

Interfacial Phenomena

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.

Several types of interface can exist, depending on whether the two adjacent phases are in the solid, liquid, or gaseous state as shown in the table. For convenience, these various combinations are divided into two groups, namely, liquid interfaces and solid interfaces.

liquid interfaces involve the association of a liquid phase with a gaseous or another liquid phase, while the 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)

The term **surface** is customarily used when referring to either a gas–solid or a gas–liquid interface. Thus, a table top surface forms a gas–solid interface with the atmosphere above it, and the surface of a rain drop constitutes a gas–liquid interface.

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

where the subscript L stands for liquid, V for vapor or gas, and S for solid

Liquid Interfaces

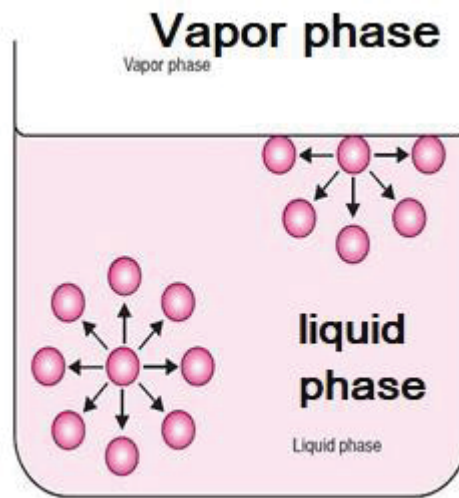
Surface and Interfacial Tensions

Surface tension :-

It is a property of the surface of the liquid that causes it to behave as an elastic sheet. It is caused by the attraction between molecules of the liquid by various intermolecular forces.

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. 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 the Figure. Such a force pulls the molecules of the interface together and, as a result, contracts the surface, resulting in a surface tension.



Unequal attractive forces acting on molecules at the surface of a liquid as compared with molecular forces in the bulk of the liquid

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.

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. That's mean:-

Adhesive forces between two liquids **More than** cohesive forces with the liquids

If two liquids are completely miscible, no interfacial tension exists between them.

Some representative surface and interfacial tensions are listed in the following table

Surface Tension and Interfacial Tension (Against Water) at 20°C			
Substance	Surface Tension (dynes/cm)	Substance	Interfacial Tension (dynes/cm)
Mercury	476	Mercury	375
Water	72.8	Water	-----
Glycerin	63.4	Glycerin	Zero (miscible liquids)
Oleic acid (Carboxylic acid)	32.5	Oleic acid	15.6
Benzene	28.9	Benzene	35.0
Chloroform	27.1	Chloroform	32.8
Olive oil (Oleic acid is the chief constituent)	35.8	Olive oil	22.9
Octanol (alcohol)	26.5	Octanol	8.5

The values for surface tension reflect the nature of intermolecular forces present.

Large values for mercury (metallic bonds) and water (H-bond) and the lower values for benzene and chloroform (London forces)

Values of interfacial tensions reflect the differences in chemical structure of the two phases involved, the greater the tendency to interact, the less interfacial tension.

In each case the presence of chemical groups capable of hydrogen bonding with water markedly decrease interfacial tension.

Interfacial tension causes immiscible liquids to resist mixing. Oil and water do not mix because of interfacial tension. To disperse one in the other, it is necessary to introduce another kind of molecule that has affinity for both oil and water like an amphiphile molecule. This type of molecule is called surface active agent (S.A.A). These molecules when placed at the interface of oil and water will decrease the interfacial tension, allowing oil and water to mix

Both Surface and interfacial tensions decrease by increasing the temperature, due to increase in the kinetic energy of the molecules. They also decrease by addition of S.A.A

Adsorption at Liquid Interfaces

Adsorption is a spontaneous phenomenon, adsorption can occur at the surface or interfaces of liquid with other liquids (**positive adsorption**).

It is the amphiphilic nature of surface-active agents that causes them to be adsorbed at interfaces, whether these are liquid–gas or liquid–liquid interfaces

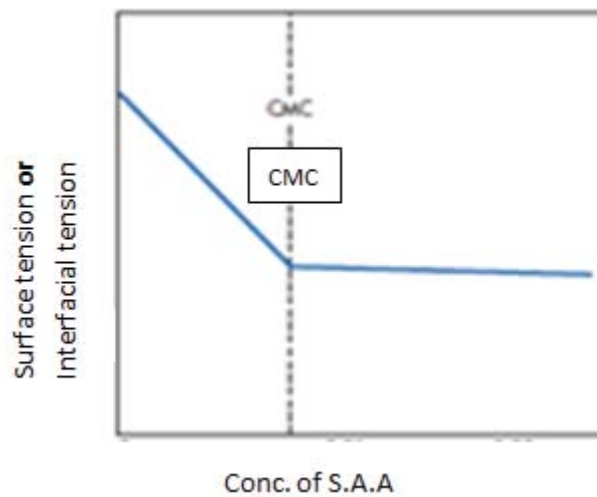
For the amphiphile to be concentrated at the interface, it must be balanced with the proper amount of polar and nonpolar groups. If the molecule is too hydrophilic, it remains within the body of the aqueous phase and exerts no effect at the interface. Likewise, if it is too lipophilic, it dissolves completely in the oil phase and little appears at the interface

On the other hand, **negative adsorption** is related to materials that are found in the bulk of liquid.

Effect of Surface active agents on surface and interfacial tension of water

The surface active agents reduce surface tension because when surfactant molecules adsorb at the water surface, 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 (interfere with hydrogen of water), hence the contraction force is reduced.

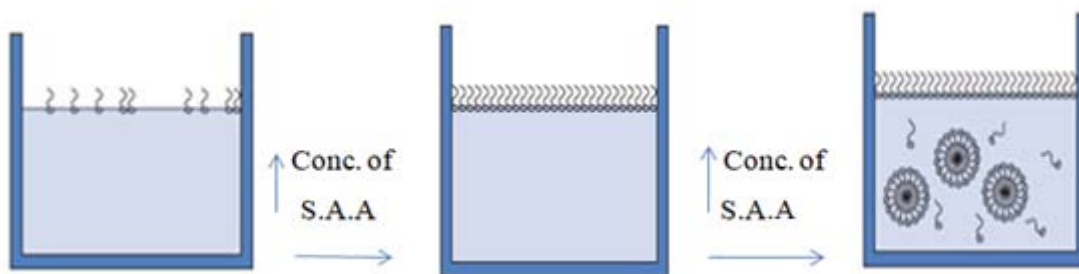
The surface tension decreases with increasing concentrations of the surface active agent; however, after a certain concentration of the surface active agent, the surface tension stops decreasing and reaches a plateau. This concentration is called critical micelle concentration (CMC).



(**Note:-** materials that concentrated in the bulk of liquid increase the surface tension of a liquid and they are called surface inactive agents like (e.g., inorganic electrolytes such as NaCl and sugar)

Why surface tension stops decreasing and reaches a plateau?

This is because at this concentration the surface is saturated with surface active molecules and any increase in their concentration will cause them to form micelles in the bulk



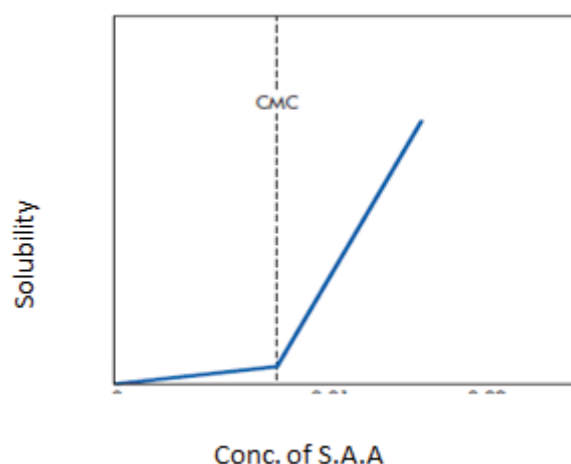
As more surface active agent is added to water, the surface of the water is covered by molecules of the surface active agent, and then micelles start forming

Why micells are formed?

To protect their hydrophobic groups from the aqueous environment

Effect of surfactant on solubility of slightly soluble substance

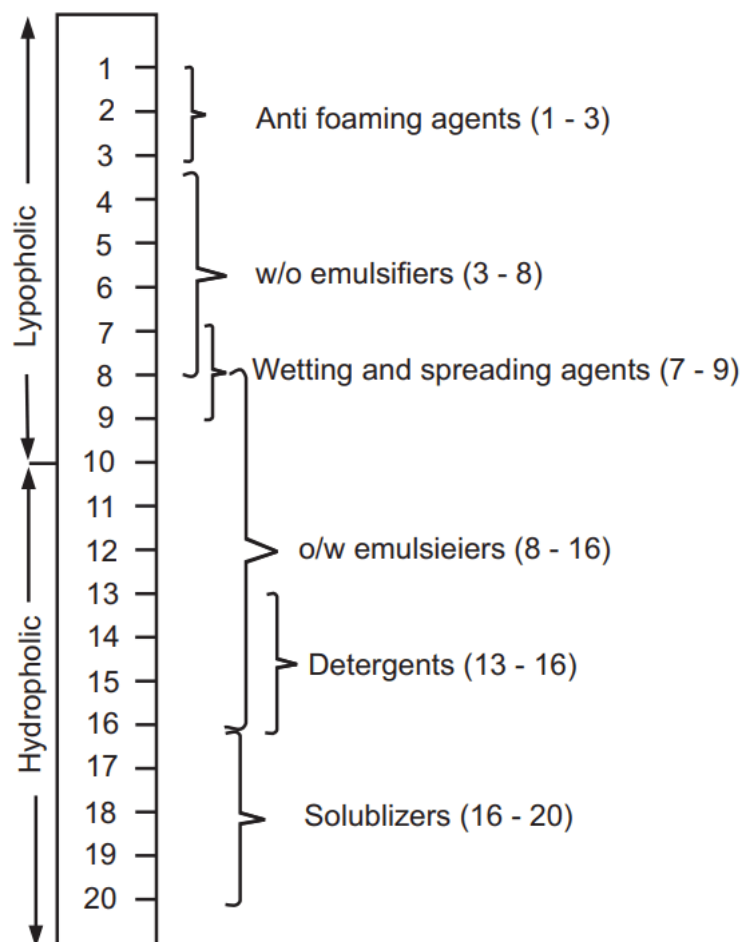
The ability of the solution to solubilize a drug, increase sharply when the concentration of the surface active agent increases beyond the CMC concentration since the nonpolar molecules in aqueous systems would be located in the hydrocarbon core of the micelle

**Hydrophile-Lipophile Balance**

The hydrophile–lipophile balance (HLB) number is a measure of the balance between hydrophobic and hydrophilic portions of a surfactant.

The HLB of a surfactant is expressed using an arbitrary scale which ranges from 0 to 20. At the higher end of the scale, the surfactants are hydrophilic and act as solubilizing agents, detergents and oil-in-water emulsifiers.

Oil-soluble surfactants have low HLB and act as water-in-oil emulsifiers.



A scale showing surfactant function on the basis of hydrophilic–lipophilic balance (HLB) values. Key: O/W = oil in water, w/o= water in oil

Wetting phenomena and wetting agents

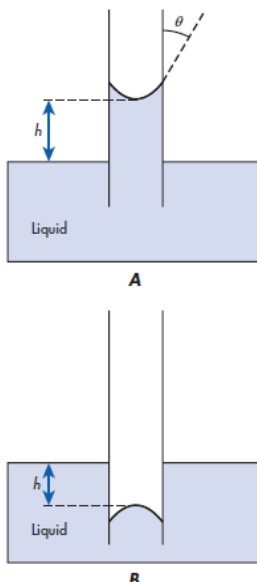
Wettability: - is the property that indicate the affinity between solid and fluid phase
Talc or charcoal sprinkled on the surface of water, they will float despite the fact that their densities are higher than that of water.

In order for wetting of solid to occur, the liquid must displace air and spread over the surface of the solid, otherwise, we say that the solid is NOT wetted

When a liquid comes into contact with the solid, the behavior of the liquid will depend on the balance between the forces of attraction of molecules in the liquid (cohesion) and the forces of attraction between the liquid and the solid phases (adhesion) .

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, 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.



A. Water can wet the glass

Because Adhesive forces more than cohesive
So water rise in side the capillary tube with concave surface

B .Mercury cannot wet the glass

Because cohesive forces more than adhesive
So mercury rise in side the capillary tube with convex surface

Many pharmaceutical preparations require dispersion of solid in liquids

Example: The preparation of **suspension** requires that the fine solid particles **immersed** and then **dispersed** in a liquid vehicle, that is mean the solid particles have to be wetted in order to be dispersed in a liquid.

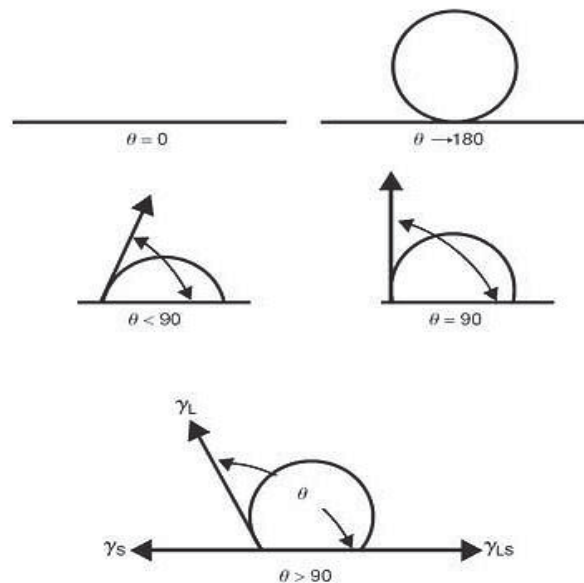
The parameter that reflects the degree of wetting is known as contact angle

Contact angle (Θ): - which is the angle between a liquid droplet and surface over which it spread it range from 0- 180° **(Figure below)**

$\Theta = 0$ means complete wetting (glass and water)

$\Theta = 180^\circ$ means no wetting (water and greasy surface)

The contact angle may also have any value between these limits (partial wetting)



Contact angles between 0° - 180°

Hydrophilic materials have small contact angle with water while hydrophobic material have large contact angle

To increase wetting, the contact angle should be decreased this is done by adding surfactant which is called wetting agent

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

Examples of the application of wetting to pharmacy and medicine:-

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 dirt 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

Spreading Coefficient

Lotions, creams, sunscreens, and many cosmetics have to be spread on the skin to exert their effect.

When a liquid spreads over the surface of a substrate, it covers all or a part of the surface. The substrate can be a solid or another liquid that is immiscible with the spreading liquid.

When a drop of oil is added on the surface of water, three things may happen:

1. The drop may spread as a thin film on the surface of water.
2. It may form a liquid lens if the oil cannot spread on the surface of water.
3. The drop may spread as a monolayer film with areas that are identified as lenses



A. Formation of a lens when a drop of oil is added to water.

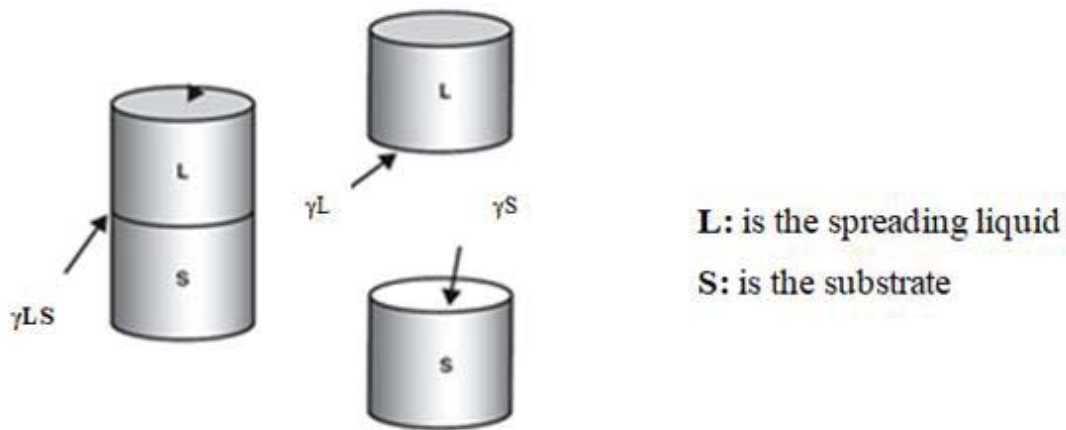
B. Monolayer of oil with a lens.

Spreading depends on the surface tension of the liquids involved and on the interfacial tension between them, that is mean spreading depends on the force of cohesion and adhesion.

For example : 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

Since spreading is dependent on the forces of adhesion and cohesion
That is mean it depend on work of adhesion and work of cohesion

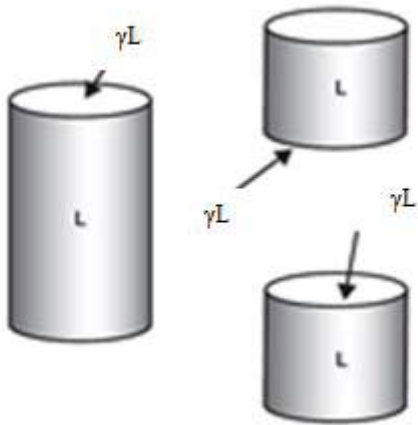
Work of adhesion: is the energy required to break the attraction between the unlike molecules. OR to separate two immiscible liquids that form an interface



The work of adhesion : is equal to the newly created surface tensions, γ_L and γ_S , minus the interfacial tension, γ_{LS} , that has been destroyed in the process. The work of adhesion is thus

$$W_a = \gamma_L + \gamma_S - \gamma_{LS}$$

The work of cohesion: is the work required to separate the molecules of the spreading liquid so that it can flow over the substrate



$$W_c = 2 \gamma_L$$

For spreading to occur the work of adhesion should be greater than the work of cohesion

$$W_a - W_c = S \quad (S \text{ is known as spreading coefficient})$$

OR

$$\begin{aligned} S &= W_a - W_c \\ &= (\gamma_L + \gamma_S - \gamma_{LS}) - 2 \gamma_L \\ &= \gamma_L + \gamma_S - \gamma_{LS} - 2 \gamma_L \\ &= \gamma_S - \gamma_{LS} - \gamma_L \\ S &= \gamma_S - (\gamma_L + \gamma_{LS}) \end{aligned}$$

$S = +ve$ value ; the liquid spread as a film

$S = -ve$ value ; the liquid form globules or floating lens and fail to spread over the liquid

Example : Which liquid is spread over the other?

$$\gamma_{\text{Hexane}} = 18 \text{ dyne/cm} \quad \gamma_{\text{water}} = 72.8 \text{ dyne/cm} \quad \gamma_{\text{Hexane/water}} = 50.8$$

If we want to spread hexane over water

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

$$S = 72.8 - (18 + 50.8)$$

$$S = 4.0 \text{ dyne/cm}$$

If we want to spread water over hexane

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

$$S = 18 - (72.8 + 50.8)$$

$$S = -105.6 \text{ dyne/cm}$$

Therefore the fact that both liquids are the same, the high surface tension of water prevent its spreading over hexane, while hexane with low surface tension and low cohesive forces can spread over water

Home Work

If you know that

$$\gamma_{\text{water}} = 72.8 \text{ dyne/cm} \quad \gamma_{\text{oleic acid}} = 32.5 \text{ dyne/cm} \quad \gamma_{\text{water/oleic acid}} = 15.6 \text{ dyne/cm}$$

Which liquid can spread over the other ? Explain

Sometimes spreading will occur only initially, and later the spreading liquid will be converted and a lens will form.

The conversion of the liquid to a lens occurs because the two substances in contact with each other become mutually saturated and their respective surface tensions become different from the initial surface tensions (when the liquids were pure).

If we use a prime (') to denote the values following equilibration (saturation) (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**

Example 16-7 :-If the surface tension of water γS is 72.8 dynes/cm at 20°C, the surface tension of benzene, γL , is 28.9 dynes/cm, and the interfacial tension between benzene and water, γLS , 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?

$$S = \gamma S - (\gamma L + \gamma LS)$$

$$S = 72.8 - (28.9 + 35)$$

$$S = 8.9 \text{ dyne/cm}$$

After equilibrium

$$S' = \gamma S' - (\gamma L' + \gamma LS)$$

$$S' = 62.2 - (28.8 + 35)$$

$$= -1.6 \text{ dyne/cm}$$

Therefore when benzene is added to water, one will observe an initial rapid spreading of benzene on the surface of the water, but later when benzene and water become mutually saturated with each other, the benzene retracts and forms a lens

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In the case of organic liquids spread on water, it is found that although the initial spreading coefficient may be positive or negative, the final spreading coefficient always has a negative value

It is important to consider the types of molecular structures that lead to high spreading coefficient.

Initial Spreading Coefficient, S, at 20°C

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

A material spreads over water because it contains polar groups such as COOH or OH.

But the carbon chain, 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

Surface active agents (SAA) increase S because they interfere with cohesive forces

Application of S.A.A

- 1- As emulsifying agents by decrease Interfacial tension
- 2- Wetting agents by decreasing the contact angle; wetting is the first step for dispersing a solid in a liquid vehicle
- 3-Detergents; which are surfactants that are used for removal of dirt
- 4- Solubilizing agents by formation of micells
- 5- A surfactant may affect the activity of a drug.

The presence of a low concentration of surfactant will potentiate the activity of anthelmintic drug. 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 the drug over the surface of the organism is facilitated. When the concentration of surface-active agent present exceeds that required amount it will form micelles and 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. or may itself exert drug action

6- A surfactant may exert a drug action

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

Electrical Properties of interfaces

Electric Properties - charge on the surface of a particle

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 because the hydronium ion is more hydrated than hydroxyl ion, so they have greater tendency to be in the bulk of aqueous medium, whereas the less hydrated hydroxyl ion have greater tendency to be adsorbed at the surface of particle

Second, charges on particles arise from ionization of groups that may be situated at the surface of the particle. In these cases, the charge is a function of pH and pKa.

Example amino acid and protein (have COOH and NH₂) groups on their structure

At low pH, the protein will have +ve charge due to ionization of -NH₂ groups to -NH₃⁺

At high pH the protein will have -ve charge due to ionization of -COOH groups to -COO⁻

At certain pH (specific for each protein), the total no. of +ve charge equal to the total no. of -ve charge and the net charge will be zero

This pH is termed as isoelectric point of protein and the protein exists as Zwitterion

The Electric Double Layer

Consider a solid surface in contact with a polar solution containing ions, for example, an aqueous solution of an electrolyte. Furthermore, 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, whereas the remainders 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. 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 the Figure 1, where 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' in the Figure 1. These ions, having a charge opposite to that of the potential-determining 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 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, 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' .

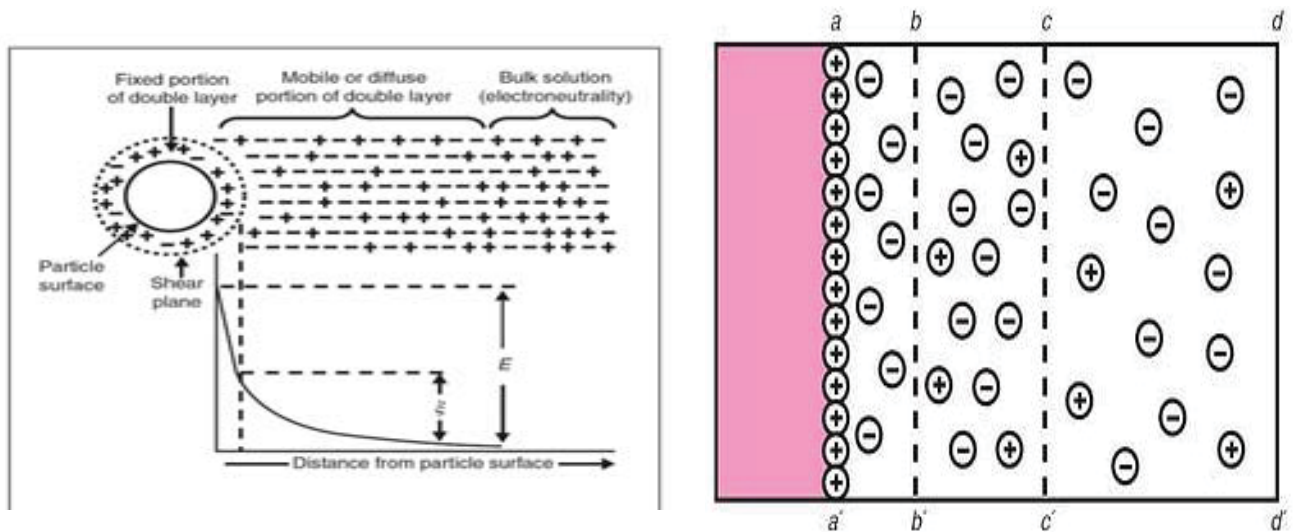


Fig. 1. The electric double layer at the surface of separation between two phases, showing distribution of ions. The system as a whole is electrically neutral.

Two situations other than that represented by the figure are possible:

- 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' .
- 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 the figure 2. 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.

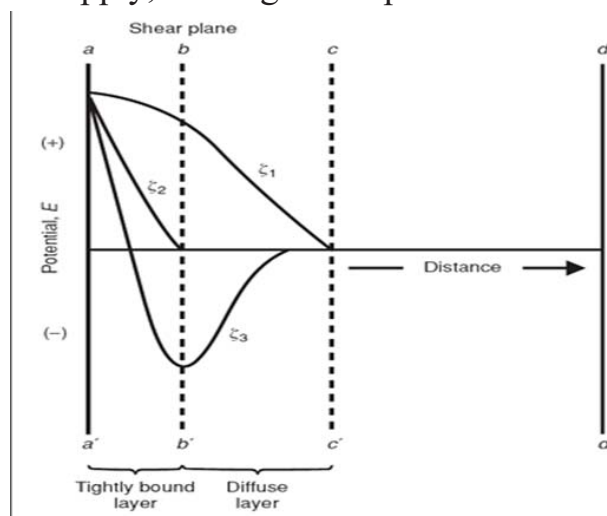


Fig. 2. Electrokinetic potential, E , at solid-liquid boundaries. Curves are shown for three cases characteristic of the ions or molecules in the liquid phase. Note that although E is the same in all three cases, the zeta potentials are positive (ζ_1), zero (ζ_2), and negative (ζ_3).

Nernst and Zeta Potentials

The changes in potential with distance from the surface for the various situations discussed in the previous section can be represented as shown in Figure 2.

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, **The zeta potential**, ζ 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 2, 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.

The zeta potential has practical application in the stability of systems containing dispersed particles because this potential, rather than the Nernst potential, it 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 potential falls off more rapidly with distance and the thickness of the double layer decreased. 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.

Application of Zeta potential

1- Interfacial Properties of Suspended Particles

The particles in a liquid suspension tend to **flocculate**, that is, to form light, fluffy conglomerates that are held together by weak van der Waals forces, but under certain conditions, the particles may adhere by stronger forces to form what are termed **aggregates** or **cake**

When the repulsion energy (zeta potential) is high, the collision of the particles is opposed. The system remains **deflocculated** (dispersed or suspended), and, when sedimentation is complete, the particles form a close-packed arrangement with the smaller particles filling the voids between the larger ones. Those particles lowest in the sediment are gradually pressed together by the weight of the ones above and they will adhere together by strong forces to form **aggregates or cake** .To resuspend and redisperse these particles, it is again necessary to overcome these forces .Because this is not easily achieved by agitation, the particles tend to remain strongly attracted to each other and form a hard **cake**.

Flocculated particles are weakly bonded, settle rapidly, do not form a cake, and are easily resuspended.

Therefore, a very high +ve or -ve zeta potential is not preferred in preparation of suspension, but its value should be controlled within certain limit as shown in the figure below, and this is done by adding a flocculating agents

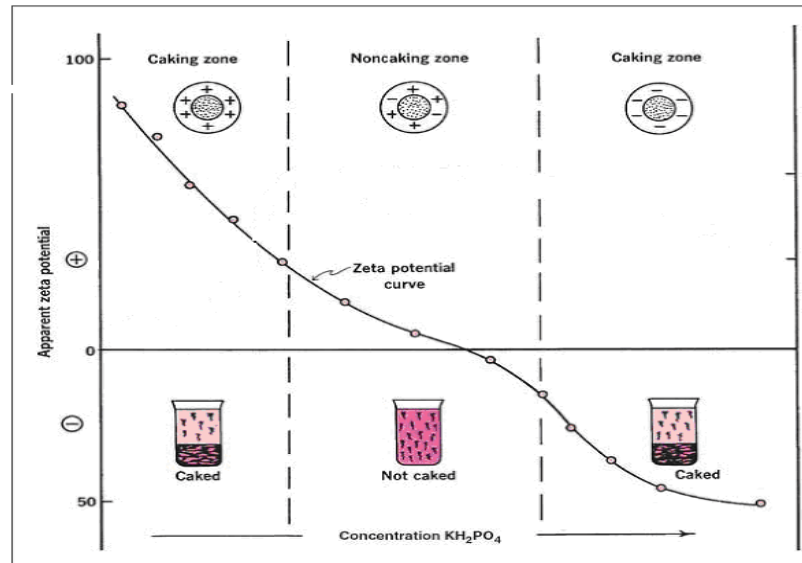


Fig. 3. Caking diagram, showing the flocculation of suspension by means of the flocculating agent monobasic potassium phosphate

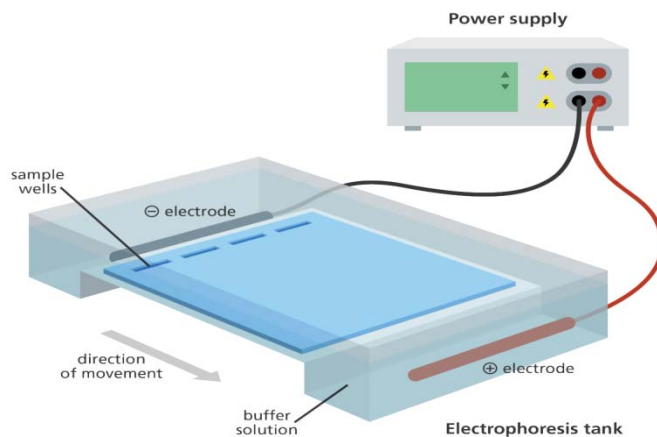
2- Electrokinetic Phenomena

The movement of a charged surface with respect to an adjacent liquid phase .
The most important application of this phenomena is electrophoresis

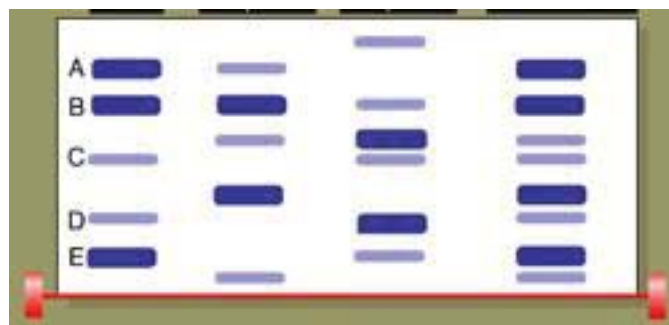
3- Electrophoresis:

Involves the movement of a charged particle through a liquid under the influence of an applied potential difference. An electrophoresis cell fitted with two electrodes contains the dispersion. When a potential is applied across the electrodes, the particles migrate to the oppositely charged electrode. From knowledge of the direction and rate of migration, the sign and magnitude of zeta potential can be determined

It is mainly used for separation of plasma protein



Electrophoresis tank



Electrophoresis sheet