



Serbian Tribology
Society

SERBIATRIB '25

19th International Conference on
Tribology



Faculty of Engineering
University of Kragujevac

Kragujevac, Serbia, 14 – 16 May 2025

Research paper

DOI:10.24874/ST.25.143

INVESTIGATION OF TRIBOLOGICAL PROPERTIES OF PROTIC IONIC LIQUIDS AS VERSATILE ADDITIVES FOR ENVIRONMENTALLY FRIENDLY WATER-BASED LUBRICANTS

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Abstract: Water as a base lubricating fluid is popular due to its low cost, nontoxicity, fire resistance, and availability. However, water as a base fluid needs to be enhanced to meet the requirements of specific applications. Therefore, this study aims to evaluate the potential of protic ionic liquids (PILs) to improve the tribological properties of water-based lubricants. The lubricity of several PILs, namely diethanolamine oleate and erucate, and tert-octylamine oleate in the water-based lubricating fluid was experimentally investigated using a ball-on-plate tribometer. In addition, kinematic viscosity, corrosiveness, and wettability were investigated. Environmental compatibility, such as soil phytotoxicity, was evaluated. The results show that the wear and friction reduction ability was significantly improved by using up to 1 wt. % of PILs. It was speculated that the polar molecules of PIL adsorb on the lubricated surface. Introducing PILs reduces the surface tension of water, resulting in better wettability. The investigated PILs showed no phytotoxicity, which makes them attractive as environmentally friendly additives.

Keywords: lubrication, additives, protic ionic liquid, wear, friction, phytotoxicity

1. INTRODUCTION

Lubricants are essential for minimising friction and wear, as well as being critical for energy efficiency and environmental protection [1]. Traditional petroleum-based lubricants pose environmental and health issues. Due to their availability and excellent thermal conductivity, water-based lubricants (WBLs) are being positioned as a more promising, eco-friendly alternative [2,3]. WBLs are particularly attractive for industries that need efficient cooling and reduced environmental impact [3]. Despite these advantages, water-based lubricants frequently demonstrate less effective lubrication properties when compared

to petroleum-based lubricants [2]. The primary reason is the limitations of water as the main component. Pure water, although it possesses excellent thermal conductivity, has inadequate viscosity and a tendency to cause corrosion, particularly when in contact with steel surfaces [2]. These properties reduce the effectiveness of WBLs in tribological systems where consistent surface separation and wear protection are essential. Therefore, effective additives are crucial for enhancing the tribological and anti-corrosion properties of WBLs [3,4]. Among contemporary additives, ionic liquids (ILs), especially protic ionic liquids (PILs), are receiving considerable attention as such additives [2,4,5].

ILs, being liquid organic salts, provide unique properties for lubrication, such as low vapour pressure and high thermal stability; notably, they can also form protective tribo-films on metal surfaces [1,4]. PILs, with their proton and hydrogen bonding capability, are well-suited for water-based systems. They improve lubrication and even provide anti-corrosion benefits [2,4]. PILs provide a route to more sustainable lubrication technologies [1,3]. Therefore, these experiments aim to investigate PILs as potential tribological properties improving additives for water-based lubricating fluids.

2. MATERIALS AND METHODS

The lubricity of several protic ionic liquids (PILs), diethanolamine oleate (P1), tert-octylamine oleate (P2), and diethanolamine erucate (P3) in deionised water (W) was experimentally investigated. The investigated PILs were synthesised following the procedure described in our previous paper [6]. A magnetic stirrer dispersed 1 wt.% of each PIL in water.

The tribological tests were conducted using a ball-on-plate tribometer. In this tribo-test, a 6 mm bearing steel ball (hardness 850 HV, roughness 0.05 μm) was rubbed against the 10x3 mm bearing steel disc-plate (hardness 190 HV, roughness 0.02 μm). The tribo-test parameters were as follows: reciprocation frequency 15 Hz, load 4 N, temperature 30 °C, duration 30 min. After tribo-tests, the specimens were inspected using optical and scanning electron microscopy. The wear scars were measured using a tip profilometer.

Kinematic viscosity, cast iron chip corrosion prevention, and wettability were investigated using standard test methods. Soil phytotoxicity evaluated environmental compatibility. The spring onions were grown in soil with a particular PIL concentration. The development of plants was monitored and compared with the conventional ionic liquid.

3. RESULTS AND DISCUSSION

Despite the low concentration, the introduction of PILs increased the viscosity of water (Table 1). The increase in viscosity varied due to differing molecular structures. It is believed that such a slight difference will not significantly affect lubricity.

Table 1. Kinematic viscosity of lubricants

Kinematic viscosity at 30 °C [mm/s ²]			
W	W+P1	W+P2	W+P3
0.801	1.746	0.981	1.631

The introduction of PILs improved the water's corrosion-prevention ability. However, the effect was not the same. Additive-free deionised water could not inhibit the corrosion of cast iron chips. The best results were observed in the case of P2, while other PILs showed less improvement (Figure 1). The ability to prevent the corrosion of iron-based metals is assigned to the nitrogen-containing spaces. Moreover, the formation of an adsorbed layer prevents oxygen from reaching the metal surface.

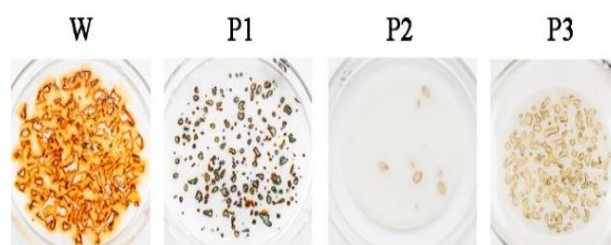


Figure 1. Cast iron chip corrosion prevention test results

The polarity of the PIL molecules is responsible for improved wettability. The polar molecules reduce water's surface tension and enable its penetration into the most minor cavities between interacting surfaces. Table 2 presents the wettability represented as the contact angle, which was measured between the surface and the edges of the droplet of lubricating fluid. The smaller the angle, the greater the wettability. The improved wettability allows us to make assumptions that the lubricity of additised samples will also be improved.

Table 2. Contact angle of lubricating fluids

Contact angle [degrees]			
W	W+P1	W+P2	W+P3
64	32	39	33

Figure 2 presents the mean coefficient of friction obtained during the tribological tests. Additive-free water demonstrated an extremely high COF. Introducing PILs significantly improved friction reduction, and the investigated additives demonstrated similar COF. The adsorbed layers of ionic liquid molecules are well known to reduce friction [5].

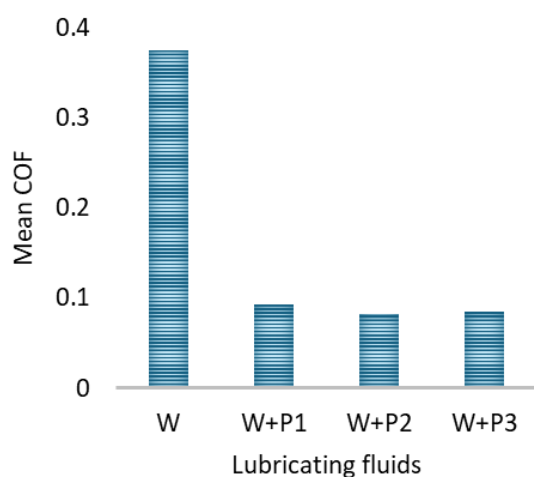
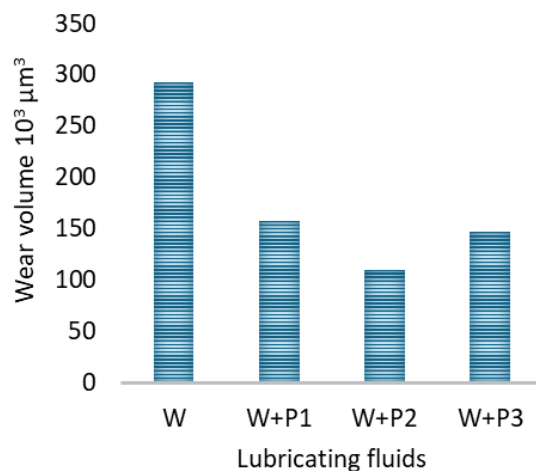
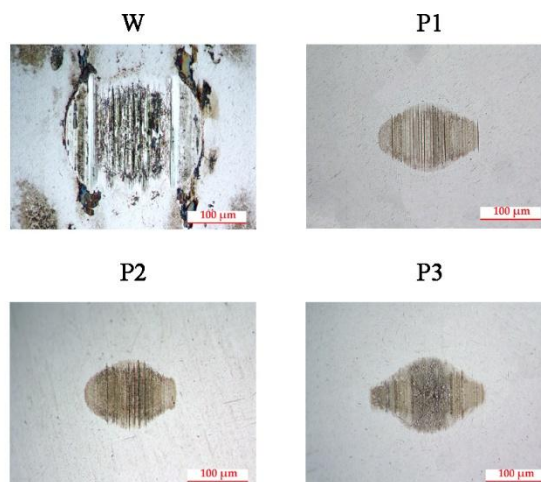
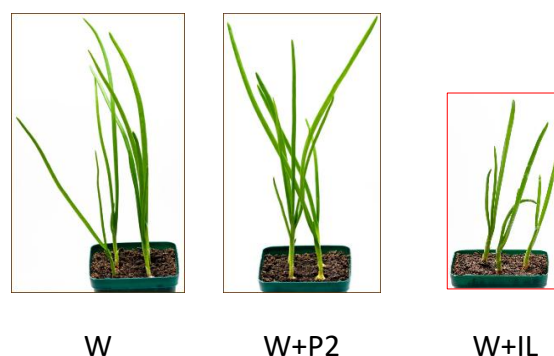
**Figure 2.** Mean COF observed in the tribological tests

Figure 3 presents the wear volume observed after the tribo-tests. Similar to COF, the wear was considerably reduced. However, in the present case, the P2 additive demonstrated better performance. It could be speculated that molecules of tert-octylamine oleate possess better adsorption, which also led to better corrosion prevention in the above-discussed tests.

The optical microscope images of wear scars observed on the balls confirm the abovementioned results (Figure 4). The lubrication with additive-free water produced a highly abraded and oxidised bearing steel surface. Lubrication with additised water resulted in smaller and smoother worn surfaces. The wear scars are similar in appearance. They all have minor scratches, residues of tribo-film, and similar shapes, which occur from the

specific contact with the plate. The relatively harder balls undergo only polishing, while the softer plate has a wear track.

**Figure 3.** Wear volume observed in the tribological tests**Figure 4.** Wear scar appearance**Figure 5.** Growing spring onions in the phytotoxicity test

Lubricating fluids accidentally spilt into the soil must not harm the environment. The phytotoxicity tests compared the growth in intact soil, soil with a P2 additive, and soil with a conventional halogen-

containing ionic liquid (Figure 5). The PIL additive did not influence the growth of spring onions, while the halogen-containing ionic liquid sowed the growth. Moreover, the onion leaves look unhealthy in the case of conventional ionic liquid.

4. CONCLUSIONS

Introducing protic ionic liquids to the deionised water improved its tribological properties. The improvement was disclosed by using a set of essential properties, namely viscosity, wettability, corrosion prevention ability, and, most importantly, lubricity. The presence of 1 wt. % of PILs increased the viscosity and improved wettability and lubricity. The corrosion prevention ability was also improved, but further investigation is needed to determine the optimal concentration of PIL. The performed soil phytotoxicity experiments reveal the environmentally friendly nature of tert-octylamine oleate PIL. Considering the similar nature of investigated PILs, it was speculated that other investigated PILs would possess similar phytotoxicity.

ACKNOWLEDGEMENT

This research was funded by grant No. S-MIP-21-61 from the Research Council of Lithuania.

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