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Measurement of dynamic molecular adsorption onto liquid surface by on-substrate droplet horizontal oscillation method

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1. Introduction

In recent years, there has been a surge in research and development related to droplet behavior, which has significant industrial importance in applications such as inkjet printing and spray painting. Therefore, it is crucial to measure the surface tension and viscosity under actual environmental conditions. For example, paint is applied to various kinds of substrates, and in recent years, there has been an increase in the practice of applying paint on an insufficiently dried, wet paint film. In such situations, material transfer occurs between the wet film and the newly applied droplets. Additionally, the painting environment is not always pristine; impurities may adsorb to the droplet. As a result, the physical properties of the droplet are changed. Understanding the temporal changes in the properties of droplets after application on a substrate is a highly interesting research topic for the industry. We have developed the method to measure the surface tension and viscosity of droplets from the horizontal oscillation behavior on a flat substrate. This new measurement technique was employed to study the dynamic molecular adsorption onto droplets. In this abstract, we show the adsorption of the surfactant in the liquid with different viscosity and surface tension.

2. Experiment

We introduce our experimental system. We set the droplets on the substrate connected with a piezo actuator to drive the horizontal vibration. We set approximately 3μL droplet on the substrate with micro syringe. The holizontal oscillations of droplets after impulsive oscillation of the substrate was detected by a laser light. We measured the resonance frequency f_l from the droplet oscillation and obtained the surface tension σ by following equation:

$$\sigma = 4\pi^2 A\rho R^3 f_l^2 / B\,, \tag{1}$$

where

$$A = \frac{1}{30}\cos^5\alpha - \frac{1}{3}\cos^3\alpha + \frac{2}{3}\cos^2\alpha - \frac{1}{2}\cos\alpha + \frac{2}{15}$$

$$B = -\frac{1}{5}\cos^5\alpha + \frac{2}{3}\cos^3\alpha - \cos\alpha + \frac{8}{15}.$$

ρ and R are density and radius of the droplet, respectively.[1)] We verified the influence of solvent viscosity and surface tension on the adsorption of surfactants in droplets. The solute is polyoxyethylene(20) sorbitan monooleate, which is nonionic surfactant and dinoted as POE. The solvents are distilled water, 25wt% and 63wt% glycerin aqueous solution, and 85wt% ethylene glycol aqueous solution, of which physcal properties are listed in **Table 1**. All solutions had a POE concentration of 57 μM.

Table 1 Physical properties of solvent.

Sample name	Water	Gly25%	Gly63%	EG85%
Viscosity [mPa s]	1	2	12	11
Surface tension [mN/m]	72	71	68	52

We measured the change in the surface tension of each solution droplet after being set on the substrate. The measurement results are shown in **Fig. 1**. The colored symbols are the measured values by this new method, and dashed lines are simulation results to be discussed later. The measurement results by maximum bubble pressure method are presented with symbols in white.

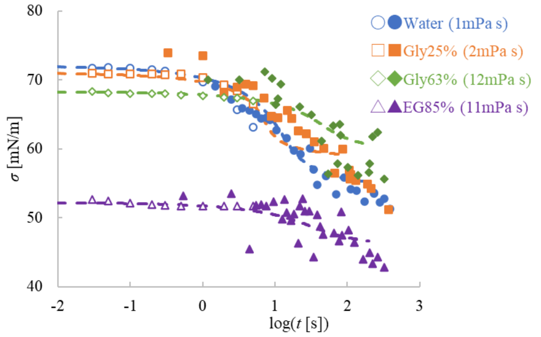

Fig. 1 Time revolution of surface tension of the droplet including a surfactant.

The measured surface tension values need to be converted to surface adsorption concentrations of surfactants to judge the adsorption speed. According to the Frumkin model, the relationship between surface tension, surface adsorption concentration $\gamma(t)$, and surfactant concentration c in the bulk is given by the following equations.

$$\sigma = \sigma_0 + RT\gamma_0\left\{\ln\left(1 - \frac{\gamma}{\gamma_0}\right) + \frac{b}{RT}\left(\frac{\gamma}{\gamma_0}\right)^2\right\}, \tag{2}$$

$$c = a\frac{\gamma/\gamma_0}{1-\gamma/\gamma_0}e^{\left(-\frac{2b}{RT}\frac{\gamma}{\gamma_0}\right)}. \tag{3}$$

Here σ_0, R and T are the surface tension of the solvent, the gas constant, and the temperature, respectively. γ_0 is the saturation surface adsorption concentration. a and b are the values related with the adsorption and desorption rate constants. γ_0, a and b

are specific parameters of each solution, and determined to match the static surface tension of solutions with various POE concentrations measured by the plate method. **Figure 2** shows the time evolution of the surface adsorption concentration. The symbols are the measured values, and dashed lines are simulation results to be discussed later. It was observed that higher viscosity results in slower adsorption rate of surfactants to the surface.

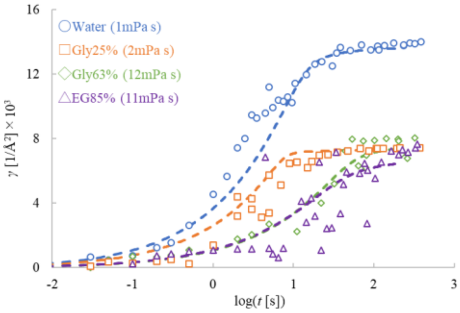

Fig. 2 Time revolution of surface adsorption concentration.

Here, the simulation results represented by dashed lines are explained. Simulations were conducted based on the assumptions that the surfactant solution filled an infinitely spreading container with a depth of L, instead of droplets. The movement speed of surfactant molecules was represented by a diffusion equation, as shown below.

$$\frac{\partial}{\partial t}c = D\nabla^2 c, \tag{4}$$

where D is the diffusion coefficient. According to the diffusion equation, the substance moves from high to low concentration areas. Since surfactants have both hydrophilic and hydrophobic groups, it is more stable for the hydrophobic groups to be oriented towards the air surface than in the solvent. Therefore, a shift occurs from a uniform concentration distribution to a biased concentration distribution towards the surface in the adsorption phenomenon of surfactants. Appropriate boundary conditions need to be defined at the liquid surface to reproduce this dynamics using the diffusion equation. Therefore, the concept of a quasi-surface was introduced. The quasi-surface represents an imaginary top layer of the liquid that is always equilibrium with the liquid surface. When there is no surfactant on the surface, the concentration of the imaginary layer c_0 is equal to 0. As the surface concentration γ increases, c_0 also increases. In addition, c_0 becomes equal to the bulk concentration when γ reaches the equilibrium concentration. The change in diffusion speed during the adsorption process can be described by introducing c_0 as a boundary condition in the diffusion equation. The relationship between the surface concentration γ and c_0 is given by Eq. (3) in setting c=c_0. The solution is divided into layers of the same thickness as the quasi-surface, and the concentration $c_n(t)$ of each layer (starting from the layer closest to the quasi-surface with n=1, 2, 3, ...) is calculated as the surfactant undergoes random walk. $\sigma(t)$ and $\gamma(t)$ were calculated from $c_0(t)$ by Eq. (2) and Eq. (3). The relationship between the thickness of each layer Δx, time interval Δt, probability of movement m, and diffusion coefficient can be expressed by discretizing Eq. (4) as follows:

$$D = \frac{m(\Delta x)^2}{\Delta t} \tag{5}$$

First, the diffusion coefficient in distilled water was determined as D_w=1×10^{-10}[m^2/s] to fit the data. This value was considered reasonable as it is of the same order as the value calculated using the Stokes-Einstein equation D=$k_B T/6\pi\eta_0 r$, where D=2.6×10^{-10}[m^2/s] based on the radius of polystyrene, which has the same molecular weight as POE, and the viscosity of water. Here, k_B is the Boltzmann constant, η_0 the solvent viscosity, and r the radius of the solute. The diffusion coefficients in other solvents were determined based on the Stokes-Einstein equation, resulting in D_W×η_w/η_x (x=Gly25%, Gly63%, EG25%), where η_w, η_x are the viscosity of distilled water and each solvent. The simulation results agreed with the measured results in short time (<10 seconds), however, they are not in agreement in the long time. When we determined γ_0, a and b, in regions where c is large, i.e., where γ is large, the theoretical values of surface tension are lower than the experimental values. In other words, the surface adsorption concentration is larger than the actual value. Therefore, the constants need to be changed. By changing the value of a, the simulation results in the short-time domain remained almost unchanged, but the results in the long-time domain changed and matched the experimental results. The theoretical values represented by the dashed lines in Fig. 1, 2. In addition, we clarified that modified a has relationship with the difference in surface tension between solvent and solution.

3. Summary

We have utilized the developed device to elucidate the relationship between physical properties of droplets and adsorption rate. Although not described in this abstract, we have also conducted measurements on phenomena such as the adsorption of solvent vapors onto liquid droplets, which will be reported at USE2024.

References

1) S. Ishida, S. Mitani and K. Sakai, Jpn. J. Appl. Phys. **63**, 03SP02 (2024).

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