Tribology International 116 (2017) 440–448

Contents lists available at ScienceDirect

Tribology International

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

# Tribological properties and surface interaction of novel water-soluble ionic liquid in water-glycol

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ARTICLE INFO

*Keywords:*
Water-soluble ionic liquids
Phosphite
Phosphate
Surface analysis

ABSTRACT

Two kinds of novel water-soluble ILs were synthesized and applied as lubricant additives in water-glycol. ILs, as the multifunctional and high efficiency additive, could drastically improve antiwear, friction-reducing and extreme pressure properties of water-glycol. SEM and EDS results indicated that the sample lubricated by PEG600MO phosphate-ammonium IL (P1) acquires higher active element content in the area with heavy wear, while that lubricated by PEG600MO phosphite-ammonium IL (P2) is relatively homogeneous on the worn surface with heavy and mild wear. L-edge XANES results showed that the tribofilm is composed of polyphosphate, and the increase of the polyphosphate chain length could improve the tribological properties. Additionally, the additive concentration, the rubbing time and the load could change the chain length of polyphosphate.

## 1. Introduction

Comparing with oil, water has many advantages, such as outstanding fire-resistant property, environmental friendliness and relatively low cost [1]. Water-glycol is one of the most widely used fire-resistant fluids in the industrial application. Due to the poor lubricating property of water-glycol fluid [2,3], we need to add a variety of additives to meet the protection against friction, wear, extreme pressure and so on. All additives must be water soluble and compatible with each other. Additives designed for water-glycol should possess excellent water solubility and tribological properties in order to prevent wear, reduce friction, and more importantly, avoiding lubrication failure of mechanical system. Various additives such as carboxylic containing additives [4,5], S containing additives [6,7], P containing additives [8,9], P-S containing additives [10,11], etc., are developed to solve the problem above. However, only few lubricant additives could be practically applied for their poor tribological performance, severe corrosion, high P-S content, complicated preparation process or questionable stabilities in water.

Ionic liquids (ILs) have become a promising candidate for high performance lubricant and additive because of their unique physicochemical properties such as high thermal stability, negligible volatility, nonflammability, low melting point and promising tribological properties [12–14]. Their promising tribological properties are derived from their unique dipolar structure and tribochemical behaves during the rotating process [15]. ILs are extensively studied in synthetic and mineral oils or greases for ceramic and metal materials lubrication [16]. Their tribological properties and tribochemical mechanism have been the research hotspot. However, there is still room for further innovation. Firstly, the majority of ILs are composed of halogen-containing anions, which may decompose to toxic and corrosive products [17]. Secondly, most studies focus on synthetic and mineral oils or greases, while few researchers focus on the tribological performance and tribochemical mechanism of ILs as additives in water [18,19]. Thirdly, water is unfavorable for the application of traditional ionic liquids [17,18,20]. Fourthly, the relationship between the tribological properties and the polyphosphate chain length is still vague in the water-based system [21].

A new family of ILs based upon carboxylate anions and quaternary ammonium cations are developed recently [22]. This ILs with halogen-free anion can replace conventional ILs by combining different cations, which has the advantages of low toxicity, low cost and simple synthetic route [23]. In the present paper, we reported polyethylene glycol 600 monooleate (PEG600MO) derived phosphite (or phosphate) anions based ILs, in which cations come from quaternary ammonium salts. Acid originated from vegetable oil and provided a lubricating environment

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http://dx.doi.org/10.1016/j.triboint.2017.08.001
Received 1 June 2017; Received in revised form 1 August 2017; Accepted 2 August 2017
Available online 4 August 2017

similar to the oil-based system. Phosphite and phosphate were used to provide reasonable tribological properties under rigorous conditions. The acid-base neutralization formed an ionic bond, which endowed the water-soluble ionic liquids with good adsorption characteristics on the worn surface. These ILs were synthesized and used as antiwear, friction-reducing and extreme pressure agents in water-glycol base liquid. SEM, EDS and XANES were used to investigate the morphology and chemical composition of the worn surface. The change of chain length of poly-phosphate was also discussed under different frictional conditions.

## 2. Materials and experimental details

### 2.1. Materials

Polyethylene glycol 600 monooleate (PEG600MO) was purchased from Haian Petrochemical Plant without further treatment. Other chemicals used in this article were all chemically pure grade and without any further purification. The steel balls (φ12.7 mm, HRC59-61) used in this work were made of GCr15 (chemical composition: 0.95–1.05 wt % C; 0.15–0.35 wt % Si; 0.20–0.40 wt % Mn; 0.027 wt % P; 0.020 wt % S; 1.30–1.65 wt % Cr; 0.30 wt % Ni; 0.25 wt % Cu), supplied by Shanghai Ningxing steel ball Co., Ltd.

### 2.2. Chemicals preparation

The synthetic route of the additives was presented in Fig. 1. The products generated from phosphate ester (or phosphite ester) was designed as P1 (or P2). Fig. 1 represents the molecular structure of P1 and P2, which are similar to the previous reported ILs [24].

### 2.3. Physical properties of lubricants

The main physical properties of lubricants were shown in Table 1. The addition of water-soluble ILs into water-glycol could not significantly change the viscosity of base liquid.

### 2.4. Characterization

The constitution of P1 and P2 were characterized by Fourier transform infrared (FT-IR) spectroscopy, Inductively Coupled Plasma Mass Spectrometer (ICP), respectively. The IR spectrum of P1 and P2 were given in Fig. 2, and the corresponding absorption peaks were summarized in Table 2. The results of elemental analysis (EA) from ICP were presented in Table 3.

The measured content of C, H, P, N elements were close to their calculated value. ICP and FT-IR results indicated that the designed molecules are successfully synthesized.

**Table 1**
Main physical properties of the lubricants.

| Items | Kinematic viscosity ($mm^2/s$) | | Viscosity index | Density ($kg/m^3$) at 25 °C |
|---|---|---|---|---|
| | 40 °C | 100 °C | | |
| Water-glycol | 1.93 | | | 1055.5 |
| P1 | 174.55 | 21.36 | 145 | 1392.85 |
| P2 | 258.67 | 29.16 | 150 | 1468.16 |
| 0.10 wt % P1 | 1.94 | | | 1056.90 |
| 0.10 wt % P2 | 2.00 | | | 1057.91 |
| 0.50 wt % P1 | 1.98 | | | 1062.49 |
| 0.50 wt % P2 | 1.94 | | | 1062.84 |
| 1.5 wt % P1 | 2.31 | | | 1076.38 |
| 1.5 wt% P2 | 2.12 | | | 1077.32 |

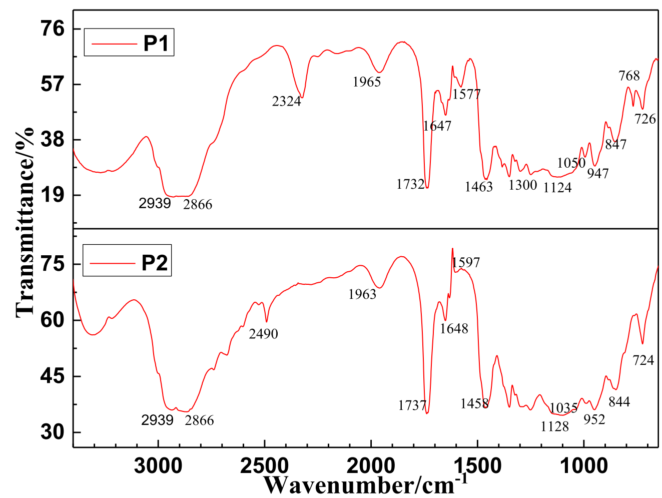


**Fig. 2.** The main absorption peaks of P1 and P2.

**Table 2**
IR spectra data of P1 and P2.

| Adsorption peaks | P1($cm^{-1}$) | P2($cm^{-1}$) |
|---|---|---|
| $-CH_3$,$-CH_2$ | 2939, 2866,726 | 2939, 2866,724 |
| C=C | 1647 | 1648 |
| -COO- | 1732,1251 | 1737,1250 |
| C-O-C | 1124 | 1128 |
| $-C-N^+$ | 947 | 952 |
| O-P-O | 847 | 844 |
| P-O | 947 | 952 |
| P=O | 1298 | – |

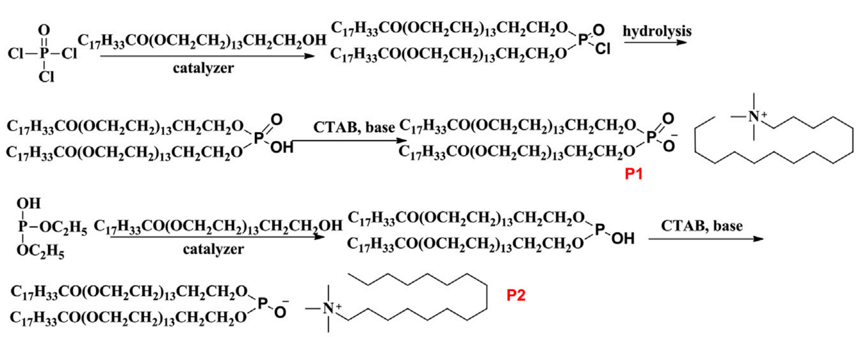


**Fig. 1.** Preparation of P1 and P2.