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## SURFACE AND INTERFACIAL PHENOMENON

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### BP302T- UNIT-III

**Surface and interfacial phenomenon:** Liquid interface, surface & interfacial tensions, surface free energy, measurement of surface & interfacial tensions, spreading coefficient, adsorption at liquid interfaces, surface active agents, HLB Scale, solubilisation, detergency, adsorption at solid interface.

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### Introduction

When phases exist together, the boundary between two of them is known as an interface. Surface is the term used to describe either a gas-solid or a gas-liquid 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 [1]. 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.

### Liquid interface

Different types of interface can exist depending on whether the two adjacent phases are in the solid, liquid, or gaseous state. For convenience, these various combinations are divided into two groups such as liquid interfaces and solid interfaces. Solid interfaces will deal with systems containing solid–gas and solid–liquid interfaces. In the liquid state, the cohesive forces between adjacent molecules are well developed. Molecules in the bulk liquid are surrounded in all directions by other molecules for which they have an equal attraction. But 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. There are various interfaces exist. The classification is shown in Table 1:

**Table 1: Classification of Interfaces**

Phase	Types and	Examples of Interfaces
Gas-Gas	No interface possible	.....
Gas-Liquid	Liquid interface	Body of water exposed to atmosphere
Gas-Solid	Solid surface	Table top
Liquid-Liquid	Liquid-Liquid interface	Emulsion
Liquid-Solid	Liquid-Solid interface	Suspension
Solid-Solid	Solid-Solid interface	Powder particles

**Surface and interfacial tensions**

The tension of the surface film of a liquid caused by the attraction of the particles in the surface layer by the bulk of the liquid, which tends to minimize surface area is known as surface tension. Molecules in the bulk liquid have an equal attraction because in all directions [2] by other molecules are surrounded. Molecules at the surface (i.e., at the liquid–air interface) creates attractive cohesive forces. Other liquid molecules that are situated below and adjacent to them generate adhesive forces of attraction with the molecules constituting the other phase involved in the interface. The adhesive force of attraction is minimum in the case of the liquid–gas interface. The net result of the molecules at the surface of the liquid experience an inward force toward the bulk. The force pulls the molecules of the interface together, resulting contracts the surface. The force per unit length is the surface tension which is applied parallel to the surface so as to counterbalance the net inward pull. Hence the cohesive forces between liquid molecules are responsible for the phenomenon of surface tension.

The interfacial tension is between two immiscible liquids arises as a result of imbalance of forces. It is the force per unit length existing at the interface between two immiscible liquid phases. 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. Generally 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. The unit of surface tension and interfacial tension is shown in Table 2 and some examples are shown in Table 3.

**Table 2: Units surface tension and interfacial tension**

Force	CGS system	SI system
Surface tension	dynes/cm	N/m
Interfacial tension	dynes/cm	N/m

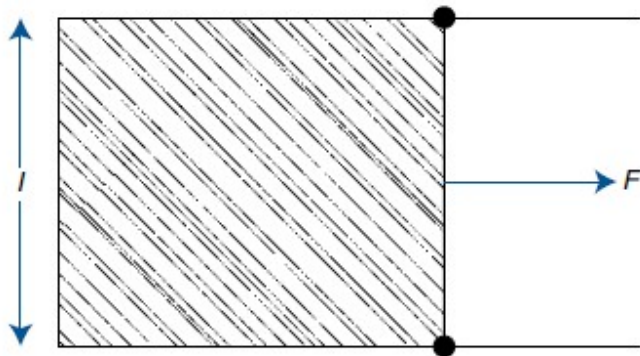
**Table 3: The surface tensions of some common liquids and their interfacial tensions against water at 20°C**

Liquids	Surface tension (dynes/cm)	Interfacial tensions against water (dynes/cm)
Water	72	-----
n-Octanol	27	8.5
CCl <sub>4</sub>	27	45
Olive oil	36	33
n-Hexane	18	51

**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. Surface free energy describes the excess energy [3] that the surface has compared to the bulk of the material. This energy is proportional to the size of the free surface; it is called a surface free energy.

Let us consider a rectangular wire with one movable side (Fig. 1). Assume further that by dipping this wire into a liquid, a film of liquid will form within the frame when it is removed and exposed to the air. As seen earlier in Fig. 1, when it comes in contact with air, the liquid surface will tend to contract with a force  $F$  as molecules leave the surface for the bulk. To keep the movable side in equilibrium, an equal force must be applied to oppose this tension in the surface. The surface tension  $\gamma$  of the liquid may be defined as  $F/2l$ , where  $2l$  is the distance of surface over which  $F$  is operating. The factor 2 arises out of considering two surfaces, top and bottom.



**Fig. 1: A movable wire frame containing a film of liquid being expanded with a force F**

Upon expansion of the surface by a very small distance,  $\Delta x$  the work done (W) is

$$W = F\Delta x \dots\dots\dots (1)$$

and, therefore,

$$W = \gamma 2l\Delta x \dots\dots\dots (2)$$

Since

$$\Delta A = 2l \Delta x \dots\dots\dots (3)$$

where  $\Delta A$  is the change in area due to the expansion of the surface, it may be concluded that

$$W = \gamma \Delta A \dots\dots\dots (4)$$

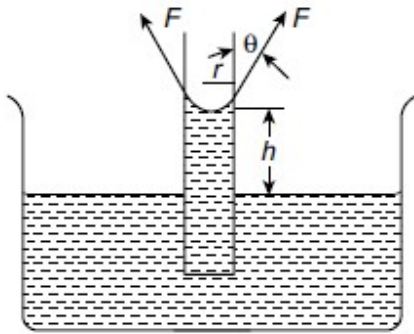
where W is the work done, or surface free energy increase, expressed in ergs,  $\gamma$  is the surface tension in dynes/cm, and  $\Delta A$  is the increase in area in  $\text{cm}^2$ .

**Measurement of surface & interfacial tensions**

1. Capillary Rise Method
2. The DuNouy Ring Method
3. Drop count (Drop weight) method
4. Wilhelmy plate methods

**1. 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. Because 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. By measuring this rise in a capillary [4], 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.



**Fig. 2: Capillary rise for a liquid exhibiting a contact angle ( $\theta$ )**

If the contact angle of liquid is not 0 (Fig. 2), except the vertical component of  $F$ , which opposes the weight of the column, is  $F \cos \theta$  and, therefore surface tension is given by

$$\gamma = \frac{rdgh}{2\cos\theta} \dots\dots\dots(5)$$

If the contact angle of liquid is 0 then surface tension is given by

$$\gamma = \frac{1}{2} rdgh \dots\dots\dots (6)$$

Where

$r$  = Radius of capillary tube

$d$  = Density of the liquid

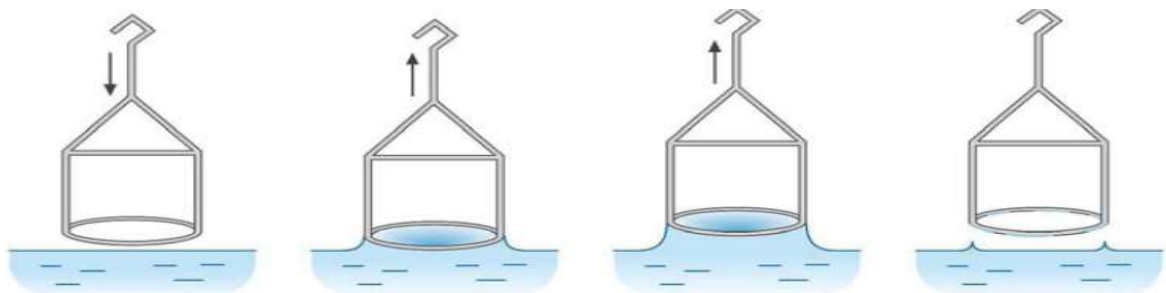
$h$  = Height of the liquid rise

$g$  = Acceleration due to gravity

$\gamma$  = Surface tension of liquid.

**2. The DuNouy Ring Method**

The DuNouy tensiometer [5] 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



**Fig. 3: Schematic of the DuNouy ring pulling a column of water above the surface**

$$\gamma = \frac{\text{Dial reading in dynes}}{2 \times \text{Ring circumference}} \times \text{Correction factor} \dots \dots \dots (7)$$

In effect, the instrument measures the weight of liquid pulled out of the plane of the interface immediately before the ring becomes detached (Fig. 3). A correction factor is necessary in equation 7 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.

**3. Drop count (Drop weight) method**

In this method stalagmometer is used. Surface tension measures the strength of the cohesive forces of liquids. The lower the surface tension of the liquid, the smaller the size of drops formed. Then more number of drops are formed for the given volume of liquid when compared to water. Therefore simply counting the number of drops for unknown liquid and water is sufficient to calculate the surface tension. This is applicable when the densities of liquids are same, as the falling of drops depends on their weights. Hence drop weight method can be used. The ratio of the weight of a drop of the liquid (X1) to that of a reference substance (X2) falling from the same capillary orifice is equal to the ratio of their surface tensions.

**Drop count method derivation**

If  $\gamma_1$  and  $\gamma_2$  are the surface tensions of liquid and reference standard (water) respectively then

$$\frac{\gamma_1}{\gamma_2} = \frac{X_1}{X_2} \dots \dots \dots (8)$$

The weight of single drop is equal to  $vd/n$  where  $v$  is the volume of liquid delivered,  $n$  is number of drops and  $d$  is density.

Hence the above equation becomes

$$\frac{\gamma_1}{\gamma_2} = \frac{\frac{vd}{n_1}}{\frac{vd_2}{n_2}} \dots \dots \dots (9)$$

The same volume of liquid and reference substance is allowed to flow from the same stalagmometer then the above equation becomes

$$\frac{\gamma_1}{\gamma_2} = \frac{d_1}{d_2} \times \frac{n_2}{n_1} \dots\dots\dots (10)$$

Rearranging the above equation

$$\gamma_1 = \frac{d_1}{d_2} \times \frac{n_2}{n_1} \times \gamma_2 \dots\dots\dots(11)$$

**Where**

$d_1$  = Density of experimental liquid

$d_2$  = Density of water

$\gamma_2$  = Surface tension of water 72 dynes/cm

**Drop weight method derivation**

The ratio of the weight of a drop of the liquid ( $W_1$ ) to the reference substance ( $W_2$ ) falling from the same capillary orifice is equal to the ratio of their surface tensions.

If  $\gamma_1$  and  $\gamma_2$  are the surface tensions of experimental liquid and reference standard respectively then

$$\frac{\gamma_1}{\gamma_2} = \frac{W_1}{W_2} \dots\dots\dots (12)$$

The weight of the drop in mg of a test liquid ( $W_1$ ) =  $2\pi r \gamma_1$

The weight of the drop in mg of a reference liquid ( $W_2$ ) =  $2\pi r \gamma_2$

As the same apparatus is used for both the liquids the correction factor is same assuming that the drop volumes are not different.

Hence

$$\frac{W_1}{W_2} = \frac{2\pi r \gamma_1}{2\pi r \gamma_2} \dots\dots\dots (13)$$

Rearranging the equation

$$\gamma_1 = \frac{W_1}{W_2} \times \gamma_2 \dots\dots\dots (14)$$

Where

$\gamma_1$  = Surface tension of experimental liquid/test liquid

$\gamma_2$  = Surface tension of water

N.B. The surface tension of water is taken as 72 dyne/cm

**4. Wilhelmy plate methods**

The apparatus consists of a thin mica, glass or platinum plate attached to a suitable balance. When used as a detachment method, the plate is immersed in the liquid, and the liquid container is gradually lowered. The reading on the balance immediately prior to detachment is noted. The

detachment force is equal to the surface tension multiplied by the perimeter of the surface detached:

$$W_L - W = 2(L + T)\gamma \dots\dots\dots(15)$$

Where

$W_L$  is the reading on the balance prior to detachment,  $W$  is the weight of the plate in air and  $L$  and  $T$  are the length and the thickness of the plate, respectively. Immersion of the plate into the lower of two liquids in a container and subsequent detachment will give the interfacial tension.

### **Spreading Coefficient (S)**

The ability of one liquid to spread over another can be assessed in terms of the spreading coefficient. It is observed for instance, that some liquids, when placed in contact with other liquid or solid surfaces, will remain retracted in the form of a drop while other liquids may exhibit a tendency to spread and cover the surface of this liquid or solid. It is apparent that the individual phases will exhibit a tendency to minimize the area of contact with other phases, thus leading to phase separation.

### **Work of adhesion (W<sub>a</sub>)**

The work of adhesion, which is the energy required to break the attraction between the unlike molecules. The work of adhesion is defined as the free energy/cm<sup>2</sup> required to separate two phases at their boundary and is equal but opposite in sign to the free energy/cm<sup>2</sup> released when the interface is formed.

### **Work of cohesion (W<sub>c</sub>)**

The work of cohesion is required to separate the molecules of the spreading liquid. The work of cohesion for a pure substance is the work/cm<sup>2</sup> required to produce two new surfaces, as when separating different phases, but now both surfaces contain the same molecules. This is equal and opposite in sign to the free energy/cm<sup>2</sup> released when the same two pure liquid surfaces are brought together and eliminated.

When the work of adhesion between two substances A and B exceeds the work of cohesion for one substance (e.g. B), spontaneous spreading of B over the surface of A should occur with a net loss of free energy equal to the difference between  $W_a$  and  $W_c$ . If  $W_c$  exceeds  $W_a$ , no spontaneous spreading of B over A can occur. The difference between  $W_a$  and  $W_c$  is known as the spreading coefficient,  $S$ . Only when  $S$  is positive spreading will occur.



The values for  $W_a$  and  $W_c$  may be expressed in terms of surface and interfacial tensions, when one considers that upon separation of two phases A and B,  $\gamma_{AB}$ , the interfacial tension is lost but that  $\gamma_A$  and  $\gamma_B$  are surface tensions of A and B respectively.

$W_a$  is given by

$$W_a = \gamma_A + \gamma_B - \gamma_{AB} \dots\dots\dots (16)$$

$W_c$  is given by

$$W_c = 2\gamma_A \text{ or } 2\gamma_B \dots\dots\dots (17)$$

for B spreading on the surface of A. Therefore,

$$S_B = W_a - W_c \dots\dots\dots (18)$$

Or

$$S_B = \gamma_A + \gamma_B - \gamma_{AB} - 2\gamma_B \dots\dots\dots (19)$$

Or

$$S_B = \gamma_A - (\gamma_B + \gamma_{AB}) \dots\dots\dots (20)$$

**Adsorption at liquid interfaces [6]**

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 an 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 is 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 are 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.

## Types of Monolayer at Liquid Surfaces

Absorbed 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. For example amyl alcohol may be said to form a soluble monolayer on water, whereas 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.

Liquid interfaces are affected by certain parameters such as surface tension, 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 the concentration of amphiphile in the bulk of the liquid. It is relatively easy with soluble monolayers to measure surface tension and concentration to compute the surface excess. With insoluble monolayers, concentration is taken to be zero, whereas surface tension and surface excess can be obtained directly. This study involves Gibbs adsorption isotherm.

The number of molecules per unit area of the surface can be estimated using Gibbs equation. The Gibbs equation is expressed as

$$\Gamma = \frac{-a}{RT} \left[ \frac{d\gamma}{da} \right] \dots \dots \dots (21)$$

Where

$\Gamma$  = Moles of solute adsorbed / unit area or surface excess

R = Ideal gas constant

T = Absolute temperature

$d\gamma$  = Change in surface tension

$da$  = Change in solute activity

Surface excess is the amount of the amphiphile per unit area of surface in excess of that in the bulk liquid.

For dilute solutions of nonelectrolytes activity term is replaced by concentration (c)

Hence the equation becomes

$$\Gamma = \frac{-c}{RT} \left[ \frac{d\gamma}{dc} \right] \dots \dots \dots (22)$$

N.B. Cetyl alcohol would form an insoluble film on the water. The addition of amphiphiles to a liquid leads to reduction in surface tension and these molecules adsorbed as monolayer this phenomenon first expressed quantitatively by Gibbs by the above equation 22.

### **Surface active agents (SAA)**

Molecules and ions that are absorbed [7] at interfaces are termed SAA or surfactants. Surfactants have two distinct regions in their chemical structure, one of which is water-liking or hydrophilic and the other of which is water-hating or hydrophobic. These molecules are referred to as amphiphilic or amphipathic molecules or simply as surfactants or SAA. An alternative expression is amphiphile, which suggests that the molecule or ion has a certain affinity for both polar and nonpolar solvents.

### **Reduction of surface and interfacial tension**

When surfactants are dissolved in water they orientate at the surface so that the hydrophobic regions are removed from the aqueous environment. The reason for the reduction in the surface tension when surfactant molecules adsorb at the water surface is that the surfactant molecules replace some of the water molecules in the surface and the forces of attraction between surfactant and water molecules are less than those between two water molecules, hence the contraction force is reduced.

Surfactants will also adsorb at the interface between two immiscible liquids such as oil and water and will orientate themselves with their hydrophilic group in the water and their hydrophobic group in the oil. The interfacial tension at this interface, which arises because of a similar imbalance of attractive forces as at the water surface, will be reduced by this adsorption.

### **Classification**

Depending on their charge characteristics the surface-active molecules may be anionic, cationic, zwitterionic (ampholytic) or non-ionic.

#### **Anionic Agents**

The most commonly used anionic surfactants are those containing carboxylate, sulfonate, and sulfate ions. Those containing carboxylate ions are known as soaps and generally are prepared by the saponification of natural fatty acid glycerides in alkaline solution. The most common cations associated with soaps are sodium, potassium, ammonium, and triethanolamine; the chain length of the fatty acids ranges from 12 to 18.

#### **Cationic Agents**

A number of long-chain cations, such as amine salts and quaternary ammonium salts, often are used as surface-active agents when dissolved in water; however, their use in pharmaceutical preparations is limited to that of antimicrobial preservation rather than as surfactants. This arises because the cations adsorb so readily at cell membrane structures in a nonspecific manner, leading to cell lysis (e.g., hemolysis), as do anionics to a lesser extent. It is in this way that they act to destroy bacteria and fungi.

### Amphoteric Agents

The major groups of molecules falling into the amphoteric category are those containing carboxylate or phosphate groups such as the anion, and amino or qua-ternary ammonium groups such as the cation. The former group is represented by various polypeptides, proteins, and the alkyl betaines; the latter group consists of natural phospholipids, such as the lecithins and cephalins.

### Nonionic Agents

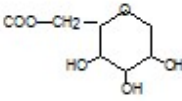
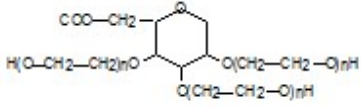
The major class of compounds used in pharmaceutical systems is the nonionic surfactants, for their advantages with respect to compatibility, stability, and potential toxicity are quite significant. It is convenient to divide these compounds into those that are relatively water insoluble and those that are quite water soluble. The major types of compounds making up this first group are the long-chain fatty acids and their water-insoluble derivatives.

Some examples of surface active agents are shown in Table 4.

**Table 4: Classification of SAA**

Class	SAA	Chemical formula (in aqs. soln.)		
		Lipophilic group	Hydrophilic group	Surface inactive ion
<b>1. Anionic</b>				
Alkali soap	Potassium stearate	$C_{17}H_{35}$	$COO^-$	$K^+$
Organic sulphates	Sodium lauryl sulphate (Sod. dodecyl sulphate)	$C_{12}H_{25}$	$OSO_3^-$	$Na^+$

Organic sulphonates	Sodium cetyl sulphonate (Sod. hexadecane sulfonate)	$C_{16}H_{33}$	$SO_3^-$	$Na^+$
<b>2. Cationic</b>				
Quaternary ammonium compounds	Cetyl trimethyl ammonium bromide (or cetrimide)	$C_{16}H_{33}$	$N^+(CH_3)_3$	$Br^-$
Pyridinium compounds	Dodecyl pyridinium chloride	$C_{12}H_{25}$	$N^+C_5H_5$	$Cl^-$
<b>3. Ampholytic</b>				
Amino acids	N-dodecyl alanine	$C_{12}H_{25}$	In alkaline soln. – anionic $NH - CH_2 - CH_2 - COO^-$	$Na^+$
		$C_{12}H_{25}$	In acid solution – cationic $N^+H_2 - CH_2 - CH_2 - COOH$	$Cl^-$
		$C_{12}H_{25}$	At isoelectric point – zwitterion $N^+H_2 - CH_2 - CH_2 - COO^-$	None
<b>4. Non-ionic</b>				
Alcohol- polyethylene glycol ethers	Polyethylene glycol 1000 monocetyl ether (cetomacrogol	$CH_2-(CH_2)_n$ (n= 15 to 17)	$(O-CH_2-CH_2)_m-COO^-$ (m = 20 to 24)	none

	1000)				
Fatty acid-polyethylene glycol ethers	Polyethylene glycol 40 monostearate	C <sub>17</sub> H <sub>33</sub>		CO-(O-CH <sub>2</sub> -CH <sub>2</sub> ) <sub>40</sub> -OH	none
Fatty acid-polyhydric alcohol esters	Sorbitan mono-oleate (Tween)	C <sub>17</sub> H <sub>33</sub>			none
	Polyoxyethylene sorbitan mono-oleate	C <sub>17</sub> H <sub>33</sub>			none

### HLB Scale [8]

Griffin in 1947 devised an arbitrary scale of values to serve as a measure of the hydrophilic-lipophilic balance (HLB) of SAA. The hydrophile-lipophile balance (HLB) number is a measure of the balance between hydrophobic and hydrophilic portions of a surfactant. The HLB number of a SAA is given using an arbitrary scale which for non-ionic surfactants ranges from 0 to 20. The HLB value of an emulsifier can be determined experimentally or can be computed as long as the structural formula of the surfactant is known. In general molecules that are oil soluble have low HLB values, those that are water soluble have high HLB values. Some HLB value range of SAA is shown in Table 5.

**Table 5: SAA and their HLB values**

Category	HLB value
Antifoaming agent	1-3
w/o emulsifier	3-8
Wetting agent/spreading agent	7-9
o/w emulsifier	8-16
Detergent	13-16
Solubilising agent	16-18

### Calculation of HLB values

**I. For simple alkyl ethers in which the hydrophile consists only of ethylene oxide**

$$\text{HLB} = E/5 \dots\dots\dots(23)$$

where E is the weight percentage of ethylene oxide groups

**II. For polyhydric alcohol fatty acid esters (e.g. glyceryl monostearate)**

$$\text{HLB} = 20 \left( 20 - \frac{S}{A} \right) \dots\dots\dots (24)$$

Where

S = Saponification number of ester

A = Acid number of fatty acid

**III. Materials not having saponification numbers (e.g. beeswax and lanolin derivatives)**

$$\text{HLB} = (E + P)/5 \dots\dots\dots(25)$$

where P is the weight percentage of polyhydric alcohol groups (glycerol or sorbitol) in the molecule.

**IV. For group contributions:**

$$\text{HLB} = \Sigma (\text{hydrophilic group numbers}) - \Sigma (\text{lipophilic group numbers}) + 7 \dots\dots\dots(26)$$

**V. For a mixture of two surfactants containing fraction *f* of A and (1 - *f*) of B it is assumed that the HLB is an algebraic mean of the two HLB numbers:**

$$\text{HLB}_{\text{mixture}} = f \text{HLB}_A + (1 - f) \text{HLB}_B \dots\dots\dots(27)$$

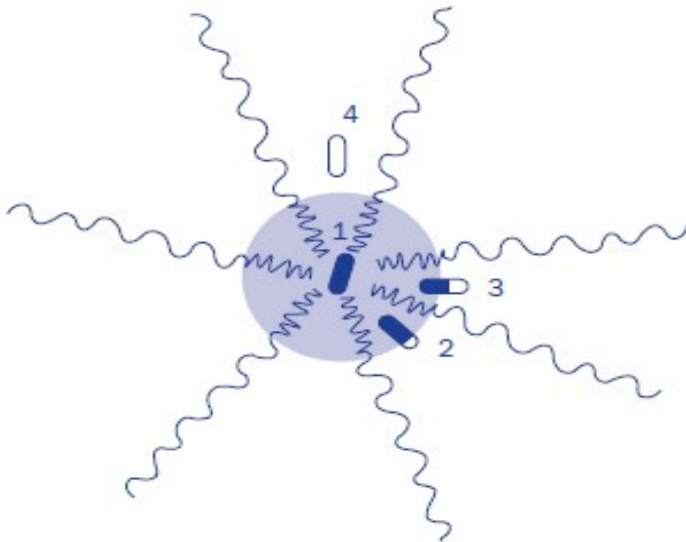
**Solubilisation**

The maximum amount of solubilisate that can be incorporated into a given system at a fixed concentration is termed the maximum additive concentration (MAC). Solubility data are expressed as solubility versus concentration curve or as three-component phase diagrams, which describe the effect of varying all three components of the system (solubilisate, solubiliser and solvent).

The site of solubilisation within the micelle is closely related to the chemical nature of the solubilisate (Fig. 4):

- ✓ Non-polar solubilisates (aliphatic hydrocarbons, for example) are dissolved in the hydrocarbon core of ionic and non-ionic micelles (position 1).
- ✓ Water-insoluble compounds containing polar groups are orientated with the polar group at the core–surface interface of the micelle, and the hydrophobic group buried inside the hydrocarbon core of the micelle (position 2 and 3).

- ✓ In addition to these sites, solubilisation in non-ionic polyoxyethylated surfactants can also occur in the poly- oxyethylene shell (palisade layer) which surrounds the core (position 4).



**Fig. 4: Schematic representation of sites of solubilisation depending on the hydrophobicity of the solubilise**

### **Factors affecting solubilisation capacity**

#### **1. Nature of the surfactant**

When the solubilise is located within the core or deep within the micelle structure the solubilisation capacity increases with increase in alkyl chain length up to about C16; further increase has little effect on solubilisation capacity.

The effect of an increase in the ethylene oxide chain length of a polyoxyethylated non-ionic surfactant on its solubilising capacity is dependent on the location of the solubilise within the micelle and is complicated by corresponding changes in the micellar size. The aggregation number decreases with increase in the hydrophilic chain length so there are more micelles in a given concentration of surfactant and, although the number of molecules solubilised per micelle decreases, the total amount solubilised per mole of surfactant may actually increase.

#### **2. Nature of the solubilise**

For a simple homologous series of solubilisates a decrease in solubilisation occurs when the alkyl chain length is increased. A relationship between the lipophilicity of the solubilise, expressed by the partition coefficient between octanol and water, and its extent of solubilisation has been noted for several surfactant systems.



### 3. Temperature

With most systems the amount solubilised increases as temperature increases. This increase is particularly pronounced with some non-ionic surfactants where it is a consequence of an increase in the micellar size with temperature increase. In some cases, although the amount of drug that can be taken up by a surfactant solution increases with temperature increase, this may simply reflect an increase in the amount of drug dissolved in the aqueous phase rather than an increased solubilisation by the micelles.

### Detergency

Surfactants in aqueous solutions [9] are used to remove the dirt from substrates such as glass, fabric, skin etc. Effective detergents are required for the cleaning of production, equipment, containers for packing and also in order to maintain hygiene in industry. The term Detergency is mostly used in the cleaning/removing of grease, oil and dirt from the solid surface. The principle of detergency is based on the formation of micelle.

Detergency is a complex process and a number of steps are simultaneously involved. These are

1. Initial wetting of the dirt from the surface
2. Solubilising the dirt
3. Removing the insoluble dirt as deflocculation particles
4. Suspending the particles in the detergent solution
5. Removing the oil soluble materials and convert into emulsion
6. Converting the dirt into foam so as wash easily

The HLB requirement for the detergency is about 13 to 16.

**Cationic type:** Zephiran, Cetrimide

**Anionic type:** Soaps, Sodium lauryl sulphate

This property is achieved by lower the surface tension of the medium in which surfactants is dissolved. By lowering this interfacial tension between two media or interfaces (e.g. air/water, water/stain, stain/fabric) the surfactant plays a key role in the removal and suspension of dirt. The lower surface tension of the water makes it easier to lift dirt and grease off of dirty dishes, clothes and other surfaces, and help to keep them suspended in the dirty water. The water-loving or hydrophilic head remains in the water and it pulls the stains towards the water, away from the fabric. The surfactant molecules surround the stain particles, break them up and force them away

from the surface of the fabric. They then suspend the stain particles in the wash water to remove them. If the dirt is oily it may be emulsified or solubilized by the surfactant.

### **Adsorption at Solid Interfaces [10]**

Adsorption of material at solid interfaces can take place from either an adjacent liquid or gas phase. The adsorption of gases in pharmacy has many applications such 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.

If a gas or vapour is brought into contact with a solid, some of it will become attached to the surface. This reduces the imbalance of attractive forces and hence the surface free energy. 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. Adsorption is classified into two types such as physical adsorption and chemical adsorption (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 can be desorbed from a solid by increasing the temperature and reducing the pressure.

**Chemisorption** is specific in which the adsorbate is attached to the adsorbent by primary chemical bonds and it is irreversible unless the bonds are broken. Only monomolecular chemisorbed layers are possible.

**Table 6: Difference between physical adsorption and chemical adsorption**

<b>Physical adsorption</b>	<b>Chemical adsorption</b>
Reversible	Irreversible
Weak van der Waals forces	Strong chemical bonds
Nonspecific	Specific
Common at low temperature	Occurs at high temperature
Heat of adsorption is low	Heat of adsorption is high
e.g.Adsorption of gases in charcoal	e.g.Adsorption of O <sub>2</sub> on gold

### **Adsorption isotherm**

Adsorption isotherm is defined as the plots drawn between the amount of gas adsorbed on a solid (Y axis) against the equilibrium pressure (in case of gases) or concentrations (in case of solutions) (X axis) at constant temperature.

The isotherms obtained can generally be classified into five types, shown in Fig. 5.

**Type I:** These isotherms exhibit a rapid rise in adsorption up to a limiting value. They are referred to as Langmuir-type isotherms and are due to the adsorption being restricted to a monolayer. Hence adsorption of the chemisorption type will give this type of curve.

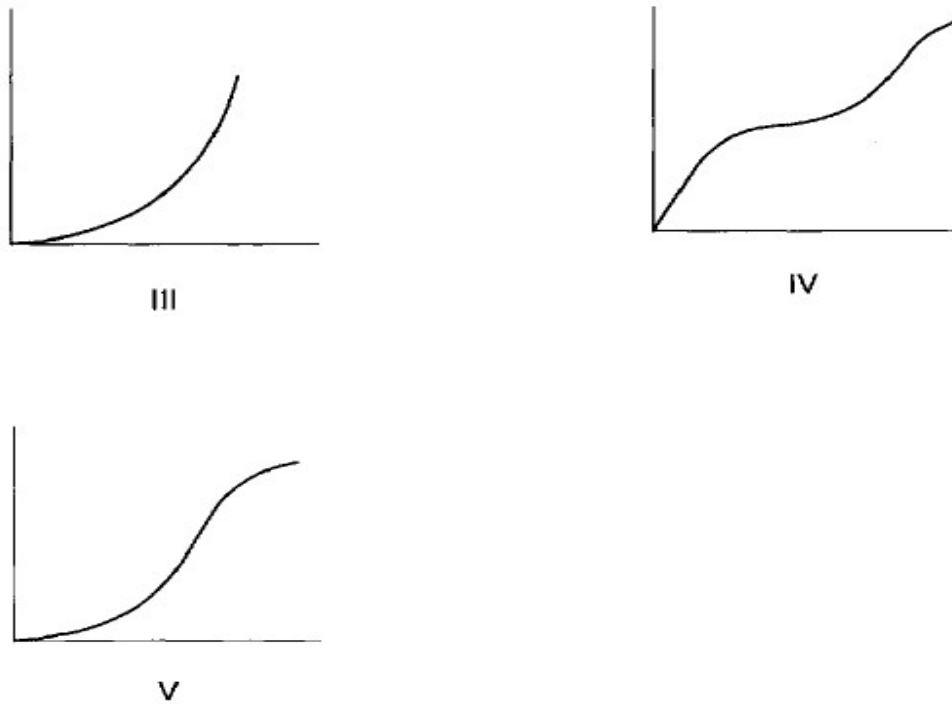
**Type II:** This isotherm is sigmoidal in shape and occurs when gases undergo physical adsorption on non-porous materials. The first inflection point represents the formation of monolayer. When the pressure is increased further multilayer formation is obtained. This isotherm is explained by BET equation. In BET equation the constant  $b$  is greater than 2. When the monolayer is formed the plot reduces to Langmuir adsorption isotherm.

**Types III:** This is seen rarely. The heat of adsorption of gas in the first layer is less than the latent heat of condensation of subsequent layers. In the BET equation the constant  $b$  is smaller than 2. For example adsorption of  $\text{Br}_2$  on silica or alumina.

**Type IV:** First point of inflection extrapolated to zero represents the monomolecular layer adsorption. Condensation within the pores of the solid and the multimolecular layer is represented by further adsorption. It is considered to be due to condensation of vapour in fine capillaries within a porous solid.

**Type V:** These occur when the adsorption in the first layer is weak, and are rare. It indicates capillary condensation. Here the adsorption reaches a limiting value before  $P_0$  is attained.





**Fig. 5: Classification of isotherms for the adsorption of vapours by solids. Ordinates  $x/m$ , abscissae  $p/p_0$**

There have been many attempts to develop equations to fit the experimentally observed isotherm. Among the most widely used expressions are the following [11-13].

1. Langmuir adsorption isotherm
2. Freundlich adsorption isotherm
3. Brunauer, Emmett and Teller (BET) equation

### **1. Langmuir adsorption isotherm**

In this theory the following assumptions are made.

- ✓ The surface of solid possesses fixed number of active sites for the adsorption of gases.
- ✓ At maximum adsorption the gas layer that is found around the solid is of only one molecule thick.
- ✓ The rate of adsorption (condensation) is proportional to number of sites unoccupied.
- ✓ The rate of evaporation (desorption) is proportional to number of sites occupied

Langmuir isotherm equation is given by

$$y = \frac{y_m b P}{1 + b} \dots \dots \dots (28)$$

Where  $y$  is the mass of gas adsorbed per gram of adsorbent and  $y_m$  is the mass of gas that 1 g of adsorbent can take up when a monolayer is complete.  $P$  is pressure of the adsorbate and  $b$  is constant.

**2. Freundlich adsorption isotherm**

Freundlich adsorption isotherm represents the variation in extent of adsorption with a equilibrium pressure or concentration of adsorbate at fixed temperature. The relationship between pressure of the gas and amount adsorbed at constant temperature has been expressed by many equations. For Freundlich isotherm the equation is

$$y = x/m = kP^{1/n} \dots \dots \dots (29)$$

Where  $x$  is weight of gas adsorbed per unit weight of adsorbent ( $m$ ),  $P$  is equilibrium pressure,  $k$  and  $n$  are constants.

**3. The Brunauer-Emmett-Teller (BET) Isotherm**

**Assumptions:**

- (1) Multilayer adsorption;
- (2) Adsorption of first layer has a heat of adsorption,  $\Delta H_A$ ;
- (3) The subsequent layers are controlled by heat of condensation,  $\Delta H_L$ .

This equation takes into account multilayer adsorption and so describes type II isotherms. It is usually

written in the form:

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{C - 1}{V_m C} \times \frac{P}{P_0} \dots \dots \dots (30)$$

Where  $p_0$  is the saturation vapour pressure,  $V$  is the equilibrium volume of gas adsorbed per unit mass of adsorbent,  $V_m$  is the volume of gas required to cover unit mass of adsorbent with monolayer, and  $c$  is a constant. The equation reduces to the Langmuir equation if adsorption is restricted to monolayer formation. One direct practical application of the adsorption of gases of pharmaceutical interest is the determination of the surface area of powders.

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