

Lateral Force Microscopy Study of the Friction between Silica Surfaces in Electrolyte Solutions

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Abstract: Lateral force measurements between a polished silica wafer and a colloidal silica particle in monovalent electrolyte solution environment (LiCl, NaCl, CsCl) were performed using an Atomic Force Microscope (AFM). Analysis of the friction versus load data, in LiCl case, indicates that increasing the electrolyte concentration, the intensity of the friction force decreases. The effects of the counterions on lateral forces show that friction coefficients gradually decrease from pure DI water to 1.0M LiCl. Lateral forces versus scan rate graphs show a typical behavior for all investigated systems: transition and saturation region. These results are consistent with the idea that strongly hydrated ions have a lubrication effect in silica-silica interactions.

INTRODUCTION

Understanding of the tribological phenomena at the nanoscale level is of critical importance for the fast development of existing and emerging technologies such as the Chemical Mechanical Planarization (CMP) and microelectromechanical systems (MEMS). The colloidal and frictional behavior of the silica, which is an important component in these technologies have been known to be far more complex than expected for smooth, chemically inert surfaces (Cook, 1990; Vigil et al., 1994; Israelachvili, 1992). The Atomic Force Microscope (AFM), used in Friction Force Microscopy (FFM) mode proves to be an ideal instrument to study the frictional phenomenon down to atomic scale. The influence of monovalent electrolyte solution on interaction forces between surfaces has been extensively studied for mica systems (Pashley, 1981, 1982; Raviv and Klein, 2002) and for mica-silica systems (Vakarelski et al., 2000), proving the existence of short-range repulsive force caused by the hydrated cations adsorbed on the surface. The strength of this force was demonstrated to increase in the order of $Cs^+ < K^+ < Na^+ < Li^+$. However, when the silica surfaces were employed instead of mica, the dependence of the interaction force shows opposite behavior: the strength and range of hydration forces decrease with increasing the degree of hydration of the counterion (Horn et al., 1989; Chapel, 1994).

The purpose of the present work is to provide systematic and reproducible data of the lateral forces recorded while sliding a colloidal particle on a flat surface in electrolyte solutions using an AFM in lateral force microscopy (LFM) mode and the colloidal probe technique.

MATERIALS AND METHODS

The 6.84- μm (diameter) monodispersed nonporous silica particles were purchased from Bangs Laboratories, as 10% vol. suspension in Deionized Water (DI). Prior to usage, small amounts of suspension were slowly dried in a vacuum chamber (70°C). The silica wafers (P-type, <100> crystal orientation, producer provided root mean square roughness about 0.2nm over $1\mu\text{m}^2$ area) have provided by Shin-Etsu Chemical Co., Japan. The solutions were prepared using analytical grade LiCl, NaCl and CsCl and the water used for all the

experiments was produced by a Milipore filtration system, with an internal specific resistance no less than $17.0 \pm 0.1 \text{ M}\Omega/\text{cm}$. The pH of solutions was determined to be 5.6 ± 0.5 .

All the experiments were done using a Digital Instruments Nanoscope III Multimode Atomic Force Microscope, equipped with a fused silica liquid cell. In friction measurements sessions, tipless rectangular cantilevers (MikroMasch Co., nominal spring constant $K_N=1.75\text{N/m}$) were used. Before starting, the wafers were thoroughly washed in acetone, ethanol and pure water. After the washing procedure, the wafers were plasma treated for 3 minutes in Ar-moisture atmosphere, using a combined system consisting in a Basic Plasma Kit-BP1 (Samco Co.) and a Radio Frequency Plasma Generator-ENI ACG 98(13.6 MHz, 1W). Contact angle measurements done after each cleaning step, showed gradual improvement of the surface decontamination and after plasma treatment, the wafers become fully hydrophilic. Silica particles were attached to the cantilever end using thermoplastic epoxy adhesive (Shell Epikote 1004) and alternatively washed in ethanol and DI water. In a typical friction force experiment, the colloidal probe is pressed against the substrate at a constant applied force while the substrate slides horizontally. The recorded data represents trace minus retrace (TMR) values of the lateral detector signal in one complete scan loop.

RESULTS

Friction trends in water and data reproducibility.

In order to obtain a reference basic behavior we have measured, at first, lateral force trends in pure water. Figure 1 illustrates the lateral force versus loading force curves for the case of silica surfaces interacting across pure water, which exhibit a linear behavior, in agreement with Amontons's Law. Each point is the conversion result of a friction loop at specific load. Typically, we started the experiment at 43 nN loading force and after allowing the system to stabilize, we recorded the voltage difference between trace and retrace. After each step in the normal force rise, the lateral force level was allowed to reach an approximately constant value. The lateral force dependence with loading force was recorded for three different colloidal probes. We observed that the resulting trends were keeping their shape. Slight scatter of the friction magnitude in the case of dissimilar probes is usual due to the local surface roughness in the contact region. For clarity, we chose to show three sets of friction trends recorded with the same colloidal probe, at different locations. The repeatability of trends, in consecutive experiments, leads us to conclude that the sliding process does not promote a detectable change in investigated system roughness, even though wearing cannot be excluded.

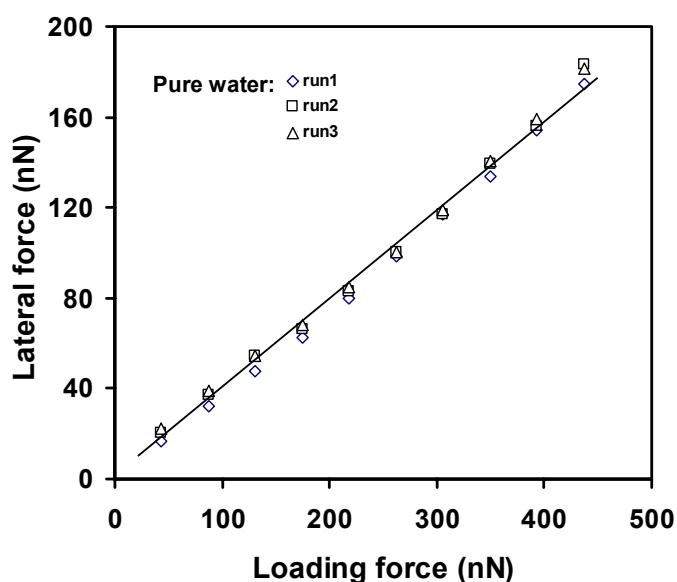


Figure 1. Lateral force as a function of the applied load for a $6.84\mu\text{m}$ silica sphere attached to a rectangular cantilever interacting with a polished silica wafer in pure DI water.

Salt concentration effect

The next step in our investigation was to study LiCl concentration effect on lateral force (Figure 2). Increasing the number of adsorbed ionic species (Li^+) on the negatively charged silica surface has a drastic effect on the lateral forces magnitude (from pure water to 1.0M LiCl there is a 75% drop in friction coefficient).

Cation type influence.

The friction force vs. load trends for three types of solutions (Figure 3), at the same concentration (1.0M), show that the lubrication effect is in close relation with the size and hydration properties of the involved cation. Knowing that in our experiments we could not exert enough pressure to remove the cations we can assume that cesium remains trapped in contact region and it is responsible for high values of friction coefficient (compared with lithium) because of its weak ability to structure water and to prevent direct contact.

The intermediary behavior of friction in presence of sodium, between lithium and cesium, comes to consolidate the hypothesis about cation series influence on friction.

Scanning velocity effect

The scanning rate influence on lateral force was studied at specific value of loading force (175nN), between $0.4\mu\text{m/s}$ and $55\mu\text{m/s}$, for metallic chloride solutions (1.0M) and pure DI water (Figure 4). Each experimental point was obtained after we allowed the system to equilibrate for a given value of scan rate (at least 10 trace/retrace loops were allowed to continue until we recorded the voltage). The shape of the curves follows the same pattern for all four systems: a steep, almost linear zone (Feiler et al., 2003) where lateral force is decreasing fast with

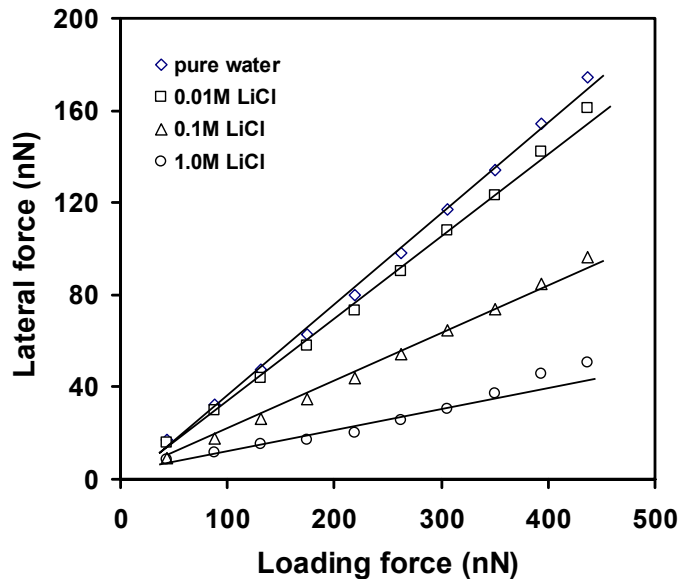


Figure 2. Lateral force as a function of the applied load for a $6.8\mu\text{m}$ silica sphere interacting with a polished silica wafer in pure DI water, 0.01M LiCl, 0.1M LiCl and 1.0M LiCl.

lithium) because of its weak ability to structure

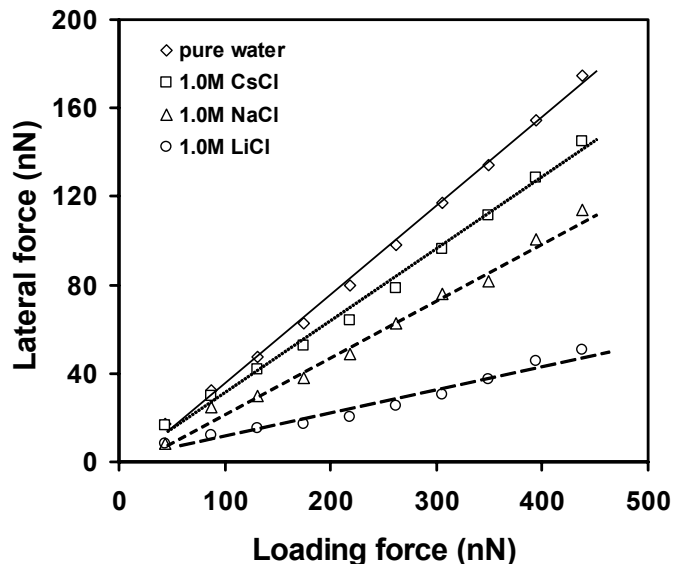


Figure 3. Lateral force as a function of the applied load for a $6.8\mu\text{m}$ silica sphere interacting with a polished silica wafer in pure DI water, 1.0 M CsCl, 1.0M NaCl and 1.0M LiCl.

scan rate and a saturation zone. These trends resemble the generic Stribeck curve (Persson, 2000) of lubricated solid bodies. Beyond certain values of scan rate (15 $\mu\text{m/s}$), the four systems reach a level of equilibrium: the scanning colloidal particle is much more separated from the wafer by hydrated counterions, which act as lubricants. Going back to the first value of scan rate, at the end of each measurement session, we could attain approximately the same value for friction force, proving that the possible wearing effect is negligible. The trends confirmed in Figure 3 and Figure 4 suggests that the more hydrated cations produce a stronger lubrication effect: the thicker the hydration shell – the stronger is the effect.

CONCLUSIONS

Lateral force measurements across aqueous electrolyte solutions reveal lubrication effects when the counterion concentration is increasing.

The presence metallic ions of different types at the silica-silica interface induce gradually, the reduction of friction coefficient in order: $\mu_{\text{Cs}^+} > \mu_{\text{Na}^+} > \mu_{\text{Li}^+}$.

For all electrolyte solutions, the dependence of lateral force with scanning velocity shows typical behavior: transition and saturation region.

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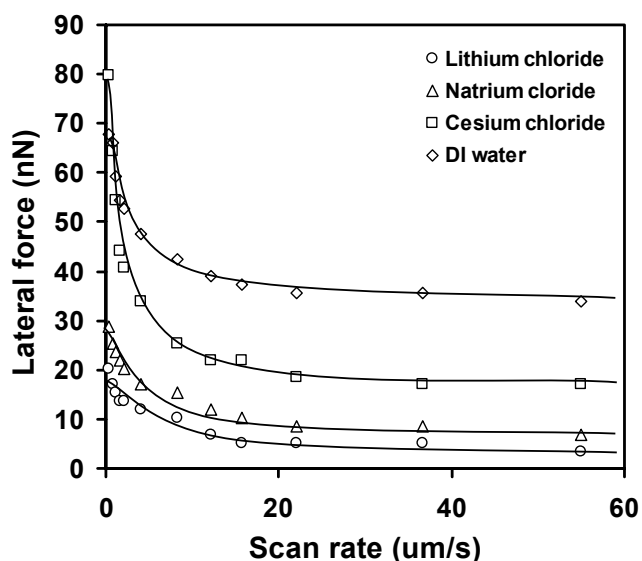


Figure 4. Lateral force as a function of the scan rate for a 6.8 μm silica sphere interacting with a polished silica wafer in pure DI water, 1.0M LiCl, 1.0M NaCl and 1.0M CsCl.