ACS APPLIED MATERIALS & INTERFACES

Research Article

www.acsami.org

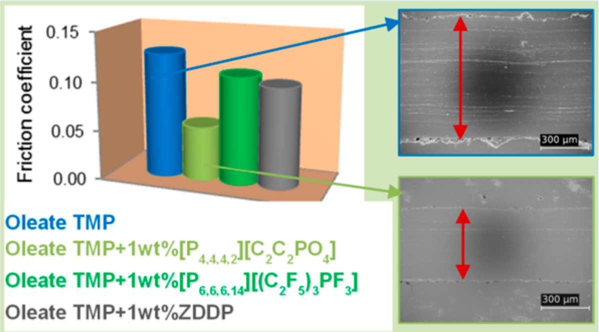
Ionic Liquids Based on Phosphonium Cations As Neat Lubricants or Lubricant Additives for a Steel/Steel Contact

Inés Otero,[†] Enriqueta R. López,[†] Manuela Reichelt,[‡] María Villanueva,[†] Josefa Salgado,[†] and Josefa Fernández*,[†]

[†]Laboratory of Thermophysical Properties of Fluids and Biomaterials, Department of Applied Physics, Faculty of Physics, University of Santiago de Compostela, 15782 Santiago de Compostela, Spain

[‡]Wilhelm Ostwald Institute for Physical and Theoretical Chemistry, University Leipzig, Linnéstr. 2, 04103 Leipzig, Germany

Supporting Information



ABSTRACT: After doing several miscibility essays with eight ionic liquids (ILs) and four base oils, the ILs tri(butyl)ethylphosphonium diethylphosphate [$P_{4,4,4,2}$][$C_2C_2PO_4$] and trihexyl(tetradecyl)phosphonium tris(pentafluoroethyl)trifluorophosphate [$P_{6,6,6,14}$][$(C_2F_5)_3PF_3$] were selected to be studied as lubricant additives. The neat IL [$P_{4,4,4,2}$][$C_2C_2PO_4$], the base oils, and several blends were characterized in terms of density, viscosity, and thermal stability. The tribological performance of the miscible base oil/IL blends (1 wt %) and the neat [$P_{4,4,4,2}$][$C_2C_2PO_4$] were evaluated for the lubrication of an AISI 420 steel−100Cr6 steel contact pair. The friction coefficients and wear volumes obtained are also compared with those corresponding to the pure base oils and their mixtures with conventional additive zinc dialkyldithiophosphate (ZDDP). As neat lubricants, [$P_{4,4,4,2}$][$C_2C_2PO_4$] showed the best antifriction ability, whereas in terms of wear, better results were obtained with [$P_{6,6,6,14}$][$(C_2F_5)_3PF_3$]. However, higher improvements in both friction and wear were found for blends containing [$P_{4,4,4,2}$][$C_2C_2PO_4$]. XPS analyses of the worn surfaces lubricated with these mixtures indicated the presence of phosphorus in the tribofilm formed on the wear track. However, this compound was slightly detected on tribosamples lubricated with blends containing [$P_{6,6,6,14}$][$(C_2F_5)_3PF_3$].

KEYWORDS: *ionic liquid, friction, antiwear additives, base oil miscibility, tribology, surface analysis, thermal stability*

1. INTRODUCTION

The lubrication industry needs to be in continuous development to deal with the technological advances and also to improve their performance in terms of efficiency and environmental considerations.[1] Currently biodegradable based oils are used in the formulation of hydraulic fluids, tractor transmission oils, industrial and marine gear oils, and total loss lubricants, among others. The applications of biodegradable lubricants should be broadly increased in the near future. In the past decade several ILs have been evaluated as lubricants and lubricant additives with promising results.[2−5] However, the replacement of traditional base oils by ILs is currently limited by their cost, as ILs are considerably more expensive. Therefore, the application of ILs as lubricant additives could have much more opportunities, being their use as neat lubricant restricted to specific requirements.[6−8] Nowadays, the environmental restrictions and operational problems of ZDDP (zinc dialkyldithiophosphate),[9] one of the most common lubricant antiwear additives for steel/steel contacts, create a need in the additive field which could be solved by using ILs.[1] Furthermore, there is a trend to use more biodegradable oils and the European Ecolabel, for instance, excludes some elements like Zn in several lubricant formulations.

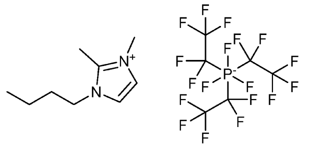
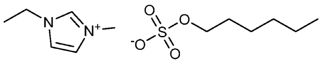
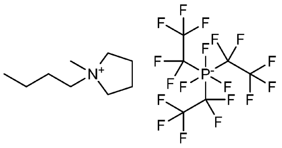
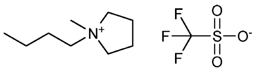
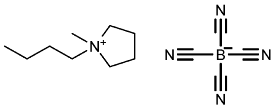
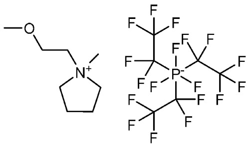
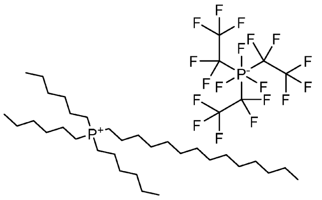
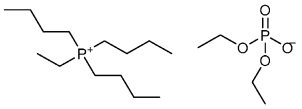
Several ILs have been investigated as lubricant additives showing higher friction reduction and wear protection abilities than the base oil.[10−21] However, the low miscibility of ILs with base oils is an important issue for their application as additives.[22] In general, the ILs miscibility increases with the polarity of the base stock.[12,13] Therefore, a better compatibility was found when ILs were mixed with base oils like ester,[22−24] poly(ethylene glycol),[11,19,21,25] or glycerol.[16,26,27] However, studies with mineral oils[13,17,18,22,28−32] and polyalphaolefins (PAO)[12,14,15,20,22] have also been performed.

In some cases, the IL−base oil mixtures were not completely stable and a creaming phenomenon appeared after a few hours of the mixtures being prepared.[14,15,18,20] In other studies, fully miscibility was found, as reported by Qu et al.[12] for the IL trihexyltetradecylphosphonium bis(2-ethylhexyl) phosphate with different mineral and PAO base oils. Yu et al.[13] have found that this IL and another phosphonium based IL (trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)

Received: May 14, 2014
Accepted: July 21, 2014
Published: July 21, 2014

dx.doi.org/10.1021/am502980m | *ACS Appl. Mater. Interfaces* 2014, 6, 13115−13128

Table 1. Ionic Liquids Used in This Work

IL Name	Reduced name	Structure	Water content (ppm)
1-butyl-2,3-dimethylimidazolium tris(pentafluoroethyl)trifluorophosphate	$[C_4C_1C_1Im][(C_2F_5)_3PF_3]$		35
1-ethyl-3-methylimidazolium hexylsulfate	$[C_2C_1Im][C_6SO_4]$		140
1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate	$[C_4C_1Pyrr][(C_2F_5)_3PF_3]$		45
1-butyl-1-methylpyrrolidinium trifluoromethanesulphonate	$[C_4C_1Pyrr][CF_3SO_3]$		57
1-butyl-1-methylpyrrolidinium tetracyanoborate	$[C_4C_1Pyrr][B(CN)_4]$		81
1-(2-methoxyethyl)-1-methyl-pyrrolidinium tris(pentafluoroethyl)trifluorophosphate	$[C_1OC_2C_1Pyrr][(C_2F_5)_3PF_3]$		26
trihexyl(tetradecyl)phosphonium tris(pentafluoroethyl)trifluorophosphate	$[P_{6,6,6,14}][(C_2F_5)_3PF_3]$		77
tri(butyl)ethylphosphonium diethylphosphate	$[P_{4,4,4,2}][C_2C_2PO_4]$ (Cyphos® 169)		70

phosphinate) were fully miscible in a mineral base SAE 10W and a synthetic PAO at any blend ratio. Recently, Somers et al.[22] studied seven phosphonium based ILs as lubricant additives to a vegetable oil, two polyol esters, a mineral oil, and a PAO base oil. These ILs were the two phosphonium ILs mentioned above, $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$, two pyrrolidinium based ILs and two imidazolium based ILs. Generally, their results showed that only the trihexyltetradecylphosphonium based ILs were miscible in the most polar base oils, whereas those previously studied by Yu et al.[13] and Qu et al.[12] were further miscible in the mineral and PAO base oils. The miscibility of these ILs in nonpolar base oils could be attributed to the three-dimensional quaternary structures with long alkyl chains, that decrease the charge density of the ion, and to the strong interionic interactions, which would reduce the effective polarity of the IL.[12,13,22]

As regards to the tribological behavior of the IL-base oil blends, Somers et al.[22] tested their mixtures for a steel on aluminum contact. The results showed that the friction and wear reduction ability of the ILs as additives was dependent on the performance of the base oil. These authors obtained better results with base oils which were able to keep low values of friction and wear on their own. In the case of the mixtures corresponding to the mineral and PAO base oils, the blends showed lower friction coefficients and wear than the pure base oils. However, this was not always true for the vegetable and polyol ester base oils.[22] The studies made by Ju et al.[13] and Qu et al.[12] with phosphonium ILs as additives for a steel—cast iron contact pair revealed better friction and wear ability in comparison with the behavior of the neat base oil. In addition to the phosphonium based ILs, imidazolium,[11,19,21,23−25,29,33] pyrrolidinium,[16,17,20,26,27] and tetraalkylammonium[14−17,26] based ILs have been also evaluated as lubricant additives in tribological tests showing sometimes significant improvements.

The interest in phosphonium based ILs has increased in the last years. They have been studied for several applications, such as corrosion protection, and their commercial availability has also increased.[34] Regarding their use in lubrication, apart from the above-mentioned use as additives, they have been also tested as neat lubricants, showing better results than imidazolium ILs[35−37] and conventional oils.[38−40]

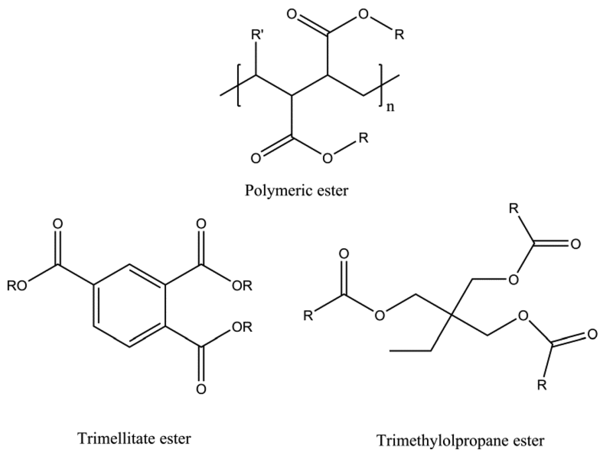
In this fundamental work, with the main aim to find suitable antiwear additives for environmentally acceptable lubricants, several ILs were studied. First, the miscibility of eight imidazolium, pyrrolidinium, and phosphonium based ILs with three synthetic ester base oils and a vegetable oil is analyzed. From them, only the ILs tri(butyl)ethylphosphonium diethylphosphate ($[P_{4,4,4,2}][C_2C_2PO_4]$) and trihexyl(tetradecyl)-phosphonium tris(pentafluoroethyl)trifluorophosphate

($[P_{6,6,6,14}][(C_2F_5)_3PF_3]$) show enough miscibility to be studied as 1 wt % lubricant additives. These two selected ILs, their blends with base oils and the neat base oils are characterized in terms of density, viscosity, and thermal stability. In the case of neat $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$, some of these properties have already been determined.[41,42] The viscosity measurements allow us to verify the single-phase of the blends and to estimate the glass transition temperatures. The tribological performances of the miscible samples and the neat IL $[P_{4,4,4,2}][C_2C_2PO_4]$ are determined in terms of friction coefficient and wear volume for an AISI 420 stainless steel-100Cr6 steel contact pair. To our knowledge $[P_{4,4,4,2}][C_2C_2PO_4]$ has not been previously studied as a lubricant or lubricant additive. The tribological performance of neat $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ under the same conditions was previously reported.[40] These results are also compared to those obtained in this work with the neat base oils and their mixtures with conventional additive ZDDP, as the tribofilms formed with this compound are well-known for their antiwear ability.[43−45] Furthermore, surface analyses using scanning electron microscopy, SEM, and X-ray photoelectron spectroscopy, XPS, are reported.

2. EXPERIMENTAL SECTION

The names, reduced names and structures of the ILs investigated in this work are shown in Table 1. All IL samples were kindly supplied by Merck KGaA (Germany) with specified purities higher than 98% except $[C_4C_1Pyrr][CF_3SO_3]$, which was purchased from IOLITEC (Germany) with a specified purity of 99%, and $[P_{4,4,4,2}][C_2C_2PO_4]$, which was kindly provided by Cytec Industries Inc. (US) with a purity of 96.3%. Prior to being used, ILs were dried under reduced pressure (10 Pa) for at least 48 h in order to remove most water and volatile impurities. The water content after drying was measured by coulometric titration using a Karl Fisher Mettler Toledo DL32. These values are reported in Table 1.

Four base oils were used in this work, a vegetable oil and three synthetic esters. The vegetable oil (VO) is a high oleic sunflower oil with the following composition expressed in mass fraction: palmitic acid ($C_{16:0}$) 4.17%, stearic acid ($C_{18:0}$) 3.30%, oleic acid ($C_{18:1}$) 85.55%, linoleic acid ($C_{18:2}$) 5.43%, arachidic acid ($C_{20:0}$) 0.78%, and behenic acid ($C_{22:0}$) 0.77%.[46] The synthetic esters are a biodegradable polymeric ester (BIOE), a trimethylolpropane trioleate (TMP), and an isotridecyl trimellitate (TTM). General structures of these esters are shown in Figure 1. VO sample was kindly provided by Instituto de la Grasa (Spain) and BIOE, TMP, and TTM were provided by Verkol Lubricantes (Spain).



Polymeric ester

Trimellitate ester

Trimethylolpropane ester

Figure 1. Structures of the polymeric, trimellitate, and trimethylolpropane esters. R = alkyl groups.

Mixtures with a 2 wt % IL in base oils were prepared and homogenized with a sonicator Bandelin Sonopuls HD 2200 for 30 s and 40% power. Three replicates of each blend sample were uprightly stored at 50 °C for 7, 14, and 42 days in order to check their stability. After each period of time, samples were centrifuged (10 min, 1400 rpm) to promote the separation of the immiscible phases. Finally, after around 18 h at room temperature, the concentration of phosphorus or sulfur in the oil-rich phase was determined with an X-ray fluorescence spectrometer. In the case of mixtures with $[C_4C_1Pyrr][B(CN)_4]$, the amount of nitrogen was analyzed by elemental analysis. This procedure allows following the miscibility evolution. Only the miscible samples at least in a concentration of 1 wt % (hereinafter referred to as base oil+1% IL), which remained stable after 42 days, were considered for further measurements. One wt % concentration value was also chosen according to miscibility results and previous literature studies and results with other ILs.[11,15,24,29,32,33]

Thermal analysis techniques were used to know the effect of the ILs on the melting and glass transition points, as well as degradation temperatures, of the mixtures. Differential scanning calorimetry (DSC) was used to check this influence at low temperatures. The experiments were performed on a DSC Q100 TA Instruments under nitrogen atmosphere at a heat rate of 10 °C/min. Each sample was subjected to three dynamic scans: (a) heating from 25 to 100 °C, (b) cooling from +100 °C to −85 °C, and (c) heating from −85 to +25 °C. Among the scans, the sample was isothermally kept for 5 min.

Moreover, thermogravimetric analyses (TGA) were performed on a TGA 7- PerkinElmer to determine the decomposition temperatures. Dynamic scans at 10 °C/min in air atmosphere of the IL ($[P_{4,4,4,2}][C_2C_2PO_4]$), base oils and the miscible blends were carried out. The onset temperature for each sample was determined using the thermal analysis software according to Salgado et al.[47] The thermogravimetric analysis for the neat IL $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ was previously reported.[42]

Density and viscosity measurements, in a temperature range of 5−100 °C and at atmospheric pressure, were performed in a rotational Couette viscometer Anton Paar Stabinger SVM3000, which includes a vibrating tube density meter. A further description of the device can be found in literature.[41] The uncertainty in this equipment is 1% for viscosity and 0.0005 $g\cdot cm^{-3}$ for density. These values were verified measuring reference fluids from Cannon Instrument Comp., N100 and S60. This apparatus also provides the viscosity index (VI).

Tribological tests were performed in a CSM Standard tribometer with a ball-on-plate configuration and reciprocating motion for (a) the neat IL $[P_{4,4,4,2}][C_2C_2PO_4]$, (b) the miscible mixtures containing 1 wt % of ILs, (c) the corresponding four pure base oils, and (d) the mixtures of three of these base oils with 1 wt % ZDDP; ZDDP was not miscible at 1 wt % in the VO oil. The ball, made of 100Cr6 steel, was slid against an AISI 420 stainless steel plate. This tribopair combination, the plate being softer than the ball, was selected due to the experimental procedure for wear volume measurement. The test parameters and the tribopair characteristics are summarized in Table 2. Before each test, plates were ultrasonically cleaned for 20 min in hexane and dried in warm air. Then, five drops of lubricant were spread at the interface prior to start the test. At least four replicates were performed for each operation condition. The friction coefficients were recorded throughout the experiments, but only the values after a duration test of 1000 s were considered to calculate the mean friction coefficient. The wear volume of a track was calculated through the cross sectional area. This was measured with a diamond-tipped stylus profilometer DEKTAK[3] at five equidistant points on the worn track. Then, the mean cross sectional area was calculated. Finally, according to the ASTM G 133-05 standard test method, the wear volume was obtained multiplying the wear track length by the average area. The wear volume reported for each lubricant and load condition is an average of the wear volume obtained in at least four worn tracks.

Surface analyses were performed on the worn tracks obtained under the 22 N load, as greater morphological changes and reactivity were expected than under lower loads. The worn surface morphology was examined, after being rinsed with acetone and hexane, with a Carl Zeiss FESEM ULTRA Plus Scanning Electron Microscope (SEM). In addition, X-ray photoelectron spectroscopy (XPS) was applied to

Table 2. Test Conditions and Tribopairs

tests parameters		tribopairs		
normal load (N)	max. contact pressure (GPa)		ball	plate
14	1.60	material	steel 100Cr6	stainless steel AISI 420
18[a]	1.74			
22	1.86			
26[a]	1.96			
stroke	10 mm	dimensions (mm)	ø6	40.5 × 21 × 5
max. sliding speed	0.1 $m \cdot s^{-1}$	hardness	803 HV	194 HV
sliding distance	100 m	surface roughness	<0.032 μm	<0.080 μm
sliding time	1570 s			
frequency	3.2 Hz			
lubricant volume	5 drops			
temp	room temp			

[a] Only for the neat ILs.

investigate the tribochemical reactivity and film composition. For this purpose, the most reactive elements from the ILs and iron were analyzed on the wear scars. Previously, samples were ultrasonically cleaned in acetone (neat ILs) or only rinsed with acetone (base oils and mixtures). XPS analyses was executed with the nonmonochromatic Mg Kα X-ray source XR 50 (1253.6 eV) and the hemispherical analyzer PHOIBOS 100-MCD5. The equipment was manufactured by SPECS and is described in detail elsewhere.[48] First, a survey spectrum at a pass energy of 100 eV and a step size of 1 eV was recorded for each tribo sample to get the different expected signals and to exclude any impurities. The core level spectra of each element were performed at 50 eV pass energy, 0.1 eV step size and good counting statistics (average over 15 times). For the neat IL $[P_{4,4,4,2}][C_2C_2PO_4]$, the survey spectrum at 50 eV pass energy and the core level spectra, at pass energy of 50 and 10 eV, were obtained. Further information about the used procedure can be found in literature.[40,48]

3. RESULTS AND DISCUSSION

Blending. From all the ILs tested (Table 1), only the phosphonium based ILs, IL $[P_{4,4,4,2}][C_2C_2PO_4]$ and $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$, lead to stable mixtures with almost all the base oils tested, as above commented. Somers et al.[22] have recently also found that imidazolium and pyrrolidinium based ILs are not miscible in base oils similar to those used in this study. Yu et al.[13] explain this behavior assuming that the three-dimensional quaternary structures of phosphonium cation with long alkyl chains diminish the charge density of the ions and improve the compatibility with oil molecules.

In the case of $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$, it was miscible in the four base oils tested. Their mixtures were stable during the 42 days. The IL $[P_{4,4,4,2}][C_2C_2PO_4]$ was miscible, in a concentration of 2 wt %, in all the base oils tested except TTM. For this base oil, the mixture showed turbidity when it was prepared, whereas the others were completely transparent. After 7 days of being prepared and centrifugation, the IL was settled at the bottom of the mixture with TTM base oil. In contrast, for all the other base oils, $[P_{4,4,4,2}][C_2C_2PO_4]$ settling was not observed and their concentration was uniform for the 42 days. All base oils are ester type containing long alkyl chains, but the TTM molecule contains a benzene ring (Figure 1). For aromatic esters the carbon−oxygen double bond is conjugated with the π-bonding. This could be the reason for the lower miscibility of $[P_{4,4,4,2}][C_2C_2PO_4]$ in this oil compared to that in nonaromatic ester base oils. The longer hydrocarbon chains in $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ may be responsible for its miscibility in TTM. Accordingly to Somers et al.[22] and Yu et al.,[13] ILs with long hydrocarbon chains are well matched with base oil structures. Besides, the long alkyl chains lower polarity because of their shielding effect against the charges and the inductive effects which weaken the positive charge of phosphorus.

Density and Viscosity. The viscosity index (VI), density at 20 °C, and viscosity at two temperatures (40 and 100 °C) for the selected neat ILs, base oils and blends are summarized in Table 3. A table containing all density and viscosity data measured in the temperature range of 5 to 100 °C is shown in the Supporting Information SI 1. $[P_{4,4,4,2}][C_2C_2PO_4]$ has higher viscosity than $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ but a lower viscosity index. Therefore, the difference between their viscosity values becomes narrower as the temperature increases. The VI for the neat ILs and neat base oils increases in this order: TTM < $[P_{4,4,4,2}][C_2C_2PO_4]$ < $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ < BIOE < TMP < VO. The low VI for TTM compared to the other base oils could be explained by the presence of a cyclic group, as it is known that they decrease this property.[49] For all the blends tested, the addition of IL slightly

Table 3. Properties at Atmospheric Pressure of the Lubricants Tested: Base Oils, ILs, and Blends[a]

lubricant	T_{onset}/°C[b]	T_g/°C[c]	VI	ρ /$kg \cdot m^{-3}$	ν/cSt	
				20 °C	40 °C	100 °C
$[P_{4,4,4,2}][C_2C_2PO_4]$	296	−73	82.3	1012.8	224.9	17.53
$[P_{6,6,6,14}][(C_2F_5)_3PF_3]$	363[42]	−93[41]	128[41]	1186[41]	131.4[d]	15.67[d]
BIOE	427	−79	155.4	942.4	487.3	47.37
BIOE+1%$[P_{4,4,4,2}][C_2C_2PO_4]$	411	−80	153.6	942.6	503.7	48.07
BIOE+1%$[P_{6,6,6,14}][(C_2F_5)_3PF_3]$	427	−80	154.1	944.0	487.4	47.15
TMP	397	−94	186.2	916.0	48.52	9.568
TMP+1%$[P_{4,4,4,2}][C_2C_2PO_4]$	337	−94	183.5	917.1	51.00	9.837
TMP+1%$[P_{6,6,6,14}][(C_2F_5)_3PF_3]$	388	−94	183.6	918.3	50.25	9.681
TTM	360	−66	73.6	954.4	317.3	20.69
TTM+1%$[P_{6,6,6,14}][(C_2F_5)_3PF_3]$	350	−66	73.1	956.3	316.1	20.53
VO	390	−93	196.6	914.1	41.95	8.799
VO+1%$[P_{4,4,4,2}][C_2C_2PO_4]$	380	−93	194.8	915.1	43.64	9.026
VO+1%$[P_{6,6,6,14}][(C_2F_5)_3PF_3]$	376	−93	194	916.4	43.17	8.948

[a] % means wt%. Onset temperature, T_{onset}; glass transition temperature, T_g; viscosity index, VI; density, ρ; kinematic viscosity, ν. [b] Expanded standard uncertainties are U(T_{onset}) = ±6 °C. [c] Calculated from the VFT correlation. [d] Calculated from ref 41.

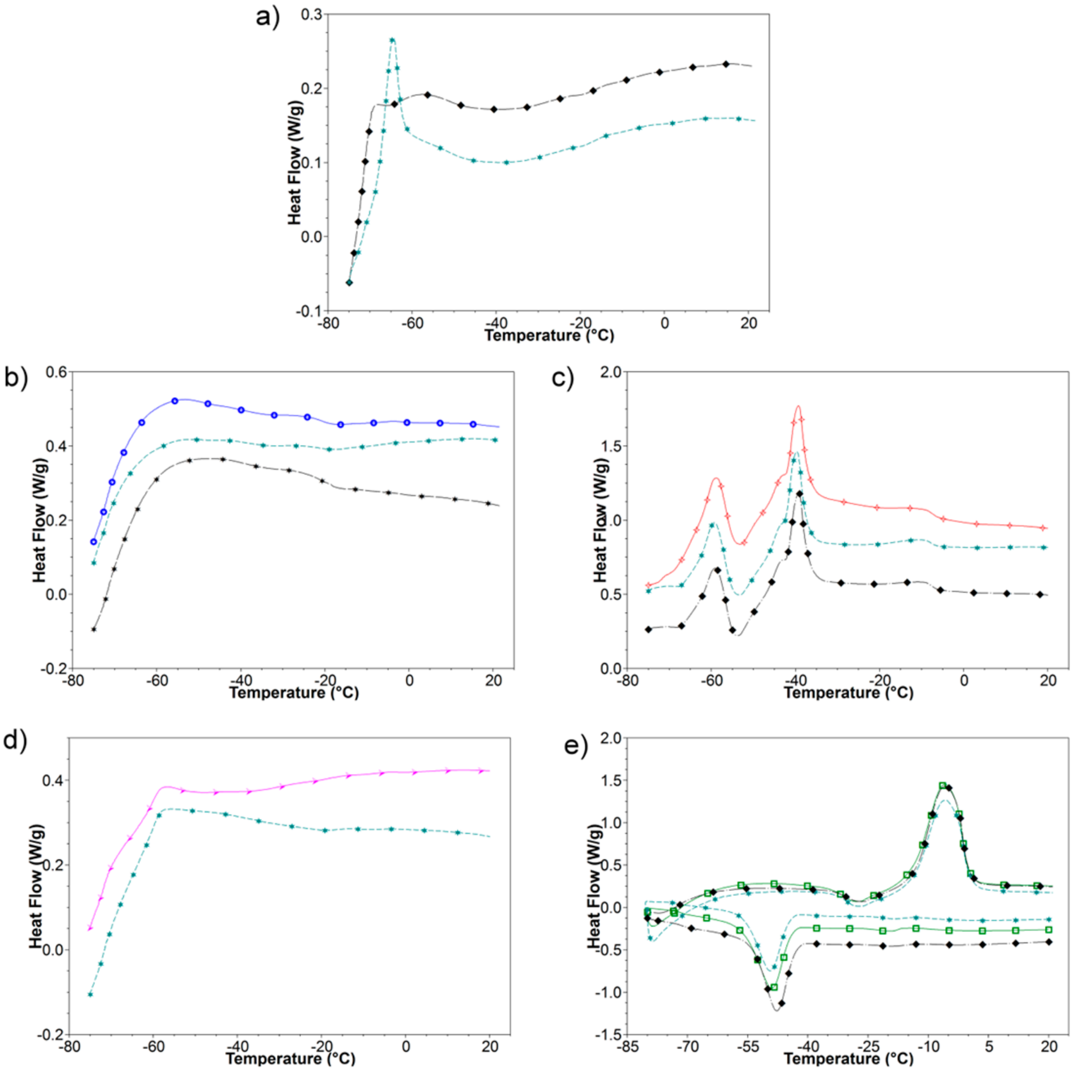


Figure 2. DSC curves for the (a) neat ILs and (b-e) neat base oils and corresponding blends (exothermic: down). (a–d) on heating and (e) heating (superior) and cooling (inferior) cycle. Symbols are only used to facilitate the identification of the curves. (a) $[P_{4,4,4,2}][C_2C_2PO_4]$ ♦, $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ blue *. (b) BIOE blue circle, BIOE+1%$[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ blue *, BIOE+1%$[P_{4,4,4,2}][C_2C_2PO_4]$ ♦. (c) TMP red diamond, TMP+1%$[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ blue *, TMP+1%$[P_{4,4,4,2}][C_2C_2PO_4]$ ♦. (d) TTM pink triangle, TTM+1%$[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ blue *. (e) VO green box, VO+1%$[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ blue *, VO+1%$[P_{4,4,4,2}][C_2C_2PO_4]$ ♦.

reduces the VI compared to the neat base oil. In general, blends for both ILs have higher viscosity than the corresponding base oil (except BIOE+1%$[P_{6,6,6,14}][(C_2F_5)_3PF_3]$), the difference being larger for mixtures with $[P_{4,4,4,2}][C_2C_2PO_4]$. On the other hand, the analysis of the density data shows that the addition of both ILs increases also the values compared to the base oil, but in this case are the blends containing $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ those with higher density.

The experimental viscosity values of the blends were compared with those obtained through the Refutas equation[50] in order to verify that they are single phase fluids (not emulsions). The viscosity of a blend of two or more liquids (single phase) can be estimated as a function of their individual viscosities and the blend ratio as indicated in the Supporting Information (SI 2). This procedure has been previously used by other authors.[12,13] The experimental and calculated viscosity values of the blends are shown in Figure 1 in SI 2. The experimental data are in good agreement with those calculated using the Refutas method. Therefore, this fact indicates that ILs are miscible in the base oils and their blends are single-phase mixtures.

The experimental viscosity data of all the samples were also well correlated using the model of Vogel−Fulcher−Tammann (VFT). The parameters and deviations of this correlation are shown in the Supporting Information (SI 3, Table 3). Using this correlation, the glass transition temperatures (T_g) were calculated taking into account that T_g can be defined as that of the liquid when its shear viscosity is 10^{12} Pa·s.[41,51,52] These calculated T_g values are shown in Table 3.

Thermal Analysis. DSC curves corresponding to the heating step experiments for the different studied lubricants are plotted in Figure 2. For the $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ IL (Figure 2a), it can be observed a narrow endothermic peak with a maximum at −65 °C, which can be attributed to a melting transition. The second IL, $[P_{4,4,4,2}][C_2C_2PO_4]$ also shows an endothermic peak at −58 °C, likely associated with a melting transition, but in this case is wider and smaller than the above-mentioned. Glass transition around −72 °C was detected for $[P_{4,4,4,2}][C_2C_2PO_4]$ whereas for $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ this kind of transition was not found in the studied temperature interval. According to the calculated T_g values (Table 3), the glass transition for $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ occurs at −93 °C, which is out of the DSC measurement range. The glass transition detected for $[P_{4,4,4,2}][C_2C_2PO_{4,}]$ agrees with the calculated T_g value (−73 °C) in Table 3 and also with the value (−69 °C) reported by Green et al.[53] from DSC.

Regarding to the mixtures (Figure 2b−e), the addition of 1 wt % of $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ or $[P_{4,4,4,2}][C_2C_2PO_4]$ to the base oils almost did not affect their thermal behavior. In case of BIOE and TTM base oils and blends (Figure 2b,d) neither glass transitions nor melt processes were distinguished. However, the calculated T_g values indicate that the glass transition occurs at around −80 °C for the three BIOE samples and −66 °C for the TTM samples. The values obtained for T_g from viscosity can differ from those determined by DSC, as already explained in literature.[54−56] In addition, the small heat flux associated with glass transitions is difficult to detect near the limits of the temperature range of our apparatus. For TMP and VO samples (base oil and blends) glass transitions and melting peaks were observed (Figure 2c,e). In case of TMP samples (neat oil and mixtures), two endothermic peaks at −59 and −39 °C were recorded. These can be related to a cold crystallization and a further melt process in the samples, respectively. For VO samples (neat oil and mixtures), an exothermic peak at −25 °C was registered, and it could be associated with a solid−solid transition previous to a melting process, at −6 °C. As regard to the cooling processes, no freezing peaks were detected except for the VO base oil and mixtures (around −48 °C). Large differences between the freezing and melting points (in this case 42 °C) were also observed for several ILs. This could be the reason why no freezing points were detected for samples with the lowest melting points.

TGA curves for $[P_{4,4,4,2}][C_2C_2PO_4]$ IL, base oils and their blends are presented in Figure 3. As it can be seen, only the degradation of the IL was a multiple-step process, whereas for the base oils and blends only a single degradation step was observed. An initial early weight loss was found only for the neat IL, which could be related to its hygroscopicity. A similar behavior for $[P_{4,4,4,2}][C_2C_2PO_4]$ was reported by Green et al.,[53] although these authors obtained an onset temperature value of 313 °C, which is 17 °C higher than that here presented (Table 3). This difference can be due to the different experimental conditions employed;[47,57] as example, in this work air atmosphere was used instead of nitrogen atmosphere employed by Green et al. A multiple step degradation process was also reported by Salgado et al.[47] for $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$, although in that case, the different steps were not as resolved as those of $[P_{4,4,4,2}][C_2C_2PO_4]$. The TGA curves of blends with $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ also showed a single degradation step. The thermal stabilities of both ILs are not as good as $[NTf_2]^-$ based ILs.[47,58]

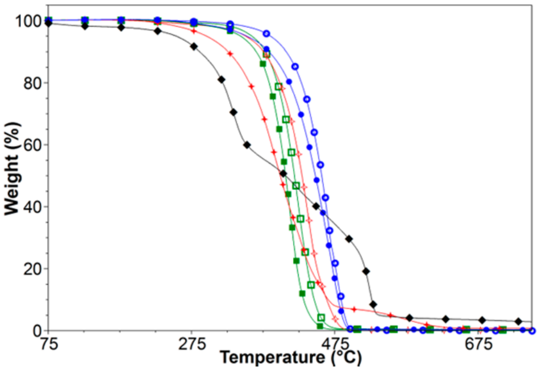


Figure 3. TGA curves for the neat IL $[P_{4,4,4,2}][C_2C_2PO_4]$ ♦, base oils (BIOE open blue circle, TMP open red diamond, and VO open green square) and their blends (BIOE+1% $[P_{4,4,4,2}][C_2C_2PO_4]$ filled blue circle, TMP+1%$[P_{4,4,4,2}][C_2C_2PO_4]$ filled red diamond, and VO +1%$[P_{4,4,4,2}][C_2C_2PO_4]$ filled green square). Symbols are only used to facilitate the identification of the curves.

Table 3 summarizes the onset temperatures obtained in TGA scans for $[P_{4,4,4,2}][C_2C_2PO_4]$, $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$, the base oils, and the corresponding blends. As it was above-mentioned, although this temperature never can reflect the maximum temperature operation, it can be used as a relative parameter to compare the thermal stability of different materials.[47] As it can be seen, ILs show lower stability than the base oils, except for $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ and the base oil TTM which have comparable results (363 and 360 °C, respectively). Taking into account the values reported in Table 3, the thermal stability of base oils and ILs is in the temperature range of 296−427 °C and follows the trend: $[P_{4,4,4,2}][C_2C_2PO_4]$ < TTM ≈ $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ < VO < TMP < BIOE. In general, it can be concluded that the addition of the studied ILs to the selected base oils seems to reduce slightly the thermal stability of the base oils, being this reduction usually higher for blends with $[P_{4,4,4,2}][C_2C_2PO_4]$.

As it is well-known, the thermal stability of a sample depends strongly on the experimental conditions; thus, for a closer study of this property, isothermal scans are recommended by several authors.[47,57,59] For this reason, thermogravimetric essays at 200 °C, which is more close to the maximum lubricant temperature in the current applications for this kind of biodegradable base oils, were performed for the IL, base oil and the corresponding blend that presents the highest difference on the T_{onset}, i.e., $[P_{4,4,4,2}][C_2C_2PO_4]$, TMP and the mixture TMP+1% $[P_{4,4,4,2}][C_2C_2PO_4]$. The results are shown in Figure 4 and it can be seen that, despite the IL presents lower thermal stability than the base oil, with a weight loss higher than 10% in 5 h, no significant differences between the base and the corresponding blend were observed.

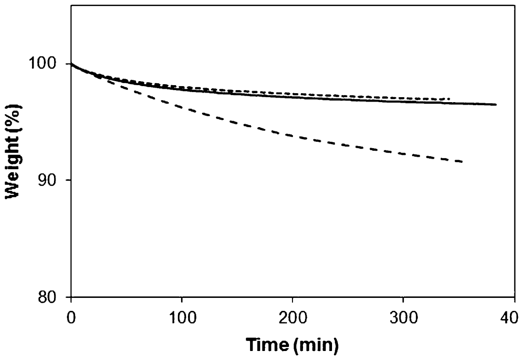


Figure 4. Isothermal scans of IL $[P_{4,4,4,2}][C_2C_2PO_4]$ (long dashed line), TMP (solid line) and TMP+1% $[P_{4,4,4,2}][C_2C_2PO_4]$ (short dashed line).

Friction and Wear. The average friction coefficients and wear volume results for the neat ILs tested under four different loads (14, 18, 22, and 26 N) are summarized in Figure 5. It can be observed that $[P_{4,4,4,2}][C_2C_2PO_4]$ has a good friction reduction ability, as the friction coefficients obtained are below 0.08 for all the loads applied. On the other hand, $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ shows a higher dependency on the load applied, reaching the

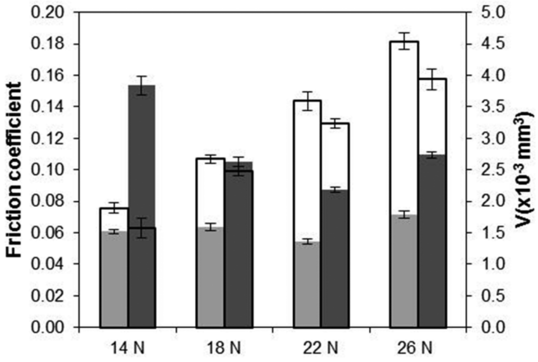


Figure 5. Friction coefficients (in gray) and wear volumes (without fill color) for the neat ILs (light gray box) $[P_{4,4,4,2}][C_2C_2PO_4]$ and (dark gray box) $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ under four different loads. The results for $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ have been published before[40] and are included here just for an easier comparison. Bars show the standard error of the mean.

highest value (0.153) under a load of 14 N and the lowest one (0.088) at 22 N. In any case, its friction protection is worse than that obtained with $[P_{4,4,4,2}][C_2C_2PO_4]$. Regarding to the wear volume results, $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ led to lower values than $[P_{4,4,4,2}][C_2C_2PO_4]$ for all the loads, except for 18 N where both reach almost the same value.

The friction coefficients and wear volumes under 14 and 22 N loads for the neat base oils and their blends with 1 wt % IL and ZDDP are plotted in Figure 6. Regarding to the base oils, it can be observed that BIOE (Figure 6a) leads to much lower friction coefficients than the other three base oils, which have shown similar behavior. In terms of wear volume, BIOE and TTM (Figure 6c) were the most protective, obtaining comparable values as those measured for the neat ILs (Figure 5). However, the base oils TMP (Figure 6b) and VO (Figure 6d) led to huge wear volumes, which were approximately 20 times higher than those of the other base oils. This behavior could be related with the viscosity values of the base oils (Table 3). In fact, those more viscous lead to lower wear volumes. In addition, similar base oils as VO and TMP were tested by Somers et al.[22] for a steel-aluminum contact pair. These authors have also obtained a poor wear performance for them, which was attributed to tribocorrosion due to the oxygen reactivity of the ester groups.[22] Therefore, it could be expected that the same problem affects the steel surface. In the case of the TTM base oil, the carbon−oxygen double bond is conjugated with the aromatic ring and thus it is more stable.[49]

Regarding to the BIOE blends (Figure 6a) the friction coefficient was slightly reduced (around 19% for both loads) when $[P_{4,4,4,2}][C_2C_2PO_4]$ was used as additive compared to the results from the base oil. This reduction was similar to that reached using ZDDP as additive and under a load of 14 N. However, under a load of 22 N, the blend BIOE+1%$[P_{4,4,4,2}][C_2C_2PO_4]$ was slightly better than BIOE+1%ZDDP. With regard to the other IL, $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ almost did not improve the friction coefficient. In fact, the blend BIOE +1%$[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ under a load of 14 N showed worse friction behavior than the base oil. However, only this IL as additive to BIOE was able to reduce the wear volume (about 13% under a load of 22 N) almost in the same order as the ZDDP mixture.

On the other hand, higher friction and wear reductions can be observed for the blends corresponding to TMP base oil (Figure 6b). Both ILs as additives reduced the friction coefficient compared to this base oil. This reduction was higher with the

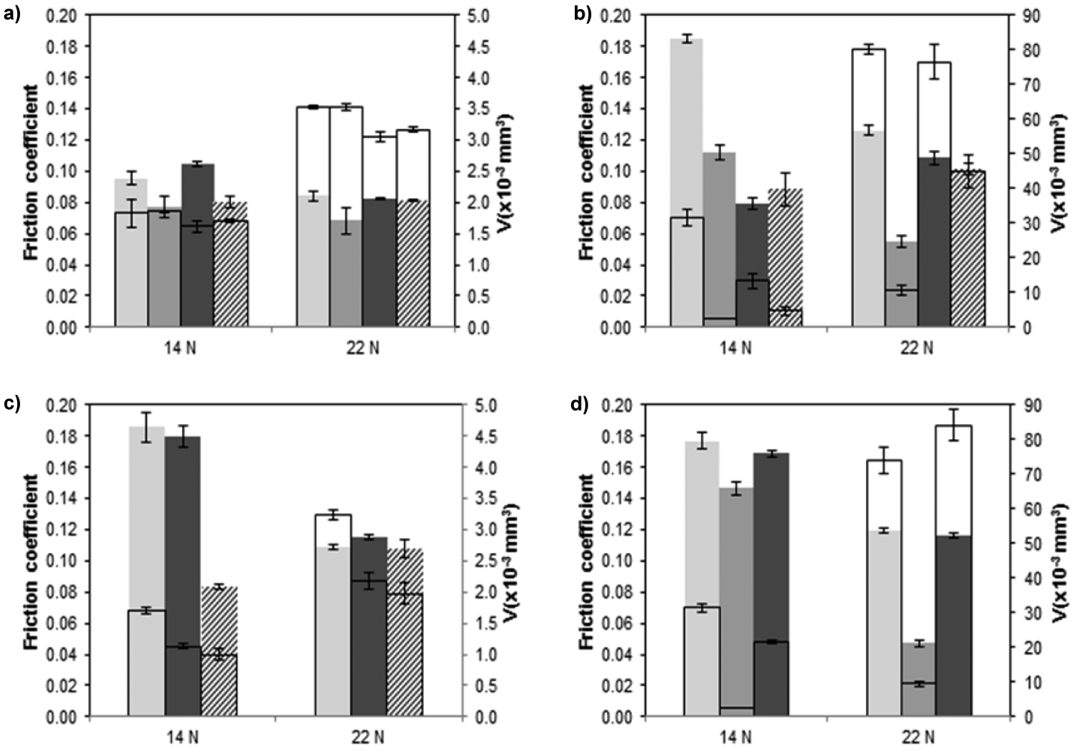


Figure 6. Friction coefficients (in gray) and wear volumes (without fill color) obtained for the neat base oils (light gray) (a) BIOE, (b) TMP, (c) TTM, and (d) VO and their respective mixtures with (medium gray) $[P_{4,4,4,2}][C_2C_2PO_4]$, (dark gray) $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$, and (lined gray) ZDDP. Bars show the standard error of the mean.

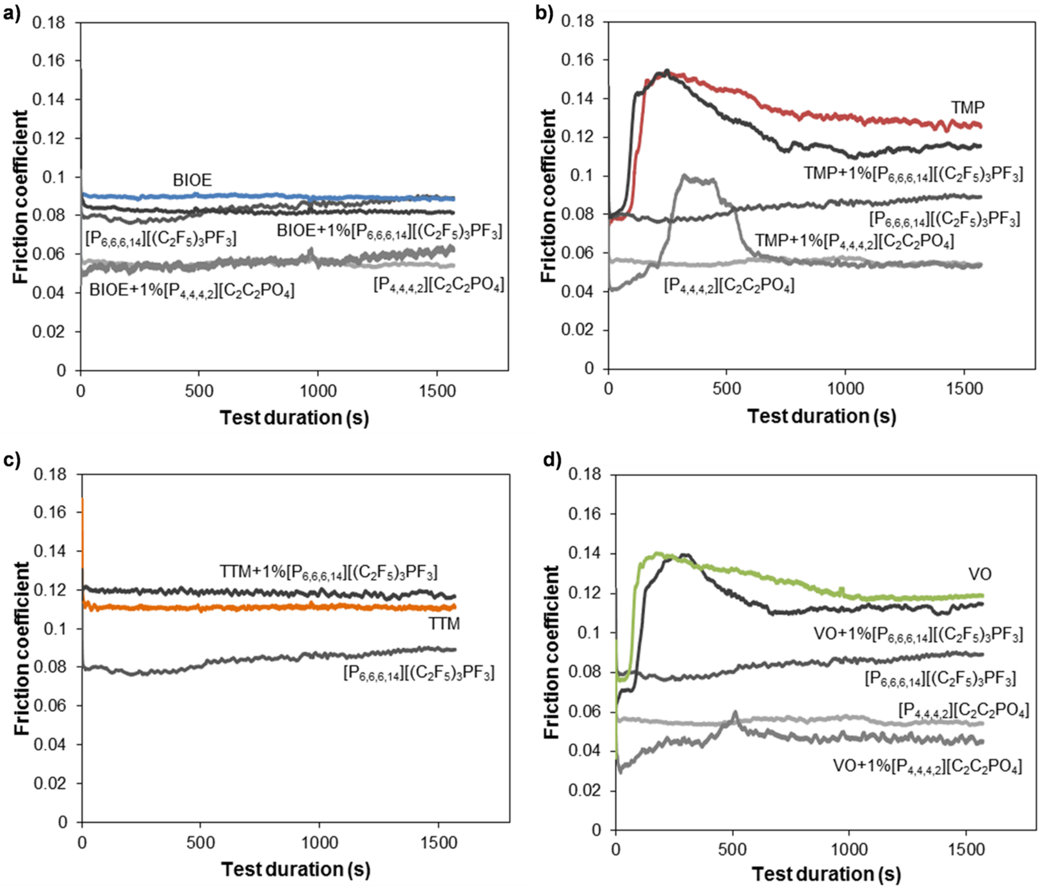


Figure 7. Friction-time records under a load of 22 N for the base oils BIOE (a), TMP (b), TTM (c), and VO (d), neat ILs and their mixtures, respectively.

blend containing $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ under a load of 14 N (decrease of 57%), whereas under a load of 22 N the lowest value was obtained with the blend corresponding to $[P_{4,4,4,2}][C_2C_2PO_4]$ (decrease of 57%). In addition, the friction coefficient reached under a load of 22 N with the blend containing $[P_{4,4,4,2}][C_2C_2PO_4]$ was 45% lower than that obtained with TMP+1%ZDDP. However, as it has been pointed out before, the problem with this base oil is the great wear volume. High wear reductions were found specially for the blend with $[P_{4,4,4,2}][C_2C_2PO_4]$ at 14 N, although this value (2.5 x10^{-3} mm^3) was higher than the obtained with the other neat base oils BIOE and TTM or the neat ILs.

The base oil TTM, which mixtures were only studied loaded with $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ and ZDDP, was almost not improved in terms of friction coefficient using this IL as additive. In fact, with this blend higher friction coefficient was obtained than with the neat base oil for a load of 22 N. On the other hand, the wear reduction (32%) was more noticeable, although lower than the obtained for the mixture with ZDDP (40%).

Finally, for the base oil VO it can be seen (Figure 6d) that the addition of $[P_{4,4,4,2}][C_2C_2PO_4]$ shows a good friction reduction at a load of 22 N, as the friction coefficient was 0.047. However, the wear volume, which was reduced by 87% is still high (9.5×10^{-3} mm^3). The use of $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ as additive to this base oil had less positive effects. Thus, despite of the qualitative wear reduction at a load of 14 N, for the load of 22 N the wear volume measured was even slightly higher than that obtained with the neat base oil. Our results agree with those reported by Somers et al.[22] as we have also seen that (1) the tribological behavior of blends depends on the performance of the base oils and (2) the addition of fluorine-containing ILs to VO and TMP base oils does not improve their performance. As explanation for this fact it has been proposed that the IL may strongly interact with the VO and TMP oils and therefore is less available to form films at the metal surface.[22]

In order to better understand the friction protection ability of the base oils and their blends with ILs, representative friction-time records corresponding to the tests under 22 N are shown in Figure 7. It can be seen that for the base oils TMP (Figure 7b) and VO (Figure 7d) the friction coefficient increases during the first 250 s and then decreases slowly until reaches a steady state. However, this high friction coefficient period was not observable with the base oils BIOE (Figure 7a) or TTM (Figure 7c). The different behavior found in the tests lubricated with TMP and VO could be related to tribocorrosion and changes in the plate surface, like the formation of wear debris. This hypothesis is in agreement with the wear volume results, as TMP and VO led to huge wear volume compared with TTM and BIOE oils. Similar time-friction coefficient variations, where a sharp increment in the friction coefficient can be seen, were reported by Jimenez et al.[29] for a steel-aluminum contact lubricated with a neat ionic liquid. These authors explain that the sudden increment in friction was at the same time as the formation of large amounts of wear debris. Then, the friction coefficient decreased again when the wear debris was removed from the test path.

In the case of the IL blends, it can be observed that the use of $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ as additive did not lower the initial high friction coefficient reached with the neat base oils TMP or VO.

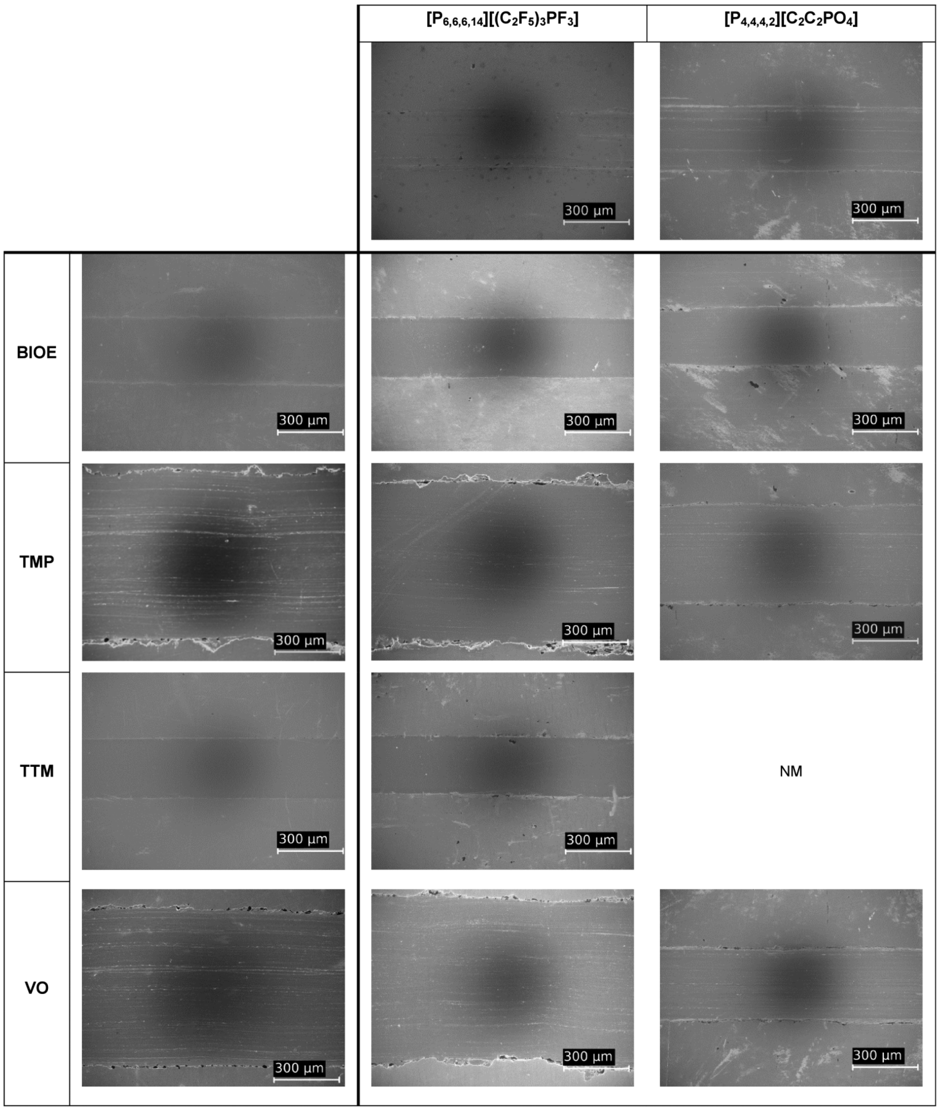


Figure 8. SEM images (250×) of the worn steel plates lubricated with neat ILs (first row), neat base oils (first column), and blends (row and column combination) after tribological test under a load of 22 N. The total width of the worn track is shown. NM: not measured.

However, for the blends containing $[P_{4,4,4,2}][C_2C_2PO_4]$ the friction coefficient increment was significantly smaller, especially for the blend with VO base oil.

Surface Analysis. After the tribological tests, SEM images of the worn steel plates tested under the load of 22 N were taken. The total width of the worn tracks obtained with all the lubricants studied can be compared in Figure 8. These SEM images are in agreement with the wear volume results (Figure 6). It can be easily appreciated the significant wear reduction when $[P_{4,4,4,2}]$-$[C_2C_2PO_4]$ was used as additive to TMP and VO base oils. In addition, it can be also noted that the base oils TMP and VO lead to the highest wear and surface damage, such as ploughing. SEM images with higher magnification are presented for the base oil VO and the blend VO+1%$[P_{4,4,4,2}][C_2C_2PO_4]$ in Figure 9. Stronger fractures on the surface lubricated with VO (Figure 9a) compared to the one lubricated with VO+1%$[P_{4,4,4,2}][C_2C_2PO_4]$ (Figure 9b) can be seen.

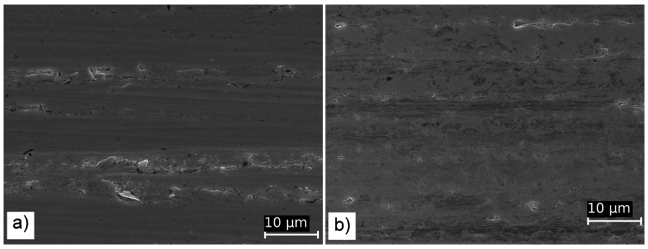
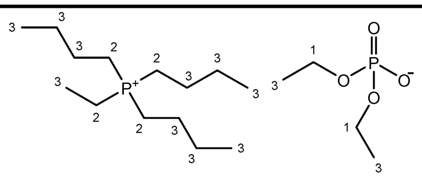
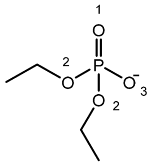


Figure 9. SEM images (5000×) of the worn steel plates lubricated with a) VO and b) VO+1%$[P_{4,4,4,2}][C_2C_2PO_4]$ after tribological test under a load of 22 N.

XPS analyses were performed on the wear tracks of the plates lubricated with the neat ILs ($[P_{4,4,4,2}][C_2C_2PO_4]$ and $[P_{6,6,6,14}]$-$[(C_2F_5)_3PF_3]$), neat base oils and blends. For all these lubricants, the worn plates obtained under a load of 22 N were analyzed. In addition, for $[P_{4,4,4,2}][C_2C_2PO_4]$, the sample tested under the load of 26 N was also examined. The XPS results for the same tribo-conditions lubricated with $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ have been already published.[40] Besides, XPS analyses were conducted on the neat IL $[P_{4,4,4,2}][C_2C_2PO_4]$ liquid sample. The corresponding XPS results for the neat IL $[P_{4,4,4,2}][C_2C_2PO_4]$ are summarized in Table 4. The equivalent XPS results for neat $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ have been already reported by the authors.[40] The Fe 2p, F 1s, P 2p, and O 1s core level spectra

Table 4. XPS Results for the Neat IL $[P_{4,4,4,2}][C_2C_2P]$

IL	Spectrum	Species	Binding Energy (eV)
$[P_{4,4,4,2}][C_2C_2PO_4]$	C 1s		1) 286.5 2) 285.6 3) 285.0
	O 1s		1) 532.5 2) 531.9 3) 530.0
	P 2p	1) P from the anion 2) P from the cation	1) 132.9 2) 132.5

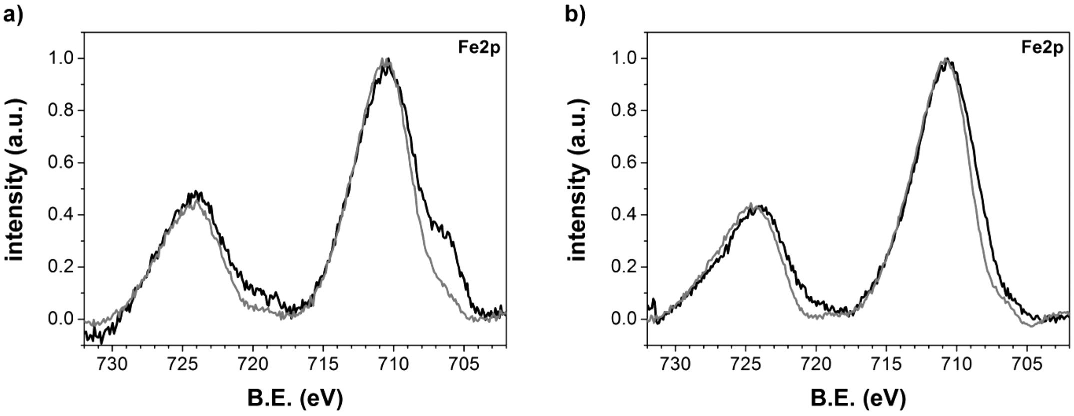


Figure 10. Fe 2p core level spectra of worn surface on steel plate lubricated with (a) $[P_{4,4,4,2}][C_2C_2PO_4]$ and (b) $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ under loads of 22 N (gray line) and 26 N (black line).

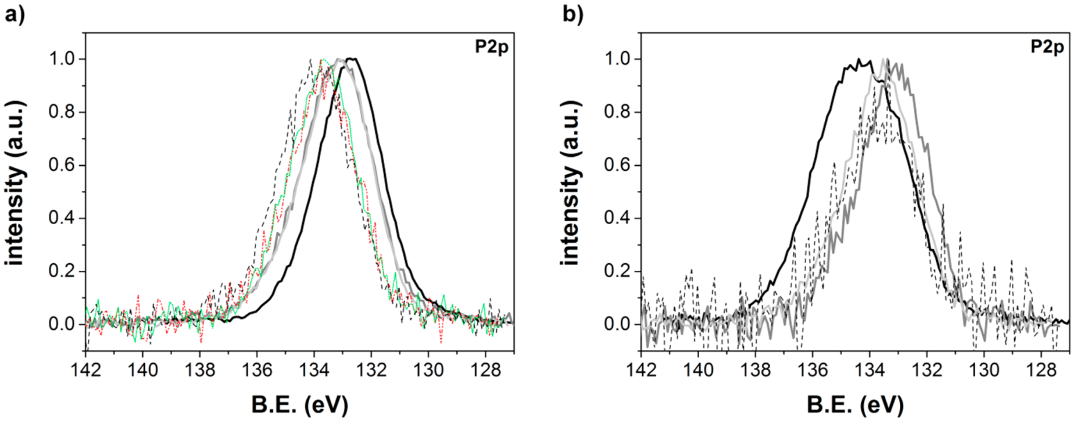


Figure 11. (a) P 2p core level spectra of neat $[P_{4,4,4,2}][C_2C_2PO_4]$ (black line) and worn surfaces on steel plate lubricated with $[P_{4,4,4,2}][C_2C_2PO_4]$ under the loads of 22 N (light gray line) and 26 N (dark gray line) and with the mixtures (22 N) BIOE+1%$[P_{4,4,4,2}][C_2C_2PO_4]$ (red dash-dot line), TMP +1%$[P_{4,4,4,2}][C_2C_2PO_4]$ (green dotted line) and VO+1%$[P_{4,4,4,2}][C_2C_2PO_4]$ (black dashed line). (b) P 2p core level spectra of neat $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ (black line) and worn surfaces on steel plate lubricated with $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ under the loads of 22 N (light gray line) and 26 N (dark gray line) and with the mixture VO+1%$[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ (black dashed line).

obtained on the wear tracks of each lubricant were compared to determine the influence of the addition 1 wt % IL to the base oils on the tribochemical reactivity. In addition, the load effect was also investigated for neat ILs.

The Fe 2p spectra from the neat IL tribosamples (Figure 10) show a fourth iron species which was not found on the worn surfaces lubricated with the neat base oils nor with the blends (The Fe 2p spectra for the latter are shown in Figure S2 in the Supporting Information SI 4). The above-mentioned iron species at a binding energy (B.E.) of approximately 706.6−707.1 eV might be attributed to Fe_2P[39] or FeP.[60,61] Elemental iron exhibits also a B.E. within this energy region. If the found signal results from elemental iron it can only be an effect of material removal during the tribotest. Indeed, we have not found any correlation between the wear volume and the fourth iron species. Therefore, it is more probably that this signal originates from Fe_2P or FeP. The most intense signal was obtained in case of $[P_{4,4,4,2}][C_2C_2PO_4]$ at a load of 26 N. Under a lower load, the intensity decreases. It has been reported that the IL reactivity might be inhibited, if the load applied is not high enough.[35] For $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ under 22 N load, the existence of a fourth species (a really small amount) was found during data evaluation (fitting procedure). In fact, in our previous article,[40] where the XPS data for $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ corresponding to a load of 26 N were published, only three species were identified. However, after seeing the results for the load of 22 N, a marginally better fit was achieved with four species. The Fe 2p spectrum for the load of 26 N is also slightly different compared to the 22 N load sample. But the effect is much weaker than for $[P_{4,4,4,2}][C_2C_2PO_4]$. Likely, the longer alkyl chains of the cation $[P_{6,6,6,14}]^+$ compared to $[P_{4,4,4,2}]^+$ have a moderating effect on the $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ reactivity. The three common species found on the wear scars for all lubricants were Fe_2O_3 and/or Fe_3O_4 at a B.E. around 710.4−710.5 eV; FeO at a B.E. of approximately 709.5−709.6 eV; and a third species at a B.E. of 713.0 eV which could be attributed to different surface structures.

The P 2p core level spectra for the neat $[P_{4,4,4,2}][C_2C_2PO_4]$, the tribosamples lubricated with this IL (loads of 22 and 26 N) and with the corresponding blends (load of 22 N) are shown in Figure 11a. The analogous figure for the IL $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ is presented in Figure 11b. In both figures it can be seen that the corresponding P 2p signal at a B.E. of 129.5 eV, which could be attributed to Fe_2P or FeP,[60] was not found on the wear scars lubricated with any IL. P 2p exhibits a very low photoionization cross section. On the other hand, if the results from the tribosamples are compared with those from the neat ILs, some differences can be seen. In the case of $[P_{4,4,4,2}][C_2C_2PO_4]$ (Figure 11a), the maximum position is shifted to larger binding energies for all the tribosamples. This shift is slightly higher in the case of the mixtures than in the samples lubricated with neat $[P_{4,4,4,2}][C_2C_2PO_4]$. Besides, for the tribosamples lubricated with this IL no load effects can be observed. The shift detected indicates that the cation is stronger modified during the tribological experiments than the anion, as the contribution of the cation to the P 2p signal is at the lowest energies (see Table 4). Regarding to the mixtures, a major proportion of cation has been modified. The opposite results were obtained for the $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ samples (Figure 11b). First, it should be pointed out that only the P 2p signal from tribosample lubricated with VO+1%$[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ was evaluable. The signal-to-noise ratio of the P 2p signal of the other three mixture samples was too low for data evaluation or rather fitting. The P 2p signals from the wear scars lubricated with the neat IL under loads of 22 and 26 N show that the maximum position is shifted to lower binding energy. Besides, the peaks become narrow after the tribotests. A small effect of load can be seen, as the signal from the sample tested under 26 N is slightly more shifted. The intensity of both phosphorus species (in anion and cation) of the P 2p signal of the neat IL is equal. Then, as the lower binding energy value is originated from the cation,[40] it can be concluded that the cation is not or only very weak modified. However, the intensity of the anionic phosphorus is decreased strongly.

The F 1s signal for neat $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ and the tribosample tested under a load of 26 N lubricated with this IL was published in our previous article.[40] However, this signal was not detected on the wear scars lubricated with $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ for a load of 22 N nor on those lubricated with the four blends. Somers et al.[22] reported that fluorine-containing IL blends may interact with similar base oils as those studied in this article. These authors also explained that if this interaction is strong, the IL will not be available to reach the surface and form a protective IL film. The same idea about competition between IL solvation and adsorption processes was also indicated by Jimenez et al.[23] for a mixture of trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide and propylene glycol dioleate. So, this effect could be responsible for the lack of F 1s signal on the tribosamples lubricated with the mixtures. Regarding to the tribosample tested with neat $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ under a load of 22 N, probably the load applied is not enough to breakdown and initiate the anion reactivity.[35,62]

The influence of ILs as additives on the base oils was analyzed through the O 1s signal. To do this, first an averaged O 1s core level spectrum of neat steel was determined, because the O 1s signal of the wear track is composed of the oxygen contribution of the lubricant and those of the neat steel (beam diameter larger than width of the wear track). Then, the measured spectra from the wear scars was forced to be fitted with two peaks, being one of them the same as that from the O 1s of neat steel. Therefore, the other is the corresponding one to the contribution from the lubricant. An influence of both ILs as additives on the base oils is only probable for TMP (see Figure 12). The O 1s signals for the samples lubricated with the other base oils and corresponding mixtures did not show differences (Figure S3 in the Supporting Information SI 4). However, for TMP base oil and its mixtures the peak is shifted (Figure 12). In addition, only for the mixture with $[P_{4,4,4,2}][C_2C_2PO_4]$, the shape of the signal becomes narrow. Therefore, some of the oxides formed with TMP base oil were not formed with its mixture with 1 wt % $[P_{4,4,4,2}][C_2C_2PO_4]$. This could contribute to the friction and wear reduction achieved with this blend (see Figure 6b).

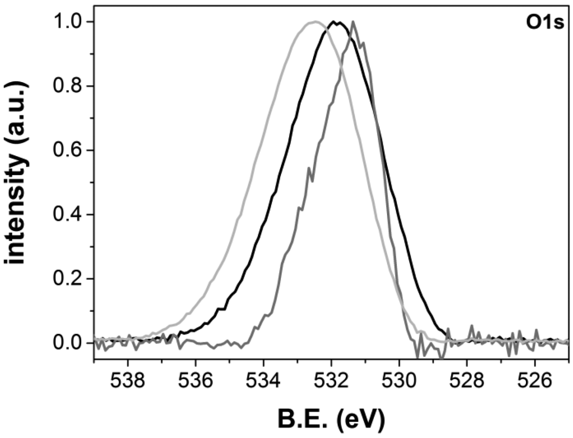


Figure 12. O 1s core level spectra of tribosamples tested under the load of 22 N and lubricated with the TMP base oil (black line) and its mixtures with $[P_{4,4,4,2}][C_2C_2PO_4]$ (dark gray line) and $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ (light gray line).

4. CONCLUSIONS

Several ILs were studied with the objective to find a reliable antiwear additive for some environmentally adapted lubricants. For this aim, the miscibility of eight ILs (imidazolium, pyrrolidinium, and phosphonium based ILs) with three ester base oils and a vegetable oil was checked. From them, only the ILs $[P_{4,4,4,2}][C_2C_2PO_4]$ and $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ were miscible with three and four of the base oils, respectively. The viscosity measurements performed in a Stabinger viscometer of these blends at 1 wt % confirm that the mixtures were single phase and not emulsions. The VI of these blends is quite close to those of the corresponding base oils. The thermal behavior of these base oils, selected blends and neat $[P_{4,4,4,2}][C_2C_2PO_4]$ was analyzed with DSC and TGA techniques. The friction coefficients of these lubricants for a steel−steel contact were measured with a tribometer in reciprocating motion. The corresponding wear volume was measured with a profilometer Dektak^3 and surface analyses were also performed with SEM and XPS.

As neat lubricants, both ILs can be used at very low temperatures because their melting points are around −60 °C. The neat IL $[P_{4,4,4,2}][C_2C_2PO_4]$ shows a high antifriction ability but less wear protection and worse thermal stability than $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$. Thus, its onset temperature is lower than all the base oils studied. So, $[P_{4,4,4,2}][C_2C_2PO_4]$ could be only used as lubricant for low temperature applications. The XPS analyses revealed the formation of a protective film mainly composed of iron phosphides and oxides on the worn plates lubricated with $[P_{4,4,4,2}][C_2C_2PO_4]$ and $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$.

As additives, the thermal behavior of the base oils at low temperature was not affected by the addition of 1 wt % of IL. In general, both ILs as additives slightly reduce the T_{onset} compared to those of the base oils. However, for TMP+1%$[P_{4,4,4,2}][C_2C_2PO_4]$ the reduction was around 60 °C. Nevertheless, the long-term thermal stability assays at 200 °C reveal that there is no significant difference between the base oil and the mixture. $[P_{4,4,4,2}][C_2C_2PO_4]$ shows, in general, a higher improvement in the tribological properties than $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$. This enhancement is especially significant for the mixtures with the base oils TMP and VO. The SEM images corroborate the ability of $[P_{4,4,4,2}][C_2C_2PO_4]$ as antiwear additive. Despite of the low amount of IL (only 1 wt %), also a tribofilm with phosphorus compounds was detected. However, the signal from mixtures containing 1 wt % $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ was very low. For these last blends, the IL seems not to be able to reach the surface, which could explain the lowest tribological performance of the blends containing $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ compared to those with $[P_{4,4,4,2}][C_2C_2PO_4]$. In conclusion, $[P_{4,4,4,2}][C_2C_2PO_4]$ is a good antiwear and antifriction additive for BIOE, TMP, and VO base oils and could be used in the same tribological applications.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Density and viscosity measured data in the temperature range of 278.15−373.15 K for $[P_{4,4,4,2}][C_2C_2PO_4]$, base oils, and blends studied. The estimation of the viscosity of the blends through Refutas equation and their comparison with the measured values. The parameters of the correlation of viscosity data using the model of Vogel−Fulcher−Tammann (VFT) for $[P_{4,4,4,2}][C_2C_2PO_4]$, base oils, and blends studied. The Fe 2p spectra from the worn surfaces lubricated with base oils (BIOE, TMP, TTM, and VO) and with the respective blends with 1 wt % $[P_{4,4,4,2}][C_2C_2PO_4]$ and 1 wt % $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$. The O 1s spectra from the worn surfaces lubricated with base oils (BIOE, TTM, and VO) and with the corresponding blends with 1 wt % $[P_{4,4,4,2}][C_2C_2PO_4]$ and 1 wt % $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: josefa.fernandez@usc.es. Phone: +34881814046. Fax: +34881814112.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Authors acknowledge Merck KGaA and Cytec Industries Inc. for providing us some of the IL samples. We are also grateful to Verkol and Instituto de la Grasa for the base oil samples and the useful advice. I.O. acknowledges the financial support provided by Xunta de Galicia under the program Plan I2C. The authors gratefully acknowledge partial financial contribution from COST project CM1206 on “Exchange on Ionic Liquids”. This work was supported by Ministerio de Economía y Competitividad (Spain) through the CTQ2011-23925 project.

■ REFERENCES

(1) Cai, M.; Guo, R.; Zhou, F.; Liu, W. Lubricating a Bright Future: Lubrication Contribution to Energy Saving and Low Carbon Emission. *Sci. China Technol. Sci.* **2013**, *56*, 2888−2913.

(2) Somers, A. E.; Howlett, P. C.; MacFarlane, D. R.; Forsyth, M. A Review of Ionic Liquid Lubricants. *Lubricants* **2013**, *1*, 3−21.

(3) Zhou, F.; Liang, Y.; Liu, W. Ionic Liquid Lubricants: Designed Chemistry for Engineering Applications. *Chem. Soc. Rev.* **2009**, *38*, 2590−2599.

(4) Minami, I. Ionic Liquids in Tribology. *Molecules* **2009**, *14*, 2286−2305.

(5) Bermúdez, M. D.; Jiménez, A. E.; Sanes, J.; Carrión, F. J. Ionic Liquids as Advanced Lubricant Fluids. *Molecules* **2009**, *14*, 2888−2908.

(6) Suzuki, A.; Shinka, Y.; Masuko, M. Tribological Characteristics of Imidazolium-Based Room Temperature Ionic Liquids under High Vacuum. *Tribol. Lett.* **2007**, *27*, 307−313.

(7) Street, K. W.; Morales, W.; Koch, V. R.; Valco, D. J.; Richard, R. M.; Hanks, N. Evaluation of Vapor Pressure and Ultra-High Vacuum Tribological Properties of Ionic Liquids. *Tribol. Trans.* **2011**, *54*, 911−919.

(8) Nainaparampil, J. J.; Eapen, K. C.; Sanders, J. H.; Voevodin, A. A. Ionic-Liquid Lubrication of Sliding MEMS Contacts: Comparison of AFM Liquid Cell and Device-Level Tests. *J. Microelectromech. Syst.* **2007**, *16*, 836−843.

(9) Zhang, J.; Liu, W.; Xue, Q. A Study of 2-(Dibutylaminomethyl)-Thiobenzimidazole as an Oil Additive. *Wear* **1999**, *231*, 279−284.

(10) Schneider, A.; Brenner, J.; Tomastik, C.; Franek, F. Capacity of Selected Ionic Liquids as Alternative Ep/Aw Additive. *Lubr. Sci.* **2010**, *22*, 215−223.

(11) Cai, M.; Liang, Y.; Yao, M.; Xia, Y.; Zhou, F.; Liu, W. Imidazolium Ionic Liquids as Antiwear and Antioxidant Additive in Poly(Ethylene Glycol) for Steel/Steel Contacts. *ACS Appl. Mater. Interfaces* **2010**, *2*, 870−876.

(12) Qu, J.; Bansal, D. G.; Yu, B.; Howe, J. Y.; Luo, H.; Dai, S.; Li, H.; Blau, P. J.; Bunting, B. G.; Mordukhovich, G.; Smolenski, D. J. Antiwear Performance and Mechanism of an Oil-Miscible Ionic Liquid as a Lubricant Additive. *ACS Appl. Mater. Interfaces* **2012**, *4*, 997−1002.

(13) Yu, B.; Bansal, D. G.; Qu, J.; Sun, X.; Luo, H.; Dai, S.; Blau, P. J.; Bunting, B. G.; Mordukhovich, G.; Smolenski, D. J. Oil-Miscible and Non-Corrosive Phosphonium-Based Ionic Liquids as Candidate Lubricant Additives. *Wear* **2012**, *289*, 58−64.

(14) Blanco, D.; Battez, A. H.; Viesca, J. L.; González, R.; Fernández-González, A. Lubrication of CrN Coating with Ethyl-Dimethyl-2-Methoxyethylammonium Tris(Pentafluoroethyl)Trifluorophosphate Ionic Liquid as Additive to PAO 6. *Tribol. Lett.* **2011**, *41*, 295−302.

(15) Blanco, D.; González, R.; Hernández Battez, A.; Viesca, J. L.; Fernández-González, A. Use of Ethyl-Dimethyl-2-Methoxyethylammonium Tris(Pentafluoroethyl)Trifluorophosphate as Base Oil Additive in the Lubrication of TiN PVD Coating. *Tribol. Int.* **2011**, *44*, 645−650.

(16) Pejakovic, V.; Kronberger, M.; Mahrova, M.; Vilas, M.; Tojo, E.; Kalin, M. Pyrrolidinium Sulfate and Ammonium Sulfate Ionic Liquids as Lubricant Additives for Steel/Steel Contact Lubrication. *Proc. Inst. Mech. Eng., Part J.* **2012**, *226*, 923−932.

(17) Viesca, J. L.; García, A.; Hernández Battez, A.; González, R.; Monge, R.; Fernández-González, A.; Hadfield, M. FAP$^-$ Anion Ionic Liquids Used in the Lubrication of a Steel−Steel Contact. *Tribol. Lett.* **2013**, *52*, 431−437.

(18) Viesca, J. L.; Battez, A. H.; González, R.; Reddyhoff, T.; Pérez, A. T.; Spikes, H. A. Assessing Boundary Film Formation of Lubricant Additivised with 1-Hexyl-3-Methylimidazolium Tetrafluoroborate Using ECR as Qualitative Indicator. *Wear* **2010**, *269*, 112−117.

(19) Cai, M.; Liang, Y.; Zhou, F.; Liu, W. Anticorrosion Imidazolium Ionic Liquids as the Additive in Poly(Ethylene Glycol) for Steel/Cu-Sn Alloy Contacts. *Faraday Discuss.* **2012**, *156*, 147−157.

(20) González, R.; Battez, A. H.; Blanco, D.; Viesca, J. L.; Fernández-González, A. Lubrication of TiN, CrN and DLC PVD Coatings with 1-Butyl-1-Methylpyrrolidinium Tris(Pentafluoroethyl)-Trifluorophosphate. *Tribol. Lett.* **2010**, *40*, 269−277.

(21) Zhang, H.; Xia, Y.; Yao, M.; Jia, Z.; Liu, Z. The Influences of Methyl Group at C2 Position in Imidazolium Ring on Tribological Properties. *Tribol. Lett.* **2009**, *36*, 105−111.

(22) Somers, A. E.; Khemchandani, B.; Howlett, P. C.; Sun, J.; MacFarlane, D. R.; Forsyth, M. Ionic Liquids as Antiwear Additives in Base Oils: Influence of Structure on Miscibility and Antiwear Performance for Steel on Aluminum. *ACS Appl. Mater. Interfaces* **2013**, *5*, 11544−11553.

(23) Jiménez, A. E.; Bermúdez, M. D. Imidazolium Ionic Liquids as Additives of the Synthetic Ester Propylene Glycol Dioleate in Aluminium-Steel Lubrication. *Wear* **2008**, *265*, 787−798.

(24) Jiménez, A. E.; Bermúdez, M. D. Short Alkyl Chain Imidazolium Ionic Liquid Additives in Lubrication of Three Aluminium Alloys with Synthetic Ester Oil. *Tribol.-Mater., Surf. Interfaces* **2012**, *6*, 109−115.

(25) Yao, M.; Liang, Y.; Xia, Y.; Zhou, F. Bisimidazolium Ionic Liquids as the High-Performance Antiwear Additives in Poly(Ethylene Glycol) for Steel-Steel Contacts. *ACS Appl. Mater. Interfaces* **2009**, *1*, 467−471.

(26) Kronberger, M.; Pejaković, V.; Gabler, C.; Kalin, M. How Anion and Cation Species Influence the Tribology of a Green Lubricant Based on Ionic Liquids. *Proc. Inst. Mech. Eng., Part J.* **2012**, *226*, 933−951.

(27) Pejaković, V.; Kronberger, M.; Kalin, M. Influence of Temperature on Tribological Behaviour of Ionic Liquids as Lubricants and Lubricant Additives. *Lubr. Sci.* **2013**, *26*, 107−115.

(28) Qu, J.; Truhan, J. J.; Dai, S.; Luo, H.; Blau, P. J. Ionic Liquids with Ammonium Cations as Lubricants or Additives. *Tribol. Lett.* **2006**, *22*, 207−214.

(29) Jiménez, A. E.; Bermúdez, M. D.; Iglesias, P.; Carrión, F. J.; Martínez-Nicolás, G. 1-N-Alkyl −3-Methylimidazolium Ionic Liquids as Neat Lubricants and Lubricant Additives in Steel-Aluminium Contacts. *Wear* **2006**, *260*, 766−782.

(30) Jiménez, A. E.; Bermúdez, M. D. Ionic Liquids as Lubricants for Steel−Aluminum Contacts at Low and Elevated Temperatures. *Tribol. Lett.* **2007**, *26*, 53−60.

(31) Qu, J.; Blau, P.; Dai, S.; Luo, H.; Meyer, H. Ionic Liquids as Novel Lubricants and Additives for Diesel Engine Applications. *Tribol. Lett.* **2009**, *35*, 181−189.

(32) Battez, A. H.; González, R.; Viesca, J. L.; Blanco, D.; Asedegbega, E.; Osorio, A. Tribological Behaviour of Two Imidazolium Ionic Liquids as Lubricant Additives for Steel/Steel Contacts. *Wear* **2009**, *266*, 1224−1228.

(33) Jiménez, A. E.; Bermúdez, M. D.; Carrión, F. J.; Martínez-Nicolás, G. Room Temperature Ionic Liquids as Lubricant Additives in Steel-Aluminium Contacts: Influence of Sliding Velocity, Normal Load and Temperature. *Wear* **2006**, *261*, 347−359.

(34) Fraser, K. J.; MacFarlane, D. R. Phosphonium-Based Ionic Liquids: An Overview. *Aust. J. Chem.* **2009**, *62*, 309−321.

(35) Minami, I.; Inada, T.; Sasaki, R.; Nanao, H. Tribo-Chemistry of Phosphonium-Derived Ionic Liquids. *Tribol. Lett.* **2010**, *40*, 225−235.

(36) Liu, X.; Zhou, F.; Liang, Y.; Liu, W. Tribological Performance of Phosphonium Based Ionic Liquids for an Aluminum-on-Steel System and Opinions on Lubrication Mechanism. *Wear* **2006**, *261*, 1174−1179.

(37) Minami, I.; Kita, M.; Kubo, T.; Nanao, H.; Mori, S. The Tribological Properties of Ionic Liquids Composed of Trifluorotris-(Pentafluoroethyl) Phosphate as a Hydrophobic Anion. *Tribol. Lett.* **2008**, *30*, 215−223.

(38) Somers, A. E.; Howlett, P. C.; Sun, J.; MacFarlane, D. R.; Forsyth, M. In *Phosphonium Ionic Liquids as Lubricants for Aluminium-Steel*, Tribology & design: Proceedings of the 3rd International Conference on Tribology in Environmental Design 2010, Algarve, Portugal, WIT: 2010; pp 273−284.

(39) Weng, L.; Liu, X.; Liang, Y.; Xue, Q. Effect of Tetraalkylphosphonium Based Ionic Liquids as Lubricants on the Tribological Performance of a Steel-on-Steel System. *Tribol. Lett.* **2007**, *26*, 11−17.

(40) Otero, I.; López, E. R.; Reichelt, M.; Fernández, J. Friction and Anti-Wear Properties of Two Tris(Pentafluoroethyl)-Trifluorophosphate Ionic Liquids as Neat Lubricants. *Tribol. Int.* **2014**, *70*, 104−111.

(41) Gaciño, F. M.; Regueira, T.; Lugo, L.; Comuñas, M. J. P.; Fernández, J. Influence of Molecular Structure on Densities and Viscosities of Several Ionic Liquids. *J. Chem. Eng. Data* **2011**, *56*, 4984−4999.

(42) Salgado, J.; Villanueva, M.; Parajó, J. J.; Fernández, J. In *Long-Term Thermal Stability of Ionic Liquids and Other Synthetic Lubricant Bases*, Conference Lubmat'12, Bilbao, Spain, 6−8 June, 2012.

(43) Nicholls, M. A.; Do, T.; Norton, P. R.; Kasrai, M.; Bancroft, G. M. Review of the Lubrication of Metallic Surfaces by Zinc Dialkyl-Dithiophosphates. *Tribol. Int.* **2005**, *38*, 15−39.

(44) Spikes, H. The History and Mechanisms of Zddp. *Tribol. Lett.* **2004**, *17*, 469−489.

(45) Barnes, A. M.; Bartle, K. D.; Thibon, V. R. A. A Review of Zinc Dialkyldithiophosphates (Zddps): Characterisation and Role in the Lubricating Oil. *Tribol. Int.* **2001**, *34*, 389−395.

(46) Regueira, T.; Lugo, L.; Fandino, O.; Lopez, E. R.; Fernandez, J. Compressibilities and Viscosities of Reference and Vegetable Oils for Their Use as Hydraulic Fluids and Lubricants. *Green Chem.* **2011**, *13*, 1293−1302.

(47) Salgado, J.; Villanueva, M.; Parajó, J. J.; Fernández, J. Long-Term Thermal Stability of Five Imidazolium Ionic Liquids. *J. Chem. Thermodyn.* **2013**, *65*, 184−190.

(48) Hammer, T.; Reichelt, M.; Morgner, H. Influence of the Aliphatic Chain Length of Imidazolium Based Ionic Liquids on the Surface Structure. *Phys. Chem. Chem. Phys.* **2010**, *12*, 11070−11080.

(49) Totten, G. E.; Liang, H. *Surface Modification and Mechanisms: Friction, Stress, and Reaction Engineering*; Marcel Dekker: New York, 2004.

(50) Maples, R. E. *Petroleum Refinery Process Economics*, 2nd ed.; Pennwell Books: Tulsa, OK, 2000.

(51) Mauro, J. C.; Yue, Y.; Ellison, A. J.; Gupta, P. K.; Allan, D. C. Viscosity of Glass-Forming Liquids. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 19780−19784.

(52) Gupta, P. K.; Mauro, J. C. Composition Dependence of Glass Transition Temperature and Fragility. I. A Topological Model Incorporating Temperature-Dependent Constraints. *J. Chem. Phys.* **2009**, *130*, 0945031−0945038.

(53) Green, M. D.; Schreiner, C.; Long, T. E. Thermal, Rheological, and Ion-Transport Properties of Phosphonium-Based Ionic Liquids. *J. Phys. Chem. A* **2011**, *115*, 13829−13835.

(54) Angell, C. A.; Smith, D. L. Test of the Entropy Basis of the Vogel-Tammann-Fulcher Equation. Dielectric Relaxation of Polyalcohols near Tg. *J. Phys. Chem.* **1982**, *86*, 3845−3852.

(55) Grocholski, B.; Jeanloz, R. High-Pressure and -Temperature Viscosity Measurements of Methanol and 4:1 Methanol:Ethanol Solution. *J. Chem. Phys.* **2005**, *123*, 2045031−2045036.

(56) Pensado, A. S.; Pádua, A. A. H.; Comuñas, M. J. P.; Fernández, J. Relationship between Viscosity Coefficients and Volumetric Properties Using a Scaling Concept for Molecular and Ionic Liquids. *J. Phys. Chem. B* **2008**, *112*, 5563−5574.

(57) Villanueva, M.; Coronas, A.; García, J.; Salgado, J. Thermal Stability of Ionic Liquids for Their Application as New Absorbents. *Ind. Eng. Chem. Res.* **2013**, *52*, 15718−15727.

(58) Salgado, J.; Parajó, J. J.; Fernández, J.; Villanueva, M. Long-Term Thermal Stability of Some 1-Butyl-1-Methylpyrrolidinium Ionic Liquids. *J. Chem. Thermodyn.* **2014**, *74*, 51−57.

(59) Kosmulski, M.; Gustafsson, J.; Rosenholm, J. B. Thermal Stability of Low Temperature Ionic Liquids Revisited. *Thermochim. Acta* **2004**, *412*, 47−53.

(60) http://srdata.nist.gov/xps/ (accessed 2 September, 2013).

(61) Philippon, D.; De Barros-Bouchet, M. I.; Le Mogne, T.; Vacher, B.; Lerasle, O.; Martin, J. M. A Multi-Technique Approach to the Characterization of Iron Phosphide Tribofilm. *Thin Solid Films* **2012**, *524*, 191−196.

(62) Somers, A. E.; Howlett, P. C.; Sun, J.; MacFarlane, D. R.; Forsyth, M. Transition in Wear Performance for Ionic Liquid Lubricants under Increasing Load. *Tribol. Lett.* **2010**, *40*, 279−284.