

Adsorption at Fluid–Fluid Interfaces: Part I

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4.1.1 Adsorption

- ◆ Adsorption is a very important interfacial phenomenon. When the concentration of any component of a heterogeneous system is higher at the interface than in the bulk, the phenomenon is called *adsorption*.
- ◆ The surface of a liquid is in a state of strain (see Lecture 1 of Module 2). Similarly, the surface of a solid has a residual field of force. Therefore, the free energy of the surface has a tendency to decrease. This tendency is responsible for adsorption.
- ◆ An example is the adsorption of surfactant molecules at the interface between water and oil. Adsorption has importance in the stability of solid colloidal matters, emulsions and foams, and a large number of separation and purification techniques such as purification of drinking water, removal of toxic substances from wastewater, and reactions at the interfaces.
- ◆ Adsorption of surfactant molecules at gas–liquid or liquid–liquid interfaces alters the surface or interfacial tension drastically. A mathematical model that describes the variation of surface or interfacial tension with the concentration of surfactant in the solution is known as the *surface equation of state* (EOS). The surface EOS also involves the excess concentration of the surfactant at the interface.
- ◆ In case of the nonionic surfactants, the EOS is rather simple. However, for ionic surfactants, electrostatic interactions exist between the surfactant molecules. In addition, when a salt is present in the system, the electrostatic interaction becomes more complicated. As the concentration of electrolyte is increased, nonideality of the solution also needs to be considered. The most commonly used surface equations of state are derived from the Langmuir and Frumkin adsorption isotherms.

4.1.2 Gibbs dividing surface

- ◆ Let us consider a system of two immiscible liquids such as water and oil. There hardly any liquid–liquid system which is immiscible in the absolute sense.

However, for the discussion at hand, the liquids are considered as *immiscible* if their mutual solubility is very small.

- ◆ Such a system is made of three parts: the two phases of volume V_1 and V_2 , and the interface separating them, as shown in Fig. 4.1.1.

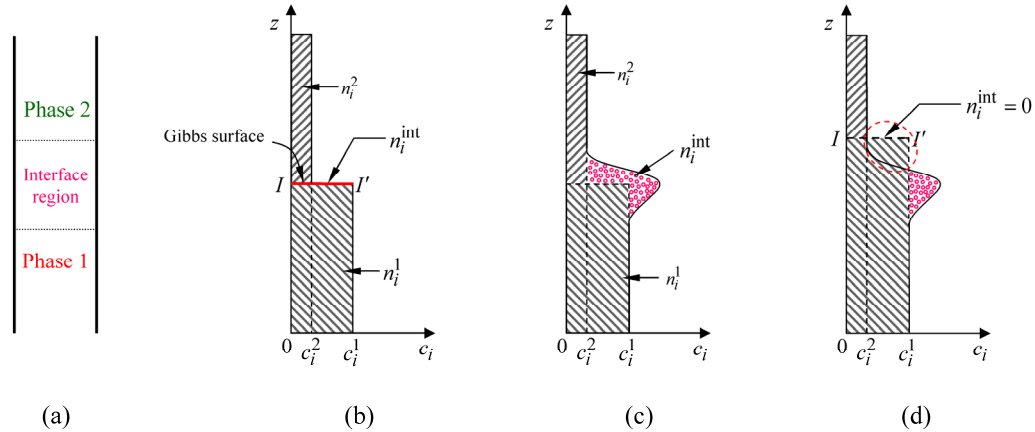


Fig. 4.1.1 (a) Illustration of the interfacial region between two phases, (b) Gibbs dividing surface, (c) concentration profile of the component i in the two phases and the interface, and (d) the location of Gibbs surface shifted so that the number of moles of component i at the interface is zero. The distance, z , is measured normal to the interface.

- ◆ Any of the extensive properties of the system such as energy, volume and surface area can be distributed between these parts. If we designate the total energy of the system by E , the energies per unit volume in the two bulk phases by e_1^b and e_2^b , and the energy of the interface by E^{int} , then we can write,

$$E^{int} = E - e_1^b V_1 - e_2^b V_2 \quad (4.1.1)$$

- ◆ The model presented above is known as *Gibbs convention*. In this approach, the two phases are separated by an infinitesimally thin dividing surface. The densities of the respective phases are constant up to the interface.
- ◆ However, the real system is somewhat different from this model system. It has a finite dividing (interfacial) region where the density changes rapidly and continuously. The model system is, therefore, a simplified but convenient system where we can think of energy and volume in discrete lumps rather than continuously varying quantities.

- ◆ The intensive properties such as pressure and density are given definite values in each phase, even for curved interfaces. The imaginary dividing surface is known as the *Gibbs dividing surface*, shown by the line II' in Figure (b). The compositions of both the phases are constant up to the dividing surface.
- ◆ Let us consider a two phase multicomponent system in which the concentration of the i^{th} component in the two phases is represented by c_i^1 and c_i^2 , respectively. The number of moles of the i^{th} component are $n_i^1 (= c_i^1 V_1)$ and $n_i^2 (= c_i^2 V_2)$ in the two phases. Therefore, the number of moles of component i at the interface is,

$$n_i^{\text{int}} = n_i - n_i^1 - n_i^2 \quad (4.1.2)$$

where n_i is the total number of moles of the i^{th} component in the entire system. The interface concentration (which is known as *surface excess*) is represented per unit area of the interface, i.e.,

$$\Gamma_i = \frac{n_i^{\text{int}}}{s} \quad (4.1.3)$$

The quantity Γ_i is expressed in mol/m^2 .

- ◆ The excess amount of material for the component i has been shown in Figure (c). According to the Gibbs model, this excess amount is ascribed to the infinitesimally thin Gibbs surface, II' , shown in Figure (b). The choice of Gibbs surface can make the surface excess zero, or even negative.
- ◆ It is often convenient to choose it in a manner such that n_i^{int} for the solvent is zero as illustrated in Figure (d) (the dotted area and the marked portion of the hatched area are equal so that $n_i^{\text{int}} = 0$). In general, the profile of each interfacial quantity is different. Therefore, a particular location of the dividing surface that makes $n_i^{\text{int}} = 0$ will not, in general, reduce another interfacial quantity to zero. The location of the dividing surface is decided depending on which properties of the system are most amenable for evaluation.

4.1.3 Gibbs adsorption equation

- ◆ The exact relationship between adsorption and surface tension was derived by J. W. Gibbs. The Gibbs adsorption equation is one of the most important equations of surface science. It is used to determine the surface activity of a surfactant at air–water or oil–water interface. It is also a basis for deriving the surface equations of state, which describe the variation of surface tension with the concentration of surfactant.
- ◆ Many derivations of varying rigidity and complexity are available in the literature. The following derivation is based on the method of Gibbs involving the use of the thermodynamic potential.
- ◆ If γ is the surface energy per unit area and s is the surface area, then the free energy of a two component system is given by the Gibbs–Duhem equation,

$$G = \gamma s + \mu_1 n_1 + \mu_2 n_2 \quad (4.1.4)$$

where the μ -terms represent chemical potentials and the n -terms represent the number of moles. The subscript ‘1’ stands for the solvent and the subscript ‘2’ stands for the solute. The term, γs , represents the surface contribution to the free energy.

- ◆ Upon differentiation of Eq. (4.1.4), we get,

$$dG = \gamma ds + s d\gamma + \mu_1 dn_1 + n_1 d\mu_1 + \mu_2 dn_2 + n_2 d\mu_2 \quad (4.1.5)$$

From another Gibbs–Duhem equation at constant temperature and pressure, we have,

$$dG = \gamma ds + \mu_1 dn_1 + \mu_2 dn_2 \quad (4.1.6)$$

where the increase in surface area is ds .

- ◆ Now, from Eqs. (4.1.5) and (4.1.6) we get,

$$s d\gamma + n_1 d\mu_1 + n_2 d\mu_2 = 0 \quad (4.1.7)$$

- ◆ Let us imagine to divide the system into two parts: one part consists of the surface region, and the other part consists of the remainder of the solution. The former is called the *surface phase* and the latter is called the *bulk phase*, which is free from the surface effects. If the number of moles of the two components in the bulk

phase are denoted by n_1^0 and n_2^0 (corresponding to n_1 and n_2 in the surface phase), the following relationship applies to the bulk phase [whereas Eq. (4.1.7) holds for the surface phase],

$$n_1^0 d\mu_1 + n_2^0 d\mu_2 = 0 \quad (4.1.8)$$

- ◆ Let us multiply Eq. (4.1.8) by n_1/n_1^0 to obtain,

$$n_1 d\mu_1 + n_1 \left(\frac{n_2^0}{n_1^0} \right) d\mu_2 = 0 \quad (4.1.9)$$

Subtracting Eq. (4.1.9) from Eq. (4.1.7) we get,

$$s d\gamma + \left(n_2 - \frac{n_1 n_2^0}{n_1^0} \right) d\mu_2 = 0 \quad (4.1.10)$$

Therefore,

$$-\frac{d\gamma}{d\mu_2} = \frac{n_2 - \frac{n_1 n_2^0}{n_1^0}}{s} \quad (4.1.11)$$

- ◆ Now, n_2 moles of the solute are associated with n_1 moles of the solvent in the surface phase, and $n_1 n_2^0 / n_1^0$ moles of the solute are associated with n_1 moles of the solvent in the bulk phase. Therefore, the right side of Eq. (4.1.11) may be regarded as the excess amount of solute per unit area of surface. This excess concentration is denoted by Γ_2 .

Therefore,

$$\Gamma_2 = -\frac{d\gamma}{d\mu_2} \quad (4.1.12)$$

- ◆ Although the arbitrary amount n_1 was used to define Γ_2 , it is independent of this quantity, since the quantity $d\gamma/d\mu_2$ depends on the nature of the surface phase only, not on its amount. The actual amount of the surface phase does not affect the value of Γ_2 as long as the entire part of the system that comes under the influence of the surface forces is included.
- ◆ The chemical potential of the solute is related to its activity by the relation,

$$\mu_2 = \mu_2^0 + RT \ln a_2 \quad (4.1.13)$$

- ◆ At constant temperature we have,

$$d\mu_2 = RT d \ln a_2 \quad (4.1.14)$$

Therefore, from Eq. (4.1.12) we get,

$$\Gamma_2 = -\frac{1}{RT} \frac{d\gamma}{d \ln a_2} \quad (4.1.15)$$

- ◆ In practice, this equation is usually applied to the solute. However, it should hold for either component of a binary system. The subscript, therefore, can be omitted giving the following equation.

$$\Gamma = -\frac{1}{RT} \frac{d\gamma}{d \ln a} = -\frac{a}{RT} \frac{d\gamma}{da} \quad (4.1.16)$$

- ◆ Equation (4.1.16) is known as the *Gibbs adsorption equation*. In its derivation, we have not made any assumption regarding the system or the surface. Its obvious application is to a gas–liquid or liquid–liquid interface. Therefore, γ represents surface tension in the former case and interfacial tension in the latter.
- ◆ Since Γ is expressed in mol/m², it is not a conventional concentration term. Nonetheless, it is a definite quantity, which can be measured by radiotracer (Tajima, 1970) and neutron reflection (Lu *et al.*, 1993) techniques.
- ◆ If the slope of the plot of γ versus $\ln a$ is negative (which is commonly observed in surfactant solutions), then Γ is positive, and there is an actual surface excess of solute. However, if the slope is positive (e.g., aqueous solutions of salts such as NaCl) Γ will be negative, which indicates surface deficiency of the solute.
- ◆ If the solute is a uni-univalent electrolyte (such as sodium dodecyl sulfate or cetyltrimethylammonium bromide) then the activity can be expressed as,

$$a = f_{\pm}^2 c^2 \quad (4.1.17)$$

where $f_{\pm}$ is the *mean activity coefficient* of the electrolyte and c is its concentration in solution. In a dilute solution, the value of $f_{\pm}$ approaches unity. Therefore, from Eq. (4.1.16), the Gibbs adsorption equation can be written as,

$$\Gamma = -\frac{1}{2RT} \frac{d\gamma}{d \ln c} \quad (4.1.18)$$

Example 4.1.1: The following data on the variation of surface tension of aqueous solution of cetyltrimethylammonium bromide (CTAB) with the concentration of the surfactant were obtained at 298 K by tensiometry.

γ (mN/m)	67.3	65.2	62.3	59.5	56.8	54.5	52.3	50.2
c (mol/m ³)	0.06	0.10	0.15	0.20	0.25	0.30	0.35	0.40

Calculate the values of Γ at 0.1 mol/m³ and 0.25 mol/m³ concentrations. Comment on your results.

Solution: The given surface tension data are plotted in Fig. 4.1.2 as γ versus $\ln(c)$.

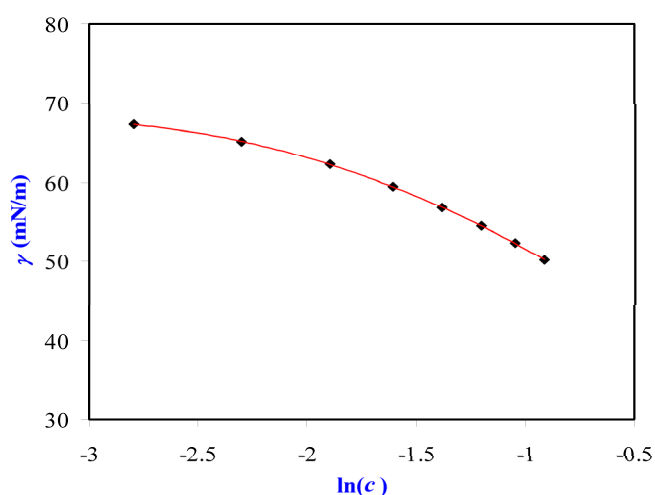


Fig. 4.1.2 Variation of surface tension with logarithm of concentration.

The data were fitted by a third-order polynomial as shown in the Fig. 4.1.2. The following equation was obtained.

$$\gamma = -0.0846(\ln c)^3 - 4.0439(\ln c)^2 - 23.15(\ln c) + 32.328$$

Therefore,

$$\frac{d\gamma}{d \ln c} = -0.2538(\ln c)^2 - 8.0878 \ln c - 23.15$$

At $c = 0.1 \text{ mol/m}^3$, we have,

$$\frac{d\gamma}{d \ln c} = -0.2538[\ln(0.1)]^2 - 8.0878[\ln(0.1)] - 23.15 = -5.8727$$

Therefore, $\Gamma = \frac{5.8727}{2 \times 8.314 \times 298} = 1.18 \times 10^{-3} \text{ mmol/m}^2 = 1.18 \times 10^{-6} \text{ mol/m}^2$

At $c = 0.25 \text{ mol/m}^3$ we have,

$$\frac{d\gamma}{d \ln c} = -0.2538[\ln(0.25)]^2 - 8.0878[\ln(0.25)] - 23.15 = -12.4257$$

$\therefore \Gamma = 2.51 \times 10^{-3} \text{ mmol/m}^2 = 2.51 \times 10^{-6} \text{ mol/m}^2$

These results indicate that the concentration of the surfactant molecules at the air–water interface increases with increasing concentration of CTAB in the solution.

4.1.4 Monolayers at fluid–fluid interfaces

- ◆ The effect of a layer of oil on calming the rampaging waves of the sea was well known to the seafarers nearly 2000 years ago, which is evident from the accounts of Pliny the Elder (AD 77). In recent years, we have seen several examples of oil-spill over sea (see Fig. 4.1.3), which has enormous effect on the ecosystem.



Fig. 4.1.3 Oil-spill over sea causing widespread layer of oil over water.

- ◆ A more comprehensive account was made by Benjamin Franklin (in 1757) when he observed that the waves of some of the ships of his fleet were remarkably smooth because ‘the cooks had emptied their greasy water through the scupper’. Later, he performed experiments in the pond at Clapham Common (in London)

on a windy day. He observed that a teaspoon of oil produced ‘an instant calm over a space several yards square, which spread amazingly and extended itself gradually until it reached the leese, making all that quarter of the pond, perhaps half an acre, as smooth as a looking glass’.

- ◆ More than a century later, Agnes Pockels did experiments in her kitchen in a rectangular trough made of tin filled with water. She observed streaming of currents when materials such as camphor and sugar were put into water and, by attaching a float to a balance, measured the change in surface tension (Pockels, 1891).
- ◆ She also showed in these experiments how films could be confined by barriers. Based on her work, it was found that the minimum area occupied by a monomolecular surface film was about 0.2 nm^2 per molecule of fatty acid (which is known as the *Pockels point*).
- ◆ It was concluded that the molecules of the fatty acid at the surface were touching each other at this point, and the picture of a surface monolayer emerged. Later Langmuir found that for the fatty acids, $\text{CH}_3(\text{CH}_2)_n\text{COOH}$, where n lies between 14 and 24, the Pockels point does not change to any significant extent. Therefore, these molecules take up similar space in the monolayer.
- ◆ The surface balance technique developed by Pockels became useful in physical chemistry for determining the size and shape of organic molecules at a time when X-ray diffraction was not yet available. Her technique formed the basis for the method later developed by Langmuir, which is often referred to as the *Langmuir trough*. This technique is still widely used by the surface chemists for various applications.

4.1.5 Types of monolayers and their applications

- ◆ If the substance that forms the monolayer is insoluble in the liquid subphase, the monolayer is called *Langmuir layer* (e.g., a monolayer of stearic acid at air–water interface). On the other hand, if the substance is soluble in the bulk phase, the

monolayer is termed *Gibbs layer* (e.g., a monolayer of sodium dodecyl sulfate at air–water interface).

- ◆ The monolayers are important in detergency, foams, emulsions, food processing and minerals processing. Therefore, the monolayers constitute an important part of modern interfacial engineering. Fundamental studies on monolayers are related to the condensed matter physics. Life scientists have investigated phospholipid Langmuir monolayers in order to gain insight into the structure and properties of bilayers, which serve as models for cell membranes.
- ◆ In 1919, Langmuir mentioned that it was possible to transfer fatty acid monolayers from water surfaces to solid supports such as glass slides. He emphasized the important effects of such single monolayers on the properties of the solid surface, such as its wettability.
- ◆ In 1934, Katherine Blodgett showed that monolayers could be transferred sequentially to build-up multilayer films. These structures are now universally referred to as *Langmuir–Blodgett films*. The controlled transfer of organized monolayers of amphiphilic molecules from the air–water interface to a solid surface was the first molecular scale technology for the creation of new materials. The Langmuir–Blodgett films are used in many high-technology applications such as molecular electronics, piezoelectric organic films, nonlinear optics and optical information storage, apart from many other common applications such as prevention of corrosion and catalysis (see Lecture 5 of Module 2).
- ◆ An interesting application of monolayers is in retardation of evaporation of water from open reservoirs and lakes in arid climates. Evaporation can be markedly reduced by spreading an insoluble monolayer of a long chain alcohol over the water surface.
- ◆ The monolayers are formed on the water surface by scattering the solid alcohol powder by boat on the lake, or by continuous addition of alcohol slurries from floating dispensers. Wind conditions and the activities of aquatic birds are important factors on the stability of the monolayer.

4.1.6 Properties of monolayers

- ◆ Following the experiment of Benjamin Franklin on spreading one teaspoonful of oil ($\sim 5 \text{ cm}^3$) on half-an-acre ($\sim 2000 \text{ m}^2$) surface area of the pond, it can be calculated that the thickness of the film on the surface of water must be about 2.5 nm.
- ◆ A hundred years later, Lord Rayleigh suggested that the maximum extension of an oil film on water represents a layer one molecule thick. At the same time, the foundation for our ability to characterize monolayers on an air–water interface was set by Agnes Pockels.
- ◆ Publication of Pockels’ work prepared the stage for Langmuir’s quantitative work on fatty acid, ester and alcohol monolayers (1917). The term “Langmuir film” is usually reserved for a floating monolayer. It was recognized by Langmuir that the force which causes the spreading of oil on the surface of water was due to the attraction between the molecules of oil and water. This attraction, however, does not emanate from the entire oil molecule but certain atoms in the molecule. Therefore, an active group of the oil molecule that has marked affinity for water is responsible for the spreading of oil on water.
- ◆ There exists a wide range of water-insoluble surfactants with an amphiphilic nature, such as the long-chain fatty acids. Many of these amphiphilic substances can easily be spread on a water surface with the help of a volatile water insoluble solvent (e.g., hexane) to form an insoluble monolayer at the air–water interface. The amphiphilic nature of the surfactant molecules dictates the orientation of the molecules at the interface in such a way that the polar head-group is immersed in the water and the long hydrocarbon chain points towards air, as shown in Fig. 4.1.4.

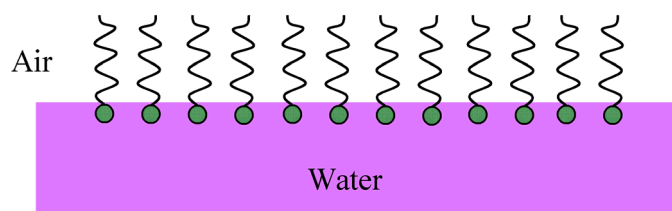


Fig. 4.1.4 An illustration showing a spread monolayer at the air–water interface.

- ◆ Long-chain fatty acids are typical examples of molecules which form the Langmuir monolayers. Chains longer than that constituted by 12 carbon atoms are necessary to keep the solubility low. However, if the hydrophobic character of the chain is dominant, the substance forms a lens rather than a monolayer at the surface.
- ◆ When the available area for the monolayer is large, the distance between the adjacent molecules is large and their interactions are weak. The monolayer can then be regarded as a two dimensional gas. If the available surface area of the monolayer is reduced by a barrier system (as shown in Fig. Fig. 4.1.5) the molecules begin to exert a repulsive effect on each other.

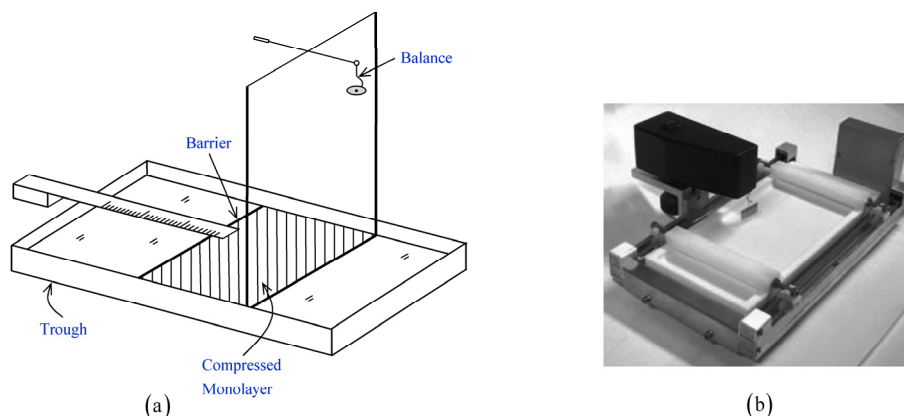


Fig. 4.1.5 Langmuir film balance: (a) schematic of the original Langmuir balance, and (b) KSV MiniMicro Langmuir-Blodgett System (courtesy: KSV Instruments Ltd. © 2008).

- ◆ This two-dimensional analogue of a pressure is termed *surface pressure*. It is defined as,

$$\pi_s = \gamma_0 - \gamma \quad (4.1.19)$$

where γ_0 is the surface tension of pure water in absence of the monolayer and γ is the surface tension with the monolayer present. Surface pressure is expressed in N/m.

- ◆ We know that the presence of surfactant lowers the surface tension of water. From Eq. (4.1.19), it is evident that the surface pressure is a measure of the

lowering of surface tension by the surfactant. If the monolayer is compressed by some means (such as the movement of the barrier shown in Fig. 4.1.5), γ decreases and consequently the surface pressure, π_s , increases.

4.1.6.1 Measurement of surface pressure

- ◆ The film-balance method developed by Langmuir measures the surface pressure directly. The shallow trough made of an inert material (e.g., glass or silica vessel with waxed edges) contains water on which the monolayer is formed. A light mica ‘boom’ waxed to prevent wetting and attached to a torsion wire separates two regions of the trough, as shown in Fig. 4.1.6.

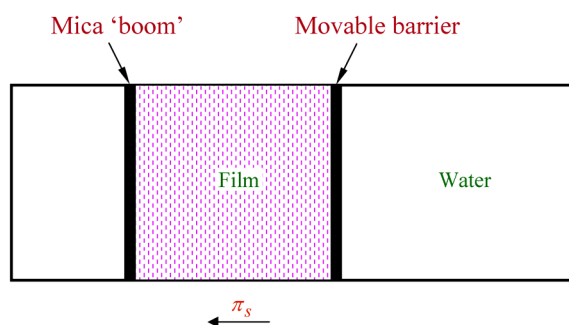


Fig. 4.1.6 Schematic of the monolayer formed in the Langmuir trough.

- ◆ The surfactant (e.g., stearic acid) is spread on one side of the ‘boom’ from a volatile liquid such as petrol ether. The solvent evaporates quickly and forms the monolayer. This film exerts a pressure π_s on the ‘boom’. It can be measured by putting weight on the pan. The movable barrier on the right is used to compress the film as required. This barrier is made of waxed glass. It is moved very slowly and smoothly while compressing the film.
- ◆ In the modern version of the Langmuir film-balance, the trough holding the subphase is usually made of Teflon. It is designed and fabricated carefully to prevent any leakage of the subphase over the edges. The temperature is controlled by circulating water in channels placed underneath the trough. The surface area of the trough can be varied by sweeping movable barriers over the surface of the

trough. The barrier is made of a polymer such as Delrin. It is heavy enough to prevent any leakage of the monolayer beneath the barrier.

- ◆ The Wilhelmy plate method (see Lecture 1 of Module 2) is used to measure the surface tension. The surface pressure is determined by measuring the change in force measured by the electrobalance for a stationary plate between a clean surface and the same surface with a monolayer present. The modern instruments are computer-controlled and give the π_s versus molecular area isotherm directly. The surface pressure and the molecular area are continuously monitored during the compression. It is also possible to hold the monolayer at a constant surface pressure, which is enabled by a computer-controlled feedback system between the electrobalance and the motor that controls the movements of the compressing barrier. This is useful for producing the Langmuir–Blodgett films deposited on a solid substrate.
- ◆ The most important precaution to be taken while studying the properties of a monolayer in a Langmuir trough is the elimination of all possible sources of contamination. A very small amount of contamination present either in the instrument or the chemicals can cause serious error in the results.

Exercise

Exercise 4.1.1: The variation of surface tension of aqueous solution of tritiated sodium dodecyl sulfate (TSDS) with the concentration of the surfactant at 298 K is given below (Tajima *et al.*, 1970).

c (mol/m ³)	γ (mN/m)	c (mol/m ³)	γ (mN/m)
0.30	70.4	0.86	65.2
0.40	70.1	0.98	63.8
0.50	69.5	1.97	55.1
0.58	67.6	2.91	49.5
0.70	66.4	4.00	46.0

From these data, calculate the Gibbs surface excess at 0.5 mol/m³, 1 mol/m³ and 3 mol/m³ concentrations of TSDS.

Exercise 4.1.2: The surface tension data for an aqueous solution of Tween 20 are presented in the following table.

Concentration of Tween 20 (mol/m ³)	Surface Tension (N/m)
0.000	0.072
0.001	0.060
0.004	0.048
0.008	0.043
0.016	0.037
0.024	0.034
0.033	0.031

Compute the surface excess concentrations in this range of surfactant concentration and present your results graphically.

Exercise 4.1.3: Answer the following questions clearly.

- (a) Explain the term adsorption.
- (b) Explain the significance of adsorption of surface active molecules at the air–liquid and liquid–liquid interfaces.
- (c) Explain Gibbs dividing surface.
- (d) Define surface excess. How would you correlate surface excess with surface tension and the concentration of surfactant in the solution?
- (e) Write the Gibbs adsorption equation applicable to: (i) a dilute solution of sodium dodecyl sulfate, and (ii) dilute solution of Tween 20.
- (f) Explain the difference between Langmuir and Gibbs monolayers.
- (g) Give five applications in which monolayers are important.
- (h) What is Langmuir–Blodgett film?
- (i) Following Benjamin Franklin’s experiment, if 5 cm^3 of oil covers half-acre surface area of a pond in the form of a monolayer, what is the thickness of the monolayer?
- (j) What is surface pressure? How is it related to surface tension?
- (k) Explain how surface pressure is measured in a Langmuir trough. What is the main modification that has been made in modern troughs as compared to Langmuir’s original trough?

Suggested reading

Textbooks

- ◆ A. W. Adamson and A. P. Gast, *Physical Chemistry of Surfaces*, John Wiley, New York, 1997, Chapter 15.
- ◆ P. C. Hiemenz and R. Rajagopalan, *Principles of Colloid and Surface Chemistry*, Marcel Dekker, New York, 1997, Chapter 7.
- ◆ P. Ghosh, *Colloid and Interface Science*, PHI Learning, New Delhi, 2009, Chapters 6 & 8.

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