

**FACULTY OF PHARMACEUTICAL SCIENCES
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**B.PHARM 3rd SEM
PHYSICAL PHARMACEUTICS-I
BP302T**

Surface and interfacial tension phenomena

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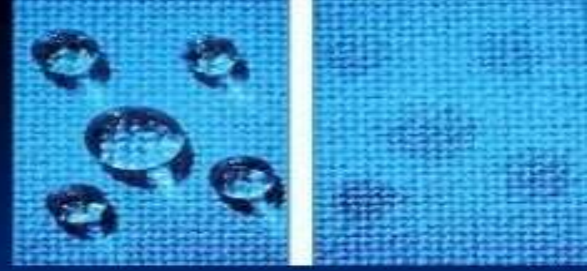
Classification of Surface Active Agents

Functional Classification

According to their pharmaceutical use, surfactants can be divided into the following groups:

- Wetting agents**
- Solubilizing agents**
- Emulsifying agents**
- Dispersing, Suspending and Deflocculating agents**
- Foaming and antifoaming agents**
- Detergents**

Wetting agents



❖ **Wetting agent is a surfactant that when dissolved in water, lower the contact angle and aids in displacing the air phase at the surface and replacing it with a liquid phase.**

❖ **Solids will not be wetted if their critical surface tension is exceeded than the surface tension of the liquid. Thus water with a value of 72 dynes/cm will not wet polyethylene with a critical surface tension of 31 dynes/cm.**

❖ **Based on this concept we should expect a good wetting agent to be one which reduces the surface tension of a liquid to a value below the solid critical surface tension.**

According to the nature of the liquid and the solid, a drop of liquid placed on a solid surface will adhere to it or no. which is the wettability between liquids and solids.

When the forces of adhesion are greater than the forces of cohesion, the liquid tends to wet the surface and vice versa. Place a drop of a liquid on a smooth surface of a solid. According to the wettability, the drop will make a certain angle of contact with the solid.

A contact angle is lower than 90° , the solid is called wettable

A contact angle is wider than 90° , the solid is named non-wettable.

A contact angle equal to zero indicates complete wettability.



The contact angle of a liquid with a solid is used as wettability index. For $\alpha < 90^\circ$ the liquid wet the wall (eg: water on glass), for $\alpha > 90^\circ$ the liquid does not wet the wall (eg: mercury on glass). If $\alpha = 0^\circ$ the liquid perfectly wet the wall.

**complete
wetting**

incomplete wetting

**no
wetting**



$$\theta = 0^\circ$$

$$\theta < 90^\circ$$

$$\theta = 90^\circ$$

$$\theta > 90^\circ$$

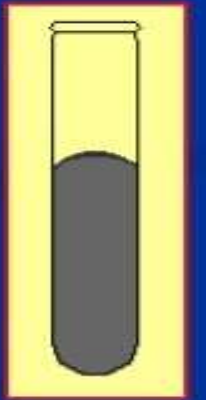
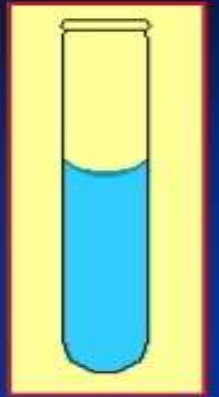
$$\theta = 180^\circ$$

$$\gamma_s - \gamma_{sL} > 0$$

$$\gamma_s - \gamma_{sL} \approx 0$$

$$\gamma_s - \gamma_{sL} < 0$$

- ❖ **The surface of liquid water (meniscus) has a **concave shape** because water wets the surface and creeps up the side**
- ❖ **The surface of Mercury has a **convex shape** it does not wet glass because the cohesive forces within the drops are stronger than the adhesive forces between the drops and glass.**



Micellar Solubilization

- **Surfactant molecules accumulate in the interfaces between water and water insoluble compound. Their hydrocarbon chains penetrate the outermost layer of insoluble compound which combine with the water-insoluble molecules. Micelles form around the molecules of the water-insoluble compound inside the micelles' cores and bring them into solution in an aqueous medium. This phenomenon is called micellar solubilization.**
- **The inverted micelles formed by oil-soluble surfactant which dissolves in a hydrocarbon solvent can solubilize water-soluble compound which is located in the center of the micelle, out of contact with the solvent.**

● **Micelles of nonionic surfactants consist of an outer shell containing their polyethylene glycol moieties mixed with water and an inner core formed by their hydrocarbon moieties. Some compounds like phenols and benzoic acid form complexes with polyethylene glycols by hydrogen bonding and/or are more soluble in liquids of intermediate polarity like ethanol or ethyl ether than in liquids of low polarity like aliphatic hydrocarbons. These compounds locate in the aqueous polyethylene glycol outer shell of nonionic micelles on solubilization.**

Drugs which are soluble in oils and lipids can be solubilized by micellar solubilization.

● **As Micellar solubilization depends on the existence of micelles; it does not take place below the CMC. So dissolution begins at the CMC. Above the CMC, the amount solubilized is directly proportional to the surfactant concentration because all surfactant added to the solution in excess of the CMC exists in micellar form, and as the number of micelles increases the extent of solubilization increases .**

● **Compounds that are extensively solubilized increase the size of micelles in two ways:**

- **The micelles swell because their core volume is augmented by the volume of the solubilizate.**
- **The number of surfactant molecules per micelle increases.**

Foaming and Anti Foaming agents

❖ ***Foams are dispersion of a gas in a liquid (liquid foams as that formed by soaps and detergents) or in a solid (solid foams as sponges).***



❖ **Foaming agents**

Many Surfactants solutions promote the formation of foams and stabilize them, in pharmacy they are useful in toothpastes compositions.

❖ **Anti Foaming agents**

They break foams and reduce frothing that may cause problems as in foaming of solubilized liquid preparations. in pharmacy they are useful in aerobic fermentations, steam boilers.

Detergents

- **Detergents are surfactants used for removal of dirt.**
- **Detergency involves:**
 - **Initial wetting of the dirt and the surface to be cleaned.**
 - **Deflocculation and suspension, emulsification or solubilisation of the dirt particles**
 - **Finally washing away the dirt.**

The molecules insert their hydrophobic tail inside the fat.



How surfactants remove the dirt



The polar and hydrophilic heads, carry the dirt in the water. The agitation of the fluid make easier the process.

Structural Classification

- **A single surfactant molecule contains one or more hydrophobic portions and one or more hydrophilic groups.**
- **According to the presence of ions in the surfactant molecule they may be classified into:**
 - ☐ **Ionic surfactants**
 - **Anionic surfactants: the surface active part is anion (negative ion) e.g. soaps, sodium lauryl sulfate**
 - **Cationic surfactants: the surface active part is cation (positive ion) e.g. quaternary ammonium salts**
 - **Ampholytic surfactants: contain both positive and negative ions e.g. dodecyl-B-alanine.**

Ionic surfactants

Anionic surfactants

- ➡ They are the metal salts of long - chain fatty acids as lauric acid.
- ➡ *Sodium dodecyl sulfate or Sodium Lauryl Sulfate* is used in toothpaste and ointments
- ➡ *Triethanolamine dodecyl sulfate* is used in shampoos and other cosmetic preparations.
- ➡ *Sodium dodecyl benzene sulfonate* is a detergent and has germicidal properties.
- ➡ *Sodium dialkylsulfosuccinates* are good wetting agents.

Cationic surfactants

- ➔ **These are chiefly quaternary ammonium compounds.**
- ➔ **They have bacteriostatic activity probably because they combine with the carboxyl groups in the cell walls and of microorganisms by cation exchange, causing lysis.**
- ➔ **Among the most popular antiseptics in this category are benzalkonium chloride, cetylpyridinium chloride and cetyltrimethylammonium bromide,**

Ampholytic Surfactants

- ➔ **These are the least common, e.g. dodecyl- β -alanine**

Non-ionic surfactants

➔ **Widely used in pharmaceutical formulations e.g. Tweens, Spans, Brij and Myrj.**

➔ **They are polyethylene oxide products.**

➔ **Surfactants based on sorbitan are of pharmaceutical importance.**

➔ **Esterification of the primary hydroxyl group with lauric, palmitic, stearic or oleic acid forms sorbitan monolaurate, monopalmitate, monostearate or monooleate**

These are water-insoluble surfactants called Span 20, 40, 60 or 80, respectively.

➔ **Addition of about 20 ethylene oxide molecules produces the water-soluble surfactants called polysorbate or Tween 20, 40, 60 or 80.**



Oriented Adsorption of surfactant at Interfaces

As a Surface active substance contains a hydrophilic and a hydrophobic portions, it is adsorbed as a monolayer at the interfaces.

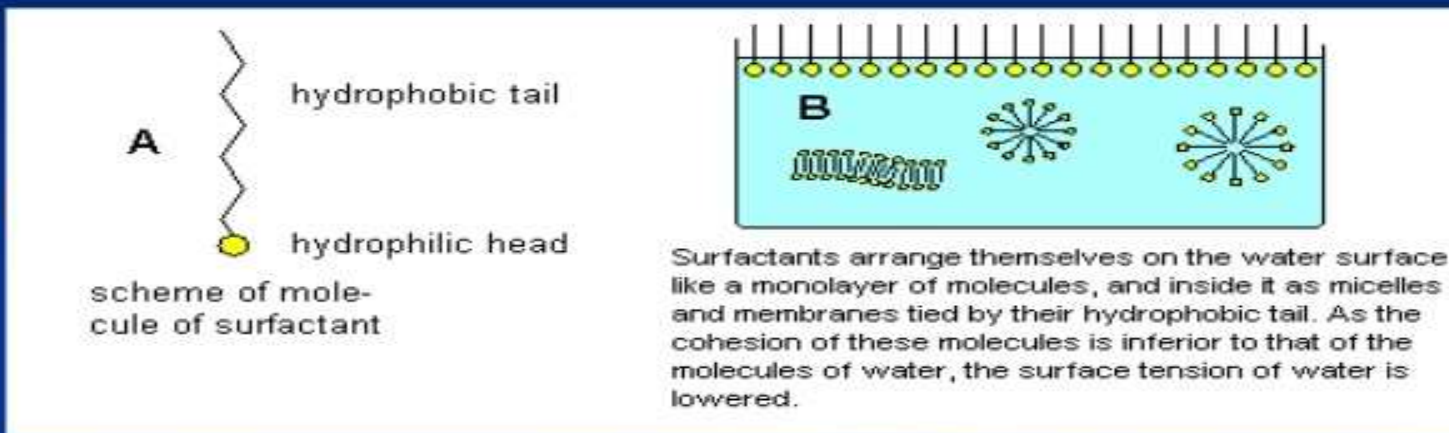
At water-air interface

Surface-active molecules will be adsorbed at water-air interfaces and oriented so

that the hydrocarbon chains of are pushed out of the water and rest on the surface, while the polar groups are inside the water. Perhaps the polar groups pull the hydrocarbon chains partly into the water.

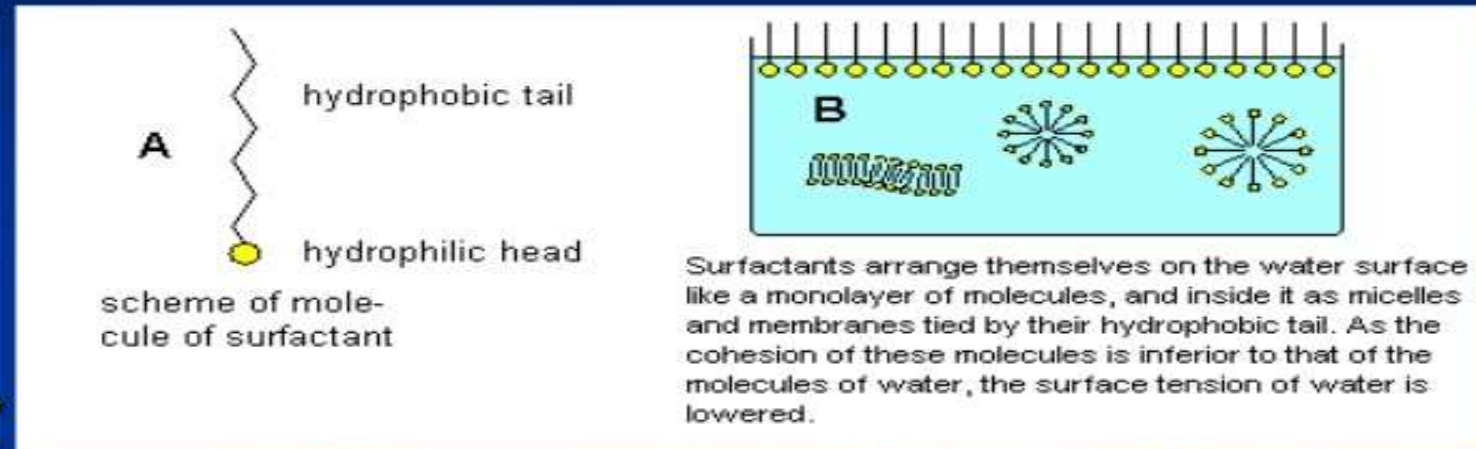
At oil-water interface

Surface-active molecules will be oriented so that the hydrophobic portion is inside the oil phase and the hydrophilic portion inside the water phase.



At low surfactant concentrations:

The hydrocarbon chains of surfactant molecules adsorbed in the interface lie nearly flat on the water surface.



At higher concentrations:

They stand upright because this permits more surfactant molecules to pack into the interfacial monolayer.

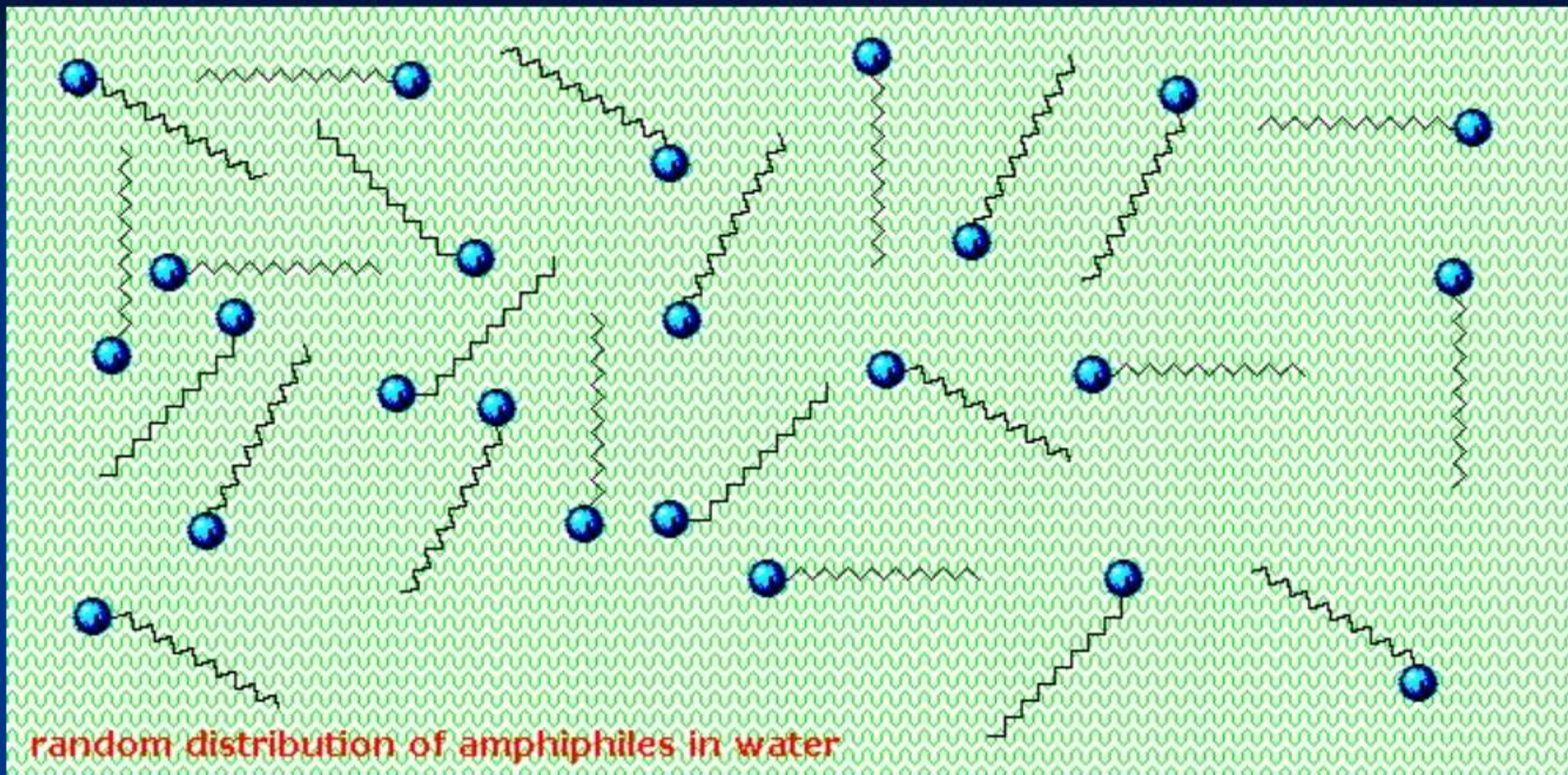
As the number of surfactant molecules adsorbed at the water-air interface increased, they tend to cover the water with a layer of hydrocarbon chains. Thus, the water-air interface is gradually transformed into a non polar-air interface. This results in a decrease in the surface tension of water.

◆ **At a given concentration, temperature, and salt content, all micelles of a given surfactant usually contain the same number of molecules, i.e. they are usually monodisperse. For different surfactants in dilute aqueous solutions, this number ranges approximately from 25 to 100 molecules.**

◆ **The diameters of micelles are approximately between 30 and 80 Å. Because of their ability to form aggregates of colloidal size, surfactants are also called association colloids.**

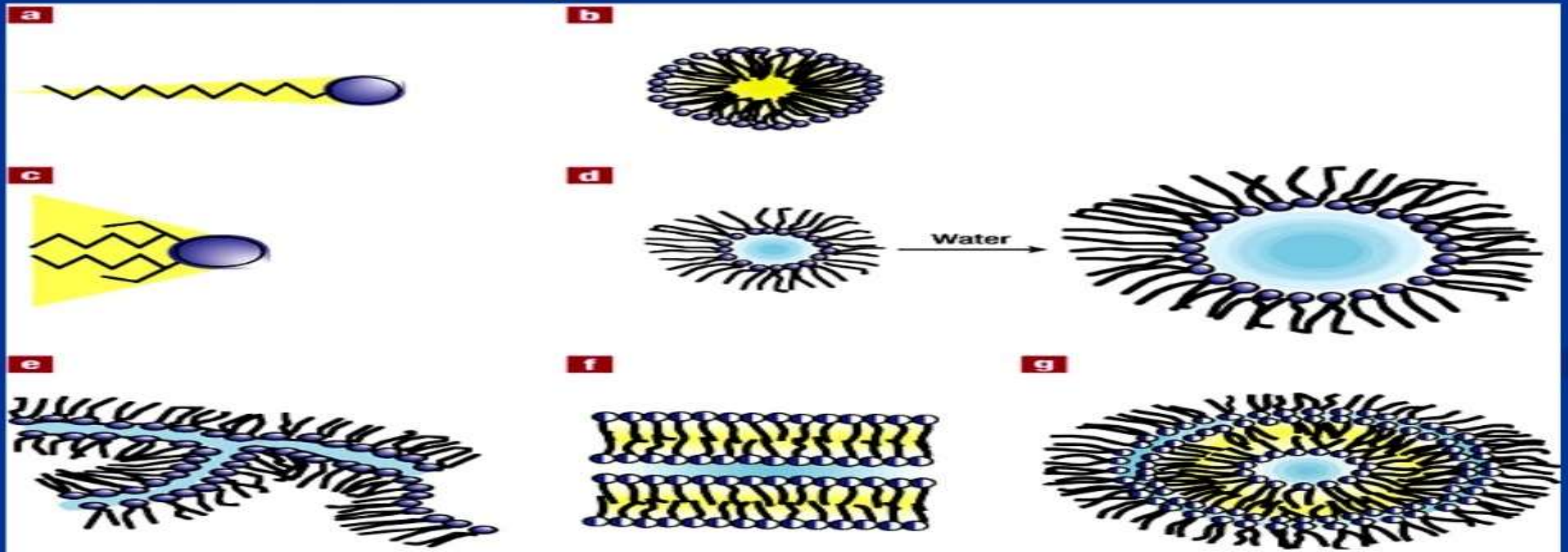
◆ **Micelles are not permanent aggregates. They form and disperse continually.**

Please wait



Surfactant shapes in colloidal solution

- a**- Cone-shaped surfactant resulting in **b**-normal micelles
- c**- Champagne cork shaped surfactant resulting in **d**-reverse micelles with control of their size by the water content
- e**- Interconnected cylinders .
- f**- Planar lamellar phase .
- g**- Onion-like lamellar phase.



➤ **Normal spherical micelles**

In dilute aqueous solutions micelles are approximately spherical. The polar groups of the surfactants are in the periphery and the hydrocarbon chains are oriented toward the center, forming the core of the micelles

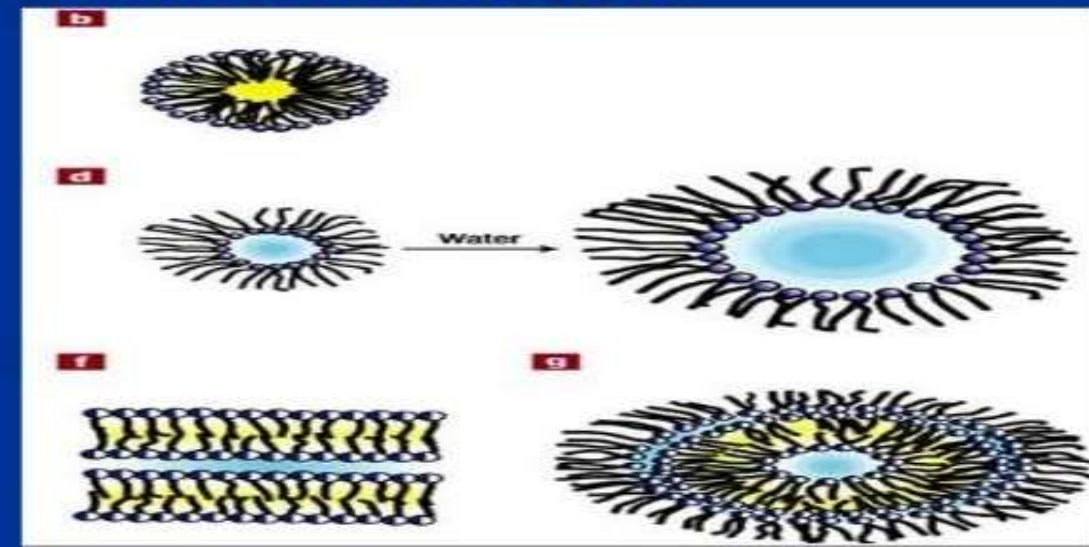


➤ **Inverted spherical micelles**

In solvents of low polarity or oils micelles are inverted. The polar groups face inward to form the core of the micelle while the hydrocarbon chains are oriented outward

➤ **Cylindrical and lamellar micelles**

In more concentrated solutions of surfactants, micelles change from spherical either to cylindrical or lamellar phase.



Incompatibilities Involving Surfactants

Nonionic surfactants

Nonionic surfactants have few incompatibilities with drugs and are preferred over ionic surfactants, even in formulations for external use, except when the germicidal properties of cationic and anionic surfactants are important.

Nonionic surfactants form weak complexes with some preservatives as phenols, including esters of p-hydroxybenzoic acid (Parabenzes) and with acids like benzoic and salicylic via hydrogen bonds. This reduces the antibacterial activity of these compounds.



Ionic surfactants

Ionic surfactants capable of reacting with compounds possessing ions of the opposite charge. These reactions may bind the surface active ions, sometimes with precipitation. The compounds which react with the surface active ions are also changed, and this may be harmful from the physiological or pharmacological point of view.

- ❖ Incompatibility of surface active quaternary ammonium compounds with bentonite, kaolin, talc, and other solids having cation exchange capacity.**

❑ Define the following terms:

[solid, liquid, gas, pure substance, compound, mixture, element, heterogeneous mixture, homogeneous mixture, extensive properties, intensive properties, chemical properties, physical properties, density, color, texture, conductivity, malleability, ductility, boiling point, melting point, flammability, corrosiveness, volatility, pounding, tearing, cutting, dissolving, evaporating, fermenting, decomposing, Exothermic, endothermic, mass, density, gravity, adhesive force, cohesive force, interface, adsorption, catalyst, dipole, physisorption, Chemisorption, hydrophilic, hydrophobic, detergent, surfactant, surface tension, adsorbate, adsorbent, etc]

❑ Respond to the following questions:

- Give a descriptive account of the phases of matter with logical relevance to state of medicines as they are taken for their respective therapeutical values
- What is viscosity and its relation with fluids
- What are surface and Inter-facial tension forces and respective association with activities of a substance material with surface area
- Describe some key phase changes of materials substance when exposed to some environmental conditions .
- How is a chemical change different from a physical change at the surface of a material
- What is contact angle of a substance and its significant role when two materials surface are in contact
- Describe the role of contact angle during the wetting process of a material substance
- What is a detergent and justified reasons for its variable composition
- Differentiate the role of adsorption process of a material substance in surface and interfacial tension
- State and explain the factors that have direct adsorptive effect on surface and interfacial tension process
- Describe some practical applications of surface and interfacial tension process with some examples
- What is the micelle made up of in terms of its physical form and shape
- What are some of the practical uses of micellular material
- State and explain some of the medical and pharmaceutical applications of named surface active agents.