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# Vacuum tribological performance of phosphonium-based ionic liquids as lubricants and lubricant additives of multialkylated cyclopentanes



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## ABSTRACT

The tribological effects of tetraalkylphosphonium phosphate ionic liquids (PP-ILs) as lubricants and lubricant additives of multialkylated cyclopentanes (MACs) was evaluated in vacuum ( $10^{-4}$  Pa) by a vacuum four-ball tribometer. Results showed that the transient seizure-like high friction appearing for MACs could be effectively eliminated by neat PP-ILs or by adding the PP-ILs with long alkyl chain into MACs. Confirmed by the surface analysis, the improved tribological performances could be ascribed to the high load-carrying capacity of ionic liquids and the protective films formed on the contact surfaces through the tribochemical reaction between the PP-ILs and fresh steel surfaces under the boundary lubrication.

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## 1. Introduction

Liquid lubricants have been frequently used in spacial moving mechanisms due to their low mechanical noise, no wear in the elastohydrodynamic regime, ease of replenishment, ability to remove wear debris, and insensitivity to environmental factors [1]. However, the application of liquid lubrication under high vacuum conditions has been a technical challenge for many years. The rapid evaporation of the liquid lubricants employed and the absence of oxide films may result in failure of the spacial moving mechanisms [2].

In recent years, multialkylated cyclopentanes (MACs) have been widely used as a kind of space liquid lubricant [3,4]. However, under vacuum conditions, it was found that the MACs and PFPE might show initial seizure-like high friction under the boundary lubrication condition, and correspondingly they would also suffer the initial high wear volume [5–8]. High friction and severe surface damage caused by high contact pressure and temperature under vacuum condition can be reduced by applying friction–reduction and anti-wear additives. However, for the aerospace application, high vapor pressure of the traditional additives leads to the decrease in the effective lifetime of the system by volatilization and loss of anti-wear properties.

Due to the attractive properties, such as negligible volatility, interesting solvating properties, excellent thermal stability, and non-flammability [9–13], the ionic liquids (ILs) are organized as

the promising candidates of liquid lubricants or lubricant additives for spacial moving mechanisms. Ye et al. [14] presented the first paper about the use of ILs as lubricants and found excellent tribology performance of alkylimidazolium tetrafluoroborates for the contact of steel/steel, steel/aluminum, steel/cooper, steel/SiO<sub>2</sub>, steel/Si, steel/sialon ceramics, Si<sub>3</sub>N<sub>4</sub>/sialon ceramics. Then, Suzuki et al. [15] found low friction coefficient, good anti-wear performance, and a high load-carrying capability of imidazolium-based ILs under high vacuum ( $10^{-5}$  Pa), while Wang et al. [16] reported the excellent tribological property of alkylimidazolium hexafluorophosphate type ILs both in air and vacuum. Nevertheless, due to the little or no solubility ( $\leq 1\%$ ) of the most ILs in nonpolar hydrocarbon oils, most of previous works used the unstable oil-ILs emulsions or the nonpolar base oils with extremely low concentrations of ILs as lubricants [17–21], while the others applied the polar base oils for better compatibility with ILs [22–24]. In the latest researches, Yu et al. [25,26] investigated phosphonium-based ionic liquids as candidate lubricant additives in air and showed good tribology performance. Therefore, there would be a good idea developing phosphonium-based ionic liquids with good solubility in nonpolar hydrocarbon oil as additives to improve the load-carrying capacity of MACs, and to eliminate the transient seizure-like high friction of MACs in vacuum.

In current research, a series of tetraalkylphosphonium phosphate ionic liquids (PP-ILs) were synthesized and their tribological properties were studied under vacuum condition. We also choose tri(2-ethylhexyl)tetradecylphosphonium bis(2-ethylhexyl) phosphate as lubricant additives, which is not only soluble but fully

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miscible in common nonpolar hydrocarbon oils. By means of scanning electron microscopy (SEM), energy dispersive X-ray analyzer attachment (EDX) and X-ray photoelectron spectroscopy (XPS) analysis, the seizure-like high friction elimination, friction-reduction, and anti-wear mechanisms of the PP-ILs for a steel/steel frictional pair were discussed.

## 2. Experimental details

### 2.1. Synthesis of PP-ILs

Fig. 1 shows the molecular structure of the selected PP-ILs. All the lubricants were synthesized in our laboratory through the method reported in the literatures [27,28]. Take the PP-IL 3 as an example, 37.064 g (0.1 mol) trioctylphosphine was added dropwise to the substrate of 43.463 g (0.1 mol) trioctyl phosphate under nitrogen and stirred at a temperature ranging from 180 to 200 °C over 30 h. After the reaction was completed, the products were purified through reduced pressure distillation. The yield was ~75%. PP-ILs 1 and 2 were prepared with the reactants of tributylphosphine and trialkyl phosphate through the similar procedures as that for PP-IL 3.

The main properties of MACs, PP-ILs, and specimens used in the experiments are listed in Table 1. PP-IL 4 was dispersed in MACs in concentration of 1 wt% using an ultrasonic bath for 2 min.

### 2.2. Friction and wear test

The tribological properties of MACs, PP-ILs and PP-IL 4 as additive of MACs in vacuum ( $\sim 10^{-4}$  Pa) were investigated on a vacuum four-ball tribometer which was designed based on the configuration of a traditional four-ball tribometer and manufactured by the State Key Laboratory of Solid Lubrication, Lanzhou

Institute of Chemical Physics, Chinese Academy of Sciences. As shown schematically in reference [8], the vacuum chamber was evacuated by using a series of a turbo molecular pump and a mechanical pump. The tribological characteristics of liquid lubricants for space applications were evaluated by this tribometer under the pressures of  $2 \times 10^{-4}$  Pa. It can also be run at low vacuum (about 10 Pa) and at atmospheric pressure with air or nitrogen.

The tribological tests were performed under the load of 392 N with a rotating speed of 1450 rpm at 25 °C for 30 min. Before and after each test, the test specimen were ultrasonically cleaned in ethanol and petroleum ether (normal alkane with a boiling point of 60–90 °C) sequentially. For each sample, three tests were performed to minimize data scattering. At the end of each test, the wear scar diameters of the three lower balls were measured with an optical microscope to an accuracy of 0.01 mm, and then the average wear scar diameter of the three identical tests was calculated as the wear scar diameter (WSD) in this paper.

### 2.3. Analysis instruments

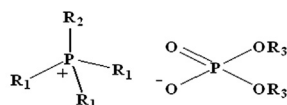
Several instruments were used to examine the lubricants and the worn surfaces of specimens for more detailed analysis of the tribological properties. The structure of PP-ILs was characterized by the IFS 66v/s Fourier transformation infrared spectroscopy (FTIR). The topography of wear scar surfaces were examined with the JSM-5600LV SEM. The Kevex EDX and XPS were employed to analyze the composition of chemical elements on the rubbing surfaces.

## 3. Results and discussion

### 3.1. Physical properties of PP-ILs

PP-IL 4 was discovered to be fully miscible with nonpolar organic solvents like MACs at any blend ratio. All blends (1–50 wt% PP-IL 4 in MACs) appear clear without clouds or phase separation by visual inspection after weeks of storage. In contrast, although having similar molecular structures, PP-ILs 2 and 3 showed limited solubility ( $< 1$  wt%) in hydrocarbon oils, while PP-IL 1 appeared to be fully miscible with water.

In general, ions and non-polar neutral organic molecules are immiscible, because ions are attracted by polar force and sometimes hydrogen bonding while non-polar molecules are held together by dispersion forces [29]. ILs are salts in which the ions are poorly coordinated, which results in these solvents being liquid at about room temperature. At least one ion has a delocalized charge and



PP-IL 1 (Water miscible):  $R_1 = (\text{CH}_2)_3\text{CH}_3$ ,  $R_2 = R_3 = \text{CH}_3$   
Tributylmethylphosphonium dimethyl phosphate

PP-IL 2 (Limited oil-solubility):  $R_1 = (\text{CH}_2)_3\text{CH}_3$ ,  $R_2 = R_3 = \text{CH}_2\text{CH}(\text{C}_2\text{H}_5)(\text{CH}_2)_3\text{CH}_3$   
Tributyl(2-ethylhexyl)phosphonium bis(2-ethylhexyl) phosphate

PP-IL 3 (Limited oil-solubility):  $R_1 = R_2 = R_3 = \text{CH}_2\text{CH}(\text{C}_2\text{H}_5)(\text{CH}_2)_3\text{CH}_3$   
Tetra(2-ethylhexyl)phosphonium bis(2-ethylhexyl) phosphate

PP-IL 4 (Oil miscible):  $R_1 = R_3 = \text{CH}_2\text{CH}(\text{C}_2\text{H}_5)(\text{CH}_2)_3\text{CH}_3$ ,  $R_2 = (\text{CH}_2)_{13}\text{CH}_3$   
Tri(2-ethylhexyl)tetradecylphosphonium bis(2-ethylhexyl) phosphate

Fig. 1. Molecular structure of the selected PP-ILs.

Table 1  
Material properties.

Lubricants	Average molecular weight	Kinematic viscosity (cSt)		Vapor pressure, 20 °C (Pa)
		40 °C	100 °C	
MACs	630	56	9.3	$5.6 \times 10^{-6}$
PP-IL 1	342	105.6	8.9	NM
PP-IL 2	636	326.8	37.4	NM
PP-IL 3	804	420	37.4	NM
PP-IL 4	888	416.3	79.1	NM
Specimens	Properties			
Test ball	Steel: AISI 52100 $d = 12.7$ mm Chemical composition: 0.95–1.05% C, 0.25–0.45% Mn, 0.15–0.35% Si, 1.40–1.65% Cr, ~0.30% Ni, ~0.25% Cu, ~0.025% S, ~0.025% P	Hardness: 60~63 HRC $R_a = 0.025$ $\mu\text{m}$		

NM—not measured.

one component is organic, which prevents the formation of a stable crystal lattice. As a result, most ILs previously reported in literatures have poor solubility in nonpolar base oils. The exceptional oil-miscibility of the PP-IL 4 gives an opportunity for using ILs as additives of nonpolar base oil. The oil-miscibility should be attributed to the high steric hindrance (long hydrocarbon chains) of PP-ILs which can dilute the charge of the ions. The phosphate ILs reported by Mori's group [30] and Qu's group [26] have similar structures to PP-IL 4, but the alkyls on the cation and anion are so short (not more than four carbons each) that they show limited solubility in oil or even miscibility in water. Besides high steric hindrance, oil-miscible ILs need to contain the three-dimensional quaternary structures for cations which can further dilute the charge due to high steric hindrance effect. For example, the 1-methyl-3-hexadecylimidazolium tetrafluoroborate ionic liquids crystal reported by Zhang's group [31] have long carbon chains with 21 carbons, but contain two-dimensional imidazolium cations and thus cannot miscible with hydrocarbon oils.

Fig. 2 shows the structure of PP-IL 4 as an example of the molecular structures of the PP-ILs by FTIR. It can be found that  $\nu_{\max}/\text{cm}^{-1}$ : 2956, 2925, 2871 and 2855 [ $\nu(\text{C-H})$ ]; 1247 [ $\nu(\text{P=O})$ ]; 1041 and 1062 [ $\nu(\text{P-O-C})$ ]. No signals of O-H flex oscillation are observed in the ranges of 3200–3700  $\text{cm}^{-1}$  from FTIR spectrum.

### 3.2. Tribological behavior

#### 3.2.1. PP-ILs as lubricating oil

Fig. 3 shows the mean friction coefficients and the WSD values of PP-ILs and MACs at 25 °C under vacuum. It can be seen that all four PP-ILs exhibit lower friction coefficients and smaller WSD values in comparison with MACs. Meanwhile, the PP-ILs with

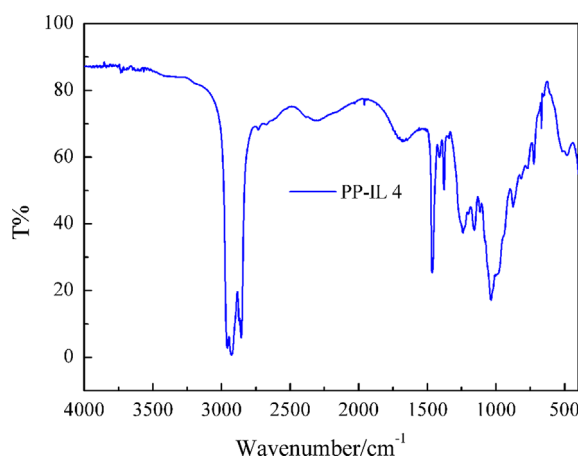


Fig. 2. IR-spectrum of PP-IL 4.

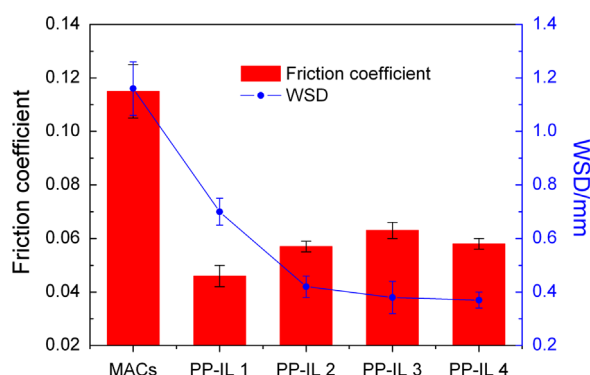


Fig. 3. Mean friction coefficients and the WSD values of MACs and PP-ILs under vacuum at 25 °C.

longer chain show better anti-wear property. The lowest friction coefficient and the highest WSD value were both obtained by PP-IL 1, among the PP-ILs.

Fig. 4 shows the friction coefficient as a function of rotating time lubricated by MACs and PP-ILs at 25 °C under vacuum. A transient seizure-like high friction could be observed for MACs under vacuum. After showing the transient seizure-like high friction, MACs showed a low friction coefficient of approximately 0.1 that is indicative of good lubrication. This result should be explained as that some species, such as carbon coating, might be produced during the high friction period to lubricate surfaces and to facilitate return to a low friction condition [7]. It can also be found that PP-ILs 2–4 exhibit steady and low friction coefficient without any transient high friction compared with MACs. A reasonable explanation is that PP-ILs with longer chain show higher carrying capacity than MACs and the PP-ILs happen to react with the fresh steel surface to form protective films under boundary lubrication during the friction process. PP-IL 1 shows the fluctuant friction coefficient in a relatively high level at the first 10 min. After that, PP-IL 1 gives an extremely low and steady friction coefficient about 0.03.

Fig. 5 shows the SEM images of wear scar surfaces lubricated by PP-ILs and MACs. The dominating pit-like features on the worn surface (Fig. 5a and b) confirmed the adhesive wear and plastic deformation lubricated by MACs. In contrast, PP-ILs 2–4 produced smooth wear scar surfaces (Fig. 5e–j) with no signs of adhesive wear and plastic deformation. In Fig. 5c and d, it could be found that PP-IL 1 gave a relatively serious damage worn surface with many pits caused by corrosive wear, which was very different from PP-ILs 2–4.

More analysis of the wear scar surfaces by EDX was done in order to detect the formation of the protective films. Results showed that less than 1 wt% P elements were detected on the worn surfaces lubricated by PP-ILs 2–4. However, as shown in Fig. 6, which is the EDX spectrum of the marked area of the wear scar surfaces lubricated by PP-IL 1, 6.35 wt% P elements were detected on the worn surface. It could also be found that P elements were bogged down along the friction direction.

Considering the results from Figs. 4, 5c, d, and 6 together, the fluctuant friction coefficient of PP-IL 1 could be ascribed to the corrosive wear caused by the relatively violent reaction between the molecular and the fresh steel surfaces at the beginning. A tribochemical film with a certain thickness was produced to separate the frictional pairs from each other, which led to an extremely low friction coefficient and a relatively high WSD value. Since PP-IL 1 is very reactive to form metal phosphides, as discussed

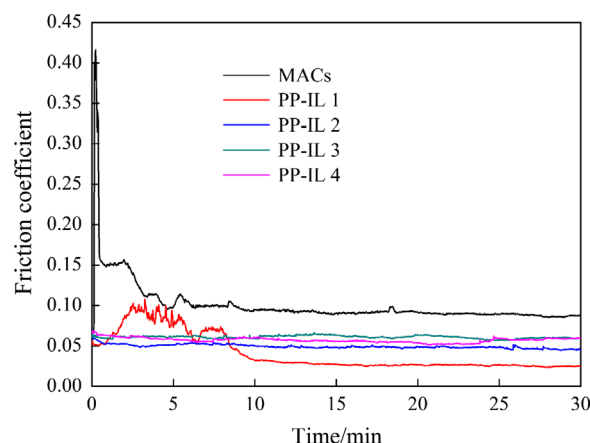
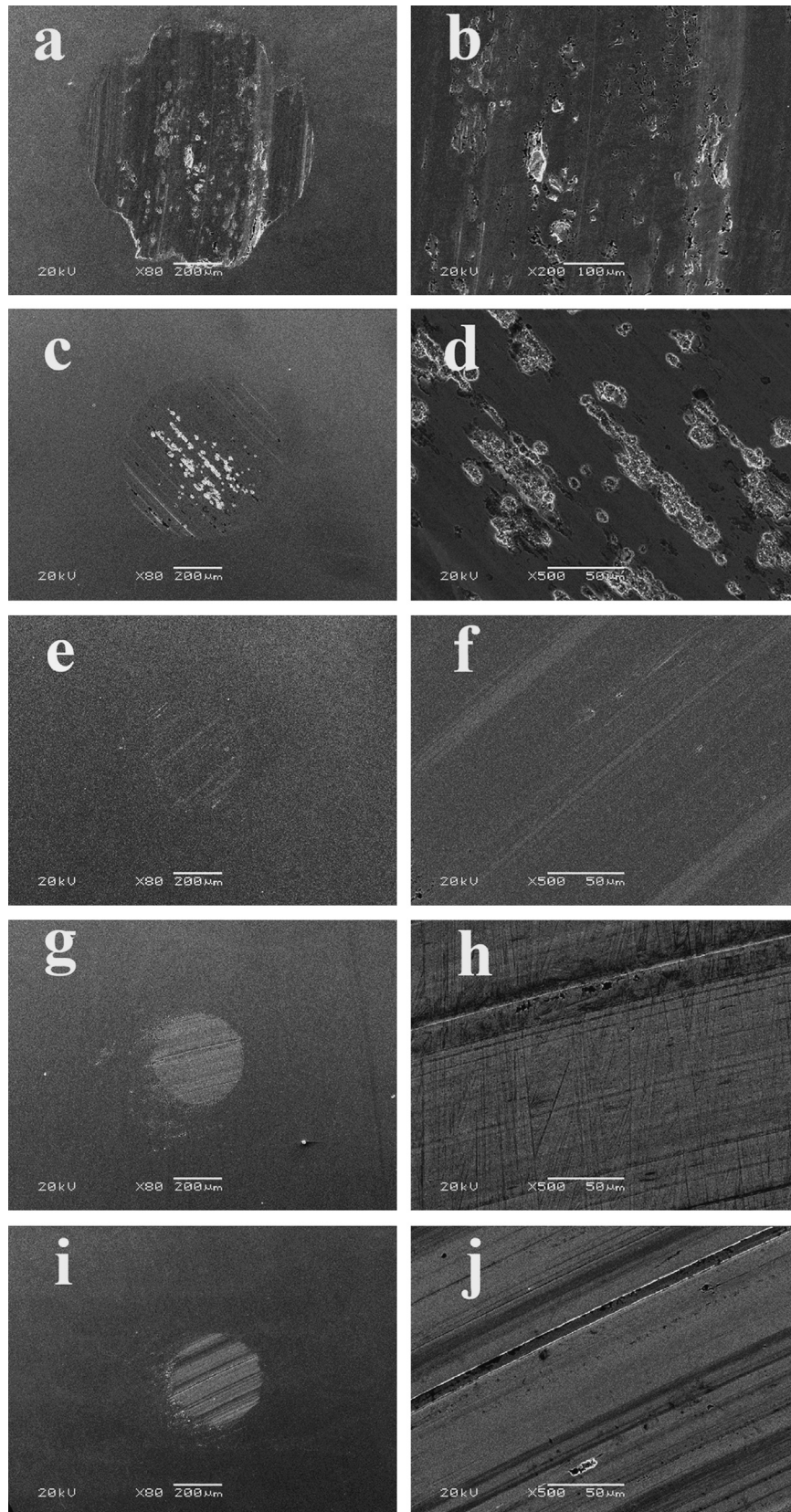


Fig. 4. Friction coefficient as a function of rotating time lubricated by MACs and PP-ILs under vacuum at 25 °C.





**Fig. 5.** SEM images of the wear scar surfaces lubricated by PP-ILs and MACs: (a) and (b) MACs, (c) and (d) PP-IL 1, (e) and (f) PP-IL 2, (g) and (h) PP-IL 3, (i) and (j) PP-IL 4.

above, the tribological characteristics of PP-IL 1 are similar to that of EP additives. Comparatively speaking, as shown in Figs. 4, and 5e–j, PP-ILs 2–4 give steady and low friction coefficient during the entire test because of the relatively mild reaction between the

PP-IL molecular and the fresh steel surfaces. So the protective boundary films were producing and consuming throughout the whole test, which led steady friction coefficient and mild wear.

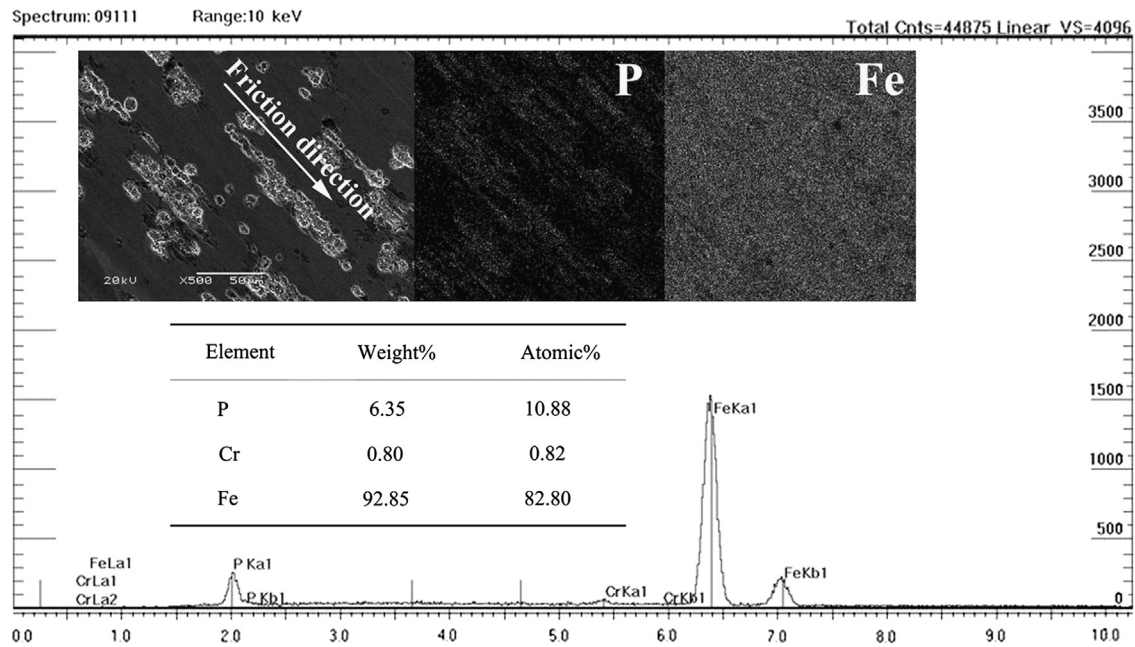


Fig. 6. EDX spectrum of the marked area of the wear scar surfaces lubricated by PP-IL 1 under vacuum at 25 °C.

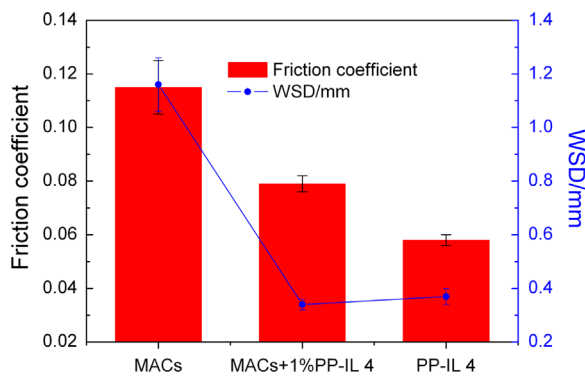


Fig. 7. Friction-reduction and anti-wear properties of PP-IL 4 under vacuum at 25 °C.

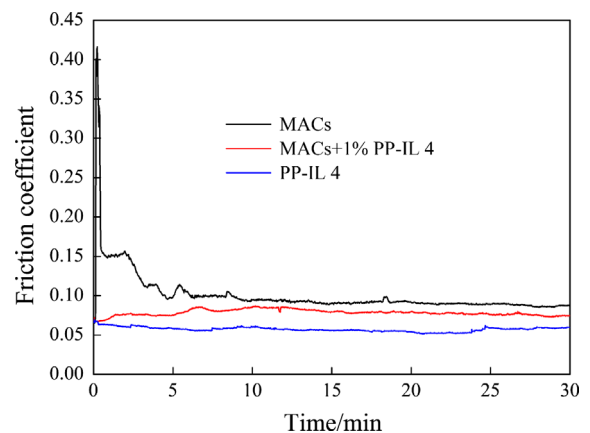


Fig. 8. The seizure-like high friction elimination effect of PP-IL 4 under vacuum at 25 °C.

### 3.2.2. PP-ILs as lubricating additives of MACs

Fig. 7 shows the friction-reduction and anti-wear properties of PP-IL 4 under vacuum at 25 °C. It can be seen that the mean friction coefficient was reduced by 31% and the WSD value was reduced by 71% when adding 1 wt% PP-IL 4 in MACs. Comparing with the pure PP-IL 4, the MACs+1% PP-IL 4 sample exhibited lower anti-wear property.

Fig. 8 shows the seizure-like high friction elimination effect of PP-IL 4 indicating that adding PP-IL 4 into MACs could totally eliminate the transient seizure-like high friction of MACs under vacuum. MACs+1 wt% PP-IL 4 produced a stable friction coefficient around 0.08 throughout the entire test indicating good lubrication.

Fig. 9 shows the SEM images of the wear scar surface lubricated by MACs+1% PP-IL 4. In comparison with MACs, MACs+1% PP-IL 4 gave a much smaller and smoother wear scar surface with no signs of adhesive wear and plastic deformation, which was even smaller than pure PP-IL 4. EDX analysis of the wear scar surface was still done in order to detect the formation of the protective films. Results showed that less than 1 wt% P elements were detected on the worn surface.

Finally, the worn scar surface was further analyzed by XPS. As shown in Fig. 10, the XPS peak P2p (133.7 eV) detected on the worn scar surface was assigned to FePO<sub>4</sub> [32]. Therefore, the tribochemical

reaction is related to the formation of FePO<sub>4</sub>. Excellent tribological behavior and formation of FePO<sub>4</sub> was also found for the contact of steel/cast iron surface lubricated with PP-ILs-containing lubricants in air [25,26]. It is referred that FePO<sub>4</sub> as a surface protective film formed on the friction surfaces to improve the tribological behavior.

## 4. Conclusions

Sliding friction experiments of PP-ILs as lubricants and additives in MACs were carried out under vacuum. Based on the above experimental results, following conclusions could be drawn.

1. Four kinds of tetraalkylphosphonium phosphate ionic liquids were synthesized, characterized, and evaluated as candidate lubricants or lubricant additives. Besides, tri(2-ethylhexyl)tetradecylphosphonium bis(2-ethylhexyl) phosphate with long alkyl chain distinguishes itself from most other ionic liquids by the oil-miscibility property.



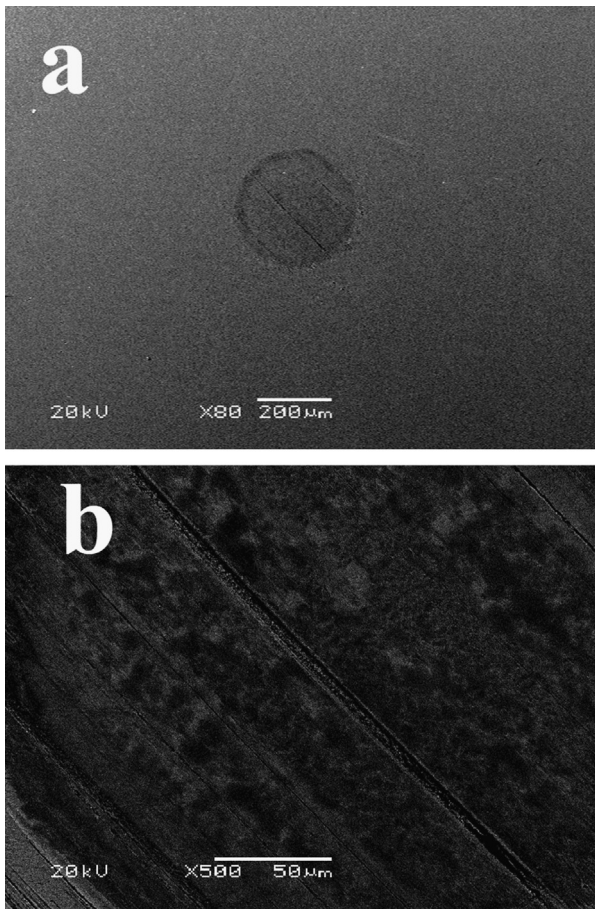


Fig. 9. SEM images of the wear scar surfaces lubricated by MACs+1 wt% PP-IL 4.

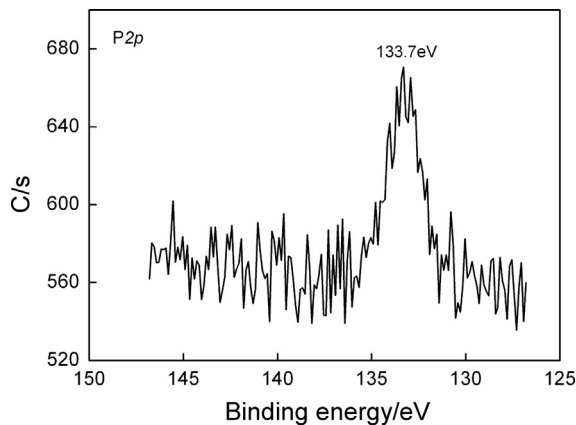


Fig. 10. XPS spectra of the wear scar surface lubricated by MACs+1 wt% PP-IL 4.

pressure, seizure-like high friction elimination, and excellent lubricity make the PP-IL 4 a promising candidate of lubricant additive for space mechanisms.

## Acknowledgements

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2. Tribological tests demonstrated superior seizure-like high friction elimination, friction-reduction, and anti-wear functionality for the PP-ILs as lubricants or PP-IL 4 as additive in MACs.
3. The surface analysis indicated that the PP-ILs with long hydrocarbon chains as lubricants or lubricant additives experienced tribochemical reaction to form the protective films on the worn surfaces during the sliding of steel against steel.
4. The characterization and testing results suggest that the prominent properties such as good oil-miscibility, low vapor

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