Chapter 4
Surface Pressure

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Abstract The basic concept of the Langmuir–Blodgett trough by measuring the surface pressure of monolayers on water was developed by Irving Langmuir. With this surface pressure measurement, we can evaluate the molecular orientations and interactions of lipids, oils, proteins, and surfactants spreading over liquids as a monolayer. Explorations of the functions of biomembranes utilizing interactions between specific lipid molecules and bioactive molecules at air/water interfaces are research targets based on this technology and are closely related to the advancement of the basics and applications for life science and medical fields. Moreover, the Langmuir–Blodgett film (LB film) as accumulated monolayers on the solid substrate is expected to be a useful module to develop molecular memory or molecular electronic devices.

Keywords Surface pressure · Area per molecule · Monolayers · Langmuir–Blodgett film

4.1 Introduction

The history of research on monolayer surfaces dates back to Benjamin Franklin's experiment in 1774. Franklin poured just a spoonful of olive oil onto the Clapham pond in England, which spread over as a thin film and seized the wave. Later in the 1880s, Agnes Pockels conducted a surface tension measurement in her kitchen by attaching a floating button to a balance, and the results were published in *Nature* in 1891 from the request of Rayleigh. In 1917, Irving Langmuir introduced the basic concept of the Langmuir–Blodgett trough by measuring the surface pressure of monolayers on water. With this surface pressure measurement, we can evaluate the molecular orientations and interactions of lipids, oils, proteins, and surfactants

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spreading over liquids (mainly water) as a monolayer. Explorations of the functions of biomembranes utilizing interactions between specific lipid molecules and bioactive molecules at air/water interfaces, or development of biomimetic materials and bio-interface devices, are typical research targets based on this technology and are closely related to the advancement of the basics and applications for life science and medical fields. The Langmuir–Blodgett film (LB film) as accumulated monolayers on the solid substrate is expected to be a useful module to develop molecular memory or molecular electronic devices.

4.2 What You Get

1. Surface pressure (π) – the area per molecule (*A*) isotherm as a two-dimensional state equation
2. Investigation of molecular orientations and interactions of monolayers at air/water interfaces
3. Evaluation of molecular interactions and miscibility in binary systems
4. The Langmuir–Blodgett film (LB film) accumulated on the solid substrate

4.3 Essentials and Tips

There are two types of surface pressure devices. One is the Wilhelmy type with a platinum or paper plate vertically hung onto the water surface to measure the vertical force, and the other is the Langmuir type, with a Teflon-coated float shorter than the trough width that moves on the water to measure the horizontal force. The Wilhelmy plate is a rather common device due to its simpler structure and easiness to handle, and this type of instrument will be explained here in this chapter. Figure 4.1 shows a

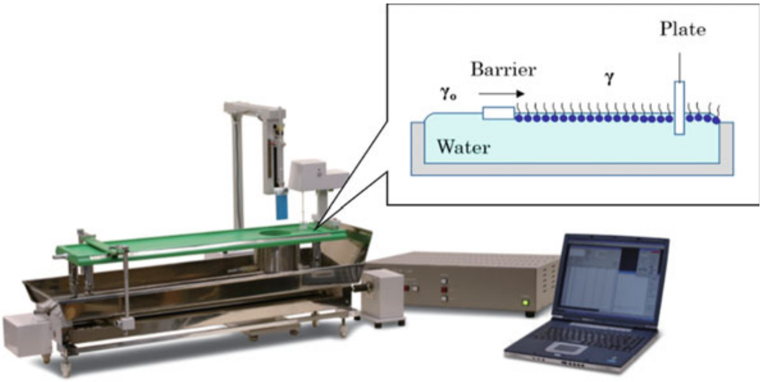

Fig. 4.1 Surface pressure meter (HBM-700. Photo credit Kyowa Interface Science Co. Ltd.)

Wilhelmy-type surface pressure instrument (HBM-700, Kyowa Interface Science Co., Ltd) with Langmuir–Blodgett trough. In the measurement procedure, first fill water over the edge of the clean trough, then prepare clean water surface, and level it (0.5–1 mm) by sweeping excess water off with a clean partition plate (barrier) or by sucking water out with an aspirator. After adjusting the trough temperature with a temperature-controlled bath, immerse the platinum plate after red heating with an alcohol lamp for cleansing, and then cool to room temperature. Next, calmly but rapidly drop the sample solution in the volatile solvent, such as chloroform, with a micro syringe. Keep still for over 10 min. to make the monolayer at the air/water interface from solvent evaporation.

The monolayer generates a spreading force at the air/water interface from the compression of the surface area with the partition plate (barrier). This force is called surface pressure (π), which is expressed by the difference of surface tension of pure water (γ_0) and the surface tension of the monolayer (γ) as $\pi = \gamma_0 - \gamma$.

Thus, π (mN/m) can be obtained by measuring the surface tension of the monolayer (γ).

4.4 Understanding Your Data

A surface pressure (π)–area per molecule (A) isotherm can be plotted using this instrument as shown in Fig. 4.2, where the monolayer area per molecule (A) is calculated by dividing the surface area by the number of molecules consisting the monolayer. This isotherm corresponds to the pressure (p) and volume (v) isotherm, so the (π)–(A) isotherm is regarded as a two-dimensional state equation, and the molecular interactions and orientations or miscibility of molecules composing the monolayer can be obtained.

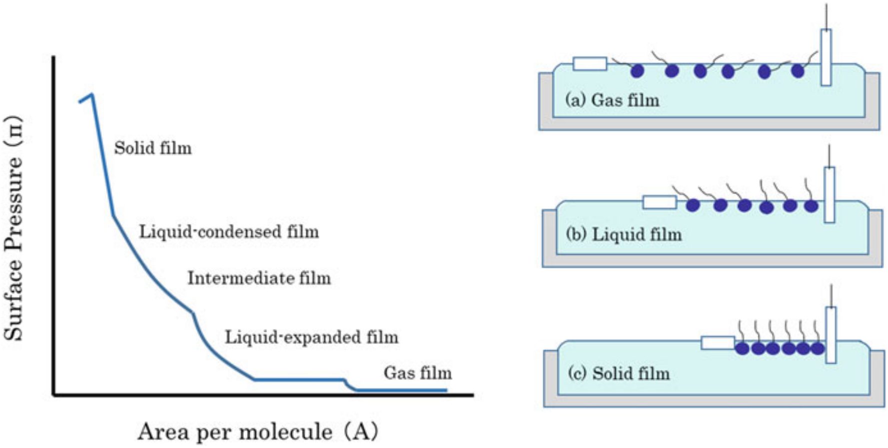

Fig. 4.2 Surface pressure (π)–area per molecule (A) isotherm

The profile of (π)–(A) isotherm (Fig. 4.2) shows the state condition of the monolayer. When the monolayer is not compressed by a partition plate (barrier), the molecules are free to move on the water surface; thus this region is called a gas film, as shown in Fig. 4.2a where the surface pressure (π) is small enough to be negligible. By compressing with a partition plate (barrier), the isotherm passes through a gas/liquid coexisting range where π stays constant regardless of the change in molecular area (A) and then reaches the liquid-expanded film where π increases compression while decreasing A. Further compression gives a liquid-condensed film through the intermediate film. Under these liquid film (Fig. 4.2b) regions, molecules are as mobile as liquids. With further compression, the two-dimensional state changes to solid film (Fig. 4.2c) and eventually reaches a collapsing pressure (γ_c) with the loss of its three-dimensional structure. As such, the (π)–(A) isotherm can be seen as a two-dimensional state equation. Its characteristics have a liquid expansion and intermediate regions (Fig.4.2) that do not exist in a three-dimensional state.

The surface compression ratio (β^s) can be calculated using Eq. 4.1 and the (π)–(A) isotherm, and the reciprocal number of β^s gives the Gibbs's modulus of the elasticity of the monolayer.

$$\beta^s = \; - \; \frac{1}{A}\left(\frac{\partial A}{\partial \pi}\right)_T \tag{4.1}$$

Here, A is molecular area, π is surface pressure and T is temperature.

As β^s is a numerical differentiation from the (π)–(A) isotherm, the phase transition of the monolayer can be accurately obtained by plotting β^s *vs* A.

4.5 What to Look Out for

Surface tension measurement using the Wilhelmy plate is based on the premise that the contact angle of the plate to water is zero. Therefore, any contamination and deformation or flaws of the plate that can affect the wettability would interfere with accurate measurement. Other than chloroform, organic solvents such as hexane and ethyl ether are commonly used to spread the monolayer molecule onto the water surface. If the solubility of the monolayer molecule is not sufficient with these solvents, water-soluble solvents such as ethyl alcohol can be used, but caution should be paid as molecules of the monolayer can dissolve into the lower aqueous phase and can interrupt accurate molecular area measurement. Other care is needed when using chloroform, whose density is larger than water due to chloroform solution sinking under the water, and can prevent solvent evaporation and the partition of the molecule for the monolayer in the water or in the chloroform solution at the bottom. To avoid this, put the tip of a micro syringe as close as possible to the water surface to spread the solution on the surface.

As the (π)–(*A*) isotherm is intended for insoluble monolayers, this method is not ideal for water-soluble materials such as hydrophilic surfactants.

4.6 Useful Hints

Monolayers at the air/water interface can be collected on to the solid surface, such as mica under constant surface pressure (π). This results in a film called the Langmuir–Blodgett film (LB film), which has been gaining attention as a potential molecular device with its nonconductive, piezo electric, and nonlinear optical properties. Atomic force microscope (AFM) observation is applicable by fixing the film on the solid base, and information relating to the orientation and miscibility of the monolayer at the molecular level can be obtained. Caution should be paid since the LB film does not always directly represent the condition of monolayer at the air/water interface. There are other instrumental methods to investigate monolayers at the air/water interface, such as the Brewster angle microscope (BAM), although its resolution is lower than AFM.