1P1-4

Proceedings of Symposium on Ultrasonic Electronics, Vol. 36 (2015)
5-7 November, 2015

Measurement of viscoelasticity of condensed molecular layer on water surface by EMS system

EMS 法による液体表面凝集膜の粘弾性測定

M. Hosoda[1†], T. Fujimoto, T. Hirano[2], and K. Sakai[2]
([1] Tokyo Denki Univ.; [2] Inst. Indust. Sci., Univ. of Tokyo)
細田 真妃子 [1†], 藤本 健夫 [1], 平野 太一 [2], 酒井 啓司 [2]
([1] 東京電機大, [2] 東大生研)

1. Introduction

Formation of a skin layer on liquid surfaces is well known and often seen phenomena in our dairy life. One of the most common examples would be the Ramsden phenomenon, which is the emergency of the layer of the proteins on the hot milk surface. It would be a problem in the industrial fields, how we can observe the precursory phenomenon of the formation of the slayer; for instance, the emergency of the solid layer on the paints through the drying process would causes a serious damage of the coating layer, since the solvent included below the surface layer would evaporate in the baking process and the bubbles thus generated destroys the expected flatness of the surface of the products.

Various kinds of physical processes are related to the formation of the surface layer. As for the Ramsden phenomenon, the surface layer is believed to be generated due to the evaporation of the water; the condensation of the protein molecules due to the evaporation are considered to be the major process of forming the solid layer, however, conformation change of the protein molecules as well as the molecular association and cross-linking would also play an important role in the layer formation.

Recently, we developed a new system for the measurement of the mechanical properties of the fluids, such as the viscosity and the elasticity for the bulk materials.[1-3] It is also effective for the layers formed on the liquid surface; we could successfully observe the two-dimensional viscosity of the adsorbed surface layer of the surfactant molecules on the aqueous solutions. The surface viscosity is important property of the monomolecular layers called Langmuir films, and its accurate determination would provide unique information of the condensation state of these two-dimensional materials.

The detail of the system would be introduced later in this report, and here, we explain the feature of the method. The most remarkable point 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 probe is set on the liquid surface. No serious mechanical disturbance is added during the measurement.

In this report, we introduce the sensitive observation of the precursory phenomenon of the formation of the surface skin layer through the measurement of the apparent viscosity of the sample liquids. An important experimental result is also demonstrated, in which the rapid increase in the apparent viscosity occurs far before the formation of the solid surface layer.

2. Observation of skin layer by disk-type EMS viscometer

Let us simply consider the contribution of the viscous properties of the bulk and surface 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 ϕ_B~-1/r., while that in the surface flow ϕ_S is given by ϕ_S~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.

3. Experiment and Results

The experimental setup is the same as that reported in our previous paper[1,2]. The sample is commercially available nonfat milk, which includes 3.0 % of protein, the lact-lecithin. The Ramsden Phenomenon is thought to be the aggregation of the proteins and fats included in milk due to the condensation following the evaporation of the solvent. In the present measurement, we especially

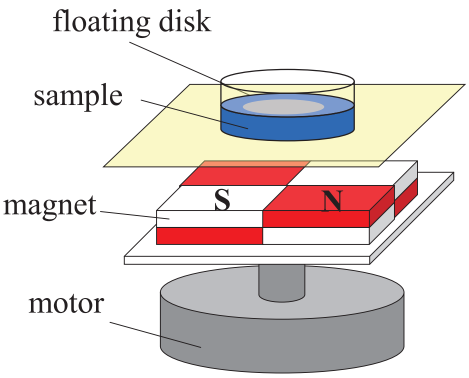

Fig.1. Schematic view of floating disk type electro-magnetically spinning viscometer.

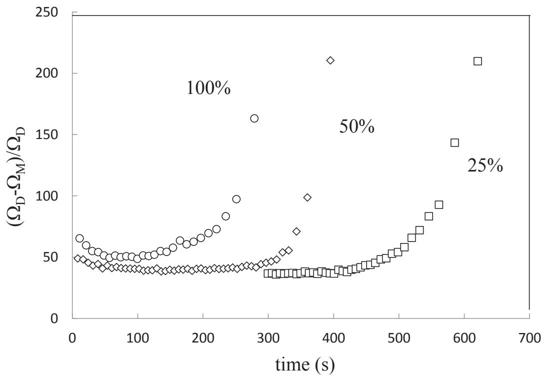

Fig.2 Time evolution of the apparent viscosity of the milk. The symbols, circles, rhombuses, and squares indicate the data obtained for whole, 1/2, and 1/4 dilution of milk, respectively. The ordinate shows the ratio between the applied torque and the rotational speed of the rotor, which is proportional to the bulk viscosity of the sample, when the surface is free from the adsorbed molecular layer.

payed attention to the aggregation and the molecular conformation of proteins, therefore, nonfat milk was chosen as a sample. The viscosity of the sample was measured by the sphere-type EMS viscometer and the values are 2.50, 2.35 and 1.89 mPa· s, at 20, 25 and 30 °C , respectively.

Figure 1 shows a schematic view of the experimental setup. A couple of magnets set below the sample cell generate the horizontal magnetic field and its rotation induces the eddy current in the probe disk. The disk is made of aluminum, whose diameter is 20 mm and the thickness is 0.3 mm. The disk floats on the sample surface by the surface tension and the buoyancy. The Lorentz interaction between the temporally modulated magnetic field and the induced current applies the torque to the disk to rotate on the sample surface following the motion of the magnetic field. The driving torque is proportional to the difference in the rotational velocities of the magnetic field Ω_M and that of the disk Ω_D, and the typical shear deformation rate is given by $\gamma=R\Omega_D/d$, R and d being the radius of the probe disk and the depth of the sample, therefore, the viscosity is proportional to the value of $(\Omega_M - \Omega_D)/\Omega_D$.

The quantity of the sample is 0.4 mm and the thickness of the sample is 2.5 mm. The rotational velocity of the magnets is fixed to 6.0 turns/s and the sample with s initial temperature of 28 °C is set on the thermo-bath with the temperature of 80 °C set on the viscometer. The change of the rotational velocity after the sample heating was measured as a function of time. We observed in advance the formation of the surface skin layer for the samples in the above condition and confirmed that the skin is formed at more than 10 minutes after the heating.

Figure 2 shows the temporal change of the value, $(\Omega_M - \Omega_D)/\Omega_D$, which is proportional to the viscosity. We can see the increase in the viscosity of the sample due to the increase in the sample temperature. Note here that the shear rates are also changed due to the slowing of the rotation of the disk, however, the sample milk is dilute solution of the protein and does not show remarkable shear rate dependence of the viscosity. As seen especially for the whole milk sample, the viscosity once decreases owning to the increase in the temperature and then shows rapid increase within only a few minutes. At the time of the rapid viscosity increase, we cannot observe the formation of the skin layer at all. The increase in the viscosity is, therefore, considered to be brought about by the local condensation of the protein molecules in the vicinity of the surface, or the conformation and the molecular shape of the protein, and the phenomenon is the precursory process of the skin formation.

We can also see the time of the increase in the apparent viscosity strongly depends on the concentration of the protein. In the presentation, we would discuss the plausible mechanism of the precursory increase before the formation of the protein skin layer.

References

1. K. Sakai, T. Hirano and M. Hosoda, Appl. Phys. Exp., 3, 016602 (2010).
2. K. Sakai, T. Hirano, and M. Hosoda, Appl. Phys. Express 5, 036601 (2012).
3. M. Hosoda, T. Hirano, and K. Sakai, Jpn. J. Appl. Phys. 51, 07GA05 (2012).