

# Ionic Enhancement of Silica Surface Nanowear in Electrolyte Solutions

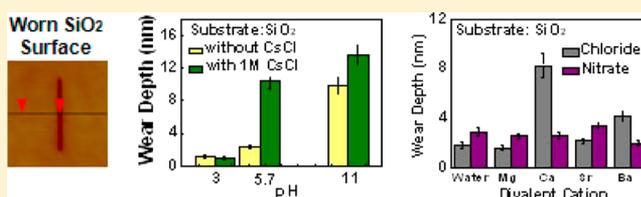
Ivan U. Vakarelski,<sup>†,‡</sup> Naofumi Teramoto,<sup>†</sup> Cathy E. McNamee,<sup>§</sup> Jeremy O. Marston,<sup>‡</sup> and Ko Higashitani<sup>\*,†</sup>

<sup>†</sup>Department of Chemical Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

<sup>‡</sup>Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia

<sup>§</sup>Shinshu University, Tokida 3-15-1, Ueda-shi, Nagano-ken 386-8567, Japan

**ABSTRACT:** The nanoscale wear and friction of silica and silicon nitride surfaces in aqueous electrolyte solutions were investigated by using sharp atomic force microscope (AFM) cantilever tips coated with silicon nitride. Measurements were carried out in aqueous solutions of varying pH and in monovalent and divalent cation chloride and nitrate solutions. The silica surface was shown to wear strongly in solutions of high pH ( $\approx 11.0$ ), as expected, but the presence of simple cations, such as  $\text{Cs}^+$  and  $\text{Ca}^{2+}$ , was shown to dramatically effect the wear depth and friction force for the silica surface. In the case of monovalent cations, their hydration enthalpies correlated well with the wear and friction. The weakest hydrated cation of  $\text{Cs}^+$  showed the most significant enhancement of wear and friction. In the case of divalent cations, a complex dependence on the type of cation was found, where the type of anion was also seen to play an important role. The  $\text{CaCl}_2$  solution showed the anomalous enhancement of wear depth and friction force, although the solution of  $\text{Ca}(\text{NO}_3)_2$  did not. The present results obtained with an AFM tip were also compared with previous nanotribology studies of silica surfaces in electrolyte solutions, and possible molecular mechanisms as to why cations enhance the wear and friction were also discussed.



## 1. INTRODUCTION

The understanding and control of friction and wear on the nanoscale is of growing importance for the rapid developments in industries employing microelectronics and nanotechnology. An example is the process of chemical mechanical polishing (CMP) used in the multilayer fabrication of integrated circuits and semiconductor devices. In CMP, the nanoscale smoothness of the wafer surface is achieved by the combined action of chemical etching and mechanical abrasion with slurries of nanosize abrasive particles.<sup>1–3</sup> Another example is the development of microelectromechanical and nanoelectromechanical systems (MEMS and NEMS), where surface wear is a major concern to the limitation of the lifetime of the devices.<sup>4</sup> The atomic force microscope (AFM) is a fitting tool for the investigation of friction and wear on small length scales.

A large number of AFM nanotribology studies have been conducted by employing the lateral force mode of the AFM either with a nanoscale bare tip or with a micrometer-scale colloid probe with a spherical particle glued on the top of the cantilever. In most experiments, a bare tip has been used as the probe, because the friction and wear experiments are very simple and efficient to conduct.<sup>5–10</sup> On the other hand, the colloid probes have the advantage of better reproducibility and limits the wear even for the measurement between bare surfaces.<sup>11–19</sup> Previously, we have performed a series of studies on the nanotribology of silica surfaces in aqueous electrolyte solutions using colloidal probes with a silica particle of 6–20

$\mu\text{m}$  in diameter and silica substrates. It was found that the lateral interaction between silica surfaces is extremely sensitive to the solution conditions, such as pH,<sup>11,12</sup> the concentration, and type of electrolyte,<sup>13,14</sup> and even the pretreatment of surface cleaning.<sup>15</sup> One of the significant effects found was that hydrated cations adsorbed on the silica surface can act as a highly effective boundary lubricant.<sup>13,14</sup> A similar effect was also reported for the lateral interaction between mica surfaces in electrolyte solutions measured using a modified surface force apparatus (SFA) and was explained by the preserved lateral mobility of the water molecules in the hydration shell of surface-adsorbed cations.<sup>20</sup>

Although the above-mentioned experiments using colloidal probes are somewhat related to the CMP polishing performance,<sup>21–23</sup> the colloid probe is not appropriate for wear experiments, as its size is too large to scratch the surface. Hence a bare tip, whose radius of curvature is close to that of CMP abrasive particles, was used in the present study, and both the friction and wear of silicon dioxide (silica) and silicon nitrate surfaces in aqueous electrolyte solutions were investigated by using an AFM tip coated with silicon nitrate. We found that even the simplest electrolyte additives, which are almost omnipresent in natural and industrial dispersions and are

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normally not considered to be active etching agents, can have a drastic effect on the nanoscale wear of the silica surfaces, and that the features of wearing correlated well with those of friction. We also correlated the results of this present study with those we previously obtained using a colloid probe.

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** All salts employed in this study (LiCl, NaCl, KCl, CsCl, LiNO<sub>3</sub>, NaNO<sub>3</sub>, KNO<sub>3</sub>, CsNO<sub>3</sub>, 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>) were purchased from Wako (Japan) and were of analytical grade. Organic contaminants in the salts were removed by roasting them for several hours in a high temperature furnace whenever possible. The water used was purified using a Millipore filtration system and had a specific resistivity of 18.2 MΩ cm.

Two kinds of wafers with different surface properties were employed as substrates: a silicon wafer with a 10 μm thick silicon dioxide (SiO<sub>2</sub>) layer (Silicon Quest Int.) and a silicon wafer with an LPCVD-deposited silicon nitride (Si<sub>3</sub>N<sub>4</sub>) layer (Silicon Quest Int.). The root-mean-square roughness of these substrate surfaces was determined via the AFM to be less than 0.3 nm over 1 μm<sup>2</sup>. Before commencing an experiment, the substrates were washed with acetone, ethanol, and water, and then plasma cleaned for 3 min in an argon–water moisture atmosphere. These treatments caused the substrate surface to be completely wetted by pure water.

**2.2. Experimental Apparatus.** The AFM measurements were made using a Digital Instruments Nanoscope III MultiMode atomic force microscope equipped with a liquid cell. Friction measurements were performed using a rectangular cantilever with the nominal normal spring constant,  $K_N = 0.03$  N/m (CSC38/Si<sub>3</sub>N<sub>4</sub>, MikroMasch), and the wear tests were done using a rectangular cantilever with the higher nominal constant  $K_N = 4.5$  N/m (NSC35/Si<sub>3</sub>N<sub>4</sub>, MikroMasch). The exact values of  $K_N$  were determined by the loaded cantilever frequency method.<sup>24</sup> Both the cantilevers have an integrated etched silicon conical tip coated with a ~10 nm thick layer of silicon nitride, where the height is 25–30 μm, the cone angle is 40°, and the tip radius is approximately 20 nm. Standard silicon nitride cantilever tips resist wear better than silicon tips, but have lower sensitivity to lateral measurements because of the short tip height. Etched silicon tips coated with silicon nitride were employed in the present study to provide the optimal combination of lateral sensitivity, wear resistance, and the wide range of spring constants needed for the friction and wear measurements.

**2.3. Experimental Procedure of Friction Measurement.** Friction force (also referred as lateral force) measurements were performed using the “friction force” mode of the AFM. In this mode, the cantilever tip is pressed against the substrate at a constant applied load, while the substrate slides horizontally underneath the cantilever. The lateral force on the tip is proportional to the cantilever twist registered by the AFM laser-photodiode system. The magnitude of the lateral force,  $F_L$ , is determined from half of the difference in the lateral force detector signal in one complete scan cycle (friction force loop),  $V_L$ , according to

$$F_L = \frac{1}{2} V_L S_L \frac{K_L}{H} \quad (1)$$

where  $S_L$  is the lateral detector sensitivity,  $K_L$  is the lateral spring constant, and  $H$  is the scanning cantilever tip height. The lateral sensitivity of the detector was determined to be  $S_L = 3.1 \times 10^{-4}$  rad/V,<sup>25</sup> and the lateral spring constant  $K_L$  was calculated by<sup>19</sup>

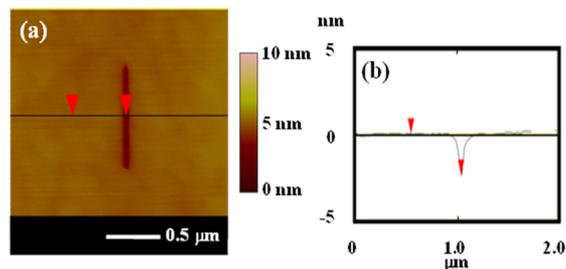
$$K_L = \frac{2K_N L^2}{3(1 + \nu)} \quad (2)$$

where  $\nu$  is Poisson's ratio ( $\approx 0.27$ ),  $K_N$  is the normal spring constant, and  $L$  is the cantilever length accounting for the cantilever tip position.<sup>26</sup>

Friction measurements were consecutively repeated at three different positions on the same substrate to confirm the reproducibility.

The averaged values were plotted against the applied load in the figures of the present study.

**2.4. Experimental Procedure of Wear Experiment.** The wear measurements were performed using the “imaging mode” (contact mode) of the AFM. First, the same place on the substrate surface was continuously scanned for a predetermined number of times by disabling the “slow scan” function and setting the scan angle to 90°. A scan size of 1 μm, scan rate of 10 Hz, scan time of 30 s (300 scan cycles), and applied load of approximately 720 nN (4 V deflection of 4.5 N/m cantilever) were used. Next, the wear trace was imaged with the same tip, but this time the scan direction was changed to 0°, the slow scan was enabled, and a much lower force was applied to the cantilever. The wear depth was determined from the height profile of the cross section line in the image, as shown in Figure 1. These wear

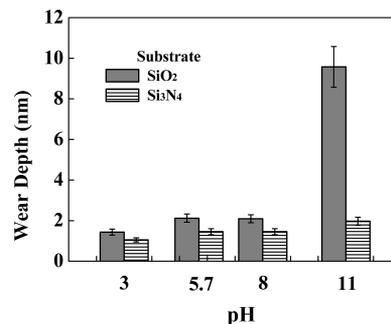


**Figure 1.** AFM image of a typical worn silica surface and the cross section profile.

test parameters were selected to allow consecutive measurements with the same tip before the wearing of the tip started to affect the results. The effect of tip wearing was checked by comparing the results between the first and the last measurements in pure water in a series of experiments. Consistent results were obtained whenever the same tip was used. However, it is not appropriate to compare the absolute values between different sets of data when different cantilevers were used. This is because each AFM tip may have a different radius of curvature. Hence, the data obtained using different cantilevers should be compared in terms of their relative differences with the values for pure water, which acts as a reference. We indicated in the figure captions when different probes were used to compare the data in one graph.

## 3. RESULTS AND DISCUSSION

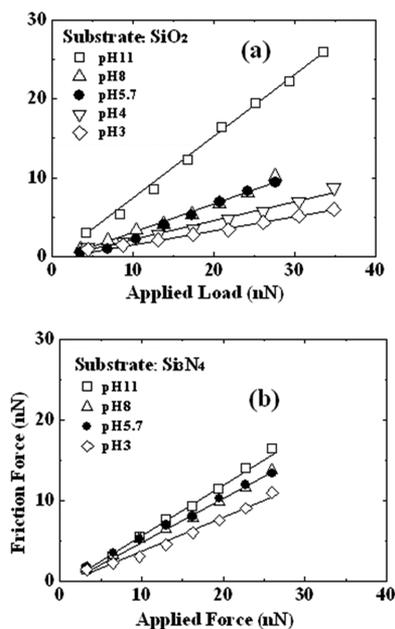
**3.1. Effect of the Solution pH.** The effect of the solution pH on the wear of the silica (SiO<sub>2</sub>) and silicon nitride (Si<sub>3</sub>N<sub>4</sub>) substrates was investigated, as shown in Figure 2. The silica substrate was seen to wear more in solutions of high pH. This result is expected as silica is known to dissolve faster in water solutions of pH > 10.0, because of the attack of excessive OH<sup>-</sup>



**Figure 2.** Dependence of the wear depth of silica and silicon nitride substrates on the solution pH. (Measurements for the silicon nitride and silica surfaces were conducted using different AFM tips.)

ions on the surface Si–O bonds.<sup>27</sup> Although this silica wear enhancement at high pH can be anticipated, the data in Figure 2 provides a quantitative estimation of the magnitude of the effect: the wear depth of the silica surface increased about 4-fold from 2.4 nm at normal pH to 9.2 nm at pH 11.0. In contrast, the silicon nitride surface gave only a slight increase in the wear depth with the same increase in pH. The difference in the wear depths between the SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub> surfaces implies that the weakening of the Si–O bonds or the partial dissolution of the surface layer will cause the easily worn gel layer on the SiO<sub>2</sub> surface, whose thickness increases substantially with increasing solution pH.

The results for the friction force measured between a Si<sub>3</sub>N<sub>4</sub> tip and a SiO<sub>2</sub> or a Si<sub>3</sub>N<sub>4</sub> surface in pure water of various pH are shown in Figure 3a and b, respectively. The friction data for



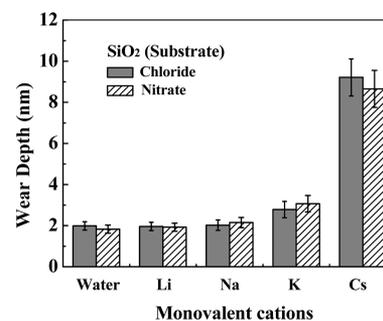
**Figure 3.** Dependence of the friction force on the applied force in solutions of various pH. The substrate is silica (a) and silicon nitride (b).

each solution condition shows a linear dependence on the applied load, as predicted by Amonton's law. The friction for the SiO<sub>2</sub> surface increased moderately from pH 3.0 to pH 5.7, remained constant for pH 5.7–8.0, and then significantly increased for pH 11.0. On the other hand, the friction for the Si<sub>3</sub>N<sub>4</sub> surface only increased slightly with the pH increase. The important finding in these measurements is that the wear dependence on pH is in good agreement with the friction results, especially with respect to their significant increase at high pH. This indicates that the friction measurement can be used as a measure to predict the wear depth.

Our previous studies on the friction between a 6.8–20  $\mu\text{m}$  silica particle and a silica plate in solutions<sup>11,12</sup> indicate that the friction is independent of the pH and increases linearly with the applied load for pH between 3.6 and 8.6. However, for pH > 9.0, the friction dependence on the load becomes nonlinear, whereby the friction is greatly reduced at low applied loads but increases rapidly above a critical load to eventually become higher than the friction at lower pH. We assumed that this behavior was due to the high pH enhanced development of a gel layer composed of polymer-like segments of silicic acid

anchored on the surface. At the lower applied load, the gel layer acts as a boundary lubricant between the surfaces, but at the higher applied load, the entanglements of these segments leads to the increase of the friction. However, in the present measurements using a Si<sub>3</sub>N<sub>4</sub> tip, the dependence of the friction on the applied load is linear and the value at high pH 11.0 is always higher than that of low pH. The reason for this difference is probably due to the chemically inert sharp tip readily penetrating the gel layer even at the lowest applied loads. This penetration of the tip pushes out the lubricant molecules from the gap between the tip and substrate, so that the lubrication region at low loads disappears, causing only the characteristics at the high load region to appear in the present experiments.

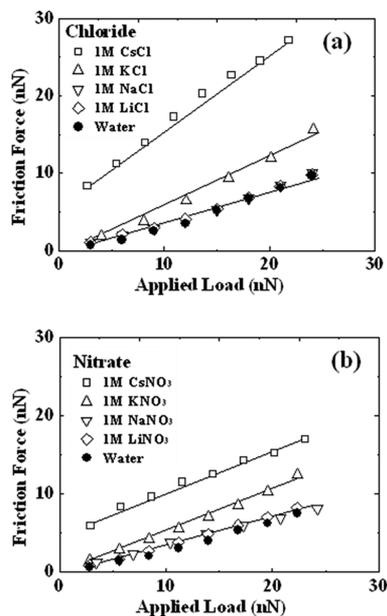
**3.2. Effect of the Monovalent Cations.** The effect of the presence and type of monovalent cations in aqueous solutions on the wear and friction of silica surfaces were studied by using alkali metal chlorides (LiCl, NaCl, KCl, CsCl) and alkali metal nitrates (LiNO<sub>3</sub>, NaNO<sub>3</sub>, KNO<sub>3</sub>, CsNO<sub>3</sub>). The measurements were done using pure water and 1.0 M electrolyte solutions. The wear results given in Figure 4 show a pronounced



**Figure 4.** Dependence of the wear depth on the type of monovalent cation in 1 M aqueous solutions. (A series of measurements for the chloride and nitrate salts were carried out using different AFM tips.)

dependence on the type of the monovalent cation. Compared with pure water, Li<sup>+</sup> and Na<sup>+</sup> did not seem to affect the wear substantially, whereas K<sup>+</sup> increased the depth of the wear by 40–60%, and Cs<sup>+</sup> greatly increased the wear depth by more than four times. The same trends were observed for the chloride and the nitrate salts. The corresponding friction data for the chloride and the nitrate salts are shown in Figure 5a and b, respectively. It is clear that the friction data are in good agreement with the wear data: regardless of whether the anion was a chloride or nitrate salt, the friction for Li<sup>+</sup> and Na<sup>+</sup> was nearly identical to the friction of pure water, whereas K<sup>+</sup> showed an increase in the friction force and Cs<sup>+</sup> gave a substantially higher value.

The order in which the monovalent cation type affects the wear rate and friction force can be correlated with the degree of cation hydration (hydration enthalpy), which is inversely proportional to the size of the cation: Li<sup>+</sup> < Na<sup>+</sup> < K<sup>+</sup> < Cs<sup>+</sup>. It is known that the highly hydrated cations adsorb weakly to a negatively charged silica surface, because of the strongly structured layers around them. However, the weakly hydrated cations (structure-breaking ions) adhere more directly and strongly to the silica surface, destroying the structured layer of water molecules on the surface. It is a little difficult to imagine that the molecular-scale adsorption of cations affects the macroscopic friction and especially the wear. We consider, however, that weakly adsorbed cations will be easily removed

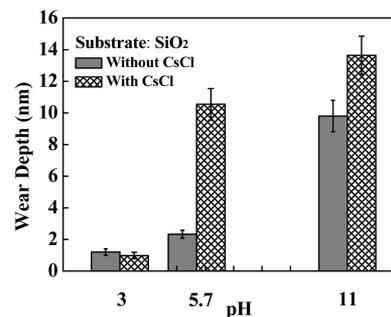


**Figure 5.** Dependence of the friction force on the type of monovalent cation in 1 M aqueous solutions. The anions are chlorides (a) and nitrates (b).

from the substrate by the lateral movement of the tip, so that the values of friction force and the wear depth will coincide nearly with those of pure water. On the other hand, much work will be required to remove strongly adsorbed cations from the gel layer on the silica surface. This implies that the cations will be removed from the substrate, together with the scratched gel layer. We believe that this is the main mechanism for the dependence of the friction force and the wear depth on the type of cations.

There are many experimental reports claiming that the molecular-scale adsorption of cations affects the macroscopic interactions between surfaces in solutions.<sup>28–37</sup> It was shown that the adsorption of hydrated cations on mica surface gives rise to a short-ranged hydration force which prevents the adhesive contact between the surfaces.<sup>28</sup> The same trend was reported for the interaction between silica surfaces, although the dependence on the type of cations and the concentration differ from that of mica and can also vary depending on the type and pretreatment of silica surfaces used.<sup>29–31</sup> The hydration enthalpy of cations was also shown to affect the time-dependent adhesive force between a silica and a mica surface.<sup>32–34</sup> The type of cation has been demonstrated to dictate the bulk-scale rheological behavior of silica and alumina slurries.<sup>35–37</sup>

**3.3. Effect of Cs<sup>+</sup> Cations.** The reason as to why the Cs<sup>+</sup> cations caused the greatest wear and friction was further investigated. The wear depths for 1.0 M CsCl solutions at pH 3.0, 5.6, and 11.0 are compared with those for water in Figure 6. The wear was clearly enhanced by the addition of Cs<sup>+</sup> cations at pH 5.7 and 11.0, pHs known to cause the silica surfaces to be negatively charged. However, no enhancement was found at pH 3.0, a state where the charge of silica surface is known to be nearly zero.<sup>38</sup> This implies that the Cs<sup>+</sup> adsorption to the silica surface is electrostatically driven and that the absence of adsorbed Cs<sup>+</sup> results in no enhancement of the wear at pH 3.0. It is also interesting to note that the enhancement caused by the addition of Cs<sup>+</sup> at pH 5.7 is much greater than that at pH



**Figure 6.** Comparison of wear depth between the solutions with and without 1 M CsCl at pH 3.0, 5.7, and 11.0.

11.0, although the negative charge of the silica surface at pH 11.0 should be higher than that at pH 5.7. We consider that this result is due to the fact that the wear enhancement is weakened by a lubricant effect, due to the high gelation of the silica surface at pH 11.0. This is confirmed by the separate experiments in which the wear depth and the friction strength increased with the increasing addition of Cs<sup>+</sup> at pH 5.7.<sup>39</sup> These results indicate that the amount of adsorbed Cs<sup>+</sup> is vital in determining the wear enhancement of the silica surface.

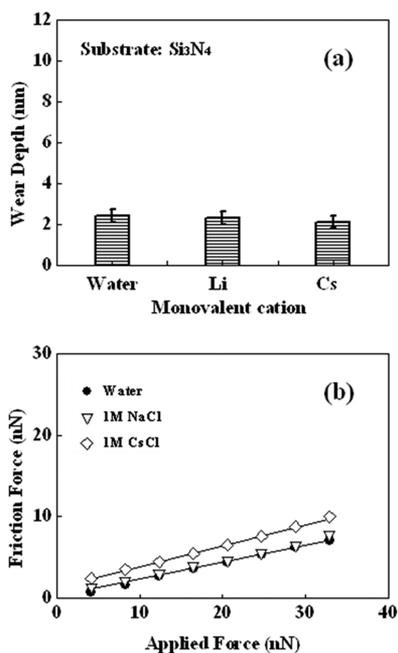
We further investigated how deeply the adsorbed Cs<sup>+</sup> cations could migrate into the SiO<sub>2</sub> surface by using the X-ray photoelectron spectroscopy (XPS). We also performed CMP tests using a tabletop polisher, in which silica nanoparticle slurries were used as abrasives. The details of the experiments are given elsewhere.<sup>21–23</sup> CsCl of 1 M was added to the pure water slurries of pH 5.7, immediately before the polishing test in order to minimize the effect of agglomeration. The silica wafer samples were thoroughly washed with water after polishing and inspected by XPS. If Cs<sup>+</sup> migrated into the SiO<sub>2</sub> surface due to the CMP abrasion procedure, some indication for the presence of Cs must be found in the XPS data. However, no indication was found under our experimental conditions. This implies that the adsorbed Cs<sup>+</sup> neither sticks on the gel layer forming a chemical complex, nor diffuses into the solid silica surface. It, however, becomes worn out as silica complexes into the solution by the abrasion procedure.

**3.4. Effect of Substrate Property.** In order to determine the reason for the substantial enhancements of wear and friction of the silica surface at high pH and by the Cs<sup>+</sup> adsorption, the characteristics of the wear and friction for the SiO<sub>2</sub> surface were compared with those for the strong wear-resistant Si<sub>3</sub>N<sub>4</sub> surface.

As for the pH dependence, the comparison was made already in Figures 2 and 3. Hence, in this section, only the slight increase of the wear depth and the friction strength of the Si<sub>3</sub>N<sub>4</sub> surface with a pH increase is discussed. It is known that the Si<sub>3</sub>N<sub>4</sub> surface is oxidized in a natural environment and is mostly covered with a thin SiO<sub>2</sub> layer of several Ångströms to a few nanometers thick, the amount depending on the conditions of the surface and environment, and that the surface oxidation increases with increasing pH.<sup>40–43</sup> The slight increase of the wear depth with pH that is shown in Figure 2 can be explained by the mechanism that only the thin SiO<sub>2</sub> layer on the Si<sub>3</sub>N<sub>4</sub> substrate becomes worn and not the strong wear-resistant Si<sub>3</sub>N<sub>4</sub> underneath.

The effects caused by the poorly hydrated cation Cs<sup>+</sup> can be seen by comparing their wear and friction data for the Si<sub>3</sub>N<sub>4</sub> substrate with those obtained with the highly hydrated cation Li<sup>+</sup> by using the 1.0 M chloride solutions. The comparison of

the wear depth is shown in Figure 7a and that of the friction force in Figure 7b. There is no substantial difference in the wear

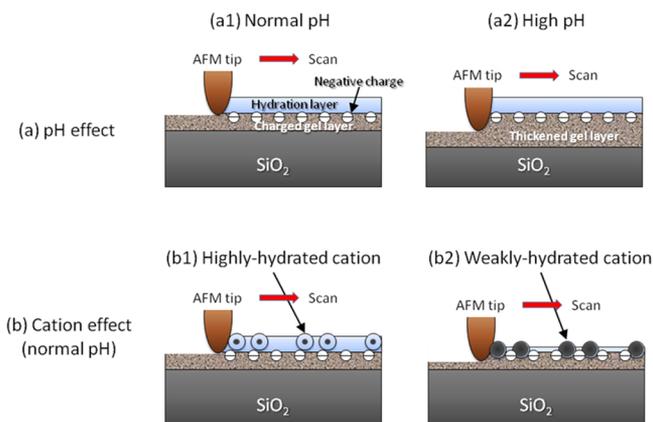


**Figure 7.** Comparison of the wear depth and friction force for the silicon nitrate substrate for 1 M LiCl, 1 M CsCl solutions, and pure water. (a) Comparison of wear depth; (b) comparison of friction force.

depth for both electrolytes and for pure water, but the friction measurements showed some increase only for the CsCl solution, albeit not as strong as that for the  $\text{SiO}_2$  surface. The  $\text{Si}_3\text{N}_4$  surface is considered to be coated with a thin layer of natural  $\text{SiO}_2$ , as explained above. As a small pressure is applied in the friction experiments, the similar trend, which was seen in the friction data of the  $\text{SiO}_2$  surface in Figure 5a, also appeared in the data of  $\text{Si}_3\text{N}_4$  surfaces shown in Figure 7b: the strongly adsorbed  $\text{Cs}^+$  enhanced the friction force. In the case of the wear experiments, however, all the wear depths were nearly identical. We believe that this is because the thin layer of  $\text{SiO}_2$  of the same thickness on the  $\text{Si}_3\text{N}_4$  surface was worn out in all cases, because of the high pressure of the wearing tip.

**3.5. Possible Mechanism.** It is important to postulate a possible mechanism for the friction and wear for silica surfaces in solutions from the data obtained in the present experiments, although further experiments are needed to clarify a more detailed mechanism.

Figure 8 is schematizing the general concepts we assume to explain the results obtained so far. The  $\text{SiO}_2$  surface is known to be negatively charged in the solution of  $\text{pH} > 3$ , and its dissolution rate into the solution increases with  $\text{pH}$ . Hence, it is plausible to assume that the silica surface is more or less covered by a gel layer whose charge and thickness increases with the solution  $\text{pH}$ . Additionally, the charge of the gel layer will attract polarized water molecules to form a thin layer of adsorbed water molecules, as illustrated as the hydration layer in Figure 8. We believe that the structure of the hydration layer is mechanically weak enough to be easily broken by the scanning of the sharp AFM tip, but the gel layer network underneath is not. Hence, the friction strength and wear depth will essentially depend on the penetration of a chemically inert AFM tip into the gel layer on the  $\text{SiO}_2$  surface. The thickening

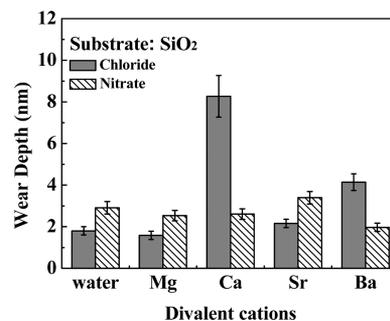


**Figure 8.** Schematic drawing describing the possible mechanisms for the effects of solution  $\text{pH}$  and Cs ions on the wear and friction of  $\text{SiO}_2$  surfaces.

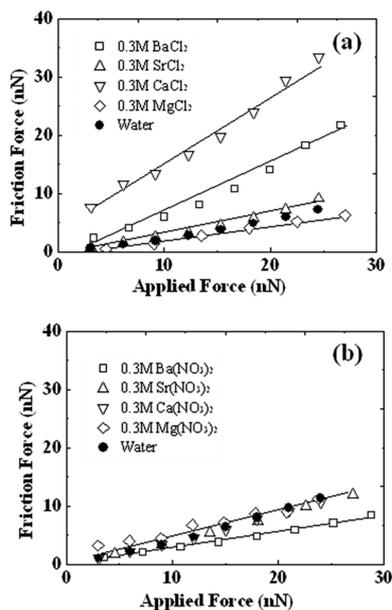
and softening of the gel layer on the  $\text{SiO}_2$  surface with increasing  $\text{pH}$  is considered to allow the AFM tip to penetrate deeper into the gel layer, which results in the increase of the friction force and the wear depth, as illustrated in Figure 8a.

As for the effects of cations, the strongly hydrated cations, such as  $\text{Li}^+$ , will be incorporated within the hydration layer, as illustrated in Figure 8b1, and can easily be removed from the surface. On the other hand, the poorly hydrated cations, such as  $\text{Cs}^+$ , will directly and strongly adsorb on the gel layer of the silica surface by breaking the hydration layer. This strong adhesion enhances the friction force and also removes the adsorbed ions from the surface, accompanied by the silica complexes of the gel layer. This results in the deepening of the wear depth.

**3.6. Effects of Divalent Cations.** In order to further determine the contributions of cations to the wear and friction of  $\text{SiO}_2$  surfaces, the effects of divalent cations were investigated by using divalent chlorides ( $\text{BaCl}_2$ ,  $\text{SrCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ ) and nitrates ( $\text{Ba}(\text{NO}_3)_2$ ,  $\text{Sr}(\text{NO}_3)_2$ ,  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{Mg}(\text{NO}_3)_2$ ). The salt concentration was chosen to be 0.3 M, because this concentration roughly matches the ionic strength of 1.0 M of the monovalent salts. The wear depths in 0.3 M divalent chloride and nitrate solutions are shown in Figure 9, and the corresponding friction data in Figure 10. It is clear that the trends of the wear in Figures 9 agree well with those of the friction in Figure 10.



**Figure 9.** Dependence of the wear depth on the type of divalent cation in 0.3 M aqueous solutions, and the comparison of the dependence of chloride and nitrate solutions. (A series of measurements were carried out for the chloride and nitrate salts using different AFM tips.)



**Figure 10.** Dependence of the friction force on the type of divalent cation in 0.3 M aqueous solutions. The anions are chlorides (a) and nitrates (b).

In the case of chloride solutions, both the wear depth and the friction strength increase with the inverse of the order of the hydration enthalpy of cations:  $\text{Mg}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$ , as in the case of monovalent cations. An exception was the case of the  $\text{CaCl}_2$  solution, in which exceptionally significant enhancements appeared. In the case of nitrate solutions, however, the wear depth and the friction strength were nearly constant and independent of the divalent cations, except for the case of the  $\text{Ba}(\text{NO}_3)_2$  solution in which both the wear depth and the friction force were lower than the others, as shown in Figures 9 and 10b.

As far as monovalent cations are concerned, the data of the wear depth and friction force can be correlated with the hydration enthalpy and successfully explained by the mechanism illustrated in Figure 8b. This result is consistent with those of our previous experiments on the friction force between silica surfaces.<sup>14,44</sup> However, the trends for the divalent cations in Figures 9 and 10 show more complex features, suggesting that other factors such as the anion type may also be involved. The most striking and important finding among the behaviors of divalent cations is the significant enhancement of the wear depth and friction force for the 0.3 M  $\text{CaCl}_2$  solution, although the 0.3 M  $\text{Ca}(\text{NO}_3)_2$  solution exhibits no special features. The similar complexity of divalent cations was also observed in our previous friction force measurements between silica surfaces in solutions: although the chloride salts of  $\text{Mg}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ , and  $\text{Ca}^{2+}$  of low concentration showed the similar behavior as the nitrates, a 0.3 M  $\text{CaCl}_2$  solution showed an anomalously stronger friction than a 0.3 M  $\text{Ca}(\text{NO}_3)_2$  solution.<sup>44</sup> This trend agrees well the behaviors of wear and friction of the present experiments.

Tanaka and Takahashi have carried out a series of experiments to clarify the effects on the dissolution of silica gel by the solution pH (alkaline) and alkaline earth metals by using fast atom-bombardment mass spectrometry (FAB-MS).<sup>45–47</sup> The dissolution of silica gel was found to increase and then to decrease with an increasing concentration of  $\text{LiCl}$ ,  $\text{NaCl}$ ,  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ , and  $\text{SrCl}_2$ , where the peak of the

dissolution appeared in the region of 0.01–1 M. Among these chloride solutions, the  $\text{CaCl}_2$  solution of ca. 0.3 M showed an exceptionally high solubility of silica. This is explained in terms of the high complexation energy of silicic acid with  $\text{Ca}^{2+}$  in the chloride solution. We believe that this will be the reason why the wear depth and friction force in 0.3 M  $\text{CaCl}_2$  solutions of the present investigation showed the high values shown in Figures 9 and 10. The effect of the anions,  $\text{Cl}^-$  and  $\text{NO}_3^-$ , were also investigated, but only for  $\text{Na}^+$ . The results indicate that there is no essential difference in the solubility of silica in  $\text{NaCl}$  or  $\text{NaNO}_3$  solutions. These results are consistent with the present wear and friction experimental results. Hence, we consider that the complex interaction between the silica surface and electrolytes, the mechanism of which is out of the scope of the present study, is the controlling factor of the wear depth and the friction force of silica surfaces in electrolyte solutions. We also leave the reason as to why the wear depth and friction force of the 0.3 M  $\text{Ba}(\text{NO}_3)_2$  solution is exceptionally smaller than the others as an unsolved problem, due to the complex solubility of silica in chloride and nitrate solutions of  $\text{Ba}^{2+}$ .

We would like to mention another anomalous behavior of  $\text{CaCl}_2$  observed in our recent CMP study. We added  $\text{CsCl}_2$  to a cationic surfactant dispersant (dodecyltrimethylammonium bromide ( $\text{C}_{12}\text{TAB}$ )) in order to regulate the polishing rates in silica-based CMP.<sup>23</sup>  $\text{C}_{12}\text{TAB}$  is an efficient silica slurry dispersant when used alone, but acts as boundary layer lubricant that decreases the polishing rates at the same time. The addition of  $\text{CaCl}_2$  to the dispersant increased the polishing rates without compromising the stability of the slurry. We also observed that when solutions of pH 11.0 were used, the surfactant lubrication effect was reduced and the addition of  $\text{CaCl}_2$  eventually caused the polishing rates to be greater than the slurries without any additives. We also saw in the same study that the adsorption of  $\text{Ca}^{2+}$  to the surface was reversible and that the XPS measurement did not show any evidence for the formation of a chemical complex of  $\text{Ca}^{2+}$  with the silica surface.<sup>23</sup> There remains the possibility that  $\text{Ca}^{2+}$  can complex with the silica dissolved in the solution, although the concentration of such complexes seem to be too low to significantly affect the wear rates.

These anomalous phenomena of  $\text{CaCl}_2$  that we observed are consistent with the solubility tests made by Tanaka and Takahashi. Although it is out of scope of the present study to understand the detailed chemistry between silica surface and electrolytes, we can conclude that the weakening of Si–O–Si network by the attack of specific simple ions will be the main mechanism for the enhancements of the wear and friction.

#### 4. CONCLUSIONS

We conducted a series of AFM friction and wear measurement between a silicon nitride coated AFM tip and a silicon dioxide or silicon nitride surface in various aqueous monovalent and divalent electrolyte solutions. Water was confirmed to enhance the wear and friction of a silica surface when the solution pH > 11.0, while a much weaker dependence on the solution pH was observed for the silicon nitride substrate. The wear and friction of a silica surface was also seen to be greatly enhanced by the presence of electrolytes in the solution. In the case of monovalent cations, the friction and wear depth increased with the decreasing hydration enthalpy of the cations. It was found that  $\text{Cs}^+$  showed the strongest effect, which was explained by the fact that the strong adsorption on the surface by the poorly hydrated  $\text{Cs}^+$  cation results in the enhancement

of the significant wear and friction. In the case of divalent cations, the dependence on the cation type was more complex: the  $\text{CaCl}_2$  displayed the anomalous enhancement of wear and friction, while  $\text{Ca}(\text{NO}_3)_2$  did not. The anomalous enhancement by  $\text{CaCl}_2$  was explained by the exceptionally high solubility of silica caused by the 0.3 M  $\text{CaCl}_2$  solution. We consider that the complex interaction between the silica surface and electrolytes, the mechanism of which is out of the scope of the present study, is the controlling factor of the wear depth and friction force of the silica surface in electrolyte solutions. Irrespective of the mechanism, it is extremely important for the effective CMP processing to know the fact that the simple cations of  $\text{Cs}^+$  and  $\text{Ca}^{2+}$  do significantly affect the wear and friction of silica surfaces.

## AUTHOR INFORMATION

### Corresponding Author

\*Mailing address: Int'tech Center #209, Graduate School of Engineering, Kyoto University-Katsura, Nishikyoku, Kyoto 615-8530, Japan. Telephone: +81-(0)75-383-2811. Fax: +81-(0)75-383-2147. E-mail: k\_higa@cheme.kyoto-u.ac.jp.

### Notes

The authors declare no competing financial interest.

## REFERENCES

- (1) Singh, R. K.; Lee, S. M.; Choi, K. S.; Basim, G. B.; Choi, W. S.; Chen, Z.; Moudgil, B. M. Fundamentals of Slurry Design for CMP of Metal and Dielectric Materials. *MRS Bull.* **2002**, *27*, 752–760.
- (2) Liang, H.; Craven, D. *Tribology in Chemical Mechanical Planarization*; CRC Press: Boca Raton, FL, 2005.
- (3) Krishnan, M.; Nalaskowski, J. W.; Cook, L. M. Chemical Mechanical Planarization: Slurry Chemistry, Materials, and Mechanisms. *Chem. Rev.* **2010**, *110*, 178–204.
- (4) Wang, W.; Wang, Y.; Bao, H.; Xiong, B.; Bao, M. Friction and Wear Properties in MEMS. *Sens. Actuators, A* **2002**, *97–98*, 486–491.
- (5) Bhushan, B. *Handbook of Micro/Nanotribology*; 2nd ed.; CRC Press: Boca Raton, FL, 1995.
- (6) Carpick, R. W.; Salmeron, M. Scratching the Surface: Fundamental Investigations of Tribology with Atomic Force Microscopy. *Chem. Rev.* **1998**, *97*, 1163–1194.
- (7) Maw, W.; Stevens, F.; Langford, S. C.; Dickinson, J. T. Single Asperity Tribochemical Wear of Silicon Nitride Studied by Atomic Force Microscopy. *J. Appl. Phys.* **2002**, *92*, 5103–5109.
- (8) Koinkar, V. K.; Bhushan, B. Microtribological Studies of Unlubricated and Lubricated Surfaces using Atomic Force/Friction Force Microscopy. *J. Vac. Sci. Technol., A* **1996**, *14*, 2378–2390.
- (9) Katsuki, F.; Saguchi, A.; Takahashi, W.; Watanabe, J. The Atomic-Scale Removal Mechanism during Si Tip Scratching on Si and  $\text{SiO}_2$  Surfaces in Aqueous KOH with an Atomic Force Microscope. *Jpn. J. Appl. Phys.* **2002**, *41*, 4919–4923.
- (10) Hu, J.; Xiao, X.-d.; Ogletree, D. F.; Salmeron, M. Atomic Scale Friction and Wear of Mica. *Surf. Sci.* **1995**, *327*, 358–370.
- (11) Taran, E.; Donose, B. C.; Vakarelski, I. U.; Higashitani, K. pH Dependence of Friction Forces between Silica Surfaces in Solutions. *J. Colloid Interface Sci.* **2006**, *297*, 199–203.
- (12) Taran, E.; Kanda, Y.; Vakarelski, I. U.; Higashitani, K. Nonlinear Friction Characteristics between Silica Surfaces in High pH Solution. *J. Colloid Interface Sci.* **2007**, *307*, 425–432.
- (13) Donose, B. C.; Vakarelski, I. U.; Higashitani, K. Silica Surfaces Lubrication by Hydrated Cations Adsorption from Electrolyte Solutions. *Langmuir* **2005**, *21*, 1834–1839.
- (14) Donose, B. C.; Vakarelski, I. U.; Taran, E.; Shinto, H.; Higashitani, K. Specific Effects of Divalent Cation Nitrates on the Nanotribology of Silica Surfaces. *Ind. Eng. Chem. Res.* **2006**, *45*, 7035–7041.
- (15) Donose, B. C.; Taran, E.; Vakarelski, I. U.; Shinto, H.; Higashitani, K. Effects of Cleaning Procedures of Silica Wafers on Their Friction Characteristics. *J. Colloid Interface Sci.* **2006**, *299*, 233–237.
- (16) Butt, H.-J.; Cappella, B.; Kappl, M. Force Measurements with the Atomic Force Microscope: Technique, Interpretation and Applications. *Surf. Sci. Rep.* **2005**, *59*, 1–152.
- (17) Biggs, S.; Cain, R. G.; Page, N. W. Lateral Force Microscopy Study of the Friction between Silica Surfaces. *J. Colloid Interface Sci.* **2000**, *232*, 133–140.
- (18) Feiler, A.; Larson, I.; Jenkins, P.; Attard, Ph. A Quantitative Study of Interaction Forces and Friction in Aqueous Colloidal Systems. *Langmuir* **2000**, *16*, 10269–10277.
- (19) Vakarelski, I. U.; Brown, S. C.; Rabinovich, Y. I.; Moudgil, B. Lateral Force Microscopy Investigation of Surfactant-Mediated Lubrication from Aqueous Solution. *Langmuir* **2004**, *20*, 1724–1731.
- (20) Raviv, U.; Klein, J. Fluidity of Bound Hydration Layers. *Science* **2002**, *297*, 1540–1543.
- (21) Basim, G. B.; Vakarelski, I. U.; Moudgil, B. M. Role of Interaction Forces in Controlling the Stability and Polishing Performance of CMP Slurries. *J. Colloid Interface Sci.* **2003**, *263*, 506–515.
- (22) Basim, G. B.; Brown, S. C.; Vakarelski, I. U.; Moudgil, B. M. Strategies for Optimal Chemical Mechanical Polishing (CMP) Slurry Design. *J. Dispersion Sci. Technol.* **2003**, *24*, 499–515.
- (23) Vakarelski, I. U.; Brown, S. C.; Basim, G. B.; Rabinovich, Y. I.; Moudgil, B. M. Tailoring Silica Nanotribology for CMP Slurry Optimization:  $\text{Ca}^{2+}$  Cation Competition in C(12)TAB Mediated Lubrication. *ACS Appl. Mater. Interfaces* **2010**, *2*, 1228–1235.
- (24) Cleveland, J. P.; Manne, S.; Bocker, D.; Hansma, P. K. A Nondestructive Method for Determining the Spring Constant of Cantilevers for Scanning Force Microscopy. *Rev. Sci. Instrum.* **1993**, *64*, 403–405.
- (25) Bogdanovic, G.; Meurk, A.; Rutland, M. W. Tip Friction-Torsional Spring Constant Determination. *Colloids Surf., B* **2000**, *19*, 397–405.
- (26) Vakarelski, I. U.; Edwards, S. A.; Dagastine, R. R.; Chan, D. Y. C.; Stevens, G. W.; Grieser, F. Atomic Force Microscopy: Loading Position Dependence of Cantilever Spring Constants and Detector Sensitivity. *Rev. Sci. Instrum.* **2007**, *78*, 116102.
- (27) Iler, R. K. *The Chemistry of Silica*; Wiley: New York, 1979.
- (28) Pashley, R. M. Hydration Forces between Mica Surfaces in Electrolyte Solutions. *Adv. Colloid Interface Sci.* **1982**, *16*, 57–62.
- (29) Horn, R. G.; Smith, D. T.; Haller, W. Surface Forces and Viscosity of Water Measured between Silica Sheets. *Chem. Phys. Lett.* **1989**, *162*, 404–408.
- (30) Grabbe, A.; Horn, R. Double-Layer and Hydration Forces Measured between Silica Sheets Subjected to Various Surface Treatments. *J. Colloid Interface Sci.* **1993**, *157*, 375–383.
- (31) Chapel, J. P. Electrolyte Species-Dependent Hydration Forces between Silica Surfaces. *Langmuir* **1994**, *10*, 4237–4243.
- (32) Vakarelski, I. U.; Ishimura, K.; Higashitani, K. Adhesion between Silica Particle and Mica Surfaces in Water and Electrolyte Solutions. *J. Colloid Interface Sci.* **2000**, *227*, 111–118.
- (33) Vakarelski, I. U.; Higashitani, K. Dynamic Features of Short-range Interaction Force and Adhesion in Solutions. *J. Colloid Interface Sci.* **2001**, *242*, 110–120.
- (34) Li, Y.; Kanda, Y.; Shinto, H.; Vakarelski, I. U.; Higashitani, K. Fragile Structured Layers on Surfaces in Highly Concentrated Solutions of Electrolytes of Various Valencies. *Colloids Surf., A* **2005**, *260*, 39–43.
- (35) Franks, G. V.; Colic, M.; Fisher, M. L.; Lange, F. Plastic-to-Brittle Transition of Consolidated Bodies: Effect of Counterion Size. *J. Colloid Interface Sci.* **1997**, *193*, 96–103.
- (36) Colic, M.; Fisher, M. L.; Franks, G. V. Influence of Ion Size on Short-range Repulsive Forces between Silica Surfaces. *Langmuir* **1998**, *14*, 6107–6112.

- (37) Franks, G. V.; Johnson, S. B.; Scales, P. J.; Boger, D. V.; Healy, T. W. Ion-Specific Strength of Attractive Particle Networks. *Langmuir* **1999**, *15*, 4411–4420.
- (38) Hartley, P. G.; Larson, I.; Scales, P. J. Electrokinetic and Direct Force Measurements between Silica and Mica Surfaces in Dilute Electrolyte Solutions. *Langmuir* **1977**, *13*, 2207–2214.
- (39) Teramoto, N. M.S. Thesis, Kyoto University, 2008.
- (40) Laarz, E.; Zhmud, B. V.; Bergstrom, L. Dissolution and Deagglomeration of Silicon Nitride in Aqueous Medium. *J. Am. Ceram. Soc.* **2000**, *83*, 2394–2400.
- (41) Wang, L.; Sigmund, W.; Aldinger, F. Systematic Approach for Dispersion of Silicon Nitride Powder in Organic Media: I, Surface Chemistry of the Powder. *J. Am. Ceram. Soc.* **2000**, *83*, 691–696.
- (42) Hackley, V. A.; Malghan, S. G. The Surface Chemistry of Silicon Nitride Powder in the Presence of Dissolved Ions. *J. Mater. Sci.* **1994**, *29*, 4420–4430.
- (43) Hackley, V. A.; Wang, P. S.; Malghan, S. G. Effects of Soxhlet Extraction on the Surface Oxide Layer of Silicon Nitride Powders. *Mater. Chem. Phys.* **1993**, *36*, 112–118.
- (44) Donose, B. C. Ph.D. Thesis, Kyoto University, 2005.
- (45) Tanaka, M.; Takahashi, K. Characterization of Silicate Monomer with Sodium, Calcium and Strontium but not with Lithium and Magnesium Ions by Fast Atom Bombardment Mass Spectrometry. *J. Mass Spectrom.* **2002**, *37*, 623–630.
- (46) Tanaka, M.; Takahashi, K. Characterization of Silicate Complexes in Aqueous Sodium Sulfate Solutions by FAB-MS. *Solution Chem.* **2005**, *34*, 617–630.
- (47) Tanaka, M.; Takahashi, K. Study on the Salting-out Effect using Silica Species by FAB-MS. *J. Solution Chem.* **2007**, *36*, 27–37.