

## Significant enhancement of anti-friction capability of cationic surfactant by phosphonate functionality as additive in water

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### ABSTRACT

A new N-(3-(diethoxyphosphoryl)propyl)-N,N-dimethyloctadecan-1-ammonium bromide (NP) surfactant was synthesized. The NP together with 1 wt% sodium D-gluconate or 1 wt% triethanolamine displays remarkable lubricating property as the water-based lubricant additive and provides a non-corrosive environment for steel in aqueous solution. The lubricating mechanism was tentatively discussed according to electrical contact resistance, X-ray photoelectron spectroscopy and Quartz Crystal Microbalance measurement. These results show a stable protective film is formed on the contact surface by physical adsorption and tribo-chemical reactions. Surprisingly, the water-based additive has excellent anti-friction properties comparable to oil-based lubricants and superior to cationic surfactant analogue. Therefore, this NP is a potential efficient additive in water-based lubricating fluids.

### 1. Introduction

Machineries and equipments in industries cannot normally operate without the effective lubrication. Human being will eventually run out of energy resources because of the friction and wear, not to mention the serious energy shortage now. Therefore, the lubrication has become an indispensable technology to delay the process. The petroleum-based lubricants are widely used in industries and can make equipment operate smoothly, reduce the energy consumption and extend the life [1]. However, these petroleum-based lubricants have low flash point, flammability and poor thermal conductivity, which make them unable to be applied in some working conditions with fire and explosion danger, such as metal processing, coal mining and etc [2]. Furthermore, the shortage of petroleum resources and adverse environmental impact also constrain the use of petroleum-based lubricants. To this end, the real eco-friendly, non-flammable, high heat capacity, availability and cheap water based lubricants have become the choice in these particular areas. Water as a cooling and lubricating fluid has the advantages of incombustibility, excellent cooling ability, environmental compatibility and low cost [3] and its formulations are widely used as the metalworking fluids [4,5]. However, the low viscosity and viscosity-pressure coefficient of water is difficult to form the effective viscoelastic lubricating film in the friction parts like oils and has serious corrosion on metal as a friction material. These drawbacks greatly limit

their practical applications.

Additive as the essence of lubricants can improve the defective lubricants of the stability and functionality, so it obviously enhances the efficiency and durability of industrial equipment. Meanwhile, the effective additive like a mechanical heart device plays an irreplaceable role in the field of water-based lubricants. To solve the above-mentioned drawbacks, more and more effective additives including friction modifier, antiwear, antioxidant, viscosity modifier, dispersant, detergent are used in water-based lubricant [3,5–8]. It is always required to develop more efficient, non-corrosive and low cost water-based additives.

Ionic liquids (ILs) have unique physicochemical properties, such as high thermal stability, flexible molecular design, excellent lubricating and AW performances. [9–14]. It was widely used as a potential efficient material in many fields [15–20] and also as high performance synthetic lubricants and additives [10,18,21–31]. For example, previously reported ILs as oil additives have superior extreme-pressure and antiwear properties, noncorrosiveness and friction reduction [18,19,32]. Some ILs have been successfully applied as oil-based additives in industrial equipment. Moreover, it was also reported that ILs could be used for ceramic lubrication as water-based additives [7,8,33]. However, ILs as water-based additives for metal lubrication are very rare because of routine serious corrosion [3]. So it is of great significance to prepare an efficient non corrosive IL as the water-based

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additive.

The application of ILs as an efficient lubricant additive in water-based fluids has drawn great interests due to their unique physico-chemical properties comparable to other additives. In this paper, a novel kind of ionic liquids analogue, N-(3-(diethoxyphosphoryl) propyl)-N,N-dimethyloctadecan-1-ammonium bromide (denoted as NP) surfactant was synthesized and evaluated as the water-based lubrication additives. The introduction of phosphonate functionality significantly improves the friction reduction, anti-wear and anti-corrosive properties. A synergistic effect of nitrogen and phosphorus element was found. It provides us an energy-efficient non-corrosive alternative to the traditional ILs as water-based lubricant additive for the metal cutting fluids applications.

## 2. Experimental section

### 2.1. Chemicals and NMR characterization

The N-(3-(diethoxyphosphoryl)propyl)-N,N-dimethyloctadecan-1-ammonium bromide, NP was synthesized by N,N-Dimethyl-*n*-octadecylamine and intermediate, which was prepared by 1,3-dibromopropane and triethyl phosphite. The molecular structure of NP is displayed in Fig. 1. These feedstocks including N,N-Dimethyl-*n*-octadecylamine, 1,3-dibromopropane, triethyl phosphite, sodium D-gluconate (GAS), triethanolamine (TEA) and hexadecyl trimethyl ammonium bromide (CTAB) are obtained from Energy Chemical, Tianjin Heowns Biochem LLC. The deionized water is used in the whole experiment and all the percentage content refers to the mass concentration in this article.

The preparation of NP was confirmed by  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  NMR and elemental analysis.  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$  (ppm): 4.33–4.00 (m, 4 H,  $\text{OCH}_2\text{CH}_3$ ), 3.45 (d, 4 H,  $\text{NCH}_2\text{CH}_2$ ), 3.18 (s, 6 H,  $\text{NCH}_3$ ), 2.04 (d, 4 H,  $\text{NCH}_2\text{CH}_2$ ), 1.79 (s, 2 H,  $\text{PCH}_2$ ), 1.60–1.08 (m, 36 H,  $\text{N}(\text{CH}_2)_2(\text{CH}_2)_{15}$ ,  $\text{OCH}_2\text{CH}_3$ ), 0.90 (t, 3 H,  $\text{N}(\text{CH}_2)_{17}\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 Hz,  $\text{D}_2\text{O}$ )  $\delta$  (ppm): 63.37, 62.93, 62.87, 51.43, 32.02, 30.08, 29.97, 29.87, 29.68, 29.53, 29.2, 26.11, 22.68, 22.35, 21.64, 20.24, 16.06, 16.01, 13.89.  $^{31}\text{P}$  NMR (162 MHz,  $\text{D}_2\text{O}$ )  $\delta$  (ppm): 32.48. Elem. Anal. Calcd for  $\text{C}_{27}\text{H}_{59}\text{BrNO}_3\text{P}$ : P, 5.56. Found P, 5.43.

### 2.2. Viscosity and corrosion test

In order to understand the physical properties of different lubri-

cants, the kinematic viscosity was examined by a SYP1003-III viscometer at 25 °C. According to GB6144-85 procedure, it was used to detect the corrosion resistance of different lubricant by the cast iron strip corrosion test. Put three pieces of cast iron strips immerse into 16 ml of water, NP consisting of 1 wt% GAS, NP consisting of 1 wt% TEA, respectively. Then, put them into a constant container of 55 °C  $\pm$  2 °C. After 24 h, take out the cast iron strips immersed in samples and the corrosion level was evaluated according to the corrosion standards.

### 2.3. Friction and wear test

In order to get the different mass concentrations ILs analogue (0, 0.05%, 0.1%, 0.5%, 1%, 2%, 3%, and 4%), different mass NP consisting of 1 wt% GAS or 1 wt% TEA was respectively added to the same quality of water.

The tribological properties of NP consisting of 1 wt% GAS or 1 wt% TEA as the water-based lubricant additives at different mass concentration were evaluated by an Optimal SRV-IV oscillating reciprocating friction and wear tester. In this experiment, the friction coefficient (COF) and wear volume losses (WV), two parameters for the determination of reducing-friction and anti-wear properties of different lubricants, were carried out applying a load of 100 N, a frequency of 25 Hz, and 1 mm-amplitude at 25 °C for 30 min. Each specimen was measured for 3 times at a relative humidity of 40–50% for 3 times. The hardness of AISI 52100 bearing steel ball was 700–800 HV and its diameter was 10 mm. The lower stationary disc was  $\phi$  24 mm $\times$ 7.9 mm and made up of AISI52100 bearing steel with hardness of 750–850 HV. The mean roughness ( $R_a$ ) of the lower steel discs and steel ball were polished to about 0.02  $\mu\text{m}$  with CW400 -CW2000 SiC abrasive paper.

The best concentration of NP consisting of 1 wt% GAS or 1 wt% TEA was select from different mass concentrations under the above conditions and then measured on the frequency conversion and the variable load experiment. It was used to record automatically the corresponding friction curves and electrical contact resistance by a computer using a data-acquiring system linked to the SRV-IV tester. A MicroXAM-3D noncontact surface mapping profiler was used to examine the wear volumes on steel surfaces.

The worn surface morphologies of wear scars on steel surfaces lubricated different lubricants were examined on a JEOL JSM-5600LV scanning electron microscope (SEM) (JEOL, Japan). After SRV-IV tests, the chemical composition of the wear scars on steel surfaces

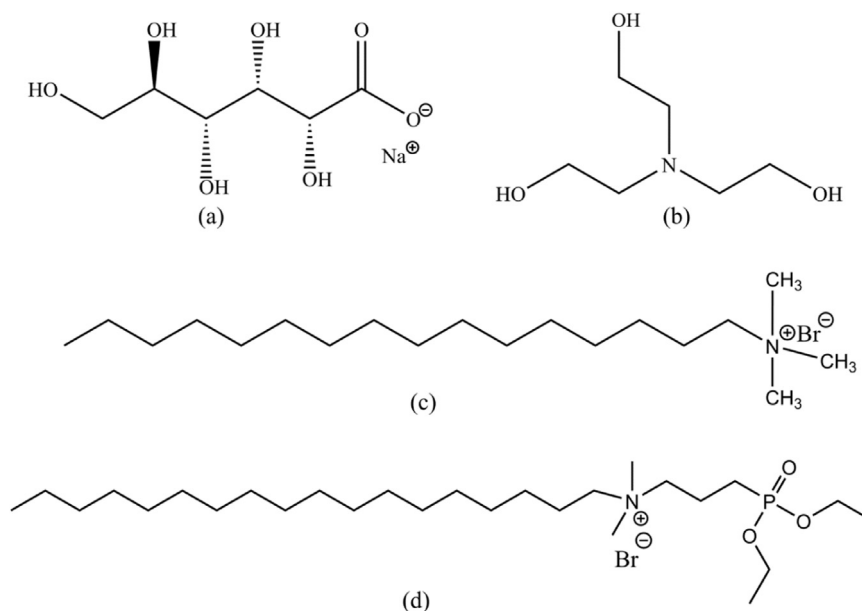


Fig. 1. Molecular structures of (a) sodium D-gluconate (GAS), (b) triethanolamine (TEA), (c) hexadecyl trimethyl ammonium bromide (CTAB) and (d) N-(3-(diethoxyphosphoryl) propyl)-N,N-dimethyl octadecan-1-ammonium bromide (NP).

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