Chapter 2
Static Surface Tension

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Abstract Surfactants (surface-active agent) are defined as substances capable of changing the surface or interfacial properties significantly. Addition of small amounts of surfactants into water decreases surface tension significantly. Namely, it is not called a surfactant if it does not decrease the surface tension of aqueous solutions. This chapter introduces the physical definition of surface tension and methods to measure it, such as Wilhelmy plate method and Du Nöuy method. The most popular methods and essential points for the measurement are explained. Surface tension measurements enable to determine the critical micelle concentration (cmc) of the surfactant, calculate the amount of surfactant adsorbed on the surface, and to determine the miscibility of two surfactants in mixed micellar solutions.

Keywords Surface excess energy · Surface tension · Critical micelle concentration · Surface adsorption amount · Miscibility

2.1 Introduction

Liquid surface in a large container gives a flat surface, though intrinsic liquid surface does not always behave so, as the shape of dew drops on leaves or on solid surface shows. This is because surface molecules of a pure liquid has larger free energy than bulk molecules, so that the surface shape tends to be spherical to minimize surface excess energy with the least number of molecules on the surface. Surface tension is a force to shrink the surface with dimension of force per unit length (mN/m), which is equal to the surface free energy per area (mJ/m^2). Figure 2.1 shows the physicochemical means of surface tension. Let's focus on the single molecule in the bulk (shown by a black dot in Fig. 2.1a). This molecule is surrounded by the same molecules around with same intermolecular force from all directions. As a result, the total amount of intermolecular force with surrounding molecules become zero. When these molecules

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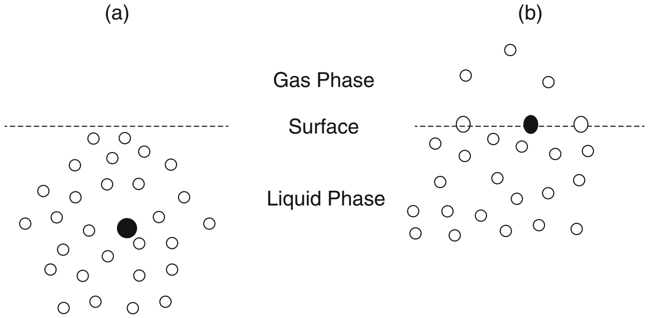


Fig. 2.1 Differences of molecular density at gas/liquid interface. The black dot shows single molecule in the bulk (**a**) or at the surface (**b**)

are brought closer from infinity, potential energy will be reduced to negative corresponding to the total amount of intermolecular forces with surrounding molecules. Thus each single molecule in the bulk (shown by black dot in Fig. 2.1a) is stable.

On the contrary, a molecule at the surface shown as a black dot in Fig. 2.1b has smaller intermolecular forces with molecules in the gas phase toward the outside of surface. As a result, the total intermolecular forces can not be cancelled to zero so that surface molecule has excess higher energy than the molecule in the bulk. This reflects to the required work force to make new surface by bringing bulk molecule to the surface. This work force, corresponding to the surface excess energy and, namely, surface tension, is smaller than the difference of potential energy between bulk molecule and surface molecule, because of the larger entropy of surface molecule. As a result, surface tension (surface energy) is larger for the molecule with strong intermolecular interaction. Surface tension of solid material, which is called as critical surface tension, comes from the same origin, and it can be measured by the contact angles of liquids dropped on the solid surface as explained in Chap. 18. Critical surface tension can be empirically calculated from the sum of contact angle dependency on the length of hydrophobic groups for liquid A with only dispersion force component, liquid B with both dispersion force component and polar component, and liquid C with dispersion force component, polar component, and hydrogen bond component.

As explained above, surface tension (γ) is expressed with dimension of force per unit length (mN/m) and can be also converted as

$$\begin{aligned}(\gamma)\ [\mathrm{mN/m}] &= [\mathrm{force}]/[\mathrm{length}] = [\mathrm{force}] \times [\mathrm{length}]/[\mathrm{length}] \times [\mathrm{length}] \\ &= [\mathrm{work}]/[\mathrm{area}] \quad \text{or} \quad [\mathrm{energy}]/[\mathrm{area}]\end{aligned}$$

Thus, γ(mN/m) can be expressed by (mJ/m^2) which corresponds to the work to make a new unit area. As surface tension reflects the strength of intermolecular interaction, it is closely related to the chemical structure as shown in Table 2.1. Surface tension is dependent on the temperature as temperature increase corresponds

Table 2.1 Surface tension for liquid materials

Material	Surface tension (mN/m)
Water	72.75
Glycerin	63.4
Benzene	28.9
Toluene	28.5
Acetone	23.7
Ethanol	22.8
Methanol	22.6
n-Hexane	18.4
Ethyl ether	17.0

to the incremental thermal motion and requires less work to bring bulk molecule to the surface. Also, surface tension depends on the solute concentration at the surface.

There are various methods for static surface tension measurement. The most popular methods are drop weight method (stalagmometric method), capillary rise method, maximum bubble pressure method, Du Nöuy method, Wilhelmy plate method, and pendant drop method. Those methods measure static surface tension at the equilibrium which closely relates to the forming capacity. The foam stability by drainage velocity depends on the dynamic surface tension, which can be measured by oscillation jet method and Hiss method (Chap. 3). Foam stability also depends on the surface viscosity (Chap. 5).

When new molecule as a surfactant is synthesized, it is a common practice to measure the level of surface tension reduction for water to evaluate the potential of this molecule. It can be found in the traditional textbook that says “addition of tiny amount of surfactant (surface active agent) can reduce water surface tension significantly,” as a reflection common perception has been that not to say surfactant without surface tension reduction. As time passes by, polymer surfactant with poor surface tension reduction but superior dispersibility of materials in the water was developed, which made surfactant definition been changed as “material capable of changing surface or interfacial properties significantly.” As explained later, critical micelle concentration (cmc) can be determined from the plot of surface tension vs concentration. In order to get accurate cmc, the relationship between equivalent conductivity and concentration is desirable, though it would not be applicable for nonionic surfactant by currently available electrodes. The methods explained here for the surface tension measurement are the most convenient way because they are independent from the ionic properties of surfactant.

2.2 What You Get

1. The cmc in water can be determined regardless of the types of surfactant.
2. Surface adsorption amount of surfactant in the solution (mostly in water) can be measured.

Fig. 2.2 Surface tensiometer DY-300. (Photo credit Kyowa Interface Science Co. Ltd.)

3. Molecular cross-sectional area at the air/liquid interface can be calculated.
4. Miscibility conditions of binary surfactant in aqueous solution can be determined.

2.3 Method

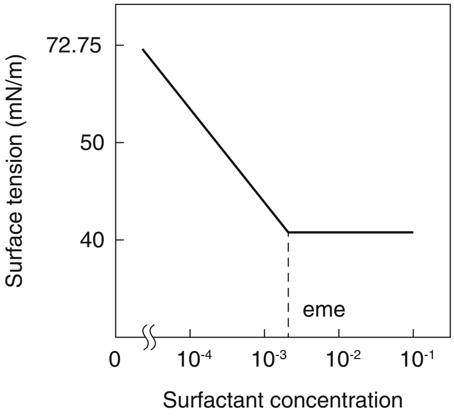
The most popular methods are the Wilhelmy plate method and Du Nöuy method. The pendant drop method, drop weight method (stalagmometric method), capillary rise method, and maximum bubble pressure method are commonly used. To get detailed methodology, operation manual for each method should be referred as each has their own principle. For the Wilhelmy plate method, one of the most popular methods, it is very important to prepare absolutely clean platinum or glass plate by complete cleansing and drying and avoiding contamination and surface disruption of sample solution by breath (Fig. 2.2). If fluorinated surfactants are the object of measurement, wetting control of the plate surface by chemical treatment is necessary.

2.4 Essentials and Tips

Du Nöuy method with a platinum ring has been the most widely used, even out of chemical industry, because of its simple and easy handling. The Wilhelmy plate method with a platinum or glass plate has been used more like professional field for its accuracy. The drop weight method (stalagmometric method) is also popular, and will be explained in the next chapter for the dynamic surface tension measurement.

Table 2.1 shows the surface tension of typical liquids. Data acquired by the method explained are surface tension vs surfactant concentration as shown in Fig. 2.3. In order for scientific analysis, concentration should be expressed by

Fig. 2.3 Relationship between surface tension and surfactant concentration in water



molar concentration (mol/l). Critical micelle concentration (cmc) can be determined from the cross section as shown in Fig. 2.3 over which surface tension becomes constant, which can be explained as a saturation concentration of monomeric surfactant solution. Smaller in cmc means higher in surface activity. For the single-tailed surfactant, cmc is 10^{-4}–10^{-3} mol/l for ionic, regardless of ionic type, and 10^{-5}–10^{-6} mol/l for nonionic surfactants. Gemini-type surfactants with double tail cmc sometime decreases to 2–3 orders smaller. Ionic surfactants with EO (polyoxyethylene) tend to show lower cmc as nonionics.

2.5 Understanding Your Data

As clear from Eq. 2.1, the adsorption amount of the surfactant at the air/water interface can be calculated from the surface tension slope toward cmc. The important point here is to use the slope as close to the cmc. In case the slope of surface tension vs concentration is not in uniformity but stepwise, the range of concentration can be divided to discuss adsorption and desorption of surfactant.

$$\Gamma = \frac{1}{A} = -\frac{1}{R}\frac{\mathrm{dr}}{d\ln C} \tag{2.1}$$

where Γ is the amount of surfactant adsorbed on the surface per unit area, R is gas constant, γ is surface tension, C is molar concentration (mol/l), and A is surface area per single surfactant molecule adsorbed.

As this equation stands for at the equilibrium, the surface tension value should be an equilibrium value. As surface tension is dependent on time duration and sometime requires quite a long period to reach equilibrium, special care should be paid for the measurement. In case concentration is not low enough to use mol/l, activity should be used instead.

It is realized that mixed surfactant system performs better than single and became quite popular for practical use. Two books are published for these characteristics of mixed surfactant system [1, 2]. Theoretical equations for the interaction between surfactants in aqueous mixed surfactant solution have been proposed by Funasaki [3], Rubingh [4], and Motomura [5]. A summary of representative two examples is explained here based on the Funasaki's equation for the binary mixed surfactant micelles [6].

2.5.1 *Example 1*

Mixed surfactant solutions[6] at 5.0×10^{-3} M consist either of sodium 3,6, 9-trioxaicosanoate (ECL from Nikko Chemical) or sodium dodecyl sulfate (SDS) as anionic surfactant with hexadecyl polyoxyethylene ether ($C_{16}H_{33}O(EO)_{10}H$; POE from Nikko Chemical) as nonionic surfactant. Composition of ECL (X_{2m}) and POE (X_{1m}) in the mixed micelle over cmc is calculated in Eqs. 2.2 and 2.3.

$$X_{2m} = \frac{C_1 * X_2 - C_{12} * X_{2b}}{C_t - C_{12}} \tag{2.2}$$

$$X_{1m} = 1 - X_{2m} \tag{2.3}$$

where C_t is the total surfactant concentration in the mixture (mol/l; M), C_{12} is the concentration of the total surfactant in the bulk phase (mol/l; M), X_2 is molar ratio of ECL in the mixed solution, and X_{2b} is molar ratio of ECL in the bulk phase.

Data required for the calculation can be retrieved from Fig. 2.4 as surface tension vs concentration relationship for each single component and Fig. 2.5 as surface tension vs concentration relationship for the binary mixed solutions at different ratio and Fig. 2.6 as surface tension (—○—) or concentration (—●—) vs mole fraction of ECL in the bulk phase obtained from Figs. 2.4 and 2.5. C_t in Eq. 2.2 is concentration

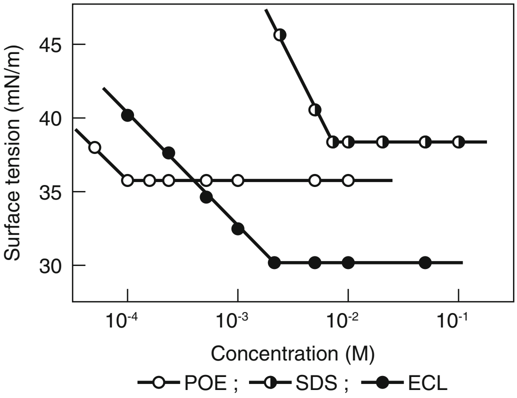


Fig. 2.4 Relationship between surface tension and concentration for single surfactant

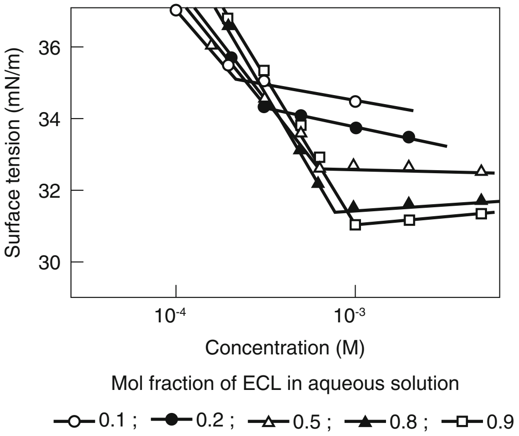


Fig. 2.5 Relationship between surface tension and concentration for binary surfactant mixture (ECL-POE) (cross point reflects cmc)

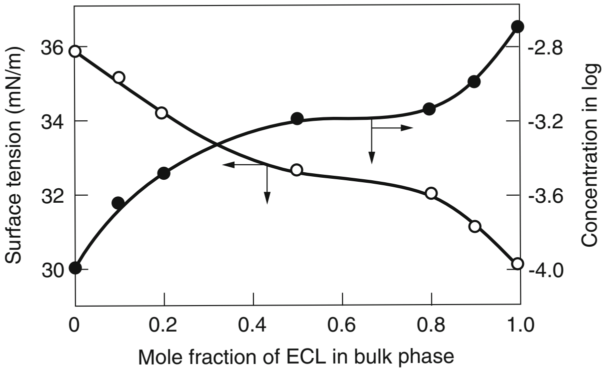


Fig. 2.6 Relationship between surface tension (—○—) or concentration (—●—) and mole fraction of ECL in the bulk phase for ECL-POE system

of mixed solution (mol/l), X_2 is composition of mixed solution, and X_{2b} and C_{12} can be determined from this figure. Applying these data to Eq. 2.3, the molar ratio of ECL or SLS in the micelle can be calculated.

The other example has been reported by Motomura et al. [5], where molar fraction of binary mixture can be calculated by Eq. 2.4 [7]. We have adapted this to the binary mixture of N^{α}, N^{α}-dimethyl-lauroyl lysine (DMLL) as amphoteric surfactant and alkyl-polyoxyethylene-ether ($C_nPOE_{20;}$ $n = 12, 14, 16, 18$) as nonionic surfactant.

$$X^{M}_{\mathrm{DMLL}} = X_{\mathrm{DMLL}} - \left(\frac{X_{\mathrm{C}_m\mathrm{POE}_{20}} {}^{*} X_{\mathrm{DMLL}}}{\mathrm{cmc}}\right) * \left(\frac{\delta_{\mathrm{cmc}}}{\delta X_{\mathrm{DMLL}}}\right)_{T*P} \tag{2.4}$$

where X_{DMLL} is molar fraction of DMLL, X_{CnPOE020} is molar faction of C_nPOE_{20} in the total solution, and cmc corresponds to the cmc of each combination.

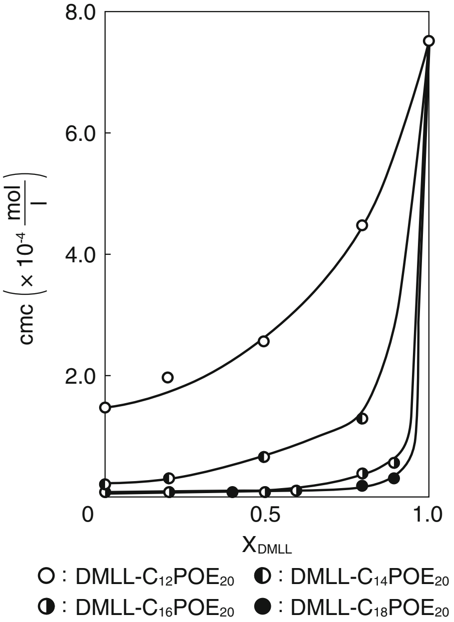


Fig. 2.7 Relationship between cmc and composition for DMLL-C_nPOE_{20} system at 40 °C

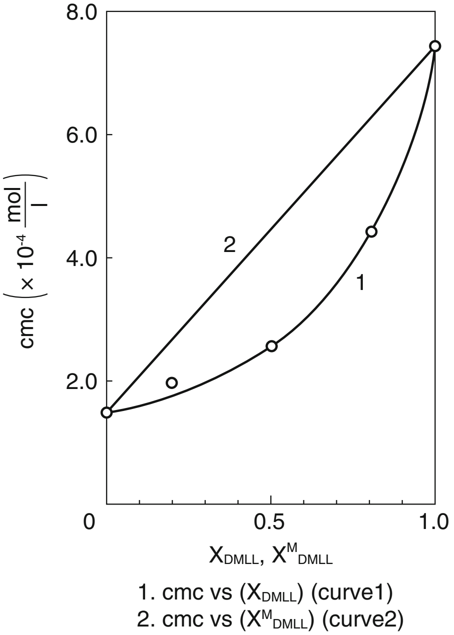


Fig. 2.8 Relationship between cmc and mol fraction of DMLL in micelle (X^M_{DMLL}) or bulk (X_{DMLL}) for DMLL-$C_{12}POE_{20}$ system at 40 °C

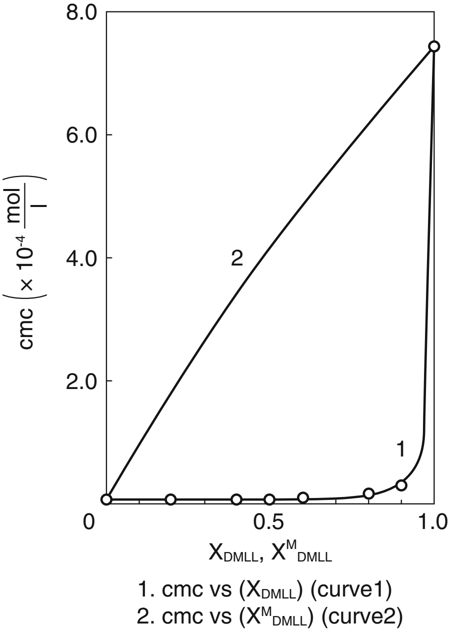


Fig. 2.9 Relationship between cmc and mol fraction of DMLL in micelle (X^{M}_{DMLL}) or bulk (X_{DMLL}) for DMLL-$C_{18}POE_{20}$ system at 40 °C

Figure 2.7 shows the relationship between cmc and composition (X_{DMLL}) for DMLL- C_nPOE_{20} system [7]. For the mixture of DMLL and $C_{12}POE_{20}$ (Fig. 2.8) or $C_{18}POE_{20}$ (Fig. 2.9) was plotted as cmc vs X^{M}_{DMLL} (curve 2) where X^{M}_{DMLL} was calculated from the value obtained from Fig. 2.4 together with the data for cmc vs X_{DMLL} from Fig. 2.7 as curve 1. Curve 1 shows cmc vs molar ratio of DMLL in the solution, and curve 2 shows cmc vs molar ratio of DMLL in the micelle obtained from Eq. 2.4. Motomura explained that ideality is smaller when separation of curve 1 and 2 is larger based on the phase separation model [5], and it is considered that interaction between surfactants is larger when difference from the ideality is larger [8]. Namely, larger in discrepancy between curve 1 and curve 2, interaction between surfactants is stronger.

2.6 What to Look Out for

Surface tension for pure water at a given condition is intrinsic physical constant, 72.75 mN/m at 25 °C, 1 atm. By Du Nöuy method, the value obtained is sometime not consistent, so that apparatus should be set as 72.75 mN/m to be maximum with pure water. Water should be clean from physical aspects which is prepared from deionized water after distillation and the surface swiped with silk thread filled in the large dish.

2.7 Useful Hints

Surface tension is closely related to the foaming property. Smaller in surface tension makes foaming easier as foaming is a process that makes new air/liquid surfaces. Foam stability relates to the surface viscosity which is a dynamic process, and dynamic surface tension should be used for the foam stability.

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