Corrosion activity and solubility in polar oils of three bis(trifluoromethylsulfonyl) imide / bis(trifluoromethylsulfonyl) amide ([NTF₂]) anion-based ionic liquids

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Abstract

The corrosion behaviour and solubility of three bis(trifluoromethylsulfonyl)amide₁ ([NTF₂]) anion-based ionic liquids: 1-dodecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([C12MIM][NTF₂]), tributylmethylylammonium bis(trifluoromethylsulfonyl)amide ([N₄₄₄][NTF₂]), and methyltrioctylammonium bis(trifluoromethylsulfonyl)amide ([N₁₈₈₈][NTF₂]), as a component in a mixture with different base oils were analysed. Six polar oils suitable for use in lubrication were utilized as base oil. Solubility tests were performed by using turbidimetry, and corrosion was checked at 4 v/v% by examining the roughness and chemical composition of the surface after 21 days. The results showed that long carbon chains in the cation improve the solubility greatly in diesters and slightly in polyolesters. Corrosion was not detected at this concentration.

Keywords: ionic liquids; corrosion; solubility; lubrication.

1. Introduction

The utilization of ionic liquids (ILs) in lubrication has been reported since 2001 [2,3]. ILs are salts with melting points below 100 °C and interest in them is growing due to the possibility of obtaining different physicochemical properties by changing the constituent ions [4]. ILs have excellent characteristics such as a large liquid range, high thermal stability, negligible vapour pressure, non-flammability, and so on, which makes them candidates for lubricant or other industrial applications [5,6]. Some researches have reviewed the increasing attention to ILs as novel lubricant fluids [7-11]. These positive features led also to the use of ILs as additives [12,13]. The first ILs used in lubrication were based on imidazolium cations and [BF₄] and [PF₆] anions [14-16], but although they improve the tribological performance, these anions decompose via hydrolysis into highly corrosive and toxic compounds [17]. This problem led to the study of new ILs based on [FAP] and [NTF₂] anions [18-27].

The inherent low solubility of the ILs in non-polar hydrocarbon oils has generated many researches [16, 28–32], where the ILs were used in oil–IL emulsions or as lubricant additives in low concentration.

¹ Although commonly referred to it as “imide” in tribology, IUPAC recommendations suggest the name bis(trifluoromethylsulfonyl)amide [1]
2009, the potential applications of phosphonium-cation-based ILs have been studied [33,34]. Some of these ILs have drawn attention due to their solubility in non-polar oils and performance as lubricant additives [31-35]. These findings are interesting and the adsorption of the ILs on the surfaces due to their polar character can be used effectively in thin film lubrication. Besides, the mechanism of boundary film formation found for a mixture formed by a component of higher viscosity and polarity (e.g. ester) in a low viscosity non-polar oil (mineral oil or polyalphaolefin) [36-38] can take place when ILs are used as additives. The advantages of this lubrication mechanism were verified by Fernandez et al. [39], who worked with a mixture of a polyalphaolefin (PAO6) and two esters (trimethylol propane trioleate and sunflower oil) at 5, 10, and 15 wt%. Taking into account the above-mentioned lubrication mechanism, a mixture of a polyalphaolefin (85 wt%) and trimethyl propane trioleate (15 wt%) was used in the formulation of oil-in-water emulsions in order to study the influence of different concentrations of emulsifiers on the lubrication under extreme pressure conditions [40].

Numerous studies refer the better solubility of ILs in polar base oils such as ester [41-43], polyethylene glycol [44-46], or glycerol [47-49]. But corrosion is also an important issue in industry [50,51], being closely related to lubrication. Some N-alkylpiridinium compounds even have anticorrosive properties [52]. Although ILs based on [NTf₂] anion trend to be resistant to hydrolysis, their solubility in different oils and corrosion activity should be addressed yet.

The present paper aims to study the solubility of three [NTf₂] anion-based ILs in six polar base oils and their corrosive action on steel. This corrosive action was studied at the maximum common solubility of the different mixtures IL and base oil. The results of this study will be of great interest due to the increasing potential of the ILs for the lubricant industry.

2. Experimental

2.1 Ionic liquids and polar oils

The ILs dodecyl-3 methylimidazolium bis(trifluoromethylsulfonyl)amide ([C12MIM][NTf₂]), tributylmethylammonium bis(trifluoromethylsulfonyl)amide ([N₃444][NTf₂]), and methyltrioctylammonium bis(trifluoromethylsulfonyl)amide ([N₃888][NTf₂]), commercially available from Ionic Liquid Technologies GmbH (Io-Li-Tec), were used as additive candidates in this work. The empirical formulae of these ILs are C₁₈H₃₇F₃O₃N₃S₂, C₁₅H₃₀F₃O₃N₃S₂, and C₂₇H₅₄F₃O₃N₃S₂, respectively. The main properties of the ILs are shown in Table 1.
Table 1. Chemical properties of the ILs.

<table>
<thead>
<tr>
<th>IUPAC name (CAS Number)</th>
<th>Acronym</th>
<th>Purity (%)</th>
<th>( \rho / 20 ^\circ C ) (g/cm(^3))</th>
<th>( M ) (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Dodecyl-3 methylimidazolium bis(trifluoromethylsulfonyl)amide (404001-48-5)</td>
<td>[C12MIM][NTf(_2)]</td>
<td>98</td>
<td>1.105</td>
<td>531.58</td>
</tr>
<tr>
<td>Tributylmethylammonium bis(trifluoromethylsulfonyl)amide (405514-94-5)</td>
<td>[N(_{4441})][NTf(_2)]</td>
<td>99</td>
<td>1.270</td>
<td>480.53</td>
</tr>
<tr>
<td>Methyltributylammonium bis(trifluoromethylsulfonyl)amide (375395-33-8)</td>
<td>[N(_{1888})][NTf(_2)]</td>
<td>99</td>
<td>1.109</td>
<td>648.85</td>
</tr>
</tbody>
</table>

Chemical structure

![Chemical structure images]

The oils used were one readily biodegradable and hydrolytically stable diester, suitable for use in high-temperature chain oil applications (Priolube 1859-Lq-(GD) coded as A1); one very hydrolytically stable and biodegradable diester (Priolube 1936 coded A2), available for a range of lubricant applications (four-stroke engines, gears and transmission, hydraulic fluids, greases); one readily biodegradable and hydrolytically stable unsaturated polyol ester (Priolube 2065-LQ-(GD) coded as A3) suitable for hydraulic fluids and greases; one biodegradable and hydrolytically saturated polyolester (Priolube 3971 coded as A4) with uses in a wide range of applications, particularly at high temperature; one biodegradable and hydrolytically stable saturated ester (Priolube 3987-LQ-(GD) coded as A5), suitable for use in a wide range of automotive and industrial applications; and one biodegradable monoester with low polarity (Priolube 1976 coded as A6), used as both a base fluid and an additive. Therefore, these base oils can be classified into four different categories according to their chemical structure: petrochemical diesters (oils A1 and A2), polyesters (A3 and A4), ester (A5), and low-polarity monoesters (A6).
monoester (A6). All of them were kindly provided by CRODA Lubricants and their main properties are shown in Table 2.

Table 2. Main physicochemical properties of the base oils.

<table>
<thead>
<tr>
<th>Base oils</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Density at 20 °C (g/cm³)</td>
</tr>
<tr>
<td>A1</td>
<td>0.928</td>
</tr>
<tr>
<td>A2</td>
<td>0.913</td>
</tr>
<tr>
<td>A3</td>
<td>0.900</td>
</tr>
<tr>
<td>A4</td>
<td>0.960</td>
</tr>
<tr>
<td>A5</td>
<td>0.920</td>
</tr>
<tr>
<td>A6</td>
<td>0.860</td>
</tr>
</tbody>
</table>

2.2. Solubility tests

Solubility can be evaluated visually by estimating the concentration of IL at which the mixture of IL and base oil becomes turbid. Turbidimetry is a suitable technique for checking solubility, and is already used with proteins in ILs [53]. Basically, a known amount of ionic liquid (ranging 20 – 200 mg) was mixed with 2 mL of base oil at room temperature and shaken in a vortex for 1 minute, and then the transmittance at 600 nm is measured in a Perkin-Elmer Lambda 900 spectrophotometer. Insoluble mixtures generate emulsions that scatter the light, thus reducing the transmittance. According to the Lambert-Beer law, the analytical expression of the transmitted light as a function of the photon mean free path is shown in Equation (1), where \( \kappa \) is a parameter depending on the geometry of the measurement cell. Likewise, parameter \( l \) can be obtained from equation (2), where \( d \) is the droplet size, \( \phi \) the volumetric fraction, and \( Q \) a constant. In addition, these both equations can be merged resulting in equation (3).

\[
T = T_0 e^{-\frac{\kappa}{\tau}} (1)
\]

\[
l = Q\frac{d}{\phi} (2)
\]

\[
\frac{\tau}{\tau_0} = e^{-\frac{\kappa\phi}{Qd}} (3)
\]

Taking into account the definition of absorbance, equation (3) is transformed into equation (4):
$$A = \frac{k \phi}{\phi} = K \frac{\phi}{d} \quad (4)$$

However, it is interesting to state that the dependence of scattered light and the concentration of IL in the emulsions with the lowest solubility was not linear as expected but followed the Equation (5), where $A$ is the absorbance at 600 nm, $\phi$ is the volumetric fraction of the IL, and $k_1$ and $k_2$ are constants.

$$A = \frac{k_1 \phi}{k_2 + \phi} \quad (5)$$

Equation (5) can be deducted from Equation (4), considering that the droplet diameter depends linearly on the concentration as $d = d_0 + \alpha \phi$, so $k_1 = K/\alpha$ and $k_2 = d_0/\alpha$. $\alpha$ is an estimation of how fast the droplet grows with concentration, whereas $d_0$ represents the size of the droplet extrapolated to $\phi = 0$.

Equation (5), once modified, can be linearized into (6):

$$\frac{1}{A} = \frac{\alpha}{K} + \frac{d_0}{K \phi} \quad (6)$$

In this way, the slope/intercept of the graphical representation $1/A$ versus $1/\phi$ is $d_0/\alpha$. The lower the value of $d_0/\alpha$, the smaller the droplets and the faster their growth with $\phi$ will be.

### 2.3. Corrosion study

The specimens used in the corrosion test were disks manufactured from AISI 52100 steel. Table 3 shows the chemical composition and mechanical properties of the disks. The disks were cleaned using heptane in an ultrasonic bath for 5 minutes before corrosion tests and later before characterization of the surface. After the above cleaning process, the disks were rinsed in ethanol and dried with hot air.

<table>
<thead>
<tr>
<th>Chemical composition (%)</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>P</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>AISI 52100 Steel disks</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></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>
<td></td>
</tr>
<tr>
<td>Dimensions</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10-mm diameter × 3-mm thickness</td>
<td>190–210 HV&lt;sub&gt;30&lt;/sub&gt;</td>
<td>0.02 μm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The corrosion performance of the ILs-base oil mixtures was studied by using the following test: 15 μL (about three drops) of the base oils or their mixtures with ILs were applied separately on the disks and they were exposed for 21 days in air at room temperature. Relative humidity and
temperature were measured at different hours during the corrosion test resulting in values of 42–59% and 12–18°C, respectively.

2.4 Surface analysis

In order to evaluate the damage on the surface after the interaction with the base oil, IL, or mixture, we analysed three different parameters of the surface: the roughness ($S_q$), estimated as the standard deviation of the height distribution $S_q = \frac{1}{A} \left[ \int_A z^2(x,y)\,dx\,dy \right]$, the skewness ($S_{sk}$), calculated as the skewness of the height distribution $S_{sk} = \frac{1}{S_q^3} \left[ \int_A z^3(x,y)\,dx\,dy \right]$, and the arithmetical mean height ($S_a$), defined as $S_a = \frac{1}{A} \int_A |z(x,y)|\,dx\,dy$. All of these parameters were estimated according to the EUR Standards [54].

Mathematical calculations were automatically performed by the stereomicroscope software.

Surfaces were also analysed using photoelectron spectroscopy (XPS) with X-ray radiation from Kα (Al) (1486.61 eV) working at 13 kV and 150 W and a SPECS Phoibos hemispherical analyser. High resolution spectra were taken with an energy step of 0.1 eV and an energy pass of 30 eV, accumulating 12 spectra.

Mathematical fitting of curves for XPS spectra was performed with CasaXPS software, using Shirley-type baselines and a Gaussian-Lorentzian (30:70) product model curve.

3. Results and discussion

3.1. Solubility

A first visual inspection of the base oil/IL mixtures is useful to know about the solubility. Table 4 shows the range of concentrations where the maximum solubility is reached. The lower limit corresponds to the highest concentration without appreciable turbidity and the higher limit corresponds to the lowest concentration where turbidity was visually evident.

<table>
<thead>
<tr>
<th>Base oil</th>
<th>Ionic liquid</th>
<th>[C12MIM][NTf₂]</th>
<th>[N4441][NTf₂]</th>
<th>[N1888][NTf₂]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td></td>
<td>≥ 30%</td>
<td>1–1.5%</td>
<td>≥ 30%</td>
</tr>
<tr>
<td>A2</td>
<td></td>
<td>≥ 30%</td>
<td>0–0.5%</td>
<td>≥ 30%</td>
</tr>
<tr>
<td>A3</td>
<td></td>
<td>0–0.5%</td>
<td>0–0.5%</td>
<td>0.5–1%</td>
</tr>
<tr>
<td>A4</td>
<td></td>
<td>0.5–1%</td>
<td>0–0.5%</td>
<td>4–4.5%</td>
</tr>
</tbody>
</table>

(*) Concentrations over 30% were not tested.
From Table 4, it seems clear that ILs [C12MIM][NTf₂] and [N₁₈₈₈][NTf₂] are easily solubilized in petrochemical diesters (A1 and A2), partially soluble in polyol esters (A3 and A4), and insoluble in esters (A5) and low-polarity monoesters (A6). On the contrary, [N₄₄₄₁][NTf₂] is only slightly soluble in A1 and insoluble in the rest of the base oils, which can be explained by taking into account the chemical structure of this IL. In organic media such as the base oils, one of the most important driving forces for solubility is the interaction between hydrophobic residues (carbon chains), and thus it is expectable that the smaller the carbon chains in the cation, the lower the amount of this kind of interaction and therefore the lower the solubility. These results are in agreement with a previous work of our research group [55].

Using the Lambert-Beer approach (Equations 1–6), a further study was performed for the most insoluble mixtures. The results listed in Table 5 show similar values of \(d_0/\alpha\) for polyolesters (A3 and A4), suggesting small droplets of IL that grow rapidly with increases in \(\phi\). Saturated ester base oil (A5), on the contrary, tends to force the IL to form big droplets, which grow slowly or even decrease in size with increases in \(\phi\) of ([N₄₄₄₁][NTf₂]) due to the different chemical nature of the base oil. Intermediate values between these two situations were found for monoester base oil (A6).

### Table 5: Values of \(d_0/\alpha\) for all mixtures.

<table>
<thead>
<tr>
<th>Base oil</th>
<th>Ionic liquid</th>
<th>(d_0/\alpha)</th>
<th>Equation 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>[C12MIM][NTf₂]</td>
<td>Highly soluble*</td>
<td>(0.90) (0.9995)</td>
</tr>
<tr>
<td>A2</td>
<td>[N₄₄₄₁][NTf₂]</td>
<td>Partially soluble*</td>
<td>(0.077) (0.9163)</td>
</tr>
<tr>
<td>A3</td>
<td>[N₁₈₈₈][NTf₂]</td>
<td>Partially soluble*</td>
<td>(d_0/\alpha = 0.079) (0.9940)</td>
</tr>
<tr>
<td>A4</td>
<td>[N₁₈₈₈][NTf₂]</td>
<td>Partially soluble*</td>
<td>(d_0/\alpha = 0.85) (0.9391)</td>
</tr>
<tr>
<td>A5</td>
<td>[N₁₈₈₈][NTf₂]</td>
<td>Partially soluble*</td>
<td>(d_0/\alpha = 0.13) (0.9327)</td>
</tr>
</tbody>
</table>

* Equation 6 is senseless in soluble systems, as they do not produce turbidity.

### 3.2. Corrosion
The previous solubility results establish that A1, A2, and A4 are the best options for solubilizing the chosen ILs. Therefore, as a next step, the corrosion effects of these base oils as well as the corrosion effects of the base-oil + IL mixtures were studied. Table 6 shows the results for samples tested with pure substances at room temperature. Since roughness ($S_q$) is a standard deviation, comparing $S_q$ from different samples requires the use of the Snedecor’s F statistic [56].

Table 6: Roughness, skewness, and mean height of the disk’s surface (stainless steel) before and after corrosion test with three of the base oils at room temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_q$ (µm)</th>
<th>$S_d$</th>
<th>$S_a$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stainless steel</td>
<td>2.17</td>
<td>0.12</td>
<td>1.64</td>
</tr>
<tr>
<td>A1</td>
<td>1.23</td>
<td>0.19</td>
<td>0.97</td>
</tr>
<tr>
<td>A2</td>
<td>0.94</td>
<td>2.08</td>
<td>0.61</td>
</tr>
<tr>
<td>A4</td>
<td>4.40</td>
<td>-0.13</td>
<td>3.51</td>
</tr>
</tbody>
</table>

However, $S_q$ is obtained from a huge number of points, and therefore $F_{crit} = 1$, meaning that any difference in $S_q$ is statistically significant. In order to evaluate whether this significant difference can be attributed to a corrosive effect, changes in skewness may be more interesting. Negative values for $S_d$ indicate that the roughness arises from deep and fine valleys in one plateau (e.g. pores), whereas positive values indicate the presence of many peaks on a plane [54].

Bulmer suggests that skewness between -0.5 and +0.5 indicates more or less symmetric distributions [57], so according to this, only the sample tested with A2 shows a significant change in $S_d$ with respect to the stainless steel, indicating a drastic change on the surface. Sample treated with neat A4 shows a change in the sign of $S_d$ with respect to stainless steel, but it is not necessarily significant.

[C12MIM][NTf$_2$], [N$_{1888}$][NTf$_2$] and [N$_{1444}$][NTf$_2$] have been described to have a corrosive effect on stainless steel, mainly as a consequence of the presence of water [55]. Taking into consideration this and the results from the experiments in the section on solubility, the corrosive effects of mixtures with 4 v/v% [C12MIM][NTf$_2$] in A1 and A2 and 4 v/v% [N$_{1888}$][NTf$_2$] in A1, A2 and A4 were tested. This concentration was chosen as it is the highest common solubility value according to Table 4. The results of the surface roughness changes are recorded in Table 7.

Table 7: Roughness, skewness, and mean height of the disk’s surface (stainless steel) before and after reaction with different mixtures at room temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_q$ (µm)</th>
<th>$S_d$</th>
<th>$S_a$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stainless steel</td>
<td>2.17</td>
<td>0.12</td>
<td>1.64</td>
</tr>
<tr>
<td>[C12MIM][NTf$_2$]-A1</td>
<td>2.03</td>
<td>-0.103</td>
<td>1.61</td>
</tr>
</tbody>
</table>
These results are mostly in accordance with those in Table 6. Mixtures with A2 show the highest values of skewness, in the limit or over the critical 0.5 value, thus indicating a significant change in the surface roughness. These values of skewness in the mixtures are probably driven by the effect of the base oil. Nevertheless, it is more likely that these changes in the surface are attributable to modification of the surface because of the diffusion of the base oil into the pores rather than a real corrosive effect. In order to check this last possibility, further experiments to analyse the chemical composition of the surface were performed.

Finally, the chemical composition of the surfaces of the samples was studied by XPS, whose results are summarized in Figures 1, 2, and 3. The difference in the high resolution spectra of Fe 2p3/2 is small, suggesting that the surfaces are very similar. All the samples can be described as showing a combination of three different peaks appearing at 706.6, 709.6, and 711.5 eV, which can be assigned, respectively, to metallic iron [58], iron oxides [58], and iron oxy-hydroxides (FeOOH) [59]. It is interesting to note that the peak at 706.6 eV (Fe⁰) is slightly higher in samples treated with a mixture of IL + base oil than in samples treated with neat base oil. This suggests either that the incorporation of IL in the base oil improves the protection offered by the mixture against atmospheric oxidation or that the ionic liquid is somehow removing Fe(III) from the surface. However, there is no chemical evidence of that nor we could find literature about this kind of reactions, being the first possibility more likely, concluding then, that there is no chemical damage in the surface. Table 8 records the curve fitting for iron in the different samples.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Fe⁰</th>
<th>Iron oxides</th>
<th>FeOOH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% Area</td>
<td>Position / eV</td>
<td>Fwhm / eV</td>
</tr>
<tr>
<td>[C12MIM][NTf₂]-A2</td>
<td>2.74</td>
<td>0.458</td>
<td>1.86</td>
</tr>
<tr>
<td>[Ni1888][NTf₂]-A1</td>
<td>2.67</td>
<td>-0.289</td>
<td>2.06</td>
</tr>
<tr>
<td>[Ni1888][NTf₂]-A2</td>
<td>0.47</td>
<td>3.68</td>
<td>0.207</td>
</tr>
<tr>
<td>[Ni1888][NTf₂]-A4</td>
<td>2.09</td>
<td>-0.264</td>
<td>1.58</td>
</tr>
</tbody>
</table>

Table 8: Curve fitting for Fe2p3/2. Percentage of the total iron.
<table>
<thead>
<tr>
<th></th>
<th>Fwhm / eV</th>
<th>2.5</th>
<th>2.5</th>
<th>2.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C12MIM][NTf2]-A2</td>
<td>% Area</td>
<td>24%</td>
<td>51%</td>
<td>25%</td>
</tr>
<tr>
<td></td>
<td>Position / eV</td>
<td>706.7</td>
<td>709.7</td>
<td>711.6</td>
</tr>
<tr>
<td></td>
<td>Fwhm / eV</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>[N1888][NTf2]-A1</td>
<td>% Area</td>
<td>25%</td>
<td>50%</td>
<td>25%</td>
</tr>
<tr>
<td></td>
<td>Position / eV</td>
<td>706.7</td>
<td>709.7</td>
<td>711.6</td>
</tr>
<tr>
<td></td>
<td>Fwhm / eV</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>[N1888][NTf2]-A2</td>
<td>% Area</td>
<td>24%</td>
<td>50%</td>
<td>25%</td>
</tr>
<tr>
<td></td>
<td>Position / eV</td>
<td>706.7</td>
<td>709.7</td>
<td>711.5</td>
</tr>
<tr>
<td></td>
<td>Fwhm / eV</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>[N1888][NTf2]-A4</td>
<td>% Area</td>
<td>25%</td>
<td>50%</td>
<td>25%</td>
</tr>
<tr>
<td></td>
<td>Position / eV</td>
<td>706.7</td>
<td>709.7</td>
<td>711.7</td>
</tr>
<tr>
<td></td>
<td>Fwhm / eV</td>
<td>2.6</td>
<td>2.6</td>
<td>2.6</td>
</tr>
</tbody>
</table>

Figure 1. High resolution Fe 2p3/2 spectra of neat base-oil corrosion samples.

Figure 2. High resolution Fe 2p3/2 spectra of [C12MIM][NTf2] in A1 and A2 corrosion samples.
4. Conclusions

The corrosion activity and solubility in polar oils of three [NTf₂] anion-based ILs were studied in this research. From the results obtained, the following conclusions can be drawn:

- The IL with short carbon chains in the cation ([N₄₄₄₄][NTf₂]) is poorly soluble in the assayed base oils. However, long carbon chains in the cation ([C12MIM][NTf₂] and [N₁₈₈₈][NTf₂]) greatly improve the solubility in petrochemical diesters (A1 and A2) or improve it slightly in polyol esters (A3 and A4).

- Turbidimetry experiments suggest that these ILs tend to form small droplets in polyol esters (A3 and A4) and bigger droplets in saturated esters (A5 and A6).

- Despite the corrosive effect of the neat ILs, XPS experiments demonstrate that there are no important chemical differences among the disk surface after 21 days of the corrosion test at 4 v/v% concentration. In fact, disk surfaces treated with a mixture of IL and base oil seem to have a slightly higher amount of Fe⁰, thus suggesting a certain protection of the surface against atmospheric oxidation.

- Only the disk surface treated with neat A2 shows changes in surface roughness after 21 days. This effect is also detected for [C12MIM][NTf₂] in A2 and [N₁₈₈₈][NTf₂] in A2, thus confirming the action of A2 on the surface.

Figure 3. High resolution Fe 2p3/2 spectra of [N₁₈₈₈][NTf₂] in A1, A2, and A4 corrosion samples.
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Graphical Abstract

Solubility test

Base oil A1
Base oil A2
Base oil A3
Base oil A4
Base oil A5
Base oil A6

IL $[\text{C}_{12}\text{MIM}][\text{NTf}_2]$:
- A1
- A2

IL $[\text{N}_{1888}][\text{NTf}_2]$:
- A1
- A2

IL $[\text{N}_{4441}][\text{NTf}_2]$:
- A1
- A2

IL $[\text{N}_{1888}][\text{NTf}_2]$:
- A1
- A2

Corrosion test

A1
A2
A4
A1 + $[\text{C}_{12}\text{MIM}][\text{NTf}_2]$
A1 + $[\text{N}_{1888}][\text{NTf}_2]$
A4 + $[\text{N}_{1888}][\text{NTf}_2]$
A2 + $[\text{C}_{12}\text{MIM}][\text{NTf}_2]$