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Evaluation of 2D viscosity with Disk-type EMS method

ディスク型 EMS 法による表面粘性の評価

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1. Introduction

Langmuir films adsorbed on liquid surfaces have attracted a great interest as the real evidence of the mono-molecular layer, which show the phase transition and critical behavior in two-dimensional system as seen in usual bulk materials. From the viewpoint of mechanical properties of material, the state of the Langmuir film is characterized by the surface pressure, which can be easily measured as the decrease in the surface tension from that of the bare water surface. The surface visco-elasticity, in addition to the surface pressure, is an important quantity as the measure of the condition of the condensed state of the Langmuir film, which gives information on the interactions between the surface molecules. However, accurate measurements of these surface properties have been difficult, since the mechanical effect of the adsorbed mono-molecular films is easily hidden by the huge contribution of the bulk properties, such as bulk viscosity and elasticity.

Up to date, many works on the surface viscosity have been reported mainly for the academic interest to the two-dimensional materials. In these days, however, demand for the accurate determination of the surface viscosity and elasticity rapidly increases, because they pay important role in the actual industrial processes of micro-fluidics, such as the inkjet technologies.

Recently, we succeeded in developing the new methodology of the rheology measurement with uniquely developed principle of the electro magnetically driving system.[1-3] The most remarkable feature of the technique is that we can remotely measure the viscosity of the sample in the completely confined environment. It would also be an advantage when it is applied for the measurement of the mechanical properties of fragile Langmuir films, since the films are quite sensitive for the external stimulation including the insertion of the mechanical probe. In our system, we can continuously observe the mechanical properties after once a small floating prove is set on the liquid surface. No serious mechanical disturbance is added during the measurement.

In this report, we introduce the accurate measurement of the surface viscosity of aqueous solutions of surfactants, which has been difficult for the conventional techniques. The surface viscosity could be successfully determined as a function of the concentration. An important experimental result is also demonstrated, in which the shear thinning phenomenon of the surface viscosity was observed for the first time.

2. Detection of the surface viscosity by disk-type EMS viscometer

Let us simply consider the contribution of the bulk and surface viscosity against the shear deformation in the vicinity of the liquid surface. We assume that a disk with a radius R is floating on the liquid with infinite depth and rotates with the angular velocity ω under an applied torque T. The fluid flow is determined by the Navier-Stokes equation, and at the steady state, the bulk flow potential ϕ_B is characterized as $\phi_B \sim -1/r$., while that in the surface flow ϕ_S is given by $\phi_S \sim \log r$. The viscous torque due to the bulk viscosity ϕ_B is roughly estimated to $T_B \sim \eta_B R^3 \omega$, while that due to the surface viscosity is $T_S \sim \eta_S R^2 \omega$. We can find that the ratio of the contributions from the bulk and the surface is given by $T_S / T_B \sim (\eta_S/\eta_B)R$, which shows that the smaller size of the probe is more sensitive for the mechanical properties of the surface.

It is shown that a typical value of the surface viscosity expected for the surfactant solutions is in the order of 10^{-6} Ns/m. According to the above discussion, the probe size less than 10^{-3} m can pick up the contribution of the surface viscosity at $\omega = 1 s^{-1}$ under the condition that the substrate is pure water and the viscosity is in the order of $\eta_B \sim 10^{-3}$ Ns/m^2, where the torque due to the bulk and surface viscosity is in almost the same order.

On the other hand, the accuracy of the disk type EMS viscometer is higher than 1%, and we can expect to detect the surface viscosity even with a larger probe size of 10^{-2} m. The experiments are planned to detect the surface viscosity of the typical surfactant solutions with the above estimations.

3. Experiment and Results

The experimental setup is the same as that reported in our previous paper[2]. We employed the disk-type EMS viscometer for the detection of the surface viscosity. The principle of the remote driving of the viscosity probe is common for all the EMS systems; the rotating magnetic field is

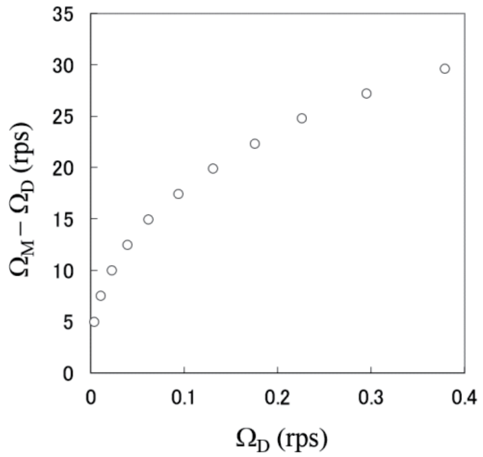

Fig.1 Torque proportional to the difference in the rotational speeds of magnetic field and the probe disk plotted against the shear deformation rate for the concentration of 5 mM SDS solution.

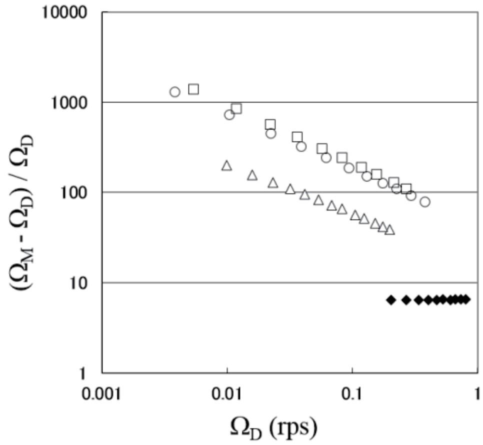

Fig.2 Torque plotted against the shear deformation rate. Open circles, squares and triangles correspond to the SDS concentrations of 10 mM, 5 mM and 1 mM, respectively. The closed squares indicate the result obtained for bare water surface.

generated by a pair of permanent magnets attached to a motor, which induces an eddy current in the metal probe. The Lorenz interaction between the magnetic field and the current drives the probe to magnetic field.

In the disk-type EMS method, the probe is a thin metal disk floating on the liquid surface by the surface tension. It has an advantage that the rotation is completely free from any mechanical friction and, therefore, it can detect quite small viscosity with a satisfactory accuracy. The sample used is aqueous solutions of sodium dodecyl sulfate (SDS), which is a most popular surfactant, with concentrations of 1, 5 and 10 mM, and pure water employed as a reference material having no surface visco-elasticity. The critical micellar concentration (CMC) of SDS solution is 8 mM, and we can expect that the surface viscosity increases with increasing concentration up to CMC, and would saturate at around it. The sample liquid is immersed in a petri-dish with 30 mm diameter to the depth of 10 mm. The probe disk is made of aluminum and has a diameter of 9 mm and a thickness of 0.1 mm. The temperature is kept 28 °C throughout the experiment.

Figure 1 shows the rotation of the probe disk on the surface of 5 mM solution, in which the vertical axis shows the difference between the rotation of the magnetic field and the probe giving the quantity proportional to the torque, while the abscissa indicates the rotation of the probe linearly dependent on the shear deformation. We can see that the ratio between the applied torque and the shear rate decreases with increasing shear rate.

Measurements were carried out for different concentrations and the results are shown in Fig.2, in which the value proportional to the surface viscosity is plotted against the shear deformation rate. The closed squares show the behavior of the probe on the bare water surface. The torque required for the probe to rotate on the adsorbed molecular layer is apparently larger than that on the water, showing the contribution of the surface viscosity. We can also see that the surface viscosity increases with the concentration blow CMC, while it does not change around it.

Another important behavior of the surface layer is that the surface viscosity decreases with increasing shear rate, which is well understood as the shear thinning in the field of rheology. Though we do not have much knowledge on the molecular dynamics of Langmuir films yet, the results would give valuable information on the relaxation of the two-dimensional viscosity. It suggests that the determination of the surface elasticity is also effective for the investigation of the inter-molecular dynamics in the mono-molecular layers. The detailed analysis of the experimental results would be given in our presentation.

References

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