Chapter 6
Interfacial Tension Between Water and Oil

Takeshi Misono

Abstract There are many products (such as cosmetics, food, etc.) in our daily life made of emulsions, mixtures of water and oil. However, water and oil are essentially immiscible, and both liquids tend to separate into two phases. Interfacial tension is the force acting between two different liquids. Higher interfacial tension means that both liquids tend to separate into two phases. The higher the interfacial tension value, the more likely the phase separation of the two liquids occurs. Thus, decreasing the interfacial tension is essential to create a stable emulsion. As such, the interfacial tension is an indicator for better understanding stable emulsion formation. Two kinds of measurement methods, the Wilhelmy and pendant drop, are usually used for evaluating interfacial tension. The Wilhelmy method using a platinum plate is a method utilizing the drawing force of liquid to the plate, and this force is converted into interfacial tension. The pendant drop method is a method of applying the curvature radius of the liquid and is often used by many researchers in recent years. The principle and detailed information of evaluating interfacial tension is described in this chapter.

Keywords Interfacial tension · Wilhelmy method · Pendant drop method · Emulsifier

6.1 Introduction

Liquid/liquid interfacial tension refers to the force contributing to the interface between two liquids (generally water and oil) which are essentially immiscible. Simply put, the principles of Chaps. 1 and 2 are applied but replacing air with liquid. However, there are many products (such as cosmetics, food, etc.) in our daily life made of emulsions, mixtures of water and oil. These emulsion products are produced by mixing water and oil and by adding emulsifiers such as surfactants. It is important

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to know the interfacial properties of an emulsifier to better understand the emulsion properties. Interfacial tension measurement is an effective indicator and will be described in this chapter.

6.2 What You Get

An understanding of the interfacial tension between different liquids and the properties of emulsifiers

6.3 Essentials and Tips

Oil-water interfacial tension measurement can be measured by methods with principles similar to surface tension methods. The two most popular methods are the Wilhelmy and pendant drop method.

6.3.1 Wilhelmy Method

When a platinum plate is immersed in the liquid solution, the wettable liquid spreads on the plate, and a drawing force of liquid occurs. The Wilhelmy method measures this force which corresponds to the interfacial tension. Figure 6.1 shows an equipment using the measurement principle shown in Fig. 6.2. In this principle, the interfacial tension is calculated by the following equation.

Fig. 6.1 Interfacial tensiometer (Photo credit Kyowa Interface Science Co., Ltd.)

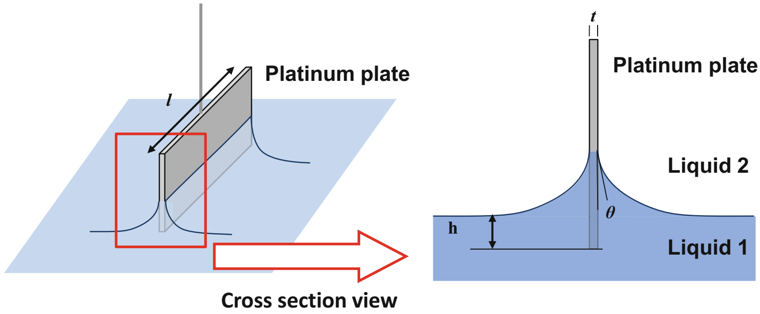

Fig. 6.2 Measurement principle of Wilhelmy method

$$P = \mathrm{mg} + 2(l + t)\gamma \cdot \cos\theta - \mathrm{lth}\Delta\rho g \tag{6.1}$$

P: tension
m: plate weight
g: gravity acceleration
l: length of plate
t: plate thickness
γ: interfacial tension
θ: contact angle between the plate and liquid
h: depth
Δρ: density difference of liquids

As seen in the equation above, The Wilhelmy method can measure the tension on the plate to calculate the interfacial tension. Therefore, it is necessary to use a hermetically sealed chamber as shown in Fig. 6.1 to avoid external factors such as wind, vibration, etc.

6.3.2 *Pendant Drop Method*

The pendant drop method is a method used to calculate the interfacial tension from the curvature radius of a droplet. The parameters for the calculation of the interfacial tension in the droplet are shown in Fig. 6.3. The relationship between the interfacial tension and each parameter can be expressed by the following equation:

$$\gamma = \Delta\rho \mathrm{gd}_e{}^2 \cdot \frac{1}{H} \tag{6.2}$$

γ: interfacial tension
Δρ: density difference of liquids
g: gravity acceleration

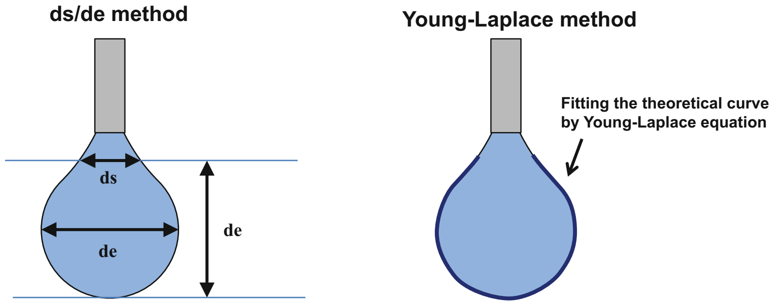

Fig. 6.3 Measurement principle of pendant drop method

d_e: maximum diameter of the droplet
1/H: correction coefficient obtained from d_s/d_e

This is called the ds/de method and is used to easily calculate the interfacial tension.

Additionally, recent development in image analysis technology has made the Young-Laplace method more popular, a method that can accurately calculate the interfacial tension by fitting the outline shape of the droplet to the Young-Laplace equation. The shape of the droplet contour can be calculated by the following simultaneous differential equation from the Young-Laplace principle.

$$\frac{\mathrm{dx}}{\mathrm{ds}} = \cos\phi, \frac{\mathrm{dz}}{\mathrm{ds}} = \sin\phi, \frac{d\phi}{\mathrm{ds}} = 2 + \beta z - \frac{\sin\phi}{x} \left(\text{where}, \beta = -\frac{\Delta\rho \mathrm{g} \mathrm{b}^2}{\gamma}\right) \tag{6.3}$$

The interfacial tension can be estimated more accurately than the ds/de method by fitting the numerical plot on the contour curve and theoretical curve.

6.4 Understanding Your Data

Higher interfacial tension value indicates that the two liquids are difficult to mix, meaning both liquids tend to separate more easily into two phases. Emulsifiers such as surfactants are often used to avoid this phase separation. The interfacial tension is decreased by adsorption of the emulsifiers into the liquid/liquid interface and, as a result, prevents phase separation. The relationship between interfacial tension and emulsifier concentration is shown in Fig. 6.4. This shows that the interfacial tension decreases by increasing emulsifier concentration so that energy required for emulsification, namely, creation of new interfaces, can be reduced. The emulsion size also depends on the interfacial tension. For example, emulsions can be prepared with normal stirring when the interfacial tension is lower than 30 mN/m, and emulsions can be prepared spontaneously (without stirring) when the interfacial tension is

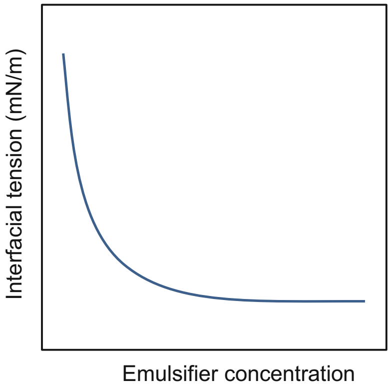

Fig. 6.4 Plots of interfacial tension as a function of emulsifier concentration

lower than approx. 2 mN/m. Furthermore, when the interfacial tension is reduced to 10^{-3} mN/m, a very fine emulsion (nano-emulsion) can be prepared.

6.5 What to Look Out for

6.5.1 Wilhelmy Method

It is common to conduct the measurement where the contact angle value θ is set to zero to avoid the influence of that angle. The contact angle θ can be set to zero by selecting the plate with a well wettable sample solution and plate surface treatment.

6.5.2 Pendant Drop Method

It is necessary to pay attention to the formation of droplets in order to calculate the interfacial tension from the droplet shape. In general, it is considered appropriate to keep de/ds ratio from 0.6 to 0.9. Furthermore, this method is not suitable for long-time measurement since the droplet curvature depends on the droplet amount.

It is necessary to fill the syringe with only the sample solution to keep the internal pressure of the syringe constant. For example, if air is contaminated in the syringe, it is impossible to keep the droplet amount constant by the change of internal pressure. It is recommended that the syringe containing the sample solution is turned upside down and the inside air is pushed out before setting it to the measuring equipment.

6.6 Useful Hints

6.6.1 Wilhelmy Method

In this method the plate is set at the interface for measurement. If either the aqueous or the oil phase is colored with a small amount of dye, the interface can be visually confirmed. In the initial setting stage of measurement, the wettability to the plate can be easily determined by this treatment.

6.6.2 Pendant Drop Method

Continuous measurement for interfacial tension against emulsifier concentration is possible with this method by successively adding emulsifier solution to the continuous phase.