

# Nanotribology of Phosphonium Phosphate Ionic Liquid: a Combined Atomic Force Microscopy and Surface Spectroscopic Study

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While phosphonium phosphate ionic liquids have been evaluated as oil additives owing to their miscibility with hydrocarbon fluids and promising tribological properties, their lubrication mechanism is still not established. Here, we perform atomic force microscopy (AFM) nanotribological experiments in trihexyltetradecylphosphonium bis(2-ethylhexyl)phosphate ionic liquid. The AFM results indicate a reduction in friction after the removal of the native oxide layer from steel. Based on laterally-resolved analyses of the steel surface, a simple phenomenological model is proposed to account for the observed nanotribological behavior.

**Keywords:** nanotribology, ionic liquids, atomic force microscopy, XPS, NEXAFS

## 1. Introduction

Ionic liquids (ILs) have gained considerable attention in the last two decades owing to their unique and tunable physico-chemical properties (*e.g.*, low vapor pressure, and high thermal stability), which have made them potentially useful for a range of applications, including batteries, fuel cells, catalysis, and lubrication. Ionic liquids are particularly attractive in lubrication, since their properties make them suitable for components working under extreme conditions (*e.g.*, high temperatures, low pressures), such as those found in engines, spacecraft, and micro-electromechanical systems. When ILs are used as lubricants, the interface between the IL and the surfaces of the components in relative motion plays a pivotal role in controlling the friction and wear response. Despite the scientific weight of published studies on the tribology of ILs, remarkably little is still known about the underpinning lubrication mechanism of ILs. The development of a fundamental understanding of the mechanism by which ILs reduce friction and/or wear requires shedding light on the processes occurring at nanoscale asperities within macroscale contacts. This constitutes a significant challenge since observing and understanding the nanoscale mechanisms at play is inhibited by the hidden nature of the buried interface and the challenge of performing observations at the nanometer scale. Here, we combined *in situ* atomic force microscopy (AFM) and *ex situ* laterally resolved surface analyses to establish a fundamental understanding of the lubrication mechanism of a class of phosphonium phosphate ionic liquids (PP-ILs), namely trihexyltetradecylphosphonium bis(2-ethylhexyl) phosphate ([P<sub>6,6,6,14</sub>][DEHP]) IL.

## 2. Results & Discussion

Here, we used AFM to visualize and quantify the

processes occurring at sliding interfaces *in situ*, in single-asperity nanocontacts<sup>1</sup>. The AFM experiments, in which a diamond tip was slid on steel in [P<sub>6,6,6,14</sub>][DEHP] IL at high contact pressure (>5 GPa), indicated a significant friction reduction only after the removal of the native surface oxide from steel. Subsequent *ex situ* laterally-resolved analysis of the surface chemistry of steel by synchrotron-based X-ray photoemission electron microscopy (X-PEEM) indicates that no stress-assisted, thermally activated chemical reaction occurred between the [P<sub>6,6,6,14</sub>][DEHP] IL and steel during the AFM experiments. The removal of the native oxide from steel led to significant variations in surface potential (measured by low energy electron microscopy, LEEM) and an increase in surface coverage of [DEHP] ions (measured by time-of-flight secondary ion mass spectrometry,ToF-SIMS). These surface modifications are proposed to be caused by a change in surface roughness, and adsorption configuration of bis(2-ethylhexyl)phosphate anions on metallic iron compared to their configuration on iron oxide, which lead to the formation of a densely packed, lubricious boundary layer only on metallic iron. The findings of this work<sup>2</sup> not only shed new light on the lubrication mechanism of ILs in general, but also provide guidance for engineering ILs with the aim of tuning their lubricating properties by controlling their interfacial structures with metal and metal oxides.

## 3. References

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