

Measurement of the mechanical properties of fatty acid solutions confined between solid surfaces

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A method has been developed with which mechanical properties of fatty acid solutions can be measured between solid surfaces. A thin film of a fatty acid solution confined between metal surfaces consists of a mobile layer and two immobile layers, and the effective viscosity of a mobile layer and the strength of an immobile layers against mechanical penetration can be estimated by measuring normal force, apparent film thickness and electrical resistance between solid specimens. The effective viscosity of a mobile layer is increased with the decrease of apparent film thickness, e.g. less than a few ten nanometers, and the effective viscosity of a solution of a fatty acid in a hydrocarbon solvent, n-hexadecane, is lower than that of the solvent. On the other hand, the mechanical strength of an immobile layer of a fatty acid solution is higher than that of its solvent, and it shows the maximum when the number of carbon atoms in a solute molecule is correspondent with that in a solvent molecule, which reminds us of the chain-matching phenomena observed in boundary lubrication.

Key words: lubrication, thin film, viscosity, mechanical strength, chain-matching phenomena

1. INTRODUCTION

A liquid molecule near a solid surface is influenced not only by surrounding liquid molecules but also by solid atoms or molecules. Therefore, liquid films confined between solid surfaces with molecular-size thickness are expected to show different mechanical properties from those in bulk, which should have large effects on tribological properties of lubricants [1-3].

In the present study, a newly-designed apparatus has been used in order to examine the mechanical properties of thin liquid films, especially of fatty acid solutions, confined between solid surfaces. Effective viscosity and mechanical strength of thin liquid films have been estimated by measuring normal force, apparent film thickness and electrical resistance between solid specimens.

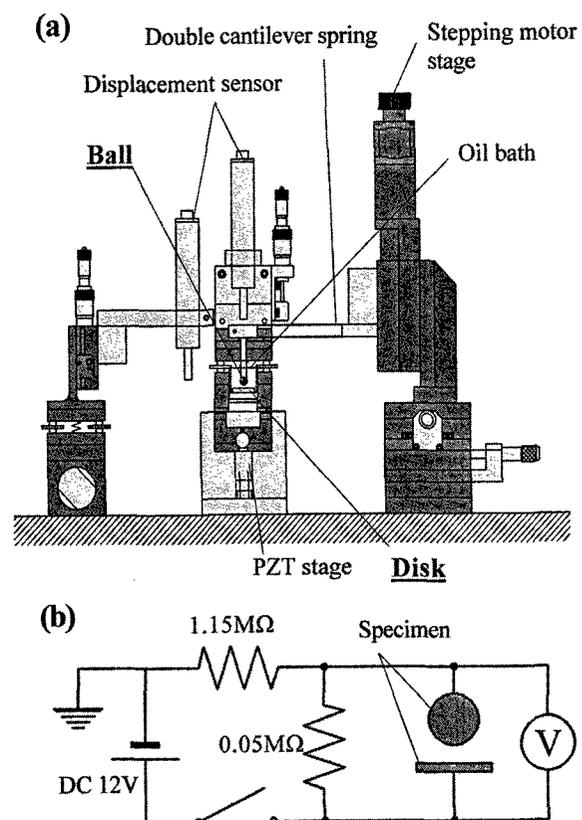
2. EXPERIMENTAL DETAILS

2.1 Apparatus

A newly-designed apparatus was used in the experiments, as shown in Fig.1 (a). Basically, this apparatus employed a point contact between two specimens, a ball and a disk.

The ball was made of SUJ2 steel and was 5 mm in diameter, which was fixed to the tip of a horizontal double-cantilever spring with a vertical rod. The stiffness of the spring was 7400 N/m, and the spring was mounted on a stepping motor stage, which moved vertically for coarse

movement with the resolution of 10 nm. The natural frequency of the vibration system was 169 Hz and the damping coefficient was 0.01.



The disk was also made of SUJ2 steel and was 16 mm in diameter, which was fixed in an oil bath. The oil bath was mounted on a PZT stage, which moved vertically for fine movement with the resolution of 0.3 nm.

Two capacitance-type displacement sensors were used for measuring the vertical displacements of two specimens with the resolution of 0.5 nm. Moreover, electrical resistance between two specimens was measured with an electrical circuit shown in Fig.1 (b) in order to examine the degree of the separation between two metal surfaces.

A physical model of the apparatus is shown in Fig.2, where x_1 , x_{10} and x_2 are the displacement of the ball, the initial position of the ball and the displacement of the disk, respectively. Apparent film thickness D is given by $D = x_1 + x_{10} - x_2$, where x_{10} did not be measured directly in the experiments.

2.2 Samples

Experiments were carried out on organic solutions with n-hexadecane as solvent. The viscosity of n-hexadecane was 0.003 Pa s at 25 °C. Eight kinds of saturated fatty acids were used as solutes. All of the chemicals were the purest obtainable commercially, and used without further treatment.

2.3 Procedure

The ball, the disk, their holders and the oil bath were first rinsed with acetone, washed thoroughly in acetone with an ultrasonic cleaner for ten minutes and then dried in a hot air stream. The ball was fixed to the double-cantilever spring. The disk was set in the oil bath, and the oil bath was mounted on the apparatus. Then, about 2 cm³ of n-hexadecane was poured into it, which is an enough amount to immerse the ball in the sample.

The ball was moved by using the stepping motor stage in order to make an initial clearance of 1 μm. After free

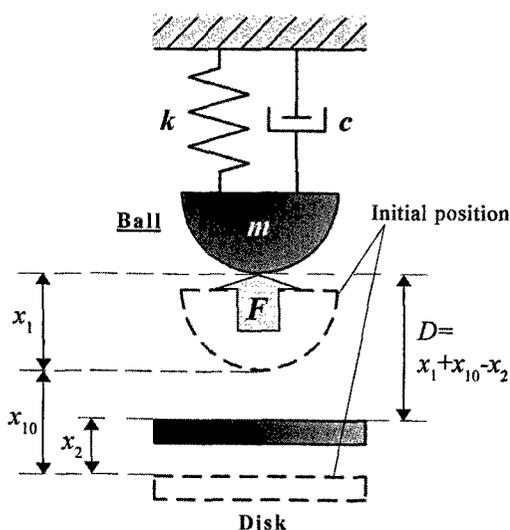


Fig.2 Physical model of the apparatus.

vibration of the ball was reduced, reciprocative movement of the disk was applied by the PZT stage, with which contact and separation between two specimens were repeated. The velocity was 1 μm/s, and the amplitude of the reciprocative movement was 1 μm. Three time-series data, the displacements of two specimens and the voltage between them, were simultaneously acquired with a digital data recorder.

After a running-in period, the time-series data become highly reproducible. Then, an adequate amount of a solute was added in the oil bath to make the concentration of the solution 0.1 wt% without stopping the reciprocative movement.

All of the experiments were carried out at 25°C by controlling the room temperature.

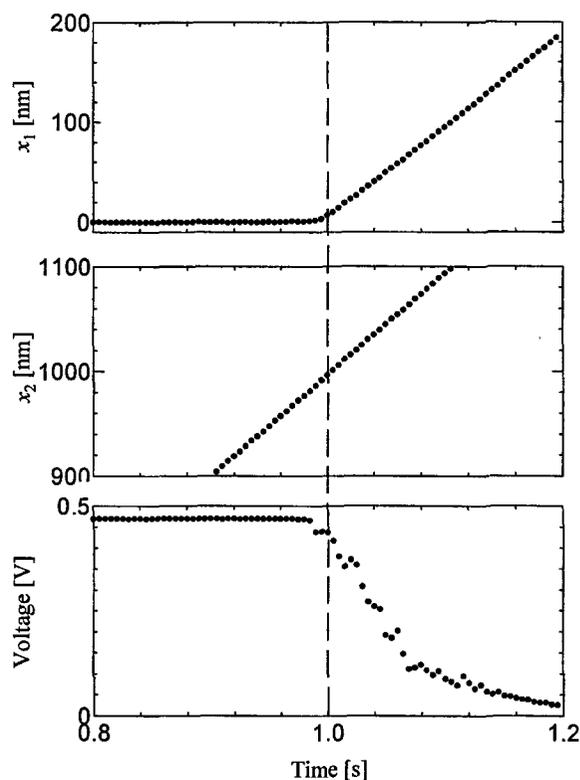


Fig.3 Change in x_1 , x_2 and voltage in time series.

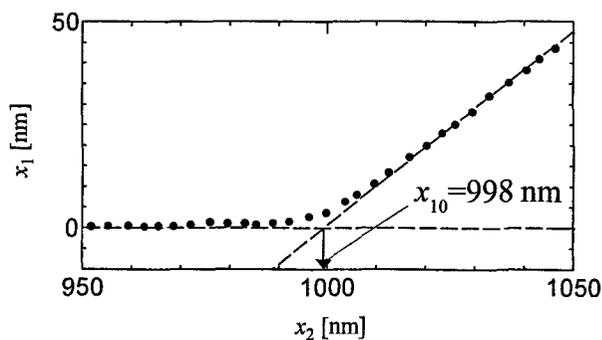


Fig.4 Determination of the initial film thickness x_{10} .

3. RESULTS AND DISCUSSIONS

3.1 An example of experimental results

Figure 3 shows an example of the time-series data obtained in the experiments, where n-hexadecane was used as a sample. The displacement of the ball x_1 is almost zero before 1 s and then increases linearly after a short transition period, whereas the displacement of the disk x_2 increases linearly. The voltage between two specimens keeps to be 0.5 V before 1 s and then slowly decreases toward zero, which indicates that the surfaces of the specimens come to contact.

By eliminating time, the relation between x_1 and x_2 is obtained, shown in Fig.4. The slope of the graph is unity when x_2 is large enough, which indicates that the two specimens move upward together. Therefore, the initial position of the ball x_{10} can be obtained as the intersection of two lines in the figure, which enables to determine the apparent film thickness D .

3.2 Mobile layer and immobile layer

Effects of adding stearic acid to n-hexadecane were investigated. Figure 5 shows the change in normal force and relative voltage against apparent film thickness before and after the addition, where the relative voltage is defined as the ratio of a voltage to the maximum voltage, 0.5 V. The relative voltage represents a degree of separation between two metal surfaces.

The normal force is decreased and the relative voltage is increased by the addition of stearic acid. For example, at the apparent film thickness of 15 nm, the relative voltage is about 0.3 for n-hexadecane, whereas almost unity for stearic

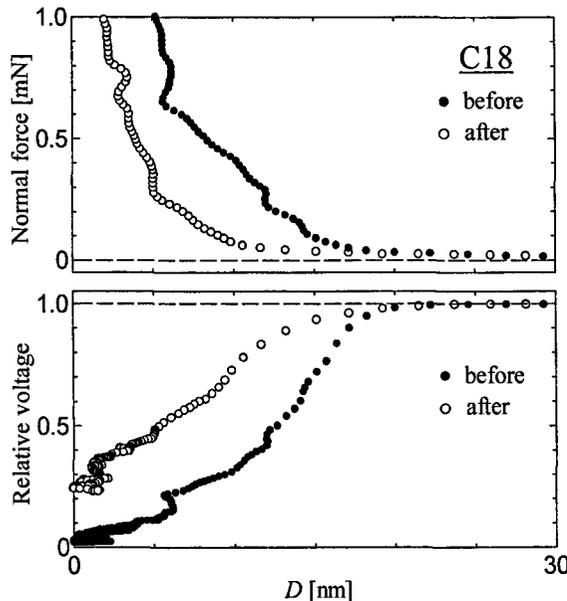


Fig.5 Change in normal force and relative voltage with the variation of D ; solid circles: results before the addition of stearic acid in n-hexadecane, open circles: those after the addition.

acid solution. This shows that organic films exist on the metal surfaces which move together with the specimens. Therefore, a thin film of stearic acid solution has a “mobile layer” and two “immobile layers” on the metal surfaces.

In order to investigate the initial contact, the rate of change in apparent film thickness dD/dt is plotted against the apparent film thickness, Fig.6. Clear bending points are recognized at 14 nm for n-hexadecane and at 7 nm for stearic acid solution, whereas dD/dt 's change smoothly for larger apparent film thickness. Therefore, the mobile layer is hydrodynamically squeezed out for the larger apparent film thickness.

3.3 Effective viscosity of mobile layer

According to the hydrodynamics, hydrodynamic force F_{hyd} of the present system is given by [3]

$$F_{hyd} = -6\pi R^2 \eta (dD/dt)/D, \tag{1}$$

where R is the diameter of the ball and η is the viscosity of the fluid. Therefore, the effective viscosity of a mobile layer can be calculated by the equation with the values in Figs.5 and 6.

Figure 7 shows the results. The effective viscosity is rapidly increased with the decrease of apparent film thickness less than a few ten nanometers. Moreover, the effective viscosity is decreased by the addition of stearic acid to n-hexadecane.

3.4 Mechanical strength of immobile layer

Experimental results for various kinds of solutes are shown in Fig.8, where the ordinates are relative voltage and the abscissas are normal force. The symbols C4, C10, C16

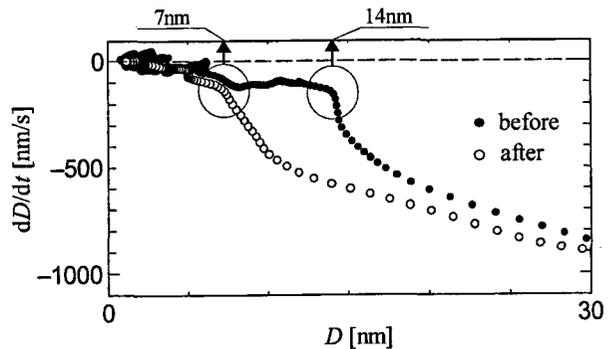


Fig.6 Change in dD/dt with the variation of D .

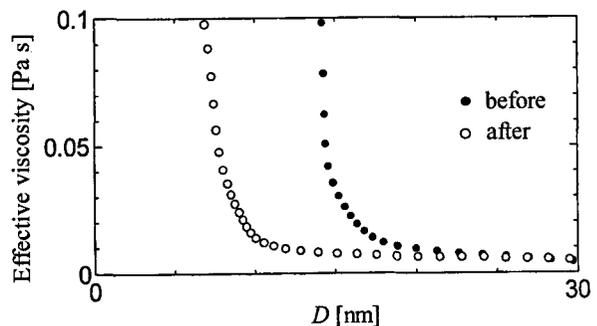


Fig.7 Change in effective viscosity with the variation of D .

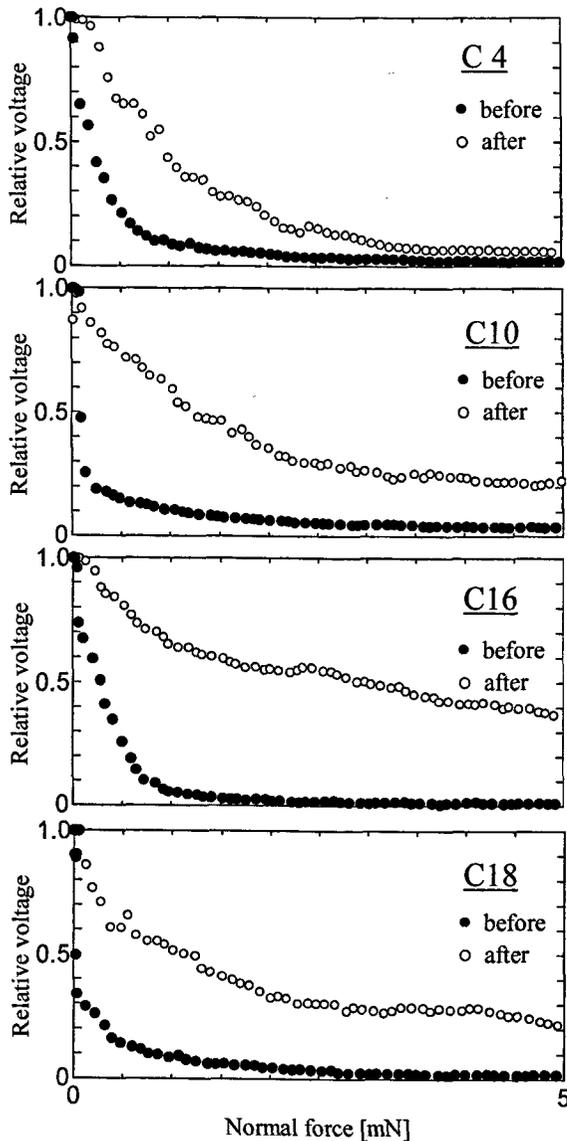


Fig.8 Change in relative voltage with the variation of normal force.

and C18 mean the kinds of solutes, butyric acid, decanoic acid, parmitic acid and stearic acid, respectively.

With increase in normal force, relative voltage is decreased, which means that the mobile layer is squeezed out and then the surface asperities penetrate the immobile layers. Curves for n-hexadecane in the four graphs are almost equivalent, however those for four kinds of solutions are clearly different each other. Moreover, the relative voltage for all solutions are higher than that for the solvent.

In order to distill the characteristics of each immobile layer, the difference of relative voltage between each solution and its solvent at 5 mN was calculated, shown in Fig.9. The quantity of the ordinates represents the mechanical strength of immobile layers.

The difference of relative voltage shows the maximum when parmitic acid is added. Therefore, the strongest immobile layers are formed on metal surfaces against the

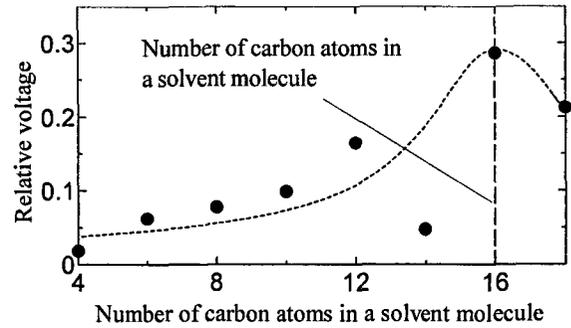


Fig.9 Effects of the number of carbon atoms in a solvent molecule on the difference of relative voltage between each solution and its solvent at 5mN.

penetration of surface asperities when the number of carbon atoms in a solute molecule is correspondent with that in a solvent molecule, which reminds us of the chain-matching phenomena observed in boundary lubrication [4].

4. CONCLUSIONS

A method has been developed with which mechanical properties of fatty acid solutions can be measured between solid surfaces.

- (1) A thin film of a fatty acid solution confined between metal surfaces consists of a mobile layer and two immobile layers.
- (2) The effective viscosity of a mobile layer is increased with the decrease of apparent film thickness, e.g. less than a few ten nanometers.
- (3) The effective viscosity of a mobile layer for the solution of stearic acid in n-hexadecane is lower than that for n-hexadecane.
- (4) The mechanical strength of an immobile layer of a fatty acid solution is higher than that of the solvent, n-hexadecane, and it shows the maximum when the number of carbon atoms in a solute molecule is correspondent with that in a solvent molecule.

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