Tribology International 116 (2017) 422–430

Contents lists available at ScienceDirect

Tribology International

journal homepage: www.elsevier.com/locate/triboint

Lubrication performance of an ammonium cation-based ionic liquid used as an additive in a polar oil

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ARTICLE INFO

Keywords:
Ionic liquid
Polar oil
Additive
Lubrication

ABSTRACT

This paper studies the tribological behavior of the ionic liquid methyltrioctylammonium bis(trifluoromethylsulfonyl)imide ($[N_{1888}][NTf_2]$) as additive at different concentrations (1.25, 2.50, 3.75 and 5.00 wt %) in a polar base oil (diester). A tribometer using a ball-on-disk reciprocating configuration under fully flooded lubrication was used at a frequency of 15 Hz, at three different loads (40, 80 and 120 N), stroke length of 4 mm, and duration of 45 min. Worn surface on the disk was studied by confocal microscopy, SEM and XPS. Main results showed similar coefficient of friction for all lubricant samples; but different wear results were found at different loads, probably related with the chemical states found for fluorine on the worn surface and the temperature-dependent adsorption-desorption processes.

1. Introduction

Ionic liquids (ILs) are molten salts consisting in cations and anions, which have excellent physicochemical properties (inherent polarity, high thermal stability, low flammability, large liquid range, high viscosity and low melting point) for using them in lubrication. The use of ILs in lubrication was explored for the first time in 2001 [1] and the attention in this subject has increased greatly over the years [2–6]. Many studies about the use of ILs as neat lubricant have showed their potential for lubricating different material pairs [7–18]. Despite the advantages of both physicochemical properties and tribological performance of the ILs, the use of them as neat lubricant or lubricant base stock is not economically feasible due to their high costs.

Due to their high costs, the feasibility of using ILs as lubricant additive has become in a prominent research topic. However, most of ILs are immiscible (≪1% of solubility) in common nonpolar oils because the nonpolar neutral molecules are attracted by van der Waals forces while ions are held together by ionic forces and occasionally also by hydrogen bonding [6]. Several studies have been published using ILs as component of oil-IL emulsions or blended at low concentrations in nonpolar oils [8,13,19–36]. Meanwhile some authors used polar base oils seeking higher solubility with ILs [33,37–51]. On the other hand, only few works have used ILs as an additive in fully-formulated oils [27,34,52–55] but more studies are necessary in order to know the compatibility of the ILs with other surface-adsorbing additives [6].

The first cations studied for tribological purpose were imidazolium-, ammonium-, pyrrolidinium-, pyridinium-, thiouronium-, and thiazolium-based. Meanwhile, anions such as $[BF_4]^-$, $[PF_6]^-$, $[Cl]^-$, $[NTf_2]^-$, $[sulfate]^-$ and $[sulfonate]^-$ were also explored first [6]. However, the main problems presented by these ILs were corrosion due to the hydrolysis of the anion and low solubility in nonpolar oils. Qu et al. reported trihexyltetradecylphosphonium bis(2-ethylhexyl) phosphate ($[P_{6,6,6,14}]$ [DEHP]) and trihexyltetradecylphosphonium bis- (2,4,4-trimethylpentyl)alkylphosphinate ($[P_{6,6,6,14}]$- [BTMPP]) as the first oil-soluble ILs [27,52], which comprise quaternary structures with relatively long hydrocarbon chains both in cations and anions. From these two works emerged a theory, which state that an IL can be soluble in nonpolar oil if both cation and anion are also soluble.

With regard to the expected solubility of the ionic liquid in polar oils, ILs comprising cations such as imidazolium and pyrrolidinium; paired with many anions have resulted soluble in rapeseed oil, poly(ethylene glycol) (PEG), trimethylolpropane (TMP) oleate, castor oil, and glycerol, or in fully-formulated oils due to synergies with other additives [6]. From a tribological point of view, the possible interference between polar base

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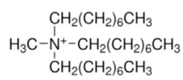
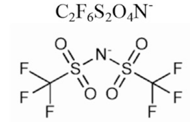
http://dx.doi.org/10.1016/j.triboint.2017.08.004
Received 31 July 2017; Accepted 3 August 2017
Available online 5 August 2017
0301-679X/

Table 1
Material properties.

IUPAC NAME (CAS NUMBER)	Purity (%)	Density 20ºC (g/cm^3)	Mol. Weight	Viscosity 40ºC (mPa·s)
Methyltrioctylammonium bis(trifluoromethylsulfonyl)imide (375395-33-8)	99	1.109	648.85	200.7

Chemical structure	
Cation	**Anion**
$C_{25}H_{54}N^+$  [N1888]	$C_2F_6S_2O_4N^-$  [NTf2]

Name	Oil type	Density 20ºC (g/cm^3)	Viscosity Index ASTM D 2270	Viscosity (mPa·s) ASTM D 445	
				40ºC	100ºC
Priolube 1936 (coded as A2)	Petrochemical diester	0.91	139	26	5.3

Table 2
Average coefficient of friction and standard deviation for tests made with all samples.

IL conc. (wt%)	40 N		80 N		120 N	
	Avg	SD ($\times10^{-3}$)	Avg	SD ($\times10^{-3}$)	Avg	SD ($\times10^{-3}$)
0.00	0.070	1.994	0.068	0.401	0.069	2.150
1.25	0.069	1.665	0.068	0.665	0.068	0.480
2.50	0.069	1.209	0.069	0.845	0.070	1.471
3.75	0.071	3.150	0.068	0.842	0.070	0.701
5.00	0.070	2.801	0.070	1.559	0.068	0.505

oils and ILs used as additive in their interaction with metallic surfaces can affect friction and wear results. This paper studies the lubrication performance of an IL based on an ammonium cation and the [NTf_2] anion used as an additive at different concentrations in a polar oil.

2. Experimental details

2.1. Lubricant samples preparation

The ionic liquid methyltrioctylammonium bis(trifluoromethylsulfonyl)imide ([N_{1888}][NTf_2]) was used as lubricant additive to a biodegradable diester with high oxidative and hydrolytical stability. The ammonium-based IL was provided by Io-Li-Tec (Ionic Liquid Technologies GmbH) and the polar base oil (Priolube 1936) was kindly supplied by CRODA, S.A. A description of the main properties of these compounds is shown in Table 1. IL-containing mixtures were prepared with the base oil and concentrations of 1.25, 2.50, 3.75 and 5.00 wt % of the IL. The solubility of the [N_{1888}][NTf_2] in the polar oil used in this work was tested using the turbidimetry technique and results showed that the IL is miscible in the oil at least 30 wt%. The corrosion activity of the IL on different substrates (steel, TiN, CrN, ZrN) was tested before [56] and no evidence of corrosion was found on these materials.

2.2. Friction and wear tests

A Bruker UMT-3 micro-tribometer with a reciprocating ball-on-disk configuration was used for friction and wear testing. The tribological tests were performed for a period of 45 min under normal loads of 40, 80 and 120 N (corresponding to maximum contact pressures of 1.67, 2.10 and 2.41 GPa, respectively), with a stroke length of 4 mm and a frequency of 15 Hz. Each test condition was repeated at least three times at room temperature using 4 ml of lubricant sample in order to ensure fully flooded lubrication condition. Commercially available AISI 52100 chrome steel balls (Ø9.5 mm, hardness 63 HRC, Ra $\leq$ 0.01 μm) were used as upper specimen and run against AISI 52100 steel disks (10 mm diameter, 3 mm thick, hardness 190–210 HV_{30}, Ra $\leq$ 0.02 μm) used as lower specimen. Coefficient of friction (COF) and electrical contact resistance (ECR) were recorded during the tests and wear volume was measured on the disk's surface using confocal microscopy (Leica DCM 3D). Both specimens were cleaned with heptane in an ultrasonic bath during 5 min before tribological tests and also before worn surface characterization. After the cleaning process, both specimens were rinsed in ethanol and then air-dried.

2.3. Surface characterization

After tribological tests worn surfaces were analyzed with a scanning electron microscope (SEM) in order to evaluate the wear mechanism. XPS measurements were also taken with a Phoibos MD5 detector, using non monochromatized Al radiation (K alpha = 1486.7 eV) at 13 kV and 200 W. Electromagnetic lenses were used in small area mode or high magnification in the case of iron and oxygen. Number of scans ranged from 10 to 40 according to the chemical elements content on the disk's surface in order to obtain high resolution spectra. Survey spectra were taken with 90 eV pass energy and 1 eV step energy (a single scan), whereas high resolution spectra were measured using 30 eV pass energy and 0.1 eV energy step. Curve fitting for high resolution XPS analysis is performed using a product 70% Gaussian-30% Lorentzian shape curve and Shirley type baseline. In case that more than one curve is used for the fitting of a single element, full width at half maximum (fwhm) is constrained so as to all curves have the same fwhm value. In the case of Fe 2p3/2 fit, an exponential tail was considered for modelling the peaks of Fe(III) (T = 1.5) and Fe(0) (T = 0.65), as done by Mangolini et al. [57].

3. Results and discussion

3.1. Tribological tests

The base oil and the IL-containing mixtures showed unexpected