

Chapter 5

Surface Viscosity



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Abstract Foam stability is closely related to the liquid's surface viscosity under non-equilibrium unstable conditions. Surface viscosity measurements for surfactants, lipids, or protein solutions give reliable indices for the foam stability such as when stable soap bubbles can be made by adding thickening agents to the soap solution. There are mainly three methods to measure surface viscosity of aqueous solutions with small amounts of surface active materials such as surfactants or proteins: the damped oscillation, rotation, and capillary methods. In this chapter, damped oscillation is focused on as it is the most common method. Foaming is a key process for industrial products such as foamed plastics and cement, while anti-foaming is also important for the engineering process of food, fermentation, textiles, dyes, paints, ink, and petrochemical production.

Keywords Surface viscosity · Foam stability · Damped oscillation method

5.1 Introduction

Foaming is a common phenomenon in our daily life, like how soap wraps up dirt due to its huge surface area or how beer foams provide antioxidation and a smooth taste. The ease of foaming is attained by less work to enlarge gas/liquid interfaces and is closely related to the surface tension of the liquid. On the other hand, foam stability is closely related to the liquid's surface viscosity under non-equilibrium unstable conditions. Surface viscosity measurements for surfactants, lipids, or protein solutions give reliable indices for the foam stability such as when stable soap bubbles can be made by adding thickening agents to the soap solution.

Foaming is a key process for industrial products such as foamed plastics and cement, while anti-foaming is also important for the engineering process of food, fermentation,

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textiles, dyes, paints, ink, and petrochemical production. The surface viscosity gives important pointers for the design and selection of anti-foaming agents.

5.2 What You Get

1. The surface viscosity for surfactants, lipids, or proteins in various solutions. Water is the most typical solvent in this application
2. The time dependence of surface viscosity, which is an important index of tracing foam stability
3. Information of molecular orientation and mobility of adsorbed layers as molecular self-assembly
4. Interfacial viscosity at liquid/liquid interfaces as an index of emulsion stability

5.3 Essentials and Tips

There are three methods to measure surface viscosity of solutions of water with small amounts of surface active materials such as surfactants or proteins: the damped oscillation, rotation, and capillary methods. The damped oscillation apparatus consists of a flat disc-shaped detector horizontally fixed to the shaft and a table to put the sample solution in the dish. Rotational oscillation is applied to the disc after placing it on top of the sample surface, and the surface viscosity can be measured from the decay rate of rotational oscillation from the viscosity resistance of the contacted liquid surface. The rotation method and capillary method are two-dimensional modifications of the Couette viscometer and capillary viscometer, respectively. In this chapter, damped oscillation is focused on as it is the most common method.

The surface viscometer SVR-A made by Kyowa Interface Science Co., Ltd. is shown in Fig. 5.1. In the measurement procedure, set the clean dish in the instrument's temperature-controlled chamber, fill up the sample solution over the edge of a

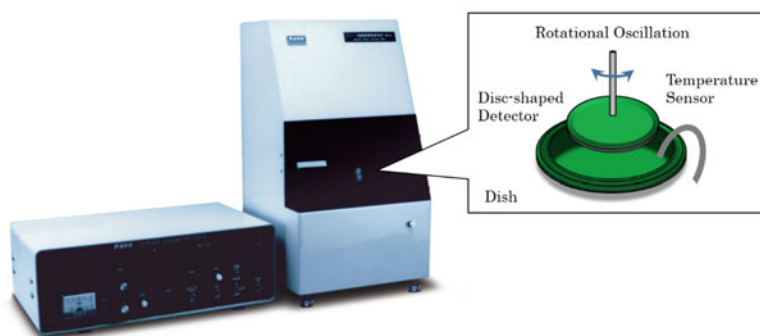


Fig. 5.1 Surface viscometer (type SVR-A. Photo credit Kyowa Interface Science Co. Ltd.)

clean dish, and then level the surface by sweeping excess sample solution off with a clean partition plate (barrier), or suck it out with an aspirator. Put the temperature sensor in the solution as surface viscosity is quite sensitive to temperature change. Move the table up so the detector contacts the solution surface, and then apply rotational oscillation to measure the surface viscosity from the decay rate of oscillation by the viscosity resistance of the contacted liquid surface.

5.4 Understanding Your Data

Data obtained by the rotational oscillator is the time dependency of oscillation displacement as a decay curve of rotational oscillation caused by surface viscosity as shown in Fig. 5.2. The decay rate (λ) is given by $\lambda = \log_e(a_1/a_2) = \log_e(a_2/a_3) = \dots$, and the surface viscosity (η^s) can be calculated by Eq. 5.1.

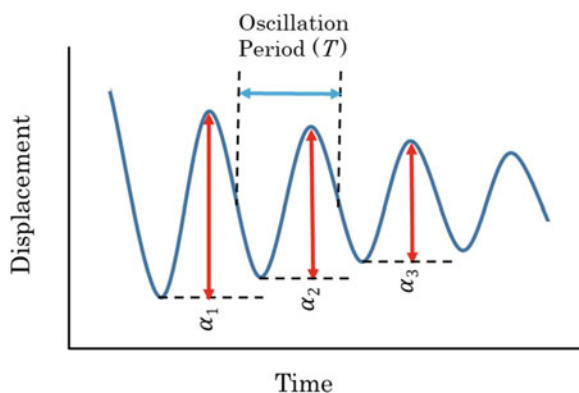
$$\eta^s = \frac{I}{2\pi} \cdot \frac{\lambda}{T} \left(\frac{1}{\gamma_1^2} - \frac{1}{\gamma_2^2} \right) \quad (5.1)$$

where I is moment inertia, λ is natural logarithmic decrement, T is oscillation period, γ_1 is disc radius, and γ_2 is dish radius. The unit of the resulted two-dimensional surface viscosity is ($N/m \cdot S$), while the unit of viscosity at three dimension is ($Pa \cdot S = N/m^2 \cdot S$).

The surface viscosity of water at 25 °C is 0.10 mN/m · S, which decreases with temperature increase due to the weakening of intermolecular hydrogen bonds. Sodium dodecyl sulfate solution (SDS; 50 mM at 25 °C), as one of the most typical anionic surfactants, shows 0.11 mN/m · S, while the surface viscosity of commercial beer is c.a. 0.16 mN/m · S at 25 °C. As such, there is common relationship between surface viscosity and foam stability.

As explained above, water has a high surface viscosity due to its strong molecular interactions. Therefore, blank correction of water contribution is required to evaluate the actual surface viscosity of the adsorbed layer of the surfactant or insoluble lipid

Fig. 5.2 Decay curve of rotational oscillation



monolayer at the water surface. This corrected surface viscosity can be calculated by Eq. 5.2.

$$\eta_s = \frac{I}{2\pi} \left(\frac{\lambda}{T} - \frac{\lambda_w}{T_w} \right) \left(\frac{1}{\gamma_1^2} - \frac{1}{\gamma_2^2} \right) \quad (5.2)$$

where I is moment inertia, λ is apparent natural logarithmic decrement observed, λ_w is natural logarithmic decrement of water, T is apparent oscillation period observed, T_w is oscillation period of water, γ_1 is disc radius, and γ_2 is dish radius. From this calibration, the surface viscosity of the actual adsorbed layer can be measured, and the molecular orientation and self-assembled states can be obtained.

5.5 Useful Hints

There are some useful hints for the measurement based on the damped oscillation method using surface viscometer SVR-A. Although the height of the sample solution in the dish does not need to be very sensitive for the measurement, it is desirable to keep the level consistent and preferably be equal to the edge of dish throughout the measurement. The contact position of the disc and sample surface significantly affects the results, and careful attention should be paid. The surface viscometer SVR-A is designed to control this positioning automatically by detecting the flow of electric current when the disc contacts the surface and stops the table elevation. (The actual stopping position is c.a. 0.5 mm above the point of contact.) As shown in Fig. 5.1, the temperature sensor works as a lead to detect electric current, so the sensor must be put in the sample solution prior to the measurement. With non-conductive solvents other than water, the table movement must be stopped manually when the sample contacts the surface with careful side view observation.

5.6 What to Look Out for

Liquid/liquid interfacial viscosity such as water and oil interface can be measured using the damped oscillation method with surface viscometer SVR-A in addition to the surface viscosity of gas/liquid interface (surface). For this measurement, put the surfactant solution in the dish with c.a. 5 mm depth, then move the table upward, and stop manually when the point disc contacts the solution surface. Gently pour oil up to the edge dish at level, and the disc should be completely in the oil phase at that point. This measurement can be done in the exact same manner with gas/liquid sample, and the interfacial viscosity can be determined by the damped oscillation method. It is well recognized that the interfacial viscosity obtained here shows a good correlation to the emulsion stability.