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INTERFACIAL PHENOMENA

15

CHAPTER OBJECTIVES

At the conclusion of this chapter the student should be able to:

1. Differentiate among different types of interfaces and describe relevant examples in the pharmaceutical sciences.
2. Understand the terms surface tension and interfacial tension and their application in pharmaceutical sciences.
3. Appreciate the different methods of surface and interface tension measurements.
4. Calculate surface and interface tensions, surface free energy, its changes, work of cohesion and adhesion, and spreading coefficient for different types of interfaces.
5. Understand the mechanisms of adsorption on liquid and solid interfaces.
6. Classify surface-active agents and appreciate their applications in pharmacy.
7. Differentiate between different types of monolayers and recognize basic methods for their characterization.
8. Recognize the electric properties of interfaces and the effects of electrolytes.

Several types of interface can exist, depending on whether the two adjacent phases are in the solid, liquid, or gaseous state (Table 15-1). For convenience, these various combinations are divided 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. Although solid–solid interfaces have practical significance in pharmacy (e.g., 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 regions 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 this chapter, the reader should appreciate that every surface is an interface. Thus, a tabletop forms a gas–solid interface with the atmosphere above it, and the surface of a raindrop constitutes a gas–liquid interface.

The symbols for the various interfacial tensions are shown in the second column of Table 15-1, where the subscript L stands for liquid, V for vapor or gas, and S for solid. Surface and interfacial tensions are defined later.

Because every physical entity, be it a cell, a bacterium, a colloid, a granule, or a human, possesses an interface at its boundary with its surroundings, the importance of the present topic is self-evident. Interfacial phenomena in pharmacy and medicine are significant factors that affect adsorption 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-active agent lining the alveoli of the lung are responsible for the efficient operation of this organ.[1–3] Several authors have 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 liquid are

KEY CONCEPT

INTERFACES

When phases exist together, the boundary between two of them is known as 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*. If a liquid and its vapors exist together in the same container, the liquid takes the bottom part of the container. The remainder of the container is filled up by the liquid vapor, which, as with any gas, has a tendency to take all available space. Molecules in both the liquid and the gas are in constant motion and can move from the liquid into the vapor and back from the vapor to the liquid. However, the distinct boundary between the vapor and the liquid is preserved under constant temperature, and the exchange of molecules does not destroy the equilibrium between these two phases due to the labile (i.e., dynamic) character of this boundary.

TABLE 15-1
Classification of Interfaces

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

surrounded in all directions by other molecules for which they have an equal attraction, as shown in **Figure 15-1**. 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 toward the bulk, as shown in **Figure 15-1**. Such a force pulls the molecules of the interface together and, as a result, contracts the surface, resulting in a *surface tension*.

This "tension" in the surface is the force per unit length that must be applied *parallel* to the surface as to counterbalance the net inward pull. This force, the surface tension, has the units of dynes/cm in the cgs system and of N/m in

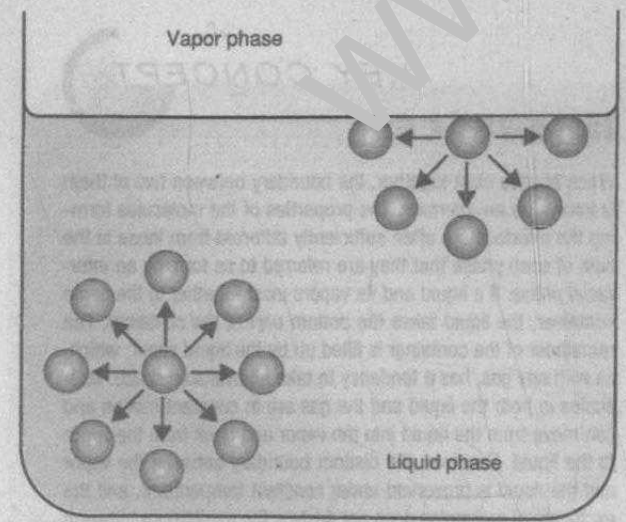

FIG. 15-1 Representation of the unequal attractive forces acting on molecules at the surface of a liquid as compared with molecular forces in the bulk of the liquid.

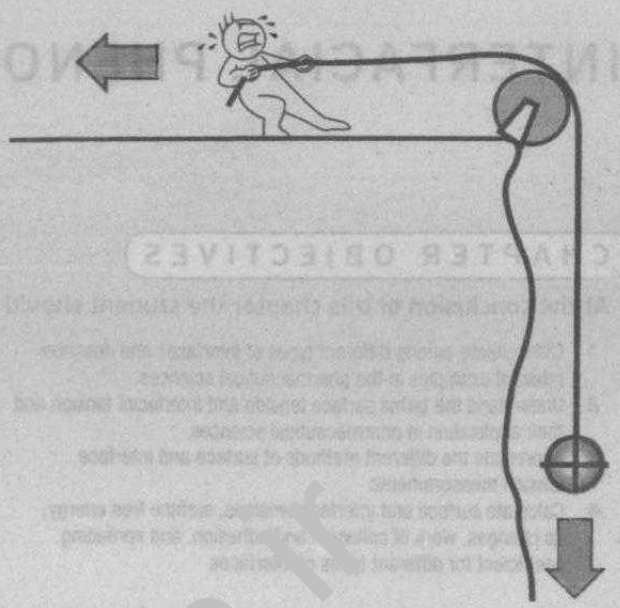

FIG. 15-2 Visualization of surface tension as akin to a person lifting a weight up the side of a cliff by pulling the rope in a horizontal direction.

the SI system. It is similar to the situation that exists when an object hanging over the edge of a cliff on a length of rope is raised up and held by a man holding the rope and walking away from the edge of the top of the cliff. This analogy to surface tension is sketched in **Figure 15-2**.

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 dynes/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, γ_{LL}, between two solids, γ_{SS}, and at a liquid–solid interface, γ_{LS}. The term *surface tension* is reserved for liquid–vapor, γ_{LV}, and solid–vapor, γ_{SV}, tensions. These are often written simply as γ_L and γ_S, respectively. 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 representative surface and interfacial tensions are listed in **Table 15-2**.

Surface tension as a force per unit length can also be illustrated by means of a three-sided wire frame across which a movable bar is placed (**Fig. 15-3**). 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 tension. The surface tension, γ, 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

TABLE 15-2

Surface Tension and Interfacial Tension (Against Water) at 20°C[a]

Substance	Surface Tension (dynes/cm)	Substance	Interfacial Tension (dynes/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
Caster 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		

[a]From P. Becher, *Emulsions: Theory and Practice*, 2nd Ed., Reinhold, New York, 1962, and other sources.

with the film. Because 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,

$$\gamma = f_b/2L \tag{15-1}$$

where f_b is the force required to break the film and L is the length of the movable bar.

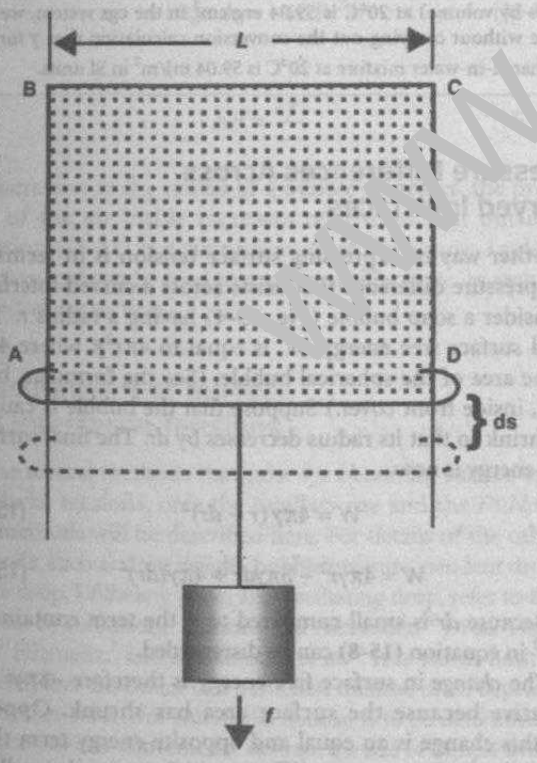

FIG. 15-3 Wire-frame apparatus used to demonstrate the principle of surface tension.

EXAMPLE 15-1

Calculating the Surface Tension of Water

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 move a molecule from the inner layers to the surface, work needs to be done against the force of surface tension. In other words, each molecule near the surface of liquid possesses a certain excess of potential energy as compared to the molecules in the bulk of the liquid. The higher the surface of the liquid, the more molecules have this excessive potential energy. Therefore, if the surface of the liquid increases (e.g., when water is broken into a fine spray), the energy of the liquid also increases. Because this energy is proportional to the size of the free surface, it is called a surface free energy. Each molecule of the liquid has a tendency to move inside the liquid from the surface; therefore, the liquid takes form with minimal free surface and with minimal surface energy. For example, liquid droplets tend to assume a spherical shape because a sphere has the smallest surface area per unit volume.

To increase the surface of the liquid without any additional changes in the liquid state, in particular without changes in liquid temperature, work must be done against the surface tension. To evaluate the amount of work in increasing the surface area, we can write equation (15-1) as $\gamma \times 2L = f$. When the bar is at a position AD in Figure 15-3 and a mass is added to extend the surface by a distance ds, the work dW (force multiplied by distance) is

$$dW = f \times \text{ds} = \gamma \times 2L \times \text{ds}$$