Ionic Liquid Lubricant Films: Solid- vs. Liquid-like Behavior

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Ionic liquids (ILs) can form strongly adsorbed films on solid surfaces and are capable of bearing heavy loads and effectively reduce friction. Here, we have combined nanorheological and tribological studies of five different ILs using an extended Surface Forces Apparatus. We discuss the effects of the chemical structure, water contamination and surface charge on the nanorheological behavior of the nanoconfined IL films and on friction.

Keywords (from 3 to 5 max): nanotribology, nanorheology, ionic liquids, lubrication.

1. Introduction

Ionic liquids (ILs) have been recognized as suitable lubricants under harsh conditions. The strongly adsorbed IL layers on solid surfaces are capable of bearing heavy loads and effectively reduce friction. Yet, the literature often mentions the solid-like behavior of ILs under the nanoconfinement provided by two countersurfaces. Here, we investigate this behavior and how it relates to the tribological performance of ILs. This work sheds light on the molecular mechanisms that govern IL-mediated lubrication.

2. Methods

We have used an extended Surface Forces Apparatus (SFA) as a nano-rheometer and as a tribometer to investigate IL films with thicknesses varying between 1.8 and 10 nm confined between mica surfaces.

In an SFA, the film thickness is controlled by moving one of the surfaces to a specific separation from the second surface very slowly (~0.5 nm/s). D is measured in real time by multiple-beam interferometry using a numerical method called Fast Spectral Correlation (FSC), which yields D with a precision better than ~30 pm and the refractive index $n(t)$ with a precision of ± 0.01. Concurrently, the SFA measures the equilibrium surface force F_s as a function of D *via* a double-cantilever spring. The temperature can be modulated in the range of 10 to 60 ºC with a stability of 0.001 ºC/h.[57] For nanorheology and tribology experiments, the lateral deflection is measured by four strain gauges assembled in a Wheatstone bridge configuration attached to the lateral spring. Using this set-up, we can subject the confined IL films to shear at a constant velocity between 0.2 nm/s and 1000 µm/s, and at a sinusoidal velocity with frequency from 0.05 to 50 Hz.

We have investigated five different ILs to examine the influence of their chemical structures on the confined behavior. The influence of water has been also studied upon equilibration of the ILs at fixed air humidity to introduce water from the gas phase. The effect of the surface charge has been also interrogated using self-assemble monolayers to control the charge density.

3. Discussion

Experimental results for dry 1-butyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide (abbrev. as [BMIM][TFSI]) are shown in Figure 1. Figure 1a shows the friction force as a function of the sliding velocity as a function of the film thickness (varying between 1.8 nm and 6.2 nm, corresponding to different loads, also given in the legend). Friction increases quasi linearly with sliding velocity at loads between 8 and 35 nN, at which the film thickness is ≥3 nm. At velocities smaller than ~ 3 µm/s, friction becomes smaller than the precision of the instrument. At the highest applied load (50 nN) friction abruptly increases; here, the equilibrium film thickness is 1.8 nm. We only show values at sliding velocities smaller than 0.3 µm/s (red), because the friction force is too high to be measured with the current set up at higher velocities. In this range of slow velocities, prominent stick-slip was measured, which correlates with the highest friction force.

Figure 1b shows the nanorheological results for the same IL as a function of the frequency. The films of dry ILs with thickness smaller than 2 nm are found to be elastic (G'>>G''), which correlates with the highest friction and stick slip in Figure 1a. Films with a thickness between 3 and 5 nm behave as viscoelastic liquids, while films with a thickness larger than 8 nm behave as viscous liquids.

We also found that the presence of water can alter the tribological and viscoelastic response of the ILs. For example, it can eliminate completely the stick slip at the highest loads and eliminate the elastic behavior of thin IL films. We also resolve the effect of the molecular composition and surface charge on the nanorheological and tribological behavior of confined IL films.

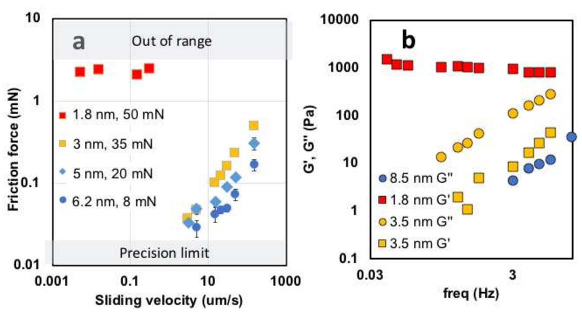

Figure 1: a) Friction force and b) nanorheological results (G' and G'') for [BMIM][TFSI]. The legend gives the thickness of the films in nanometers.