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Friction and anti-wear properties of two tris(pentafluoroethyl) trifluorophosphate ionic liquids as neat lubricants

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ABSTRACT

The tribological behaviour was evaluated for two ionic liquids (ILs) as neat lubricants for the sliding pair stainless steel AISI420 and 100Cr6 under four loads (14, 18, 22 and 26 N). The ILs contain the same anion, tris(pentafluoroethyl)trifluorophosphate $[(C_2F_5)_3PF_3]^-$ (also known as $[FAP]^-$), combined with the cations 1-butyl-2,3-dimethylimidazolium $[C_4C_1C_1Im]^+$ or trihexyl(tetradecyl)phosphonium $[P_{6,6,6,14}]^+$. The IL $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ showed always better lubricating properties than $[C_4C_1C_1Im][(C_2F_5)_3PF_3]$ in terms of friction coefficient and wear volume. Under the same conditions, tribological tests were performed with two perfluoropolyethers as reference lubricants developing, in general, higher friction coefficients and also higher wear volumes than those obtained with both ILs. Surface interactions were studied by SEM observations and XPS analyses of the neat ILs and of the wear tracks.

1. Introduction

The lubricant industry is always trying to improve the performance of their products, being focused on friction coefficients reduction, increasing durability and service and reducing emission among other factors. Furthermore, the technological advances, for example in micro-electromechanical machines (MEMs) [1,2] or aerospace industry [3], are also demanding specialised lubricants. Ionic liquids (ILs) have emerged as potential lubricants or lubricant additives [4–7] since the first publication about this topic in 2001 by Ye et al. [8]. Their excellent properties (low volatility, non-flammability, thermal stability, broad electrochemical window, low melting point) [4,6,7] make them interesting for this application, although ILs can be also found in other multiple fields like batteries [9], as solvents [10], in extraction processes [11,12] or oxygen compression [13]. Another interesting aspect is the huge number of possible ILs, due to the different combinations of cations and anions, each one with its own properties. For that, ILs have been described as tailored lubricants [14]. However, only some ILs have been studied so far in tribological works. The most common are summarised in several reviews [4–6,15].

The lubricating ability of ILs is related to their facility to form adsorbed films on the metal surface due to their high polarity [5,16] and also to their reactivity under high load [15], proved by the formation of triboproducts. Both mechanisms can contribute to the prominent anti-wear ability of ILs [6]. The study of the tribochemical reactions, which take place on surfaces lubricated with ILs, revealed that fluorinated compounds exhibit favourable tribological properties. However, ILs containing the $[PF_6]^-$ and $[BF_4]^-$ anions show corrosion problems caused by their reactivity with water, which leads to production of corrosive hydrogen fluoride acid [17–19]. For that, subsequent work was performed with more hydrophobic anions, mainly bis(trifluoromethylsulfonyl)imide $[NTf_2]^-$ and tris(pentafluoroethyl)trifluorophosphate $[(C_2F_5)_3PF_3]^-$. The $[(C_2F_5)_3PF_3]^-$ ILs have high hydrolytic and thermal stability and they are more hydrophobic than $[NTf_2]^-$ ILs [20]. Besides, ionic liquids with $[(C_2F_5)_3PF_3]^-$ anion possess better tribological properties than the bis(trifluoromethylsulfonyl)imide-derived ones [5,18]. Another advantage of $[(C_2F_5)_3PF_3]^-$ is its adaptability to multiple cation groups [18]. Minami et al. [18] evaluated the friction coefficient of several ILs with the anion $[(C_2F_5)_3PF_3]^-$ and different cations such as N,N-alkylimidazolium, tetraalkylphosphonium, N,N-dialkylpyrrolidinium, tetramethylisouronium and tetramethyl-N-alkylguanidinium as neat lubricants for steel–steel contact. These authors also compared them with two N,N-alkylimidazolium $[NTf_2]$ ILs, obtaining better results with all the $[(C_2F_5)_3PF_3]^-$ ILs.

Somers et al. [21] studied also three ILs with the anion $[(C_2F_5)_3PF_3]^-$ and the cations trihexyl(tetradecyl)phosphonium $[P_{6,6,6,14}]^+$, 1-butyl-1-methylpyrrolidinium $[C_4C_1Pyrr]^+$ and 1-ethyl-3-methyl imidazolium $[C_2C_1Im]^+$, but as lubricant for

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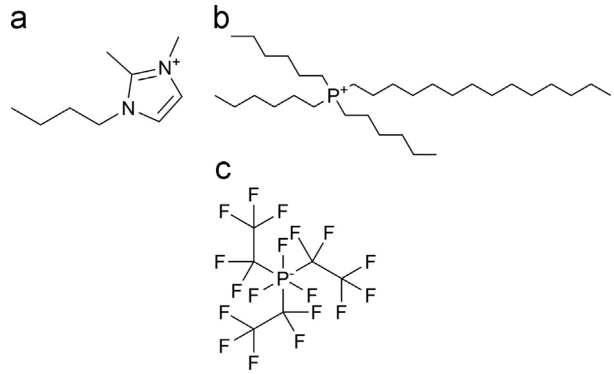

Fig. 1. Molecular structures of the cations and anion which form the ILs studied: 1-butyl-2,3-dimethylimidazolium tris(pentafluoroethyl) trifluorophosphate $[C_4C_1C_1Im][(C_2F_5)_3PF_3]$ and trihexyl(tetradecyl)phosphonium tris(pentafluoroethyl)trifluoro phosphate $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$. (a) $[C_4C_1C_1Im]^+$, (b) $[P_{6,6,6,14}]^+$ and (c) $[(C_2F_5)_3PF_3]^-$.

steel-aluminium pairs. In the same work they analysed, among others, $[NTf_2]^-$ ILs with the cations $[P_{6,6,6,14}]^+$ and $[C_4C_1Pyrr]^+$ and also an IL composed of the diphenylphosphate anion, $[DPP]^-$, and $[P_{6,6,6,14}]^+$. The lowest friction coefficients were found for $[P_{6,6,6,14}][NTf_2]$, followed by $[P_{6,6,6,14}][DPP]$ and $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$. However, this trend switches when ILs with the cation $[C_4C_1Pyrr]^+$ are compared, as the one with the anion $[(C_2F_5)_3PF_3]^-$ exhibits lower friction than the $[NTf_2]^-$ IL. In terms of wear, ILs with the anion $[(C_2F_5)_3PF_3]^-$ developed better results than the corresponding ILs with the anion $[NTf_2]^-$. A wear trend was also found by Somers et al. [21] depending on the cation type, phosphonium > pyrrolidinium > imidazolium (from better to worse performance). Their results were coherent with the Atkin et al. [22] investigations on IL/metal surfaces, because $[P_{6,6,6,14}]^+$ has a localised charge and longer alkyl chains, which lead to more coherent solvation layers.

$[C_4C_1Pyrr][(C_2F_5)_3PF_3]$ was also tested by González et al. [23] as neat lubricant and as additive to a PAO base oil for the lubrication of CrN, TiN and diamond-like carbon (DLC) coated surfaces. They obtained promising results, particularly for $[C_4C_1Pyrr][(C_2F_5)_3PF_3]$ as neat lubricants. Blanco et al. [24,25] studied the same coatings, TiN [25] and CrN [24], lubricated with a PAO base oil additivated with ethyl-dimethyl-2-methoxyethylammonium tris(pentafluoroethyl)trifluorophosphate. The aim of that study was testing the effectiveness of the IL as additive compared to the traditional additive zinc dialkyldithiophosphate (ZDDP), though better results were obtained for the mixtures with ZDDP.

Most tribological investigation work on ILs as lubricants is based on imidazolium-derived cations [5,15]. However, up to our knowledge, no IL composed of a trialkylimidazolium, $[C_nC_mC_pIm]^+$, cation and a $[(C_2F_5)_3PF_3]^-$ anion has been studied so far with respect to their suitability as lubricant. The ILs with the C2-position substituted in the imidazolium ring are much more chemically stable than the unsubstituted counterparts [26,27]. Furthermore, some tribological investigations with $[C_nC_mC_pIm][NTf_2]$ ILs revealed better friction coefficients and wear performances than the corresponding unsubstituted ILs [28,29]. On the other hand, as exposed before, tetraalkylphosphonium ILs seem to have a high thermal stability [30–32] and a great lubricating potential [18,21,33–41], with some exception [16].

In this fundamental study, the lubricating performances, in terms of friction coefficient and wear volume, of two ionic liquids with the same tris(pentafluoroethyl)trifluorophosphate anion are investigated and compared. The cations are 1-butyl-2,3-dimethylimidazolium, $[C_4C_1C_1Im]^+$, and trihexyl(tetradecyl)phosphonium, $[P_{6,6,6,14}]^+$. Whilst Somers et al. [21] tested the same $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ for a steel on aluminium, in the present work a pair of stainless steel 100Cr6-AISI 420 was used. Furthermore, those materials are different from the pair of stainless steel SUJ2–SUJ2 analysed by Minami et al. [18] with the same IL. These authors have only reported a low friction coefficient for this IL, obtained with a pendulum test under a load of 2.9 N. Neither wear results nor friction load dependencies were evaluated, whereas four different loads (14, 18, 22, and 26 N) were tested in the present work. In addition, in this work X-ray photoelectron spectroscopy (XPS) analyses for the neat ILs and the rubbed surfaces are also shown. We are not aware of any previous XPS study of these neat ILs and surfaces lubricated with them. The friction coefficients and wear volumes were compared with those obtained from two perfluoropolyethers (PFPE) of similar viscosity and under the same tribological conditions.

2. Material and methods

2.1. Chemicals

The ILs used in this study were kindly provided by Merck KGaA (Germany) with specified purity higher than 98%. To remove the residual volatile impurities, before of being used, ILs were treated under vacuum (0.1 Pa) at room temperature, for at least 48 h. This allowed a reduced water content (lower than 112 ppm for $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ and 156 ppm for $[C_4C_1C_1Im][(C_2F_5)_3PF_3]$), which was measured by coulometric titration using a Karl Fisher Mettler Toledo DL32. Molecular structures and some properties of these ILs can be found in Fig. 1 and Table 1, respectively.

Two Krytox® PFPE ($F(CF(CF_3)CF_2O)_nCF_2CF_3$) high performance commercial oils (GPL-104 and GPL-105), kindly provided by Brugarolas (Spain), were also tested for comparison. Both base oils have been chosen because they are fluorinated lubricants and their boundary film formation might be similar to the ILs studied. Some of the properties of the PFPE lubricants are also shown in Table 1.

2.2. Tribo-tests

Friction coefficients were measured with a CSM Standard Tribometer in a ball-on-plate configuration with reciprocating motion. Stainless steel balls AISI 100Cr6 were run against stainless steel plates AISI 420; the characteristics of the tribopair and the test parameters are summarised in Table 2. Before each test, plates were cleaned with hexane and dried in warm air. Then, the flat surfaces were lubricated with five drops of lubricant spread in the contact zone. The test conditions (Table 2) correspond to a boundary lubrication regime according to the lambda ratio calculated with the Hamrock and Downson formula [42], although plastic deformation may occur. At least four replicates were run for each test condition and the friction coefficient was calculated as average of their results but considering only the values after 1000 s. After those tests, the cross-sectional area of the wear tracks was measured at five equidistant points with a diamond-

Table 1
Properties of the lubricants tested. ν: kinematic viscosity at 40 °C and atmospheric pressure; VI: viscosity index; ρ: density at 15 °C and atmospheric pressure; pour point.

Lubricant	ν/cSt	VI	ρ/kg m^{-3}	Pour point/°C
$[C_4C_1C_1Im][(C_2F_5)_3PF_3]$	43.9[50]	107[50]	1609.7[50]	–
$[P_{6,6,6,14}][(C_2F_5)_3PF_3]$	131.4[50]	128[50]	1190.3[50]	–
GPL-104[51]	60	111	1750[a]	−51
GPL-105[51]	160	124	1760[a]	−36

[a] At 100 °C.