Surface Phenomena

Medical Chemistry

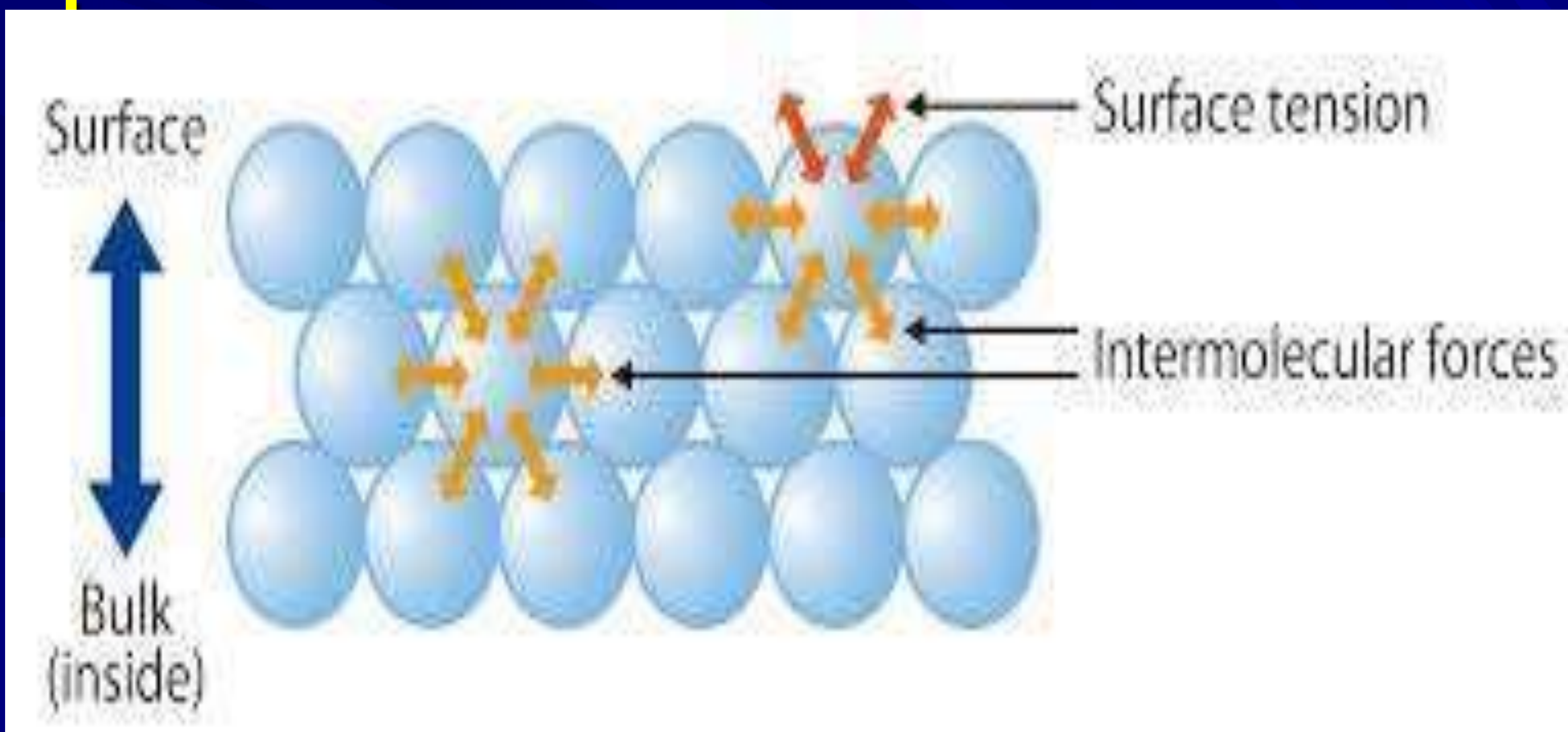
Surface phenomena

Surface phenomena are observed in heterogeneous systems at the phase interface.

Surface phenomena are caused by excess of free energy at the phase interface.

Surface phenomena

Molecules on the surface have imbalanced intermolecular forces compared to molecules in the bulk of the



Surface tension

Surface tension is the ratio of free energy of the surface to the surface area.

$$\delta = Gs/S$$

Here,

- **σ is the surface tension;**
- **G_s is the free Gibbs energy of the surface;**
- **S is the surface area.**

Surface tension of water

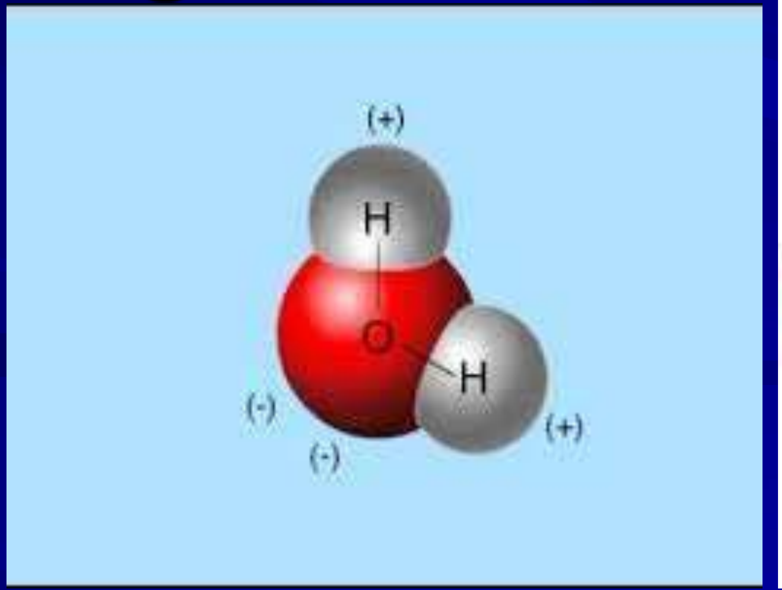
Surface tension of water is abnormally high.

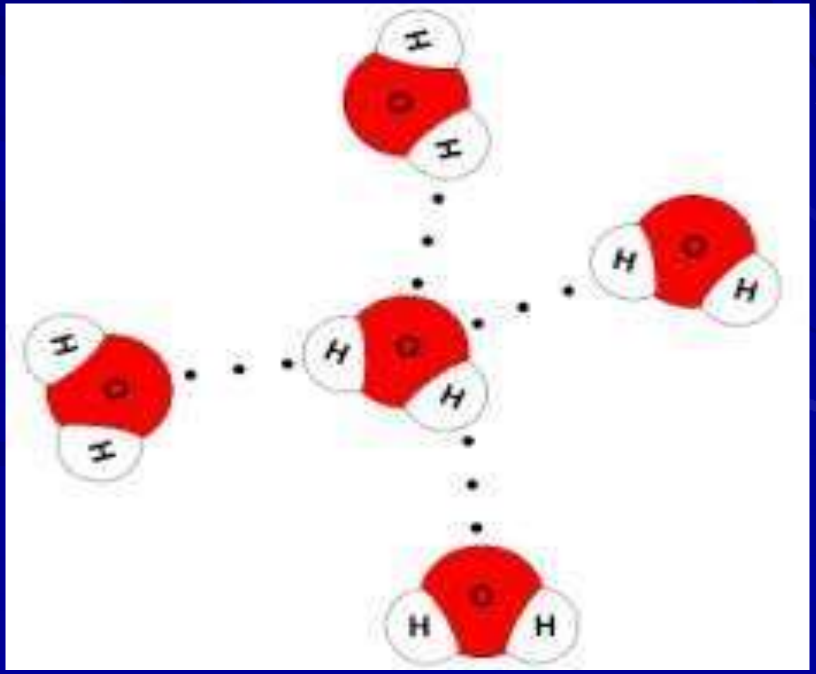
Due to it, small objects that are denser than water can float on its surface.

Surface tension of water

Two causes of high surface tension of water:

- **Polarity of water of water molecules;**
- **Ability of water molecules to form hydrogen bonds.**





Decrease of surface energy

Surface phenomena happen spontaneously, i.e with a decrease of free energy.

There are two ways to decrease free energy of the surface.

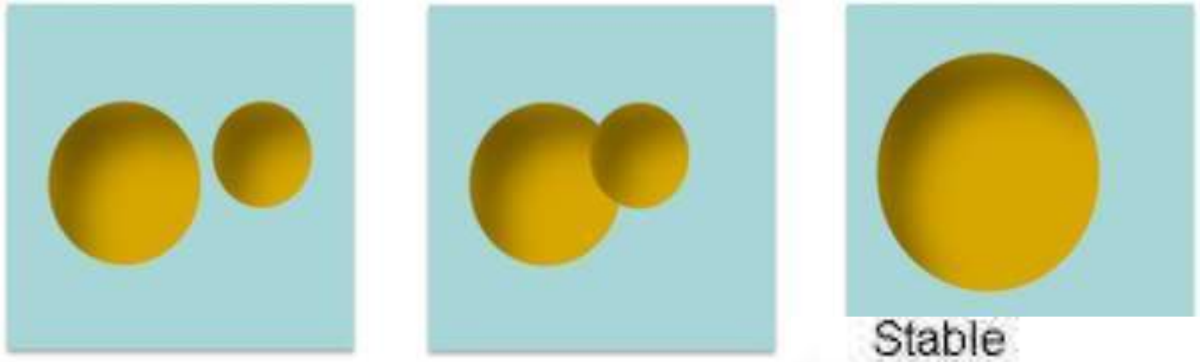
Decrease of surface energy

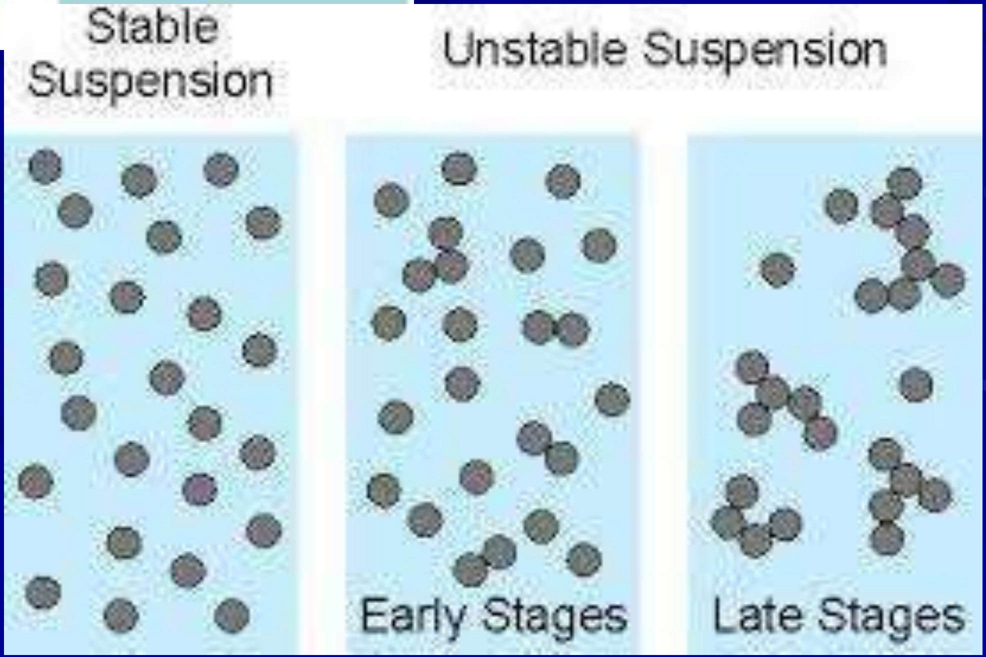
1. Decrease of surface area

a) tendency to form spherical or smooth surface

Decrease of surface energy

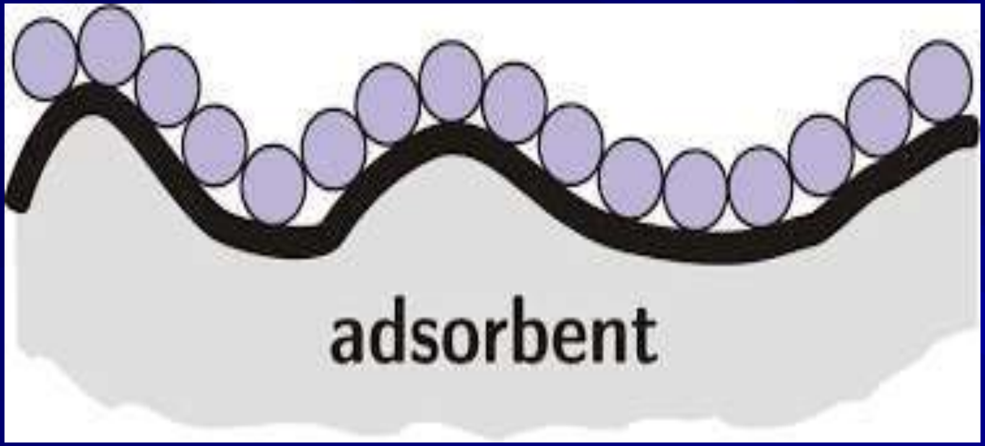
b) aggregation of particles of the solute

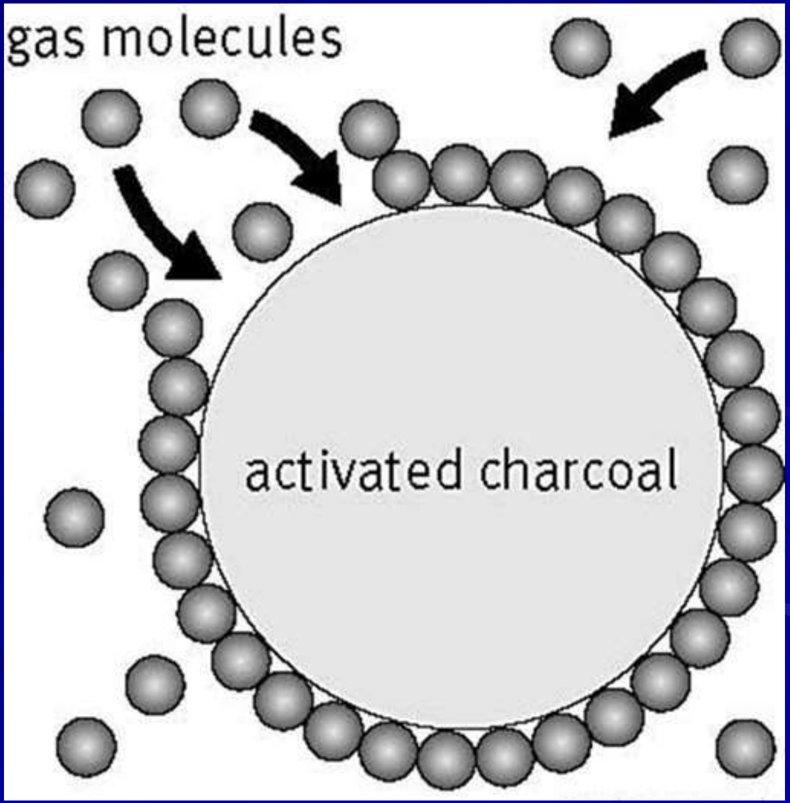




Surface phenomena

2. Decrease of surface free energy through adsorption.





Surface active compounds

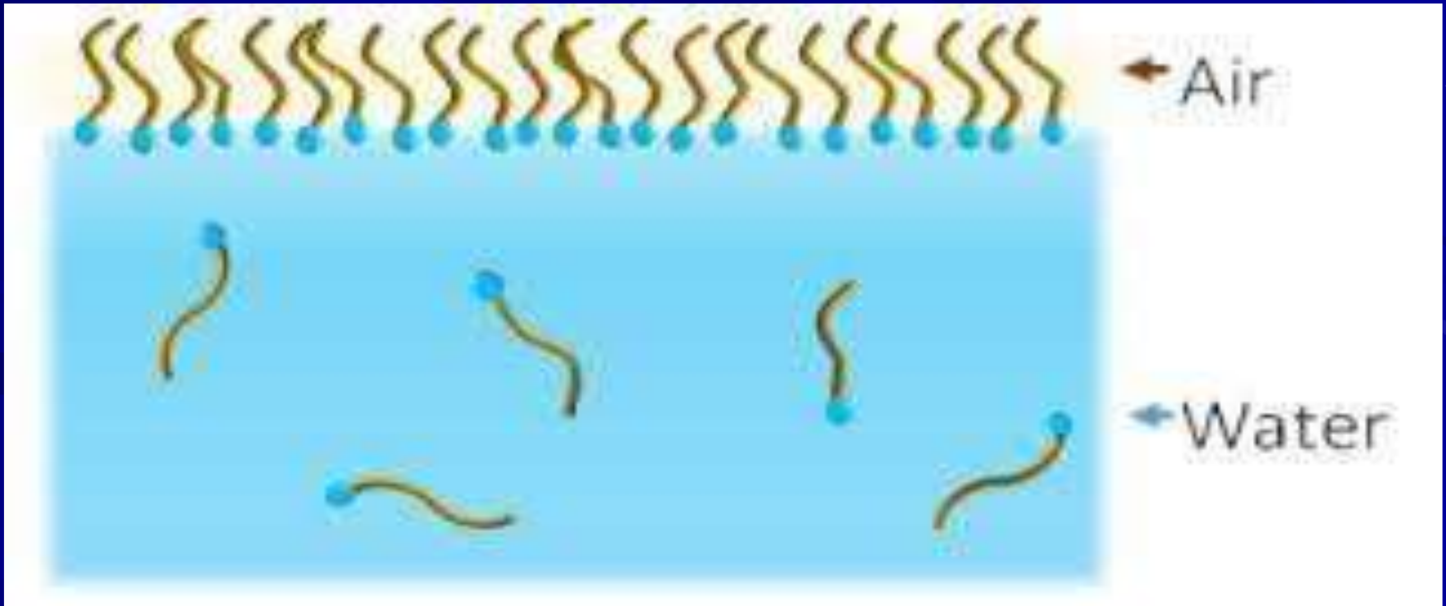
Surface active compounds (surfactants) concentrate on the surface and decrease surface tension of water.

Surfactants concentrate at the phase interface because they are amphiphilic.

Surface active compounds

Surfactants are amphiphilic, i.e the molecule has a hydrophilic (polar) part and a hydrophobic (non-polar) part.

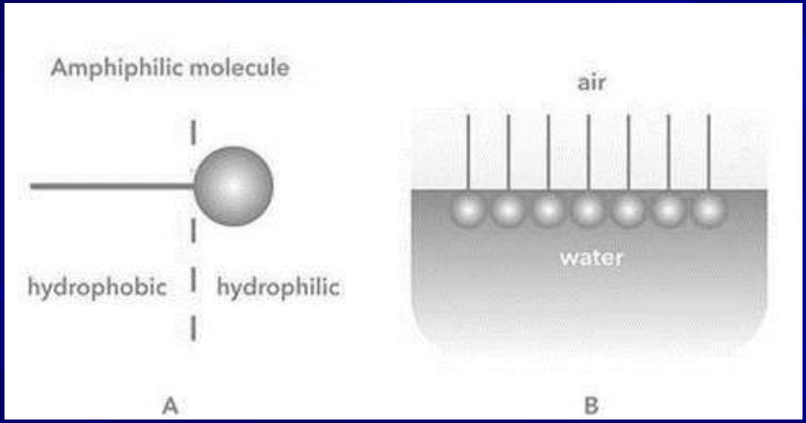
The hydrophilic part is in water, the hydrophobic part is pushed into air.

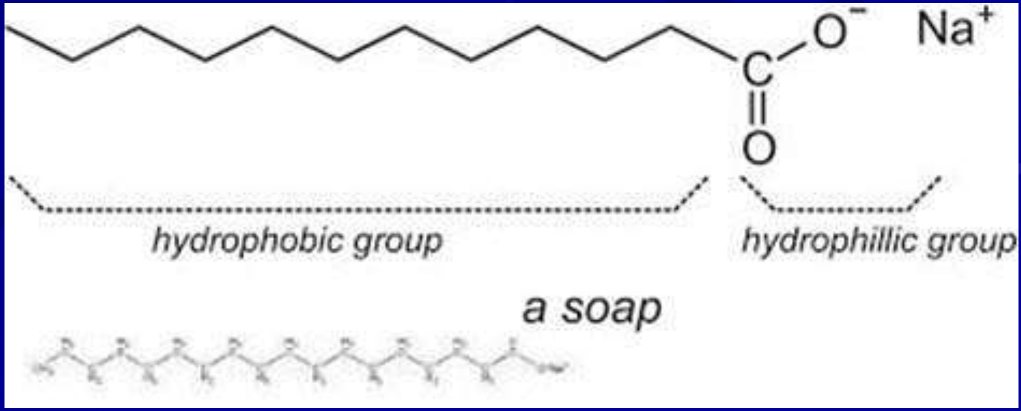


Surface active compounds

Example:

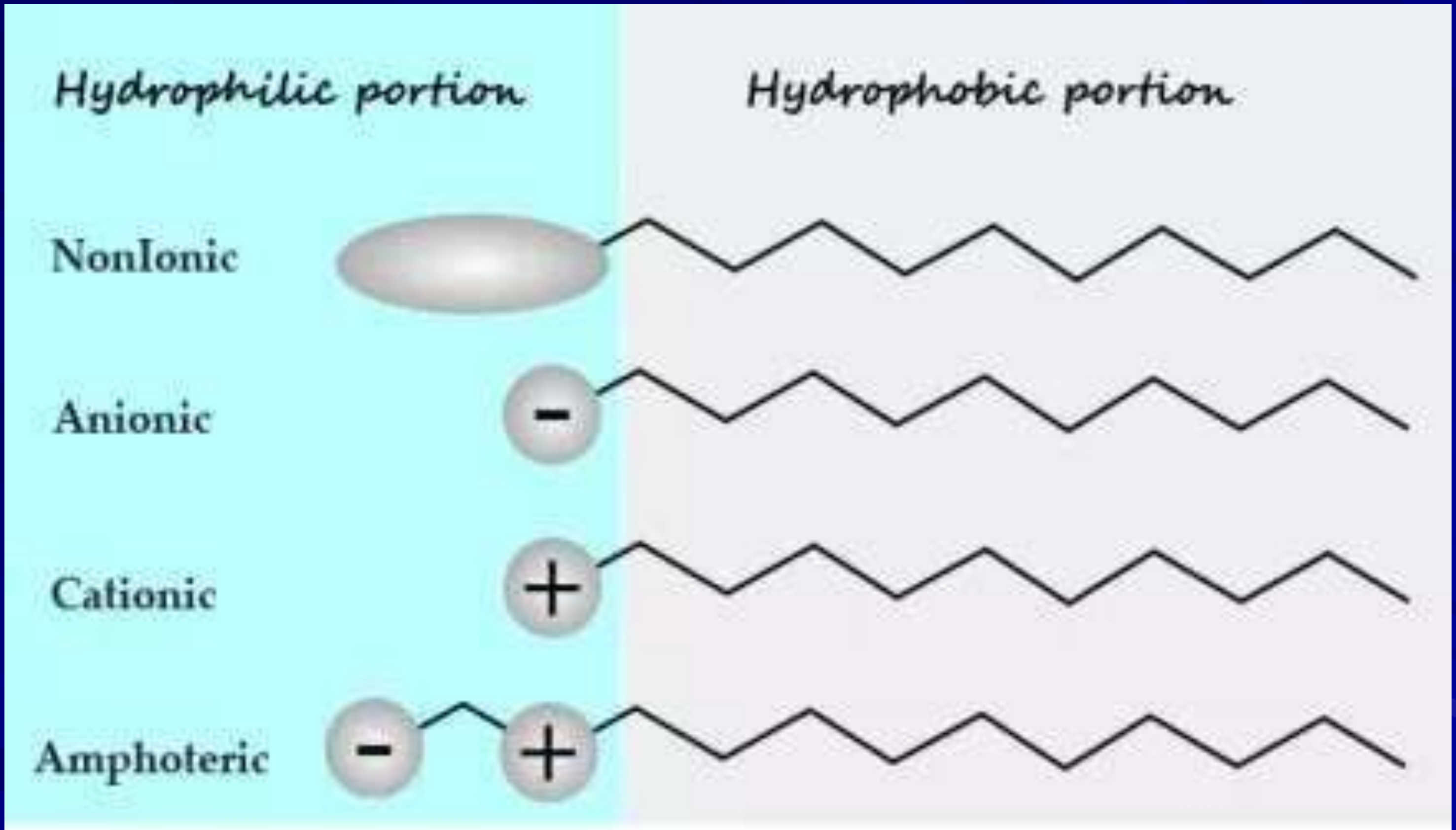
soap (sodium stearate $C_{17}H_{35}COONa$), where the carboxylate anion is the hydrophylic part, and the hydrocarbon radical is the hydrophobic part.





Surface active compounds

Surfactants are classified as:



The different types of surfactants

Traube's rule

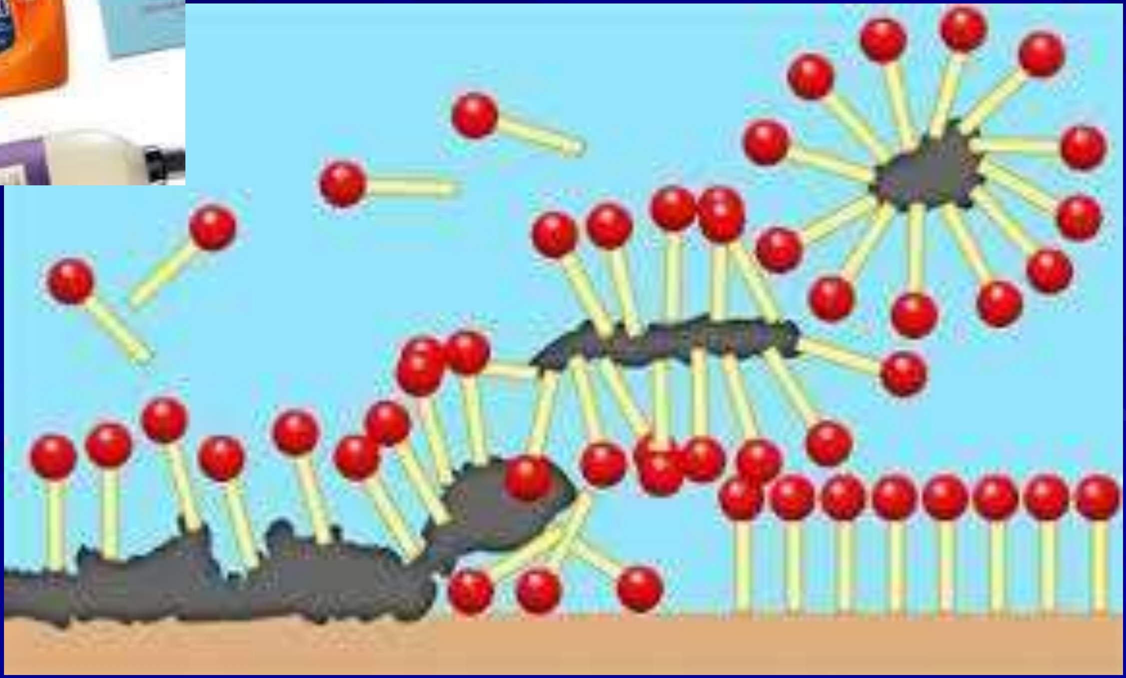
The longer hydrocarbon chain – the bigger surface activity.

Traube's rule

In dilute solutions of a homological series of surface active compounds, each next $–CH_2–$ group in the hydrocarbon chain increases the surface activity 3 - 3.5 times.

Applications of surface active compounds

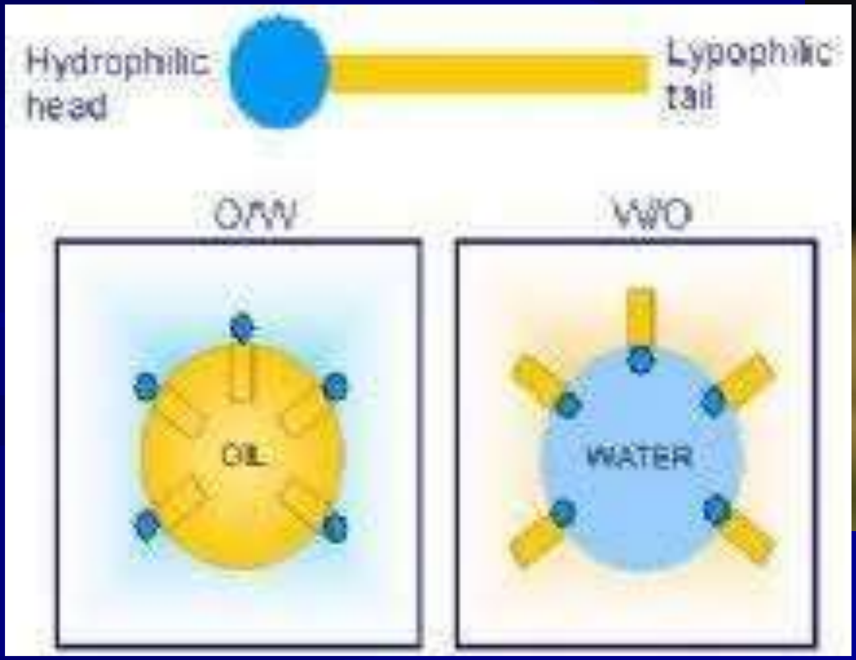
1. Detergents



Applications of surface active compounds

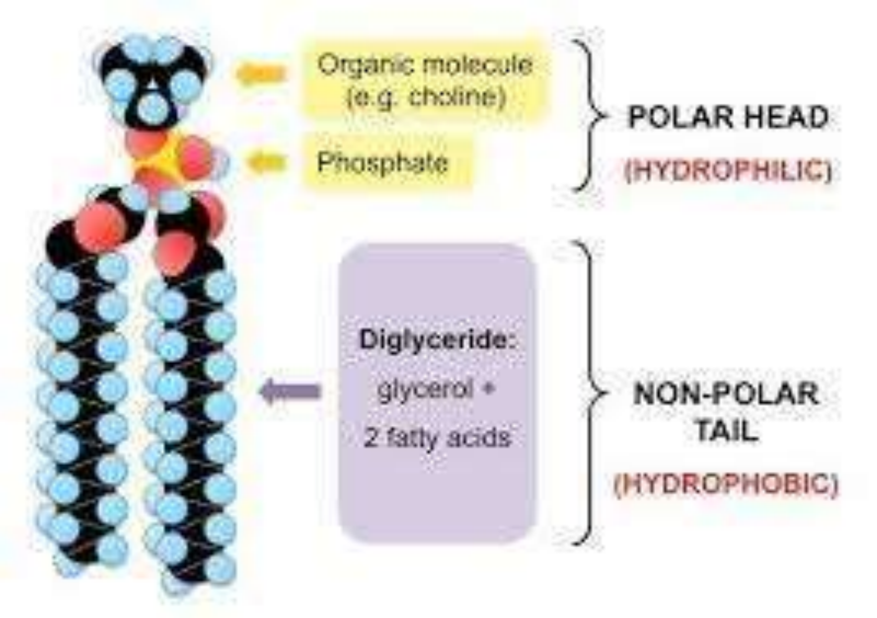
2. Emulsifiers.

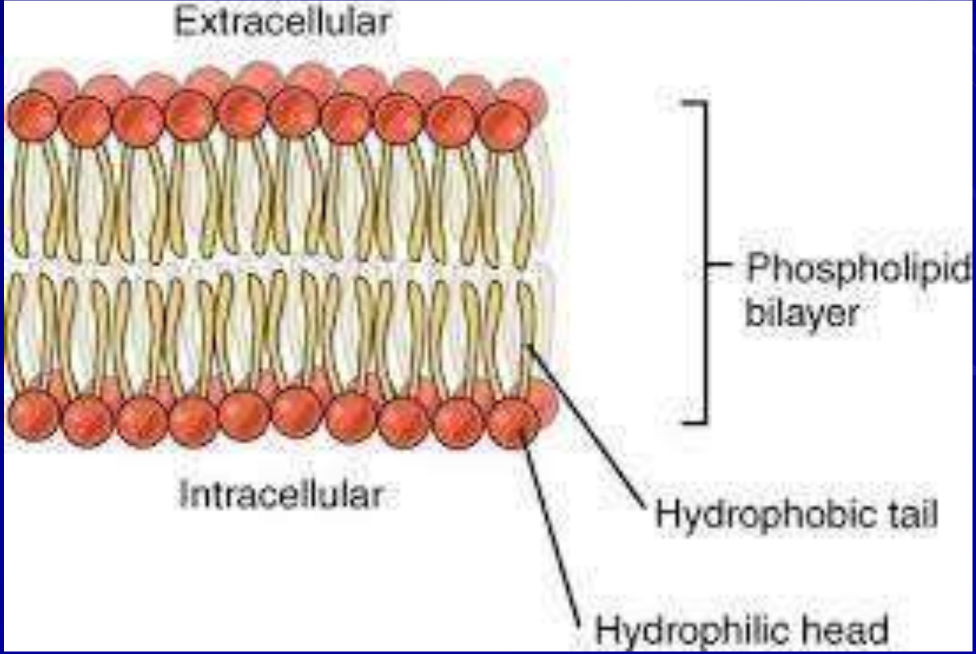
In food these are lecithins (a type of phospholipids).



Roles of phospholipids

1. Main component of the cell membrane. The other components are proteins and cholesterol



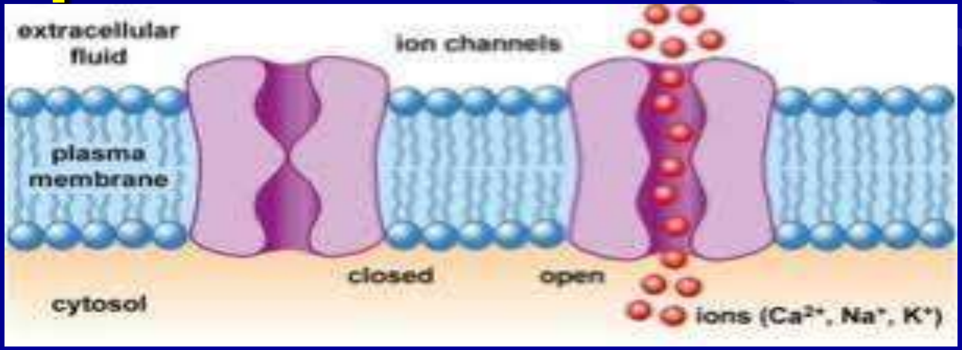


Roles of phospholipids

Phospholipids regulate transport of substances into the cell.

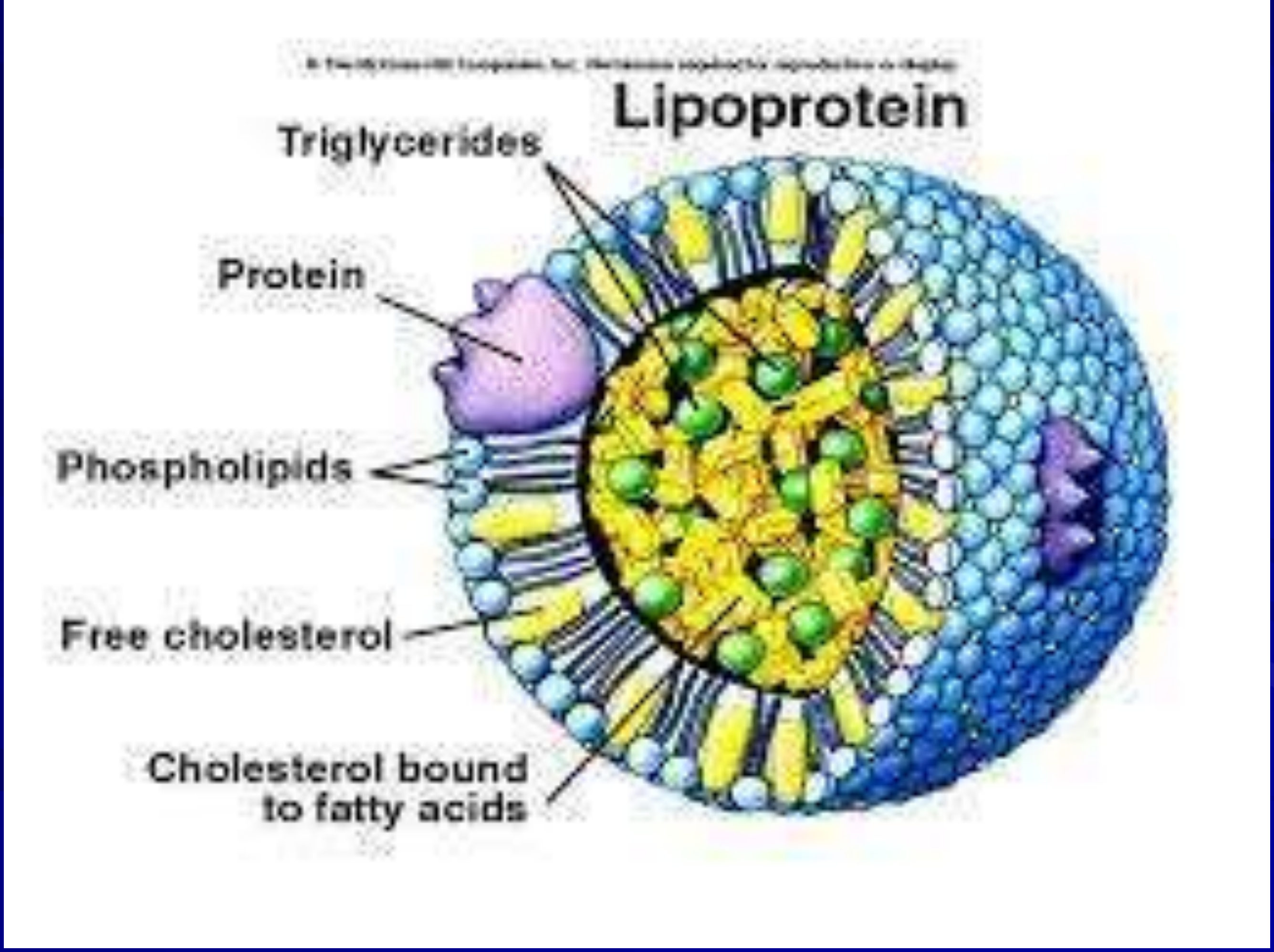
Nonpolar substances e.g. steroid hormones, oxygen, pass freely through the membrane.

Polar molecules and ions need special transporters, e.g. ion channels. Protein channels for transport of water are called aquaporins.



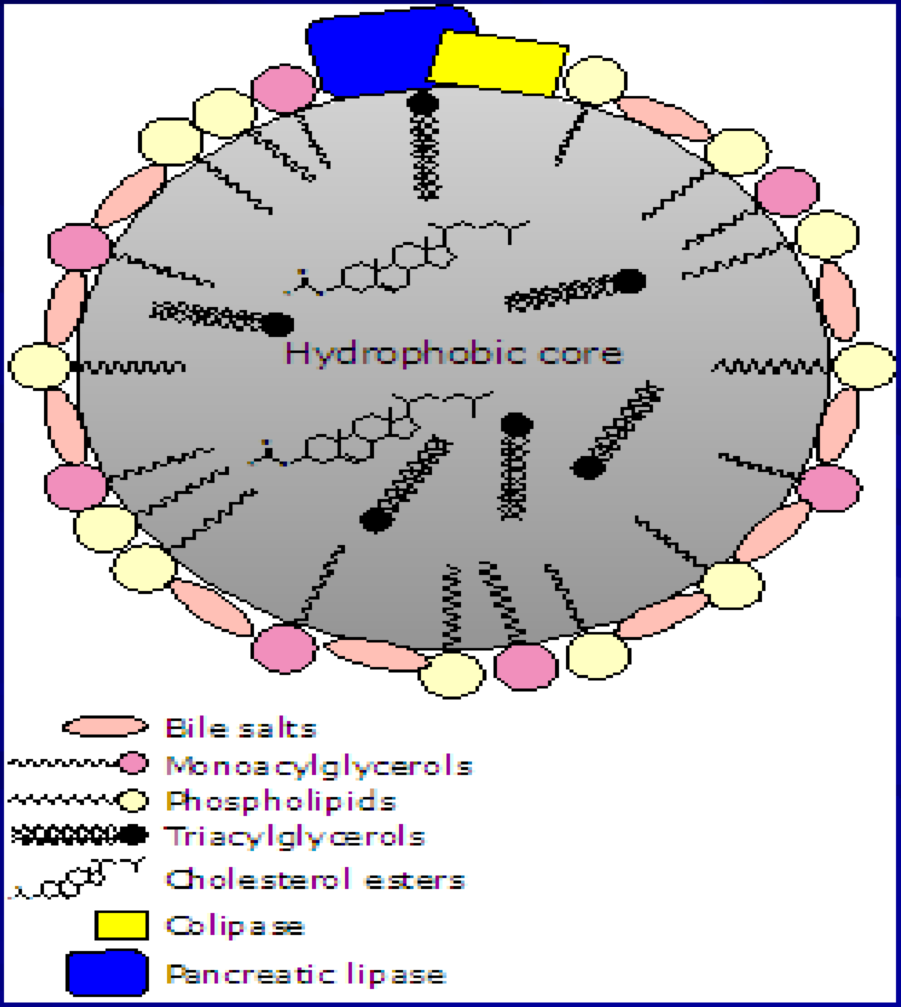
Roles of phospholipids

2. Transport of lipids in blood



Roles of phospholipids

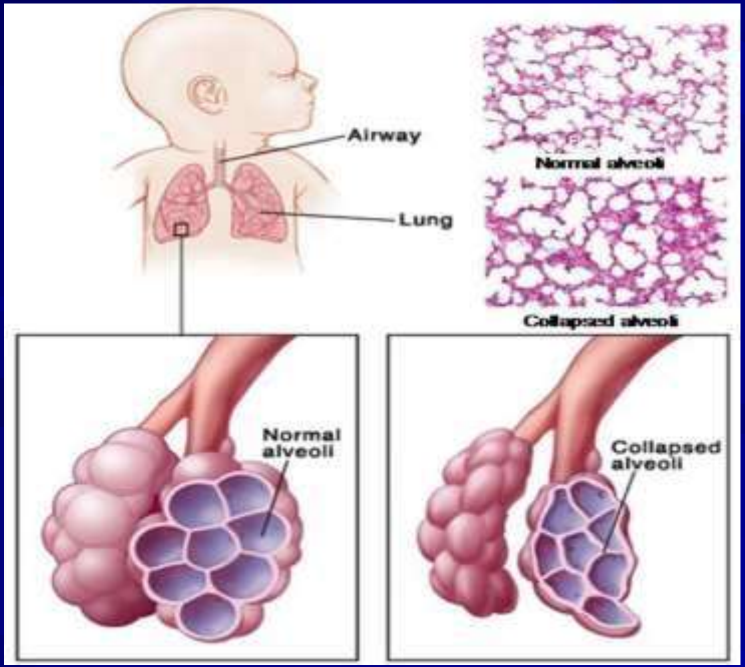
3. Emulsifiers in the small intestine, together with bile acids

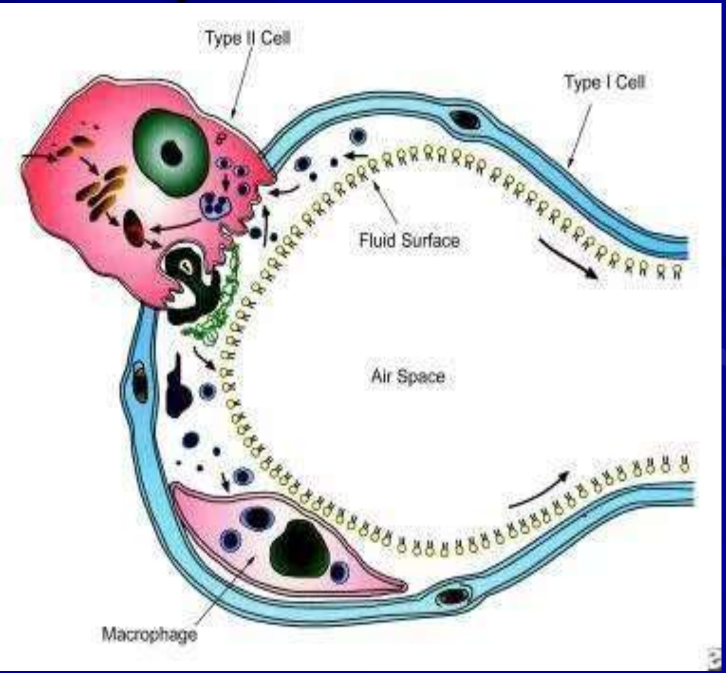


Roles of phospholipids

4. A lecithin dipalmitoylphosphatidylcholine is a surfactant in the lungs, prevents alveoli from collapsing.

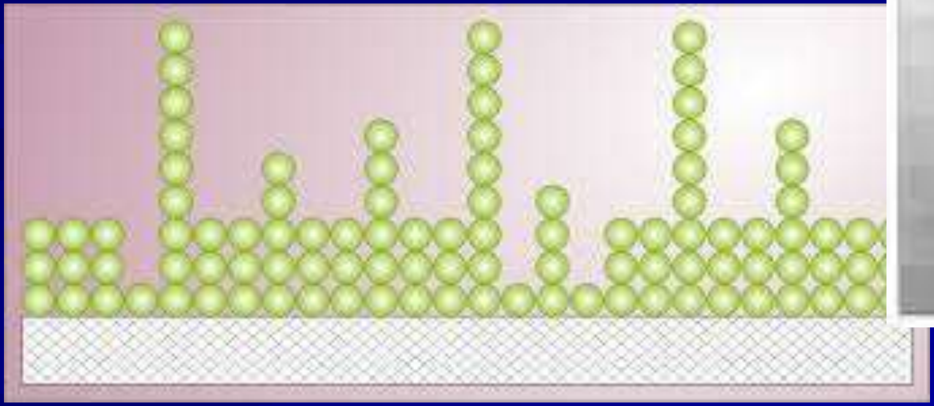
Deficiency can cause respiratory distress syndrome (in preterm infants).

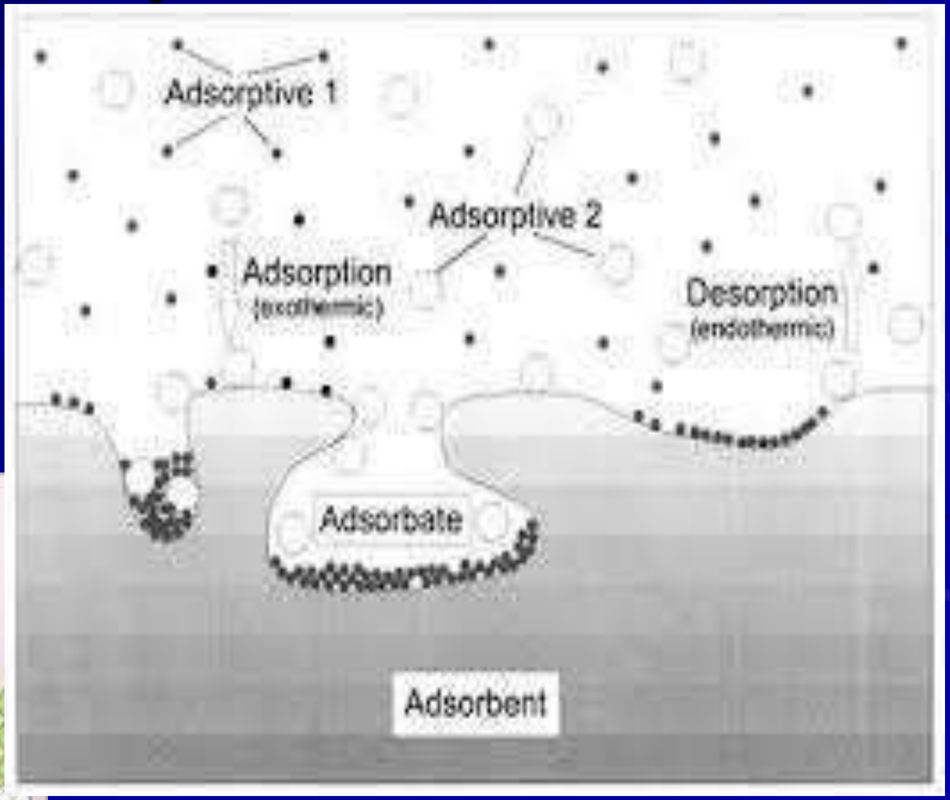




Adsorption

Adsorption is a spontaneous increase in the concentration of a substance at the phase interface as compared to the bulk phase.





Adsorption

- **Adsorbent** is a substance on which adsorption occurs.
- **Adsorbate** is a substance which is adsorbed on a phase interface.
- **Desorption** is a process reverse to adsorption.
- **Absorption** proceeds in the bulk of the substance, when atoms or molecules cross the phase interface and distribute in the bulk of an absorbent.

Physical and chemical adsorption

There are two types of adsorption: physical adsorption (physisorption) and chemical adsorption (chemisorption).

Physical adsorption

Occurs through Van der Waals forces.

Interactions between adsorbent and adsorbate are weak.

Ii is reversible.

Molecules in adsorbent and adsorbate do not change their identity.

It is not specific, i.e. same adsorbent may adsorb various substances.

The heat effect is from small to moderate.

It decreases with increasing temperature.

Chemical adsorption

Chemical adsorption (chemisorption) happens due to a chemical reaction between adsorbent and adsorbate.

Molecules of the adsorbate lose their identity.

It increases with an increase in temperature.

It is often irreversible.

It is specific.

The heat effect of chemisorption is large.

Molecular and ionic adsorption

Physical adsorption can be molecular and ionic.

Molecular adsorption depends on polarity of molecules of adsorbent and adsorbate.

Ionic adsorption can be nonselective (depends on charge of the ion), selective (depends on the identity of the ion) and ion-exchange.

Langmuir adsorption isotherm

At constant temperature, Langmuir adsorption isotherm defines ….

Assumptions:

1. Adsorption only happens on ….
2. All active sites have equal ….
3. Each site can hold …

Langmuir adsorption isotherm

$$\Gamma = \Gamma_{\infty} \frac{c}{c + B}$$

Γ is adsorption, mol/m^2;

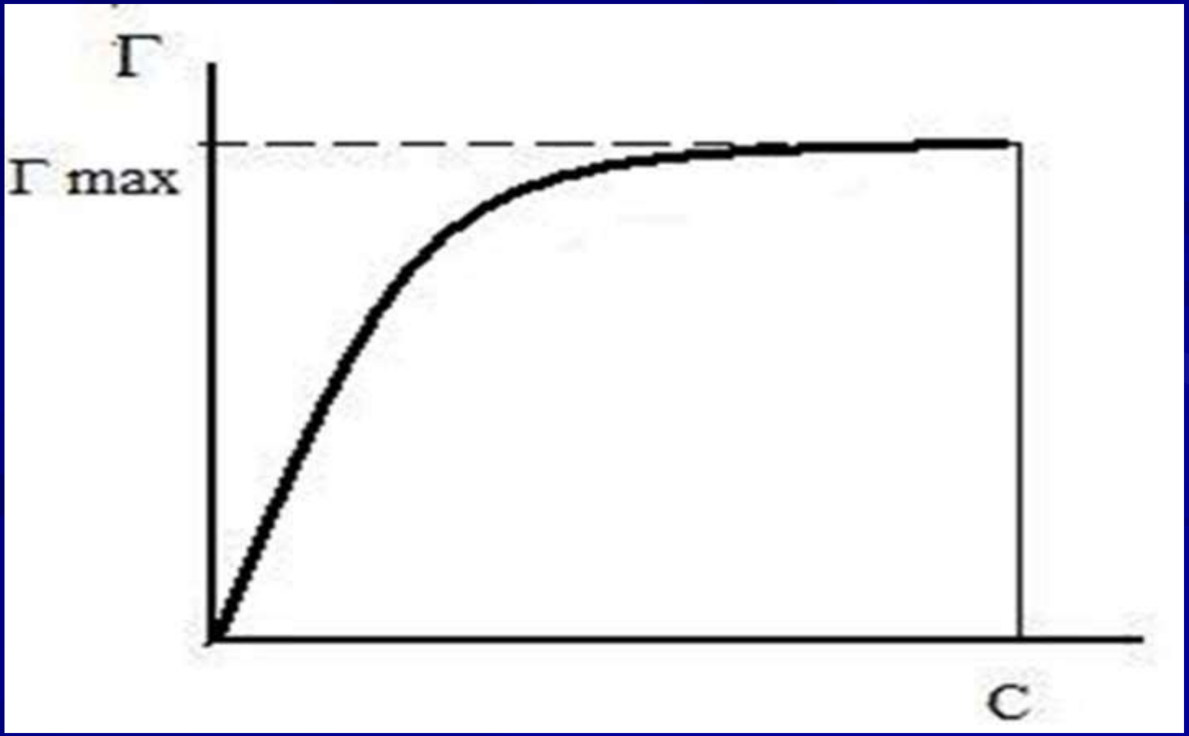
Γ_{∞} is maximum possible adsorption, mol/m^2;

c is concentration, mol/m^3;

B is the adsorption constant equal to the concentration at which the adsorption is half the maximum possible adsorption

Langmuir adsorption isotherm

When all active sites are occupied, adsorption reaches its maximum and does not increase anymore.



Molecular adsorption

Molecular adsorption depends on polarity of molecules of the adsorbent and adsorbate.

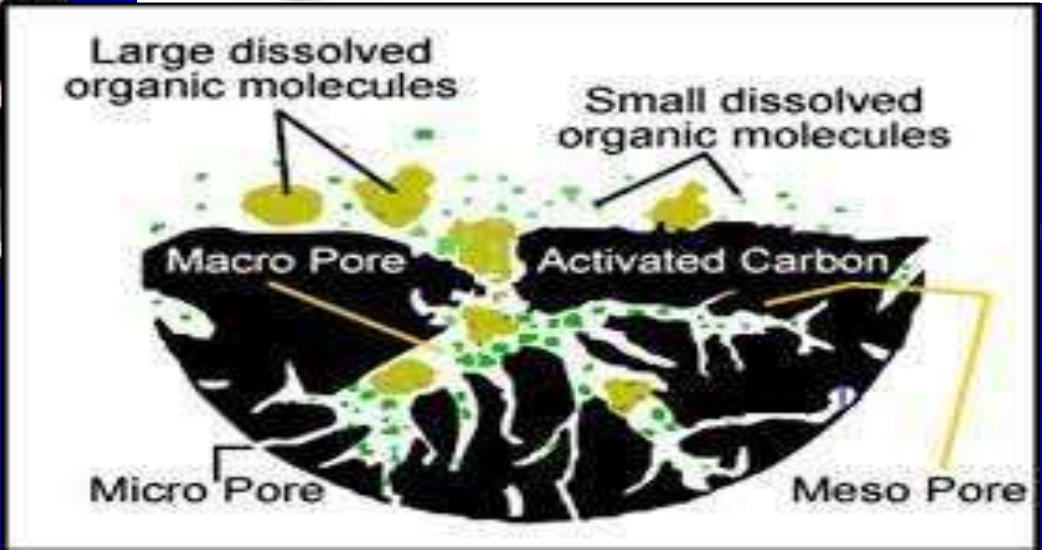
Rebinder's rule of polarities

Polar substances are adsorbed on polar adsorbents from nonpolar solvents and vice versa.

Example: of methylamine CH_3NH_2 and propylamine $CH_3CH_2CH_2NH_2$ in water, propylamine is better adsorbed on activated charcoal, because it is less polar than methylamine.

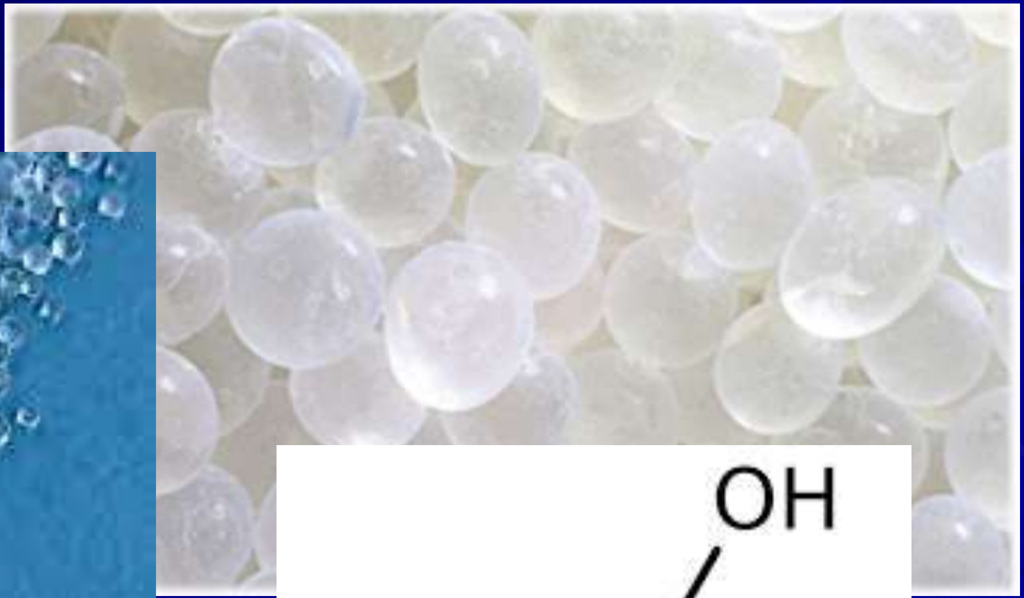
Nonpolar adsorbents

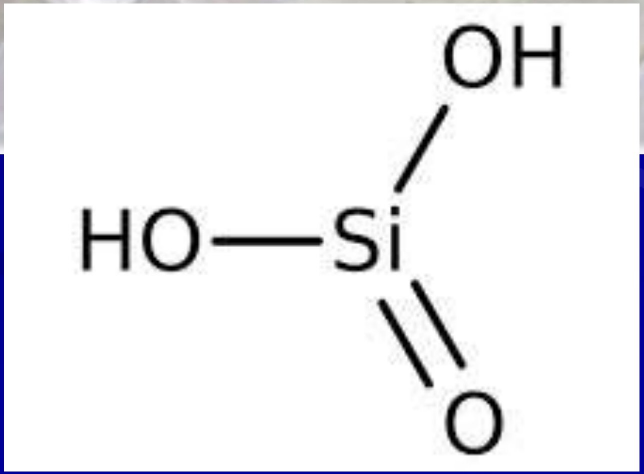
Activated charcoal is a nonpolar adsorbent. It is highly porous and has a large surface area.



Polar adsorbents

Silica gel is a polar adsorbent. It is amorphous and porous dry gel of silicic acid.





Selective ionic adsorption

Selective ionic adsorption follows the Paneth – Fajans rule.

Paneth-Fajans rule:

The ion is preferably adsorbed from a solution on the surface of a solid crystalline adsorbent when the ion is a component of the crystal lattice of the adsorbent.

Examples: on AgI surface, either Ag^{+} or I^{-} are adsorbed; on CaF_2 surface, either Ca^{2+} or F^{-} are preferably absorbed.

Ion exchange adsorption

Ion exchange adsorption is the process of exchange of equivalent amounts of ions of the same charge between adsorbent and solution.

An ion exchanger is an insoluble substance containing ions that are electrostatically bound to the functional groups of a solid matrix.

Ion exchange adsorption

Ion exchange resins are: cationite resins and anionite resins.The resins are prepared as spherical beads 0.5 to 1.0 mm in diameter.

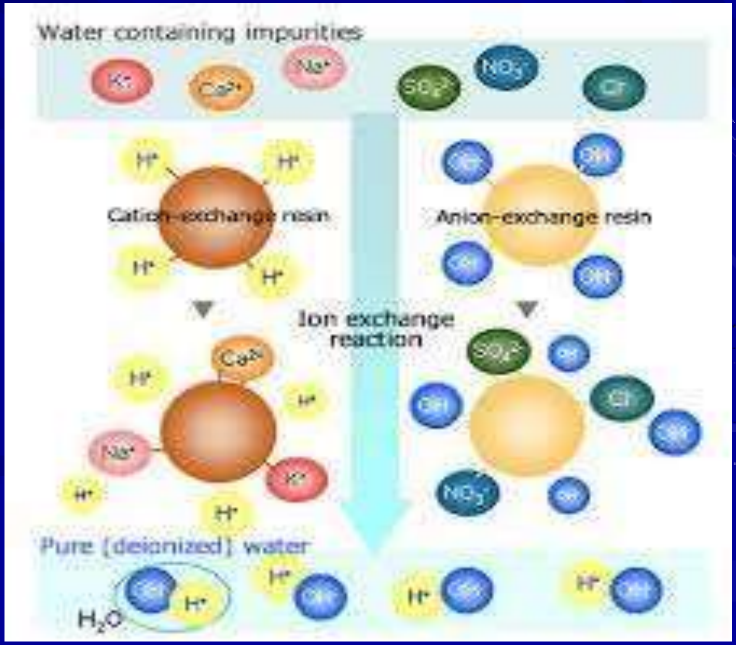
Zeolites are naturally occurring porous sands that are cation exchangers.

Ion exchange adsorption

Uses of ion exchange adsorption: ion exchange chromatography; production of high purity water; water softening.

Example of removal Na^+ and Cl^- ions from water:

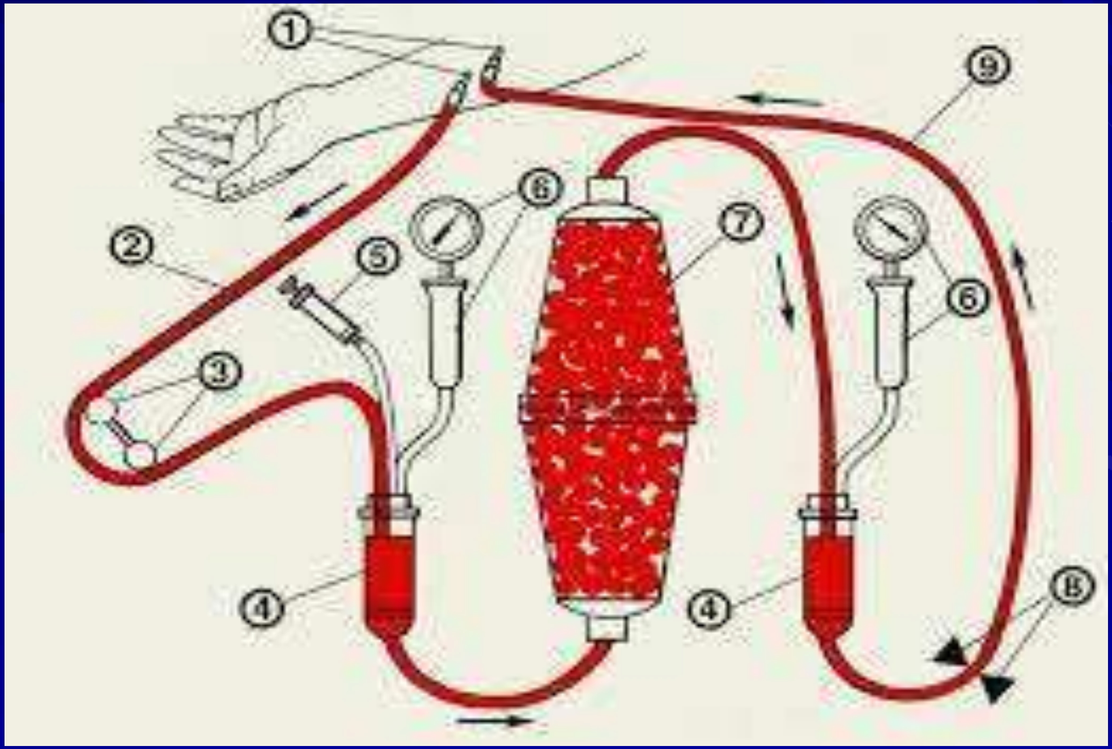
- $R_1{-}H + Na^+ \rightleftharpoons R_1Na + H^+$
- $R_2{-}OH + Cl^- \rightleftharpoons R_2Cl + OH^-$
- $2H^+ + OH^- \rightleftharpoons H_2O$



Adsorption therapy

Hemosorption

Removal of toxins from blood over adsorbents (e.g., activated charcoal) outside of the body.



Adsorption therapy

Enterosorption

Removal of toxins from the gastrointestinal tract over adsorbents.