

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]), tributylmethylammonium bis(trifluoromethylsulfonyl)amide ([N₄₄₄₁][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 petrochemical diesters and slightly in polyolesters. Corrosion wasn't 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 [1B,1]. 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 [2]. 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 [3,4]. Some researches have reviewed the increasing attention to ILs as novel lubricant fluids [5–8A]. These positive features led also to the use of ILs as additives [8B,8C]. The first ILs used in lubrication were based on imidazolium cations and [BF₄] and [PF₆] anions [9–11], but although they improve the tribological performance, these anions decompose via hydrolysis into highly corrosive and toxic compounds [15]. This problem led to the study of new ILs based on [FAP] and [NTf₂] anions [16–20].

¹ Although commonly referred to it as “imide” in tribology, IUPAC recommendations suggest the name bis(trifluoromethylsulfonyl)amide [1A]

The inherent low solubility of the ILs in non-polar hydrocarbon oils has generated many researches [11, 39–47], where the ILs were used in oil–IL emulsions or as lubricant additives in low concentration. Since 2009, the potential applications of phosphonium-cation-based ILs have been studied [48,49]. Some of these ILs have drawn attention due to their solubility in non-polar oils and performance as lubricant additives [45–47,50]. 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) [51–53] can take place when ILs are used as additives. The advantages of this lubrication mechanism were verified by Fernandez et al. [54], 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 trimethylol 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[55].

Numerous studies refer the better solubility of ILs in polar base oils such as ester [13,34,56], polyethylene glycol [30,57–59], or glycerol [60–62]. But corrosion is also an important issue in industry [63,64], being closely related to lubrication. Some N-alkylpyridinium compounds even have anticorrosive properties [64A]. Although ILs based on $[\text{NTf}_2]$ 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 $[\text{NTf}_2]$ 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.

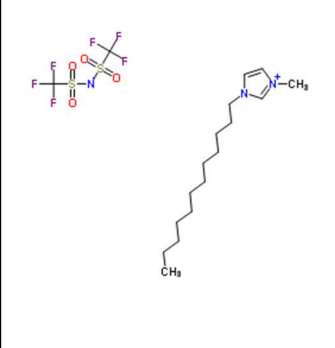
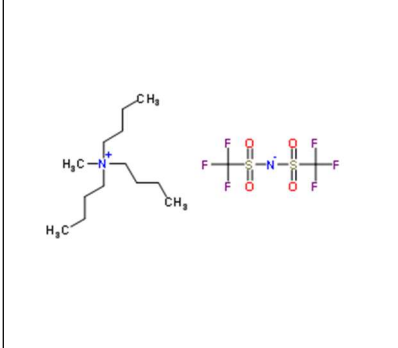
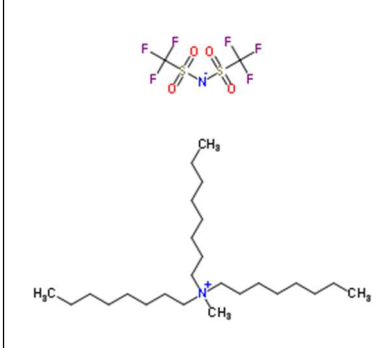
2. Experimental

2.1 Ionic liquids and polar oils

The ILs dodecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ($[\text{C}_{12}\text{MIM}][\text{NTf}_2]$), tributylmethylammonium bis(trifluoromethylsulfonyl)amide ($[\text{N}_{4441}][\text{NTf}_2]$), and methyltrioctylammonium bis(trifluoromethylsulfonyl)amide ($[\text{N}_{1888}][\text{NTf}_2]$), 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 $C_{18}H_{31}F_6O_4N_3S_2$, $C_{15}H_{30}F_6O_4N_2S_2$, and $C_{27}H_{54}F_6O_4N_2S_2$, respectively. The main properties of the ILs are shown in Table 1.

Table 1. Chemical properties of the ILs.

IUPAC name (CAS Number)	Acronym	Purity (%)	$\rho / 20\text{ }^\circ\text{C}$ (g/cm ³)	M (g/mol)
1-Dodecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide (404001-48-5)	[C12MIM][NTf ₂]	98	1.105	531.58
Tributylmethylammonium bis(trifluoromethylsulfonyl)amide (405514-94-5)	[N4441][NTf ₂]	99	1.270	480.53
Methyltrioctylammonium bis(trifluoromethylsulfonyl)amide (375395-33-8)	[N1888][NTf ₂]	99	1.109	648.85
Chemical structure				
				
[C12MIM][NTf ₂]	[N4441][NTf ₂]	[N1888][NTf ₂]		

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 polyolester (*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),

polyolesters (A3 and A4), ester (A5), and low-polarity 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.

Base oils	Properties					
	Density at 20 °C (g/cm ³)	Kinematic Viscosity (mm ² /s)		Viscosity Index	Pour Point (°C)	Flash Point (°C)
		40 °C	100 °C			
A1	0.928	9.24	2.60	116	−60	–
A2	0.913	27.30	5.40	139	−54	–
A3	0.900	48	9.80	196	−39	324
A4	0.960	30	6	144	−3	285
A5	0.920	145	19.20	151	−20	> 300
A6	0.860	26	5.60	157	−33	260

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 [65]. 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 k 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, ϕ the volumetric fraction, and Q a constant. In addition, these both equations can be merged resulting in equation (3).

$$T = T_0 e^{-\frac{k}{l}} \quad (1)$$

$$l = Q \frac{d}{\phi} \quad (2)$$

$$\frac{T}{T_0} = e^{-\frac{k\phi}{Qd}} \quad (3)$$

Taking into account the definition of absorbance, equation (3) is transformed into equation (4):

$$A = \frac{k\phi}{Qd} = K \frac{\phi}{d} \quad (4)$$

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, ϕ 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 deduced 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 $k_2 = d_0/\alpha$. α 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):

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

In this way, the slope/intercept of the graphical representation $1/A$ versus $1/\phi$ is d_0/α . The lower the value of d_0/α , the smaller the droplets and the faster their growth with ϕ 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 3. Description of the steel disks used in corrosion tests.

Chemical composition (%)						
AISI 52100 Steel disks	C	Si	Mn	Cr	P	S
	0.98–1.1	0.15–0.30	0.25–0.45	1.30–1.60	0.025	0.025
	Dimensions		Hardness		Roughness (Ra)	
	10-mm diameter × 3-mm thickness		190–210 HV ₃₀		0.02 μm	

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.

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 $S_q = \sqrt{\frac{1}{A} \iint_A z^2(x, y) dx dy}$, the skewness (S_{sk}), calculated as the skewness of the height distribution $S_{sk} = \frac{1}{S_q^3} \left[\frac{1}{A} \iint_A z^3(x, y) dx dy \right]$, 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 [66]. All of

these parameters were obtained using a Leica M205FA fluorescence stereomicroscope. Mathematical calculations were automatically performed by the stereomicroscope software.

Surfaces were also analysed using photoelectron spectroscopy (XPS) with X-ray radiation from K_{α} (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 4. Solubility ranges obtained by visual inspection expressed as v/v %. (* Concentrations over 30% were not tested)

Base oil	Ionic liquid		
	[C12MIM][NTf ₂]	[N4441][NTf ₂]	[N1888][NTf ₂]
A1	≥ 30%*	1–1.5%	≥ 30%*
A2	≥ 30%*	0–0.5%	≥ 30%*
A3	0–0.5%	0–0.5%	0.5–1%
A4	0.5–1%	0–0.5%	4–4.5%
A5	0–0.5%	0–0.5%	0–0.5%
A6	0–0.5%	0–0.5%	0–0.5%

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 [37].

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/α for polyolesters (A3 and A4), suggesting small droplets of IL that grow rapidly with increases in ϕ . 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 ϕ 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/α for all mixtures.

Base oil	Ionic liquid		
	[C12MIM][NTf ₂]	[N ₄₄₄₁][NTf ₂]	[N ₁₈₈₈][NTf ₂]
A1	Highly soluble*	Partially soluble*	Highly soluble*
A2	Highly soluble*	$d_0/\alpha = 0.90$ (0.9995)	Highly soluble*
A3	$d_0/\alpha = 0.077$ (0.9163)	$d_0/\alpha = 0.097$ (0.9980)	Partially soluble*
A4	Partially soluble*	$d_0/\alpha = 0.079$ (0.9940)	Partially soluble*
A5	$d_0/\alpha = 5.84$ (0.9975)	$d_0/\alpha = -25.9$ (0.9902)	$d_0/\alpha = 0.85$ (0.9391)
A6	$d_0/\alpha = 0.42$ (0.9894)	N/A	$d_0/\alpha = 0.13$ (0.9327)

* 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 [67].

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.

Sample	S_q (μm)	S_{sk}	S_a (μm)
Stainless steel	2.17	0.12	1.64
A1	1.23	0.19	0.97
A2	0.94	2.08	0.61
A4	4.40	-0.13	3.51

However, S_q is obtained from a huge number of points, and therefore $F_{\text{crit}} = 1$, 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_{sk} 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 [66].

Bulmer suggests that skewness between -0.5 and $+0.5$ indicates more or less symmetric distributions [68], so according to this, only the sample tested with A2 shows a significant change in S_{sk} 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_{sk} with respect to stainless steel, but it is not necessarily significant.

[C12MIM][NTf₂], [N₁₈₈₈][NTf₂] and [N₁₄₄₄][NTf₂] have been described to have a corrosive effect on stainless steel, mainly as a consequence of the presence of water [3768A]. 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][NTf₂] in A1 and A2 and 4 v/v% [N₁₈₈₈][NTf₂] 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.

Sample	S_q (μm)	S_{sk}	S_a (μm)
Stainless steel	2.17	0.12	1.64
[C12MIM][NTf₂]-A1	2.03	-0.103	1.61
[C12MIM][NTf₂]-A2	2.74	0.458	1.86
[N₁₈₈₈][NTf₂]-A1	2.67	-0.289	2.06
[N₁₈₈₈][NTf₂]-A2	0.47	3.68	0.207
[N₁₈₈₈][NTf₂]-A4	2.09	-0.264	1.58

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 2p_{3/2} 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 [69], iron oxides [69], and iron oxy-hydroxides (FeOOH) [70]. 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 8: Curve fitting for Fe2p_{3/2}. Percentage of the total iron.

SAMPLE		Fe ⁰	Iron oxides	FeOOH
A1	% Area	15%	57%	28%
	Position / eV	706.6	709.6	711.5
	Fwhm / eV	2.6	2.6	2.6
A2	% Area	15 %	56%	28%
	Position / eV	706.6	709.6	711.4
	Fwhm / eV	2.6	2.6	2.6
A4	% Area	16 %	56%	28%
	Position / eV	706.7	709.6	711.6
	Fwhm / eV	2.7	2.7	2.7
[C12MIM][NTf₂]-A1	% Area	23%	52%	26%
	Position / eV	706.7	709.7	711.6
	Fwhm / eV	2.5	2.5	2.5
[C12MIM][NTf₂]-A2	% Area	24%	51%	25 %
	Position / eV	706.7	709.7	711.6
	Fwhm / eV	2.5	2.5	2.5
[N₁₈₈₈][NTf₂]-A1	% Area	25%	50%	25%
	Position / eV	706.7	709.7	711.6
	Fwhm / eV	2.5	2.5	2.5
[N₁₈₈₈][NTf₂]-A2	% Area	24%	50%	25%
	Position / eV	706.7	709.7	711.5
	Fwhm / eV	2.5	2.5	2.5

[N ₁₈₈₈][NTf ₂]-A4	% Area	25%	50%	25%
	Position / eV	706.7	709.7	711.7
	Fwhm / eV	2.6	2.6	2.6

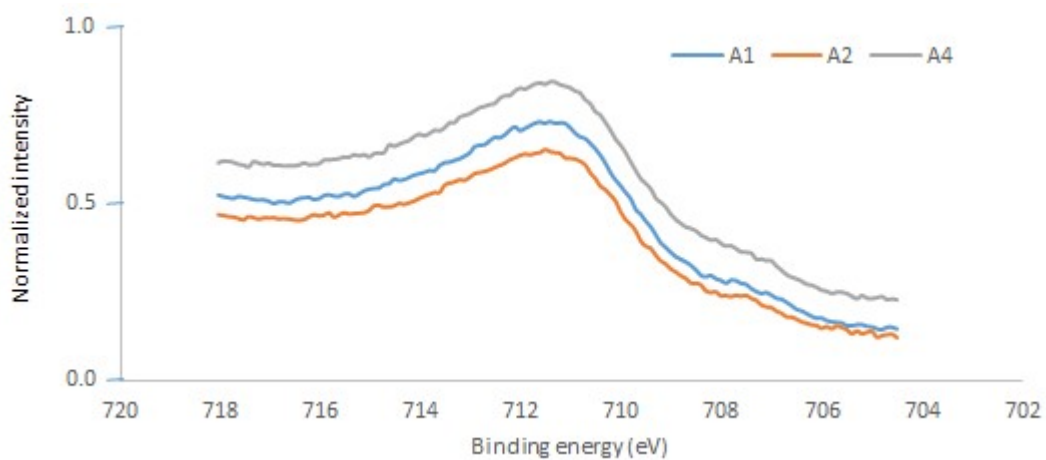


Figure 1. High resolution Fe 2p_{3/2} spectra of neat base-oil corrosion samples.

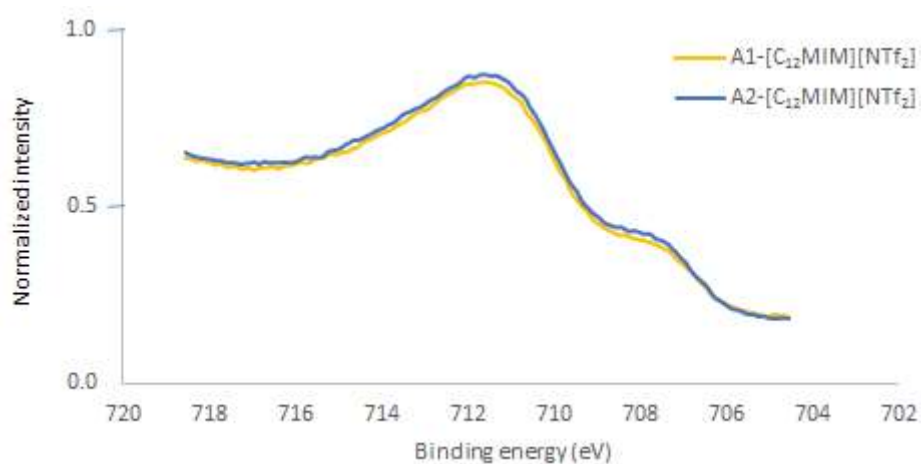


Figure 2. High resolution Fe 2p_{3/2} spectra of [C₁₂MIM][NTf₂] in A1 and A2 corrosion samples.

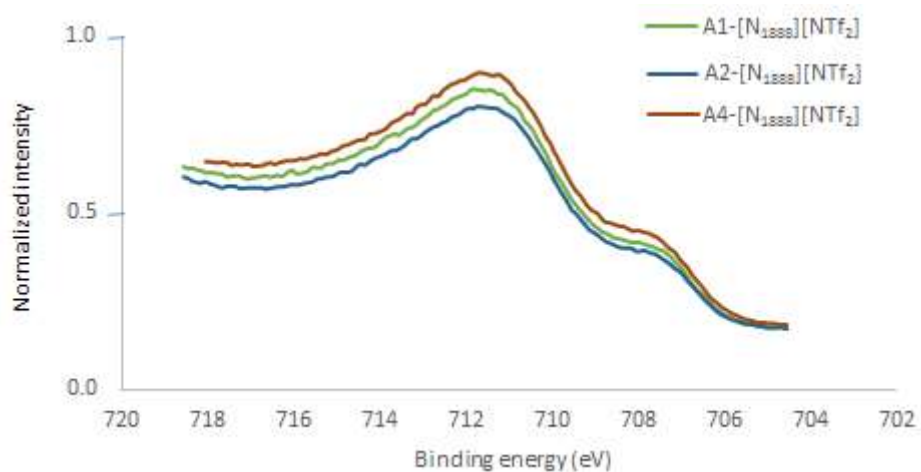


Figure 3. High resolution Fe 2p_{3/2} spectra of [N₁₈₈₈][NTf₂] in A1, A2, and A4 corrosion samples.

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 ([N₄₄₄₁][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 [68A], 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.

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References

- [1A] G.J. Willson, A.F. Hollenkamp, A.G. Pandolfo, *Chem. Int.* 29(4) (2007).
<https://www.iupac.org/publications/ci/2007/2904/ud.html>
- [1B] J. F. Brennecke, E. J. Maginn, *AIChE Journal*, 47(11) (2001) 2384-2389. doi: 10.1002/aic.690471102
- [1] C. Ye, W. Liu, Y. Chen, L. Yu, *Chem. Commun.* 21 (2001) 2244–2245. doi: 10.1039/B106935G.
- [2] M. Petkovic, K.R. Seddon, L.P.N. Rebelo, C.S. Pereira, *Chem. Soc. Rev.* 40 (2011) 1383–1403. doi: 10.1039/c004968a.
- [3] J. Van Rensselar, *Tribol. Lubr. Technol.* 66(4) (2010) 24–31.
- [4] N. Muhammad, Y.A. Elsheikh, M.I.A. Mutalib, A.A. Bazmi, R.A. Khan, H. Khan, S. Rafiq, Z. Man, I. Khan, *J. Ind. Eng. Chem.* 21 (2105) 1–10, doi: 10.1016/j.jiec.2014.01.046
- [5] M.D. Bermúdez, A.E. Jiménez, J. Sanes, F.J. Carrión, *Molecules* 14 (2009) 2888–2908. doi: 10.3390/molecules14082888.
- [6] I. Minami, *Molecules* 14 (2009) 2286–2305. doi: 10.3390/molecules14062286.
- [7] M. Palacio, B. Bhushan, *Tribol. Lett.* 40 (2010) 247–268. doi: 10.1007/s11249-010-9671-8.
- [8] A. Somers, P. Howlett, D. MacFarlane, M. Forsyth, *Lubricants* 1 (2013) 3–21. doi: 10.3390/lubricants1010003.
- [8A] Y. Zhou, J. Qu, *ACS Appl. Mat. Interf.* 9 (4) (2017) 3209-3222. doi: 10.1021/acsami.6b12489
- [8B] P. Iglesias, M.D. Bermúdez, F.J. Carrión, G. Martínez-Nicolás, *Wear* 256 (3-4) (2004) 386-392. doi: 10.1016/S0043-1648(03)00442-3
- [8C] A.E. Jiménez, M.D. Bermúdez, P. Iglesias, F.J. Carrión, G. Martínez-Nicolás, *Wear* 260 (7-8) (2006) 766-782. doi: 10.1016/j.wear.2005.04.016
- [9] W. Liu, C. Ye, Q. Gong, H. Wang, P. Wang, *Tribol. Lett.* 13 (2002) 81–85. doi: 10.1023/A:1020148514877.
- [10] B.S. Phillips, J.S. Zabinski. *Tribol. Lett.* 17 (2004) 533–541. doi: 10.1023/B:TRIL.0000044501.64351.68.
- [11] A.H. Battez, R. González, J.L. Viesca, D. Blanco, E. Asedegbega, A. Osorio, *Wear* 266 (2009) 1224–1228. doi: 10.1016/j.wear.2009.03.043.
- [12] ~~Z. Mu, F. Zhou, S. Zhang, Y. Liang, W. Liu, *Tribol. Int.* 38 (2005) 725–731. doi: 10.1016/j.triboint.2004.10.003.~~
- [13] ~~A.E. Jiménez, M.D. Bermúdez, *Wear* 265 (2008) 787–798. doi: 10.1016/j.wear.2008.01.009.~~

- [14] H. Wang, Q. Lu, C. Ye, W. Li, Z. Cui, *Wear* 256 (2004) 44–48. doi: 10.1016/S0043-1648(03)00255-2.
- [15] M.G. Freire, C.M.S.S. Neves, I.M. Marrucho, J.A.P. Coutinho, A.M. Fernandes, *J. Phys. Chem. A* 114 (2009) 3744–3749. doi: 10.1021/jp903292n.
- [16] A.E. Somers, S.M. Biddulph, P.C. Howlett, J. Sun, D.R. MacFarlane, M. Forsyth, *Phys. Chem. Chem. Phys.* 14 (2012) 8224–8231. doi: 10.1039/c2cp40736a.
- [17] I. Otero, E.R. López, M. Reichelt, J. Fernández, *Tribol. Int.* 70 (2014) 104–111. doi: 10.1016/j.triboint.2013.10.002.
- [18] I. Minami, M. Kita, T. Kubo, H. Nanao, S. Mori, *Tribol. Lett.* 30 (2008) 215–223. doi: 10.1007/s11249-008-9329-y.
- [19] R. González, A. Hernández Battez, D. Blanco, J.L. Viesca, A. Fernández-González, *Tribol. Lett.* 40 (2010) 269–277. doi: 10.1007/s11249-010-9674-5.
- [20] D. Blanco, R. González, A. Hernández Battez, J.L. Viesca, A. Fernández-González, *Tribol. Int.* 44 (2011) 645–650. doi: 10.1016/j.triboint.2011.01.004.
- [21] D. Blanco, A.H. Battez, J.L. Viesca, R. González, A. Fernández-González, *Tribol. Lett.* 41 (2011) 295–302. doi: 10.1007/s11249-010-9714-1.
- [22] A. Hernández Battez, R. González, J.L. Viesca, A. Fernández-González, M. Hadfield, *Tribol. Int.* 58 (2013) 71–78. doi: 10.1016/j.triboint.2012.10.001.
- [23] R. González, A.H. Battez, J.L. Viesca, A. Higuera Garrido, A. Fernández-González, *Tribol. Trans.* 56 (2013) 887–895. doi: 10.1080/10402004.2013.810319.
- [24] J.L. Viesca, A. García, A. Hernández Battez, R. González, R. Monge, A. Fernández-González, M. Hadfield, *Tribol. Lett.* 52 (2013) 431–437. doi: 10.1007/s11249-013-0226-7.
- [25] A. García, R. González, A. Hernández Battez, J.L. Viesca, R. Monge, A. Fernández-González, M. Hadfield, *Tribol. Int.* 72 (2014) 42–50. doi: 10.1016/j.triboint.2013.12.007.
- [26] R. Monge, R. González, A. Hernández Battez, A. Fernández-González, J.L. Viesca, A. García, M. Hadfield, *Wear* 328–329 (2015) 50–63. doi: 10.1016/j.wear.2015.01.041.
- [27] J.L. Viesca, M. Anand, D. Blanco, A. Fernández-González, A. García, M. Hadfield, *Lubricants* 4 (2016) 8–18. doi: 10.3390/lubricants4010008.
- [28] B.A. Kheireddin, W. Lu, I.C. Chen, M. Akbulut, *Wear* 303 (2013) 185–190. doi: 10.1016/j.wear.2013.03.004.

- [29] L. Pisarova, C. Gabler, N. Dörr, E. Pittenauer, G. Allmaier, *Tribol. Int.* 46 (2012) 73–83. doi: 10.1016/j.triboint.2011.03.014.
- [30] M. Cai, Y. Liang, M. Yao, Y. Xia, F. Zhou, W. Liu, *ACS Appl. Mater. Interfaces* 2 (2010) 870–876. doi: 10.1021/am900847j.
- [31] T. Murakami, K. Kaneda, M. Nakano, A. Korenaga, H. Mano, S. Sasaki, *Tribol. Int.* 41 (2008) 1083–1089. doi: 10.1016/j.triboint.2008.02.017.
- [32] A.E. Somers, P.C. Howlett, J. Sun, D.R. MacFarlane, M. Forsyth, *Tribol. Lett.* 40 (2010) 279–284. doi: 10.1007/s11249-010-9695-0.
- [33] I. Minami, T. Inada, R. Sasaki, H. Nanao, *Tribol. Lett.* 40 (2010) 225–235. doi: 10.1007/s11249-010-9626-0.
- [34] A.E. Somers, B. Khemchandani, P.C. Howlett, J. Sun, D.R. Macfarlane, M. Forsyth, *ACS Appl. Mater. Interfaces* 5 (2013) 11544–11553. doi: 10.1021/am4037614.
- [35] C. Gabler, N. Dörr, G. Allmaier, *Tribol. Int.* 80(2014) 90–97. doi: 10.1016/j.triboint.2014.06.018.
- [36] P. Bandeira, J. Monteiro, A.M. Baptista, F.D. Magalhães, *Tribol. Lett.* 59 (2015) 13–27. doi: 10.1007/s11249-015-0545-y.
- [37] D. Blanco, J.L. Viesca, M.T. Mallada, B. Ramajo, R. González, A. Hernández Battez, *Surf. Coat. Tech.* 302 (2016) 13–21. doi: 10.1016/j.surfcoat.2016.05.051
- [38] A. Hernández Battez, D. Blanco, A. Fernández González, M.T. Mallada, R. González, J.L. Viesca, *Tribol. Int.* 103 (2016) 73–86. doi: 10.1016/j.triboint.2016.06.038
- [39] A.E. Jiménez, M.D. Bermúdez, P. Iglesias, F.J. Carrión, G. Martínez-Nicolás, *Wear* 260 (2006) 766–782. doi: 10.1016/j.wear.2005.04.016.
- [40] J. Qu, J.J. Truhan, S. Dai, H. Luo, P.J. Blau, *Tribol. Lett.* 22 (2006) 207–214. doi: 10.1007/s11249-006-9081-0.
- [41] J. Qu, P.J. Blau, S. Dai, H. Luo, H.M. Meyer, *Tribol. Lett.* 35 (2009) 181–189. doi: 10.1007/s11249-009-9447-1.
- [42] K. Mistry, M.F. Fox, M.J. Priest, *Proc. Inst. Mech. Eng. Part J – J. Eng. Tribol.* 223 (2009) 563–569. doi: 10.1243/13506501JET562.
- [43] R.G. Lu, H. Nanao, K. Kobayashi, T. Kubo, S.J. Mori, *Jpn. Petrol. Inst.* 53(1) (2010) 55–60. doi: 10.1627/jpi.53.55
- [44] A. Schneider, J. Brenner, C. Tomastik, F. Franek, *Lubr. Sci.* 22 (2010) 215–223. doi: 10.1002/lis.120.

- [45] R. González, M. Bartolomé, D. Blanco, J.L. Viesca, A. Fernández-González, A. Hernández Battez, *Trib. Int.* 98 (2016) 82–93. doi: 10.1016/j.triboint.2016.02.016
- [46] J. Qu, D.G. Bansal, B. Yu, J.Y. Howe, H. Luo, S. Dai, H. Li, P.J. Blau, B.G. Bunting, G. Mordhukovich, D.J. Smolenski, *ACS Appl. Mater. Interfaces* 4 (2012) 997–1002. doi:10.1021/am201646k.
- [47] B. Yu, D.G. Bansal, J. Qu, X. Sun, H. Luo, S. Dai, D.J. Smolenski, *Wear* 289 (2012) 58–64. doi_10.1016/j.wear.2012.04.015.
- [48] K.J. Fraser, D.R. MacFarlane, *Aust. J. Chem.* 62 (2009) 309–321. doi: 10.1071/CH08558.
- [49] F. Zhou, Y. Liang, W. Liu, *Chem. Soc. Rev.* 38(9) (2009) 2590–2599. doi: 10.1039/b817899m.
- [50] W.C. Barnhill, J. Qu, H. Luo, H.M. Meyer III, C. Ma, M. Chi, B.L. Papke, *ACS Appl. Mater. Interfaces* 6 (2014) 22585–22593. doi: 10.1021/am506702u
- [51] P.M. Cann, H.A. Spikes, *Tribol. Trans.* 37 (1994) 580–586. doi: 10.1080/10402009408983332
- [52] M. Smeeth, S. Günsel, H.A. Spikes, *Tribol. Trans.* 39(3) (1996) 726–734. doi: 10.1080/10402009608983590
- [53] G. Guangteng, M. Smeeth, P.M. Cann, H.A. Spikes, *Proc. Inst. Mech. Eng. J.* 210 (1996) 1–15. doi: 10.1243/PIME_PROC_1996_210_473_02
- [54] J.E. Fernández Rico, A. Hernández Battez, D. García Cuervo, *Wear* 253 (2002) 827–831. doi: 10.1016/S0043-1648(02)00229-6
- [55] A. Cambiella, J.M. Benito, C. Pazos, J. Coca, A. Hernández, J.E. Fernández, *J. Mater. Process Tech.* 184 (2007) 139–145. doi: 10.1016/j.jmatprotec.2006.11.014
- [56] A.E. Jiménez, M.D. Bermúdez, *Tribol. – Mater. Surf. Interfaces* 6 (2012) 109–115. doi: 10.1179/1751584X12Y.0000000011
- [57] M. Yao, Y. Liang, Y. Xia, F. Zhou, *ACS Appl. Mater. Interfaces* 1 (2009) 467–471. doi: 10.1021/am800132z
- [58] M. Cai, Y. Liang, F. Zhou, W. Liu, *Faraday Discuss.* 156 (2012) 147–157. doi: 10.1039/C2FD00124A
- [59] H. Zhang, Y. Xia, M. Yao, Z. Jia, Z. Liu, *Tribol. Lett.* 36 (2009) 105–111. doi: 10.1007/s11249-009-9465-z
- [60] M. Kronberger, V. Pejakovic, C. Gabler, M. Kalin, *Proc. Inst. Mech. Eng. Part J: J Eng Tribol* 226 (2012) 933–951. doi: 10.1177/ 1350650112459012

- [61] V. Pejaković, M. Kronberger, M. Kalin, *Lubr. Sci.* 26 (2014) 107–115. doi: 10.1002/ls.1233
- [62] V. Pejakovic, M. Kronberger, M. Mahrova, M. Vilas, E. Tojo, M. Kalin, *Proc. Inst. Mech. Eng. Part J: J. Eng. Tribol.* 226 (2012) 923–932. doi: 10.1177/1350650112448978
- [63] A.K. Singh, S. Mohapatra, B. Pani, *J. Ind. Eng. Chem.* 33 (2016) 288–297. doi: 10.1016/j.jiec.2015.10.014
- [64] A.A. Gürten, H. Keleş, E. Bayol, F. Kandemirli, *J. Ind. Eng. Chem.* 27 (2015) 68–78. doi: 10.1016/j.jiec.2014.11.046
- [64A] G. Xia, X. Jiang, L. Zhou, Y. Liao, M. Duan, H. Wang, Q. Pu, J. Zhou, *J. Ind. Eng. Chem.* 27 (2015) 133–148. doi: 10.1016/j.jiec.2014.12.027
- [65] S. Strassburg, H. Bermudez, D. Hoagland, *Biomacromolecules* 17 (2016) 2233–2239. doi:10.1021/acs.biomac.6b00468.
- [66] K. J. Stout, P. J. Sullivan, W. P. Dong, E. Mainsah, N. Luo, T. Mathia, H. Zahouan, *The development of methods for the characterization of roughness in three dimensions*. Published on behalf of the Commission of the European Communities, 1993.
- [67] N.J. Miller and J. C. Miller, *Statistics and Chemometrics for Analytical Chemistry*, 4th ed., Prentice Hall, 2000. ISBN: 0130228885
- [68] M.G. Bulmer, *Principles of Statistics*, 2nd ed., Courier Corporation, Dover (1979). ISBN: 9780486637600
- [68A] D. Blanco, J.L. Viesca, M.T. Mallada, B. Ramajo, R. González, A. Hernández Battez, *Surf. Coat. Tech.* 302 (2016) 13–21. doi: 10.1016/j.surfcoat.2016.05.051
- [69] P. Marcus, J.M. Grimal, *Corros. Sci.* 33 (1992) 805–814. doi: 10.1016/0010-938X(92)90113-H
- [70] B.J. Tan, K.J. Klabunde, P.M.A. Sherwood, *Chem. Mater.* 2 (1990) 186–191. doi: 10.1021/cm00008a021