Unit III

Surface and interfacial phenomenon

Surface free energy:

The situation shown in Fig describe that free energy is present in the form of tension at the surface. Tension at the surface is helpful in maintaining the minimum surface possible. This energy is called as surface free energy. It can be defined, as the work required in increasing the area by one cm^2. The surface free energy can be derived from the following illustration.
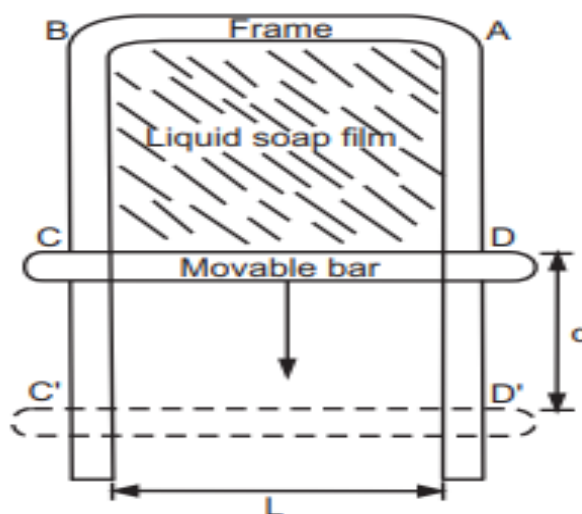

Figure 3.5: Wire Frame Apparatus

ABCD is a three-sided frame with a movable bar CD of length L. A soap film is formed over the area ABCD. Applying a force F to movable bar, the film stretches to the downward. To break the film some force is required. If the applied

force is less than what is required to break the film then the film retract due to surface tension. If the force F is applied on a movable bar CD, it shifts by a distance d to C'D'. The work done W is expressed as;

$$W = F \times d$$

While stretching of the film the force acts against the surface tension of the liquid as it try to contract the liquid. The soap film has liquid–gas interface. The total length of contact of the film is equal to double length of the bar because film has two surfaces on either side. Therefore, force acting on surface is expressed mathematically as

$$F = \gamma \times 2L$$

Substituting values of downward force F, in above equation, gives;

$$W = \gamma \times 2L \times d$$

The quantity 2L is equal to increased surface area ΔA produced by extending the film. Then the equation above changes to:

$$W = \gamma \times \Delta A \text{ or}$$

$$\Delta G = \gamma \times \Delta A$$

Where, W is work done or increased surface energy expressed in ergs.

In the thermodynamic sense any form of energy can be split into two factors namely, intensity factor and capacity factor. In film stretching surface tension is the capacity factor. The above equation is applied in gas adsorption studies on the solid surfaces, in studying physical instability of suspensions and thermodynamic instability of emulsions.

The dimensional analysis of work energy theorem shows that the unit of surface tension (N/m or dyne/cm) is equivalent to J/m^2 . This means surface tension also can be considered as surface free energy.

Pressure Differences Across Curved Interfaces:

Another way of expressing surface tension is in terms of the pressure difference that exists across a curved interface.
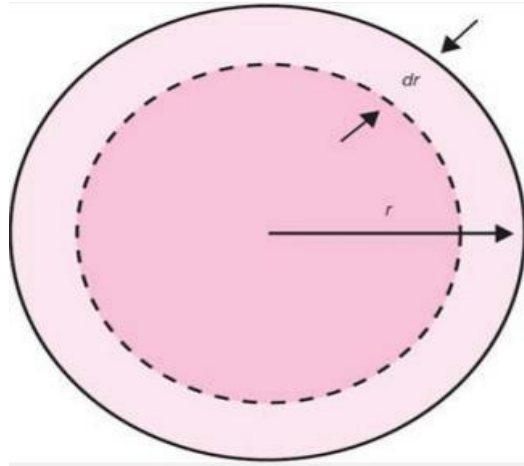
Consider a soap bubble having a radius r in Fig.

Figure: Schematic representation of the pressure difference across the curved surface of a soap bubble.

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.

Suppose that the bubble is caused to shrink so that its radius decreases by dr.

The final surface free energy is now

$$W = 4\pi r(r\text{-}dr)^2$$

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

Because dr is small compared to r, the term containing $(dr)^2$ in the above equation can be disregarded. The change in surface free energy is therefore $-8\pi\gamma r$ dr, negative because the surface area has shrunk. Opposing this change is an equal and opposite energy term that depends on the pressure difference, ΔP, across the wall of the bubble. Because pressure is a force per unit area, or force = pressure $\times$ area, the work change brought about by a decrease in radius dr is

$$W = \Delta P \times 4\pi r^2 \times -dr$$

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

$$-8\pi\gamma r dr = -4\Delta P r^2 dr \text{ (or)}$$

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

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

Prepared by:

Sridevi Murugesan

Department of Pharmaceutics

SNS College of Pharmacy and Health Sciences