

Effects of Halide Contaminants on the Lubricating Properties of Phosphorus-Based Ionic Liquids

Zixuan Li^{1,2}, Oscar Morales-Collazo³, Jerzy T. Sadowski⁴, Hugo Celio¹, Andrei Dolocan¹, Joan F. Brennecke³, Filippo Mangolini^{1,2,5}

¹) Texas Materials Institute, The University of Texas at Austin, Austin, Texas 78712, USA

²) Materials Science and Engineering Program, University of Texas at Austin, Austin Texas 78712, USA

²) Materials Science and Engineering Program, University of Texas at Austin, Austin Texas 78712, USA

³) McKetta Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas 78712, USA

⁴) Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York 11973, USA

⁵) J. Mike Walker Department of Mechanical Engineering, The University of Texas at Austin, Austin, Texas 78712, USA

*Corresponding author: filippo.mangolini@austin.utexas.edu

Ionic liquids (ILs) are a novel class of “green” lubricants that can potentially increase the energy efficiency and lifetime of automobile engines. Despite recent progress in the synthesis of lubricious ILs, their implementation in oil formulations has been hindered by their high cost, which derives from the time-consuming purification processes used to remove two common contaminants from ILs, namely water and residual halide ions from the chemical synthesis. Here, we evaluate the effect of halide ions and water on the lubricating properties of a class of non-corrosive, thermally-stable, and oil-soluble ILs, *i.e.*, phosphonium phosphate ILs (PP-ILs).

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1. Introduction

Ionic liquids (ILs) are defined as salts with melting point below 100°C. Their unique physico-chemical properties (*e.g.*, low vapor pressure, high thermal stability, low flammability) compared to molecular liquids make them useful for a range of applications, including batteries, catalysis, and lubrication. Since the first report in 2001 proposing the use of ILs as lubricants¹, a number of researchers in tribology focused on the investigation of the lubrication mechanism of ILs. In particular, studies at the macroscale provided evidence for the ability of phosphorus-containing ILs to work as surface-active ingredients able to reduce friction and wear by reacting on metallic surfaces and forming thin, protective films (“tribofilms”)². Among the ILs that have recently drawn the attention of scientists, phosphonium phosphate ILs (PP-ILs) have been investigated given their solubility in non-polar hydrocarbon oils and their effectiveness in reducing friction and wear in steel-*vs.*-steel sliding contacts. The vast majority of these studies have been carried out with high-purity PP-ILs, whose high cost mainly derives from difficult and time-consuming purification processes required to remove contaminants (*i.e.*, water and residual halide ions from the synthesis). Even though several studies published in the last decade highlighted the role of residual water in affecting the tribological performance of imidazolium-based ILs, remarkably little is known about the effect of common contaminants (*i.e.*, residual halide ions from the synthesis) on the lubricating properties of PP-ILs. The present work aims to fill this gap in our knowledge base by systematically evaluating the influence of halides on the lubricating properties of PP-ILs, while shedding light on the underpinning surface physico-chemical origin.

2. Results & Discussion

Here, we perform macroscale tribological (52100 steel-*vs.*-52100 steel) experiments in the presence of PP-ILs (tri-hexyltetradecylphosphonium bis(2-ethylhexyl) phosphate [P_{6,6,6,14}][DEHP] IL) with systematically-varied concentration of a common halide contaminant, *i.e.*, bromide, to identify its influence on the tribological response of PP-ILs. The tribological tests indicated a slight reduction of friction upon increasing the bromide-to-phosphate anion ratio from 0.05:1 to 1:1. A further increase in the bromide-to-phosphate anion ratio above 1:1 led to an increase in friction and wear together with corrosion of the steel surface.

Ex situ surface chemical analysis (X-ray photoelectron spectroscopy, time-of-flight secondary ion mass spectrometry, and synchrotron-based X-ray photoemission electron microscopy) suggested that the presence of a sufficient concentration of phosphate anions (bromide-to-phosphate anion ratio less than 1:1) is critical to create a phosphate adsorbed surface layer on steel able to prevent significant corrosion due to the presence of bromide anions (together with residual water in the ILs).

These findings not only shed new light on the effect of halides on the lubrication performance of ILs in general, but also provide guidance for efficiently using ILs in a cost-effective manner in technological applications.

3. References

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