आईएफटीएम विश्वविद्यालय, मुरादाबाद, उत्तर प्रदेश

IFTM University, Moradabad, Uttar Pradesh

NAAC ACCREDITED

E-Content

IFTM University, Moradabad

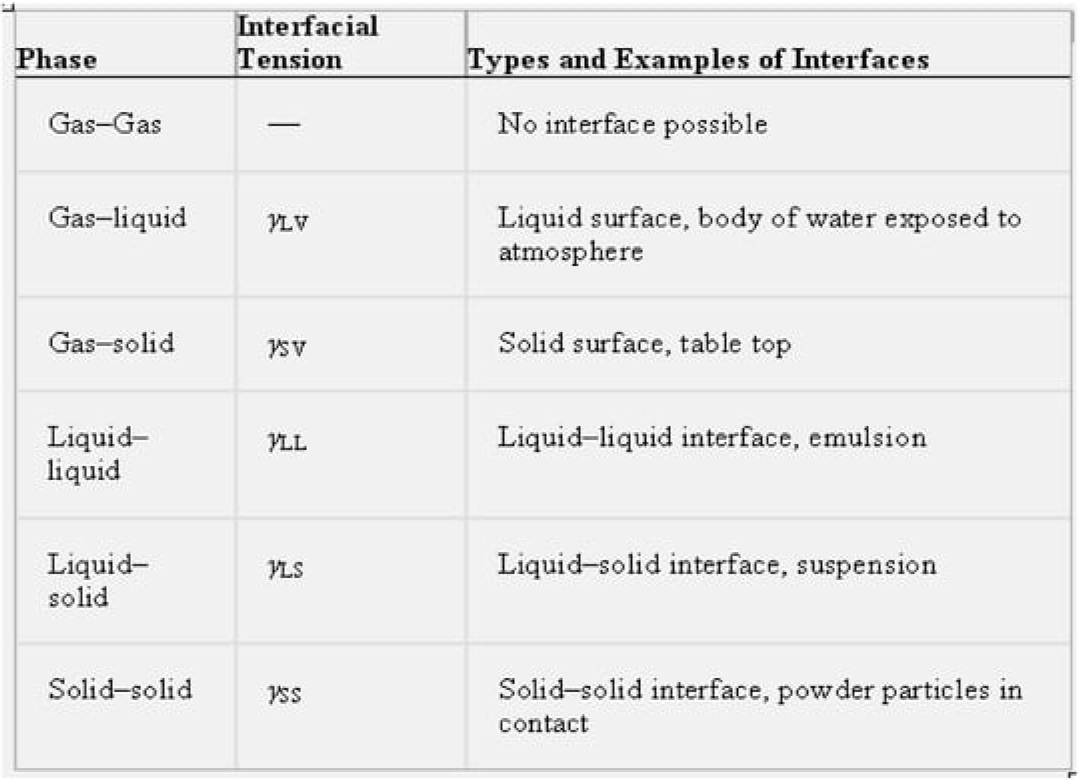
Unit 4

Interfacial Phenomena

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.
- The term *surface* is used when referring to either a gas–solid or a gas–liquid interface.

Types of interface



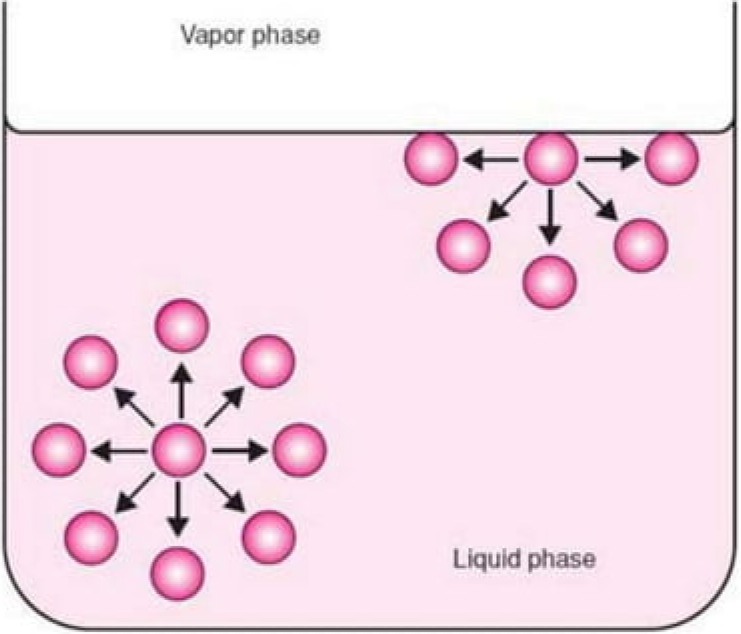
Phase	Interfacial Tension	Types and Examples of Interfaces
Gas–Gas	—	No interface possible
Gas–liquid	γ_{LV}	Liquid surface, body of water exposed to atmosphere
Gas–solid	γ_{SV}	Solid surface, table top
Liquid–liquid	γ_{LL}	Liquid–liquid interface, emulsion
Liquid–solid	γ_{LS}	Liquid–solid interface,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

Liquid Interfaces

Surface and Interfacial Tensions

- molecules in the bulk liquid are surrounded in all directions by other molecules for which they have an equal attraction.

- 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.


Vapor phase
Liquid phase

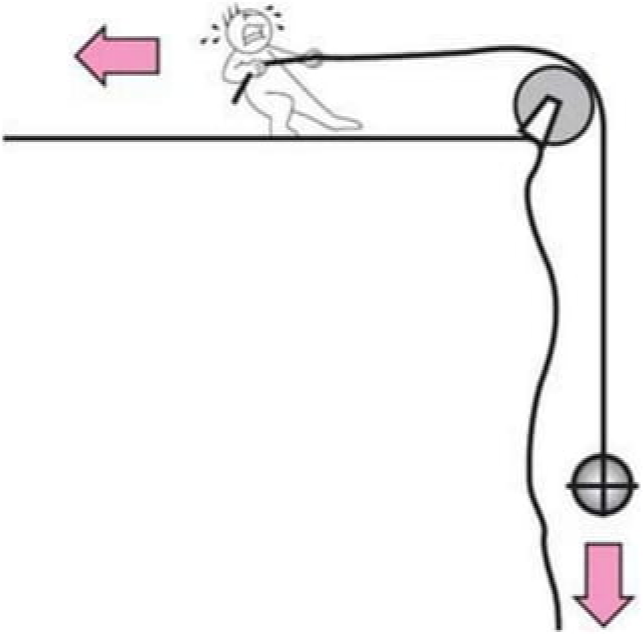
- The net effect is that the molecules at the surface of the liquid experience an inward force toward the bulk.

- 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 so as to counterbalance the net inward pull.

- *Interfacial tension* is the force per unit length existing at the interface between two immiscible liquid phases and.

- the surface and interfacial tensions, have the units of dynes/cm or N/m.



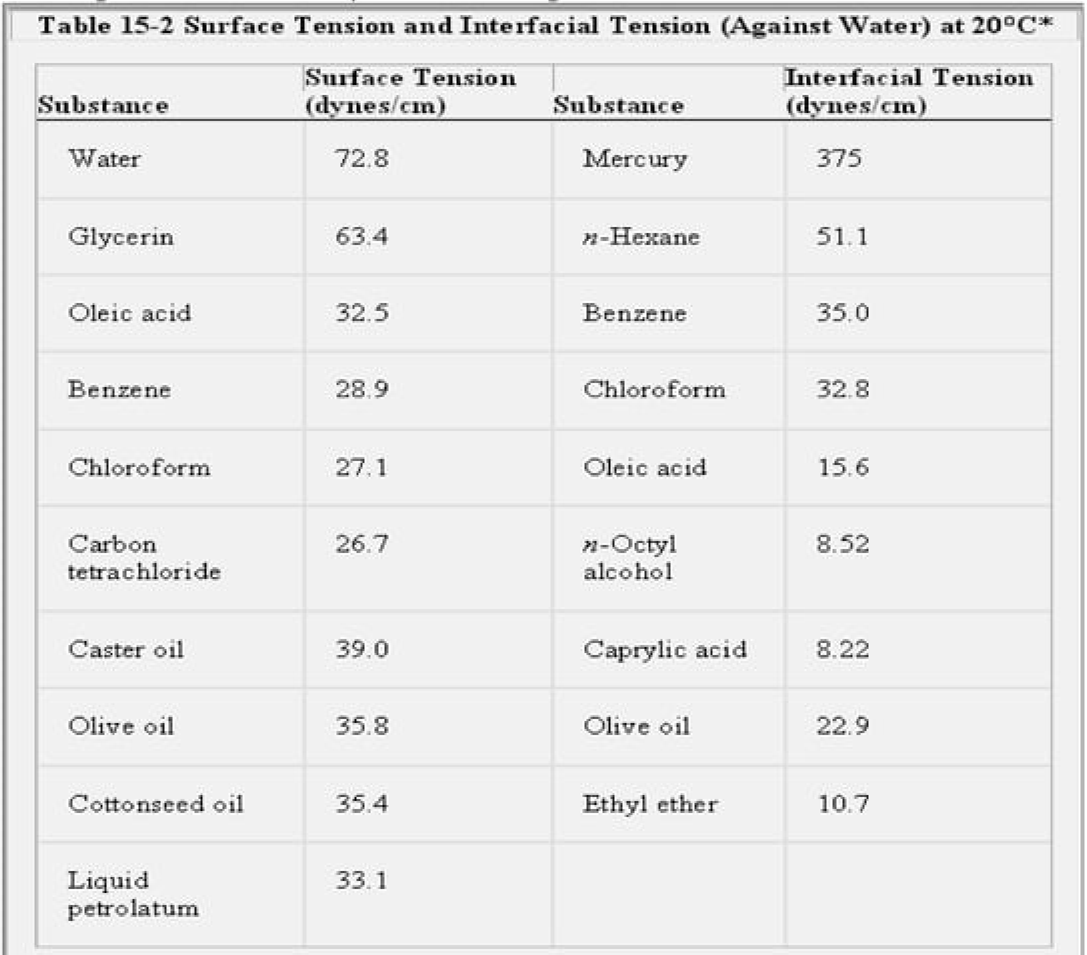


Table 15-2 Surface Tension and Interfacial Tension (Against Water) at 20°C*

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		

- 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.

Surface Free Energy and Surface Tension

- The surface layer of a liquid possesses additional energy as compared to the bulk liquid.
- This energy increases when the surface of the same mass of liquid increases and is therefore called *surface free energy*.

The work W required to create a unit area of surface is known as *SURFACE FREE ENERGY/UNIT AREA* (ergs/cm^2)

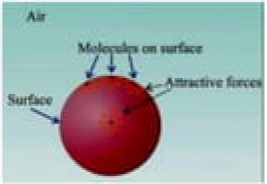
erg = dyne . cm

$$\boxed{W = \gamma \Delta A}$$

Its equivalent to the surface tension γ

Thus the greater the area A of interfacial contact between the phases, the greater the free energy.

- For equilibrium, the surface free energy of a system must be at a minimum. Thus Liquid droplets tend to assume a spherical shape since a sphere has the smallest surface area per unit volume.



Measurement of Surface and Interfacial Tensions

- **Capillary Rise Method.**
- **The DuNoüy Ring Method**
- **Drop weight method (Stalagmometer)** , bubble pressure, pendent drop, sessile drop, Wilhelmy plate, and oscillating drop,

The choice of the method for measuring surface and interfacial tension depend on:

- **Whether surface or interfacial tension is to be determined.**
- **The accuracy desired**
- **The size of sample.**

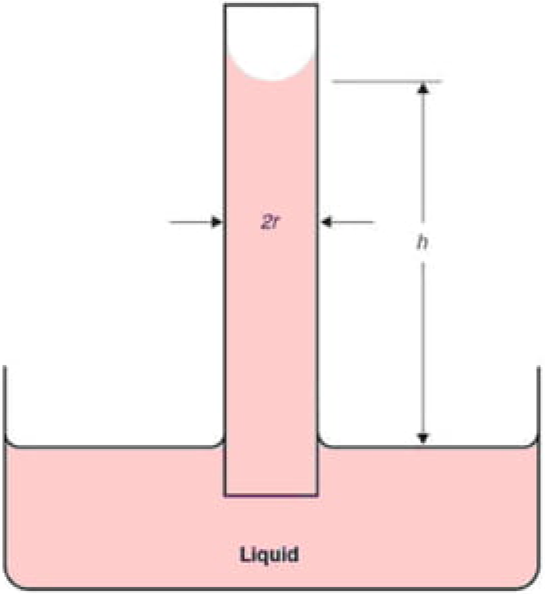
Capillary Rise Method

- When a capillary tube is placed in a liquid contained in a beaker, the liquid generally rises up the tube a certain distance.

- 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.

- Because of the surface tension, the liquid continues to rise in the tube, but because of the weight of the liquid, the upward movement is just balanced by the downward force of gravity.

$$\gamma = \frac{1}{2} r h \rho g \qquad (15\text{–}12)$$


2r
h
Liquid

- Example:
- 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/cm3.

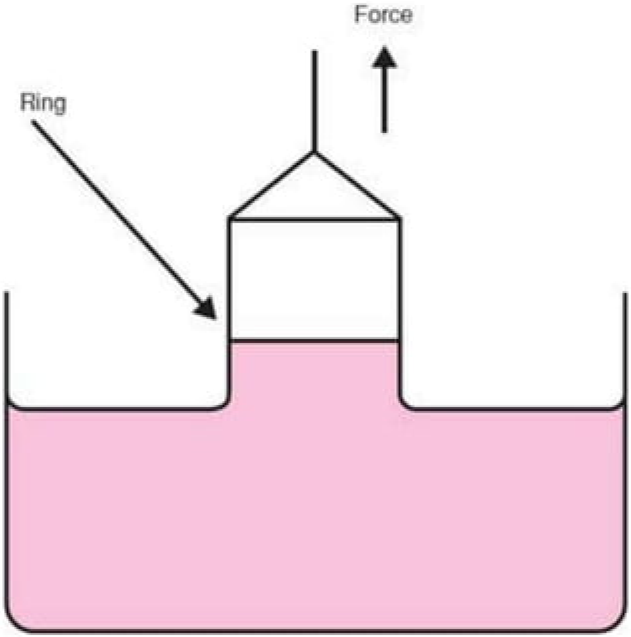
$$\gamma = \frac{1}{2} \times 0.01\,\text{cm} \times 3.67\,\text{cm} \times 1.476\,\text{g/cm}^3 \times 981\,\text{cm/sec}^2$$
$$\gamma = 26.6\,\text{g/sec}^2 = 26.6\,\text{dynes/cm}$$

The DuNoüy Ring Method

- The *DuNoüy tensiometer* is widely used for measuring surface and interfacial tensions.

- 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.


Force
Ring

$$\gamma = \frac{\text{Dial reading in dynes}}{2 \times \text{Ring circumference}} \times \text{Correction factor, } \beta \tag{15–14}$$

- A correction factor is necessary 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.

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.

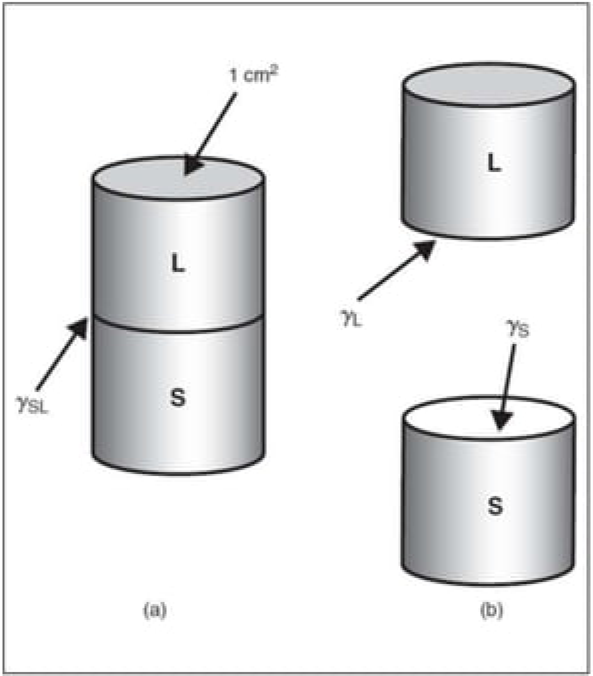
- The term *film* used here applies to a *duplex film* as opposed to a monomolecular film. Duplex films are sufficiently thick (100 Å or more) so that the surface (boundary between oleic acid and air) and interface (boundary between water and oleic acid) are independent of one another.

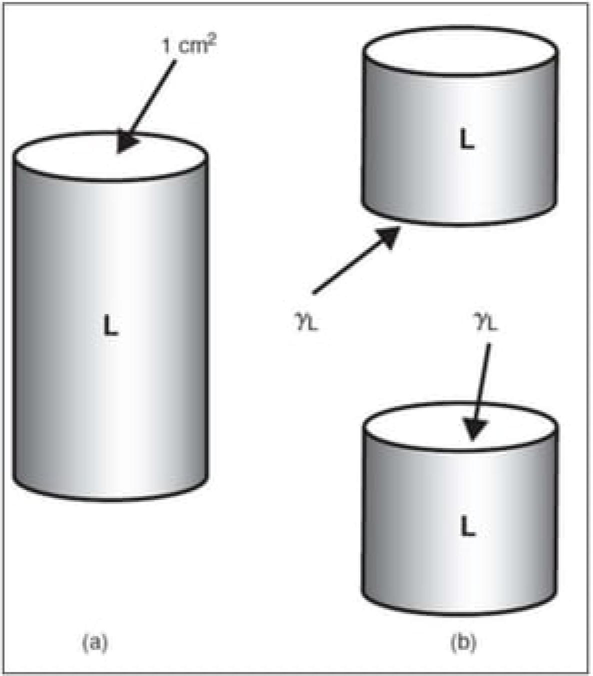
- The *work of adhesion*, is the energy required to break the attraction between the unlike molecules.

$$W_a = \gamma_L + \gamma_S - \gamma_{LS} \qquad (15\text{–}16)$$

- The *work of cohesion*, required to separate the molecules of the spreading liquid so that it can flow over the sublayer,

$$W_c = 2\gamma_L \qquad (15\text{–}17)$$


1 cm²
L
S
γSL
L
γL
γS
S
(a)
(b)


1 cm²
L
L
γL
γL
L
(a)
(b)

- The term (*W*a - *W*c) is known as the *spreading coefficient*, *S*;

- if it is positive, the oil will spread over a water surface.

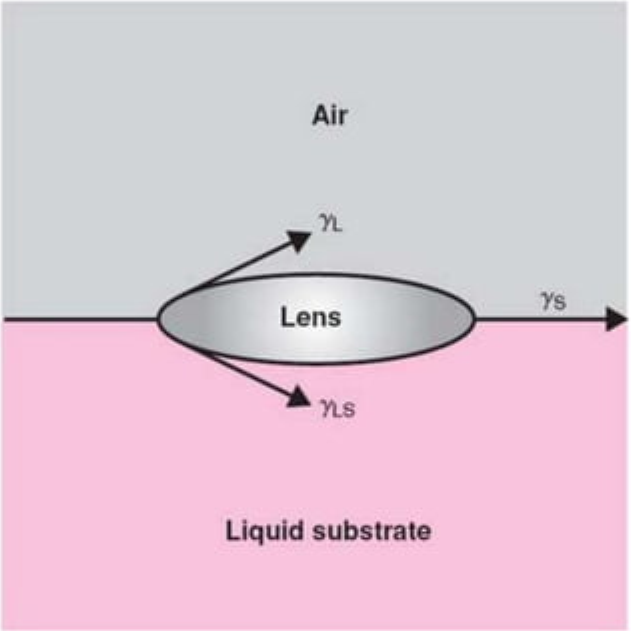
$$S = W_a - W_c = (\gamma_L + \gamma_S - \gamma_{LS}) - 2\gamma_L \quad (15\text{–}18)$$

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

- γ_S is the surface tension of the sublayer liquid,
- γ_L is the surface tension of the spreading liquid,
- γ_{LS} is the interfacial tension between the two liquids.

- 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 γ_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.


Air
γ_L
Lens
γ_S
γ_{LS}
Liquid substrate

- Example
- If the surface tension of water γ_S is 72.8 dynes/cm at 20°C, the surface tension of benzene, γ_L, is 28.9 dynes/cm, and the interfacial tension between benzene and water, γ_{LS}, is 35.0 dynes/cm, what is the initial spreading coefficient?

- Following equilibration, $\gamma_{S'}$ is 62.2 dynes/cm and $\gamma_{L'}$ is 28.8 dynes/cm. What is the final spreading coefficient?

$$S = 72.8 - (28.9 + 35.0) = 8.9 \text{ dynes/cm (or } 8.9 \text{ ergs/cm}^2\text{)}$$
$$S' = 62.2 - (28.8 + 35.0) = -1.6 \text{ dynes/cm}$$

The applications of spreading coefficients

- 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.

Adsorption at Liquid Interfaces

- Certain molecules and ions, when dispersed in the liquid, move of their own accord to the interface.

- the surface free energy and the surface tension of the system are automatically reduced.

- Molecules and ions that are adsorbed at interfaces are termed *surface-active agents* or *surfactants*. An alternative term is *amphiphile*,

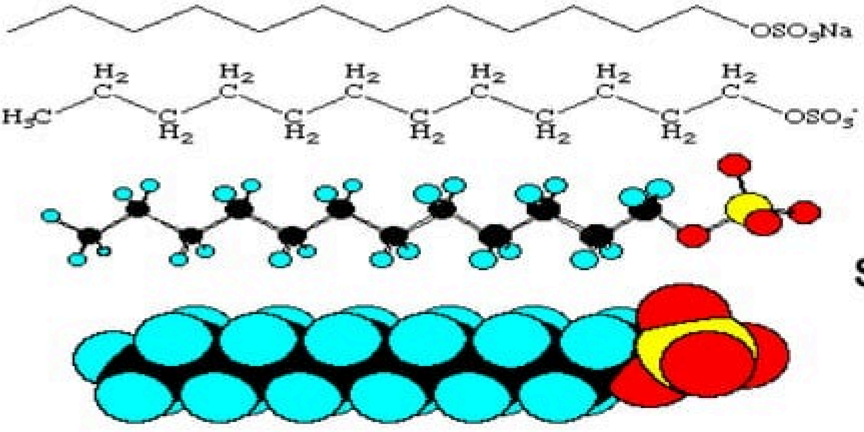
Surface Active Agents

Surface Active Agents

A surfactant molecule is depicted schematically as a cylinder representing the hydrocarbon (hydrophobic) portion with a sphere representing the polar (hydrophilic) group attached at one end.

The hydrocarbon chains are straight because rotation around carbon-carbon bonds bends, coils and twists them.

$CH_3(CH_2)_{11}OSO_3^-Na^+$



Sodium Lauryl Sulfate molecule

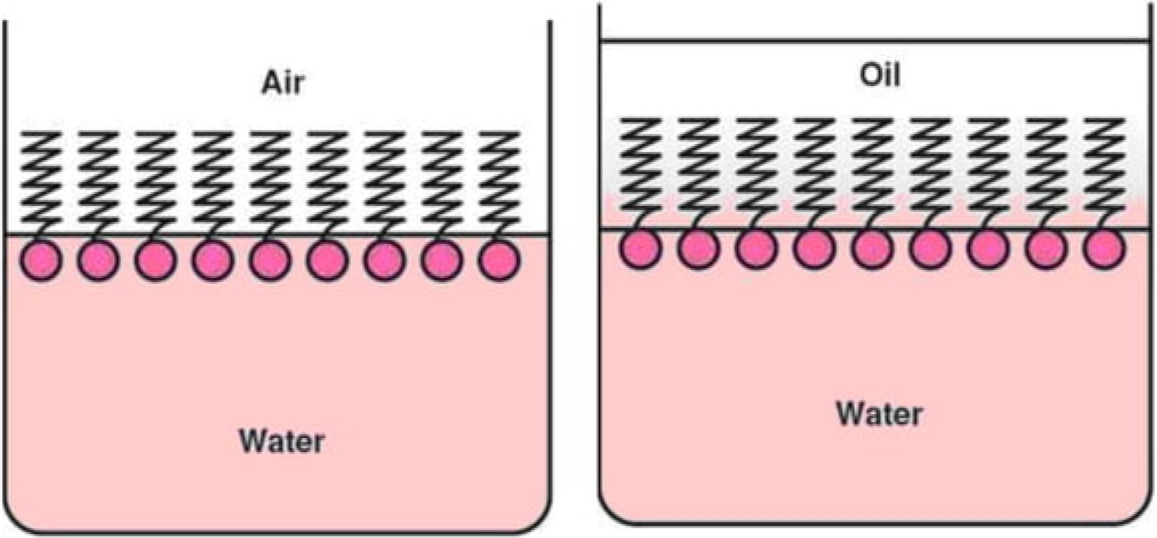
Surface-Active Agents

- It is the amphiphilic nature of surface-active agents that causes them to be absorbed at interfaces,
- Thus, in an aqueous dispersion of amphiphile, the polar group is able to associate with the water molecules. The nonpolar portion is rejected,
- As a result, the amphiphile is adsorbed at the interface.

- The situation for a fatty acid at the air–water and oil–water interface:

- At the oil–water interface, the lipophilic chains are directed upward into the air;

- at the air–oil interface, they are associated with the oil phase.


Air
Water
Oil
Water

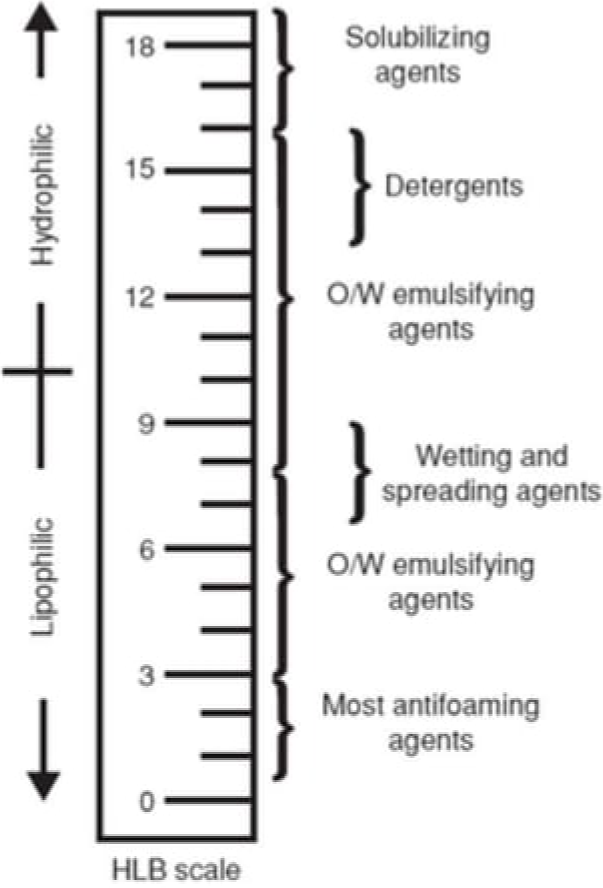
- For the amphiphile to be concentrated at the interface, it must be balanced with the proper amount of water- and oil-soluble groups.

- If the molecule is too hydrophilic, it remains within the body of the aqueous phase and exerts no effect at the interface.

- if it is too lipophilic, it dissolves completely in the oil phase and little appears at the interface

Systems of Hydrophile–Lipophile Classification

- The higher the HLB of an agent, the more hydrophilic it is.
- The Spans, sorbitan esters , are lipophilic and have low HLB values (1.8–8.6);
- The Tweens, polyoxyethylene derivatives of the Spans, are hydrophilic and have high HLB values (9.6–16.7).



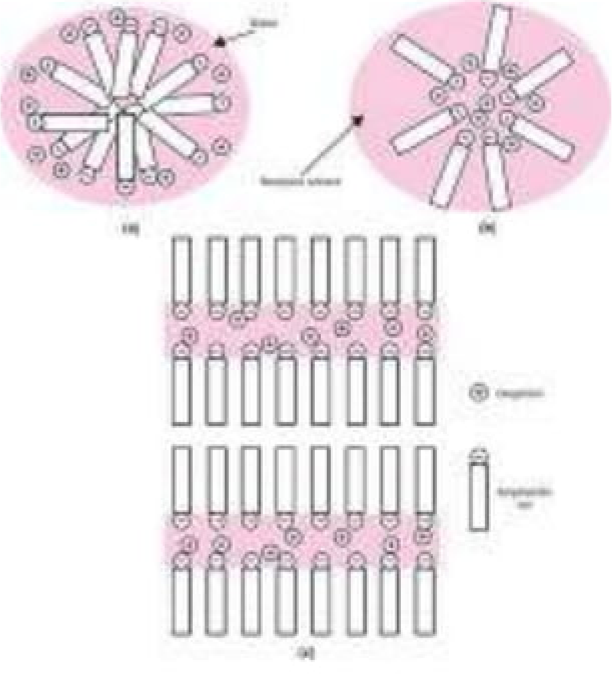
Hydrophilic
Lipophilic
18
15
12
9
6
3
0
Solubilizing agents
Detergents
O/W emulsifying agents
Wetting and spreading agents
O/W emulsifying agents
Most antifoaming agents
HLB scale

Micelles and the Critical Micelle Concentration

- When present in a liquid medium at low concentrations, the amphiphiles exist separately.

- As the concentration is increased, aggregation occurs. These aggregates, which may contain 50 or more monomers, are called *micelles*

- The concentration of monomer at which micelles form is termed the *critical micelle concentration*(*CMC*).



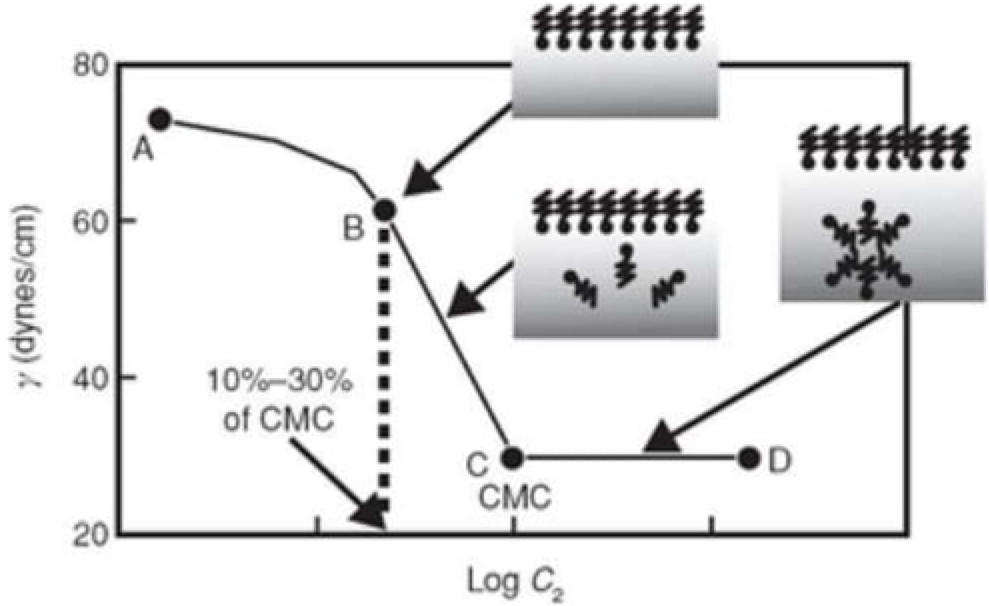
- (*a*) spherical micelle in aqueous media,
- (*b*) reversed micelle in nonaqueous media,
- (*c*) laminar micelle, formed at higher amphiphile concentration, in aqueous media.

- The surface tension decreases up to the CMC .
- When the surface tension, γ, 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.

- The initial curved segment A–B is followed by a linear segment, B–C, along which there is a sharp decrease in surface tension as log c_2 increases.

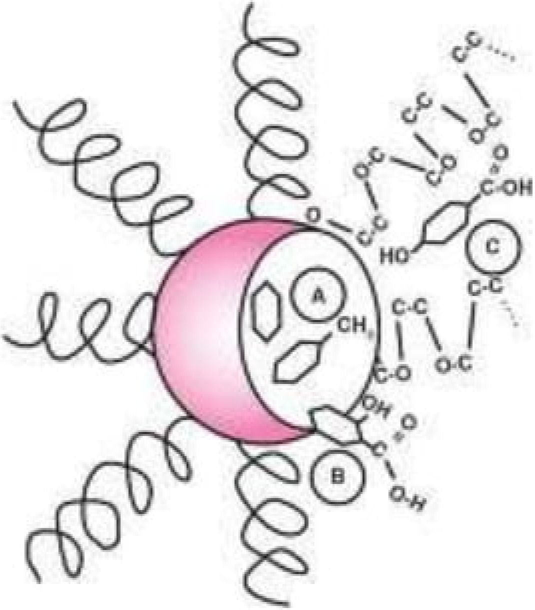
- The point C corresponds to the critical micelle concentration (CMC), the concentration at which micelles form in the solution.

- Beyond the CMC, the line becomes horizontal because further additions of surfactant are no longer being accompanied by a decrease in surface tension.


80
60
40
20
γ (dyne/cm)
A
B
C
CMC
D
10%–30%
of CMC
Log C_2

- is the ability of the micelles to increase the solubility of materials that are normally insoluble, or only slightly soluble, in the dispersion medium used.

- This phenomenon, known as *solubilization*,


C-C
C-C
O-C
C-C
C-C
O-C
O
O
C-C
C-OH
HO
C
A
CH3
C-C
C-C
C-O
O-C
OH
O
C
B
O-H

Adsorption at Solid Interfaces

- solid–gas adsorption:
- the removal of objectionable odors from rooms and food,
- the operation of gas masks,
- the measurement of the dimensions of particles in a powder.

- solid–liquid adsorption:
- decolorizing solutions,
- adsorption chromatography,
- detergency, wetting.

The Solid–Gas Interface

- the *adsorbent* : the material used to adsorb the gas)
- the *adsorbate*: the substance being adsorbed
- types of adsorption:

1. physical adsorption:

- associated with van der Waals forces,
- 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.

2. chemical adsorption or chemisorption

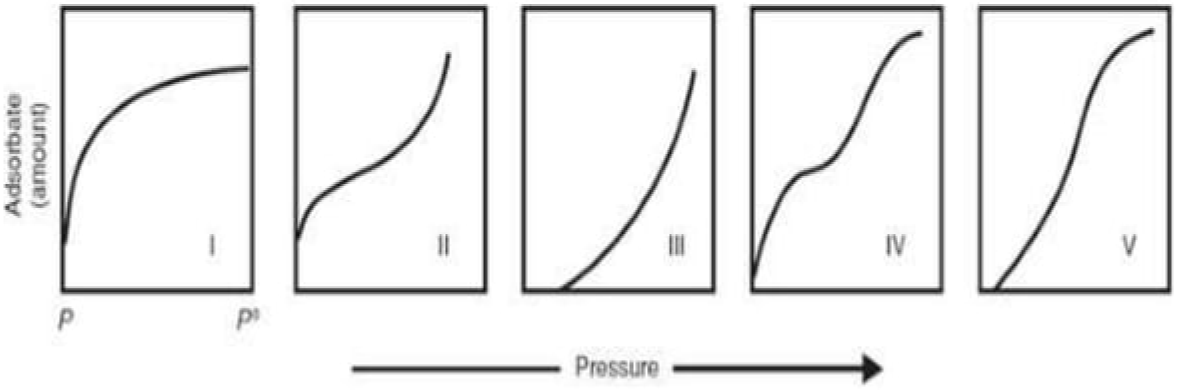
- the adsorbate is attached to the adsorbent by primary chemical bonds,
- irreversible unless the bonds are broken.

- The degree of adsorption of a gas by a solid depends on:

1. the chemical nature of the *adsorbent* and the *adsorbate*
2. the surface area of the adsorbent,
3. the temperature,
4. the partial pressure of the adsorbed gas.

- 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.

- The number of moles, grams, or milliliters, *x*, of gas adsorbed on, *m*, grams of adsorbent at standard temperature and pressure is plotted on the vertical axis against the equilibrium pressure of the gas in mm Hg on the horizontal axis,


Adsorbate (amount)
I
II
III
IV
V
P
P^0
Pressure

the *Freundlich isotherm*

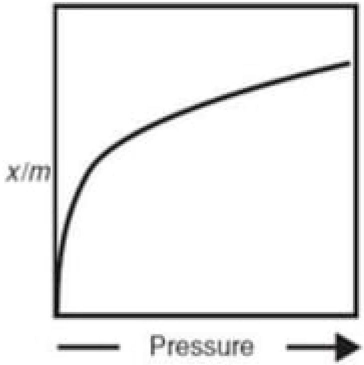
$$y = \frac{x}{m} = kp^{1/n} \qquad (15\text{–}49)$$

- *x* is the mass of gas adsorbed
- *m* is the mass of adsorbent,
- *y* is *x/m*
- *k* and *n* are constants that can be evaluated from the results of the experiment.

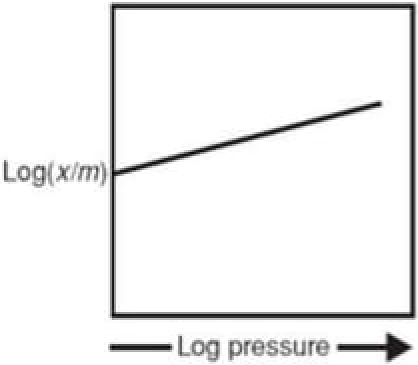
- the logarithmic form,

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p \qquad (15\text{–}50)$$

- which yields a straight line when plotted.
- The constant, log *k*, is the intercept on the ordinate,
- 1/*n* is the slope of the line.



(a)



(b)

the *Langmuir isotherm*

- 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)

$$y = \frac{y_m b p}{1 + bp} \qquad (15\text{–}55)$$

$$\frac{p}{y} = \frac{1}{by_m} + \frac{p}{y_m} \qquad (15\text{–}56)$$

- 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.

- Y_m is the quantity of vapor adsorbed per unit mass of adsorbent when the surface is covered with a monomolecular layer.

the *BET equation*

- derived by Brunauer, Emmett, and Teller.

$$\frac{p}{y(p_0 - p)} = \frac{1}{y_m b} + \frac{b-1}{y_m b}\frac{p}{p_0} \qquad (15\text{–}57)$$

The Solid–Liquid Interface

- Drugs such as dyes, alkaloids, fatty acids, and even inorganic acids and bases can be absorbed from solution onto solids such as charcoal and alumina.

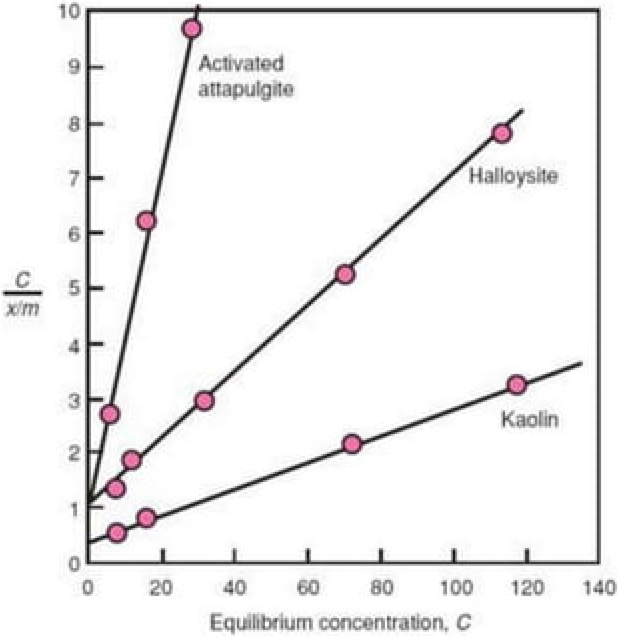
- Isotherms that fit one or more of the equations mentioned previously can be obtained by substituting solute concentration for the vapor pressure term used for solid–gas systems.

- Langmuir equation:

$$\frac{c}{y} = \frac{1}{by_{\mathrm{m}}} + \frac{c}{y_{\mathrm{m}}} \qquad (15\text{–}58)$$

- *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., $y = x/m$)

Adsorption of strychnine on various clays



- Data for adsorption of timolol from aqueous solution onto kaolin.
- ***adsorption isotherm***
- ***Calculate***

x/*m* (mg/g)	*C* (mg/100ml)
3.1	20
2.8	17
1.8	9
0.84	3

Wetting

- Adsorption at solid surfaces is involved in the phenomena of wetting and detergency.
- When a liquid comes into contact with the solid, the forces of attraction between the liquid and the solid phases begin to play a significant role.
- In this case, the behavior of the liquid will depend on the balance between the forces of attraction of molecules in the liquid and the forces of attraction between the liquid and the solid phases.

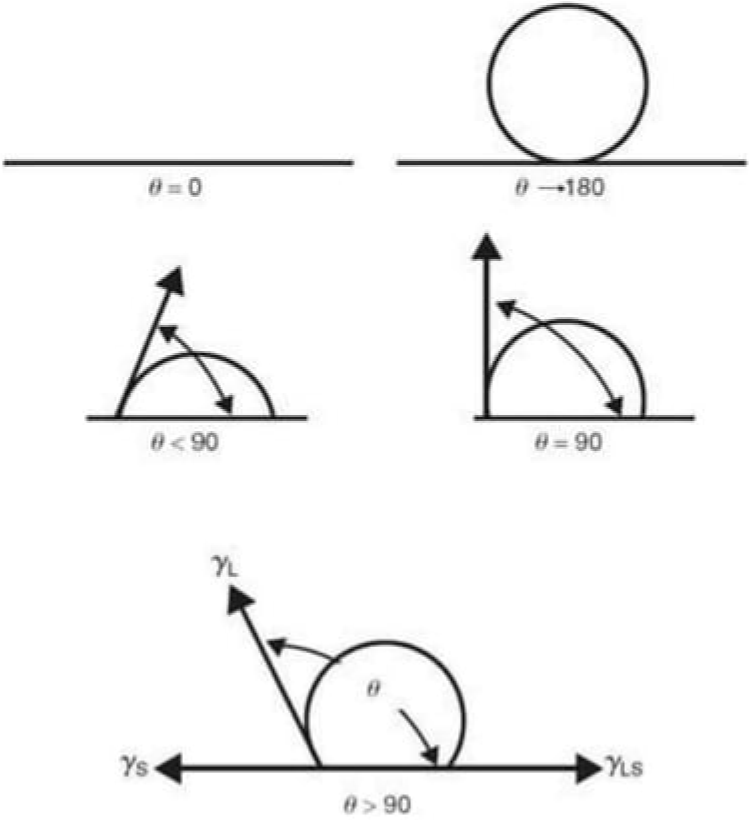
- In the case of mercury and glass, attractive forces between molecules of mercury and glass are much smaller than the forces of attraction between molecules of mercury themselves.
- As a result, mercury will come together as a single spherical drop.

- In contrast, for water and glass (or mercury and zinc), attractive forces between the solid and liquid molecules are greater than the forces between molecules of liquid themselves, and so the liquid is able to wet the surface of the glass.

- The contact angle is the angle between a liquid droplet and the surface over which it spreads.

- the contact angle between a liquid and a solid may be 0° signifying complete wetting, or may approach 180°, at which wetting is insignificant.

$$S = \gamma_L(\cos\theta - 1) \qquad (15\text{–}60)$$


θ = 0
θ → 180
θ < 90
θ = 90
γL
θ
γS
γLS
θ > 90

- The most important action of a wetting agent is to lower the *contact angle* between the surface and the wetting liquid.

- A *wetting agent* is a surfactant that, when dissolved in water, lowers the advancing contact angle, aids in displacing an air phase at the surface, and replaces it with a liquid phase.

the application of wetting

- 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 can be absorbed for application to various body areas;
- the displacement of dirt and debris by the use of detergents in the washing of wounds;
- the application of medicinal lotions and sprays to the surface of the skin and mucous membranes.

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

- The influence of tablet binders on wettability of acetaminophen tablets

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, $W = \gamma\,(1 + \cos\theta)$

PVP $W_{SL} = 71.23(1 + 0.7455) = 124.33$ N/m

Gelatin $W_{SL} = 71.23(1 + 0.7230) = 122.73$ N/m

Tapioca $W_{SL} = 71.33(1 + 0.7570) = 125.33$ N/m

Electric Properties of Interfaces

- Particles dispersed in liquid media may become charged mainly in one of two ways:

1. 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.

2. 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 p*K* 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

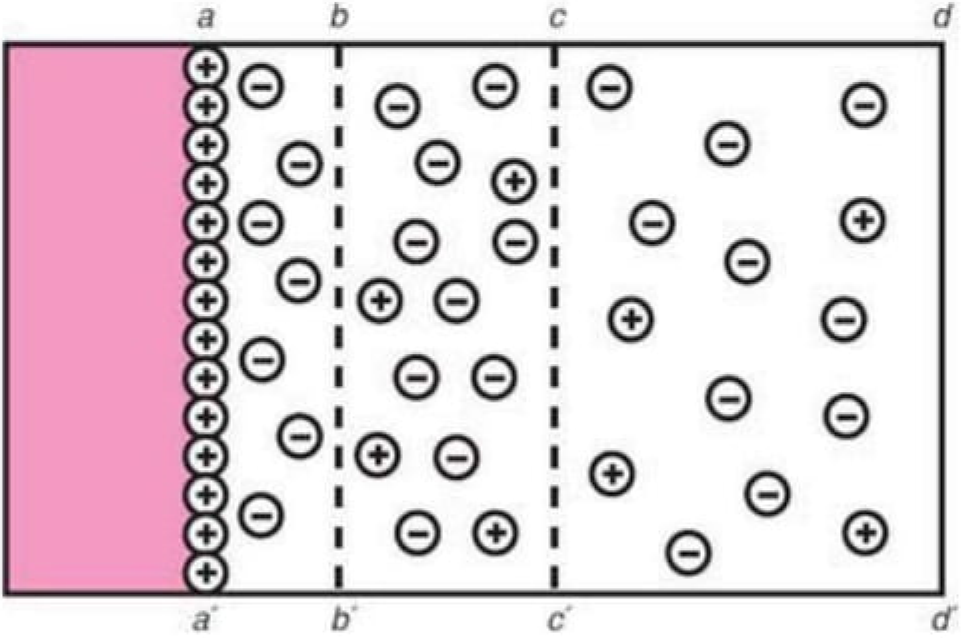
- Consider a solid surface in contact with a polar solution containing ions, for example, an aqueous solution of an electrolyte.
- suppose that some of the cations are adsorbed onto the surface, giving it a positive charge.
- Remaining in solution are the rest of the cations plus the total number of 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, whereas the remainder are distributed in decreasing amounts as one proceeds away from the charged surface.

- At a particular distance from the surface, the concentrations of anions and cations are equal, that is, conditions of electric neutrality prevail.

- the system *as a whole* is electrically neutral, even though there are regions of unequal distribution of anions and cations.


a
b
c
d
a'
b'
c'
d'

- *aa′* is the surface of the solid.
- The adsorbed ions that give 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′* .
- These ions, having a charge opposite to that of the potential-determining ions, are known as *counterions* or *gegenions*.

- In the region bounded by the lines *bb′* and *cc′*, there is an excess of negative ions.
- The potential at *bb′* is still positive because, 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:

1. the first layer (extending from *aa'* to *bb'*) tightly bound
2. a second layer (from *bb'* to *cc'*) that is more diffuse.

- The so-called diffuse double layer therefore extends from *aa'* to *cc'*.

Nernst and Zeta Potentials

- The changes in potential with distance from the surface for the various situations:

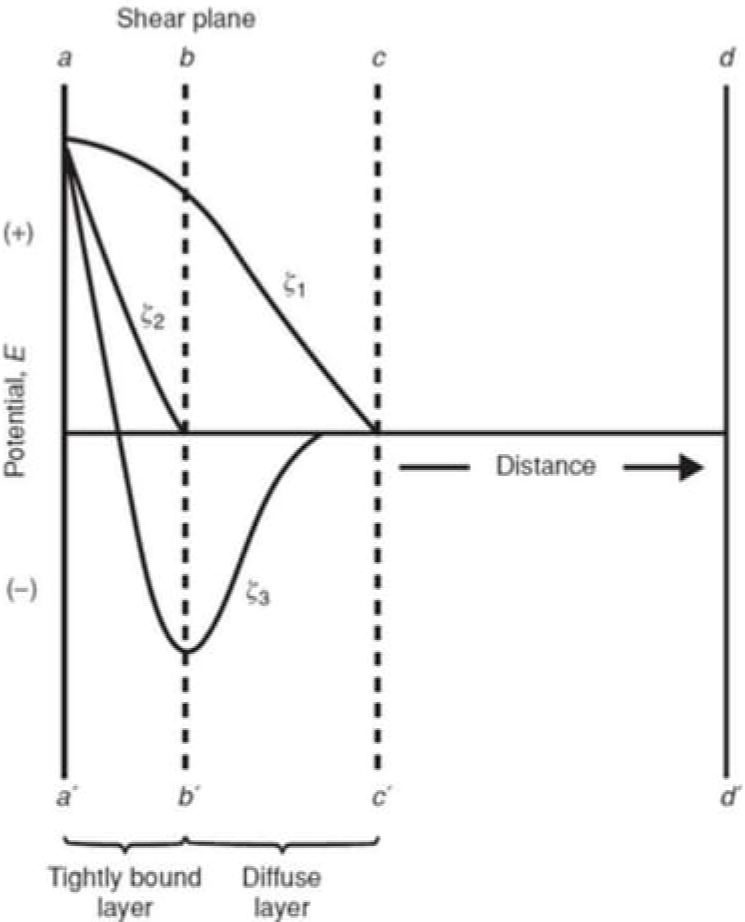
- The potential at the solid surface *aa′* due to the potential-determining ion is the *electrothermodynamic* (*Nernst*) *potential*, *E*,
- defined as the difference in potential between the actual surface and the electroneutral region of the solution.

- The potential located at the shear plane *bb'* is known as the *electrokinetic*, or *zeta*, *potential*, ζ.

- 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.

- the potential initially drops off rapidly, 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.


Shear plane
a
b
c
d
(+)
Potential, E
(−)
ζ1
ζ2
ζ3
Distance
a′
b′
c′
d′
Tightly bound layer
Diffuse layer

- The zeta potential has practical application in the stability of systems containing dispersed particles because this 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 exceed the repulsive forces, and the particles come together. This phenomenon is known as *flocculation*

- ***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.