

# How the Ionic Layer between Silica Surfaces in Solutions Affects Their Macroscopic Friction

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電解質水溶液中の清浄なシリカ表面間摩擦力を種々の条件下で測定し、その摩擦力が、シリカ表面に吸着したイオン種、イオンの価数、対イオンの種類、溶液 pH に敏感に依存することを系統的に明らかにすると共に、吸着イオンが如何にマクロな摩擦力に及ぼすかに対するメカニズムを推定した。

## 1 Introduction

We conducted a series of friction measurements between completely-hydrophilic silica surfaces in various electrolyte solutions of normal and high pH's, by using the atomic force microscope (AFM), and it was found that the friction has the molecular-scale sensitivity to the surface microstructures and the medium properties.

## 2 Experiments

Silicon wafers coated by thermal oxide silica layer were used as flat surfaces, whose root mean square (RMS) roughness was about 0.2 nm over  $1\mu\text{m}^2$ . Pure nonporous silica spheres of 6.8  $\mu\text{m}$  and 10  $\mu\text{m}$  in diameter were used as spherical particles. The surfaces of wafers and silica particles were cleaned carefully.

Electrolytes used were LiCl, NaCl, CsCl, MgCl<sub>2</sub>, CaCl<sub>2</sub>, SrCl<sub>2</sub>, BaCl<sub>2</sub>, Mg(NO<sub>3</sub>)<sub>2</sub>, Ca(NO<sub>3</sub>)<sub>2</sub>, Sr(NO<sub>3</sub>)<sub>2</sub>, Ba(NO<sub>3</sub>)<sub>2</sub>, LaCl<sub>3</sub> and La(NO<sub>3</sub>)<sub>3</sub> of analytical grade. Pure water with an internal specific resistance no less than 17.6 M $\Omega$ /cm was produced with a Millipore filtration system. The solution pH was adjusted with a 0.1M solution of HCl and a 0.5M solution of NaOH.

All the friction measurements were carried out with an AFM (Digital Instruments Nanoscope III multimode) equipped with a liquid cell. Rectangular tipless cantilevers were used to prepare colloid probes.

## 3 Results and Discussion

### 3.1 Friction in Normal pH Solutions of Mono-valent Cations

Firstly, the frictions between silica surfaces in pure water and electrolyte solutions of monovalent cations with different hydration enthalpy were measured [1]. In pure water, the friction force  $F_L$  was found to increase linearly with the applied load  $L$  at a fixed scan rate  $v$ , as shown in Figure 2. However, at a given applied load, the friction decreases with the increase of the scan velocity and reaches to a saturation value at higher scan rates, as shown in Figure 3.

When electrolytes were added, the significant lowering of the frictional coefficient occurred. An important finding was that the lubrication property can be related to the hydration enthalpy of the cations adsorbed on surfaces; the smaller and more hydrated the cations are, the stronger the lubrication effect is, as shown in Figures 2 and 3. The most probable mechanism is that the lubrication is attributable to the lateral mobility of the water molecules within the hydration shell of adsorbed cations.

### 3.2 Friction in Normal pH Solutions of Multi-Valent Cations

Here the effects of multivalent cations on the magnitude of friction were examined [2]. It was found that even very small concentrations of divalent cations could significantly change the frictional force between surfaces. The Ba<sup>2+</sup>, Sr<sup>2+</sup> and Ca<sup>2+</sup> cations were found to act effectively as lubricants, as in the cases of monovalent cations. However, in the case

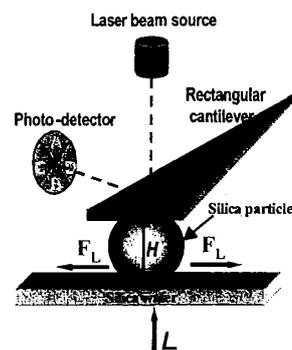


Figure 1 Schematic drawing of the principle of friction measurement by AFM

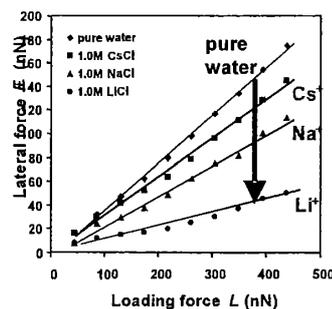


Figure 2 Dependence of  $F_L$  on  $L$  between silica surfaces in solutions of various monovalent cations at normal pH

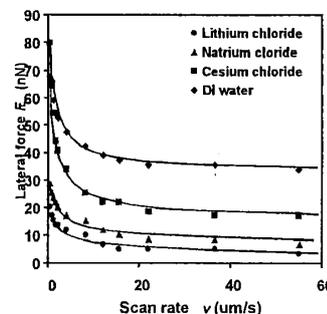


Figure 3 Dependence of  $F_L$  on  $v$  between silica surfaces in solutions of various monovalent cations at normal pH

of  $Mg^{2+}$ , the trend was reversed, as shown in Figures 4 and 5. Hence, the mechanism of friction for multi-valent cations was not so simple. It was found that these friction values were successfully correlated with a dynamic measure, that is, the relative residence time of water molecules around ions.

### 3.3 Sensitivity of Friction to Molecular-Scale Surface Properties and the Correlation with Solution pH

Here the fundamental differences of friction characteristics in solutions between a normal pH 5.6 and a high pH 10.6 were examined by using silica surfaces with the atomic-scale difference of roughness, which were prepared by the RCA cleaning procedure at different temperatures [3,4].

It is found that, in the case of normal pH, the atomic-scale roughness of surfaces influences greatly the magnitude of friction, while a master curve of friction, which is independent of the roughness, was obtained in the case of high pH, as shown in Figure 6. Because the existence of hairy layer was proven directly by the dynamic method for the normal force measurements and the thickness of the hairy layer at pH 10.6 was estimated to be at least 1.0~1.5 nm [5], the origin of the lubrication in the low loading region at pH 10.6 is considered to be due to the introduction of freely-movable water molecules into the gap between surfaces with the hairy layer, and the origin of the non-linear increase of friction at high loading force is the entanglement among the hairy chains protruding from the both surfaces. The appearance of the master curve was also considered to be attributable to the hairy layer, that is, the difference of the atomic-scale roughness at pH 5.6 was overcome by the existence of the much thicker hairy layer.

### 3.4 Conclusions

It was found that the atomic scale difference of adsorbed layers on silica surfaces in solutions influences greatly the macroscopic friction behavior between the surfaces.

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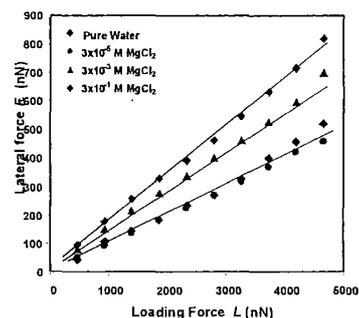


Figure 4 Dependence of  $F_L$  on  $L$  between silica surfaces in  $MgCl_2$  solutions at normal pH.

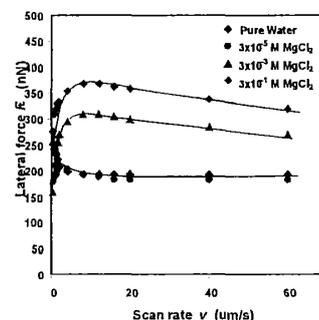


Figure 5 Dependence of  $F_L$  on  $v$  between silica surfaces in  $MgCl_2$  solutions at normal pH

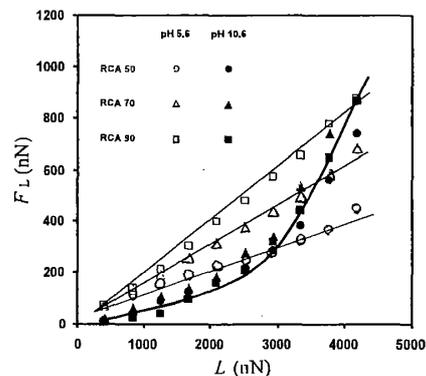


Figure 6 Dependence of surface roughness on the friction in solutions of normal and high pH's. (RCA 50 means that the surface was cleaned by RCA method at the temperature, 50 C)