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Viscosity and Lubricity of Aqueous NaCl Solution Confined between Mica Surfaces Studied by Shear Resonance Measurement

Hiroshi Sakuma,[1,2] Kenshiro Otsuki,[2] and Kazue Kurihara[1,*]

[1]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University and CREST (JST),
Katahira 2-1-1, Aoba-ku, Sendai, 980-8577, Japan*
[2]*Institute of Geology and Paleontology, Graduate School of Science, Tohoku University,
Aoba, Aramaki, Aoba-ku, Sendai, 980-8578, Japan*

We report the viscoelasticity of the thin film of aqueous NaCl solution confined between mica surfaces measured by shear resonance apparatus. The observed shear resonance curves at separations less than ca. 2 nm indicated that the solution exhibits the high lubrication effects under some loads. The effective viscosity (0.1–10 Pa s) obtained for the separations less than 1 nm from a mechanical model was $2-4$ orders of magnitude larger than the bulk value. Our study employing a novel shear measurement provided a comprehensive picture for the dynamics of confined water thinner than a few nanometers.

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There are increasing interests in clear understanding of friction and lubrication behavior at the atomic and molecular scale [1,2]. The physics to explain the fundamental origin of friction and lubrication is not sufficiently established because of the complexity of the friction. The physical property of confined liquid, especially water because of the general presence of it on Earth, between solid surfaces, is one of the most important properties to be investigated in nano to microscale phenomena. The ordering and viscosity of confined water and aqueous electrolytes have been studied using a surface forces apparatus (SFA) [3–7] and simulations [8,9]. The surface forces between hydrophilic surfaces in water and electrolyte solutions are sufficiently explained by the Derjaguin-Landau-Verwey-Overbeek and hydration forces [3,10,11], but the understanding of friction and lubrication effect of confined water is controversial, when the thickness of the water thin film becomes thinner than a few nanometers [5,6]. Zhu and Granick [5] reported the increased viscosity at the separation around 2 nm. On the other hand, Raviv and Klein [6] observed no increase even at a distance less than 1 nm and claimed that the previous observation might be due to the contamination of mica surfaces. Providing the explicit conclusions for the controversial problem and understanding the lubrication effect of confined water by the combination with simulations are needed to develop the physics of friction.

Here, we carried out the novel shear resonance measurements [12–15] to investigate the fluidity of aqueous NaCl solution confined between mica surfaces and obtained the explicit conclusion for this controversial problem. Since the shear resonance response is high and not strongly affected by noise, the measurement has a high sensitivity for any change in the fluidity of a thin liquid film between solid surfaces.

The shear resonance measurement was performed in a manner similar to that previously described [12–15]. The droplet of a liquid was confined between upper and lower mica surfaces. The upper surface was laterally oscillated

with various frequencies by applying the sinusoidal voltage (U_{in} and $-U_{in}$) to the two opposite electrodes of the four-sectored piezo tube. The movement of the upper surface is monitored by the capacitance probe, and the output voltage (U_{out}) was plotted as the amplitude ratio of U_{out}/U_{in} as a function of frequency. This is the shear resonance curve, which shows the maximum amplitude at a characteristic (resonance) frequency. When the upper and lower surfaces are in a large separation, the height of this resonance peak is sensitive to the viscosity of confined liquid and decreases with decreasing the surface separation. When the surfaces come closer, the resonance frequency usually shifts to a higher frequency due to the coupling of the upper and lower surfaces mediated by confined liquid (due to the contribution of the spring of the lower unit).

The distance between the surfaces, D, was determined using the multiple beam interferometry with a resolution of 0.1 nm [16]. The muscovite mica sheets (10×10 mm^2, thickness is 0.8–2.5 μm) were freshly cleaved, and the silver was deposited on the one side of them with a thickness of 50 nm using a standard procedure [3,17]. The sheets were then glued onto cylindrical silica disks (the radius of curvature of about 20 mm, and about 10 mm disk diameter) using epoxy resin (Shell, Epikot 1004) with the silvered sides down on the disk, and then subjected to the experiments. The twist angle indicating the crystallographic orientation between the upper and lower muscovite mica surfaces [18] was fixed at $0° \pm 5°$.

After the shear resonance curves were measured at separation and mica-mica contact in air as the reference states, the droplet of aqueous NaCl (Merck, suprapur 99.99%) solution (7 mM and ca. 60–90 μl) was injected between the mica surfaces. A salt concentration of 7 mM was chosen to be the same as in a previous experiment [6] for comparison. The pure water (NANOpure II, Barnstead; 18 MΩ/cm resistance) was added to the bottom of the chamber in order to keep the humidity in the chamber.

The measurement was started at $D = 200$–350 nm and the resonance curves were recorded at various separations. We used the input signal with the voltage $U_{in} = 20$ mV and angular frequencies of $\omega = 100$–850 rad/sec. The actual amount of the movement of the upper surface was 0.51 μm when the applied voltage was 20 mV and U_{out}/U_{in} was 10.1. We first used a $U_{in} = 200$ mV instead of 20 mV for oscillating the surface, and found by the shape of fringes of equal chromatic order (FECO) that the mica surfaces were destroyed possibly due to the instability of the instrument and/or of the structure of water molecules by the large shear velocity and long sliding distance. The normal forces between the two mica surfaces were also simultaneously measured. The normal forces were determined from deflections of double-cantilever springs (spring constant, $k_n = 130$–5000 N/m) fixed on the lower lens unit. All the measurements were carried out at room temperature ($23.8 \pm 0.1\,°C$).

The normal force profiles are shown in Fig. 1. The profiles confirmed the results of an earlier study [11] showing a long-range electric double layer repulsion and a strong repulsion due to the hydrated sodium ion layers at separations $D < \sim 2$ nm. These results of the normal force were fitted to the expression of Derjaguin-Landau-Verwey-Overbeek [electric double layer force [19] and van der Waals force $(-A_H/6D^2)$] and hydration forces $[2\pi E_h \exp(-D/D_h)]$, and we obtained the surface potential, $\psi_0 = 65$ mV, the decay length, $\kappa^{-1} = 3.7$ nm, the constant for expressing hydration energy, $E_h = 0.06$ J/m^2, and the decay length of hydration force, $D_h = 0.3$ nm. Here, A_H is the Hamaker constant (2×10^{-20} J). The decay length (3.7 nm) of the electric double layer repulsion was in good agreement with the calculated Debye length of 3.7 nm for 7 mM NaCl [3].
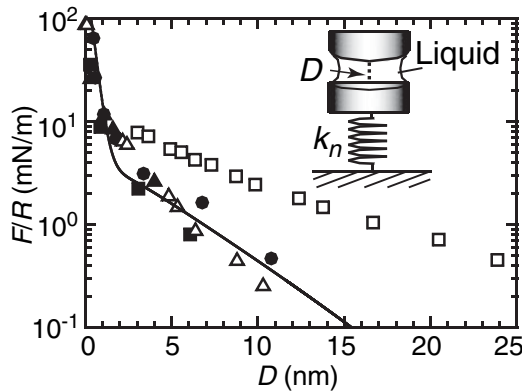
The resonance curves are plotted for various separation distances in Fig. 2. Two reference states, the curves for the separation and the mica-mica contact both in air, are also plotted for convenience. The NaCl solution at $D = 346$ nm exhibited a peak at a resonance frequency of 210 rad/sec, and the location and intensity of this peak were nearly the same as those for the reference state of separation in air even when the distance decreased until $D = 1.8 \pm 0.3$ nm. The peak intensity decreased at $D = 1.1 \pm 0.3$ nm to 85% of the value at $D = 1.8 \pm 0.3$ nm. At $D = 0.6 \pm 0.3$ nm, the resonance curve drastically changed. Instead of the sharp peak, a very broad peak emerged, which shifted toward a high frequency region with the decreasing D value down to 0.3 ± 0.2 nm. In general, the amplitude of the resonance peak is determined by both of the damping coefficients of the vibrated unit and confined liquid, and the shift in the resonance frequency to the larger values is determined by the spring constant of vibrated parts coupled through a confined liquid. Therefore, these changes indicated that (1) there was a coupling between the top and the bottom surfaces mediated by water molecules; (2) the NaCl solution confined in less than 1 nm thickness had a high viscosity and absorbed the vibration energy fed into the system under some normal loads (0.55–2.15 mN). The smaller resonance peaks at $D \leq 0.6 \pm 0.3$ nm compared with one for the mica-mica contact interestingly demonstrated that a very thin layer of water could act as a lubricant.

Eventually, the resonance curve at $D = 0.0 \pm 0.3$ nm became a sharp peak again at 650 rad/sec that was nearly the same frequency as for the case of the mica-mica contact in air. The amplitude of the resonance at the 0.0 ± 0.3 nm
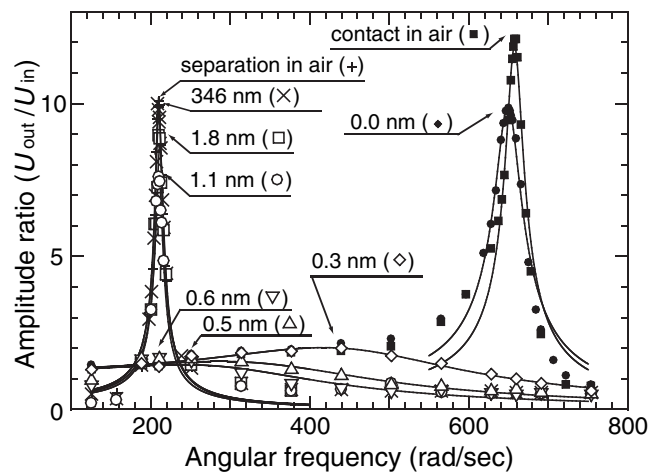

FIG. 1. Profiles of normal forces (F) between mica surfaces in NaCl solutions measured on approaching. F values are normalized by the surface curvature radius (R). The horizontal axis denotes the surface distance (D). The inset shows the schematic diagram of the normal force measurement, where k_n is the spring constant. Filled symbols are the results of this study (7 mM NaCl); empty squares and triangles are the previous study of the concentration of 1.4 and 10 mM, respectively [11]. Solid line denotes the fitting curve of our results to the theoretical expression.

FIG. 2. Resonance curves for NaCl solution (7 mM) confined between mica surfaces at seven distances: 346 nm, 1.8 ± 0.3 nm (load = 0.14 mN), 1.1 ± 0.3 nm (0.24 mN), 0.6 ± 0.3 nm (0.55 mN), 0.5 ± 0.2 nm (1.33 mN), 0.3 ± 0.2 nm (2.15 mN), 0.0 ± 0.3 nm. The reference states of the separation and mica-mica contact in air are shown together. The arrows denote the peak position of the resonance curve at the surface distances. The solid lines denote the fitting curves to our mechanical model.

thickness is slightly smaller than that for the mica contact in air. This might be attributable to the existence of a small quantity of water molecules between the surfaces. It was not clear how much water remained in the gap between the mica surfaces, though the absence of the jump-in contact, which is typical for the van der Waals interaction between mica at low salt concentrations, indicated the presence of some water. The large peak intensity suggested that such water should be highly ordered.

We took sufficient care for the preparation of the mica substrates as depicted previously [17]. They showed that the intensity of the even-order FECO spectra decreased when the Pt nanoparticles existed on the mica surfaces. In our study, no reduced intensity of the even-order fringes at mica contact in air was observed in the FECO spectra, indicating that the Pt particles were not detected on our mica surfaces. Previous studies have also reported that freshly cleaved mica in air rapidly accumulates a thin adsorbed layer of a carbon/water-vapor complex of a few angstroms thickness, e.g., [20], which is, however, soluble in water when the latter is clean and salt free [6]. In our study, the mica contact positions in pure water and NaCl solution lay between 0.0 and -1.6 nm relative to the air contact position depending on the prepared conditions, indicating that our mica could accumulate similar contamination, which was soluble in water. In this Letter, we describe the data obtained using the cleanest mica sheets (contact position: $D = 0.0 \pm 0.3$ nm) we could prepare. We may note that the identical results of the shear resonance curves were obtained for mica surfaces which showed the closer contact positions.

In order to quantitatively compare the viscoelasticity of the NaCl solution based on the shear resonance curves, we used a mechanical model [13,15] and obtained the total spring constant, k, and the total damping coefficient, b (Fig. 3). At large separations, where the resonance peak does not change thus the viscosity of NaCl solution is small, the k and b are approximated to be the spring constant, k_0, and damping coefficient, b_0, of the upper mechanical unit, respectively. When the intensity and the frequency of the peak start to change with the decreasing separation, the k and b are represented by $k = k_0 + \Delta k$ and $b = b_0 + \Delta b$, where the Δk and Δb denote the contributions in the spring constant and the damping coefficient from both the NaCl solution and the lower unit. An extreme example is the peak observed at the high frequency (corresponds to a high k value) for the mica-mica contact in air, where the strong adhesion between the mica surfaces binds the upper and lower units. The k values reflect mainly the elasticity of the apparatus (resonance unit), because the value of the apparatus should be much higher than that of NaCl solution. Therefore, the change in k is determined by the degree of connectivity between the upper and lower shear units. The results of shear resonance measurements ($U_{\text{out}}/U_{\text{in}}$ and ω) were fitted using a least-squares method to the equation derived from this mechanical model [15]:
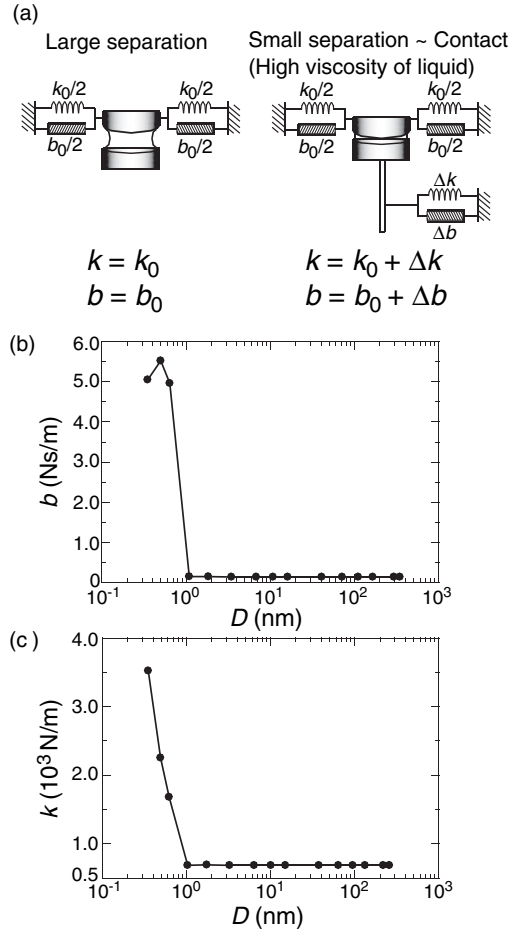

FIG. 3.   (a) Mechanical model to analyze the viscoelasticity of NaCl solution, (b) plots of changes in damping coefficient (b), and (c) spring constant (k) calculated for resonance curves in Fig. 2 as a function of the surface separation. Similar to the change of resonance curves (Fig. 2), there are drastic increases in the damping coefficient and spring constant at $D < 1$ nm.

$$\frac{U_{\text{out}}}{U_{\text{in}}} = \frac{C}{m} \frac{1}{\sqrt{(k/m - \omega^2)^2 + (b\omega/m)^2}}, \tag{1}$$

where C is the transfer coefficient and m is the effective mass of the vibrated unit. The effective mass m was the fixed constant of 15.5 g, because the difference in the m value between the separate and contact states was small compared with the changes in k and b [13]. This mechanical model indicates that the maximum amplitude of the resonance curve, $(U_{\text{out}}/U_{\text{in}})_{\text{max}}$, and the frequency, Ω_{res}, can be related to b and k, respectively [13].

At $D = 1.8 \pm 0.3$ nm, there is little change in both Ω_{res} and $(U_{\text{out}}/U_{\text{in}})_{\text{max}}$ with the large separation, and therefore, k and b are almost equal to those in the bulk state [Figs. 3(b) and 3(c)]. At $D = 1.1 \pm 0.3$ nm, $(U_{\text{out}}/U_{\text{in}})_{\text{max}}$ slightly decreased, and the b value increased by 1% from the value at $D = 1.8 \pm 0.3$ nm. From 0.6 ± 0.3 to 0.3 ± 0.2 nm, the b sharply increased and remained high while k gradually increases with the decreasing surface distance.

The large amplitude at the resonance frequency of $D = 1.8 \pm 0.3$ nm implied that the viscosity was small and almost the same as in the bulk (8×10^{-4} Pa s). This feature is consistent with previous investigations [6]. We observed an increase in the effective viscosity (η_{eff}) at $D < 1$ nm, and the η_{eff} value was obtained to be $10^{-1} \sim 10$ Pa s using the equation, $\eta_{\mathrm{eff}} = bD/A_{\mathrm{eff}}$, where A_{eff} is the effective area determined by FECO ($D < 1$ nm) [13,21,22]. This value was considerably smaller than the value reported by Zhu and Granick [5]. The η_{eff} value estimated in this study is slightly larger than the upper detection limit of the method by Raviv and Klein [6], which might be the reason why they have not seen the change at $D \geq 0.8 \pm 0.3$ nm. They vibrated the upper surface and recorded the response of the lower surface. This means that they can detect only changes when the fluid transmits the movement of the top surface to the lower one. In our experiment, we found the change of the viscosity at $D < 1$ nm as the decrease of the resonance peak, which is consistent with the results of high viscosity of water at $D = 0.92$ nm obtained by molecular dynamics simulations [23]. The shear resonance measurement can determine the viscosity and the connectivity (traction) property of a confined liquid with high sensitivity and stability because it monitors a large resonance signal. This allows us to study small changes in the viscosity of confined water.

The viscosity of a NaCl solution below a few nanometers thickness should be discussed in relation to the hydration force [6]. The origin of the hydration force has been investigated using SFA since its first observation for aqueous KNO_3 solutions [10]. In these studies it was recognized that the hydration layers (structured water molecules) of cations adsorbed on mica were preserved at high compression. The ordering of water molecules has been supported by the presence of oscillatory force in this separation range [24]. The hydration radius of the Na^+ ion adsorbed on muscovite mica surfaces was estimated to be 0.43 nm [11]. Our result for the high effective viscosity at $D \leq 0.6 \pm 0.3$ nm, which corresponded to about two opposing hydration layers of Na^+ ions, could be explained by the low mobility of structured water molecules around Na^+ ions bound on the upper and lower mica surfaces.

We directly observed the lubrication effect of molecularly thin film of water within ca. 2 nm thickness under the same load by monitoring the change of shear resonance curves in amplitude and resonance frequency. The properties of water in molecular scale strongly affect the macroscale phenomena as shown in the low frictional strength of solids containing swelling clays [25]. The clear demonstration of the relation between molecularly and macroscale phenomena would contribute to develop the physics of friction and lubrication.

*Electronic address: kurihara@tagen.tohoku.ac.jp

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[21] Typically, we obtained the effective viscosity, $\eta_{\mathrm{eff}} = 9.7$ Pa s for A_{eff} of 3.0×10^{-10} m^2, b of 4.84 Ns/m at $D = 0.6$ nm. The effective viscosities at $D = 0.6(\pm 0.3)$ nm for several experiments had the error in determining the distance and perhaps the resonance intensity, thus the estimated values lay in the range between 0.1–10 Pa s. At $D = 0.3$ nm, we cannot estimate the viscosity from the mechanical model.
[22] At $D \geq 1.0$ nm, we cannot measure the effective area by FECO, so we estimated the area assuring the viscosity of the thick water film ($D > 200$ nm) to be equal to the bulk value [15]. The obtained viscosity at $D = 1.1$ nm was 9×10^{-4} Pa s ($A_{\mathrm{eff}} = 3.1 \times 10^{-8}$ m^2, $b = 0.026$ Ns/m).
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