

# Interfacial Phenomena

Liquid Interfaces  
 Adsorption at Liquid Interfaces  
 Adsorption at Solid Interfaces

Applications of Surface Active Agents  
 Electric Properties of Interfaces

When phases exist together, the boundary between two of them is termed an *interface*. The properties of the molecules forming the interface are often sufficiently different from those in the bulk of each phase that they are referred to as forming an "interfacial phase." Although this terminology is not correct in terms of the phase rule, it is a useful concept. For example, molecules at the liquid-gas interface may exist in a two-dimensional gaseous, liquid, or solid state depending on the prevailing conditions of temperature and pressure in the interface. Their phase-like behavior is therefore apparent.

Several types of interface can exist, depending on whether the two adjacent phases are in the solid, liquid, or gaseous state (Table 14-1). For convenience, we shall divide these various combinations into two groups, namely *liquid interfaces* and *solid interfaces*. In the former group, the association of a liquid phase with a gaseous or another liquid phase will be discussed. The section on solid interfaces will deal with systems containing solid-gas and solid-liquid interfaces. While solid-solid interfaces have practical significance in pharmacy (for example, the adhesion between granules, the preparation of layered tablets, and the flow of particles), little information is available to quantify these interactions. This is due, at least in part, to the fact that the surface region of materials in the solid

state is quiescent, in sharp contrast to the turbulence that exists at the surfaces of liquids and gases. Accordingly, solid-solid systems will not be discussed here. A final section will outline the electric properties of interfaces.

The term *surface* is customarily used when referring to either a gas-solid or a gas-liquid interface. Although this terminology will be used in the present chapter, the reader should appreciate that every surface is an interface. Thus, a table top forms a gas-solid interface with the atmosphere above it, and the surface of a rain drop constitutes a gas-liquid interface.

The symbols for the various interfacial tensions are shown in the second column of Table 14-1, where the subscript *L* stands for liquid, *V* for vapor or gas, and *S* for solid. Surface and interfacial tensions are defined on p. 363.

Since every particle of matter, be it cell, bacterium, colloid, granule, or man, possesses an interface at the boundary of its surroundings, the importance of the present topic is self-evident. Interfacial phenomena in pharmacy and medicine are significant factors that affect absorption of drugs onto solid adjuncts in dosage forms, penetration of molecules through biologic membranes, emulsion formation and stability, and the dispersion of insoluble particles in liquid media to form suspensions. The interfacial properties of a surface-

TABLE 14-1. Classification of Interfaces

Phase	Interfacial Tension	Types and Examples of Interfaces
Gas-gas	—	No interface possible
Gas-liquid	$\gamma_{LV}$	Liquid surface, body of water exposed to atmosphere
Gas-solid	$\gamma_{SV}$	Solid surface, table top
Liquid-liquid	$\gamma_{LL}$	Liquid-liquid interface, emulsion
Liquid-solid	$\gamma_{LS}$	Liquid-solid interface, suspension
Solid-solid	$\gamma_{SS}$	Solid-solid interface, powder particles in contact

active agent found lining the alveoli of the lung are responsible for the efficient operation of this organ.<sup>1</sup> Felmeister<sup>2</sup> and Seeman<sup>3</sup> reviewed the relationship between surface properties of drugs and their biologic activity.

### LIQUID INTERFACES

**Surface and Interfacial Tensions.** In the liquid state, the cohesive forces between adjacent molecules are well developed. Molecules in the bulk of the liquid are surrounded in all directions by other molecules for which they have an equal attraction, as shown in Figure 14-1. On the other hand, molecules at the surface (i.e., at the liquid-air interface) can only develop attractive cohesive forces with other liquid molecules that are situated below and adjacent to them. They can develop adhesive forces of attraction with the molecules constituting the other phase involved in the interface, although, in the case of the liquid-gas interface, this adhesive force of attraction is small. The net effect is that the molecules at the surface of the liquid experience an inward force towards the bulk, as shown in Figure 14-1. Such a force pulls the molecules of the interface together and, as a result, contracts the surface, resulting in a *surface tension*. Liquid droplets tend to assume a spherical shape, since a sphere has the smallest surface area per unit volume.

This "tension" in the surface is the force per unit length that must be applied *parallel* to the surface so as to counterbalance the net inward pull. This force, the surface tension, has the units of dyne/cm in the cgs system. It is similar to the situation that exists when an object dangling over the edge of a cliff on a length of rope is pulled upward by a man holding the rope and

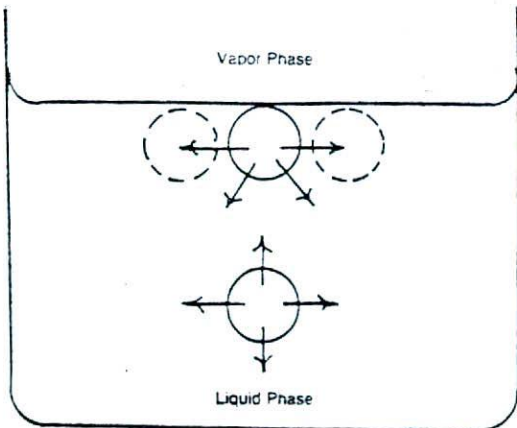


Fig. 14-1. Representation of the unequal attractive forces acting on molecules at the surface of a liquid, as compared with molecular forces in the bulk of the liquid.

walking away from the edge of the top of the cliff. This analogy to surface tension is sketched in Figure 14-2.

*Interfacial tension* is the force per unit length existing at the interface between two immiscible liquid phases and, like surface tension, has the units of dyne/cm. Although in the general sense all tensions may be referred to as *interfacial tensions*, this term is most often used for the attractive force between immiscible liquids. Later we will use the term *interfacial tension* for the force between two liquids,  $\gamma_{LL}$ , two solids,  $\gamma_{SS}$ , and for a liquid-solid interface,  $\gamma_{LS}$ . The term *surface tension* is reserved for liquid-vapor,  $\gamma_{LV}$ , and solid-vapor,  $\gamma_{SV}$ , tensions. These are often written simply as  $\gamma_L$  and  $\gamma_S$ . Ordinarily, interfacial tensions are less than surface tensions because the adhesive forces between two liquid phases forming an interface are greater than when a liquid and a gas phase exist together. It follows that if two liquids are completely miscible, no interfacial tension exists between them. Some representatives of surface and interfacial tensions are listed in Table 14-2.

That surface tension is a force per unit length may also be illustrated by means of a three-sided wire frame across which a movable bar is placed (Fig. 14-3). A soap film is formed over the area ABCD and can be stretched by applying a force  $f$  (such as a hanging mass) to the movable bar, length  $L$ , which acts against the surface tension of the soap film. When the mass is removed, the film will contract owing to its surface

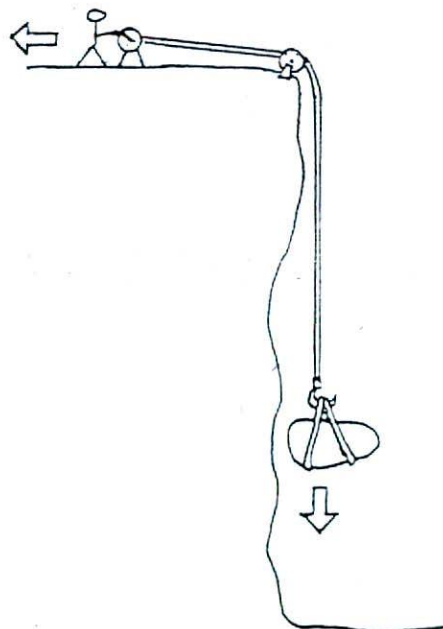


Fig. 14-2. Visualization of surface tension as a person lifting a rock by pulling the rope in a horizontal direction.

TABLE 14-2. Surface Tension and Interfacial Tension (Against Water) at 20° C\*

Substance	Surface Tension (dyne/cm)	Substance	Interfacial Tension Against Water (dyne/cm)
Water	72.8	Mercury	375
Glycerin	63.4	n-Hexane	51.1
Oleic acid	32.5	Benzene	35.0
Benzene	28.9	Chloroform	32.8
Chloroform	27.1	Oleic acid	15.6
Carbon tetrachloride	26.7	n-Octyl alcohol	8.52
Castor oil	39.0	Caprylic acid	8.22
Olive oil	35.8	Olive oil	22.9
Cottonseed oil	35.4	Ethyl ether	10.7
Liquid petrolatum	33.1		

\*From P. Becher, *Emulsions: Theory and Practice*, 2nd Edition, Reinhold, New York, 1962, and other sources.

tension. The surface tension,  $\gamma$ , of the solution forming the film is then a function of the force that must be applied to break the film over the length of the movable bar in contact with the film. Since the soap film has two liquid-gas interfaces (one above and one below the plane of the paper), the total length of contact is in fact equal to twice the length of the bar.

Thus

$$\gamma = f_b/2L \quad (14-1)$$

in which  $f_b$  is the force required to break the film and  $L$  is the length of the movable bar.

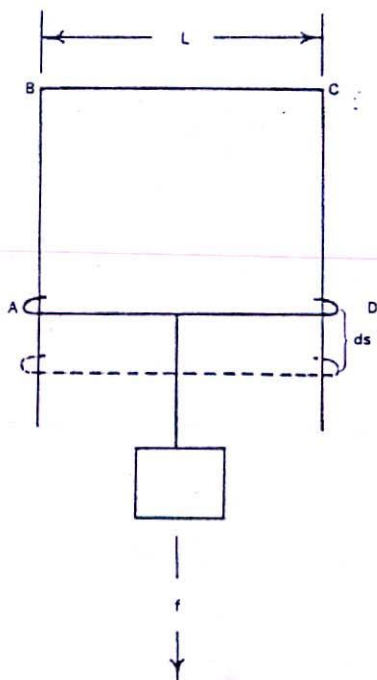


Fig. 14-3. Wireframe apparatus used to demonstrate the principle of surface tension.

**Example 14-1.** If the length of the bar  $L$  is 5 cm and the mass required to break a soap film is 0.50 g, what is the surface tension of the soap solution?

Recall that the downward force is equal to the mass multiplied by the acceleration due to gravity. Then

$$\gamma = \frac{0.50 \text{ g} \times 981 \text{ cm/sec}^2}{10 \text{ cm}} = 49 \text{ dynes/cm}$$

**Surface Free Energy.** To evaluate the work done (energy) in increasing the surface area, equation (14-1) may be written as  $\gamma \times 2L = f$ . When the bar is at a position  $AD$  in Figure 14-3 and a mass is added to extend the surface by a distance  $ds$ , the work  $dW$  (force multiplied by distance) is

$$dW = f \times ds = \gamma \times 2L \times ds$$

and, since  $2L \times ds$  is equal to the increase in surface area  $dA$  produced by extending the soap film,

$$dW = \gamma dA$$

For a finite change,

$$W = \gamma \Delta A \quad (14-2)$$

in which  $W$  is the work done or *surface free energy* increase expressed in ergs,  $\gamma$  is the surface tension in dynes/cm, and  $\Delta A$  is the increase in area in  $\text{cm}^2$ . Any form of energy can be divided into an intensity factor and a capacity factor (p. 53). Surface tension is the intensity factor, and a change in area is the capacity factor of surface free energy. Surface tension may thus be defined as the *surface free energy change per unit area increase* in conformity with equation (14-2).

**Example 14-2.** What is the work required in Example 14-1 to pull the wire down 1 cm as shown in Figure 14-3?

Since the area is increased by  $10 \text{ cm}^2$ , the work done is given by the equation

$$W = 49 \text{ dynes/cm} \times 10 \text{ cm}^2 = 490 \text{ ergs}$$

Repeat the calculations using SI units.

$$1 \text{ dyne} = 10^{-5} \text{ N, or } 49 \text{ dyne} = 49 \times 10^{-5} \text{ N}$$

$$49 \text{ dyne/cm} = 49 \times 10^{-3} \text{ N/m} = 49 \times 10^{-3} \text{ Nm/m}^2$$

Also  $1 \text{ Nm} = 1 \text{ J}$  (Table 1-3, p 3), and  $1 \text{ J} = 10^7 \text{ erg}$ . Therefore,  $W = 49 \times 10^{-3} \text{ Nm/m}^2 \times 10^{-3} \text{ m}^2 = 490 \times 10^{-7} \text{ J} = 490 \text{ erg}$ .

Equation 14-2 defines surface tension as the work per unit area required to produce a new surface. From

thermodynamics, at  $T$  and  $P$  constant, the surface tension can also be viewed as the increment in Gibbs free energy per unit area (see Hiemenz,<sup>4</sup> pp. 293–296). Thus, equation (14–2) can be written as

$$\gamma = \left( \frac{\partial G}{\partial A} \right)_{T,P} \quad (14-3)$$

This definition has the advantage that the path-dependent variable  $W$  is replaced by a thermodynamic function  $G$ , which is independent of the path. Many of the general relationships that apply to  $G$  also serve for  $\gamma$ . This fact enables us to compute the enthalpy and entropy of a surface:

$$G^s = \gamma = H^s - TS^s \quad (14-4)$$

and

$$\left( \frac{\partial G^s}{\partial T} \right)_P = \left( \frac{\partial \gamma}{\partial T} \right)_P = -S^s \quad (14-5)$$

Combining equations (14–4) and (14–5),

$$\gamma = H^s + T \left( \frac{\partial \gamma}{\partial T} \right)_P \quad (14-6)$$

Thus from a plot of surface tension against absolute temperature, one may obtain the slope of the line ( $\partial\gamma/\partial T$ ) and thus has  $-S^s$  from equation (14–5). If  $H^s$  does not change appreciably over the temperature range considered, the intercept gives the  $H^s$  value. It should be noted that the units on  $S^s$  and  $H^s$  are given in two dimensions, ergs  $\text{cm}^{-2} \text{deg}^{-1}$  for  $S^s$  and ergs  $\text{cm}^{-2}$  for  $H^s$  in the cgs system. In the SI system  $S^s$  is given in units of joule  $\text{m}^{-2} \text{deg}^{-1}$  and  $H^s$  in units of joule  $\text{m}^{-2}$ , where m stands for meters.

**Example 14–3.** The surface tension of methanol in water (10% by volume) at 20, 30, and 50° C (293.15, 303.15, and 323.15° K) is 59.04, 57.27, and 55.01 dyne/cm (or erg/cm<sup>2</sup>) (see *CRC Handbook of Chemistry and Physics*, 63rd Edition, p. F-35 for the data). Compute  $S^s$  and  $H^s$  over this temperature range.

Using linear regression of  $\gamma$  versus  $T$  according to equation (14–6),

the slope is found to be  $-0.131 \text{ erg cm}^{-2} \text{deg}^{-1} = \left( \frac{\partial \gamma}{\partial T} \right)_P = -S^s$ ; hence,

$S^s = 0.131$  and the intercept is  $97.34 \text{ erg cm}^{-2} = H^s$ . The equation is therefore

$$G^s = \gamma = 97.34 - 0.131 T$$

If we compute  $H^s$  at each temperature from equation (14–6) and if  $S^s$  remains constant at  $-0.131$ :

$$\text{At } 20^\circ \text{C, } H^s = 59.04 + (0.131 \times 293.15) = 97.44 \text{ erg cm}^{-2}$$

$$\text{At } 30^\circ \text{C, } H^s = 57.27 + (0.131 \times 303.15) = 96.96 \text{ erg cm}^{-2}$$

$$\text{At } 50^\circ \text{C, } H^s = 55.01 + (0.131 \times 323.15) = 97.34 \text{ erg cm}^{-2}$$

$H^s$  appears to be practically constant, very similar to the intercept from the regression equation,  $H^s = 97.34 \text{ erg cm}^{-2} = 97.34 \text{ mJ/m}^{-2}$ . Note that the numerical value of surface tension in the cgs system, like that for  $H^s$  in the cgs system, is the same as that in the SI system when the units mJ are used. Thus one can convert surface tension readily from cgs to SI units.<sup>4</sup> For example, if the surface tension of methanol in water (10% by volume) at 20° C is 59.04 erg/cm<sup>2</sup> in the cgs system, we can write without carrying out the conversion calculation that  $\gamma$  for the methanol-in-water mixture at 20° C is 59.04 mJ/m<sup>2</sup> in SI units.

**Pressure Differences Across Curved Interfaces.** Another way of expressing surface tension is in terms of the pressure difference that exists across a curved interface. Consider a soap bubble (Fig. 14–4) having a radius  $r$ . The total surface free energy  $W$  is equal to  $4\pi r^2 \gamma$ , where  $4\pi r^2$  is the area of the spherical bubble. (See the formulas, bottom, inside front cover.) Suppose that the bubble is caused to shrink so that its radius decreases by  $dr$ . The final surface free energy is now

$$W = 4\pi\gamma(r - dr)^2 \quad (14-7)$$

$$W = 4\pi\gamma r^2 - 8\pi\gamma r dr + 4\pi\gamma(dr)^2 \quad (14-8)$$

Since  $dr$  is small compared to  $r$ , the term containing  $(dr)^2$  in equation (14–8) may be disregarded.

The change in surface free energy is therefore  $-8\pi\gamma r dr$ , where the minus sign appears because the surface area has shrunk. Opposing this change is an equal and opposite energy term that depends on the pressure difference,  $\Delta P$ , across the wall of the bubble. Since pressure is a force per unit area, or force = pressure  $\times$  area, the work change brought about by a decrease in radius  $dr$  is

$$W = \Delta P \times 4\pi r^2 \times -dr \quad (14-9)$$

At equilibrium, this must equal the change in surface free energy, and so

$$-8\pi\gamma r dr = -4\Delta P \pi r^2 dr \quad (14-10)$$

or

$$\Delta P = 2\gamma/r \quad (14-11)$$

Therefore, as the radius of a bubble decreases, the pressure of the air inside increases relative to that outside. Equation (14–11) is a simplification of the Young–Laplace equation and can be used to explain capillary rise, as seen in the following section.

**Measurement of Surface and Interfacial Tensions.** Of the several methods that exist for obtaining surface and interfacial tensions, only the capillary rise and the DuNoüy ring methods will be described here. For details of the other methods, such as drop weight,

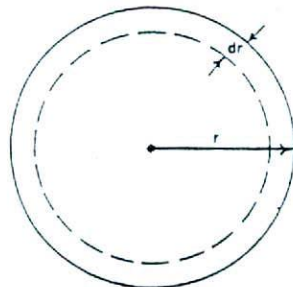


Fig. 14–4. Schematic representation of pressure difference across the curved surface of a soap bubble.

bubble pressure, pendent drop, sessile drop, and Wilhelmy plate, refer to the treatises by Adamson,<sup>5</sup> Harkins and Alexander,<sup>6</sup> Drost-Hansen,<sup>7</sup> and Hiemenz.<sup>4</sup> It is worth noting, however, that the choice of a particular method often depends on whether surface or interfacial tension is to be determined, the accuracy and convenience desired, the size of sample available, and whether or not the effect of time on surface tension is to be studied. In reality, there is no one best method for all systems.

The surface tensions of most liquids decrease almost linearly with an increase in temperature, that is, with an increase in the kinetic energy of the molecules. In the region of its critical temperature, the surface tension of a liquid becomes zero. The surface tension of water at 0° C is 75.6, at 20° C it is 72.8, and at 75° C it is 63.5 dynes/cm. It is therefore necessary to control the temperature of the system when carrying out surface and interfacial tension determinations.

**Capillary Rise Method.** When a capillary tube is placed in a liquid contained in a beaker, the liquid generally rises up the tube a certain distance. This is because when the force of adhesion between the liquid molecules and the capillary wall is greater than the cohesion between the liquid molecules, the liquid is said to *wet* the capillary wall, spreading over it, and rising in the tube (spreading is discussed in some detail on page 369). By measuring this rise in a capillary, it is possible to determine the surface tension of the liquid. It is not possible, however, to obtain interfacial tensions using the capillary rise method.

Consider a capillary tube of inside radius  $r$  immersed in a liquid that wets its surface, as seen in Figure 14-5a. The liquid continues to rise in the tube due to the surface tension, until the upward movement is just balanced by the downward force of gravity due to the weight of the liquid.

The upward vertical component of the force resulting from the surface tension of the liquid at any point on the circumference is given by

$$a = \gamma \cos \theta$$

as seen in the enlarged sketch (Fig. 14-5b). The total upward force around the inside circumference of the tube is

$$2\pi r \gamma \cos \theta$$

in which  $\theta$  is the *contact angle* between the surface of the liquid and the capillary wall, and  $2\pi r$  is the inside circumference of the capillary. For water and other commonly used liquids, the angle  $\theta$  is insignificant, that is, the liquid wets the capillary wall so that  $\cos \theta$  is taken as unity for practical purposes (see left side of Fig. 14-5b).

The counteracting force of gravity (mass  $\times$  acceleration) is given by the product of the cross-sectional area  $\pi r^2$ , the height  $h$  of the liquid column to the lowest point

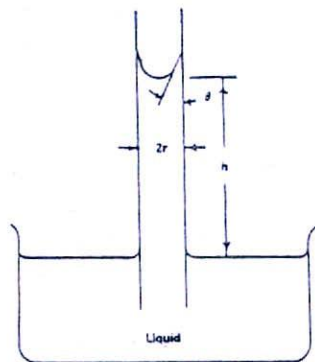


Fig. 14-5a. Measuring surface tension by means of the capillary rise principle.

of the meniscus, the difference in the density of the liquid  $\rho$  and its vapor  $\rho_0$ , and the acceleration of gravity:  $\pi r^2 h (\rho - \rho_0) g + w$ . The last term  $w$  is added to account for the weight of liquid above  $h$  in the meniscus. When the liquid has risen to its maximum height, which may be read from the calibrations on the capillary tube, the opposing forces are in equilibrium, and accordingly the surface tension can be calculated. The density of the vapor, the contact angle, and  $w$  can usually be disregarded; hence,

$$2\pi r \gamma = \pi r^2 h \rho g$$

and finally

$$\gamma = \frac{1}{2} r h \rho g \quad (14-12)$$

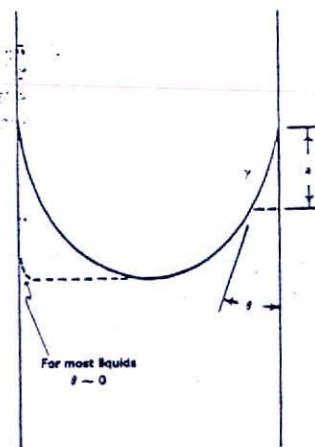


Fig. 14-5b. Enlarged view of the force components and contact angle at the meniscus of a liquid. For many liquids the contact angle  $\theta$  (exaggerated in figure) is nearly zero as shown on the left-hand side of the diagram.

**Example 14-4.** A sample of chloroform rose to a height of 3.67 cm at 20° C in a capillary tube having an inside radius of 0.01 cm. What is the surface tension of chloroform at this temperature? The density of chloroform is 1.476 g/cm<sup>3</sup>.

$$\gamma = \frac{1}{2} \times 0.01 \text{ cm} \times 3.67 \text{ cm} \times 1.476 \text{ g/cm}^3 \times 981 \text{ cm/sec}^2$$

$$\gamma = 26.6 \text{ g cm(sec}^2\text{cm)} = 26.6 \text{ dynes/cm}$$

Capillary rise may also be explained as being due to the pressure difference across the curved meniscus of the liquid in the capillary. We have already seen in equation (14-11) that the pressure on the concave side of a curved surface is greater than that on the convex side. This means that the pressure in the liquid immediately below the meniscus will be less than that outside the tube at the same height. As a result, the liquid will move up the capillary until the hydrostatic head produced equals the pressure drop across the curved meniscus. Using the same symbols as before and neglecting contact angles,

$$\Delta P = 2\gamma/r = \rho gh \quad (14-13)$$

in which  $\rho gh$  is the hydrostatic head. Rearranging equation (14-13) gives

$$\gamma = \tau\rho gh/2$$

which is identical with equation (14-12) derived on the basis of adhesive forces versus cohesive forces.

**The DuNoüy Ring Method.** The *DuNoüy tensiometer*, illustrated in Figure 14-6, is widely used for measuring surface and interfacial tensions. The principle of the instrument depends on the fact that the force necessary to detach a platinum-iridium ring immersed at the surface or interface is proportional to the surface or interfacial tension. The force required to detach the ring in this manner is provided by a torsion wire and is recorded in dynes on a calibrated dial. The

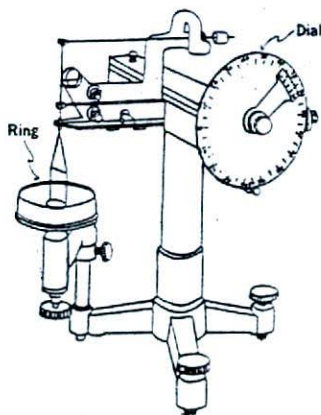


Fig. 14-6. Cenco DuNoüy tensiometer.

surface tension is given by the formula (compare with equation [14-1])

$$\gamma = \frac{\text{dial reading in dynes}}{2 \times \text{ring circumference}} \times \text{correction factor, } \beta \quad (14-14)$$

In effect, the instrument measures the weight of liquid pulled out of the plane of the interface immediately before the ring becomes detached (Fig. 14-7). A correction factor is necessary in equation (14-14) because the simple theory does not take into account certain variables such as the radius of the ring, the radius of the wire used to form the ring, and the volume of liquid raised out of the surface. Errors as large as 25% may occur if the correction factor is not calculated and applied. The method of calculating the correction factor has been described by Harkins and Jordan,<sup>5</sup> and, with care, a precision of about 0.25% can be obtained.

**Example 14-5.** The published surface tension of water at 18° C is 73.05 dyne/cm and the density  $\rho_1$  of water at this temperature is 0.99860 g/cm<sup>3</sup>. The density  $\rho_2$  of moist air—that is, air saturated with the vapor of the liquid, water, at 18° C—is 0.0012180. Therefore,  $\rho_1 - \rho_2$ , the density of water overlaid with air, is 0.99739 g/cm<sup>3</sup>. The dial reading in dynes or newtons on the tensiometer is equal to the mass  $M$  of the liquid lifted by the ring, multiplied by the gravity constant, 980.665 cm/sec<sup>2</sup>; that is,

$$\text{dial reading} = M \text{ (grams)} \times 980.665 \text{ cm/sec}^2$$

It is thus possible to obtain the mass  $M$  of liquid lifted with the ring,  $M = 0.7866$  gram, before it breaks away from the water surface. The ring must be kept absolutely horizontal for accurate measurement. The volume  $V$  of water lifted above the free surface of water is calculated from the mass of water lifted and the density at 18° C, or

$$V = \frac{M}{\rho_1 - \rho_2} = \frac{0.7866}{0.99739} = 0.78866 \text{ cm}^3$$

The ring of the tensiometer has a radius  $R$  of 0.8078 cm, and  $R^3 = 0.527122 \text{ cm}^3$ . The radius  $r$  of the wire that forms the ring is 0.1877 cm. Two values,  $R^3/V$  and  $R/r$ , are needed to enter the tables of Harkins and Jordan<sup>5</sup> to obtain the correction factor,  $\beta$ , by interpolation.

An abbreviated table of  $R^3/V$  and  $R/r$  values needed to obtain  $\beta$  is given in Table 14-3. In this example  $R^3/V = 0.527122/0.78866 = 0.66838$ , and  $R/r = 0.8078/0.1877 = 43.0368$ . Introducing these

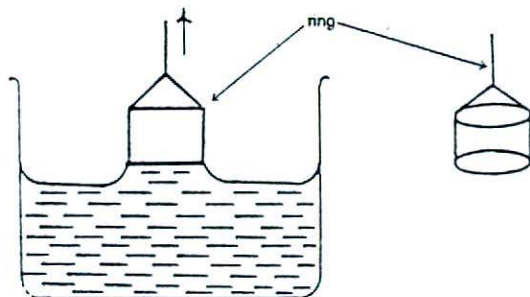


Fig. 14-7. Schematic of the tensiometer ring pulling a column of water above the surface before it breaks away.

TABLE 14-3. Some Harkins and Jordan  $\beta$  Values\*

$R^3V$ ↓ → $R/r$	30	40	50	60
0.50	0.9402	0.9687	0.9876	0.9984
1.00	0.8734	0.9047	0.9290	0.9438
2.00	0.8098	0.8539	0.8798	0.9016
3.00	0.7716	0.8200	0.8520	0.8770
3.50	0.7542	0.8057	0.8404	0.8668

\*From W. D. Harkins and H. F. Jordan, *J. Am. Chem. Soc.* 52, 1751, 1930; H. L. Cuoppes, *J. Phys. Chem.* 51, 1341, 1947.

values into Table VIII-C of Harkins and Jordan<sup>8</sup> and by interpolation, one obtains  $\beta = 0.9471$  ( $18^\circ\text{C}$ ).

Finally, using equation (14-14), the surface tension for water at  $18^\circ\text{C}$  is obtained:

$$\gamma = \frac{M \times g}{4\pi R} \times \beta = \frac{(0.7866 \text{ g})(980.665 \text{ cm/sec}^2)}{4\pi(0.3078 \text{ cm})} \times 0.9471$$

$$= 71.97 \text{ dyne/cm or } 71.97 \text{ erg/cm}^2$$

Without the correction factor,  $\beta$ ,  $\gamma$  is calculated here to be 75.99. The values of  $\gamma$  for water at  $18^\circ\text{C}$  are recorded in handbooks as approximately 73.05 dyne/cm. The error relative to the published value at  $18^\circ\text{C}$  is  $\frac{73.05 - 71.97}{73.05} \times 100 = 1.48\%$ .

The correction factor  $\beta$  may be calculated from an equation rather than obtaining it from tabulated values of  $R/r$  and  $R^3/V$  as done in *Example 14-4*. Zuidema and Waters<sup>9</sup> suggested an equation to calculate  $\beta$ , as discussed by Shaw:<sup>10</sup>

$$(\beta - a)^2 = \frac{4b}{\pi^2} \cdot \frac{1}{R^2} \cdot \frac{M \times g}{4\pi R (\rho_1 - \rho_2)} + c \quad (14-15)$$

*Example 14-6.* Use equation (14-15) to calculate  $\beta$ , the surface tension correction at  $20^\circ\text{C}$  where  $a = 0.7250$ ,  $b = 0.09075 \text{ m}^{-1}\text{s}^2$  for all tensiometer rings, and  $c = 0.04534 - 1.679^\circ\text{r}/R$ .  $R$  is the radius of the ring in meters,  $r$  is the radius of the wire from which the ring is constructed,  $M$  is the mass in kg of the liquid lifted above the liquid surface as the ring breaks away from the surface,  $g$  is the acceleration due to gravity in meters  $\cdot \text{sec}^{-2}$ ,  $\rho_1$  is the density of the liquid in kg meter $^{-3}$ , and  $\rho_2$  is the density of the air saturated with the liquid; that is, the upper phase of an interfacial system. With the following data, which must be expressed in SI units for use in equation (14-15),  $\beta$  is calculated and used in equation (14-14) to obtain the corrected surface tension. The terms of equation (14-15) in SI units are  $R = 0.012185$  meter,  $r = 0.0002008$  meter,  $M = 0.0012196$  kg,  $g = 9.80665 \text{ ms}^{-2}$ ,  $\rho_1 = 998.207 \text{ kg/m}^3$ , and  $\rho_2 = 1.2047 \text{ kg/m}^3$ . Finally,  $c = 0.04534 - 1.6790 \text{ r}/R = 0.017671$ .

Substituting into equation (15) we have

$$(\beta - a)^2 = \frac{4(0.09075 \text{ m}^{-1}\text{s}^2)}{9.869604} \cdot \frac{1}{(0.0012196 \text{ kg})(9.80665 \text{ ms}^{-2})}$$

$$+ \frac{0.04534 - (1.6790)(0.0002008 \text{ m})/0.012185 \text{ m}}{4(3.14159)(0.012185 \text{ m})(998.207 - 1.2047 \text{ kg/m}^3)}$$

$$(\beta - a)^2 = 0.0194077 + 0.0176713 = 0.0370790$$

$$\beta - 0.7250 = (0.0370790)^{1/2} = 0.192559$$

$$\beta = 0.7250 + 0.192559 = 0.918 \text{ (dimensionless) at } 20^\circ\text{C}$$

The literature value of  $\gamma$  for water at  $20^\circ\text{C}$  is 72.8 dyne/cm (or erg/cm $^2$ ) in cgs units. Using the uncorrected equation  $\gamma = M \times g/(4\pi R)$  and in SI units, we obtain for water at  $20^\circ\text{C}$

$$\gamma = \frac{0.0012196 \text{ kg} \times 9.80665 \text{ ms}^{-2}}{4 \times \pi \times 0.012185 \text{ m}} = 0.078109 \text{ kg s}^{-2}.$$

Multiplying numerator and denominator by meter $^2$  yields the result  $0.07811 \text{ Jm}^{-2}$ , and expressing the value in  $\text{mJ/m}^2$  we have  $78.11 \text{ mJ/m}^2$ . This is a useful way to express surface tension in SI units, for the value  $78.11$  is numerically the same as that in the cgs system; namely,  $78.11 \text{ erg/cm}^2$  (see *Example 14-3*). To correct the value,  $\gamma = M \times g/(4\pi R)$ , expressed either in cgs or SI units, we multiply by the Harkins and Jordan or the Zuidema and Waters value for  $\beta$  at a given liquid density and temperature,  $M$  value, and ring dimensions.

For the particular case in this example,

$$\gamma = \frac{M \times g}{4\pi R} \times \beta = 78.11 \text{ erg/cm}^2 \text{ (or } \text{mJ/m}^2) \times 0.918$$

$$= 71.7 \text{ erg/cm}^2$$

The error in the Zuidema and Waters value of  $71.7 \text{ mJ/m}^2$  relative to the literature value,  $72.8 \text{ mJ/m}^2$  at  $20^\circ\text{C}$ , is  $\frac{72.8 - 71.7}{72.8} \times 100 = 1.51\%$ .

**Spreading Coefficient.** When a substance such as oleic acid is placed on the surface of water, it will spread as a film if the force of adhesion between the oleic acid molecules and the water molecules is greater than the cohesive forces between the oleic acid molecules themselves. The term *film* used here applies to a *duplex film*, as opposed to a monomolecular film. Duplex films are sufficiently thick (100 Å or more) so that the surface (boundary between oleic acid and air) and interface (boundary between water and oleic acid) are independent of one another.

The *work of adhesion*, which is the energy required to break the attraction between the unlike molecules, is obtained by reference to Figure 14-8. Here in (a) we see a hypothetical cylinder (cross-section area,  $1 \text{ cm}^2$ ) of the sublayer liquid  $S$  overlaid with a similar section of the spreading liquid  $L$ .

By equation (14-2), surface or interfacial work is equal to surface tension multiplied by the area increment. The work required to separate the two sections of liquid in Figure 14-8, each with a cross-sectional area of  $1 \text{ cm}^2$ , is therefore numerically related to the surface or interfacial tension involved, the area increment being unity:

$$\text{Work} = \text{Surface tension} \times \text{unit area change}$$

Accordingly, it is seen in Figure 14-8b that the work done is equal to the newly created surface tensions,  $\gamma_L$  and  $\gamma_S$  minus the interfacial tension  $\gamma_{LS}$  that has been

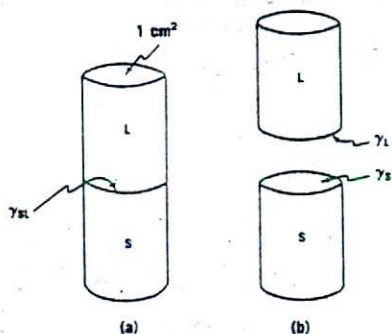


Fig. 14-8. Representation of the work of adhesion involved in separating a substrate and an overlying liquid.

destroyed in the process. The work of adhesion is thus

$$W_a = \gamma_L + \gamma_S - \gamma_{LS} \quad (14-16)$$

The work of cohesion, required to separate the molecules of the spreading liquid so that it can flow over the sublayer, is obtained by reference to Figure 14-9. Obviously, no interfacial tension exists between the like molecules of the liquid, and when the hypothetical 1 cm<sup>2</sup> cylinder in (a) is divided, two new surfaces are created in (b), each with a surface tension of  $\gamma_L$ . Therefore the work of cohesion is

$$W_c = 2\gamma_L \quad (14-17)$$

With reference to the spreading of an oil on a water surface, spreading occurs if the work of adhesion (a measure of the force of attraction between the oil and water) is greater than the work of cohesion. The term ( $W_a - W_c$ ) is known as the spreading coefficient ( $S$ ); if positive, the oil will spread over a water surface. Equations (14-16) and (14-17) may be written

$$S = W_a - W_c = (\gamma_L + \gamma_S - \gamma_{LS}) - 2\gamma_L \quad (14-18)$$

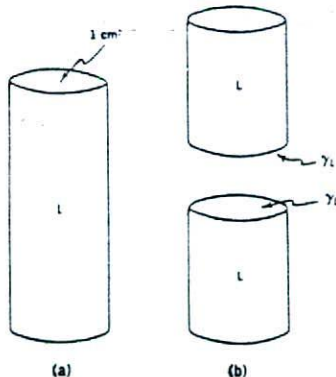


Fig. 14-9. Representation of the work of cohesion involved in separating like molecules in a liquid.

in which  $\gamma_S$  is the surface tension of the sublayer liquid,  $\gamma_L$  is the surface tension of the spreading liquid, and  $\gamma_{LS}$  is the interfacial tension between the two liquids. Rearranging equation (14-18) gives

$$S = \gamma_S - \gamma_L - \gamma_{LS} \quad (14-19)$$

or

$$S = \gamma_S - (\gamma_L + \gamma_{LS}) \quad (14-20)$$

Figure 14-10 shows a lens of material placed on a liquid surface (e.g., oleic acid on water). From equation (14-20), one sees that spreading occurs ( $S$  is positive) when the surface tension of the sublayer liquid is greater than the sum of the surface tension of the spreading liquid and the interfacial tension between the sublayer and the spreading liquid. If  $(\gamma_L + \gamma_{LS})$  is larger than  $\gamma_S$ , the substance forms globules or a floating lens and fails to spread over the surface. An example of such a case is mineral oil on water.

Spreading may also be thought of in terms of surface free energy. Thus, the added substance will spread if, by so doing, the surface free energy of the system is reduced. Put another way, if the surface free energy of the new surface and the new interface is less than the free energy of the old surface, spreading will take place.

Up to this point, the discussion has been restricted to initial spreading. Before equilibrium is reached, however, the water surface becomes saturated with the spreading material, which in turn becomes saturated with water. If we use a prime (') to denote the values following equilibration (i.e., final rather than initial values), then the new surface tensions are  $\gamma'_S$  and  $\gamma'_L$ . When mutual saturation has taken place, the spreading coefficient may be reduced or may even become negative. This means that although initial spreading of the material may occur on the liquid substrate, it can be followed by coalescence of the excess material into a lens if  $S'$  becomes negative in value. This reversal of spreading takes place when  $\gamma'_S$  becomes less than  $(\gamma'_{LS} + \gamma'_L)$ . Note that the value of  $\gamma'_{LS}$  does not change since the interfacial tension is determined under conditions of mutual saturation.

**Example 14-7.** If the surface tension of water  $\gamma_S$  is 72.8 dynes/cm at 20° C, the surface tension of benzene  $\gamma_L$  is 28.9, and the interfacial tension between benzene and water  $\gamma_{LS}$  is 35.0, what is the initial

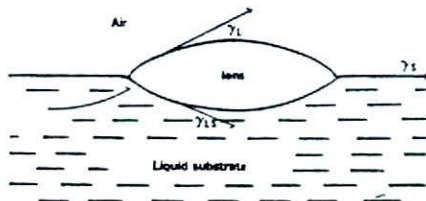


Fig. 14-10. Forces existing at the surfaces of a lens floating in a substrate liquid.



spreading coefficient? Following equilibration,  $\gamma_s$  is 62.2 dynes/cm and  $\gamma_L$  is 28.8. What is the final spreading coefficient?

$$S = 72.8 - (28.9 + 35.0) = 8.9 \text{ dynes/cm (or 8.9 ergs/cm}^2\text{)}$$

$$S' = 62.2 - (28.8 + 35.0) = -1.6 \text{ dynes/cm}$$

Therefore, while benzene spreads initially on water, at equilibrium there is formed a saturated monolayer with the excess benzene (saturated with water) forming a lens.

In the case of organic liquids spread on water, it is found that while the initial spreading coefficient may be positive or negative, the final spreading coefficient always has a negative value. Duplex films of this type are unstable and form monolayers with the excess material remaining as a lens on the surface. The initial spreading coefficients of some organic liquids on water at 20° C are listed in Table 14-4.

It is important to consider the types of molecular structures that lead to high spreading coefficients. An oil spreads over water because it contains polar groups such as COOH or OH. Hence, propionic acid and ethyl alcohol should have high values of  $S$ , as seen in Table 14-4. As the carbon chain of an acid, oleic acid for example, increases, the ratio of polar-nonpolar character decreases and the spreading coefficient on water decreases. Many nonpolar substances such as liquid petrolatum ( $S = -13.4$ ) fail to spread on water. Benzene spreads on water not because it is polar but because the cohesive forces between its molecules are much weaker than the adhesion for water.

The applications of spreading coefficients in pharmacy should be fairly evident. The surface of the skin is bathed in an aqueous-oily layer having a polar-nonpolar character similar to that of a mixture of fatty acids. For a lotion with a mineral oil base to spread freely and evenly on the skin, its polarity and hence its spreading coefficient should be increased by the addition of a surfactant. The relation between spreading, HLB (*hydrophile-lipophile balance*), and emulsion stability has been studied.<sup>11</sup> Surfactant blends of varying HLBs were added to an oil, a drop of which was then placed on water. The HLB of the surfactant blend that caused the

oil drop to spread was related to the required HLB of the oil when used in emulsification. See pages 371 and 373 for a discussion of HLB.

## ADSORPTION AT LIQUID INTERFACES

Surface free energy was defined previously as the work that must be done to increase the surface by unit area. As a result of such expansion, more molecules must be brought from the bulk to the interface. The more work that has to be expended to achieve this, the greater the surface free energy.

Certain molecules and ions, when dispersed in the liquid, move of their own accord to the interface. Their concentration at the interface then exceeds their concentration in the bulk of the liquid. Obviously, the surface free energy and the surface tension of the system is automatically reduced. Such a phenomenon, where the added molecules are partitioned in favor of the interface, is termed *adsorption*, or more correctly, *positive adsorption*. Other materials (e.g., inorganic electrolytes) are partitioned in favor of the bulk, leading to *negative adsorption* and a corresponding increase in surface free energy and surface tension. Adsorption, as will be seen later, can also occur at solid interfaces. Adsorption should not be confused with *absorption*. The former is solely a surface effect, whereas in absorption, the liquid or gas being absorbed penetrates into the capillary spaces of the absorbing medium. The taking up of water by a sponge is absorption; the concentrating of alkaloid molecules on the surface of clay is adsorption.

**Surface-Active Agents.** Molecules and ions that are adsorbed at interfaces are termed *surface-active agents*, or *surfactants*. An alternative expression is *amphiphile*, which suggests that the molecule or ion has a certain affinity for both polar and nonpolar solvents. Depending on the number and nature of the polar and nonpolar groups present, the amphiphile may be predominantly *hydrophilic* (water-loving), *lipophilic* (oil-loving), or reasonably well balanced between these two extremes. For example, straight-chain alcohols, amines, and acids are amphiphiles that change from being predominantly hydrophilic to lipophilic as the number of carbon atoms in the alkyl chain is increased. Thus, ethyl alcohol is miscible with water in all proportions. In comparison, the aqueous solubility of amyl alcohol,  $C_5H_{11}OH$ , is much reduced, while cetyl alcohol,  $C_{16}H_{33}OH$ , may be said to be strongly lipophilic and insoluble in water.

It is the amphiphilic nature of surface-active agents that causes them to be adsorbed at interfaces, whether these be liquid-gas or liquid-liquid. Thus, in an aqueous dispersion of amyl alcohol, the polar alcoholic group is able to associate with the water molecules. The nonpolar portion is rejected, however, because the adhesive forces it can develop with water are small in

TABLE 14-4. Initial Spreading Coefficients,  $S$ , at 20° C\*

Substance	$S$ (dynes/cm)
Ethyl alcohol	50.4
Propionic acid	45.8
Ethyl ether	45.5
Acetic acid	45.2
Acetone	42.4
Undecylenic acid	32 (25°)
Oleic acid	24.6
Chloroform	13
Benzene	8.9
Hexane	3.4
Octane	0.22
Ethylene dibromide	-3.19
Liquid petrolatum	-13.4

\*From W. D. Harkins, *The Physical Chemistry of Surface Films*, Reinhold, New York, 1952, pp. 44, 45.

comparison to the cohesive forces between adjacent water molecules. As a result, the amphiphile is adsorbed at the interface. The situation for a fatty acid at the air-water and oil-water interface is shown in Figure 14-11. At the air-water interface, the lipophilic chains are directed upward into the air; at the oil-water interface, they are associated with the oil phase. In order for the amphiphile to be concentrated at the interface, it must be balanced with the proper amount of water- and oil-soluble groups. If the molecule is too hydrophilic, it remains within the body of the aqueous phase and exerts no effect at the interface. Likewise, if it is too lipophilic, it dissolves completely in the oil phase and little appears at the interface.

**Systems of Hydrophile-Lipophile Classification.** Griffin<sup>12</sup> devised an arbitrary scale of values to serve as a measure of the hydrophilic-lipophile balance (HLB) of surface-active agents. By means of this number system, it is possible to establish an HLB range of optimum efficiency for each class of surfactant, as seen in Figure 14-12. The higher the HLB of an agent, the more hydrophilic it is. The Spans, sorbitan esters manufactured by ICI Americas Inc., are lipophilic and have low HLB values (1.8 to 8.6); the Tweens, polyoxyethylene derivatives of the Spans, are hydrophilic and have high HLB values (9.6 to 16.7).

The HLB of a nonionic surfactant whose only hydro-

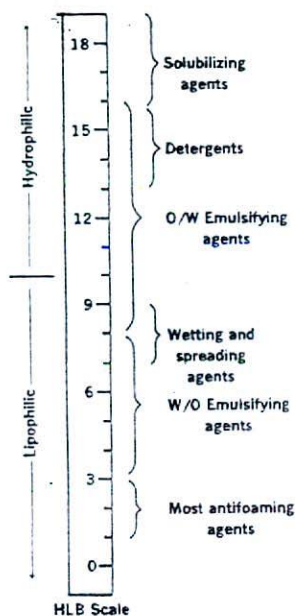


Fig. 14-12. A scale showing surfactant function on the basis of HLB values.

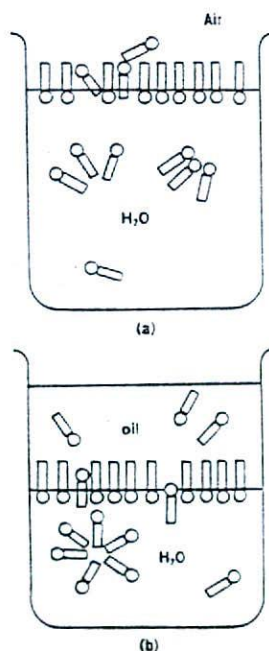


Fig. 14-11. Adsorption of fatty acid molecules (a) at a water-air interface and (b) at a water-oil interface.

philic portion is polyoxyethylene is calculated using the formula

$$\text{HLB} = E/5 \quad (14-21)$$

in which  $E$  is the percent by weight of ethylene oxide. A number of polyhydric alcohol fatty acid esters, such as glyceryl monostearate, may be estimated by using the formula

$$\text{HLB} = 20 \left( 1 - \frac{S}{A} \right) \quad (14-22)$$

in which  $S$  is the saponification number of the ester and  $A$  the acid number of the fatty acid. The HLB of polyoxyethylene sorbitan monolaurate (Tween 20), for which  $S = 45.5$  and  $A = 276$ , is

$$\text{HLB} = 20 \left( 1 - \frac{45.5}{276} \right) = 16.7$$

The HLB values of some commonly used amphiphilic agents are given in Table 14-5.

The oil phase of an oil-in-water (O/W) emulsion requires a specific HLB, called the *required hydrophile-lipophile balance*, RHLB. A different RHLB is required to form a water-in-oil (W/O) emulsion from the same oil phase. The RHLB values for both O/W and W/O emulsions have been determined empirically for a number of oils and oil-like substances, some of which are listed in Table 14-6.

TABLE 14-5. HLB Values of Some Amphiphilic Agents

Substance	HLB
Oleic acid	1
Polyoxyethylene sorbitol beeswax derivative (G-1706)	2.0
Sorbitan tristearate	2.1
Glyceryl monostearate	3.8
Sorbitan mono-oleate (Span 80)	4.3
Diethylene glycol monostearate	4.7
Glyceryl monostearate, self-emulsifying (Tegin)	5.5
Diethylene glycol monolaurate	6.1
Sorbitan monolaurate (Span 20)	3.6
Polyethylene lauryl ether (Brij 30)	9.5
Gelatin (Pharmagel B)	9.8
Methyl cellulose (Methocel 15 cps)	10.5
Polyoxyethylene lauryl ether (G-3705)	10.8
Polyoxyethylene monostearate (Myrj 45)	11.1
Triethanolamine oleate	12.0
Polyoxyethylene alkyl pnenol (Igepal Ca-630)	12.8
Polyethylene glycol 400 monolaurate	13.1
Polyoxyethylene sorbitan mono-oleate (Tween 80)	15.0
Polyoxyethylene sorbitan monolaurate (Tween 20)	16.7
Polyoxyethylene lauryl ether (Brij 35)	16.9
Sodium oleate	18.0
Potassium oleate	20
Sodium lauryl sulfate	40

Example 14-8. For the oil-in-water emulsion:

Ingredient	Amount	RHLB (O/W)
1. Beeswax	15 g	9
2. Lanolin	10 g	12
3. Paraffin wax	20 g	10
4. Cetyl alcohol	5 g	15
5. Emulsifier	2 g	
6. Preservative	0.2 g	
7. Color	as required	
8. Water, purified q.s.	100 g	

One first calculates the overall RHLB of the emulsion by multiplying the RHLB of each oil-like component (items 1 through 4) by the weight fraction that each oil-like component contributes to the oil phase. The total weight of the oil phase is 50 g. Therefore,

Beeswax	$15/50 \times 9 = 2.70$
Lanolin	$10/50 \times 12 = 2.40$
Paraffin	$20/50 \times 10 = 4.00$
Cetyl alcohol	$5/50 \times 15 = 1.50$
Total RHLB for the emulsion	$= 10.60$

Next, a blend of two emulsifying agents is chosen, one with an HLB above and the other with an HLB below the required HLB of the emulsion (RHLB = 10.6 in this example). From Table 14-5, we choose Tween 80 with an HLB of 15 and Span 80 with an HLB of 4.3.

The formula to calculate the weight percentage of Tween 80 (surfactant with the higher HLB) is

$$\% \text{ Tween 80} = \frac{\text{RHLB} - \text{HLB low}}{\text{HLB high} - \text{HLB low}} \quad (14-23)$$

where HLB high is for the higher value, 15, and HLB low is for the lower value, 4.3.

$$\% \text{ Tween 80} = \frac{10.6 - 4.3}{15.0 - 4.3} = 0.59$$

Two grams of emulsifier has been estimated as proper protection for the O/W emulsion. Therefore,  $2.0 \text{ g} \times 0.59 = 1.18$  grams of Tween 80 is needed and the remainder, 0.82 gram, must be supplied by Span 80 for the 100-gram emulsion.

TABLE 14-6. Required HLB for Some Oil Phase Ingredients, for Both O/W and W/O Emulsions\*

	O/W	W/O
Cottonseed oil	6-7	—
Petrolatum	8	—
Beeswax	9-11	5
Paraffin wax	10	4
Mineral oil	10-12	5-6
Methyl silicone	11	—
Lanolin, anhydrous	12-14	8
Carnauba wax	12-14	—
Lauryl alcohol	14	—
Castor oil	14	—
Kerosene	12-14	—
Cetyl alcohol	13-16	—
Stearyl alcohol	15-16	—
Carbon tetrachloride	16	—
Lauroic acid	16	—
Oleic acid	17	—
Stearic acid	17	—

\*From Atlas HLB System, ICI Americas; P. Becher, *Emulsions, Theory and Practice*, 2nd Edition, Reinhold, New York, 1966, p. 249.

The choice of the mixture of emulsifiers and the total amount of the emulsifier phase is left to the formulator, who determines these unknowns over time by preparation and observation of the several formulas chosen.

A mathematical formula for determining the minimum amount of surfactant mixture has been suggested by Bonadeo:<sup>13</sup>

$$Q_2 = \frac{6(\rho_s/\rho)}{10 - 0.5 \text{ RHLB}} + 4Q/1000 \quad (14-24)$$

where  $\rho_s$  is the density of the surfactant mixture,  $\rho$  is the density of the dispersed (internal) phase, and  $Q$  is the percent of the dispersant (continuous phase) of the emulsion. The required HLB, written RHLB, is the HLB of the oil phase needed to form an O/W or W/O emulsion.

Example 14-9. We wish to formulate two products, (a) a W/O and (b) an O/W emulsion containing 40 g of a mixed oil phase and 60 g of water.

(a) The oil phase consists of 70% paraffin and 30% beeswax. The density of the oil phase is  $0.85 \text{ g/cm}^3$  and the density of the aqueous phase is about  $1 \text{ g/cm}^3$  at room temperature. The density of the mixture of surfactants for the W/O emulsion is  $0.87 \text{ g/cm}^3$ . The required HLB values of paraffin and of beeswax for a W/O emulsion are 4.0 and 5.0, respectively.

The amount  $Q_2$  in grams of a mixture of sorbitan tristearate (HLB = 2.1) and diethylene glycol monostearate (HLB = 4.7) to obtain a water-in-oil emulsion is obtained by the use of equation (14-24), first calculating the RHLB of the oil phase:

$$\text{RHLB} = (4 \times 0.70) + (5 \times 0.30) = 4.3$$

$$Q_2 = \frac{6(0.87/1)}{10 - (0.5 \times 4.3)} + \frac{4 \times 40}{1000} = 0.82 \text{ g}$$

Note that for a W/O emulsion we used the density of the internal phase,  $\rho_{\text{water}} = 1$ , and the percent of dispersant, oil = 40%.

(b) The RHLB of the oil phase, 70% paraffin and 30% beeswax, for an O/W emulsion is

$$\text{RHLB} = (0.70 \times 10) + (0.3 \times 9) = 9.7$$

and the total amount of surfactant mixture is

$$Q_o + \frac{6(1.05/0.85)}{10 - (0.5 \times 9.7)} + \frac{4 \times 60}{1000} = 1.63 \text{ g}$$

For an O/W emulsion, we used the density  $\rho$  of the oil as the internal phase and the percent of dispersant as the aqueous phase.

For the amount of surfactant mixture in the W/O emulsion we can raise the value  $Q$ , roughly to 1.0 g and for the O/W emulsion to about 2.0 g. We can then calculate the weights of the two emulsifying agents for each emulsion, using the equation

$$\frac{\% \text{ surfactant of higher HLB}}{\% \text{ surfactant of lower HLB}} = \frac{\text{RHLB} - \text{HLB low}}{\text{HLB high} - \text{HLB low}} \quad (14-25)$$

For the W/O emulsion, the percent by weight of diethylene glycol monostearate (HLB = 4.7) combined with sorbitan tristearate (HLB = 2.1) is

$$\frac{\% \text{ diethylene glycol monostearate}}{\% \text{ sorbitan tristearate}} = \frac{4.3 - 2.1}{4.7 - 2.1} = 0.85 \text{ g or } 85\% \text{ of } 1 \text{ gram}$$

The fraction or percentage of sorbitan monostearate is therefore 0.15 g or 15% of the 1 gram of mixed emulsifier.

For the O/W emulsion the percent by weight of Tween 80 (HLB = 15) combined with diethylene glycol monolaurate (HLB = 6.1) is

$$\% \text{ Tween } 80 = \frac{9.7 - 6.1}{15 - 6.1} = 0.40 \text{ or } 40\%$$

The fraction or percentage of diethylene glycol monolaurate is therefore 0.60 or 60%. And 0.40 or 40% of a 2-gram mixture of emulsifier phase = 0.8 gram of Tween 80. The remainder, 1.2 grams, is the amount of diethylene glycol monolaurate in the 2-gram emulsifier phase.

Other scales of hydrophile-lipophile balance have been developed, although none of these have gained the acceptance afforded the HLB system of Griffin. A titration method, as well as other techniques, for determining the hydrophile-lipophile character of surfactants, have been proposed.<sup>14</sup>

**Types of Monolayer at Liquid Surfaces.** For convenience of discussion, adsorbed materials are divided into two groups: those that form "soluble" monolayers and those that form "insoluble" films. The distinction is made on the basis of the solubility of the adsorbate in the liquid subphase. Thus, amyl alcohol may be said to form a soluble monolayer on water, while cetyl alcohol would form an insoluble film on the same sublayer. It must be emphasized that this is really only an arbitrary distinction, for the insoluble films are, in effect, the limiting case of those compounds that form soluble monolayers at liquid interfaces. There are, however, important practical reasons why such a classification is made.

It will become apparent to the student in the following sections that three interrelated parameters are important in studying liquid interfaces. These are (1) surface tension,  $\gamma$ ; (2) surface excess,  $\Gamma$ , which is the amount of amphiphile per unit area of surface in excess of that in the bulk of the liquid; and (3)  $c$ , the concentration of amphiphile in the bulk of the liquid. As we shall see, it is relatively easy with soluble monolayers to measure surface tension and  $c$  and from these data to compute the surface excess. With insoluble monolayers,  $c$  is taken to be zero, while surface tension and surface excess can be obtained directly. Materials that lie on the borderline between soluble and insoluble systems

can be studied by either approach and, invariably, similar results are obtained.

Data obtained from such studies are of increasing biologic and pharmaceutical interest. For example, emulsions are stabilized by the presence of an interfacial film between the oil and water phases. A knowledge of the area occupied by each amphiphilic molecule at the interface is important in achieving optimum stability of the emulsion. The efficiency of wetting and detergent processes depends on the concentration of material adsorbed. Monolayers of adsorbed amphiphiles may be used as *in vitro* models for biologic membranes that are thought to consist of two monolayers placed back-to-back with the hydrocarbon chains intermeshed. Consequently, these model systems are finding increasing application for *in vitro* studies of drug absorption across biologic membranes. Studies of interfacial adsorption also provide valuable information on the dimensions of molecules, since it is possible to calculate the areas occupied by amphiphilic molecules.

**Soluble Monolayers and the Gibbs Adsorption Equation.** The addition of amphiphiles to a liquid system leads to a reduction in surface tension owing to these molecules or ions being adsorbed as a monolayer. Adsorption of amphiphiles in these binary systems was first expressed quantitatively by Gibbs in 1878 as follows:

$$\Gamma = - \frac{c}{RT} \frac{d\gamma}{dc} \quad (14-26)$$

in which  $\Gamma$  is the surface excess or surface concentration, that is, the amount of the amphiphile per unit area of surface in excess of that in the bulk of the liquid,  $c$  is the concentration of amphiphile in the liquid bulk,  $R$  is the gas constant,  $T$  is the absolute temperature, and  $d\gamma/dc$  is the change in surface tension of the solution with change of bulk concentration of the substance. The derivation of equation (14-26) is given in the following paragraphs.

Recall (equation (3-70), p. 67) that the free energy change of a bulk phase containing two components is written

$$dG = -S dT + V dp + \mu_1 dn_1 + \mu_2 dn_2$$

Two immiscible bulk phases may be considered to be separated by an interface or "surface phase" in which the contribution to the volume is ignored, and a new energy term  $\gamma dA$  (see equation (14-2)) is introduced to account for the work involved in altering the surface area  $A$ . The surface tension  $\gamma$  is the work done at a constant temperature and pressure per unit increase of surface area. The new work done on the surface phase is equal to the surface free energy increase,  $dG^s$ . Therefore, we can write

$$dG^s = -S^s dT + \gamma dA + \mu_1^s dn_1^s + \mu_2^s dn_2^s \quad (14-27)$$

At equilibrium, the free energy of the entire system is zero under the conditions of constant temperature, pressure, and surface area. Since no matter passes in or

out of the system as a whole, the chemical potential of a component  $i$  is the same in the two bulk phases as it is in the surface phase  $s$ :

$$\mu_{i\alpha} = \mu_{i\beta} = \mu_{is} \quad (14-28)$$

Such a system consisting of two immiscible liquids, water  $\alpha$  and oleic acid  $\beta$ , separated by the surface phase  $s$  is shown in Figure 14-13a. Equation (14-27) may be integrated at constant temperature and composition to give the surface free energy,

$$G^s = \gamma A + n_1^s \mu_1^s + n_2^s \mu_2^s \quad (14-29)$$

Since the surface free energy depends only on the state of the system,  $dG^s$  is an exact differential and may be obtained by general differentiation of (14-29) under the condition of variable composition.

$$dG^s = \gamma dA + A d\gamma + n_1^s d\mu_1^s + n_2^s d\mu_2^s + \mu_1^s dn_1^s + \mu_2^s dn_2^s \quad (14-30)$$

Comparing this result with equation (14-27) shows that

$$A d\gamma + S^s dT + n_1^s d\mu_1^s + n_2^s d\mu_2^s = 0 \quad (14-31)$$

and at constant temperature

$$A d\gamma + n_1^s d\mu_1^s + n_2^s d\mu_2^s = 0 \quad (14-32)$$

When equation (14-32) is divided through by the surface area  $A$ , and  $n_1^s/A$  and  $n_2^s/A$  are given the symbols  $\Gamma_1$  and  $\Gamma_2$ , respectively,

$$d\gamma + \Gamma_1 d\mu_1^s + \Gamma_2 d\mu_2^s = 0 \quad (14-33)$$

As expressed by equation (14-33), the chemical potentials of the components in the surface are equal to those in the bulk phases provided that the system is in equilibrium at constant temperature, pressure, and surface area.

Now consider a single-phase solution of oleic acid (solute or component 2) in water (solvent or component 1) as shown in Figure 14-13b. Under these circumstances, it is possible to drop the superscripts on the chemical potentials and write

$$d\gamma + \Gamma_1 d\mu_1 + \Gamma_2 d\mu_2 = 0 \quad (14-34)$$

in which  $\Gamma_1$  and  $\Gamma_2$  are the number of moles of the components per unit area in the surface and  $\mu_1$  and  $\mu_2$  are the chemical potentials of the two components in the solution.

It is possible to make an arbitrary choice of the surface, and we do so in a manner that makes  $\Gamma_1$  equal to zero, that is, we arrange the boundary so that none of the solvent is present in the surface (cf. Fig. 14-13b). Then equation (14-34) becomes

$$d\gamma + \Gamma_2 d\mu_2 = 0 \quad (14-35)$$

and

$$\Gamma_2 = - \left( \frac{\partial \gamma}{\partial \mu_2} \right)_T \quad (14-36)$$

The chemical potential of the solute can be expressed in terms of the activity using the equation

$$\mu_2 = \mu_2^s + RT \ln a_2$$

and by differentiating at constant temperature, one obtains

$$d\mu_2 = RT d \ln a_2 \quad (14-37)$$

Substituting this value in equation (14-36) produces the result

$$\Gamma_2 = - \frac{1}{RT} \left( \frac{\partial \gamma}{\partial \ln a_2} \right)_T \quad (14-38)$$

From differential calculus, if  $y = \ln a_2$ , then  $d \ln a_2 = da_2/a_2$ . Substituting this result in equation (14-38), results in the *Gibbs adsorption equation*,

$$\Gamma_2 = - \frac{a_2}{RT} \left( \frac{\partial \gamma}{\partial a_2} \right)_T \quad (14-39)$$

This is equation (14-26), which was given on page 373 in terms of concentration  $c$  instead of activity. If the solution is dilute,  $a_2$  may be replaced by  $c$  without introducing a significant error.

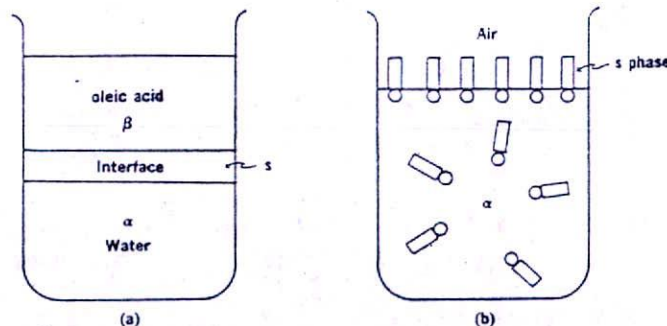


Fig. 14-13. A system consisting of oleic acid and water. (a) Graphic description of the two bulk phases,  $\alpha$  and  $\beta$ , and the interface  $s$ . (b) Condition under which only the  $\alpha$  phase and the surface or  $s$  phase need be considered.

When the surface tension  $\gamma$  of a surfactant is plotted against the logarithm of the surfactant activity or concentration,  $\log c_2$ , the plot takes on the shape shown in Figure 14-14. The initial curved segment A-B is followed by a linear segment, B-D, along which there is a sharp decrease in surface tension as  $\log c_2$  increases. The point D corresponds to the critical micelle concentration, cmc, the concentration at which micelles form in the solution (p. 396). Beyond the cmc the line becomes horizontal, further additions of surfactant no longer being accompanied by a decrease in surface tension. Along the linear segment B-D, the surface excess  $\Gamma$  is constant because from equation (14-33), replacing activity with concentration,

$$\Gamma_2 = -\frac{1}{RT} \left( \frac{\partial \gamma}{\partial \ln c_2} \right) \quad (14-40)$$

the slope  $\partial\gamma/\partial \ln c_2$  reaches a limiting value and remains constant. Saturation adsorption of the surfactant has been reached at point B; that is,  $\Gamma_2$  does not increase further as the bulk concentration increases. However, the surface tension decreases greatly until point D is reached. Within the segment B-D of the curve the surfactant molecules are closely packed at the surface and the surface area occupied per molecule is constant. Both the surface excess  $\Gamma_2$  and the area per surfactant molecule may be calculated using equation (14-40).

**Example 14-10.** The limiting slope of a plot of  $\gamma$  versus  $\ln c_2$  for a nonionic surfactant,  $C_{12}H_{25}O(CH_2CH_2O)_4H$ ,<sup>15</sup> is  $\partial\gamma/\partial \ln c_2 = -5.2937$  dyne/cm at 23.0° C. Calculate  $\Gamma_2$  and the area per molecule of this surfactant.

From the Gibbs adsorption equation (14-40),

$$\Gamma_2 = - \left( \frac{1}{8.3143 \times 10^7 \text{ erg deg}^{-1} \text{ mole}^{-1} \times 296.15 \text{ K}} \right) (-5.2937 \text{ dyne/cm})$$

$$\Gamma_2 = 2.15 \times 10^{-10} \text{ mole/cm}^2$$

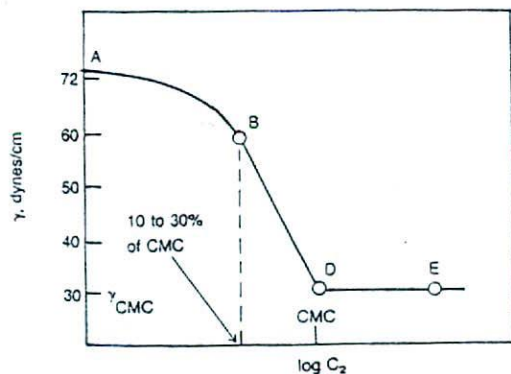


Fig. 14-14. Decrease in the surface tension of water when a straight-chain amphiphile is added. (From H. Schott, *J. Pharm. Sci.* 69, 852, 1980, reproduced with permission of the copyright owner.)

The surface excess,  $2.15 \times 10^{-10}$  mole/cm<sup>2</sup>, is multiplied by  $6.0221 \times 10^{23}$  mole<sup>-1</sup>, Avogadro's number, to obtain molecules/cm<sup>2</sup>. The reciprocal then gives the area per molecule:

$$\text{Area/molecule} = \frac{1}{6.0221 \times 10^{23} \text{ mole}^{-1} \times 2.15 \times 10^{-10} \text{ mole/cm}^2}$$

$$= 7.72 \times 10^{-15} \text{ cm}^2/\text{molecule} = 77 \text{ \AA}^2/\text{molecule}$$

The validity of the Gibbs equation has been verified experimentally. One of the more ingenious methods is due to McBain,<sup>16</sup> who literally fired a small microtome blade across a liquid surface so as to collect the surface layer. Analysis of the liquid scooped up and collected by the speeding blade agreed closely with that predicted by the Gibbs equation. More recently, radioactive techniques using weak beta emitters have been used successfully.<sup>17</sup>

**Insoluble Monolayers and the Film Balance.** Insoluble monolayers have a fascinating history that goes back to before the American Revolution. During a voyage to England in 1757, Benjamin Franklin observed, as had seamen for centuries before him, that when cooking grease was thrown from the ship's galley onto the water, the waves were calmed by the film that formed on the surface of the sea. In 1765, Franklin followed up this observation with an experiment on a half-acre pond in England and found that the application of 1 teaspoonful of oil was just sufficient to cover the pond and calm the waves. In 1899, Lord Rayleigh showed that when small amounts of certain slightly soluble oils were placed on a clean surface of water contained in a trough, they spread to form a layer one molecule thick (monomolecular layer). Prior to Rayleigh's work, a woman named Agnes Pockels, from Lower Saxony, Germany, who had no formal scientific training, developed a "film balance" for studying insoluble monolayers. She carried out a series of experiments, which she summarized in a letter to Lord Rayleigh in January, 1881. In fact, she invented the film balance in 1883, over 30 years before Langmuir, whose name is normally associated with this type of apparatus. These and other early contributions in the area of surface phenomena are described in a series of papers by Giles and Forrester.<sup>18</sup>

Knowing the area of the film and the volume of the spreading liquid, it should be possible to compute the thickness of such films. The film thickness is equal to the length of the molecules standing in a vertical position on the surface when the molecules are packed in closest arrangement. Furthermore, if the molecular weight and the density of the spreading oil are known, the cross-sectional area available to the molecules should be easily computed.

**Example 14-11.** We have noted that Benjamin Franklin placed 1 teaspoonful ( $\approx 5 \text{ cm}^3$ ) of a fatty acid "oil" on a half-acre ( $\approx 2 \times 10^7 \text{ cm}^2$ ) pond. Assume that the acid, having a molecular weight of 300 and a density of  $0.90 \text{ g/cm}^3$ , was just sufficient to form a condensed monomolecular film over the entire surface. What was the length and the cross-sectional area of the fatty acid molecule?

(a) Thickness of oil on the pond = length of the vertically oriented fatty acid molecule.

$$\frac{5 \text{ cm}^3}{2 \times 10^7 \text{ cm}^2} = 25 \times 10^{-8} \text{ cm} = 25 \text{ \AA}$$

(b)

$$5 \text{ cm}^3 \times 0.9 \text{ g/cm}^3 = 4.5 \text{ g}$$

$$\frac{4.5 \text{ g}}{300 \text{ g/mole}} = 0.015 \text{ mole}$$

$$0.015 \text{ mole} \times 6.02 \times 10^{23} \text{ molecules/mole} = 9 \times 10^{21} \text{ molecules}$$

$$\frac{2 \times 10^7 \text{ cm}^2 \text{ pond area}}{9 \times 10^{21} \text{ molecules}} = 22 \times 10^{-16} \text{ cm}^2/\text{molecule}$$

$$= 22 \text{ \AA}^2/\text{molecule}$$

We can readily see from this example that the area of cross section per molecule is given by

$$\text{Cross-sectional area/molecule} = \frac{MS}{V\rho N} \quad (14-41)$$

in which  $M$  is molecular weight of the spreading liquid,  $S$  the surface area covered by the film,  $V$  the volume of the spreading liquid,  $\rho$  its density, and  $N$  Avogadro's number.

Langmuir, Adam, Harkins, and others have made quantitative studies of the properties of films that are spread over a clear surface of the substrate liquid (usually water) contained in a trough. The film can be compressed against a horizontal float by means of a movable barrier. The force exerted on the float is measured by a torsion wire arrangement similar to that employed in the ring tensiometer. The apparatus, called a *film balance*, is shown in Figure 14-15. The compressive force per unit area on the float is known as the *surface* or *film pressure*,  $\pi$ ; it is the difference in surface tension between the pure substrate,  $\gamma_0$ , and that with a film spread on it,  $\gamma$ , and is written

$$\pi = (\gamma_0 - \gamma) \quad (14-42)$$

Surface tension (interfacial tension) is resistance of the surface (interface) to an expansion in area, and film pressure,  $\pi$ , is the lowering of this resistance to expansion, as expressed quantitatively in equation (14-42). Schott<sup>15</sup> states that the film pressure,  $\pi$ , is an expansion pressure exerted on the monolayer that opposes the surface tension,  $\gamma_0$ , or contraction of the clean (water) surface. The surface active molecules of the monolayer are thought to insert themselves into the surface of the water molecules of a film balance to reduce the resistance of the water surface to expansion. The presence of the surfactant molecules increases the ease of expansion, presumably by breaking or interfering with hydrogen bonding, van der Waals interaction, and other cohesive forces among the water molecules. These attractive forces produce the "spring-like" action in the water surface, as measured by the surface tension,  $\gamma_0$ , and the introduction of surfactant molecules into the clean water surface reduces the springiness of

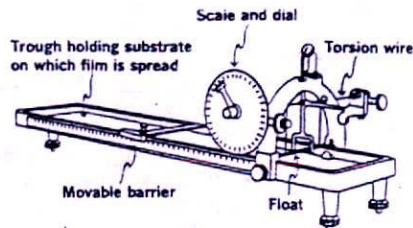


Fig. 14-15. Film balance, Cenco model.

the interacting water molecules and decreases the surface tension  $\gamma_0$  to  $(\gamma_0 - \gamma)$  or  $\pi$  (equation (14-42)).

In carrying out an experiment with the film balance, the substance under study is dissolved in a volatile solvent (e.g., hexane) and is placed on the surface of the substrate, which has previously been swept clean by means of a paraffined or Teflon strip. The liquid spreads as a film, and the volatile solvent is permitted to evaporate. A cross-sectional view of the interface after spreading is shown in Figure 14-16. The movable barrier is then moved to various positions in the direction of the float. The area of the trough available to the film at each position is measured, and the corresponding film pressure is read from the torsion dial. The film pressure is then plotted against the area of the film or, more conveniently, against the cross-sectional area per molecule in  $\text{\AA}^2$  (cf. *Example 14-11* and equation [14-41] for computing the molecule's cross-sectional area from the area of the film). The results for stearic acid and lecithin may be represented as shown in Figure 14-17.

Frequently, a variety of phase changes are observed when an insoluble film is spread at an interface and then compressed. A representation of what can occur with a straight-chain saturated aliphatic compound at the air-water interface is shown in Figure 14-18. When the film is spread over an area greater than 50 to 60  $\text{\AA}^2/\text{molecule}$  (region G), it exerts little pressure on the floating barrier. The film acts like a gas in two dimensions. As the film begins to be compressed (region L<sub>1</sub>-G), a liquid phase L<sub>1</sub> appears that coexists in

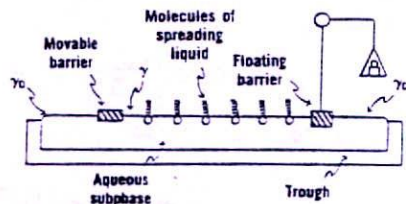


Fig. 14-16. Cross-section view of spreading liquid on the surface of a film balance.

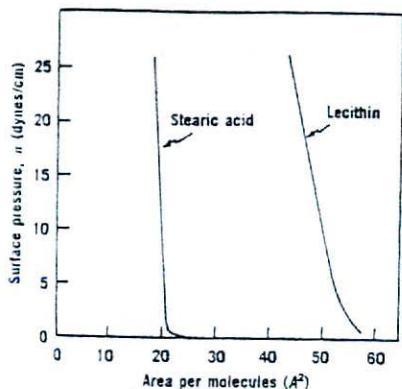


Fig. 14-17. Surface film pressure  $\pi$  for stearic acid and lecithin plotted as a function of cross-sectional area per molecule.

equilibrium with the gas phase. This occurs at a low surface pressure (e.g., 0.2 dyne/cm or less.) The liquid expanded state (region  $L_1$ ) may be thought of as a bulk liquid state, but in two dimensions. Further compression of the film often leads to the appearance of an intermediate phase (region I) and then a less compressible condensed liquid state, region  $L_2$ . This then gives way to the least compressible state (region S), where the film can be regarded as being in a two-dimensional solid state. In these latter stages of film compression,

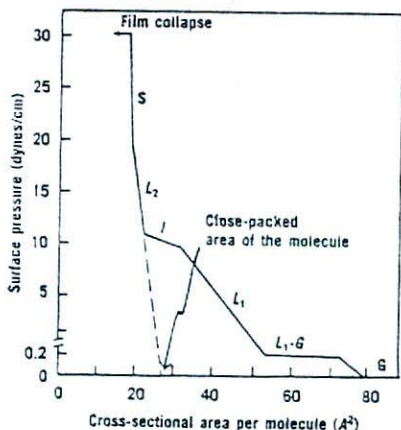


Fig. 14-18. Phase changes that occur when a liquid film is spread at an interface and then compressed. Key: G, two-dimensional gas;  $L_1 - G$ , liquid phase in equilibrium with two-dimensional gas;  $L_1$ , liquid expanded or two-dimensional bulk liquid state; I, intermediate state;  $L_2$ , condensed liquid state; S, two-dimensional solid state. When compressed by a force greater than required to form a solid surface, the film collapses, as shown by the arrow at the top of this figure. (From P. C. Heimenz, *Principles of Colloid and Surface Chemistry*, 2nd Edition, Dekker, NY 1986, p. 364, with permission of the copyright owner.)

the film or surface pressure,  $\pi = \gamma_0 - \gamma_1$  rises rapidly as the curve passes through the regions  $L_2$  and S in Figure 14-18. This increase in  $\pi$  with compression of the surfactant film results from surface active molecules being forcibly inserted and crowded into the surface. This process opposes the natural tendency of the water surface to contract, and the surface tension decreases from  $\gamma_0$  to  $\gamma_1$ . Finally the molecules slip over one another, and the film breaks when it is greatly compressed. The regions marked along the plot in Figure 14-18 can be represented schematically in terms of the positioning of the spreading molecules in the surface, as shown in Figure 14-19. In region G in Figure 14-18 the molecules in the monolayer lie on the surface with great distances between them, as in a three-dimensional gas. In the part of the curve marked  $L_1$  and  $L_2$  (see Fig. 14-18), the molecules are forced closer together, and, as shown schematically in Figure 14-19b, are beginning to stand erect and interact with one another, analogous to a three-dimensional liquid. In region S of Figure 14-18, the spreading molecules are held together by strong forces; and this condition, analogous to the solid state in three-dimensional chemistry, shows little compressibility relative to that of a gas or a liquid. The S state is shown schematically in Figure 14-19c where the molecules on the surface of the film balance are compressed together as far as possible. Further compression of the film (by a movement from right to left on the horizontal axis of the graph in Figure 14-18—that is, a movement from left to right of the movable barrier shown in Fig. 14-15) brings about a collapse of the monolayer film, one part sliding over the other, as depicted in Figure 14-19d.

The cross-sectional area per molecule of the close-packed film at zero surface pressure is obtained by extrapolating the linear portion of the curve to the horizontal axis, as seen in Figure 14-18. The values for some organic molecules, determined in this way by Langmuir,<sup>19</sup> are listed in Table 14-7. It is seen that myricyl alcohol with 30 carbons in the chain has a length almost twice that of the other molecules. Its cross-sectional area at the interface is not markedly different from other single-chain molecules, however, confirming that it is the cross-sectional area of the alkyl chain, rather than the length, that is being measured. Tristearin, with three fatty acid chains, has a cross-sectional area about three times that of the molecules with only one aliphatic chain.

The electrical potential and viscosity of monomolecular films may be studied by means of the film balance, and the molecular weight of high polymers such as proteins can be estimated by its use. The film-balance technique also has considerable significance in the study of biologic systems. Some protein molecules unfold from a spherical configuration into a flat film when spread on the surface of the film trough, and the relationship between unfolding and biologic activity can be studied.



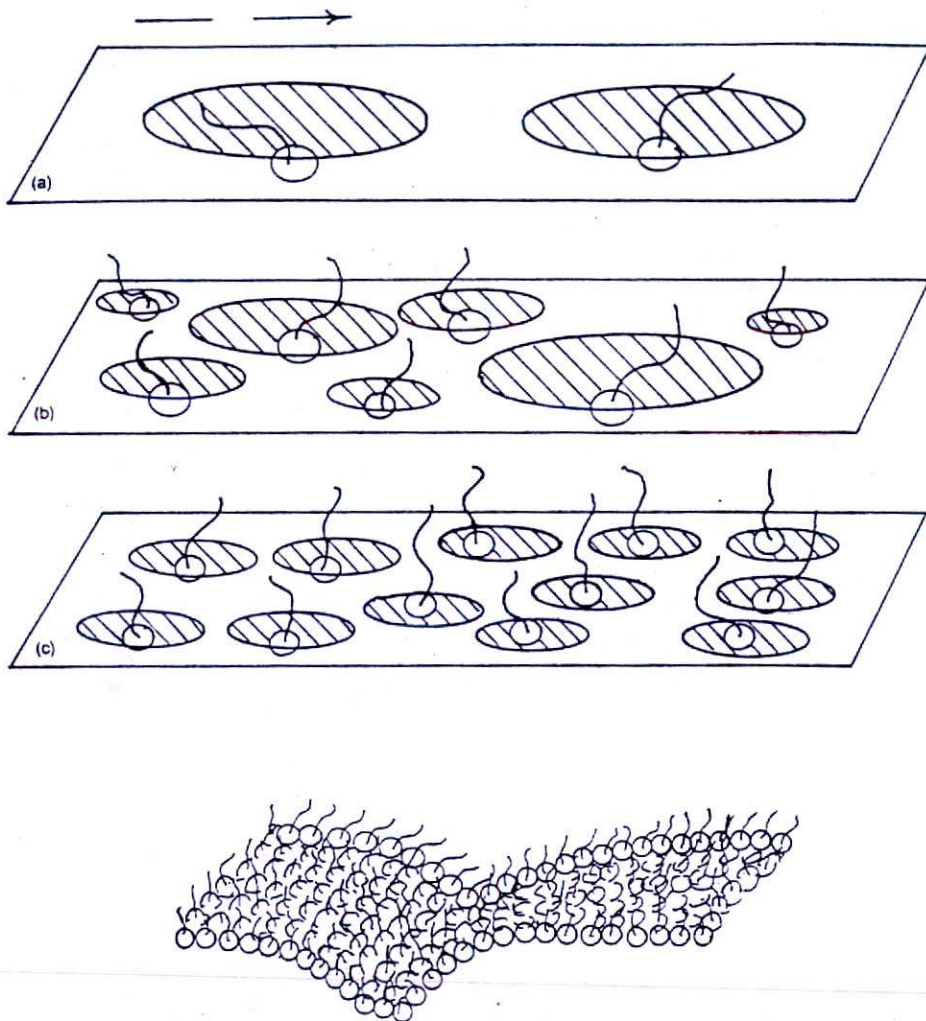


Fig. 14-19. Effective areas (cross-hatched ellipses) per molecule at the various degrees of monolayer compression. (a) gaseous state; (b) expanded liquid state; (c) condensed liquid and two-dimensional solid state; (d) film collapse. (From P. C. Hiemenz, *Principles of Colloid and Surface Chemistry*, 2nd Edition, Dekker, New York, 1986, p. 366, reproduced with permission of the copyright owner.)

The sizes and shapes of molecules of steroids, hormones, and enzymes and their interaction with drugs at interfaces can also be investigated by means of the film balance. The interaction between insulin injected under the surface layer and several lipids spread at constant surface pressure on a film balance were studied by Schwinke et al.<sup>20</sup> The film balance and its applications are discussed in the books of Adam,<sup>21</sup> Harkins,<sup>22</sup> Sobotka,<sup>23</sup> and Gaines.<sup>24</sup>

Mention has been made of the fact that materials forming an insoluble monolayer may be thought of as being in the gaseous, liquid, or solid state, depending on

the degree of compression to which the film is subjected. Thus, the surface pressure for molecules in the gaseous state at an interface is comparable to the pressure  $P$  that molecules in three-dimensional gaseous systems exert on the walls of their containers. Just as the equation of state for an ideal gas in three dimensions is  $PV = nRT$  (p. 25), that for a monolayer is

$$\pi A = nRT \quad (14-43)$$

in which  $\pi$  is the surface pressure in dynes/cm and  $A$  is the area that each mole of amphiphile occupies at the interface.

TABLE 14-7. Dimensions of Organic Molecules Determined by Means of the Film Balance

Substance	Formula	Length of Molecule (angstroms, Å)	Cross-Sectional Area (sq. angstroms, Å <sup>2</sup> )
Stearic acid	C <sub>17</sub> H <sub>35</sub> COOH	25	22
Tristearin	(C <sub>128</sub> H <sub>352</sub> O <sub>23</sub> ) <sub>3</sub> C <sub>3</sub> H <sub>5</sub>	25	66
Cetyl alcohol	C <sub>16</sub> H <sub>33</sub> OH	22	21
Myrcyl alcohol	C <sub>30</sub> H <sub>51</sub> OH	41	27

Equation (14-43), the two-dimensional ideal gas law, may be derived as follows. When the concentration of amphiphile at the interface is small, solute-solute interactions are unimportant. Under these conditions, surface tension decreases in a linear fashion with concentration. We may therefore write that

$$\gamma = bc + \gamma_0 \quad (14-44)$$

in which  $\gamma_0$  is the surface tension of the pure substrate,  $\gamma$  is the surface tension produced by the addition of  $c$  moles/liter of adsorbate, and  $b$  is the slope of the line. Since the slope of such a plot is negative, and since  $\pi = \gamma_0 - \gamma$ , equation (14-44) may be rewritten as

$$\pi = -bc \quad (14-45)$$

The Gibbs adsorption equation (14-26) can be expressed in the following form:

$$-(d\gamma/dc) = -b = \Gamma RT/c \quad (14-46)$$

since  $(d\gamma/dc)$  is the slope of the line.

Substituting for equation (14-45) in equation (14-46) and cancelling  $c$ , which is common to both sides; we obtain

$$\pi = \Gamma RT \quad (14-47)$$

Surface excess has the dimensions of moles/cm<sup>2</sup> and can be represented by  $n/A$ , in which  $n$  is the number of moles and  $A$  is the area in cm<sup>2</sup>. Thus:

$$\pi = nRT/A$$

or

$$\pi A = nRT$$

which is equation (14-43).

As with the three-dimensional gas law, equation (14-43) can be used to compute the molecular weights of materials adsorbed as gaseous films at an interface. (See Problems 14-24 and 14-25.) Nonideal behavior also occurs, and plots of  $\pi A$  versus  $\pi$  for monolayers give results comparable to those in three-dimensional systems when  $PV$  is plotted against  $P$ . Equations similar to van der Waal's equation (p. 26) for nonideal behavior have been developed.

The relation between the Gibbs adsorption equation and equation (14-43) emphasizes the point made earlier that the distinction between soluble and insoluble films is an arbitrary one, made on the basis of the experi-

mental techniques used rather than any fundamental differences in physical properties.

The variation of the surface pressure  $\pi$  with temperature at the several "phase changes" observed in the two-dimensional isotherm,  $\pi$ -area, (see Fig. 14-18) may be analyzed by a relationship analogous to the Clapeyron equation (p. 68):

$$\frac{d\pi}{dT} = \frac{\Delta H}{T(A_1 - A_2)} \quad (14-48)$$

where  $A_1$  and  $A_2$  are the molar areas (cm<sup>2</sup> mol<sup>-1</sup>) of the two phases and  $T$  and  $\Delta H$  are the temperature and enthalpy for the phase change.<sup>25</sup> Note that  $\pi$ ,  $\Delta H$ , and  $(A_1 - A_2)$  are the two-dimensional equivalents of pressure, enthalpy, and change of volume in the Clapeyron equation.

**Example 14-12.** Monolayers of insoluble amphiphilic compounds with a polymerizable group serve to investigate the polymerization behavior at the gas-water interface. The  $\pi$ - $A$  isotherms resulting from film balance experiments with *n*-hexadecyl acrylate monolayers in the temperature range 13° to 25° C showed two breaks corresponding to phase transitions (changes in state).

Compute  $\Delta H$ , the enthalpy change of transition from the condensed liquid state  $L_2$  to the liquid expanded state  $L_1$ . The areas per molecule at  $L_1$  and  $L_2$  are 0.357 and 0.265 nm<sup>2</sup>/molecule. The change of surface pressure with temperature,  $d\pi/dT = 0.91$  mN m<sup>-1</sup> °K<sup>-1</sup>, and the temperature of transition is 24.2° C.<sup>25</sup>

From equation (14-48):

$$\Delta H = T(A_1 - A_2) \frac{d\pi}{dT}$$

$$\begin{aligned} \Delta H &= 297.2^\circ \text{K} (0.357 - 0.265) \times 10^{-18} \text{ m}^2/\text{molecule} \times \\ & 0.91 \times 10^{-3} \frac{\text{N}}{\text{m} \cdot \text{K}} = 2.49 \times 10^{-20} \text{ J/molecule} \\ & 2.49 \times 10^{-20} \times 6.022 \times 10^{23} = 14,995 \text{ J/mole} \approx 15 \text{ kJ/mole} \end{aligned}$$

## ADSORPTION AT SOLID INTERFACES

Adsorption of material at solid interfaces may take place from either an adjacent liquid or gas phase. The study of adsorption of gases is concerned in such diverse applications as the removal of objectionable odors from rooms and food, the operation of gas masks, and the measurement of the dimensions of particles in a powder. The principles of solid-liquid adsorption are utilized in decolorizing solutions, adsorption chromatography, detergency, and wetting.

In many ways, the adsorption of materials from a gas or liquid onto a solid surface is similar to that discussed under liquid surfaces. Thus, adsorption of this type may

be considered as an attempt to reduce the surface free energy of the solid. The surface tensions of solids are invariably more difficult to obtain, however, than those of liquids. In addition, the solid interface is immobile in comparison to the turbulent liquid interface. The average lifetime of a molecule at the water-gas interface is about 1 microsecond, whereas an atom in the surface of a nonvolatile metallic solid may have an average lifetime of  $10^{27}$  seconds.<sup>26</sup> Frequently, the surface of a solid may not be homogeneous, in contrast to liquid interfaces.

**The Solid-Gas Interface.** The degree of adsorption of a gas by a solid depends on the chemical nature of the *adsorbent* (the material used to adsorb the gas) and the *adsorbate* (the substance being adsorbed), the surface area of the adsorbent, the temperature, and the partial pressure of the adsorbed gas. The types of adsorption are generally recognized as physical or van der Waals' adsorption, and chemical adsorption or chemisorption. *Physical adsorption*, associated with van der Waals' forces, is reversible, the removal of the adsorbate from the adsorbent being known as *desorption*. A physically adsorbed gas may be desorbed from a solid by increasing the temperature and reducing the pressure. *Chemisorption*, in which the adsorbate is attached to the adsorbent by primary chemical bonds, is irreversible.

The relationship between the amount of gas physically adsorbed on a solid and the equilibrium pressure or concentration at constant temperature yields an *adsorption isotherm* when plotted as shown in Figure 14-20. The term *isotherm* refers to a plot at constant temperature. The number of moles, grams, or milliliters  $x$  of gas adsorbed on  $m$  grams of adsorbent at STP (standard temperature and pressure) is plotted on the vertical axis against the equilibrium pressure of the gas in mm Hg on the horizontal axis, as seen in Figure 14-20a.

One method of obtaining adsorption data is by the use of an apparatus similar to that shown in Figure 14-21, which consists essentially of a balance contained within

a vacuum system. The solid, previously degassed, is placed on the pan, and known amounts of gas are allowed to enter. The increase in weight at the corresponding equilibrium gas pressures is recorded. This may be achieved by noting the extension of a calibrated quartz spring used to suspend the pan containing the sample. The data are then used to construct an isotherm based on one or more of the following equations.

Freundlich<sup>27</sup> suggested a relationship, the *Freundlich isotherm*,

$$y = \frac{x}{m} = kp^{1/n} \quad (14-49)$$

in which  $y$  is the mass of gas  $x$  adsorbed per unit mass  $m$  of adsorbent, and  $k$  and  $n$  are constants that can be evaluated from the results of the experiment. The equation is handled more conveniently when written in the logarithmic form,

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p \quad (14-50)$$

which yields a straight line when plotted as seen in Figure 14-20b. The constant,  $\log k$ , is the intercept on the ordinate, and  $1/n$  is the slope of the line.

Langmuir<sup>28</sup> developed an equation based on the theory that the molecules or atoms of gas are adsorbed on active sites of the solid to form a layer one molecule thick (monolayer). The fraction of centers occupied by gas molecules at pressure  $p$  is represented by  $\theta$ , and the fraction of sites not occupied is  $1 - \theta$ . The rate  $r_1$  of adsorption or condensation of gas molecules on the surface is proportional to the unoccupied spots  $1 - \theta$  and to the pressure  $p$ , or

$$r_1 = k_1(1 - \theta)p \quad (14-51)$$

The rate  $r_2$  of evaporation of molecules bound on the surface is proportional to the fraction of surface occupied,  $\theta$ , or

$$r_2 = k_2\theta \quad (14-52)$$

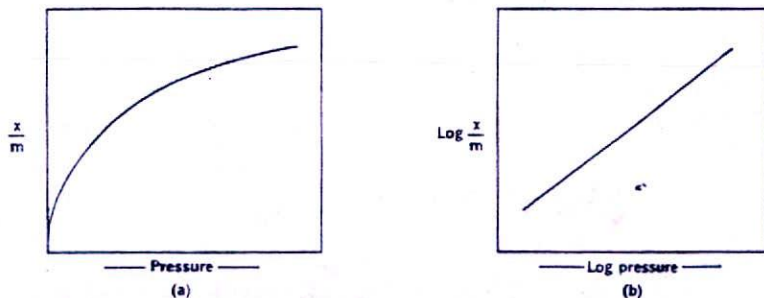


Fig. 14-20. Adsorption isotherms for a gas on a solid. (a) Amount  $x$  of gas adsorbed per unit mass  $m$  of adsorbent plotted against the equilibrium pressure. (b) Log of the amount of gas adsorbed per unit mass of adsorbent plotted against the log of the pressure.

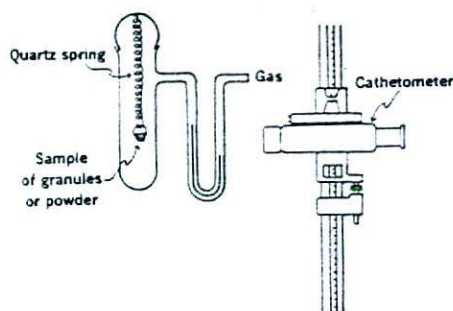


Fig. 14-21. Schematic of apparatus used to measure adsorption of gases on solids.

and at equilibrium  $r_1 = r_2$  or

$$k_1(1 - \theta)p = k_2\theta \quad (14-53)$$

By rearrangement, we obtain

$$\theta = \frac{k_1 p}{k_2 + k_1 p} = \frac{(k_1/k_2)p}{1 + (k_1/k_2)p} \quad (14-54)$$

We can replace  $k_1/k_2$  by  $b$  and  $\theta$  by  $y/y_m$ , in which  $y$  is the mass of gas adsorbed per gram of adsorbent at pressure  $p$  and at constant temperature, and  $y_m$  is the mass of gas that 1 gram of the adsorbent can adsorb when the monolayer is complete. Inserting these terms into equation (14-54) produces the formula

$$y = \frac{y_m b p}{1 + b p} \quad (14-55)$$

which is known as the *Langmuir isotherm*. By inverting equation (14-55) and multiplying through by  $p$ , it may be written for plotting as

$$\frac{p}{y} = \frac{1}{b y_m} + \frac{p}{y_m} \quad (14-56)$$

A plot of  $p/y$  against  $p$  should yield a straight line, and  $y_m$  and  $b$  can be obtained from the slope and intercept.

Equations (14-49), (14-50), (14-55), and (14-56) are adequate for the description of curves only of the type shown in Figure 14-20a. This is known as the Type I isotherm. Extensive experimentation, however,

has shown that there are four other types of isotherms, as seen in Figure 14-22, that are not described by these equations. Type II isotherms are sigmoidal in shape and occur when gases undergo physical adsorption onto nonporous solids to form a monolayer followed by multilayer formation. The first inflection point represents the formation of a monolayer; the continued adsorption with increasing pressure indicates subsequent multilayer formation. Type II isotherms are best described by an expression derived by Brunauer, Emmett, and Teller and termed for convenience the *BET equation*. This equation may be written as

$$\frac{p}{y(p_0 - p)} = \frac{1}{y_m b} + \frac{b - 1}{y_m b} \frac{p}{p_0} \quad (14-57)$$

in which  $p$  is the pressure of the adsorbate in mm Hg at which the mass  $y$  of vapor per gram of adsorbent is adsorbed,  $p_0$  is the vapor pressure when the adsorbent is saturated with adsorbate vapor,  $y_m$  is the quantity of vapor adsorbed per unit mass of adsorbent when the surface is covered with a monomolecular layer, and  $b$  is a constant proportional to the difference between the heat of adsorption of the gas in the first layer and the latent heat of condensation of successive layers. The saturated vapor pressure  $p_0$  is obtained by bringing excess adsorbate in contact with the adsorbent. For the case of simple monolayer adsorption, the BET equation reduces to the Langmuir isotherm.

Isotherms of the shape shown as IV in Figure 14-22 are typical of adsorption onto porous solids. The first point of inflection, when extrapolated to zero pressure, again represents the amount of gas required to form a monolayer on the surface of the solid. Multilayer formation and condensation within the pores of the solid are thought to be responsible for the further adsorption shown, which reaches a limiting value before the saturation vapor pressure,  $p_0$  is attained. Type III and Type V isotherms are produced in a relatively few instances in which the heat of adsorption of the gas in the first layer is less than the latent heat of condensation of successive layers. As with Type IV isotherms, those of Type V show capillary condensation, and adsorption reaches a limiting value before  $p_0$  is attained. The Type II isotherm results when  $b$  is greater than 2.0 and Type III when  $b$  is smaller than 2.0 in the

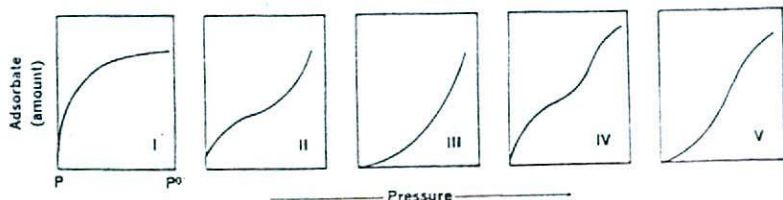


Fig. 14-22. Various types of adsorption isotherms.

BET expression, equation (14-57). Types IV and V frequently involve hysteresis and appear as shown in Figures 14-23 and 14-24, respectively.

The total surface area of the solid can be determined from those isotherms in which formation of a monolayer can be detected, that is, Types I, II, and IV. This information is obtained by multiplying the total number of molecules in the volume of gas adsorbed by the cross-sectional area of each molecule. The surface area per unit weight of adsorbent, known as the *specific surface*, is important in pharmacy since the dissolution rates of drug particles depend, in part, on their surface area (see p. 331). Other techniques for determining specific surface are discussed in Chapter 16.

**The Solid-Liquid Interface.** Drugs such as dyes, alkaloids, fatty acids, and even inorganic acids and bases may be absorbed from solution onto solids such as charcoal and alumina. The adsorption of solute molecules from solution may be treated in a manner analogous to the adsorption of molecules at the solid-gas interface. Isotherms, which fit one or more of the equations mentioned previously, may be obtained by substituting solute concentration for the vapor pressure term used for solid-gas systems. For example, the adsorption of strychnine, atropine, and quinine from aqueous solutions by six different clays<sup>29</sup> was capable of being expressed by the Langmuir equation in the form

$$\frac{c}{y} = \frac{1}{by_m} + \frac{c}{y_m} \quad (14-58)$$

in which  $c$  is the equilibrium concentration in milligrams of alkaloidal base per 100 mL of solution,  $y$  is the amount of alkaloidal base  $x$  in milligrams adsorbed per gram  $m$  of clay (i.e.,  $y = x/m$ ), and  $b$  and  $y_m$  are constants defined earlier. In later studies, Barr and

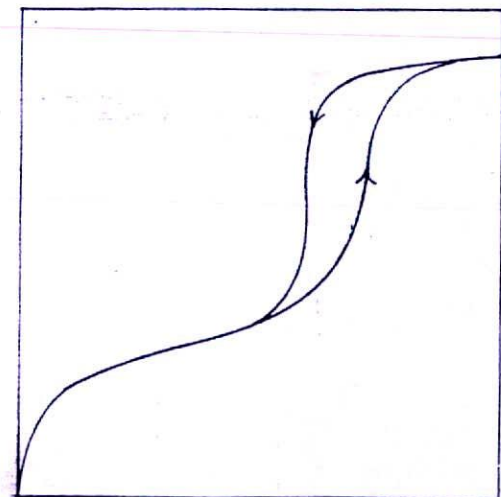


Fig. 14-23. Type IV isotherm showing hysteresis.

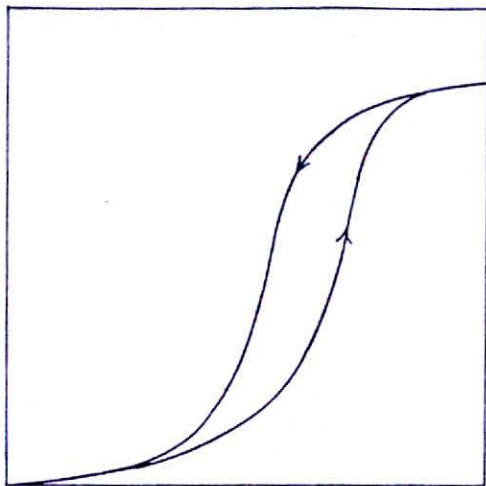


Fig. 14-24. Type V isotherm showing hysteresis.

Arnista<sup>30</sup> investigated the adsorption of diphtheria toxin and several bacteria by various clays. They concluded that attapulgite, a hydrous magnesium aluminum silicate, was superior to kaolin as an intestinal adsorbent. The results of the adsorption of strychnine on activated attapulgite, halloysite (similar to kaolinite) and kaolin, all washed with gastric juice, are shown in Figure 14-25.

The smaller the slope, the better the adsorption. Thus, it can be calculated from Figure 14-25 that an equilibrium concentration of, say, 400 mg strychnine/100 mL of solution,  $x/m$  for the three adsorbents is approximately 40, 20, and 6.7 mg/g for attapulgite, halloysite, and kaolin, respectively. When an orally administered drug causes gastrointestinal disturbances, commercial adsorbent, antacid, or antidiarrheal preparations are often taken by the patient, and these preparations may interact with the drug to reduce its bioabsorption. The absorption of quinidine salts (an antiarrhythmic agent), for example, is impaired by combining with kaolin, pectin, montmorillonite, and similar adsorbents. Moustafa et al.<sup>31</sup> found that the adsorption of quinidine sulfate by antacid and antidiarrheal preparations, Kaopectate, Simeco, magnesium trisilicate, and bismuth subnitrate, were well expressed by both Freundlich and Langmuir adsorption isotherms.

Nikolakakis and Newton<sup>32</sup> studied the solid-solid adsorption of a fine cohesive powder onto the surface of coarse free-flowing particles to form what is called an "ordered" mixture. These systems provide very homogeneous mixtures of powders ordinarily having good physical stability. Examples of "ordered" mixtures are dry blends of sucrose and antibiotics that can be reconstituted with water to provide antibiotic syrup formulations. Sorbitol can replace sucrose to prepare

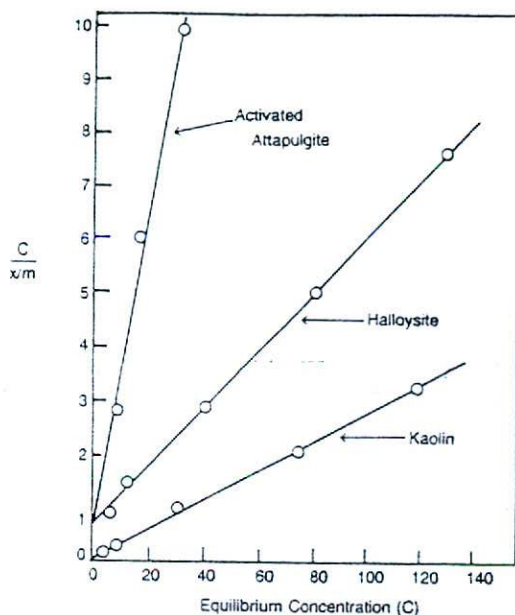


Fig. 14-25. Adsorption of strychnine on various clays. (Modified from M. Barr and S. Arnista, *J. Am. Pharm. Assoc., Sci. Ed.* 46, 486, 488, 1957.)

sucrose-free formulations for diabetic patients. During blending, a fine powder of an antibiotic is adsorbed onto the surface of coarse particles of sorbitol. Nikolakakis and Newton obtained an apparent Langmuir or Type I isotherm when the weight of drug adsorbed per unit weight of sorbitol ( $x/m$ ) was plotted against the concentration  $c$  of nonadsorbed drug at equilibrium. Thus, using the linear form, equation (14-58), the  $b$  and  $y_m$  values can be computed. The  $y_m$  value is the amount of antibiotic per unit weight of sorbitol required to form a monolayer on the surface of sorbitol particles. This can be considered as a measure of the adsorption capacity or number of binding sites of sorbitol for the antibiotic. The quantity  $b$  is an empirical affinity or binding constant that is given thermodynamic significance by some workers (see Hiemenz,<sup>4</sup> pp. 398-407).

**Example 14-13.** The values of  $c/y$  against  $c$  for the solid-solid adsorption of cephalixin monohydrate onto sorbitol are

$c$ (% (w/w))*	5	10	15	20
$c/y$ (%(w/w))	54.85	34.5	114.15	143.8
(g (adsorbate)/g (adsorbent))				

Calculate  $b$  and  $y_m$ .

\*Note that we express  $c$  as percent w/w on both the  $x$ - and the  $y$  axes. We express  $y = (x/m)$  as gram (adsorbate)/gram (adsorbent), which is dimensionless. Therefore, the units on  $c/y$  on the  $x$ -axis are simply, %/(w/w). Like  $y$ ,  $y_m$  is dimensionless and  $b$  has the units, 1/%(w/w).

Using a regression analysis of  $c/y$  ( $y$ -axis) against  $c$  ( $x$ -axis), the equation is  $c/y = 25.2 + 5.93c$ .

$$\text{Slope} = \frac{1}{y_m} = 5.93; \quad y_m = 0.169 \text{ g/g (dimensionless)}$$

$$\text{Intercept} = \frac{1}{by_m} = 25.2 \text{ \% (w/w)};$$

$$b = \frac{1}{25.2 \text{ \% (w/w)} \times 0.169 \text{ g/g}} = 0.235 \text{ \% (w/w)}^{-1}$$

**Activated Charcoal.** In an investigation of the adsorption of drugs on activated charcoal and its effects on the bioabsorption of drugs in man, Tsuchiya and Levy<sup>33</sup> concluded that reasonable in vivo predictions could be made from in vitro studies concerning the antidotal effectiveness of activated charcoal.

Activated charcoal is used as an antidote in poisonings by sulfonylureas such as tolbutamide, acetohexamide, and other drug and nondrug compounds. Contrary to earlier reports, Kannisto and Neuvonen<sup>34</sup> reported that charcoal effectively adsorbs sulfonylureas and can prevent their gastrointestinal absorption and subsequent toxicity in cases of overdose. The data were analyzed by the authors using the Langmuir adsorption isotherm.

In large overdosage, the analgesic acetaminophen (paracetamol) may cause liver damage, renal failure, and death owing to hepatotoxicity and sometimes renal tubular necrosis (15 grams may be fatal). Activated charcoal has been used to adsorb acetaminophen, and acetylcysteine to neutralize the toxic metabolites that deplete hepatic glutathione. However, there has been concern that activated charcoal will absorb the acetylcysteine as well as the acetaminophen and reduce or nullify the effectiveness of acetylcysteine in preventing liver damage and kidney failure. Ryboit et al.<sup>35</sup> have shown, however, that acetylcysteine is adsorbed by charcoal in sufficiently small amounts that the concurrent use of acetylcysteine and activated charcoal is a useful treatment for acetaminophen poisoning.

The adsorption of drugs by activated charcoal not only prevents bioabsorption from the gastrointestinal tract but also may increase the diffusion of the drug from the tissues into the gastrointestinal tract and elimination from the body by a process called *gastrointestinal dialysis*. In this process the adsorbing charcoal establishes a gradient between the systemic circulation in the body and the fluids in the gastrointestinal tract.<sup>36</sup> A rather thorough list of references to the systemic removal of drugs by charcoal adsorption is given in the 1988 paper by Huang and Tzou.<sup>36</sup>

Gessner and Hasan<sup>37</sup> studied the adsorption of solutes from aqueous solution onto activated charcoal. The adsorption data gave a good fit to the Freundlich isotherm and a poor fit to the Langmuir isotherm, even for published data that were considered earlier to adhere well to the Langmuir isotherm. Furthermore, the Freundlich isotherm accounted better for the effectiveness of activated charcoal to serve as an in vivo antidote against drug overdosing and poisoning.

Kleeman and Bailey<sup>38</sup> developed an in vitro approach for quantitatively ranking the affinity of drugs, toxicants, and suspended materials used in the treatment of public water supplies, to activated charcoal using high-performance liquid chromatography as the analytic tool. The authors provide an excellent review of the literature.

The adsorption of phenobarbital from simulated intestinal and gastric fluids by two activated charcoals of different pore size and specific surface area (pp. 430, 393) was investigated by Wurster et al.,<sup>39</sup> fitting the data to the linearized Langmuir expression (see equation [14-58]) and to a least-squares regression equation. A new activated charcoal with a specific surface of nearly 3000 m<sup>2</sup>/g was found to adsorb about three times as much phenobarbital as the charcoal with a specific surface of 1500 m<sup>2</sup>/g. It was concluded that the poorer adsorption by the older charcoal occurred because the site spacings on its surface were not sufficient for optimum arrangement of the phenobarbital molecules.

Hajratwala<sup>40</sup> referred to adsorption of drugs on charcoal, talc, and other adsorbents and discussed the manner of obtaining Langmuir and Freundlich constants from adsorption isotherms.

**Wetting.** Adsorption at solid surfaces is involved in the phenomena of wetting and detergency.

A *wetting agent* is a surfactant that, when dissolved in water, lowers the advancing contact angle and aids in displacing an air phase at the surface and replacing it with a liquid phase. Examples of the application of wetting to pharmacy and medicine include the displacement of air from the surface of sulfur, charcoal, and other powders for the purpose of dispersing these drugs in liquid vehicles; the displacement of air from the matrix of cotton pads and bandages so that medicinal solutions may be absorbed for application to various body areas; the displacement of dirt and debris by the use of detergents in the washing of wounds; and the application of medicinal lotions and sprays to the surface of the skin and mucous membranes.

The most important action of a wetting agent is to lower the *contact angle* between the surface and the wetting liquid. The contact angle is the angle between a liquid droplet and the surface over which it spreads. As shown in Figure 14-26, the contact angle between a liquid and a solid may be 0°, signifying complete wetting, or it may approach 180°, at which wetting is insignificant. The contact angle may also have any value between these limits, as illustrated in the sketches. At equilibrium, the surface and interfacial tensions can be resolved into

$$\gamma_s = \gamma_{SL} + \gamma_L \cos \theta \quad (14-59)$$

which is known as Young's equation.

When  $\gamma_s$  of equation (14-59) is substituted into equation (14-19), we have

$$S = \gamma_L (\cos \theta - 1) \quad (14-60)$$

and combining equation (14-59) with equation (14-16) results in

$$W_a = W_{SL} = \gamma_L (1 + \cos \theta) \quad (14-61)$$

which is an alternative form of Young's equation. Equations (14-60) and (14-61) are useful expressions since they do not include  $\gamma_S$  or  $\gamma_{SL}$ , neither of which can be easily or accurately measured. The contact angle between a water droplet and a greasy surface results when the applied liquid, water, wets the greasy surface incompletely. When a drop of water is placed on a scrupulously clean glass surface, it spreads spontaneously and no contact angle exists. This result can be described by assigning to water a high spreading coefficient on clean glass, or by stating that the contact angle between water and glass is zero. If the appropriate wetting agent is added to water, the solution will spread spontaneously on a greasy surface. For a wetting agent to function efficiently, in other words, to exhibit a low contact angle, it should have an HLB of about 6 to 9 (see p. 371).

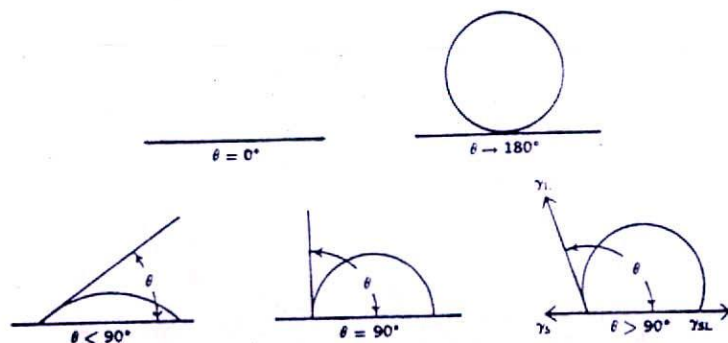


Fig. 14-26. Contact angles from 0° to 180°.

**Example 14-14.** Wettability of tablet surfaces influences disintegration and dissolution, and the subsequent release of the active ingredient(s) from the tablet.

A *tablet binder* is a material that contributes cohesiveness to a tablet so that the tablet remains intact after compression. The influence of tablet binders on wettability of acetaminophen tablets was studied by Esezobo et al.<sup>41</sup> The contact angle of water on the acetaminophen tablets, the surface tension of the liquid, and the disintegration time of the tablets are found in the following table. The water on the tablet surface is saturated with the basic formulation ingredients excluding the binder. The concentration of the tablet binders, povidone (polyvinylpyrrolidone, PVP), gelatin, and tapioca, is constant at 5% w/w.

Binder	$\gamma$ (Nm <sup>-1</sup> ) <sup>a</sup>	Cos $\theta$	t (min)
Povidone (PVP)	71.23	0.7455	17.0
Gelatin	71.23	0.7230	23.5
Tapioca	71.33	0.7570	2.0

<sup>a</sup>The surface tension  $\gamma$  is given in Jm<sup>-1</sup> or newtons, the SI force unit, divided by meters. In the cgs system  $\gamma$  is expressed in the force unit of dyne divided by cm, or in erg/cm<sup>2</sup>.

Using equations (14-60) and (14-61), compute  $S$ , the spreading coefficient, and  $W_{SL}$ , the work of adhesion, for water on the tablet surface, comparing the influence of the three binders in the formulation. Observe the disintegration times found in the table and use them to refute or corroborate the  $S$  and  $W_{SL}$  results.

	Spreading Coefficient	$S = \gamma (\cos \theta - 1)$
PVP	$S = 71.23 (0.7455 - 1) = -18.13$	
Gelatin	$S = 71.23 (0.7230 - 1) = -19.73$	
Tapioca	$S = 71.33 (0.7570 - 1) = -17.33$	

	Work of Adhesion	$W_{SL} = \gamma (1 + \cos \theta)$
PVP	$W_{SL} = 71.23 (1 + 0.7455) = 124.33 \text{ Nm}^{-1}$	
Gelatin	$W_{SL} = 71.23 (1 + 0.7230) = 122.73 \text{ Nm}^{-1}$	
Tapioca	$W_{SL} = 71.33 (1 + 0.7570) = 125.33 \text{ Nm}^{-1}$	

The spreading coefficient is negative, but the values are small. Tapioca shows the smallest negative value,  $S = -17.33$ , followed by PVP and finally gelatin. These results agree with the work of adhesion, tapioca > PVP > gelatin. The higher the work of adhesion the stronger is the bond between water and the tablet surface and the better is the wetting.

From the table, we observe the tablet disintegration times to be in the order tapioca < PVP < gelatin, which agrees qualitatively with the  $S$  and  $W_{SL}$  values. That is, the better the wetting, reflected in a larger work of adhesion and a smaller negative spreading coefficient, the shorter is the tablet disintegration time. Other factors, such as tablet porosity, which were not considered in the study, cause the relationship to be only qualitative.

Zisman and his associates<sup>42</sup> found that when the cosine of the contact angle,  $\cos \theta$ , was plotted versus the surface tension for a homologous series of liquids spread on a surface such as Teflon (polytetrafluoroethylene), a straight line resulted. The line may be extrapolated to  $\cos \theta = 1$ ; that is, to a contact angle of zero, signifying complete wetting. The surface tension at  $\cos \theta = 1$  was given the term *critical surface tension*

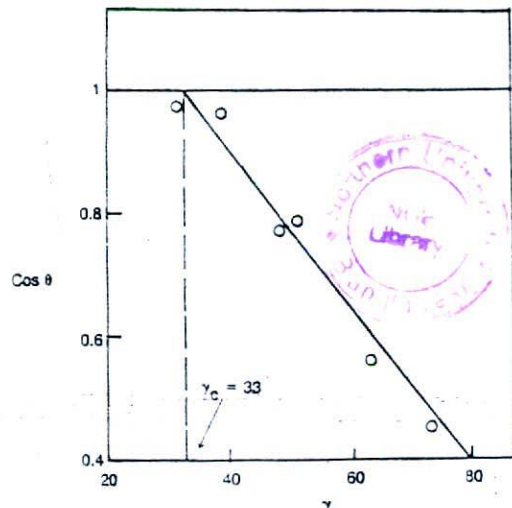


Fig. 14-27. Critical surface tension (Zisman) plot for a model skin. (From J. C. Charkoudian, *J. Soc. Cosmet. Chem.* 39, 225, 1988, reproduced with permission of the copyright owner.)

and the symbol  $\gamma_c$ . Various series of liquids on a given solid surface were all found to have about the same value of  $\gamma_c$ , as observed in Figure 14-27. Zisman concluded that  $\gamma_c$  was characteristic for each solid, Teflon, for example, having a value of about 18 erg/cm<sup>2</sup>. Since the surface of Teflon consists of  $-\text{CF}_2-$  groups, Zisman reasoned that all surfaces of this nature would have critical surface tensions of about 18 erg/cm<sup>2</sup>, and any liquid with a surface tension less than 18 erg/cm<sup>2</sup> would wet a surface composed of  $-\text{CF}_2-$  groups.<sup>43,44</sup>

**Example 14-15.** Charkoudian<sup>45</sup> designed a model skin surface with physical and chemical properties approximating those reported for human skin. The model skin consisted of a protein (cross-linked gelatin), a synthetic lipid-like substance, and water, with the protein and lipid in a ratio of 3 to 1. To further characterize the artificial skin, the surface tensions of several liquids and their contact angles on the model skin surface were determined at 20° C, as given in the following table.

Plot the  $\cos \theta$  versus  $\gamma$  and compute the critical surface tension  $\gamma_c$  for complete wetting of the artificial skin surface. The values of  $\gamma_c$  for in vivo human skin are about 26 to 28 dyne/cm.

From the results obtained, which liquid in the table above would be expected to best wet the model skin surface?

The plot is shown in Figure 14-27. Although the liquids in the table do not constitute a homologous series, they appear to fit nicely the Zisman principle, producing a straight line that extrapolates to  $\cos \theta$  corresponding to a critical surface tension of  $\gamma_c = 33$  dyne/cm.

Mineral oil, with a surface tension of 31.9 dyne/cm, most closely approximates the critical surface tension  $\gamma_c = 33$  dyne/cm of the

Liquid	Water	Glycerin	Diiodomethane	Ethylene glycol	Benzyl alcohol	Mineral oil
$\gamma$ (dyne/cm)	72.8	63.4	50.8	48.3	39.2	31.9
$\cos \theta$	0.45	0.56	0.79	0.77	0.96	0.97



model skin surface. For a more exact calculation of  $\gamma_c$ , least-squares linear regression analysis may be applied to yield

$$\cos \theta = -0.0137 \gamma + 1.450, r^2 = 0.972$$

For the specific value of  $\cos \theta = 1$ , we obtain  $\gamma_c = 33.3$  dyne/cm. It is noted that the critical surface tension  $\gamma_c$  for the artificial skin used in this study is somewhat higher ( $\gamma_c = 33.3$  dyne/cm) than values reported elsewhere in the literature for human skin ( $\gamma_c = 26-28$  dyne/cm). According to the author, this is due in part to the absence of sweat and sebaceous secretions, which lower the  $\gamma_c$  value of viable human skin.

Although one frequently desires to determine the relative efficiencies of wetting agents, it is difficult to measure the contact angle. Nor are spreading coefficients usually available, since no convenient method is known for directly measuring the surface tension of a solid surface. As a result of these difficulties, empiric tests are used in industry, one of the best known wetting tests being that of Draves. The *Draves test* involves measuring the time for a weighted skein of cotton yarn to sink through the wetting solution contained in a 500-mL graduate. No method has yet been suggested for estimating the ability of a wetting agent to promote spreading of a lotion on the surface of the skin, and the application properties of such products are ordinarily determined by subjective evaluation. However, see *Problems 14-11* and *14-14*.

**Detergents** are surfactants that are used for the removal of dirt. Detergency is a complex process involving the removal of foreign matter from surfaces. The process includes many of the actions characteristic of specific surfactants: initial wetting of the dirt and of the surface to be cleaned; deflocculation and suspension, emulsification or solubilization of the dirt particles; and sometimes foaming of the agent for entrainment and washing away of the particles. Since the detergent must possess a combination of properties; its efficiency is best ascertained by actual tests with the material to be cleaned.

Other dispersion stabilizers, including deflocculating, suspending, and emulsifying agents, are considered in Chapter 18.

#### APPLICATIONS OF SURFACE ACTIVE AGENTS

In addition to the use of surfactants as emulsifying agents, detergents, wetting agents, and solubilizing agents, they find application as antibacterial and other protective agents and as aids to the absorption of drugs in the body.

A surfactant may affect the activity of a drug or may itself exert drug action. As an example of the first case, the penetration of hexylresorcinol into the pinworm *Ascaris* is increased by the presence of a low concentration of surfactant. This potentiation of activity is due to a reduction in interfacial tension between the liquid phase and the cell wall of the organism. As a result, the adsorption and spreading of hexylresorcinol over the surface of the organism is facilitated. When the concentration of surface-active agent present exceeds that

required to form micelles, however, the rate of penetration of the anthelmintic decreases nearly to zero. This is because the drug is now partitioned between the micelles and the aqueous phase, resulting in a reduction in the effective concentration. Quaternary ammonium compounds are examples of surface-active agents that in themselves possess antibacterial activity. This may depend in part on interfacial phenomena, but other factors are also important. The agents are adsorbed on the cell surface and supposedly bring about destruction by increasing the permeability or "leakiness" of the lipid cell membrane. Death then occurs through a loss of essential materials from the cell. Both gram-negative and gram-positive organisms are susceptible to the action of the cationic quaternary compounds, whereas gram-positive organisms are attacked more easily by anionic agents than are gram-negative bacteria. Nonionic surfactants are least effective as antibacterial agents. In fact, they often aid rather than inhibit the growth of bacteria, presumably by providing long-chain fatty acids in a form that is easily metabolized by the organism.

Miyamoto et al.<sup>46</sup> studied the effects of surfactants and bile salts on the gastrointestinal absorption of antibiotics using an *in situ* rat gut perfusion technique. Polyoxyethylene lauryl ether reduced the absorption of propicillin in the stomach and increased it in the small intestine. It is a well-known fact that some surfactants increase the rate of intestinal absorption, while others decrease it. Some of these effects may result from alteration of the membrane by the surfactant. The effects of surfactants on the solubility of drugs and their bioabsorption has been reviewed by Mulley<sup>47</sup> and by Gibaldi and Feldman.<sup>48</sup>

**Foams and Antifoaming Agents.** Any solutions containing surface-active materials produce stable foams when mixed intimately with air. A foam is a relatively stable structure consisting of air pockets enclosed within thin films of liquid, the gas-in-liquid dispersion being stabilized by a *foaming agent*. The foam dissipates as the liquid drains away from the area surrounding the air globules, and the film finally collapses. *Agents* such as alcohol, ether, castor oil, and some surfactants may be used to break the foam and are known as *antifoaming agents*. Foams are sometimes useful in pharmacy but are usually a nuisance and are prevented or destroyed when possible. The undesirable foaming of solubilized liquid preparations poses a problem in formulation.

#### ELECTRIC PROPERTIES OF INTERFACES

This section deals with some of the principles involved with surfaces that are charged in relation to their surrounding liquid environment. Discussion of the applications arising from this phenomenon will be reserved for the chapters dealing with colloidal systems (Chapter 15) and suspensions (Chapter 18).

Particles dispersed in liquid media may become

charged mainly in one of two ways. The first involves the selective adsorption of a particular ionic species present in solution. This may be an ion added to the solution or, in the case of pure water, it may be the hydronium or hydroxyl ion. The majority of particles dispersed in water acquire a negative charge due to preferential adsorption of the hydroxyl ion. Secondly, charges on particles arise from ionization of groups (such as COOH) that may be situated at the surface of the particle. In these cases, the charge is a function of pK and pH. A third, less common, origin for the charge on a particle surface is thought to arise when there is a difference in dielectric constant between the particle and its dispersion medium.

**The Electric Double Layer.** Consider a solid surface in contact with a polar solution containing ions, for example, an aqueous solution of an electrolyte. Further, let us suppose that some of the cations are adsorbed onto the surface, giving it a positive charge. Remaining in solution are the rest of the cations plus the total number of anions added. These anions are attracted to the positively charged surface by electric forces that also serve to repel the approach of any further cations once the initial adsorption is complete. In addition to these electric forces, thermal motion tends to produce an equal distribution of all the ions in solution. As a result, an equilibrium situation is set up in which some of the excess anions approach the surface, while the remainder are distributed in decreasing amounts as one proceeds away from the charged surface. At a particular distance from the surface, the concentration of anions and cations are equal, that is, conditions of electric neutrality prevail. It is important to remember that the system as a whole is electrically neutral, even though there are regions of unequal distribution of anions and cations.

Such a situation is shown in Figure 14-28, where  $aa'$  is the surface of the solid. The adsorbed ions that gave the surface its positive charge are referred to as the *potential-determining ions*. Immediately adjacent to this surface layer is a region of tightly bound solvent molecules, together with some negative ions, also tightly bound to the surface. The limit of this region is given by the line  $bb'$  in Figure 14-28. These ions, having a charge opposite to the potential-determining

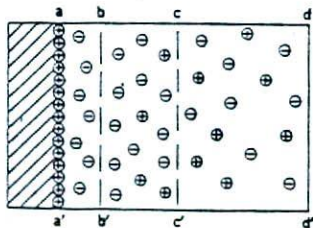


Fig. 14-28. The electric double layer at the surface of separation between two phases, showing distribution of ions. The system as a whole is electrically neutral.

ions, are known as *counterions* or *gegenions*. The degree of attraction of the solvent molecules and counterions is such that if the surface is moved relative to the liquid, the shear plane is  $bb'$  rather than  $aa'$ , the true surface. In the region bounded by the lines  $bb'$  and  $cc'$ , there is an excess of negative ions. The potential at  $bb'$  is still positive, since, as previously mentioned, there are fewer anions in the tightly bound layer than cations adsorbed onto the surface of the solid. Beyond  $cc'$ , the distribution of ions is uniform and electric neutrality is obtained.

Thus, the electric distribution at the interface is equivalent to a double layer of charge, the first layer (extending from  $aa'$  to  $bb'$ ) tightly bound, and a second layer (from  $bb'$  to  $cc'$ ) that is more diffuse. The so-called diffuse double layer therefore extends from  $aa'$  to  $cc'$ .

Two situations other than that represented by Figure 14-28 are possible. (1) If the counterions in the tightly bound, solvated layer equal the positive charge on the solid surface, then electric neutrality occurs at the plane  $bb'$  rather than  $cc'$ . (2) Should the total charge of the counterions in the region  $aa'-bb'$  exceed the charge due to the potential-determining ions, then the net charge at  $bb'$  will be negative, rather than less positive as shown in Figure 14-28. This means that, in this instance, for electric neutrality to be obtained at  $cc'$ , an excess of positive ions must be present in the region  $bb'-cc'$ .

The student should appreciate that if the potential-determining ion is negative, the arguments just given still apply, although now positive ions will be present in the tightly bound layer.

**Nernst and Zeta Potentials.** The changes in potential with distance from the surface for the various situations discussed in the previous section may be represented as shown in Figure 14-29. The potential at the solid surface  $aa'$ , due to the potential-determining ion, is the *electrothermodynamic (Nernst) potential*,  $E$ , and is defined as the difference in potential between the actual surface and the electroneutral region of the solution. The potential located at the shear plane  $bb'$  is known as the *electrokinetic, or zeta, potential*,  $\zeta$ . The zeta potential is defined as the difference in potential between the surface of the tightly bound layer (shear plane) and the electroneutral region of the solution. As shown in Figure 14-29, the potential drops off rapidly initially, followed by a more gradual decrease as the distance from the surface increases. This is because the counterions close to the surface act as a screen that reduces the electrostatic attraction between the charged surface and those counterions further away from the surface.

Zeta potential has practical application in the stability of systems containing dispersed particles since this potential, rather than the Nernst potential, governs the degree of repulsion between adjacent, similarly charged, dispersed particles. If the zeta potential is reduced below a certain value (which depends on the particular system being used), the attractive forces

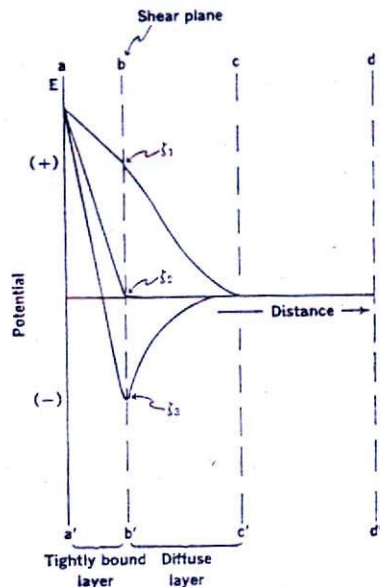


Fig. 14-29. Electrokinetic potential at solid-liquid boundaries. Curves are shown for three cases characteristic of the ions or molecules in the liquid phase. Note that although  $E$  is the same in all three cases, the zeta potentials are positive ( $\zeta_1$ ), zero ( $\zeta_2$ ), and negative ( $\zeta_3$ ).

exceed the repulsive forces, and the particles come together. This phenomenon is known as *flocculation* and is discussed in the chapters dealing with colloidal and coarse dispersions (see Chapters 15 and 18).

**Effect of Electrolytes.** As the concentration of electrolyte present in the system is increased, the screening effect of the counterions is also increased. As a result, the potential falls off more rapidly with distance because the thickness of the double layer shrinks. A similar situation occurs when the valency of the counterion is increased while the total concentration of electrolyte is held constant. The overall effect frequently causes a reduction in zeta potential.

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### Problems\*

14-1. Water has an unusually high surface tension, and like other liquids, its surface tension decreases with increasing temperature. What is your explanation for these two phenomena?

*Hint:* What kind of intermolecular forces do you believe might contribute to these observations?

14-2. You wish to formulate a sunscreen product that lowers surface tension and thus spreads easily on the skin. You choose *p*-aminobenzoic acid, a powerful sunscreen.

(a) Calculate the surface tension of a 12.35 weight percent of *p*-aminobenzoic acid solution in water at 25° C. The DuNouy tensiometer ring circumference is 12.47 cm and the correction factor  $\beta$  according to Harkins and Jordan is 0.920. The dial reading in dynes was obtained experimentally as 1989.

(b) What agent might you add to improve the spreading qualities of this product?

*Answer:* (a)  $\gamma = 73.37$  dyne/cm

14-3. Equation (14-1), page 364, considers  $\gamma$  as a force per unit length (dyne/cm) in the surface, while equation (14-2), page 364, views  $\gamma$  as an energy per unit area (erg/cm<sup>2</sup>) of the surface. Show the dimensional equivalency in both ergs and SI units for these two interpretations of the surface tension.

*Answer:* Check your answer with Hiemenz<sup>16</sup>

14-4. What is the pressure difference  $\Delta P$  in dyne/cm<sup>2</sup> across a soap bubble formed from the soap solution of *Example 14-1*, page 364? The radius of the soap bubble is 2.50 cm.

*Answer:* 39.2 dyne/cm<sup>2</sup>

14-5. A soap bubble is blown up at the bowl opening of a clay pipe; the pressure of air inside the bubble decreases as the radius of the bubble increases according to the equation

$$\Delta P = \frac{2\gamma}{r}$$

where  $\Delta P$  is the pressure difference across the soap film,  $\gamma$  is the surface free energy or surface tension of the soap solution, and  $r$  is the radius of the bubble. If the soap solution has a surface tension of 3.2 dyne/cm and the radius of the bubble expands to 7.6 cm, what is the pressure difference in dyne/cm<sup>2</sup> across the surface film of the soap bubble? Express the result both in dyne/cm<sup>2</sup> and in atmospheres.

*Answer:*  $\Delta P = 0.84$  dyne/cm<sup>2</sup> or  $8.3 \times 10^{-7}$  atm

14-6. Calculate the surface tension of a 2% (w/v) solution of a wetting agent that has a density of 1.008 g/cm<sup>3</sup> and that rises 6.60 cm in a capillary tube having an inside radius of 0.02 cm.

*Answer:* 65.2 dyne/cm

14-7. The surface tension of benzene at 20° C is 28.85 dyne/cm. In a capillary apparatus, the liquid rose to a height of 1.332 cm. The density of benzene is 0.8765 g/cm<sup>3</sup> at 20° C. Using the capillary-rise equation, calculate the diameter of the capillary tube. The acceleration of gravity is 981 cm/sec<sup>2</sup>.

*Answer:* 0.073 cm diameter. The answer is not exact since the equation is an approximate one. An iteration procedure is required to

obtain accurate results for the capillary rise problem, as discussed by Hiemenz.<sup>16</sup>

14-8. Water has a surface tension of 71.97 dyne/cm at 25° C, and its density at 25° C is 0.9971 g/cm<sup>3</sup>.

(a) How high will the water rise in a very fine capillary tube of radius 0.0023 cm?

(b) If water rises by capillary action only 64 cm in a narrow tube equivalent to a xylem tube in a living plant, how is it possible to lift aqueous nutrients to the top-most leaves in the tall trees in a forest?

*Answer:* 64.0 cm. The important process is not capillary action but rather appears to be osmosis.

14-9. (a) How high will the liquid carbon tetrachloride rise in a capillary tube of radius 0.015 cm at 20° C? The density of carbon tetrachloride is 1.595 g/cm<sup>3</sup> and its surface tension is 26.99 dyne/cm at 20° C.

(b) Could one use this experiment to estimate the acceleration,  $g$ , caused by gravity on the earth?

*Answer:* (a) 2.30 cm

14-10. Pure ethyl alcohol rises 2.48 cm in a capillary rise apparatus at 30° C. The capillary tube has a radius of 0.0230 cm, and the density of ethyl alcohol at 30° C is 0.781 g/cm<sup>3</sup>. What is the surface tension of ethyl alcohol at 30° C?

*Answer:* 21.85 dyne/cm

14-11. (a) Paruta and Cross<sup>31</sup> studied the spreading on water of a number of surfactants (spreading promoters) added to mineral oil as a laboratory test in the design of cosmetic creams and lotions. The surface tension of water at 25° C is 72.0 dyne/cm, the surface tension of a test lotion consisting of 5 g/dL (5% w/v) solution of sorbitan monooleate in mineral oil was found to be 31.2 dyne/cm and the interfacial tension  $\gamma_{il}$  of the oil-surfactant solution measured against water was 5.7 dyne/cm. Calculate the initial spreading coefficient  $S_{initial}$  of the oil-surfactant solution (the oil phase) on water.

(b) What is the significance of the positive spreading coefficient? Could you suggest a better substrate than water to test the spreadability of a cosmetic lotion? See Paruta and Cross for another approach.<sup>31</sup>

*Answer:* (a) the spreading coefficient  $S_{initial} = 35.10$  dyne/cm

14-12. The surface tension of an organic liquid is 25 erg/cm<sup>2</sup>, the surface tension of water is 72.8 erg/cm<sup>2</sup>, and the interfacial tension between the two liquids is 30 erg/cm<sup>2</sup> at 20° C. What is the work of cohesion of the organic liquid, the work of adhesion between the liquid and water, and the initial spreading coefficient of the liquid on the water surface at 20° C?

*Answer:*  $W_c = 50$  erg/cm<sup>2</sup>,  $W_a = 67.8$  erg/cm<sup>2</sup>,  $S_{initial} = 17.8$  erg/cm<sup>2</sup>

14-13. The surface tension of *n*-heptyl alcohol is 27.0 erg/cm<sup>2</sup>, the surface tension of water is 72.3 erg/cm<sup>2</sup>, and the interfacial tension between the two liquids is 8.0 erg/cm<sup>2</sup> at 20° C. Calculate  $W_c$ ,  $W_a$ , and  $S_{initial}$ .

*Answer:*  $W_c = 54$  erg/cm<sup>2</sup>,  $W_a = 91.3$  erg/cm<sup>2</sup>,  $S_{initial} = 37.8$  erg/cm<sup>2</sup>

14-14. The contact angle  $\theta$  for a skin lotion when applied to the back of the hand of a number of subjects was found to have an average value of 103° at 24° C. The surface tension  $\gamma_L$  of the lotion measured at 24° C in a capillary rise experiment was 63.2 dyne/cm, or 63.2 mN m<sup>-1</sup> in SI units (The symbol  $m$  stands for both *milli* and *meters*; 63.2 mN m<sup>-1</sup> is read "63.2 millinewtons per meter.") What is the work of adhesion  $W_{SL}$  and the initial spreading coefficient  $S_{initial}$  for this lotion on the skin?

*Answer:*  $W_{SL} = 48.98$  erg/cm<sup>2</sup> or 0.049 N/m;  $S_{initial} = -77.42$  erg/cm<sup>2</sup> or -0.077 N/m

14-15. Magnesium stearate and lactose are excipients commonly used in tablet formulation. The measured contact angles of water or of a saturated aqueous solution on the surfaces of compacts of these two powders are  $\theta = 121^\circ$  and  $\theta = 30^\circ$ . Their surface tensions (against air) are 72.3 and 71.6 dyne/cm. The surface tension of water (against air) at 20° C is 72.8 dyne/cm.

(a) Compute the interfacial tension between water and each of these compacted powders. You will need equation 14-59.

\*Problems 14-26 through 14-29 were prepared by B. Hajratwala, Wayne State University, Detroit.

(b) Compute the spreading of water on the solid surfaces. (Data from Lerk et al.<sup>53</sup>)

(c) How do you explain the quite different spreading results on these two powder compacts?

**Partial Answers:** (a) Magnesium stearate:  $\gamma_{SL} = 109.8$  dyne/cm; lactose:  $\gamma_{SL} = 8.55$  dyne/cm; (b) for magnesium stearate,  $S_{\text{max}} = -110.3$  dyne/cm; for lactose,  $S_{\text{max}} = -9.76$  dyne/cm

14-16. *p*-Toluidine, a yellow liquid used in the manufacture of dyes is only slightly soluble in water. The surface tension of para-toluidine was measured at various concentrations at 25° C (298° K) and the results were plotted. The slope  $d\gamma/dc$  of the line at  $c = 5 \times 10^{-2}$  g/cm<sup>3</sup> was found to be  $-32,800$  cm<sup>3</sup>/sec<sup>2</sup>. Using the Gibbs' adsorption equation, compute the excess surface concentration in mole/cm<sup>2</sup> and in g/cm<sup>2</sup>. The molecular weight of *p*-toluidine is 107.15 g/mole.

**Answer:**  $\Gamma = 6.6 \times 10^{-8}$  mole/cm<sup>2</sup>;  $7.1 \times 10^{-7}$  g/cm<sup>2</sup>

14-17. The surface tension of aminobutyric acid in water at 25° C is given as a function of concentration (weight per cent of aminobutyric acid) in the following table:

Data for Problem 14-17

Weight % w/w	4.96	9.34	13.43
$\gamma$ (dyne/cm)	71.91	71.67	71.40

(a) Plot the data and obtain the slope  $\partial\gamma/\partial(\text{wt}\%)$  from the two-point formula or from regression analysis. (If you use regression analysis, the intercept should be close to the surface tension value of water at 25° C, 71.97 dyne/cm.)

(b) Calculate the surface excess (the Gibbs' adsorption coefficient  $\Gamma$ ) for aminobutyric acid at the surface of water for each of these three concentrations (weight %).

(c) What is the area occupied by each molecule of aminobutyric acid at the water surface?

(d) Regarding your results, do you think that aminobutyric acid acts as a surfactant within this concentration range?

**Answers:** (a)  $\partial\gamma/\partial(\text{wt}\%) = -0.06015$  erg cm<sup>-2</sup> (wt%)<sup>-1</sup>; (b)  $\Gamma = 1.2 \times 10^{-11}$ ,  $2.27 \times 10^{-11}$ , and  $3.26 \times 10^{-11}$  mole cm<sup>-2</sup>; (c) the areas per molecule are 1383, 730, and 510 Å<sup>2</sup>; (d) Does aminobutyric acid significantly lower the surface tension of water?

14-18. The adsorption of proteins at the oil-water interfaces are of biologic interest because in cell membranes various proteins attached to polar lipid-bilayer regions control cellular aggregation and cellular growth.

The adsorption of bovine serum albumin (BSA) to a polar peanut oil-water interface varies with ionic strength and pH. At 30° C and ionic strength  $\mu = 0.1$ , the maximum adsorption (surface excess values) are  $\Gamma = 2.54$  mg m<sup>-2</sup> at pH 5, and  $\Gamma = 0.70$  mg m<sup>-2</sup> at pH 4. The isoelectric point of BSA is near 5.<sup>54</sup> Compute the area per molecule of BSA at the two different pH values and the limiting slope ( $d\gamma/d\ln c$ ). Why does A. the area per molecule of BSA, differ at these two pH values? *Hint:* Does protein conformation vary with pH? The molecular weight of BSA is about 69,000 daltons. You will need the Gibbs adsorption equation,  $\Gamma = -\frac{1}{RT} \left( \frac{d\gamma}{dc} \right)$ , and for the area per

molecule, A, you will need the equation  $A = 1/(N\Gamma)$ , where  $N$  is Avogadro's number and  $\Gamma$  is the surface excess. You will want to convert  $\Gamma$  (g/m<sup>2</sup>) into mole/m<sup>2</sup> using the molecular weight (g/mole) of BSA.

**Answer:** At pH 5,  $(d\gamma/d\ln c) = 9.28 \times 10^{-5}$  Nm;  $A = 45$  (nm<sup>2</sup>)/molecule. At pH 4,  $(d\gamma/d\ln c) = 2.5 \times 10^{-5}$  Nm;  $A = 160$  (nm<sup>2</sup>)/molecule = 16,400 Å<sup>2</sup>/molecule. Tanford et al.<sup>54</sup> calculated the area of bovine serum albumin at pH 4 using intrinsic viscosity and obtained 16,286 Å<sup>2</sup>/molecule.

14-19. The surface excess  $\Gamma$  in the limiting concentration range, B-D in Figure 14-14, page 375, for a nonionic surface active drug is  $5.45 \times 10^{-10}$  mole cm<sup>-2</sup> at 25° C. Compute the limiting slope,  $(d\gamma/d\ln c)$ , and the area per molecule for the drug. The relevant

equations are  $(d\gamma/d\ln c) = -\Gamma RT$  and for the area per molecule,  $A = 1/(N\Gamma)$ , where  $N$  is Avogadro's number.

**Answer:**  $(d\gamma/d\ln c) = -13.51$  dyne/cm; area per molecule =  $30.48 \times 10^{-16}$  cm<sup>2</sup>/molecule =  $30.48$  Å<sup>2</sup>/molecule

14-20. Korzacz et al.<sup>55</sup> studied the isotherms of surface pressure  $\pi$  versus area per molecule A for insoluble monolayers of dipalmitoylphosphatidyl choline on an aqueous substrate of pH 5.2. They obtained the following results (read from Figure 1 of their article):

Data for Problem 14-20

$\pi$ (mN/m)	60	40	20	6	4	2	1	0
$A \times 10^{-20}$ m <sup>2</sup>	40	44	50	52	68	94	95	96

Plot  $\pi$  against A as in Figure 14-18. For the several segments of the curve, extrapolate the line to the x-axis to obtain the limiting areas of the phase changes observed. Identify the phase changes that occur. Express the areas in nm<sup>2</sup> and in Å<sup>2</sup>.

**Answer:** Check your answers against Figure 1 of the article by Korzacz et al.<sup>55</sup> Extrapolating to the lower end of the curve yields an area/molecule  $A = 52 \times 10^{-20}$  m<sup>2</sup> =  $52$  Å<sup>2</sup>. Extrapolating to the end of the curve yields  $A = 96 \times 10^{-20}$  m<sup>2</sup> =  $96$  Å<sup>2</sup>.

14-21. When  $1 \times 10^{-4}$  cm<sup>3</sup> of stearic acid, dissolved in benzene, is placed on the surface of water in a trough, the stearic acid spreads over the surface and the benzene evaporates off. The monomolecular layer of acid that is formed covers an area of 400 cm<sup>2</sup>. Calculate the length in angstroms of the stearic acid molecules.

**Answer:** 25 Å

14-22. Stearic acid has a molecular weight of 284.3 g/mole and a density of 0.85 g/cm<sup>3</sup>. Using the data of Problem 14-21, compute the cross-sectional area of the acid molecule in square angstroms.

**Answer:** 22 Å<sup>2</sup>

14-23. When  $1 \times 10^{-4}$  cm<sup>3</sup> of myricyl alcohol dissolved in benzene was spread on the surface of water in a trough, the monomolecular layer of alcohol that formed when the benzene had evaporated covered an area of 250 cm<sup>2</sup>. Calculate the length in angstroms of the myricyl alcohol molecule and the cross-sectional area per molecule in square angstroms. Myricyl alcohol has a molecular weight of 453 and a density of 0.70 g/cm<sup>3</sup>.

**Answer:** 40 Å<sup>2</sup>; 27 Å<sup>2</sup>

14-24. By analogy of monomolecular films to a two-dimensional gas, the molecular weight of a substance can be obtained with the film balance using the equation  $\pi A = (w/M)RT$ . By plotting the product of the film pressure  $\pi$  and the area A against  $\pi$  and extrapolating to  $\pi = 0$ , a value of  $\pi A/w = 2.4 \times 10^6$  erg/g at 292.15° K was obtained for x grams of a synthetic gum. Compute the molecular weight M of the gum. (Note:  $R = 8.314 \times 10^7$  erg/mole deg.)

**Answer:** M = 10,121 g/mole

14-25. Insulin was spread as a film on the surface of an aqueous solution having a pH of 2.05 and an ionic strength of 0.01. The value of  $\pi A/w$  extrapolated to  $\pi = 0$  was obtained as  $4.02 \times 10^6$  erg/g at 292.15° K. Compute the molecular weight of insulin using the equation given in Problem 14-24.

**Answer:** 6042 g/mole

14-26. From the logarithmic form of the Freundlich isotherm, equation (14-50), page 380, using concentration, c, instead of pressure, p, a plot of  $\log(z/\pi)$  (y-axis) against  $\log c$  (x-axis), gives a straight line. When the value of c equals 1.0,  $\log c = 0$ , the y-intercept is  $\log(z/\pi) = \log k$ , from which the value of k is obtained. The  $\pi$  value is computed from the slope. The use of log-log graph paper allows one to read directly the k value from the y-intercept axis where the x-axis is c = 1. Caution: one cannot obtain the slope  $n$  from a direct reading on a log-log plot.

A newly synthesized steroid is adsorbed on activated charcoal at 37° C. Data are obtained for adsorption from a phosphate buffer solution at pH 7.4:

Data for Problem 14-26

Amount (mole) of steroid adsorbed per gram of charcoal, $z/m$	Equilibrium concentration, $c$ , of steroid (mole/liter)
$1.585 \times 10^{-4}$	$3.162 \times 10^{-6}$
$2.310 \times 10^{-4}$	$5.012 \times 10^{-6}$
$3.162 \times 10^{-4}$	$7.079 \times 10^{-6}$
$5.012 \times 10^{-4}$	$1.122 \times 10^{-4}$
$7.943 \times 10^{-4}$	$1.995 \times 10^{-4}$
$1.259 \times 10^{-3}$	$3.162 \times 10^{-4}$

(a) Plot  $z/m$  against  $c$  using log-log graph paper, and obtain  $k$  and  $n$ . Hint: Use 6 cycle  $\times$  6 cycle log-log graph paper because you will need to extrapolate the line to read the  $y$ -intercept at  $c = 1$ .

(b) Regress  $\log(z/m)$  against  $\log c$  and compute  $k$  and  $n$  from the intercept and the slope, respectively.

Answers: (a)  $n = 1.1$ ,  $k = 1.76$  liter/g; (b)  $n = 1.1$ ,  $k = 1.76$  liter/g  
14-27. The following data are obtained for the adsorption of timolol, an antihypertensive agent, from aqueous solution onto kaolin at 37° C.

Data for Problem 14-27\*

$z/m$ (mg adsorbed per g adsorbent)	$c$ (mg/100 mL)	$c/(z/m)$ (g/100 mL)
3.1	20	6.45
2.8	17	6.07
1.8	9	5.00
0.84	3.0	3.57

\*Data from B. C. Walker, B. Pharm. Thesis, University of Otago, New Zealand, 1976.

(a) Plot the data on log-log paper according to the Freundlich isotherm and evaluate  $n$  and  $k$  (equation (14-50)), using concentration,  $c$ , instead of pressure,  $p$ .

(b) Plot  $c/(z/m)$  ( $y$ -axis) against  $c$  ( $x$ -axis) according to the Langmuir plot as shown in Figure 14-25. Compute  $b$  and  $y_m$  according to the Langmuir equation (equation (14-58)). (The  $y_m$  value is calculated from the slope, and  $b$  is computed from the intercept.)

(c) What are the units on  $n$ ,  $k$ ,  $y_m$ , and  $b$ ?

Answer: (a) Using the 2-point formula and the Freundlich isotherm for slope,  $1/n$ ; and reading directly from the  $y$ -intercept on the log-log plot for  $k$ , one obtains  $1/n = 0.685$  (dimensionless) and  $k = 0.4$  mg/g.

The units on  $k$  are taken as mg/g because at the intercept the Freundlich equation requires that  $c = 1$  mg/mL or in logarithmic form  $\log c = \log 1 = 0$ . Then  $\log(z/m) = \log k + (1/n)\log c = \log k + 0$  and  $\log(z/m) = \log k$ . Therefore  $(z/m) = k$  and  $k$  has the same units, mg/g, as has  $z/m$ .

Using regression analysis on the Freundlich log-log equation,  $\log(z/m) = -0.4045 + 0.6906 \log c$ ;  $r^2 = 0.9999$ . The slope =  $1/n = 0.6906$  (dimensionless) and from the intercept,  $\log k = -0.4045$ ;  $k = \text{antilog}(-0.4045) = 0.394$  mg/g.

(b) Using the 2-point formula and the Langmuir isotherm for  $1/y_m$ , the slope:

$$1/y_m = \frac{(c/y_1) - (c/y_2)}{(c_1) - (c_2)} = \frac{6.45 - 3.57}{20 - 3} = 0.1694 \text{ g/mg}$$

$$y_m = 1/0.1694 = 5.903 \text{ mg/g}$$

For the intercept, one reads directly from the graph to obtain  $1/(by_m) = 3.35$  g/dl.  $1/b = \text{Intercept} \times y_m = 3.35 \text{ g/dl} \times 5.903 \text{ mg/g}$   
 $1/b = 19.78 \text{ mg/dl}$ ;  $b = 0.051 \text{ dl/mg}$ .

Using regression analysis on the Langmuir equation:

$$c/y = 1/(by_m) + (1/y_m)c;$$

$$c/y = 3.247 + 0.1653 c; r^2 = 0.978$$

$$\text{Slope} = 0.1653 \text{ g/mg} = 1/y_m; y_m = 6.0496 \text{ mg/g}$$

$$\text{Intercept} = 1/(by_m) = 3.247 \text{ g/dl}$$

$$1/b = 3.247 \times 6.0496 = 19.643 \text{ mg/dl}$$

$$b = 0.051 \text{ dl/mg}$$

14-28. Sellers et al.<sup>66</sup> reported the following constants for adsorption of various drugs by activated charcoal at 37° C:

Data for Problem 14-28

Drug	$y_m$	$b$	Tablet strength (mg)
Aspirin	262	0.012	300
Chlordiazepoxide	157	0.010	25
Diazepam	136	0.010	5

In cases of drug overdose and poisoning, one practice is to administer an aqueous slurry (suspension) of 1 g activated charcoal/kg body weight as an antidote. If the patient weighs 72 kg, how many tablets of each type is such a slurry capable of handling?

Answer: Aspirin, 63 tablets; chlordiazepoxide, 452 tablets; and diazepam, 1958 tablets.

14-29. Sturgeon et al.<sup>67</sup> studied the adsorption of doxorubicin, an anthracycline antibiotic, on tribasic calcium phosphate where  $c$  is the concentration of doxorubicin and  $x$  is its amount in mg adsorbed per mg of the adsorbent.

Data for Problem 14-29

$c/(z/m) \times 10^3$ (g/mL)	$c \times 10^5$ , mg/mL
1.25	2.0
2.25	3.5
2.90	4.5
3.40	5.3

(a) Plot the Langmuir isotherm and evaluate  $y_m$ , the maximum binding capacity in mg/g, and  $b$ , the affinity or binding constant, in mL/mg.

(b) Tribasic calcium phosphate is not used as an antidote in poisoning. Why did the authors choose to study the adsorption of doxorubicin on tribasic calcium phosphate?

Answers: (a)  $y_m = 1.56$  mg/g,  $b = \text{infinite}$ ; (b) bone tissue from patients receiving extended doxorubicin therapy were found to be stained by long-term therapy with this drug; the authors used solid tribasic calcium phosphate as a model to approximate adsorption of the drug by bone tissues samples.

14-30. From the affinity or binding constant,  $b$ , obtained from the Langmuir isotherms, the standard free energy of adsorption can be computed as

$$\Delta G^\circ = -RT \ln b$$

because the affinity  $b$  is an equilibrium constant.<sup>68</sup> The Langmuir constants for the adsorption of nadolol, an adrenergic drug, onto magnesium trisilicate were determined at two temperatures:

Data for Problem 14-30

T (°C)	$y_m$ (mg/g)	$b$	
		(liter/g)	(liter/mole)
37° C	68.2	0.33227	102.14
50° C	53.8	0.34168	105.457

(a) Compute  $\Delta G^\circ$  at the two temperatures; (b) use the integrated form of the van't Hoff equation and compute  $\Delta H^\circ$ . (c) Compute  $\Delta S^\circ$  at 37° and 50° C. (d) Using the nonlinear form of the Langmuir equation,

i.e.,  $z/m = \frac{y_{\infty}bc}{1 + bc}$ , together with the parameters  $y_{\infty}$ , mg/g and  $b$  (liter/g) given in the table at the two temperatures, compute  $z/m$  for the following concentrations,  $c$ : 0.5, 5, 20, 50 mg/100 mL. Plot the Langmuir isotherms at the two temperatures on the same graph.

**Answers:** (a)  $\Delta G^\circ = -2.9$  kcal/mole at 37° C and  $-3.0$  kcal/mole at 50° C; (b)  $\Delta H^\circ = 490$  cal/mole; (c)  $\Delta S^\circ(37^\circ) = 10.8$  u.e. and  $\Delta S^\circ(50^\circ) = 10.8$  u.e.; (d)  $z/m(37^\circ \text{ C}) = 8.3$  mg/g; at 50° C,  $z/m = 7.9$  mg/g at  $c$  (mg/100 mL) = 0.5

14-31. Use the data for the surface tension,  $\gamma$ , of glycerol at three temperatures, 20°, 90° and 150° C from a handbook of physics and chemistry,\* viz: 63.4, 58.6, and 51.9 erg/cm<sup>2</sup>. (a) Plot  $\gamma$  versus temperature (°K on the horizontal axis). Use regression analysis or a tangent drawn at each temperature to obtain the slope  $(\partial\gamma/\partial T)_p = -S^\circ$ . (b) Knowing  $\gamma$  and the entropy of the surface,  $S^\circ$ , calculate the surface enthalpy  $H^\circ$  at each of the three temperatures using the appropriate equation, page 365. Does  $H^\circ$  appear to remain constant over this temperature range? (c) What is the meaning of  $H^\circ$  in surface chemistry? How do you interpret (explain) the entropy value obtained?

**Partial Answers:** (b)  $S^\circ = 0.0879$  erg cm<sup>-2</sup> deg<sup>-1</sup>;  $H^\circ = 89.17, 90.52, \text{ and } 89.09$  erg cm<sup>-2</sup> at 20°, 90°, and 150° C, respectively. (c) See Harkins<sup>59</sup> for an interpretation of  $H^\circ$  and  $S^\circ$ .

14-32. Use the following data to obtain the entropy and formation of a surface and the surface enthalpy at 20°, 100°, and 200° C for carbon tetrachloride.

Data for Problem 14-32\*

T (°K)	293.15	373.15	473.15
$\gamma$ (dyne/cm)	26.95	17.26	6.53

Calculate  $S^\circ$  from the slope of a plot of  $\gamma$  against  $T$  and using this value, compute  $H^\circ$  at the three temperatures.

**Partial Answer:**  $S^\circ = 0.113$  erg cm<sup>2</sup> deg<sup>-1</sup>;  $H^\circ$  at 20° C = 60.08 erg cm<sup>2</sup>.

14-33. Provided that the enthalpy of a surface  $H^\circ$  does not appreciably vary over the temperature range under study,  $H^\circ$  can be computed from the intercept of a plot of  $\gamma$  against  $T$ , according to the equation

$$\gamma = H^\circ + T \left( \frac{\partial \gamma}{\partial T} \right) = H^\circ - TS^\circ$$

where  $S^\circ$ , the surface entropy, is the slope of the line.

Use the data for the surface tension of water found between -8° C (265.15° K) and 100° C (373.15° K) from CRC\* or a comparable table of data, together with linear regression analysis to obtain  $H^\circ$  and  $S^\circ$ .

**Answer:**  $S^\circ = 0.1647$  erg cm<sup>-2</sup> deg<sup>-1</sup>;  $H^\circ = 120.9$  erg cm<sup>-2</sup>

14-34. The contact angle  $\theta$  of a liquid on a solid surface can be evaluated from the Girifalco-Good-Fowkes-Young equation<sup>60</sup> and Hiemenz,<sup>4</sup> pages 339 to 345:

$$(1 + \cos \theta)\gamma_L = 2\sqrt{\gamma_s^d \gamma_L^d}$$

where  $\gamma_L$  is the total (dispersion + polar) surface tension of the liquid and  $\gamma_s^d$  and  $\gamma_L^d$  are the surface tension of the solid and the liquid due to the dispersion (weak electrostatic or London force) components,  $d$ . For relatively nonpolar liquids  $\gamma_L = \gamma_L^d$ .

(a) Compute the contact angles,  $\theta$ , of water, ethylene glycol, and benzene on teflon. The surface tensions of water, ethylene glycol, and benzene are 72.8, 49, and 29 dyne/cm, respectively, and the corresponding  $\gamma_s^d$  are 21.8, 28.6, and 29 dyne/cm;  $\gamma_s^d$  for teflon is 19.5 dyne/cm at 25° C.

(b) What significance do these values have? See Sharma and Ruckenstein<sup>60</sup> and Hiemenz<sup>4</sup> for the meaning of these values.

**Answer:** (a)  $\theta$  (water) = 115.7°,  $\theta$  (ethylene glycol) = 92°,  $\theta$  (benzene) = 50.2°

14-35. The interfacial tension between oil and water or an aqueous solution can be computed from the surface tension of the pure components by means of the Girifalco-Fowkes equation:

$$\gamma_{o,aq} = \gamma_o + \gamma_{aq} - 2\sqrt{\gamma_o^d \gamma_{aq}^d}$$

where the subscripts  $o$  and  $aq$  stand for the oil and aqueous phases and the superscript  $d$  signifies the dispersion or weak electrostatic interaction part of the surface tension of the aqueous phase.<sup>61</sup>

Compute the interfacial tension between a 10% by volume aqueous solution of ethylene glycol monomethyl ether ( $\gamma_{aq} = 56.9$  mJ/m<sup>2</sup> and  $\gamma_{aq}^d = 22$  mJ/m<sup>2</sup>) and paraffin oil ( $\gamma_o = 30.8$  mJ/m<sup>2</sup>). **Note:** mJ/m<sup>2</sup> is read, "millijoules per square meter." Also note that for a paraffin oil  $\gamma_s^d = \gamma_o$  because the paraffin oil is a nonpolar substance.

**Answer:** 35.6 mJ/m<sup>2</sup>. (Note that the numerical value 35.6 for the surface tension in the SI units of mJ/m<sup>2</sup> is the same as the numerical value for surface tension in the cgs system, namely 35.6 erg/cm<sup>2</sup>.)

\*The values are found using the data from the CRC Handbook of Physics and Chemistry, 63rd Edition, 1982, pp. F-35-37.