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AMMONIUM VS. PHOSPHONIUM CATION-BASED IONIC LIQUIDS AS NEAT LUBRICANTS: PHYSICOCHEMICAL, ENVIRONMENTAL AND TRIBOLOGICAL BEHAVIOR

TRACK OR CATEGORY

Lubrication Fundamentals

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INTRODUCTION

Ionic Liquids (ILs) are thermally stable and non-flammable salts with negligible volatility and melting point lower than 100ºC. These characteristics make them ideal candidates for different applications including lubrication [1,2]. Several studies about the application of ionic liquids as neat lubricants or lubricant additive have been published over the last years, obtaining results that proved their lubricant potential [3–9]. However, few researches have focused on others physicochemical properties of the ILs, including environmental behavior. In order to enhance the knowledge about ionic liquids in lubrication, this work explores the physicochemical and environmental properties, besides the tribological performance, of two phosphonium- and ammonium cation-based ILs, both with the anion $[NTf_2]$.

EXPERIMENTAL DETAILS

Both Ionic liquid (ILs): Trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl) imide $[P_{66614}][NTf_2]$ and Methyltrioctylammonium bis(trifluoromethylsulfonyl)imide $[N_{1888}][NTf_2]$ were provided by Ionic Liquid Technologies GmbH., chosen from an available family of phosphonium cation-based and ammonium cation-based ILs due to their potential use in lubricant applications [3,4]. A rotational Couette viscometer (Stabinger SVM3000) was used to measure **viscosity and density** according to ASTM D7042 at atmospheric pressure from 10 to 100 °C. The viscosity index (VI) was also calculated according to ASTM D2270. **Surface tension** of the ILs was measured following the Du Noüy's platinum ring method using a KSV Sigma 700 tensiometer (20−80 °C temperature range). **Contact angle** of the ILs were calculated using sessile drops with a KSV CAM 200 goniometer equipped with a micrometer syringe. The expanded drop allows measuring the dynamic advancing contact angle (θ_A), and the average value was measured using both sides of the drop. **Thermogravimetric analyses (TGA)** were made on a Mettler Toledo TGA/SDTA851, carrying out dynamic scans from room temperature to approximately 600 ºC at a heating rate of 10 ºC/min under oxygen and nitrogen atmospheres with a flow rate of 50 mL/min in both cases. **Corrosion** behavior was studied using a simple test: applying separately each ionic liquid on the surface of an AISI 52100 steel disc (previously ultrasonically cleaned in heptane and air dried) which remained at room temperature for 20 days while the corrosion activity was observed. Subsequently, the steel surfaces were analyzed by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The assessment of **bacterial toxicity** was firstly carried out with *Vibrio fischeri*. This bioluminescence assay is a standard ecotoxicological test in Europe (DIN EN ISO 11348). The bacterial toxicity of the samples was secondly evaluated using a bacterial colorimetric assay: *Toxi-ChromoTest* with *Escherichia coli.* **Biodegradability** could be estimated by the biodegradability index (BOD_5/COD). Chemical oxygen demand (COD) concentration was determined by the dichromate method (at 600 nm) using a DR2500 spectrophotometer. The biochemical oxygen demand (BOD_5) was measured using a manometric respirometric measurement system, BOD-System OxiDirect®. Finally, a reciprocating ball-on-disc configuration was used to perform the **tribological tests**, using a Bruker UMT-3 tribometer. The upper (balls) and lower (disks) specimens used are both manufactured from AISI 52100 steel. 60-min tests were conducted under a load of 40 N (corresponding to a maximum contact pressure of 1.67 GPa), 15 Hz of frequency, stroke length of 4 mm, room temperature and a relative humidity in the range 20–30%. 25 μL of the corresponding ionic liquid were used in these tests. Friction coefficient was recorded during the test and wear on the discs was measured after tests using a Leica DCM 3D confocal microscope. Scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and X-Ray photoelectron spectroscopy (XPS) were also employed to carry out the **surface characterization.**

RESULTS AND DISCUSSION

Surface tension (γ) of two [NTf_2]-based ionic liquids was measured. Values ranged between 29.327 $\pm$0.009 (20ºC) and 25.15 $\pm$0.01 (80ºC) for [P_{66614}][NTf_2] and 28.919 $\pm$0.007 (20ºC) and 25.23 $\pm$0.04(80ºC) for [N_{8881}][NTf_2]. The similar values shown by [P_{66614}][NTf_2] and [N_{8881}][NTf_2] are related to their high alkyl chain length in the cation. Regarding **contact angle** results, ionic liquids with similar surface tensions led to similar contact angles, especially with hydrophobic surfaces (steel, ZrN, CrN). Table 1 shows some thermal parameters of the ILs. The good **thermal stability** found can be explained considering the [NTf_2] anion: high degree of charge delocalisation and low nucleophilicity [10].

Table 1. Thermal results from dynamic scans in both atmospheres at 10 ºC·min^{-1}.

Ionic Liquids	Atmosphere	T_{onset} (ºC)	$T_{10\%}$ (ºC)	T_{peak1} (ºC)	T_{peak2} (ºC)	$Wt_{total\ loss*}$ (%)
[P_{66614}][NTf_2]	N_2	434	400	456	--	98.8
	O_2	401	388	422	432	96.7
[N_{8881}][NTf_2]	N_2	362	386	-	425	99.9
	O_2	286	320	-	400	99.7

Concerning the behaviour of [N_{8881}][NTf_2] compared to [P_{66614}][NTf_2], it seems that phosphonium cation is more thermally stable than ammonium cation, concluding that the mechanism of thermal decomposition was also affected by the nature of the cation. With regard to **corrosion** activity, the [P_{66614}][NTf_2] showed it on the surface, with EDS spectra showing other elements (O, S, P, F) than those observed in the steel. On the other hand, [N_{1888}][NTf_2] showed no signs of corrosion. Table 2 shows *bacterial toxicity* results based on EC_{50} and the TU data according to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS) [12].

Table 2. EC_{50} and TU values after exposure of both ILs of 2 different bacteria.

	Vibrio fischeri		*E. coli*	
IL sample	**EC_{50} (mg/L)^a**	**TU^b**	**EC_{50} (mg/L)^a**	**TU^b**
[P_{66614}][NTf_2]	1.3 $\pm$ 0.6	75.36	1.6 $\pm$ 0.2	62.37
[N_{1888}][NTf_2]	12.9 $\pm$ 0.3	7.75	6.5 $\pm$ 0.3	15.51

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

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

With *Vibrio fischeri*, [P_{66614}][NTf_2] can be placed into the category Acute 2 and [N_{1888}][NTf_2] can be classified as harmful (category Acute 3). Similar results were obtained with *E. coli:* both ILs are classified as toxic (TU between 10-100), [P_{66614}][NTf_2] being more toxic.

For both ILs, the values of BOD_5/COD were lower than 0.3 (0.050 $\pm$ 0.010 for [P_{66614}][NTf_2] and 0.060 $\pm$ 0.020 for [N_{8881}][NTf_2]), which indicated that these compounds were **poorly biodegradable**. The presence of halides in the molecule, alkyl chain branching, quaternary carbon atoms and heterocycles could worsen biodegradability [11]. The average friction coefficient of the ionic liquids tested is shown in Table 3. The results are given with the standard deviation which did not reach 5% in any case. It can be observed that the $[N_{1888}][NTf_2]$ ionic liquid shows the best antifriction behavior with friction coefficient values around 0.04, whereas the $[P_{66614}][NTf_2]$ ionic liquid showed the higher friction coefficient (~0.08).

Table 3. Mean friction coefficient in the tribological tests.

IL sample	COF	Std Dev	Error (%)
$[P_{66614}][NTf_2]$	0.0410	0.0018	4.3087
$[N_{1888}][NTf_2]$	0.0826	0.0035	4.2157

CONCLUSIONS

Two $[NTf_2]$ anion-based ionic liquids were studied from physicochemical, environmental and tribological points of view and the main conclusions that can be drawn were:

- The size, symmetry and structure of both ions had strong influence on physicochemical properties.
- Such good thermal stability of both ILs can be explained considering the $[NTf_2]$ anion.
- $[P_{66614}][NTf_2]$ and $[N_{8881}][NTf_2]$ presented low surface tension values related to their high alkyl chain length in the cation and the big size of their anion.
- Only $[P_{66614}][NTf_2]$ showed presence of corrosion activity.
- Both ILs were poorly biodegradable (BOD_5/COD values were lower than 0.3).
- $[N_{1888}][NTf_2]$ was less toxic than $[P_{66614}][NTf_2]$ according of both bacterial criteria.
- $[N_{1888}][NTf_2]$ ionic liquid showed the best antifriction behavior.

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KEYWORDS

Ionic liquids, friction coefficient, environmental properties, neat lubricant