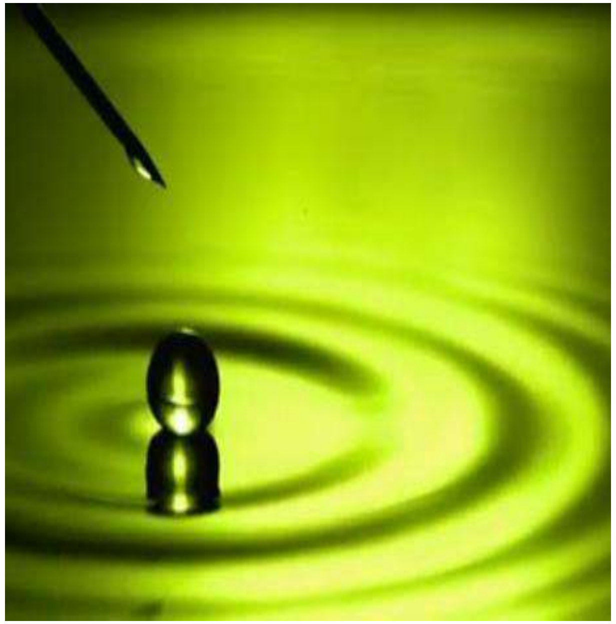
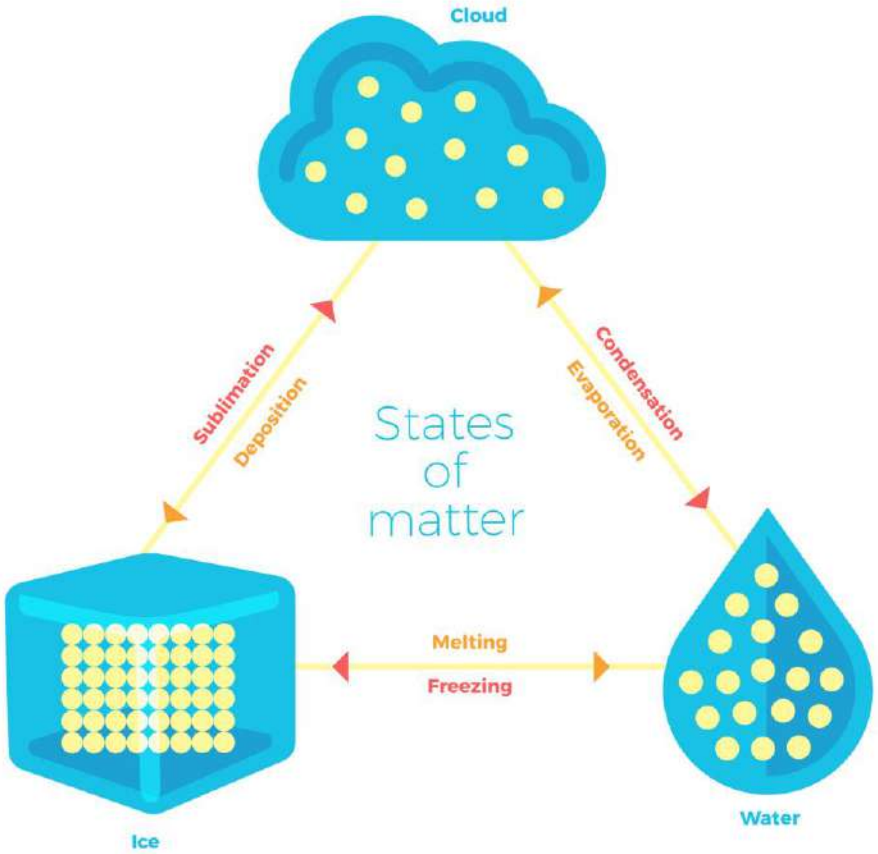
INTERFACIAL PHENOMENA

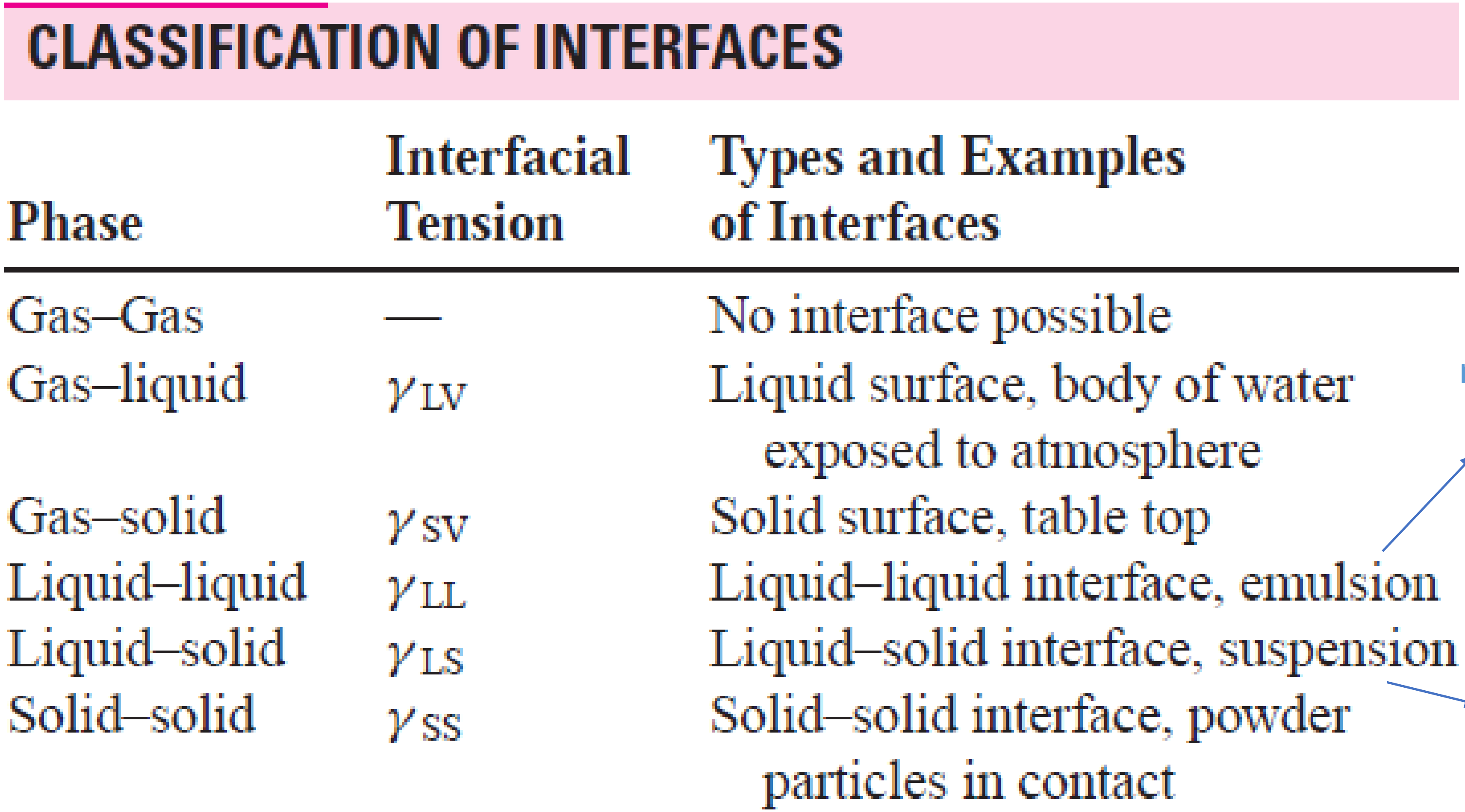


Phase vs State

O_2
CO_2
H_2
H_2O



- ✓Interface is the boundary between two or more phases exist together
- ✓Several types of interface can exist, depending on whether the two adjacent phases are in the solid, liquid, or gaseous state



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

mixture of two or more liquids in which one is present as droplets

insoluble solid particles are dispersed in a liquid medium

- The term **surface** is customarily used when referring to either a gas–solid or a gas–liquid interface.
- When phases exist together, the boundary between two of them is known as **an interface**

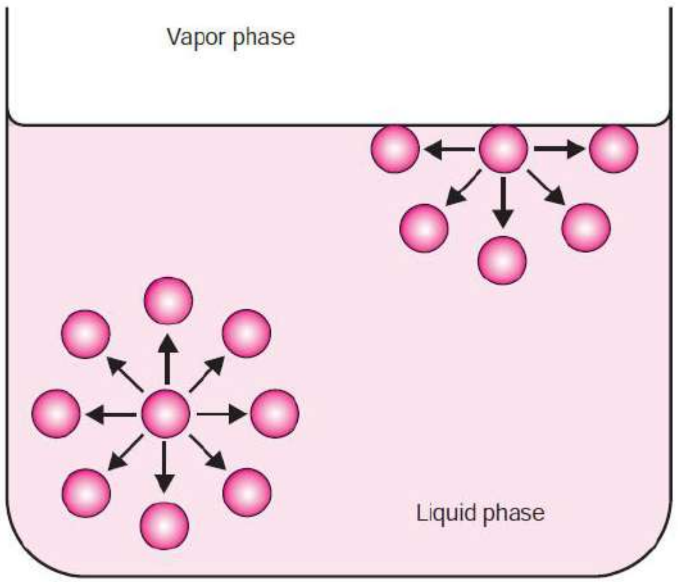
- Every surface is an interface.
  - ✓a tabletop forms a gas–solid interface with the atmosphere above it
  - ✓the surface of a raindrop constitutes a gas–liquid interface.
- **Interfacial phenomena** in pharmacy and medicine are significant factors that affect:
  - ✓ adsorption of drugs onto solid adjuncts in dosage forms,
  - ✓penetration of molecules through biologic membranes,
  - ✓emulsion formation and stability,
  - ✓dispersion of insoluble particles in liquid media to form suspensions.

LIQUID INTERFACES

A- Surface and Interfacial Tensions

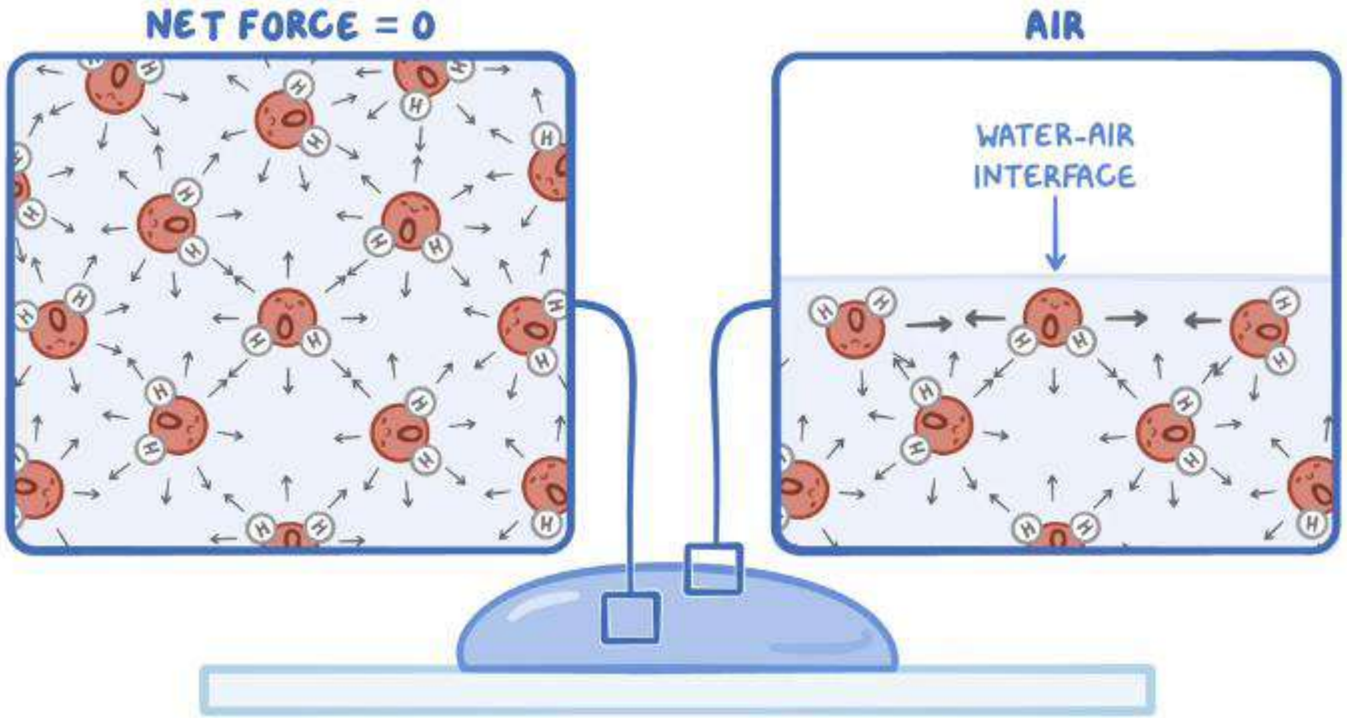
The properties of the molecules forming the interface are different from those in the bulk that these molecules are forming an interfacial phase.

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



- For the molecules at the **surface** (at the liquid/air interface):
    - attractive cohesive forces with other liquid molecules which are situated below and adjacent to them.
    - adhesive forces of attraction with the molecules of the other phase in the interface

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



- **Surface tension:** is the force per unit length that must be applied parallel to the surface so as to counterbalance the net inward pull. (The units of dynes/cm or N/m).

- **Interfacial tension:** is the force per unit length existing at the interface between two immiscible liquid phases. (The units of dynes/cm).

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

- We will use the term **interfacial tension** for the force
  - ✓between two liquids, γLL,
  - ✓between two solids, γSS,
  - ✓ at a liquid–solid interface,γLS

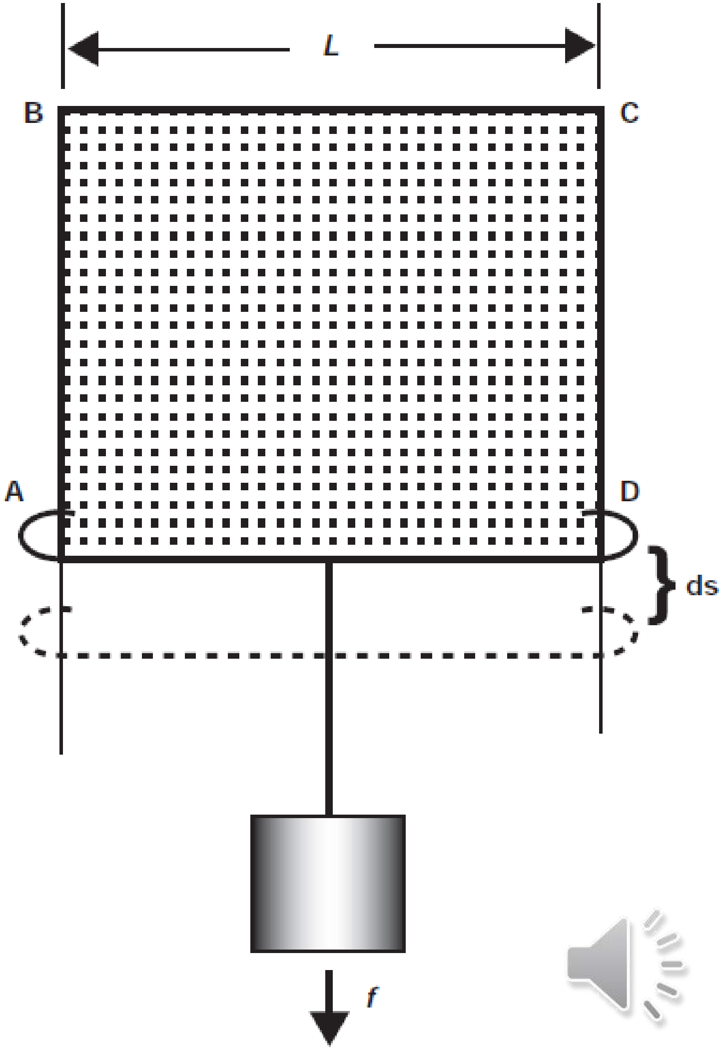
- The term **surface tension** is reserved for
  - liquid–vapor, γLV,
  - solid–vapor, γSV, tensions

- Interfacial tensions are less than surface tensions because adhesive forces between the two liquid phases forming the interface are greater than when a liquid and a gas phase exist together.

- Surface tension as a force per unit length can also be illustrated by means of a **three-sided wire frame** across which a movable bar is placed.

$$\gamma = f_b/2L$$

Where fb is the force required to break the film and L is the length of the movable bar



B- Surface Free Energy

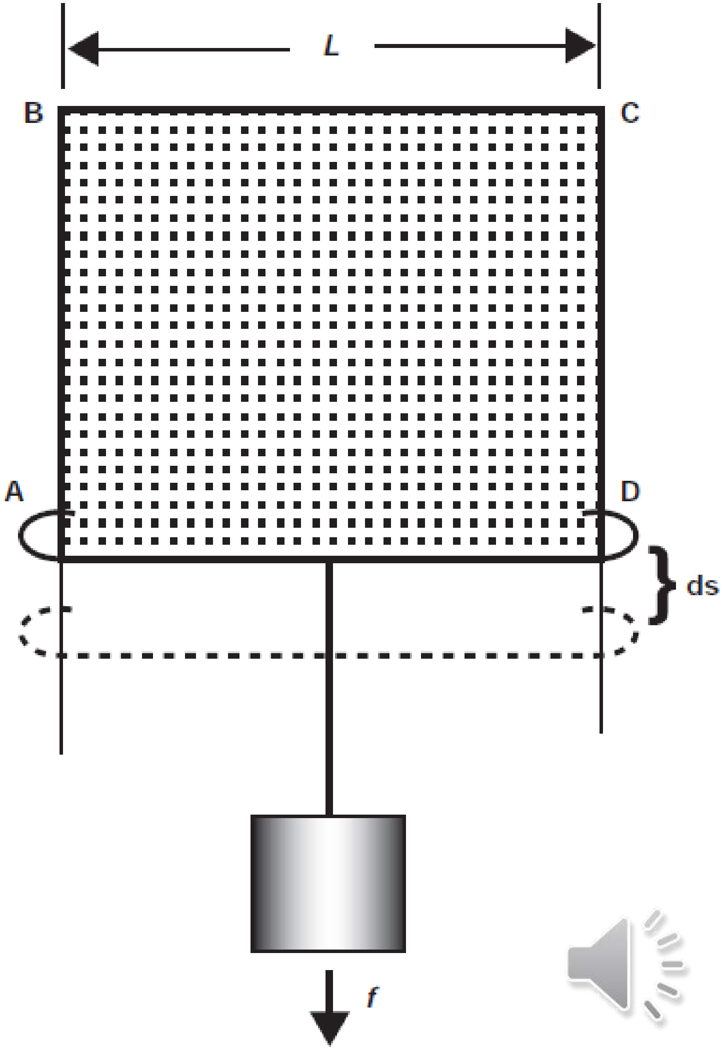
- To move a molecule from the inner layers to the surface, work needs to be done against the force of surface tension.
- In other words, each molecule near the surface of liquid possesses a certain excess of potential energy as compared to the molecules in the bulk of the liquid.
- The higher the surface of the liquid, the more molecules have this excessive potential energy.
- Therefore, if the surface of the liquid increases, the energy of the liquid also increases.
- Because this energy is proportional to the size of the free surface, it is called a **surface free energy.**

- To increase the surface of the liquid without any additional changes in the liquid state, in particular without changes in liquid temperature, work must be done against the surface tension.
- To evaluate the amount of work in increasing the surface area, we can write:

$$\gamma \times 2\mathcal{L} = f$$

- When the bar is at a position AD in the figure and a mass is added to extend the surface by a distance ds, the work dW (force multiplied by distance) is

$$dW = f \times ds = \gamma \times 2\mathcal{L} \times ds$$



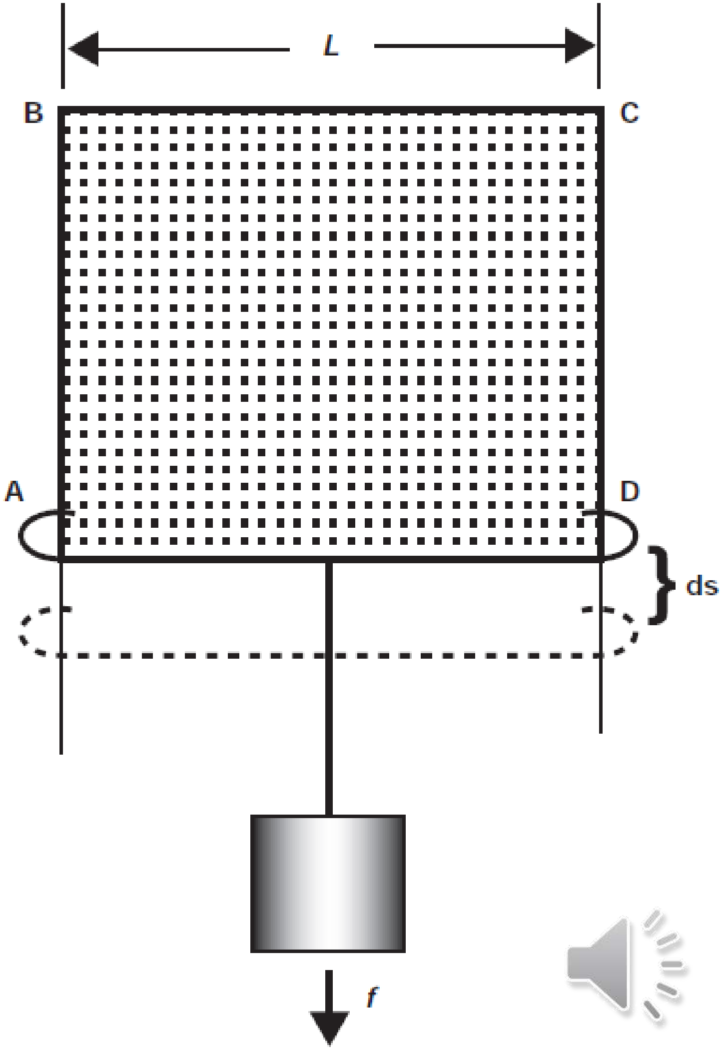
- and, because 2L × ds is equal to the increase in surface area, dA, produced by extending the soap film,

$$dW = \gamma \, dA$$

- For a finite change,

$$W = \gamma \Delta A$$

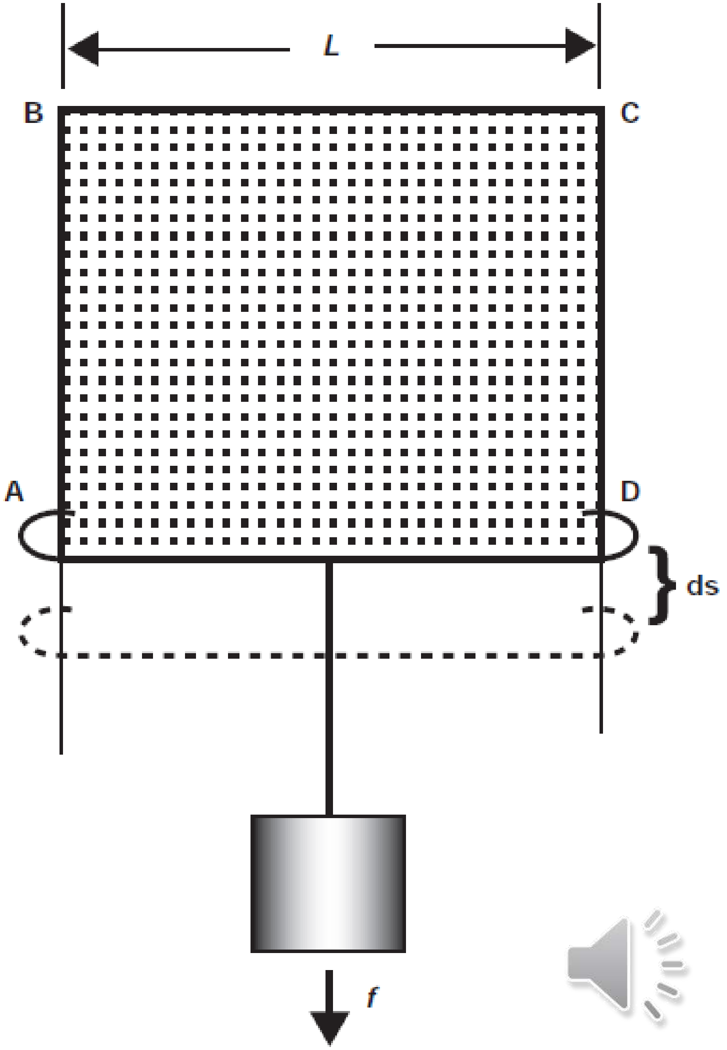
where W is the work done, or ***surface free energy*** **increase**, expressed in ergs, γ is the surface tension in dynes/cm, and A is the increase in area in cm2.



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

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

- From equation, **Surface tension** can be defined as the surface free energy change per unit area increase OR the work per unit area required to produce a new surface.



- 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.

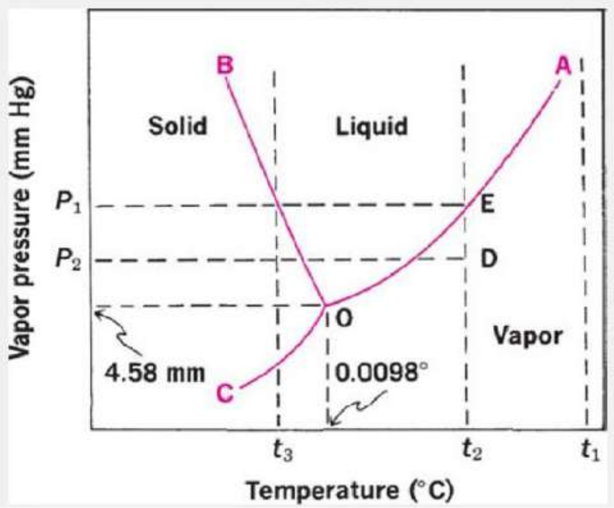
Measurement of Surface and Interfacial Tensions

Methods for Measuring Surface and Interfacial Tensions:

1. Capillary Rise Method.
2. DuNoüy Ring Method.

- The choice of a particular method often depends on:
  - a) Whether surface or interfacial tension is to be determined,
  - b) The accuracy and convenience desired,
  - c) The size of sample available,
  - d) whether the effect of time on surface tension is to be studied.

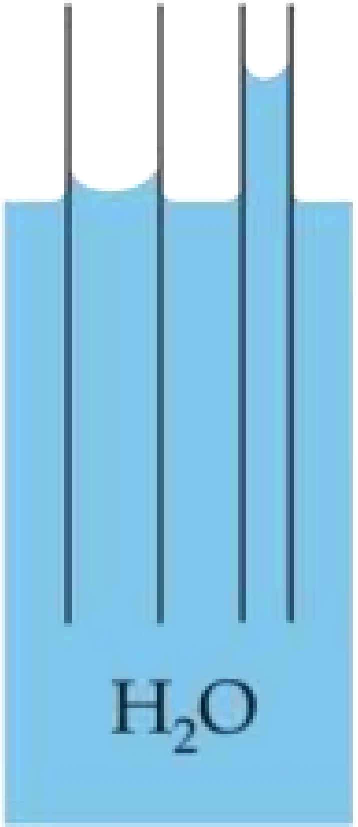
- The surface tensions of most liquids decrease almost linearly with an increase in temperature, that is, with an increase in the kinetic energy of the molecules.
- In the region of its critical temperature, the surface tension of a liquid becomes zero.
- The surface tension of water:
  - at 0°C is **75.6** dynes/cm
  - at 20°C it is **72.8** dynes/cm
  - at 75°C it is **63.5** dynes/cm

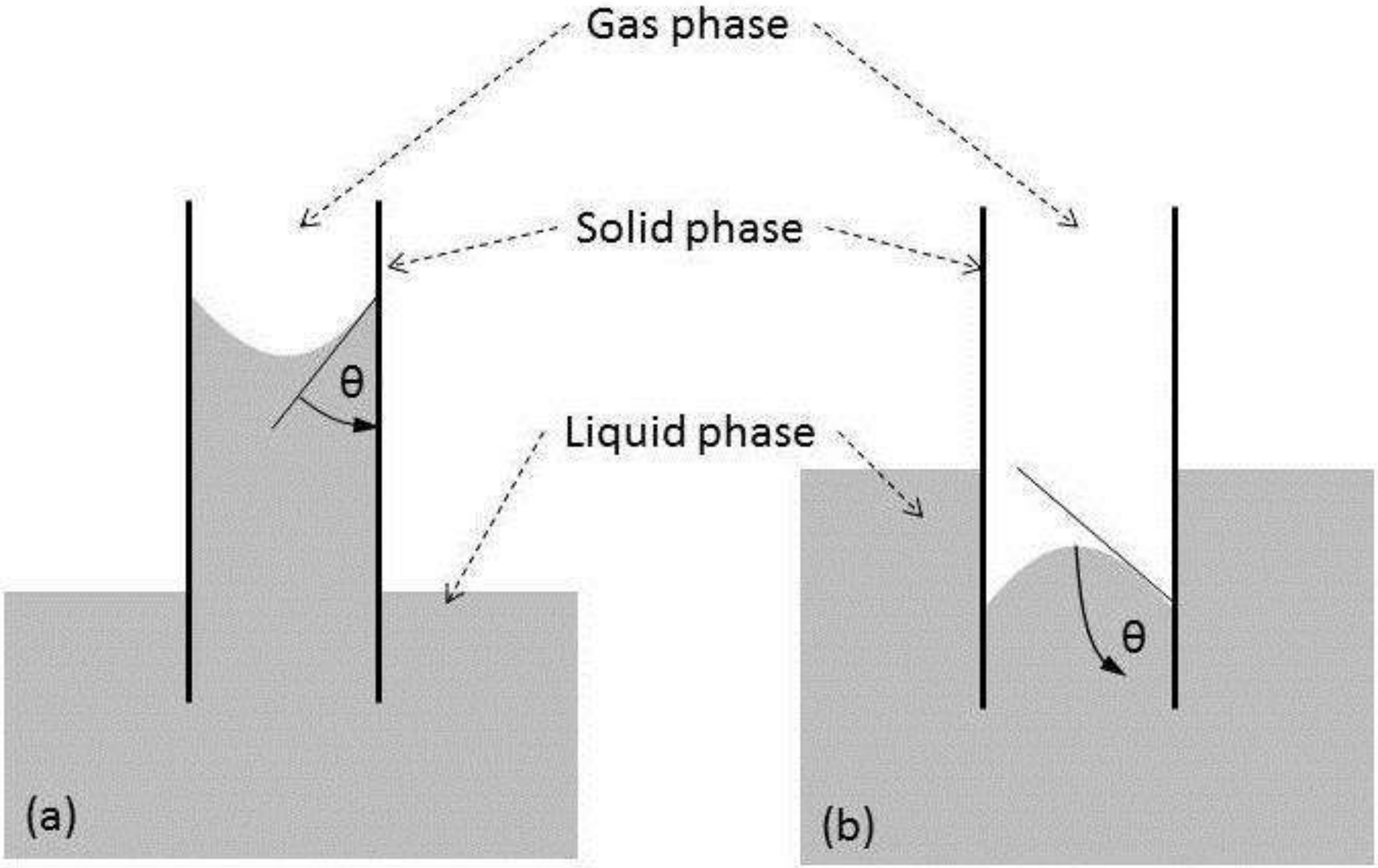


- It is therefore necessary to control the temperature of the system when carrying out surface and interfacial tension determinations.

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.
- **adhesion > cohesion→ rising**
- By measuring this rise in a capillary, it is possible to determine the surface tension of the liquid.





Gas phase

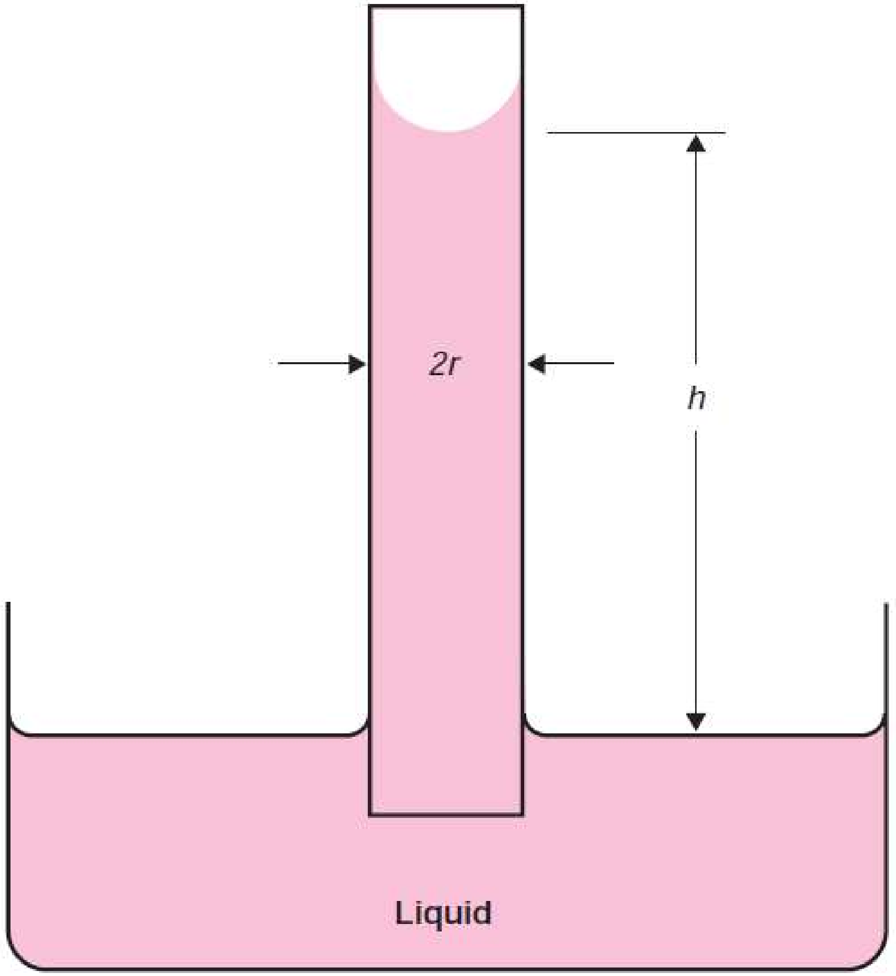
Solid phase

Liquid phase

- 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.

- Consider a capillary tube with an inside radius *r* immersed in a liquid that wets its surface.



- θ is the circumference contact angle between the surface of the liquid and the capillary wall and 2πr is the inside of the capillary.

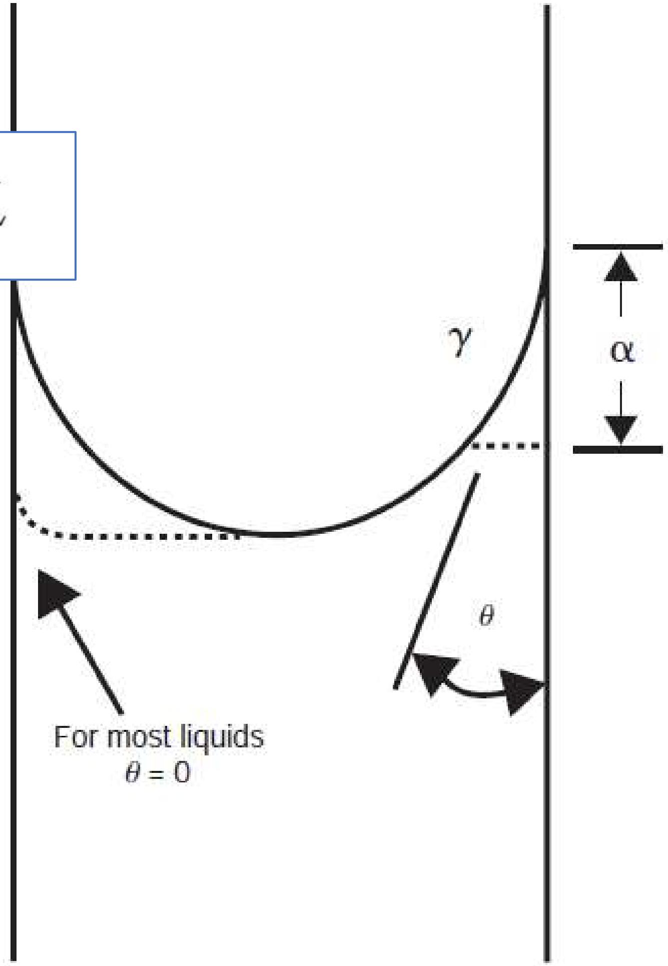
$$\gamma = f_b/2L$$

- The total upward force around the inside circumference of the tube is

$$\gamma\, 2\pi r \cos(\theta)$$

- For water and other commonly used liquids, the angle θ is insignificant

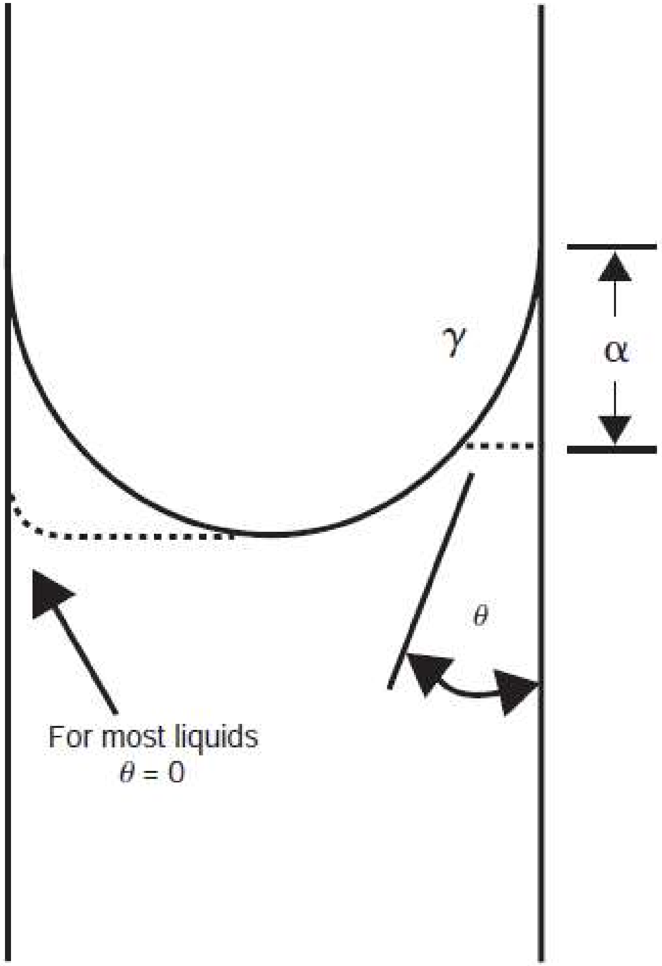
- Then, the contact angle θ (exaggerated in the figure) is nearly zero, as shown on the left-hand side of the diagram.



- The counteracting force of gravity (mass × acceleration)
- ρ = m/V → m = ρV
- $V = \pi r^2 h$
- force of gravity = $\rho \pi r^2 h g$

- the cross-sectional area, πr^2 , the height, h, of the liquid column to the lowest point of the meniscus, the density of the liquid, ρ, and the acceleration of gravity:

$$\pi r^2 h\rho g$$



- When the liquid has risen to its maximum height, the opposing forces are in equilibrium, and accordingly the surface tension can be calculated.

$$2\pi r\gamma = \pi r^2 h\rho g$$

- and finally

$$\gamma = 1/2\ rh\rho g$$

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.

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

$$\gamma = 26.6\,\text{g/sec}^2 = 26.6\,\text{dynes/cm}$$

dyne, defined as the force that imparts to a mass of 1 g an acceleration of 1 cm/sec2

2. The DuNo¨uy Ring Method

- The **DuNo¨uy tensiometer** is widely used for measuring surface and interfacial tensions.
- The principle: 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.

- The surface tension is given by the formula:

$$\gamma = f_b/2L$$

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

- A correction factor takes 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.

The surface tension can be measured with a wide range of test bodies ...

Basic tensiometry using a Du Noüy ring measure surface tension and interfacial tension

https://www.youtube.com/watch?v=dE3R5oZVML8

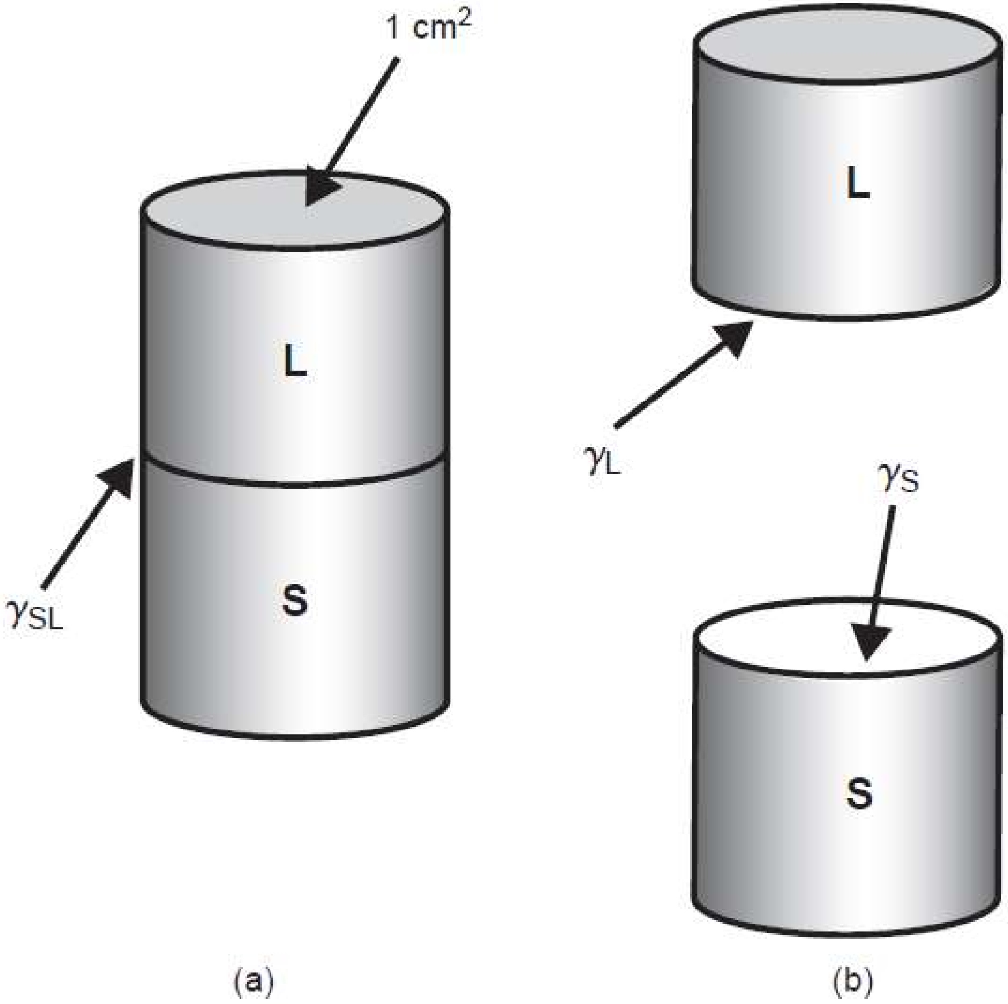
Spreading Coefficient

a monounsaturated
the predominant
fatty acid in olive oil and
avocado

- 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 °A 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**, which is the energy required to break the attraction between the unlike molecules, is obtained by reference to **Figure a** shows a hypothetical cylinder (cross-sectional area 1 cm$_2$) of the sublayer liquid, S, overlaid with a similar section of the spreading liquid, L.

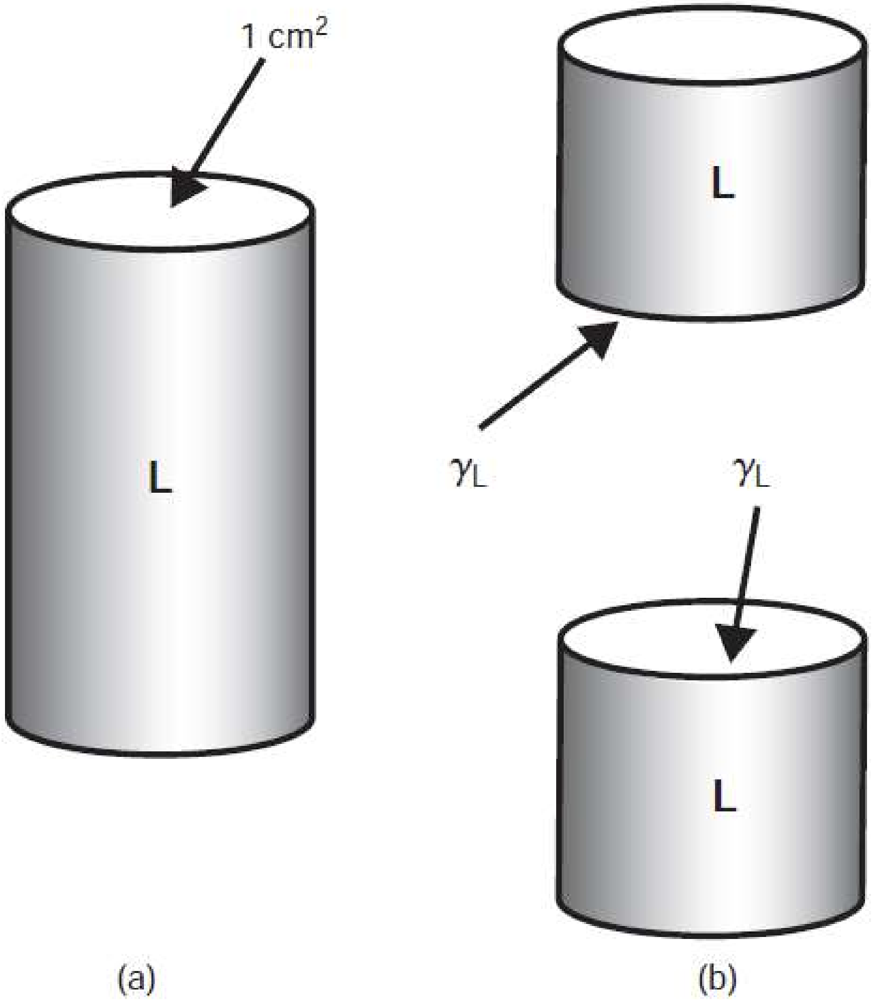


- By equation **W = γΔA,** surface or interfacial work is equal to surface tension multiplied by the area increment.
- The work of adhesion is thus
  - $W_a = \gamma_L + \gamma_S - \gamma_{LS}$

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

$$W_c = 2\gamma_L$$

- 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
  - If it is negative → it will contract
  - If it is zero → it will sit there and look at you



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

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

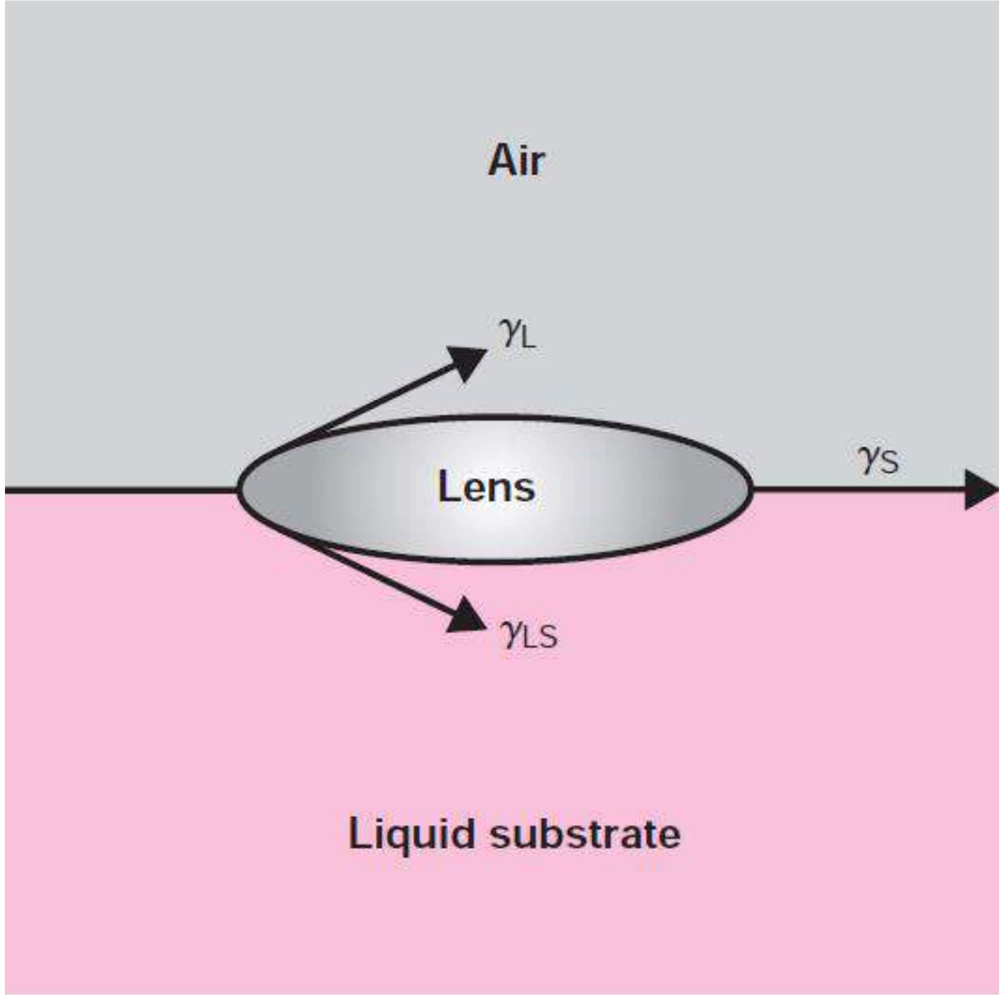
- Rearranging equation gives:

$$S = \gamma_S - \gamma_L - \gamma_{LS}$$

or

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

- 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.



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, γ_S is 62.2 dynes/cm and γ_L is 28.8 dynes/cm. What is the final spreading coefficient?

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

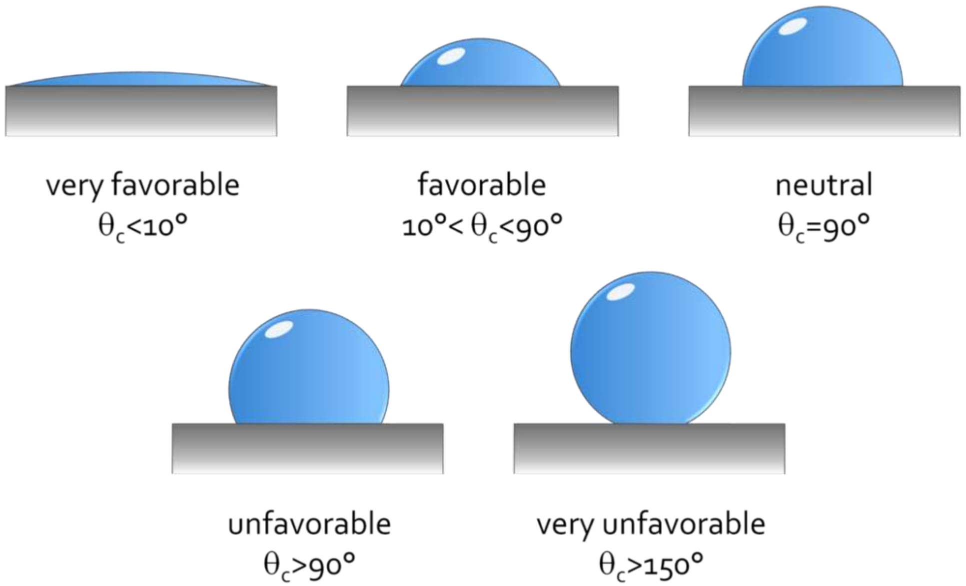
- Therefore, although benzene spreads initially on water, at equilibrium there is formed a saturated monolayer with the excess benzene (saturated with water) forming a lens.

Relation between molecular structure and spreading coefficients

- Oil spreads over water because it contains polar groups such as COOH or OH.
- As the carbon chain of an acid increases → the ratio of polar–nonpolar character decreases → 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.

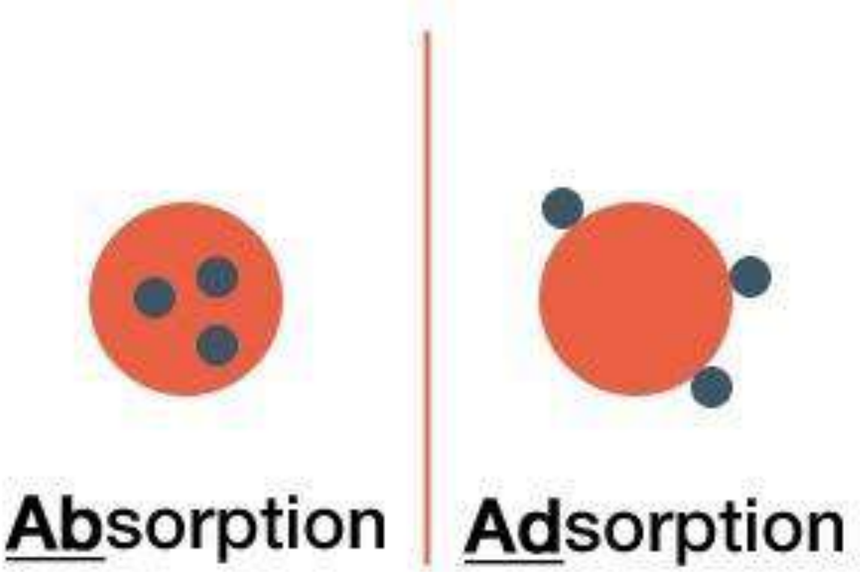
The applications of spreading coefficients in pharmacy

- 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

- The adsorption is solely a surface effect, whereas in absorption, the liquid or gas being absorbed penetrates into the capillary spaces of the absorbing medium.

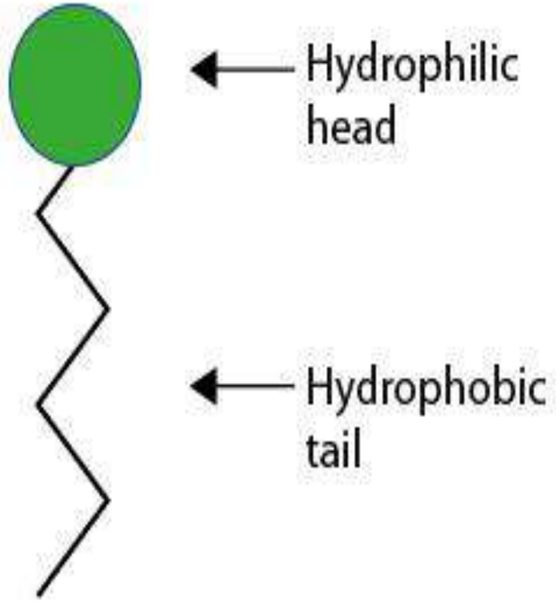


- Surface free energy was defined previously as the work that must be done to increase the surface by unit area.
- Certain molecules and ions, when dispersed in the liquid, move of their own accord to the interface.
- Their concentration at the interface then exceeds their concentration in the bulk of 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, **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.

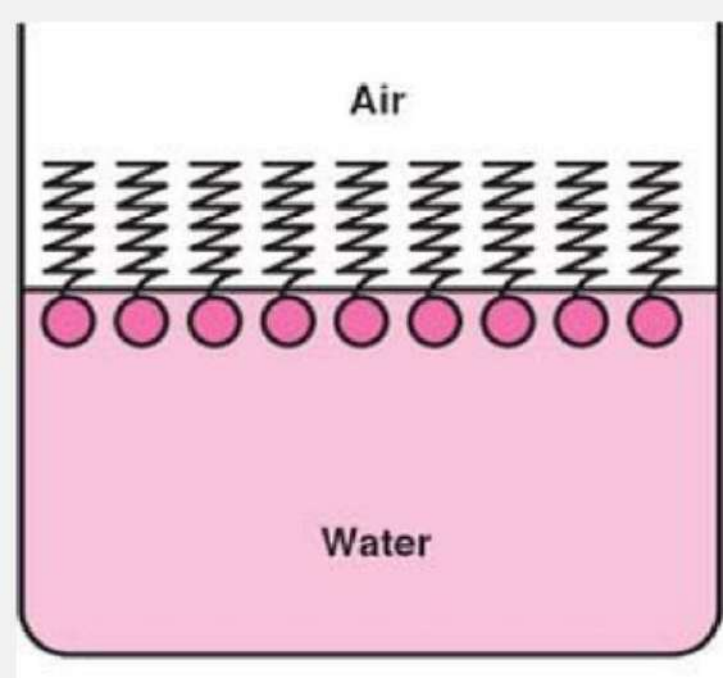
Surface-Active Agents

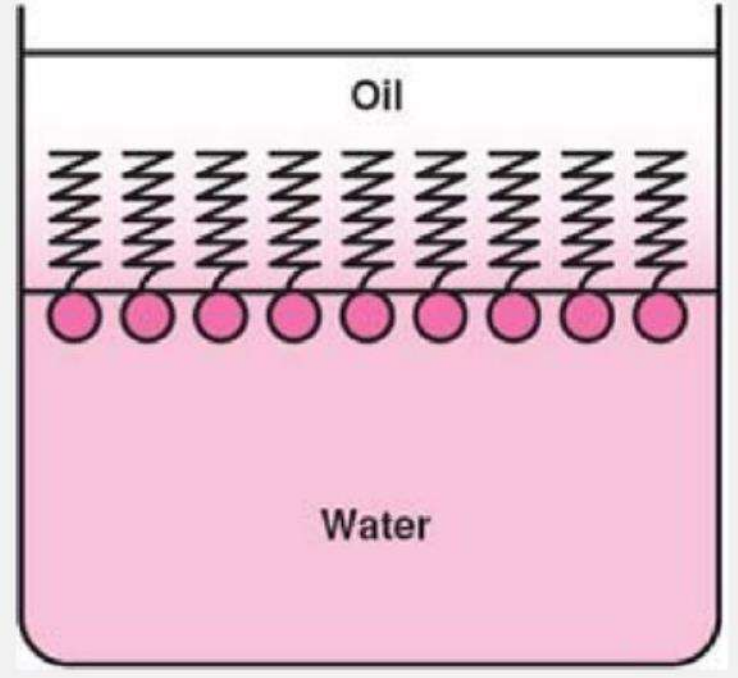
- It is the amphiphilic nature of surface-active agents that causes them to be absorbed at interfaces, whether these are liquid–gas or liquid–liquid interfaces.



- Thus, in an aqueous dispersion of amyl alcohol,
  - ✓the polar alcoholic group is able to associate with the water molecules.
  - ✓The nonpolar portion is rejected.

- The situation for a fatty acid at the air–water and oil–water interface is:
  a) At the air– water interface, the lipophilic chains are directed upward into the air; at the oil–water interface, they are associated with the oil phase.
  b) For the amphiphile to be concentrated at the interface, it must be balanced with the proper amount of water- and oil-soluble groups.

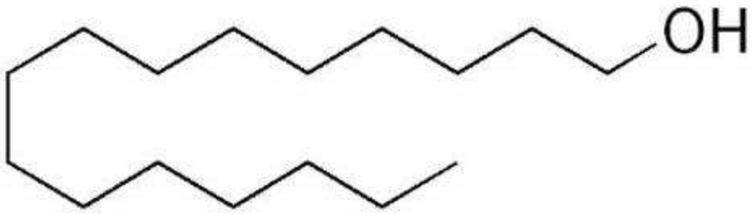




- If the molecule is too hydrophilic, it remains within the body of the aqueous phase and exerts no effect at the interface.

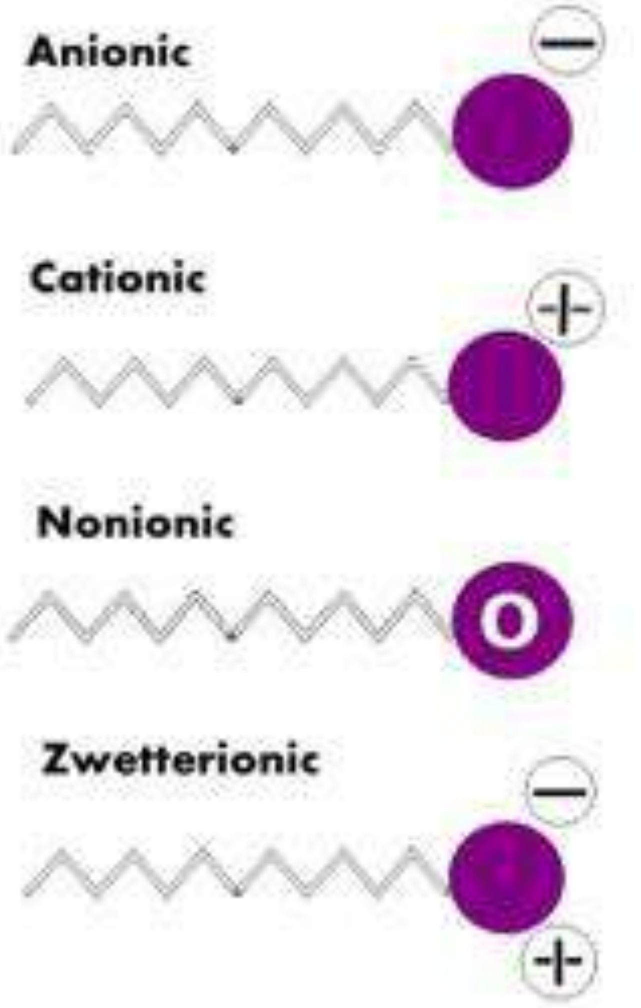
- Likewise, if it is too lipophilic, it dissolves completely in the oil phase and little appears at the interface

- Depending on the number and nature of the polar and nonpolar groups present, the amphiphile may be predominantly hydrophilic (water-loving), lipophilic (oil-loving), or reasonably well balanced between these two extremes.
- For example, straight-chain alcohols, amines, and acids are amphiphiles that change from being predominantly hydrophilic to lipophilic as the number of carbon atoms in the alkyl chain is increased.
- Thus, ethyl alcohol is miscible with water in all proportions. In comparison, the aqueous solubility of amyl alcohol, $C_5H_{11}OH$, is much reduced, whereas cetyl alcohol, $C_{16}H_{33}OH$, may be said to be strongly lipophilic and insoluble in water.



Surfactants Types:

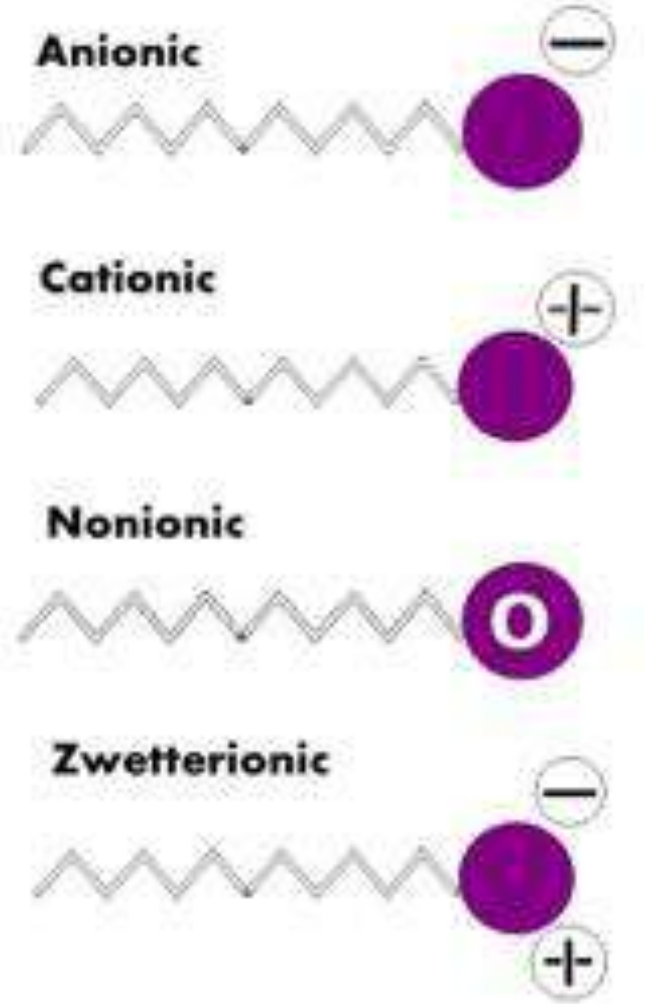
1- Anionic surfactants:



- these are the most type of surfactants.
- It contains organic tail with negative charge head and small positive molecule like ammonium.
- This consist of soaps of alkali, amines, alkyl sulphates (sodium lauryl sulfate).
- They have unpleasant taste.
- They are not suitable for internal use due to irritant action on intestinal mucosa.

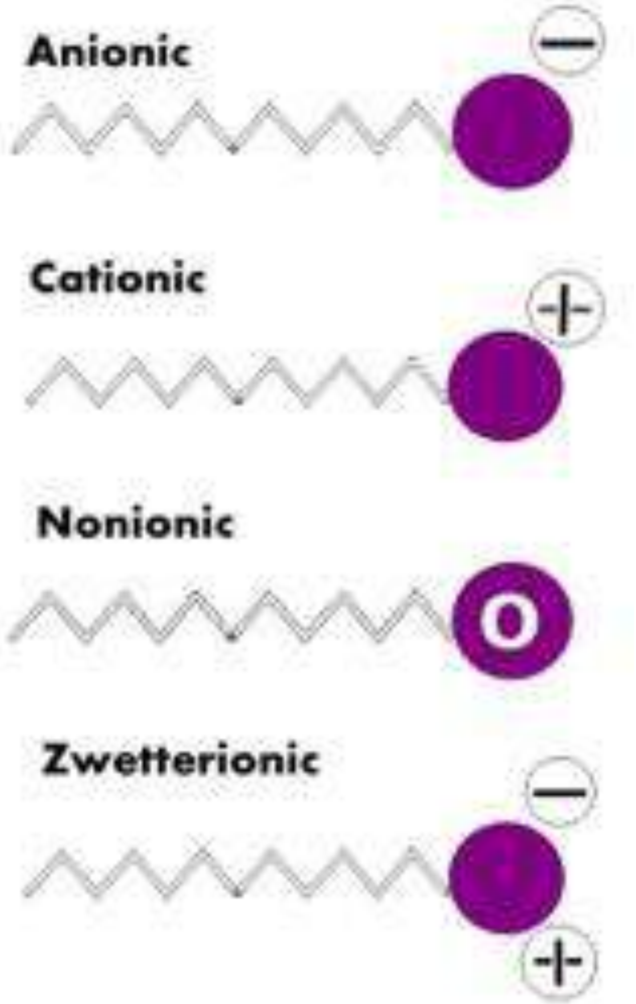
2- Cationic surfactants:

- it contains organic tail with positive charge head and small negative molecule like chloride.
- **Example** :
    - quaternary ammonium compound as cetrimide, benzalkonium chloride and benzethonium chloride.

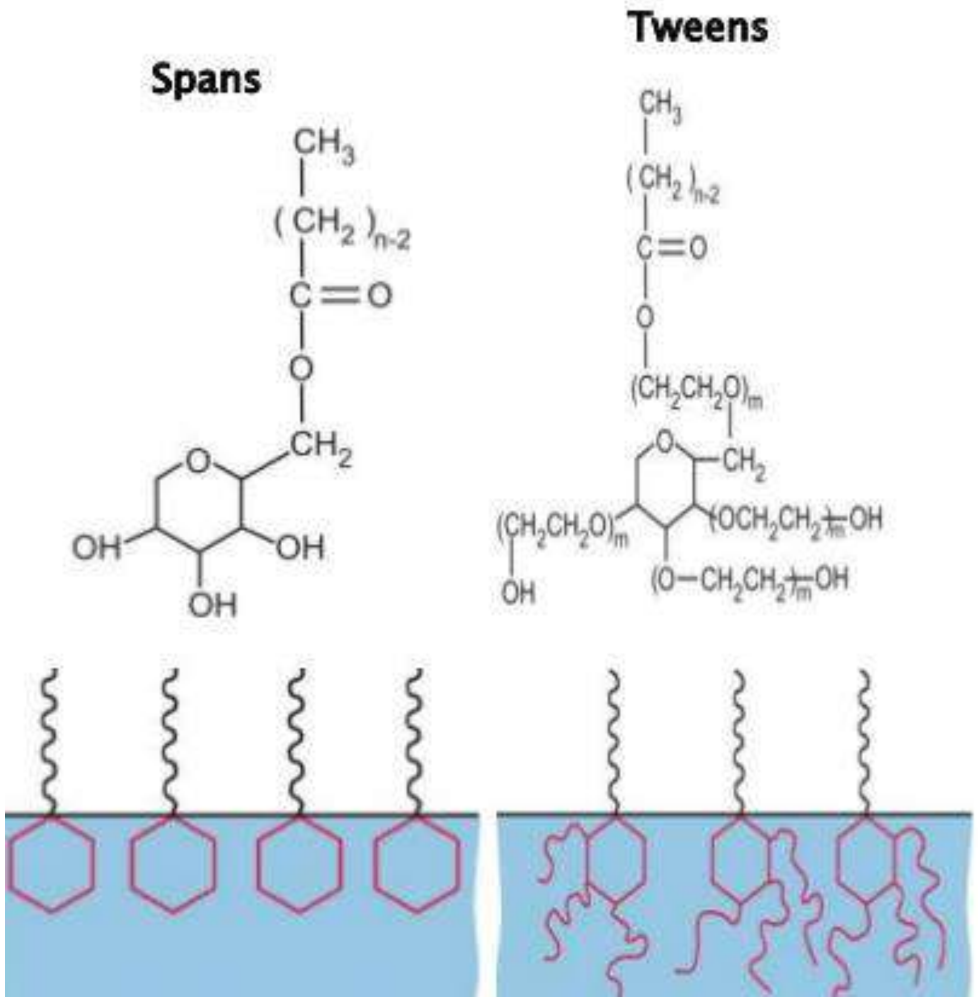


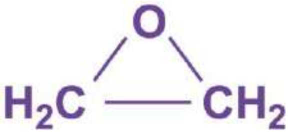
3- Non-ionic surfactants:

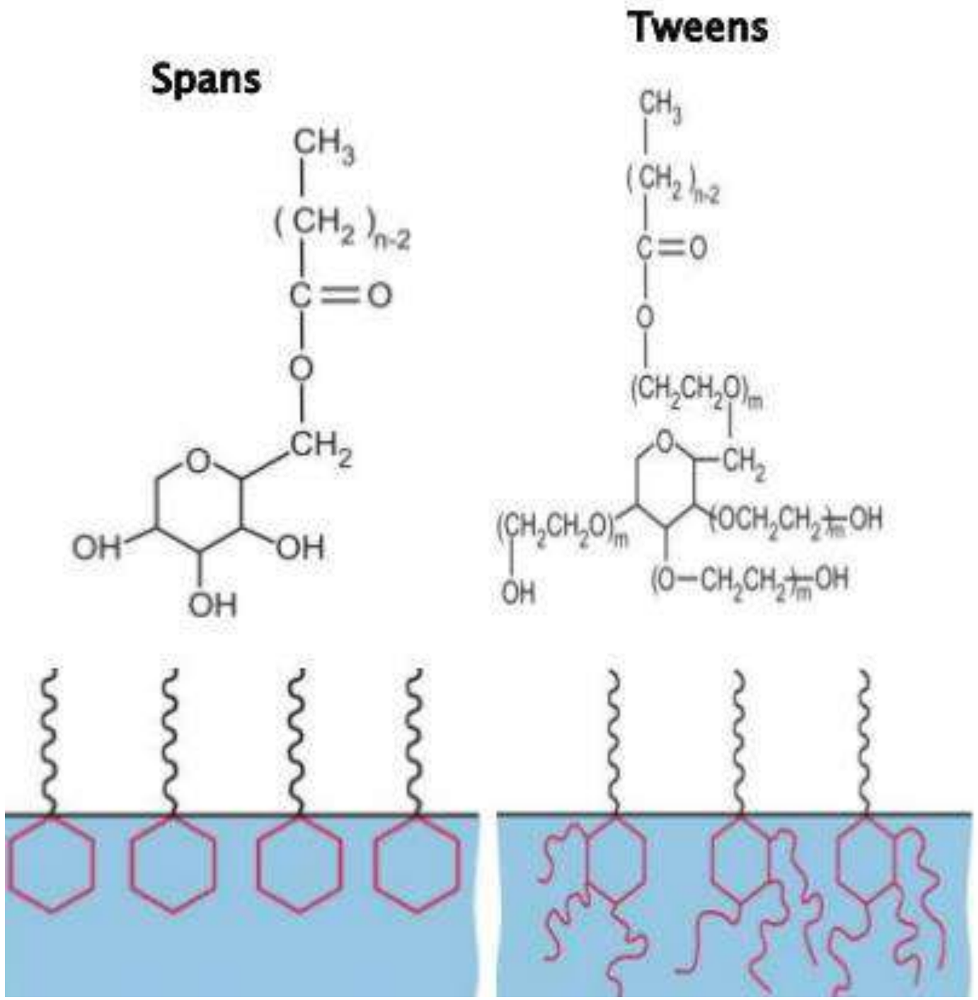
- they do not ionize in water because their hydrophilic part consist of non dissociable molecules.
- They are pharmaceutically important. They are compatible with anionic and cationic surfactants.
- They are resistant to pH change.
- **Example**
  - include glycerol and glycol esters, macrogol (polyethylene glycol (PEG)) esters such as:
    - polyoxy stearates, spans and tweens.



- The esterification of a liquid solution of **sorbitol** with fatty acids leads to a **sorbitan esters (Spans)** and have low water solubility.
- Sorbitan esters are often used in the **food industry**, especially in chocolate and margarine production,

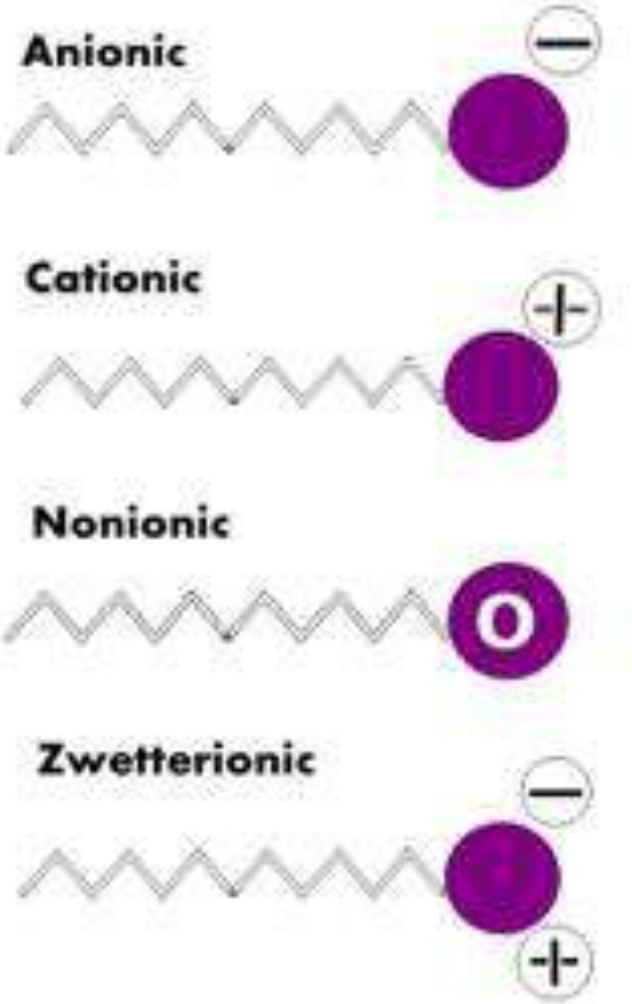


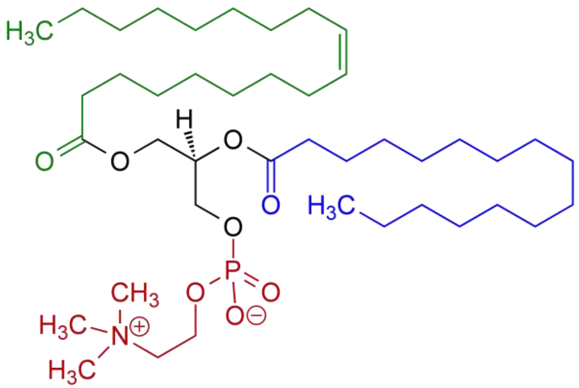
- Sorbitan esters can be further reacted with **ethylene oxide**  to introduce **polyoxyalkylene chains** (tweens or polysorbates) that results in a significant increase of the surfactant’s water solubility.
- Polysorbates are also commonly used as emulsifiers in the food industry (salad dressing, ice cream) and in cosmetics, pharmaceuticals, detergents, paints, and plastic applications.



4- Ampholytic surfactants:

- they depend on the pH of the system.
- Below a certain pH they are cationic while above a certain pH they are considered anionic and at intermediate pH act as zwitterions.
- Example: lecithin, N-dodecyl alanine.

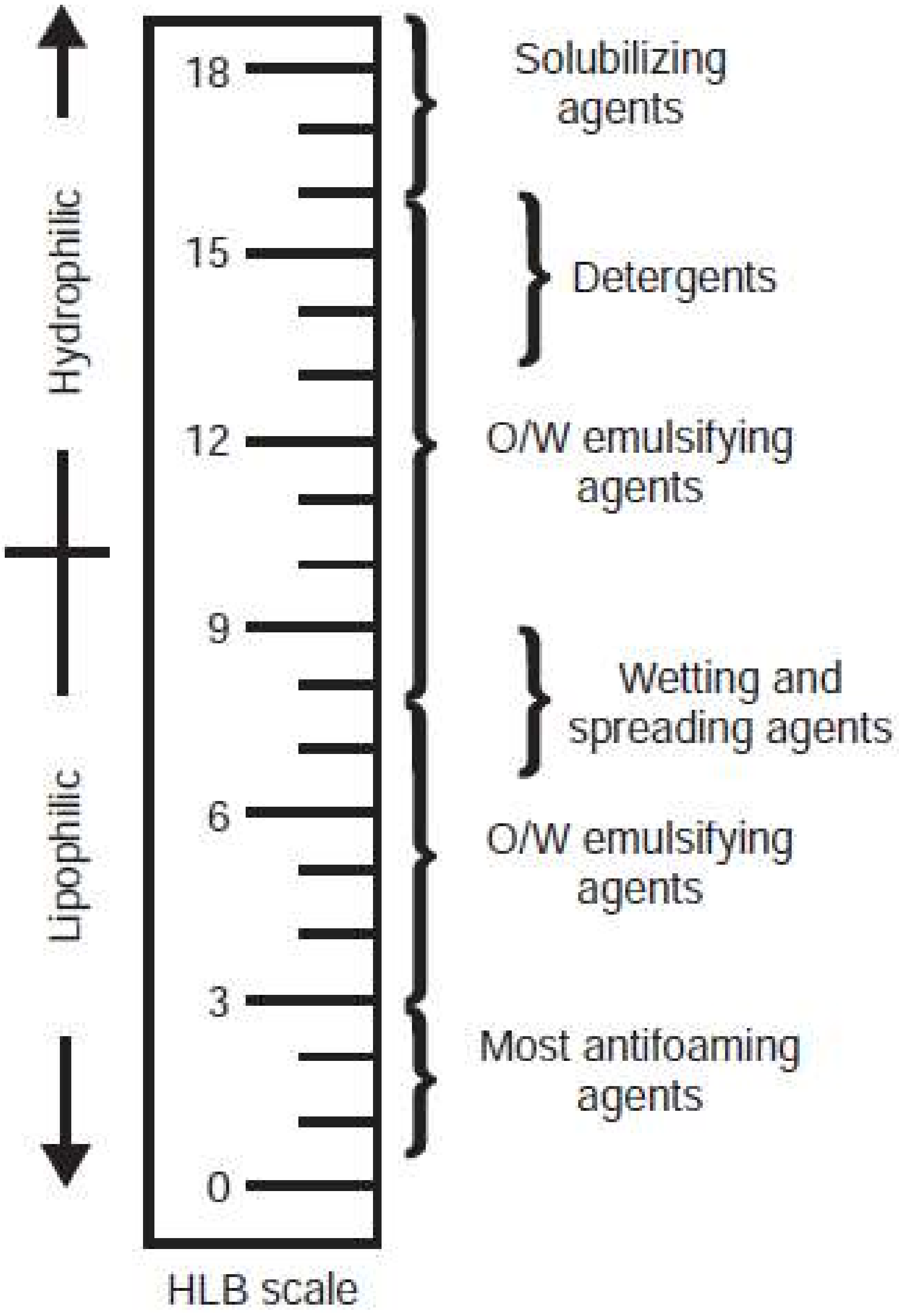




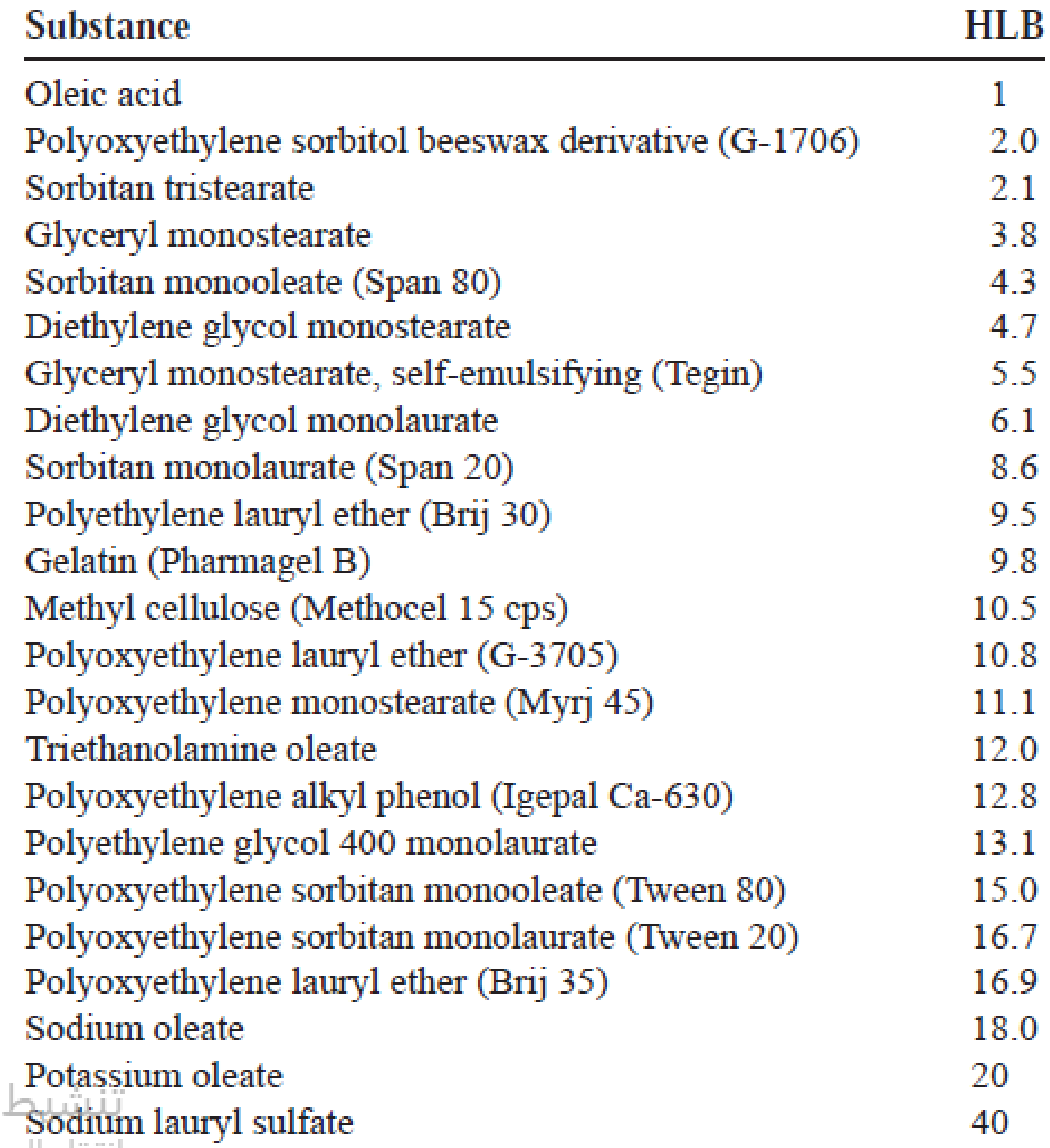
Systems of Hydrophile-Lipophile Classification

- 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).

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

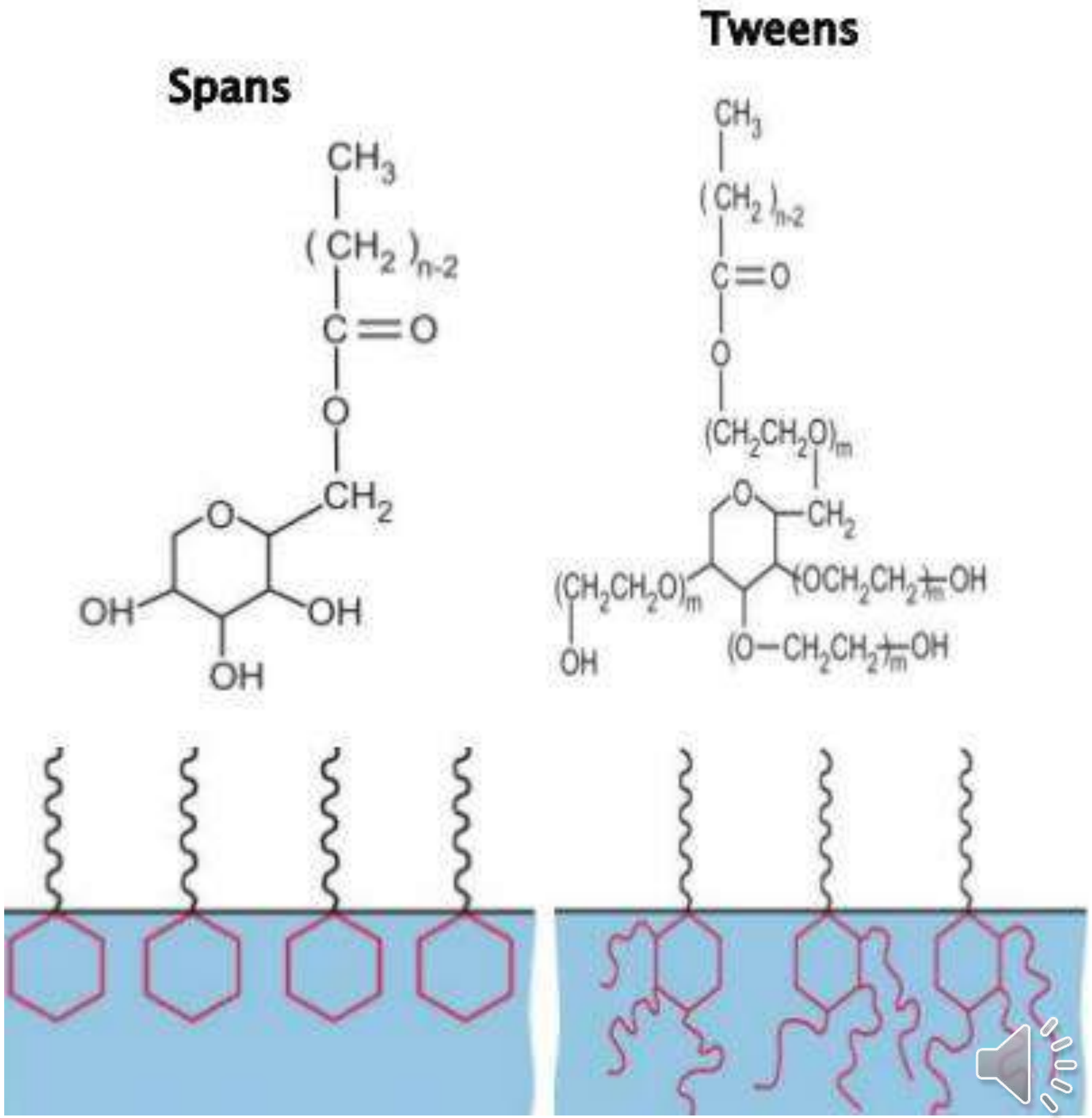


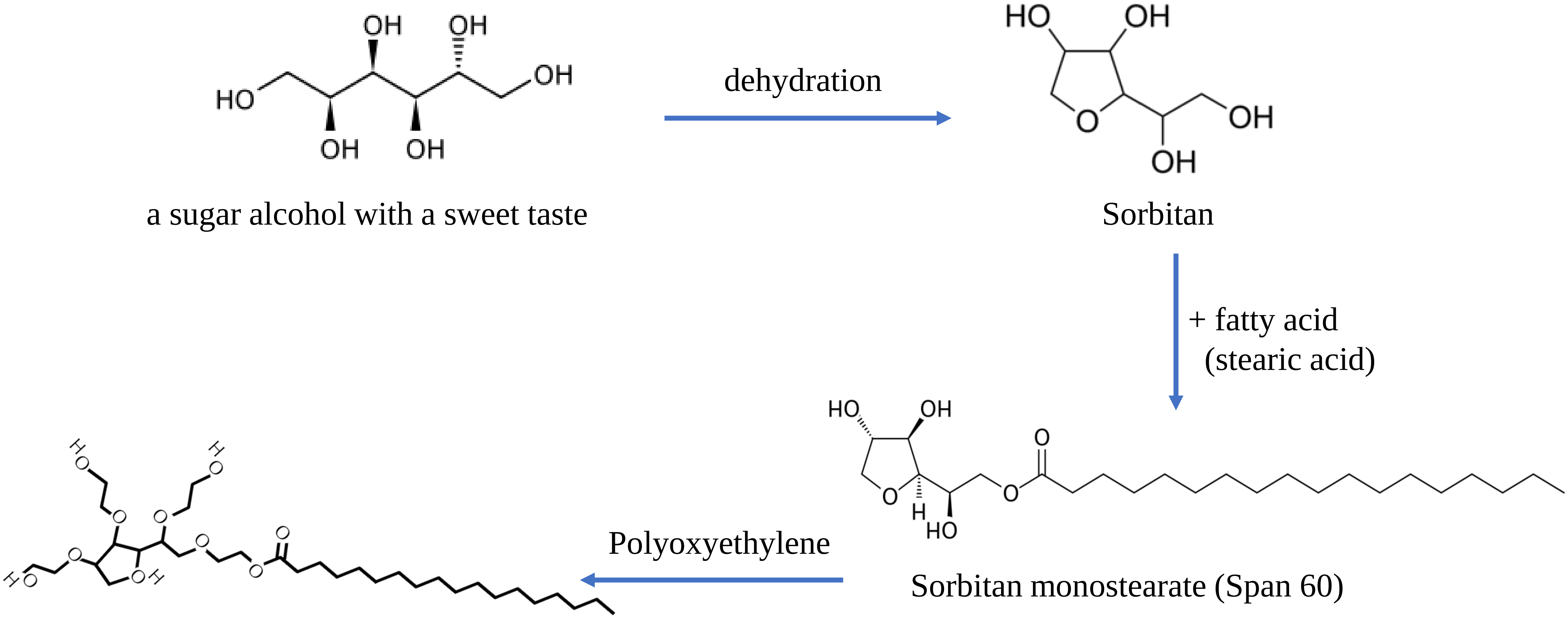
- HYDROPHILIC–LIPOPHILIC BALANCE (HLB) VALUES OF SOME AMPHIPHILIC AGENTS



Substance	HLB
Oleic acid	1
Polyoxyethylene sorbitol beeswax derivative (G-1706)	2.0
Sorbitan tristearate	2.1
Glyceryl monostearate	3.8
Sorbitan monooleate (Span 80)	4.3
Diethylene glycol monostearate	4.7
Glyceryl monostearate, self-emulsifying (Tegin)	5.5
Diethylene glycol monolaurate	6.1
Sorbitan monolaurate (Span 20)	8.6
Polyethylene lauryl ether (Brij 30)	9.5
Gelatin (Pharmagel B)	9.8
Methyl cellulose (Methocel 15 cps)	10.5
Polyoxyethylene lauryl ether (G-3705)	10.8
Polyoxyethylene monostearate (Myrj 45)	11.1
Triethanolamine oleate	12.0
Polyoxyethylene alkyl phenol (Igepal Ca-630)	12.8
Polyethylene glycol 400 monolaurate	13.1
Polyoxyethylene sorbitan monooleate (Tween 80)	15.0
Polyoxyethylene sorbitan monolaurate (Tween 20)	16.7
Polyoxyethylene lauryl ether (Brij 35)	16.9
Sodium oleate	18.0
Potassium oleate	20
Sodium lauryl sulfate	40

- Sorbitan esters and polyoxyethylene sorbitan esters are widely used in cosmetics, food products, and oral and topical pharmaceutical formulations and are generally regarded as nontoxic and non-irritant materials.





a sugar alcohol with a sweet taste

dehydration

Sorbitan

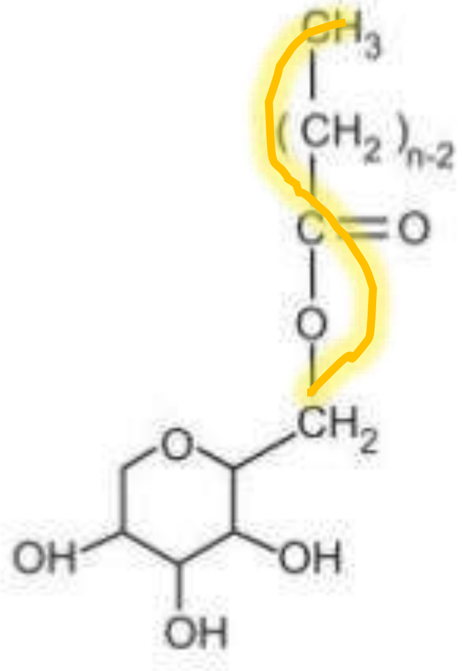
+ fatty acid
(stearic acid)

Sorbitan monostearate (Span 60)

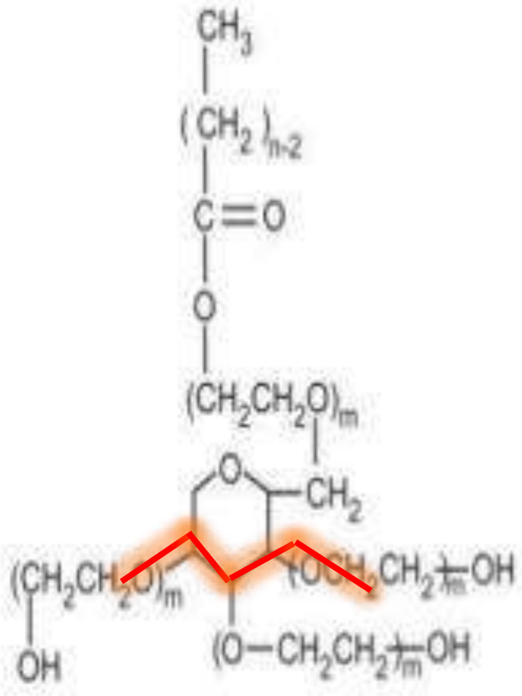
Polyoxyethylene

Polyoxyethylene Sorbitan monostearate (Tween 60)

- ✓ **Oil**-soluble and hydrophobic



Spans



Tweens

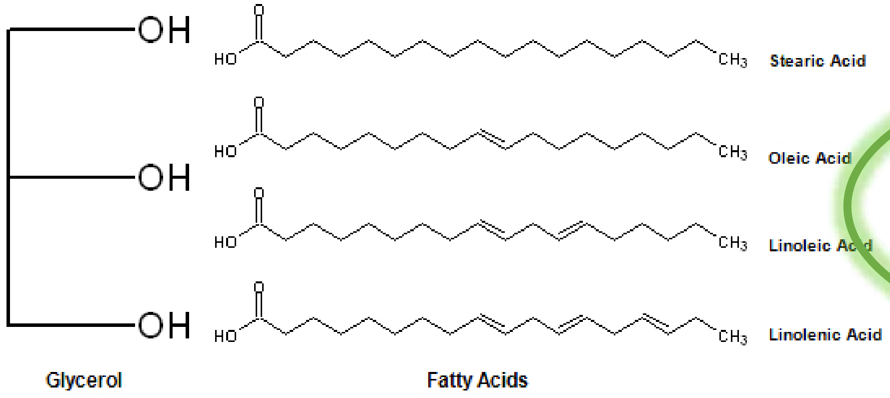
- ✓ **W**ater-soluble and hydrophilic

- The HLB of a nonionic surfactant whose only hydrophilic portion is polyoxyethylene is calculated by using the formula

$$\mathrm{HLB} = E/5$$

where *E* is the percentage by weight of ethylene oxide

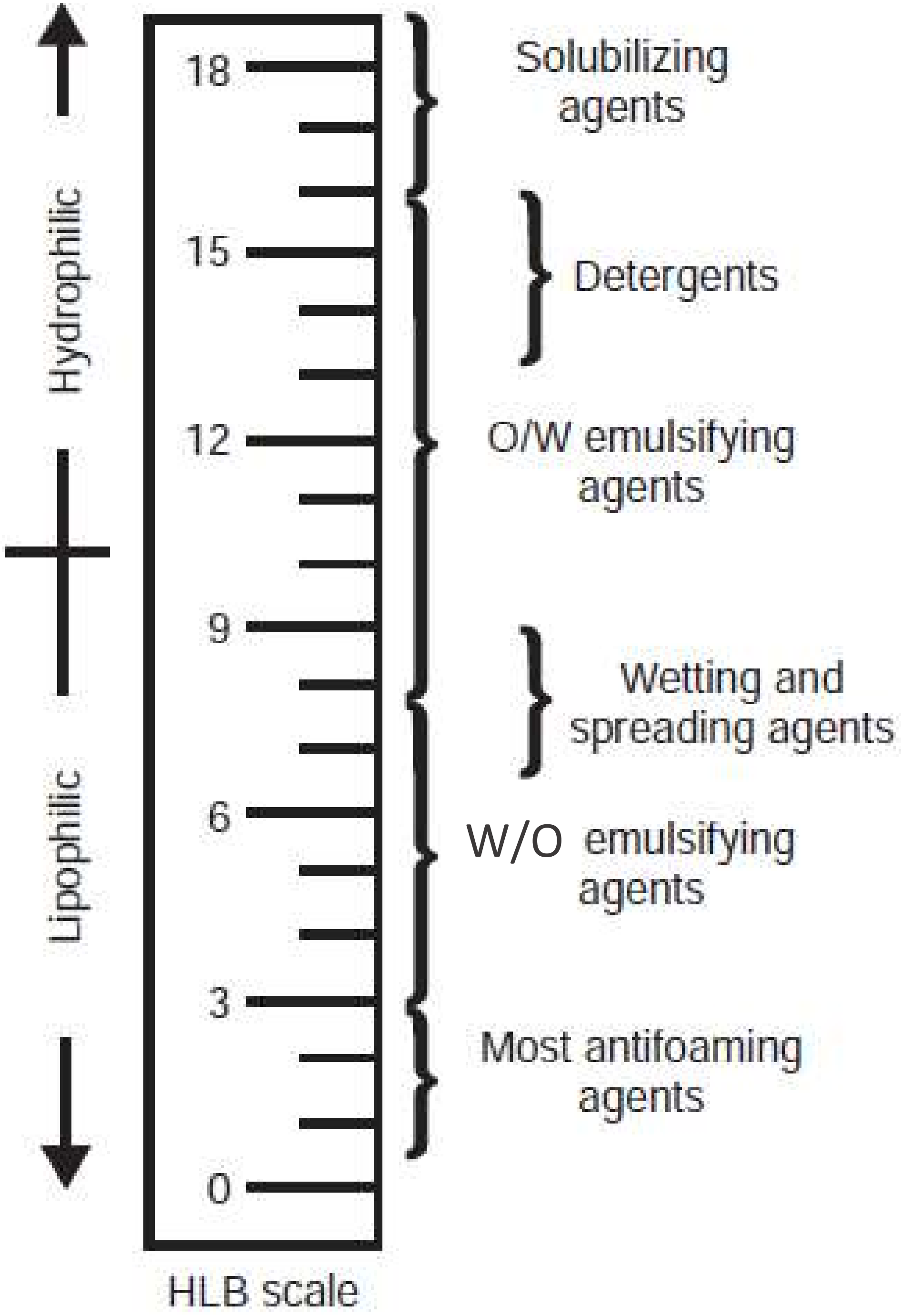
- A number of polyhydric alcohol fatty acid esters, such as glyceryl monostearate, can be estimated by using the formula:



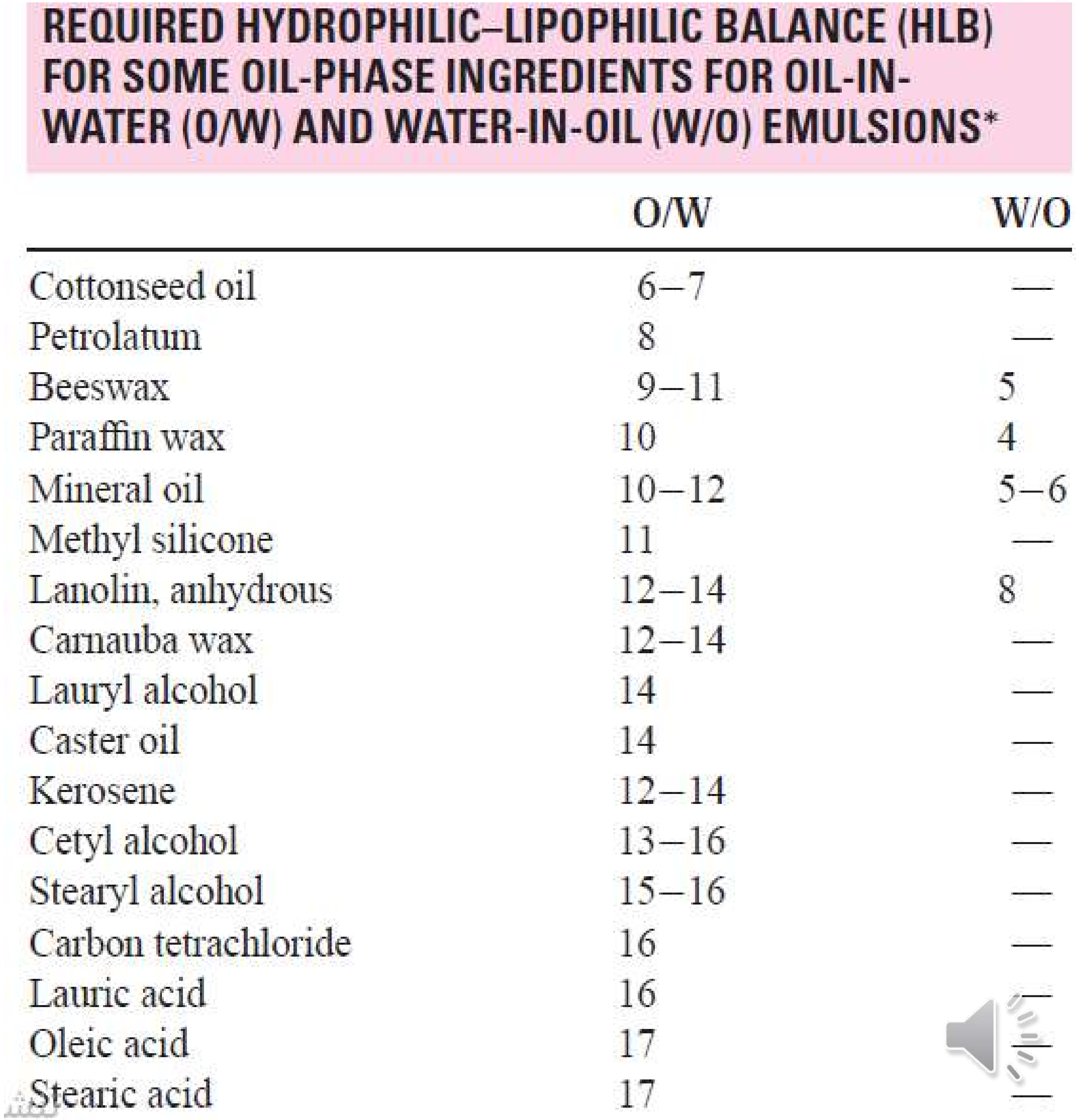
$$\mathrm{HLB} = 20\left(1 - \frac{S}{A}\right)$$

  - where S is the saponification number of the ester and A is the acid number of the fatty acid.

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



- The oil phase of an oil-in-water (O/W) emulsion requires a specific HLB, called the **required hydrophile–lipophile balance** (RHLB).
- A different RHLB is required to form a water in- oil (W/O) emulsion from the same oil phase.
- The RHLB values for both O/W and W/O emulsions have been determined empirically for a number of oils and oil-like substances, some of which are listed in the table.



REQUIRED HYDROPHILIC–LIPOPHILIC BALANCE (HLB) FOR SOME OIL-PHASE INGREDIENTS FOR OIL-IN-WATER (O/W) AND WATER-IN-OIL (W/O) EMULSIONS*

	O/W	W/O
Cottonseed oil	6–7	—
Petrolatum	8	—
Beeswax	9–11	5
Paraffin wax	10	4
Mineral oil	10–12	5–6
Methyl silicone	11	—
Lanolin, anhydrous	12–14	8
Carnauba wax	12–14	—
Lauryl alcohol	14	—
Caster oil	14	—
Kerosene	12–14	—
Cetyl alcohol	13–16	—
Stearyl alcohol	15–16	—
Carbon tetrachloride	16	—
Lauric acid	16	—
Oleic acid	17	—
Stearic acid	17	—

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- A different RHLB is required to form a water in- oil (W/O) emulsion from the same oil phase.
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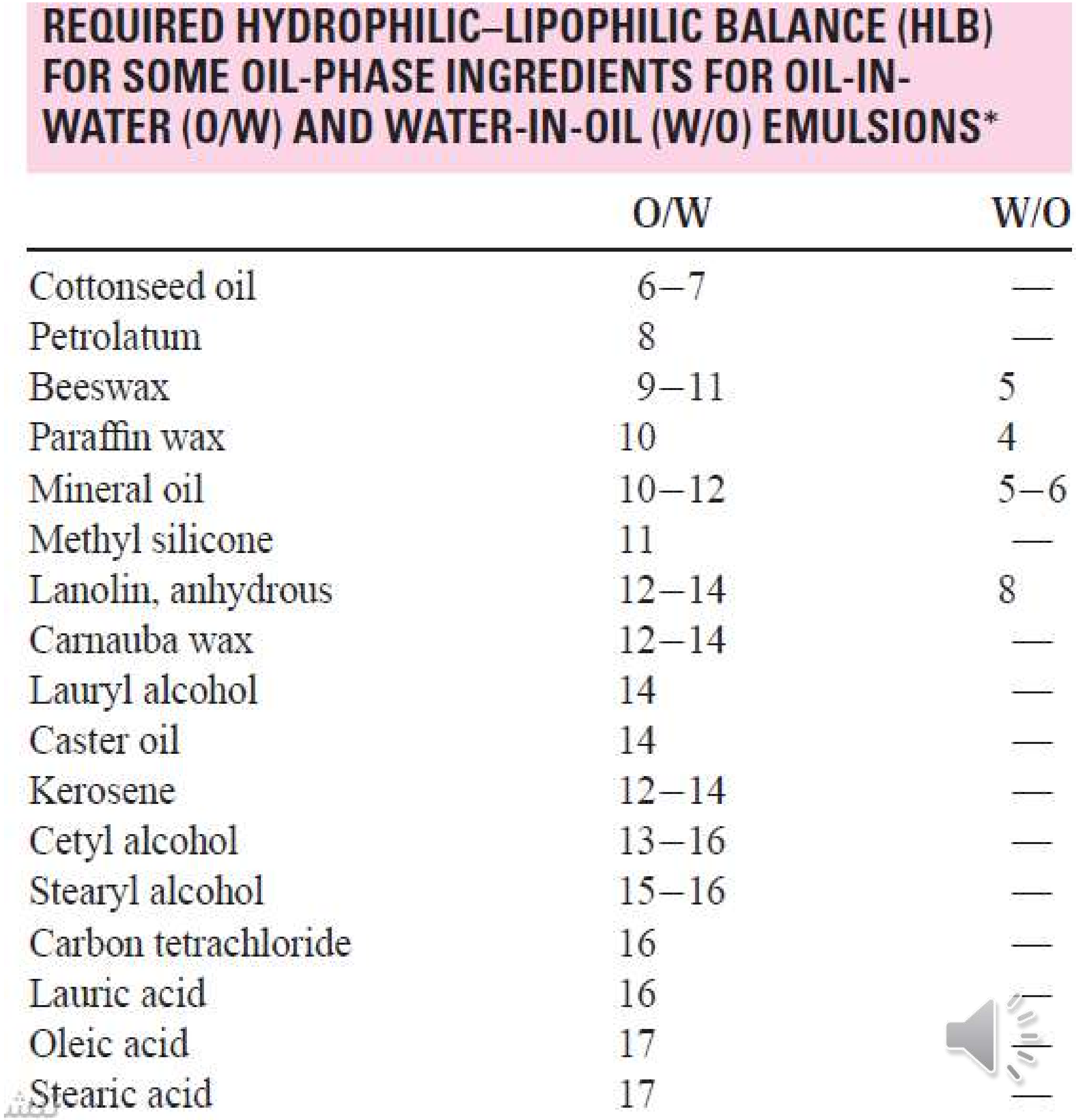

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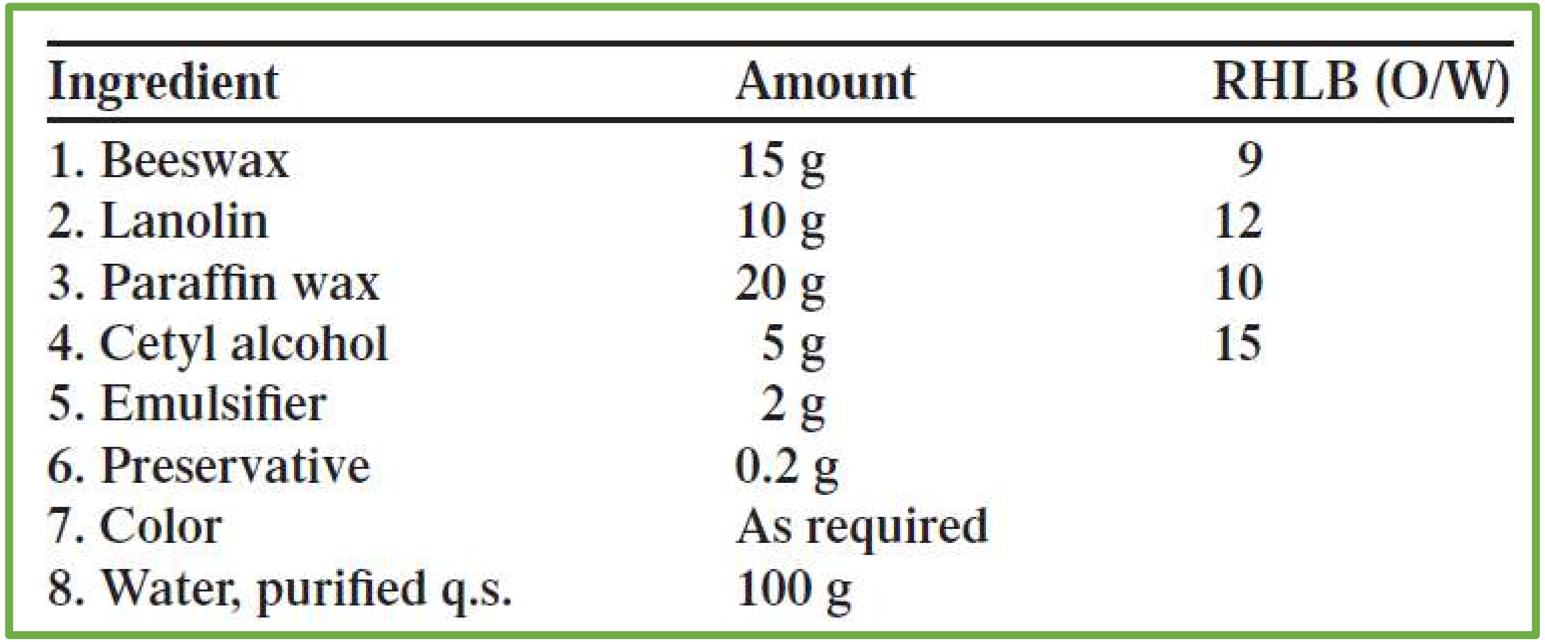
Stearyl alcohol	15–16	—
Carbon tetrachloride	16	—
Lauric acid	16	—
Oleic acid	17	—
Stearic acid	17	—

• EXAMPLE

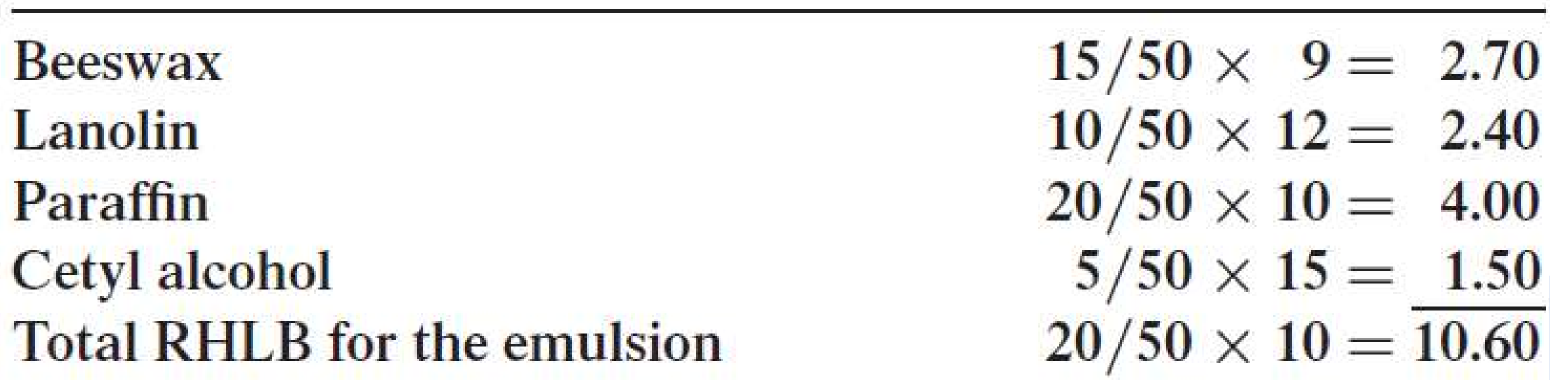
- Calculation of HLB Value for Oil-in-Water Emulsions
- For the oil-in-water emulsion,



Ingredient	Amount	RHLB (O/W)
1. Beeswax	15 g	9
2. Lanolin	10 g	12
3. Paraffin wax	20 g	10
4. Cetyl alcohol	5 g	15
5. Emulsifier	2 g	
6. Preservative	0.2 g	
7. Color	As required	
8. Water, purified q.s.	100 g	

- One first calculates the overall RHLB of the emulsion by multiplying the RHLB of each oil-like component (items 1–4) by the weight fraction that each oil-like component contributes to the oil phase. The total weight of the oil phase is 50 g.

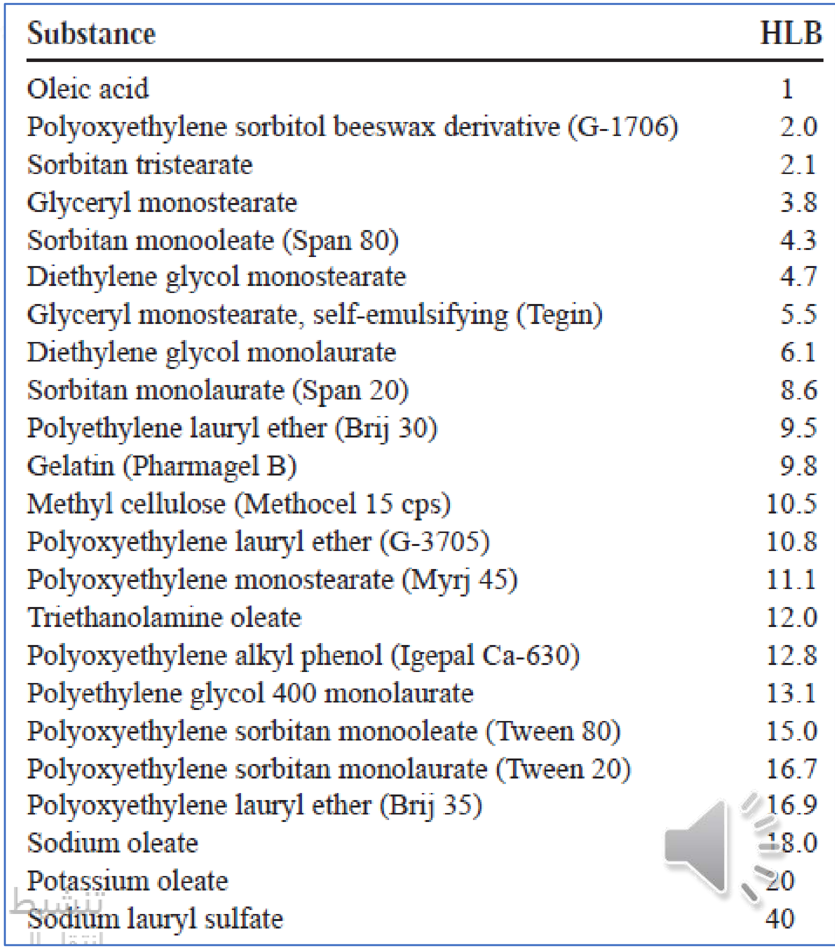
Therefore,



Beeswax	$15/50 \times 9 =$	2.70
Lanolin	$10/50 \times 12 =$	2.40
Paraffin	$20/50 \times 10 =$	4.00
Cetyl alcohol	$5/50 \times 15 =$	1.50
Total RHLB for the emulsion	$20/50 \times 10 =$	10.60

Next, one chooses a blend of two emulsifying agents, one with an HLB above and the other with an HLB below the required HLB of the emulsion (RHLB = 10.6 in this example).

From the table, we choose Tween 80, with an HLB of 15, and Span 80, with an HLB of 4.3.



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- The formula for calculating the **weight percentage** of Tween 80 (surfactant with the **higher HLB**) is

$$\%\ \text{Tween 80} = \frac{\text{RHLB} - \text{HLB low}}{\text{HLB high} - \text{HLB low}}$$

- where HLB high is for the higher value, 15, and HLB low is for the lower value, 4.3.We have

$$\%\ \text{Tween 80} = \frac{10.6 - 4.3}{15.0 - 4.3} = 0.59$$

- Two grams of emulsifier has been estimated as proper protection for the O/W emulsion.
- Therefore, 2.0 g×0.59=1.18 g of Tween 80 is needed and the remainder, 0.82 g, must be supplied by Span 80 for the 100-g emulsion.

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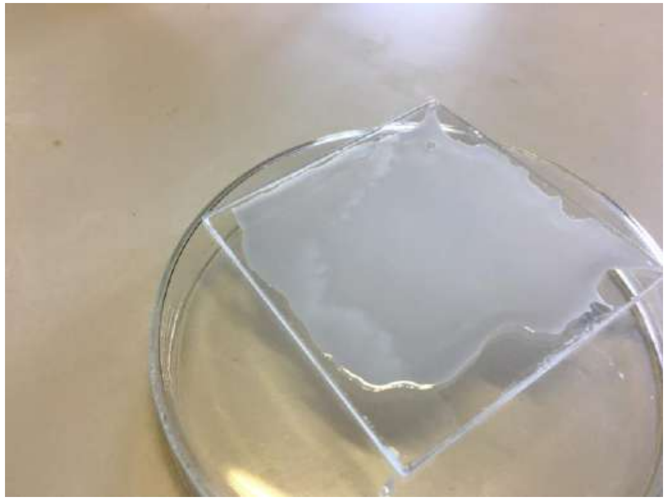
APPLICATIONS OF SURFACE-ACTIVE AGENTS

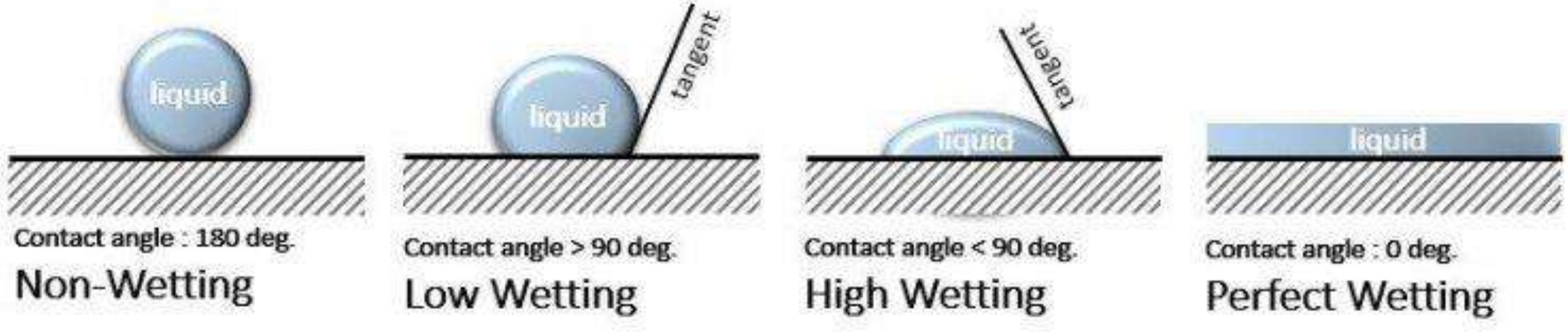
1- Wetting

- 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 most important action of a wetting agent is to lower the contact angle between the surface and the wetting liquid.
- The contact angle is the angle between a liquid droplet and the surface over which it spreads. As shown in Figure, the contact angle between a liquid and a solid may be:
  - ✓0°, signifying complete wetting, or
  - ✓180°, at which wetting is insignificant.
  - ✓The contact angle may also have any value between these limits.



- The contact angle between a water droplet and a greasy surface results when the applied liquid, water, wets the greasy surface incompletely.
- When a drop of water is placed on a clean glass surface, it spreads spontaneously and no contact angle exists.
- This result can be described by: water a high spreading coefficient on clean glass, or by stating that the contact angle between water and glass is zero.
- If the appropriate wetting agent is added to water, the solution will spread spontaneously on a greasy surface.
- For a wetting agent to function efficiently—in other words, to exhibit a low contact angle—it should have an **HLB of about 6 to 9.**

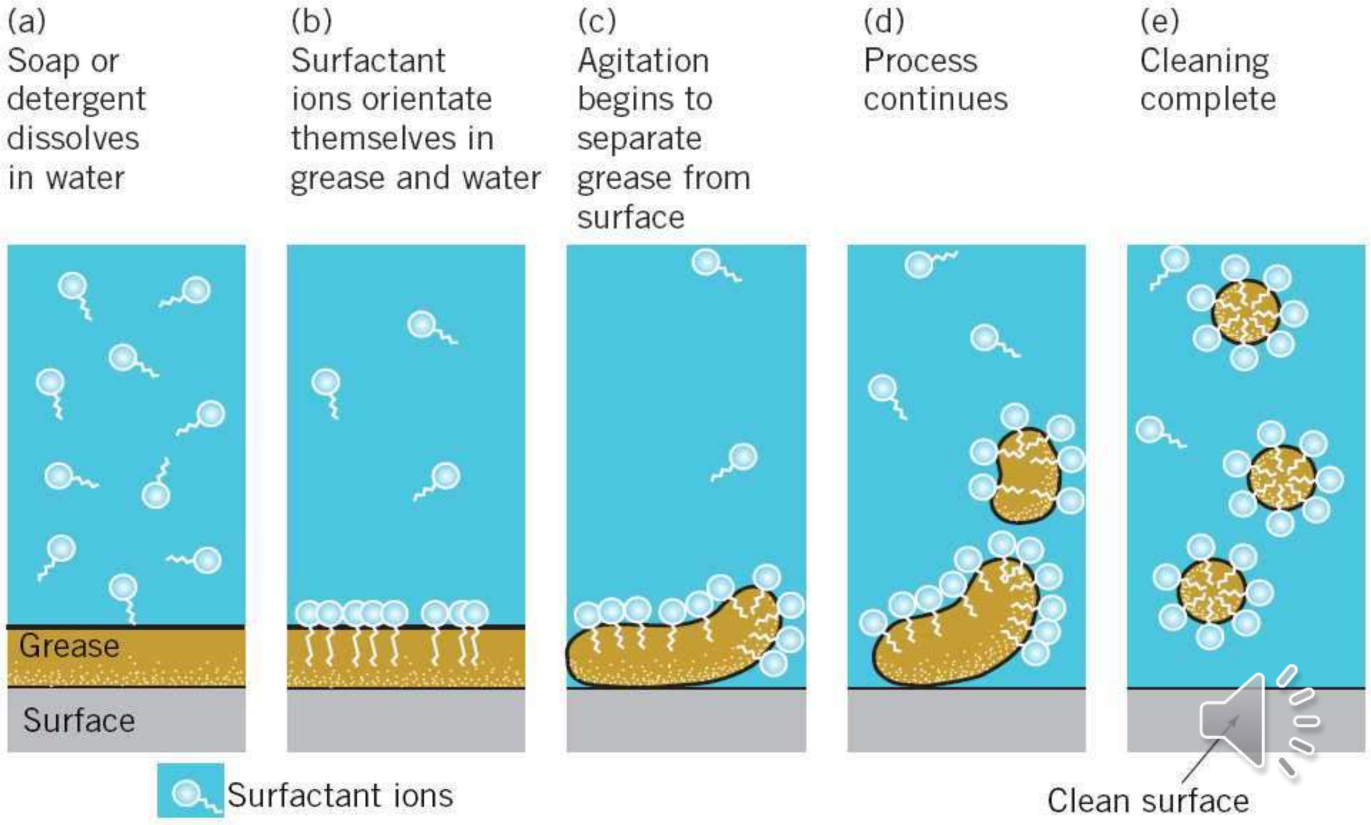
Wetting Agent

- 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.**

- Examples of the application of wetting to pharmacy and medicine include:
  a) the displacement of air from the surface of **sulfur, charcoal**, and other powders for the purpose of dispersing these drugs in liquid vehicles
  b) 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
  c) the displacement of dirt and debris by the use of **detergents** in the washing of wound
  d) the application of **medicinal lotions and sprays** to the surface of the skin and mucous membranes

2- Detergents

- are surfactants that are used for the removal of dirt.
- Detergency is a complex process involving the removal of foreign matter from surfaces.
- The process includes many of the action characteristic of specific surfactants: initial wetting of the dirt and of the surface to be cleaned; deflocculation and suspension; emulsification or solubilization of the dirt particles



- All of the soaps (sodium oleate, etc.) are fatty acid salts (anionic surfactant).
- They are characterized by:

  (a) a long hydrocarbon chain, which may be monounsaturated (i.e., have one double bond, like sodium oleate), polyunsaturated (i.e., have more than one double bond), or saturated (i.e., no double bonds),

  (b) a carboxylate group at the end.

- The cleaning action of soaps and detergents is based on the property known as **detergency**

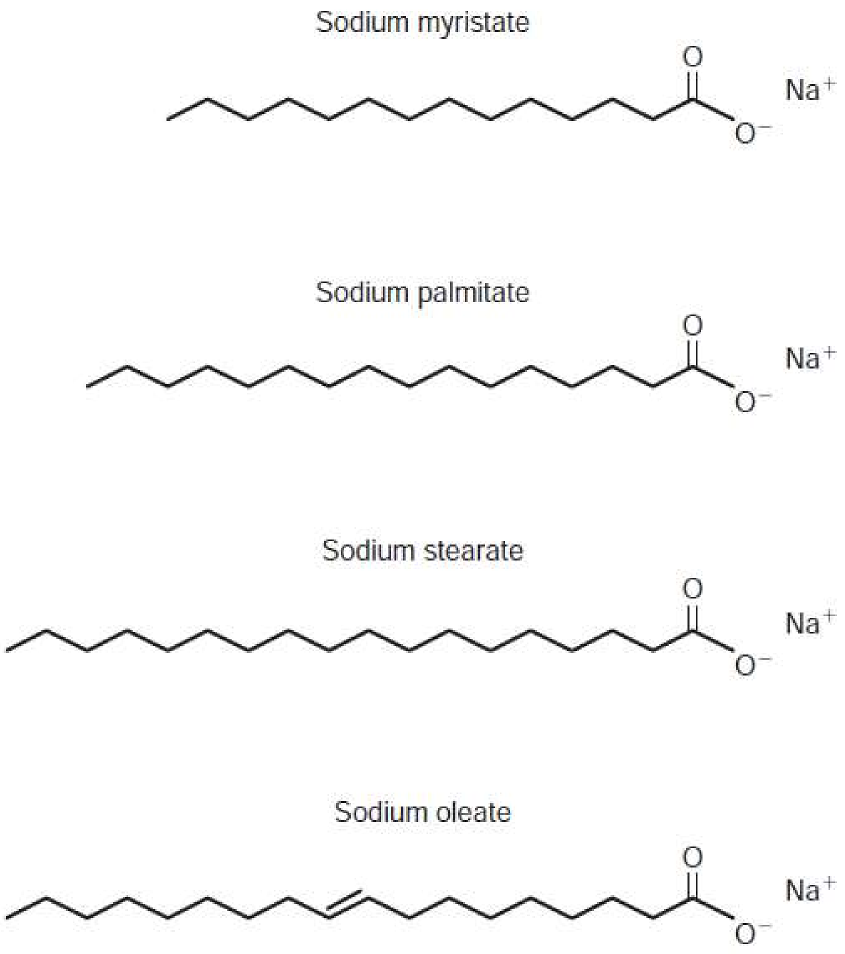


Fig. 15–26. Common soaps.

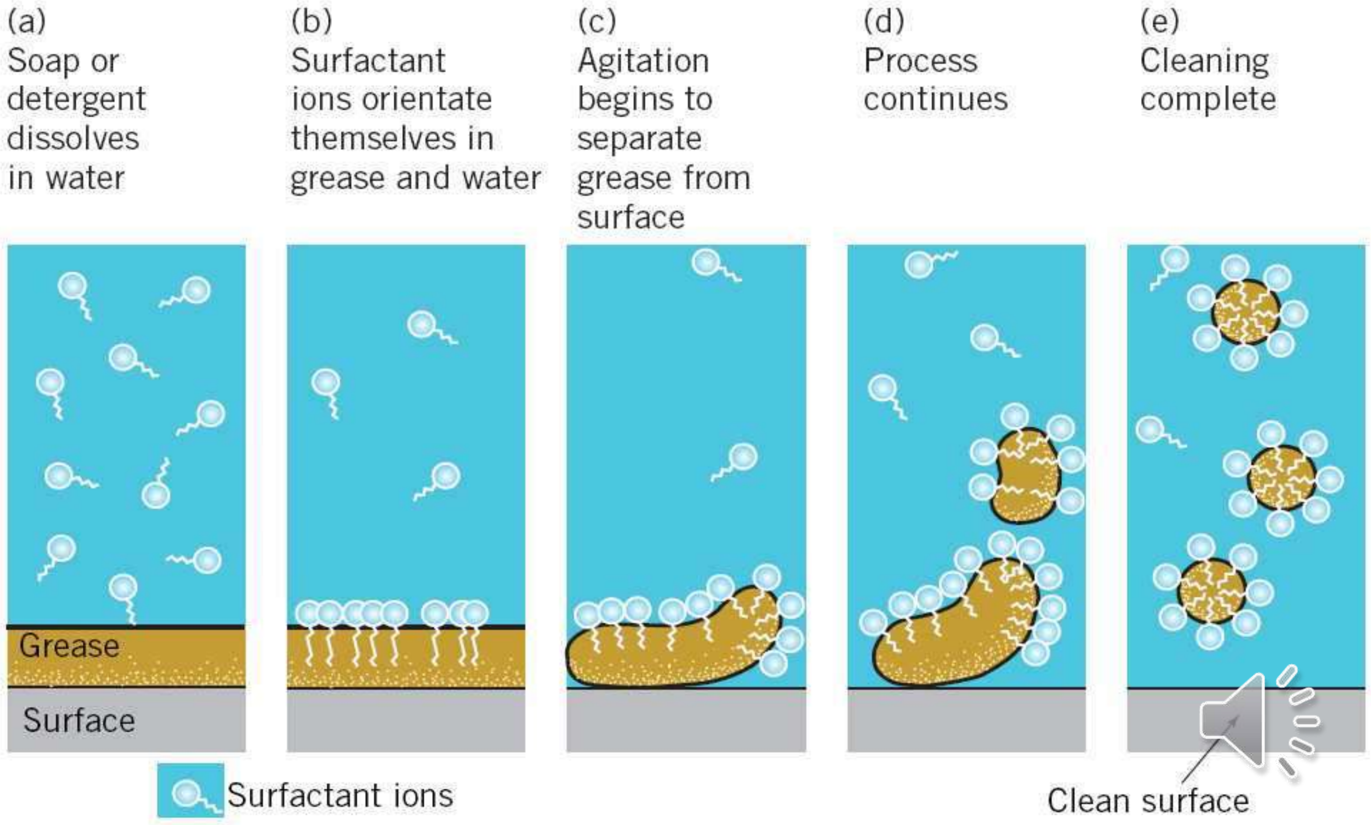
- The process includes the following main steps:

(a) The hydrocarbon tails of the detergent anions dissolve in the grease;

(b) The grease spot gradually breaks up and becomes pin cushioned by the detergent anions

(c) small bits of grease are held in colloidal suspension by the detergent.

✓ The anionic heads keep the grease from coalescing because the particles carry the same electric charge.



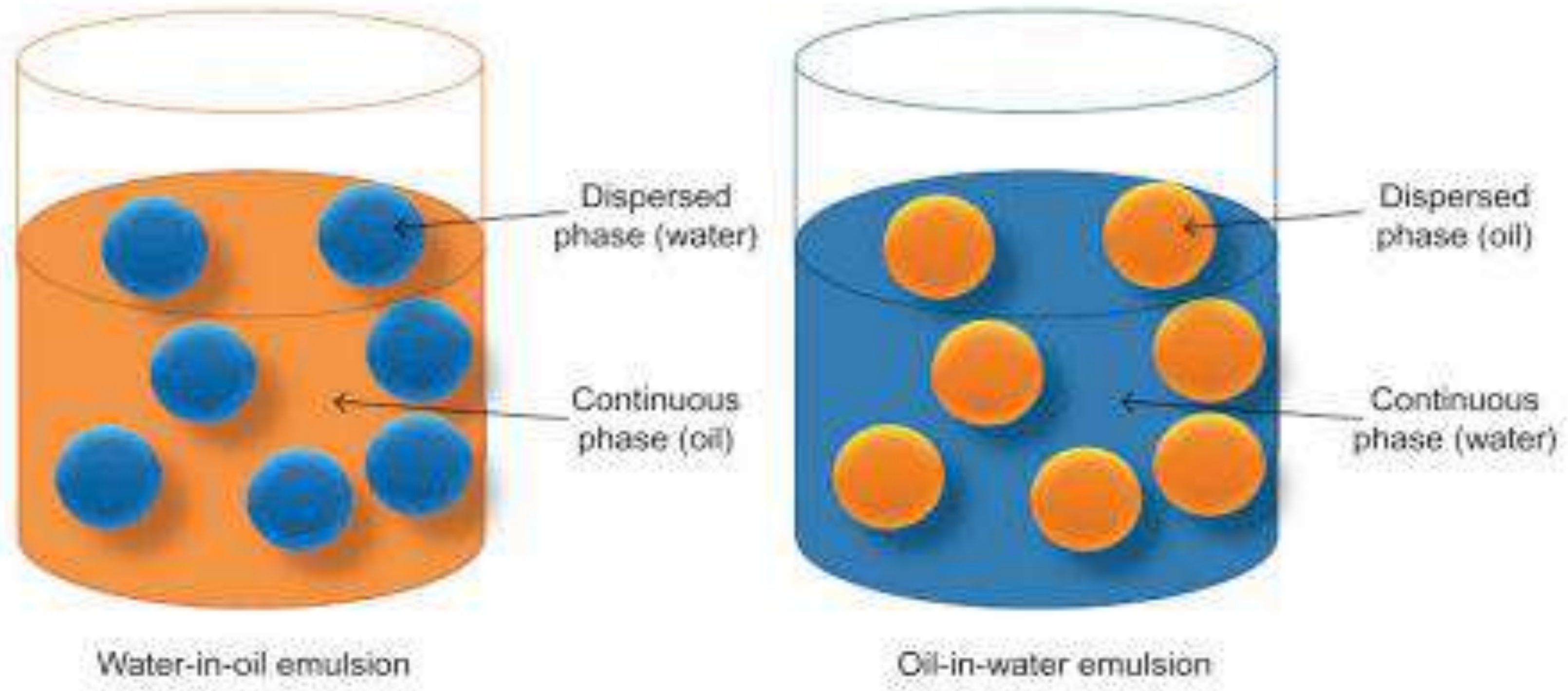
3- Foams and Antifoaming Agents

- Any solutions containing surface-active materials produce stable foams when mixed intimately with air.
- **A foam** is a relatively stable structure consisting of air pockets enclosed within thin films of liquid
- the **gas-in-liquid** dispersion being stabilized by a **foaming agent.**
- The foam dissipates as the liquid drains away from the area surrounding the air globules, and the film finally collapses.
- Agents such as alcohol, ether, castor oil, and some surfactants can be used to break the foam and are known as **antifoaming agents.**

- Foams are sometimes useful in pharmacy but are usually a nuisance and are prevented or destroyed when possible.
- The undesirable foaming of solubilized liquid preparations poses a problem in formulation.

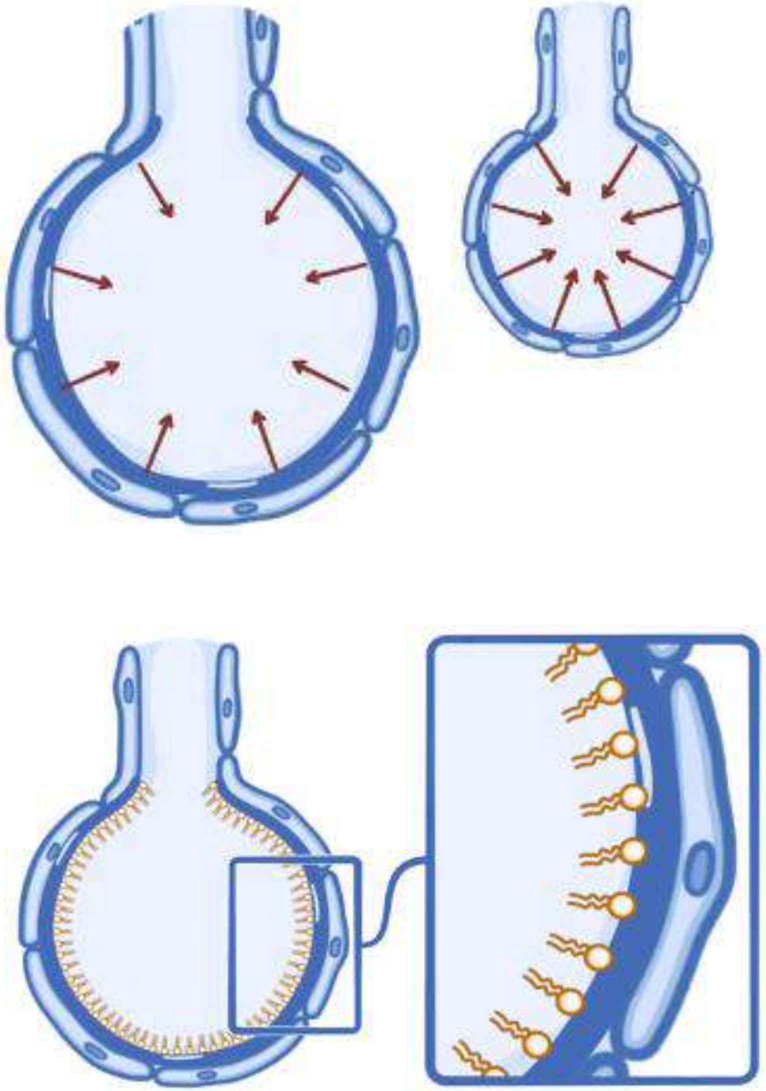
4- Emulsifying agents (Emulsifiers)

- The most important industrial role for surfactants is the formation of emulsions.
- An emulsion is a dispersion of one liquid in a second, immiscible liquid. Salad dressings, milk, and cream are emulsions, as are medicinal creams such as moisturizers.
- Emulsions are multiphase systems, even though they often look like they are just one phase.
- The phases in an emulsion are normally called the continuous phase and the dispersed phase


Dispersed phase (water)
Continuous phase (oil)
Water-in-oil emulsion
Dispersed phase (oil)
Continuous phase (water)
Oil-in-water emulsion

5- Lung Surfactant

- Lung surfactant is surface-active agent that covers the surface of alveoli contacted with air. It decreases the surface tension at the air–alveoli interface almost to zero.
- Therefore accomplishes two main tasks:
  - First, it **prevents the collapse of alveoli**.
  - Second, main surfactant function is to **decrease the pressure inside the alveoli**. Thus, lung surfactant allows us to breathe and prevents pulmonary edema.



- Lung surfactant is a complex mixture of proteins and lipids but the major component is phosphatidylcholine.
- Some pathologic conditions were found to decrease the activity of lung surfactant.
- The typical premature infant has only 1/20 of the lung surfactant needed to breathe.
- Fortunately, additional artificial lung surfactant can be administered.

ELECTRIC PROPERTIES OF INTERFACES

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

a) 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.

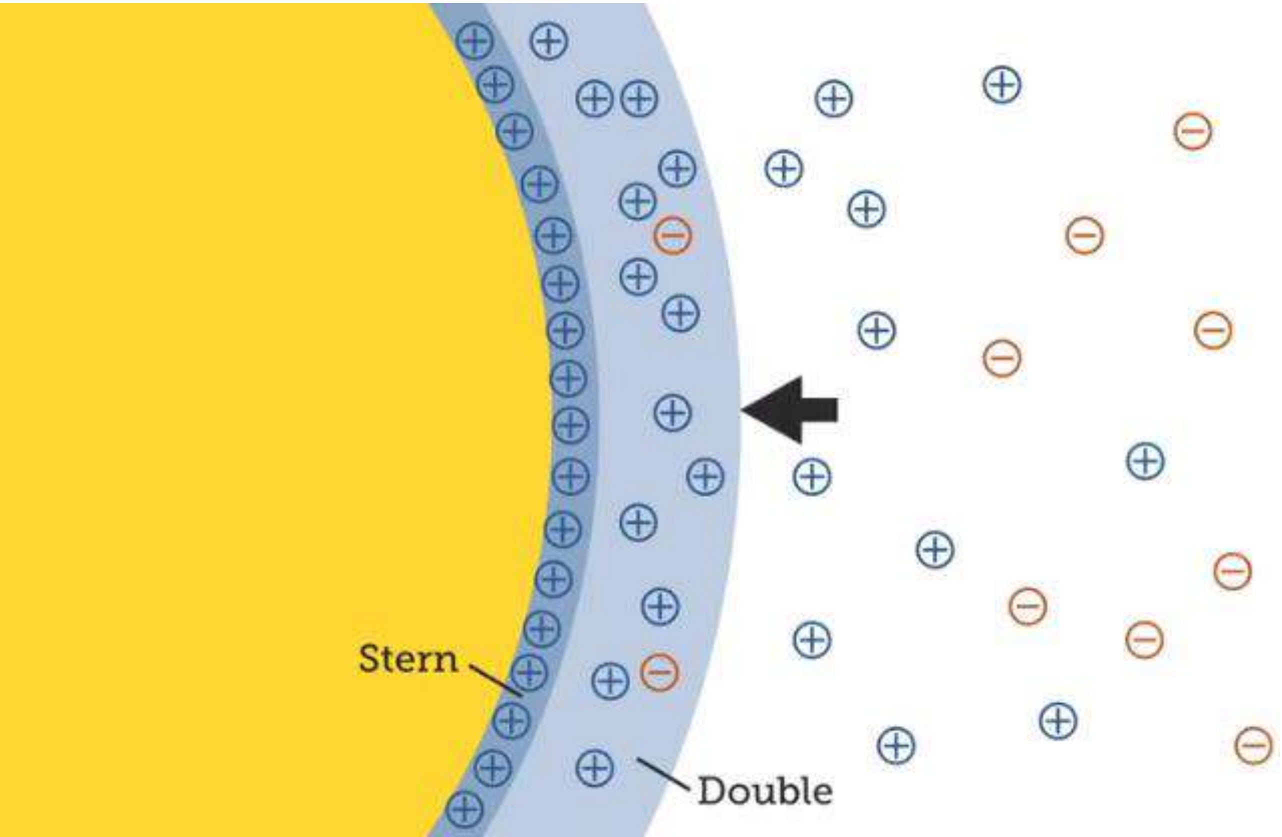
b) charges on particles arise from ionization of groups (such as COOH) that may be situated at the surface of the particle.

- In these cases, the charge is a function of p*K* and pH.

✓ 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

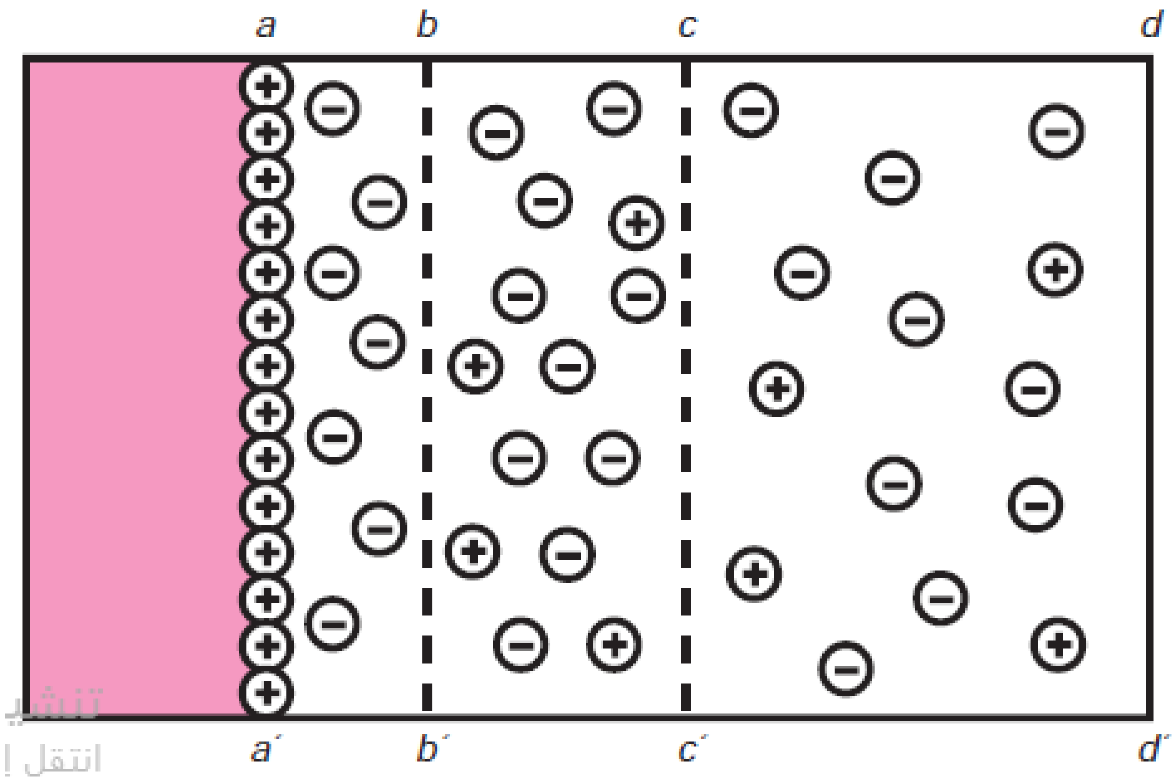
- Consider a solid surface in contact with a polar solution containing ions, for example, an aqueous solution of an electrolyte.



- the system as a whole is electrically neutral, even though there are regions of unequal distribution of anions and cations.
- The adsorbed ions that give the surface its positive charge are referred to as the **potential-determining ions.**

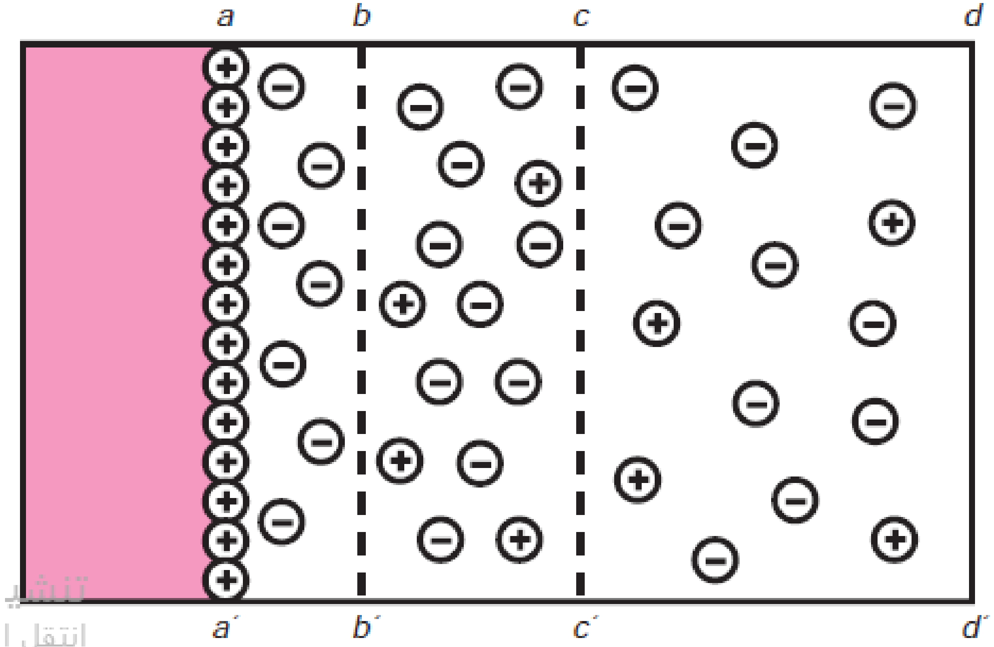
- Immediately adjacent to this surface layer is a region of tightly bound solvent molecules, together with some negative ions, also tightly bound to the surface
- The limit of this region is given by the line bb’ These ions, having a charge opposite to that of the potential-determining ions, are known as **counterions**

- if the surface is moved relative to the liquid, the **shear plane** is *bb* rather than *aa*, the **true surface.**



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.

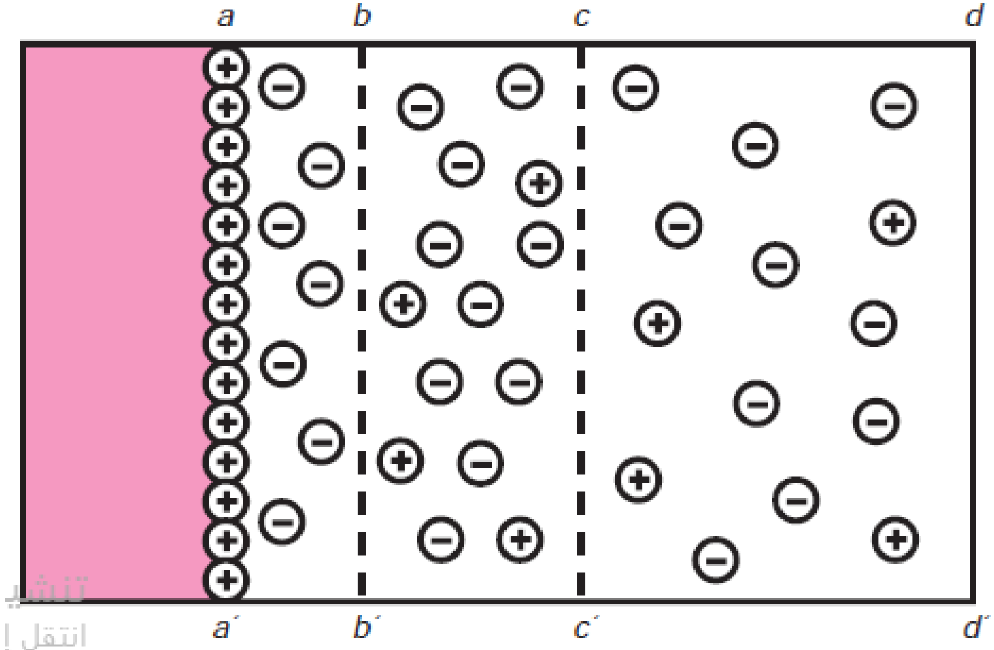
- In the region bounded by the lines *bb*and *cc*, there is an excess of negative ions.
- Beyond *cc*, the distribution of ions is uniform and electric neutrality is obtained.
- the electric distribution at the interface is equivalent to a **double layer** of charge, the first layer (extending from *aa* 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.



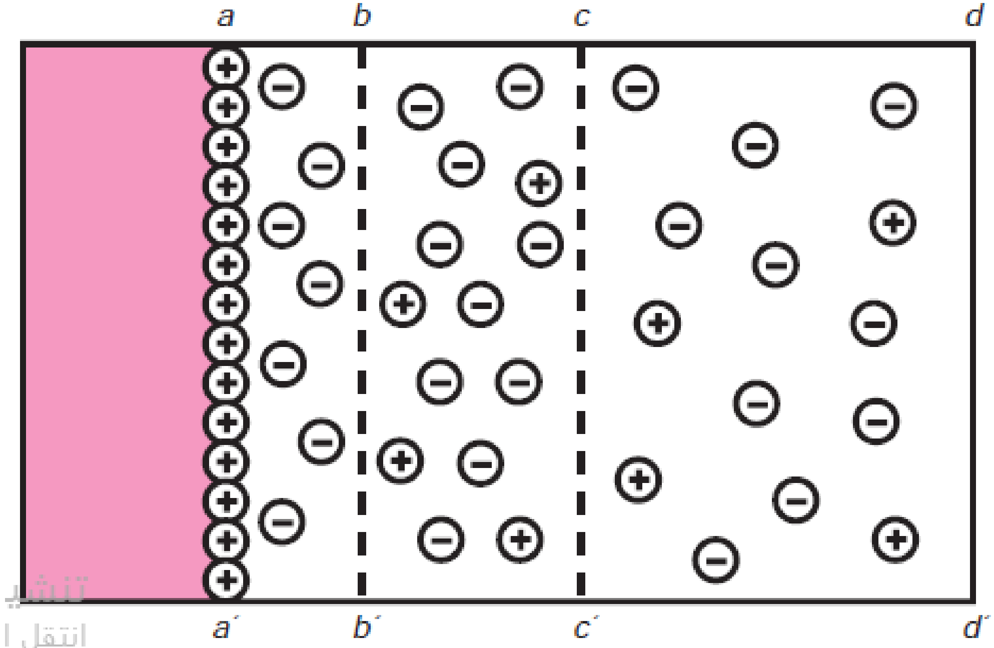
Two other situations are possible:

(*a*) 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*.

(*b*) 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

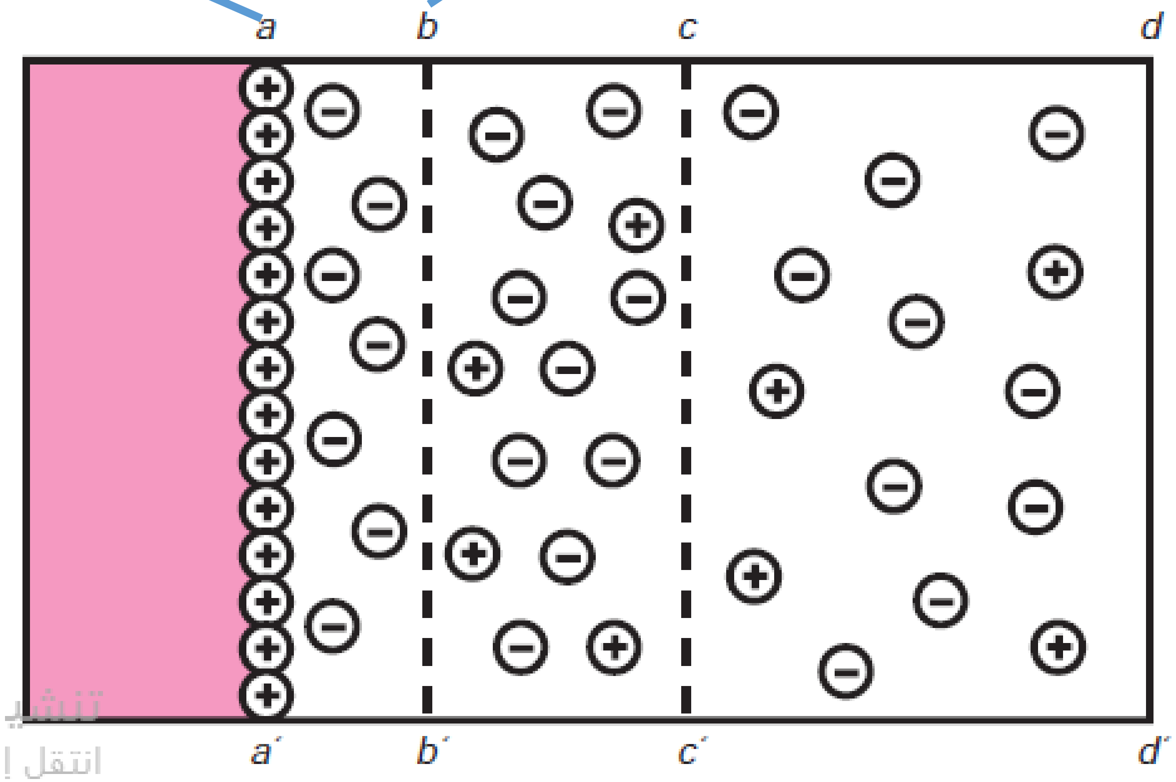


- This means that, in this instance, for electric neutrality to be obtained at *cc*, an excess of positive ions must be present in the region *bb*–*cc*.
- if the potential determining ion is negative, the arguments just given still apply, although now positive ions will be present in the tightly bound layer.



electrothermodynamic (Nernst) potential

Zeta Potentials



- the difference in potential between the actual surface and the electroneutral region of the solution

- the difference in potential between the surface of the tightly bound layer (shear plane) and the electroneutral region of the solution.

- The zeta potential has practical application in the stability of systems containing dispersed particles because this potential, rather than the Nernst 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