

Synthesis of Nanomaterials

Chemical Methods

M.Sc. Biotechnology
Part II (Semester IV)
Paper I, Unit I
Mumbai University
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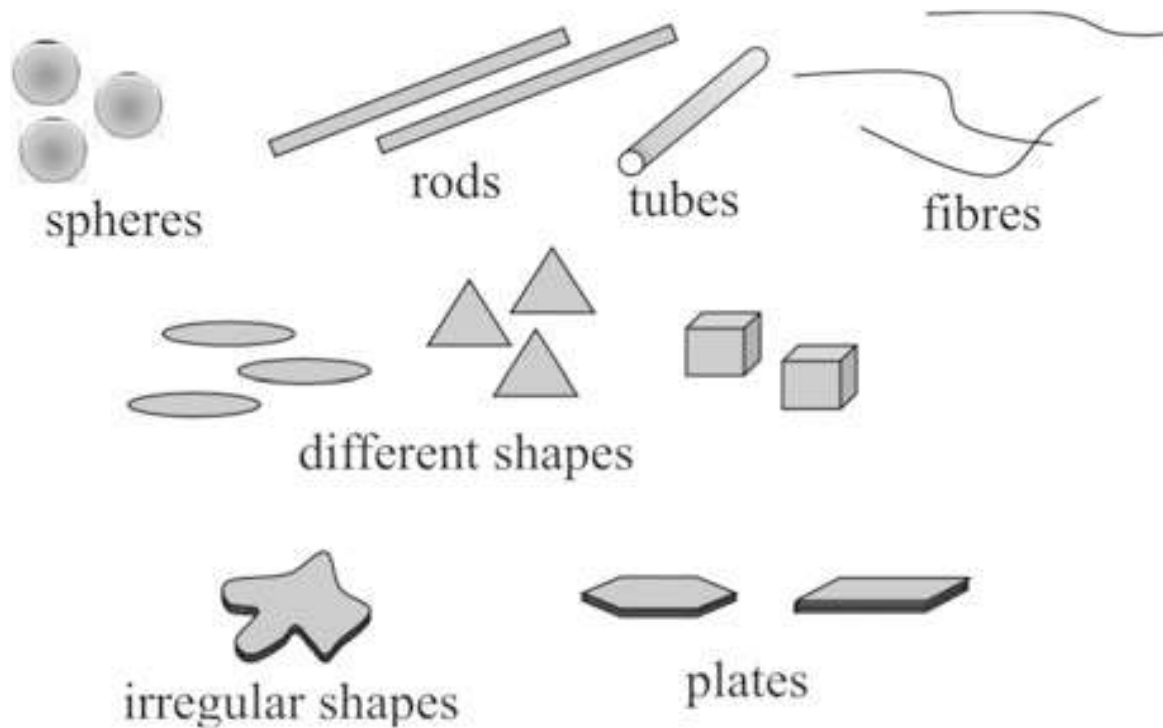
Advantages

- Simple and Inexpensive, less instrumentation compared to many physical methods
- Low temperature (<350°C) synthesis
- Doping of foreign atoms (Ions) is possible during synthesis by either coupling, coating, chemical capping.
- Large quantities of the materials can be obtained with a variety of sizes and shapes.
- Materials are obtained in the form of liquid but can be easily converted into dry powder or thin films
- Self assembly or patterning is possible

Colloids

- As in many cases nanoparticles synthesized by chemical methods form what is known as 'Colloids'
- A class of materials, in which two or more phases (solid, liquid or gas) of same or different materials co-exist with the dimensions of at least one of the phases less than a micrometre (μm) is known as colloids.

- Colloids may be particles, plates or fibres



- Nanomaterials are a subclass of colloids, in which one of the dimensions is in nanometre range.
- Examples of Colloids: liquid in gas (fog), liquid in liquid (fat droplets in milk), solid in liquid (tooth paste), solid in solid (tinted glass), gas in liquid (foam).

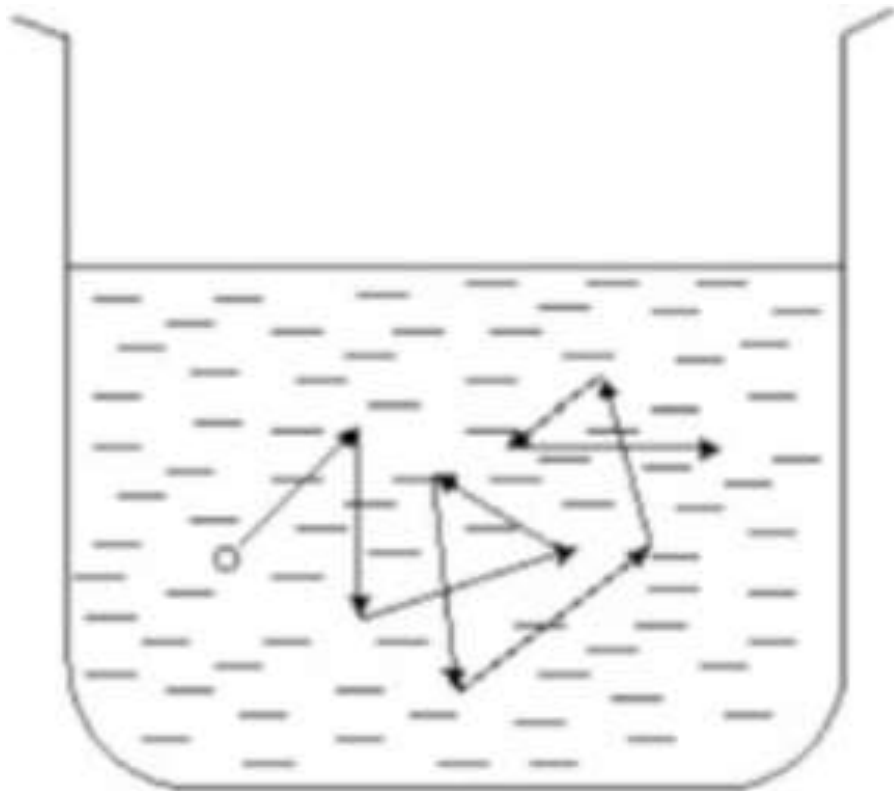
- Organic and inorganic materials can be dispersed into each other to form colloids.
- Several examples exist even of bio-colloids. Blood and bones are good examples of bio-colloids.
- Blood has corpuscles dispersed in serum and bone has colloids of calcium phosphate embedded in collagen.

- Colloids may even form networks. For example aerogels are a network of silica colloidal particles, pores of which are filled with air.

Interactions of Colloids and Medium

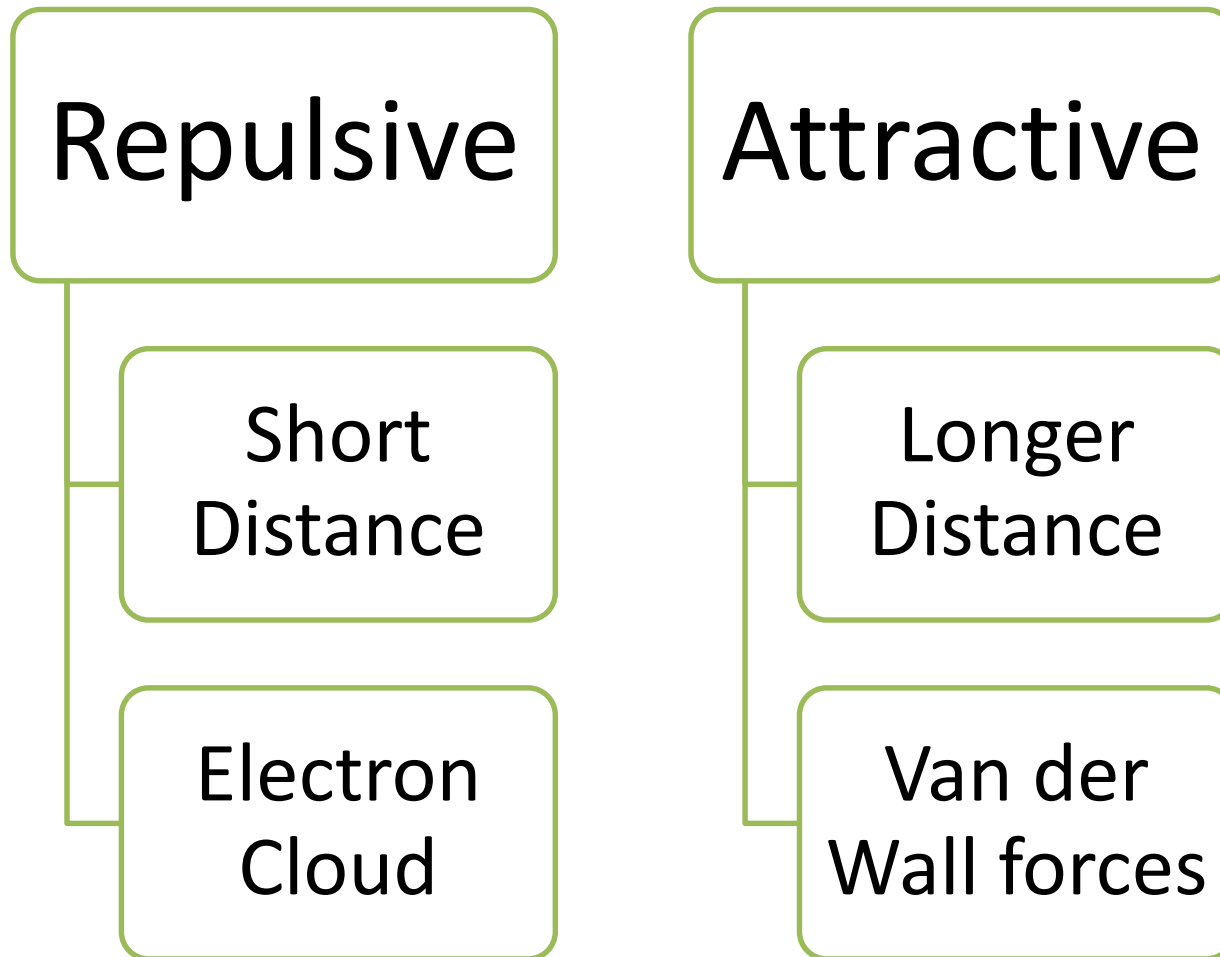
- Colloids are particles with large surface to volume ratio.
- Correspondingly there are large number of atoms/molecules on the surface of a colloidal particle, which do not have as many neighbours as those for an atom/molecule inside the interior.
- Therefore atoms on the surface are in a highly reactive state, which easily interact to form bigger particles or tend to coagulate.

- It is thus necessary to understand the stability of colloids i.e. how the colloids dispersed in a medium can remain as separated particles.
- We consider a case in which inorganic spherical colloids of equal size are dispersed in a liquid medium.
- When fine particles are dispersed in a liquid medium, it is known that they undergo *Brownian motion*.



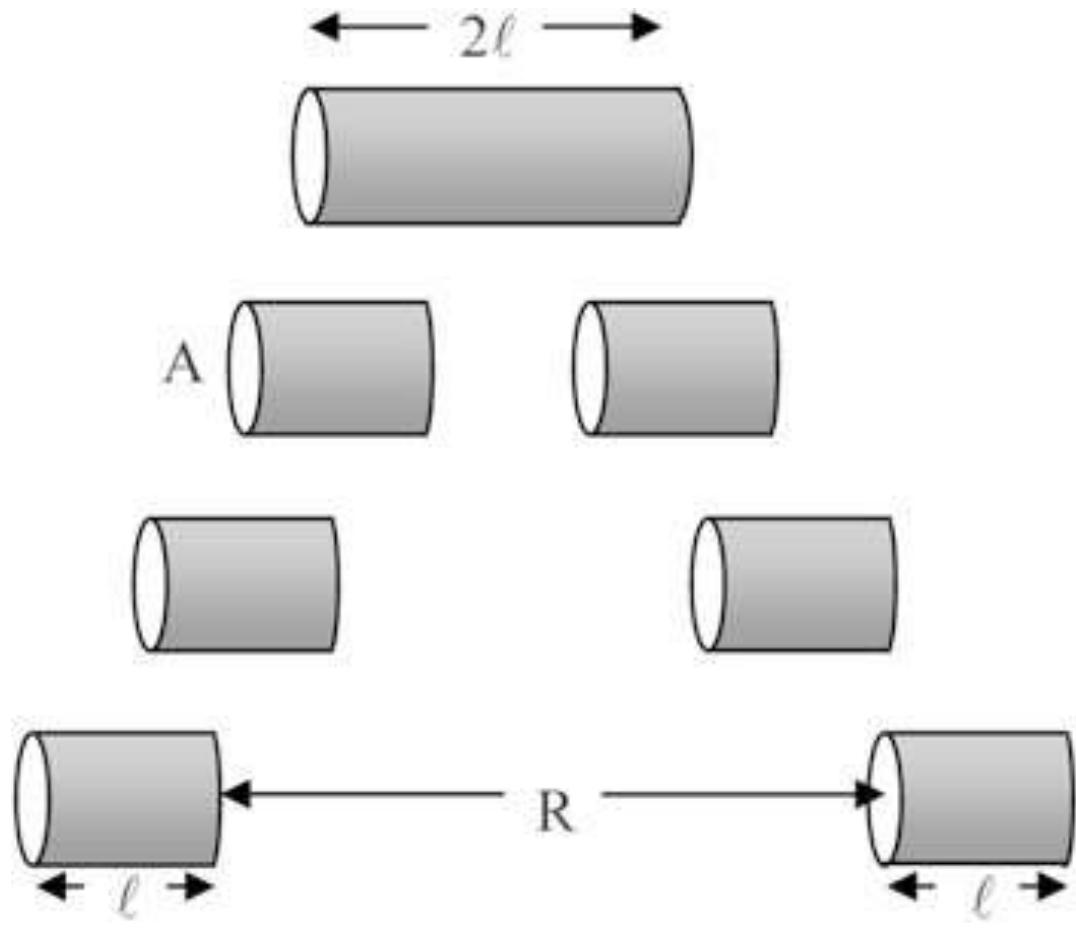
- If we are able to tag a particle in the solution, it would appear as if it is making a random motion.
- All other particles also execute random motion, hitting each other and changing direction of motion in solution.
- Distance travelled between successive collisions is random too.

Types of Interaction

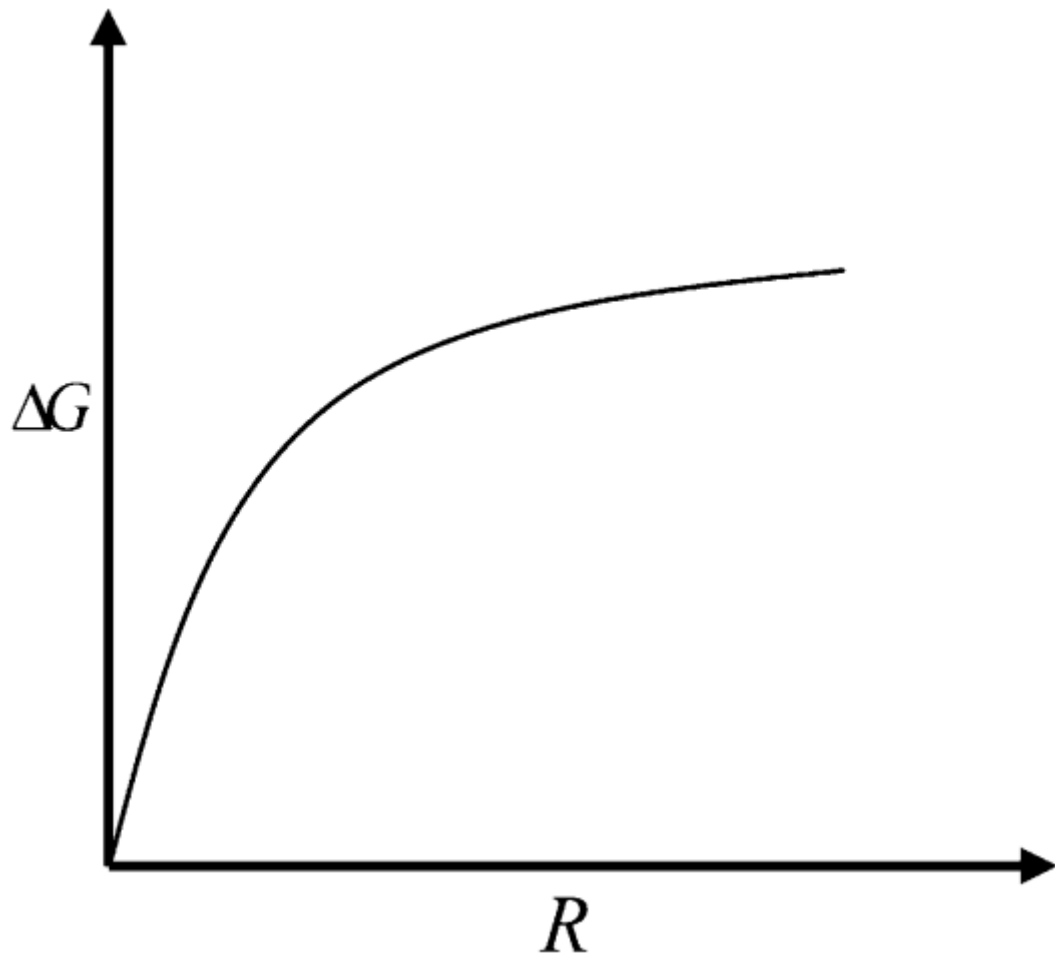


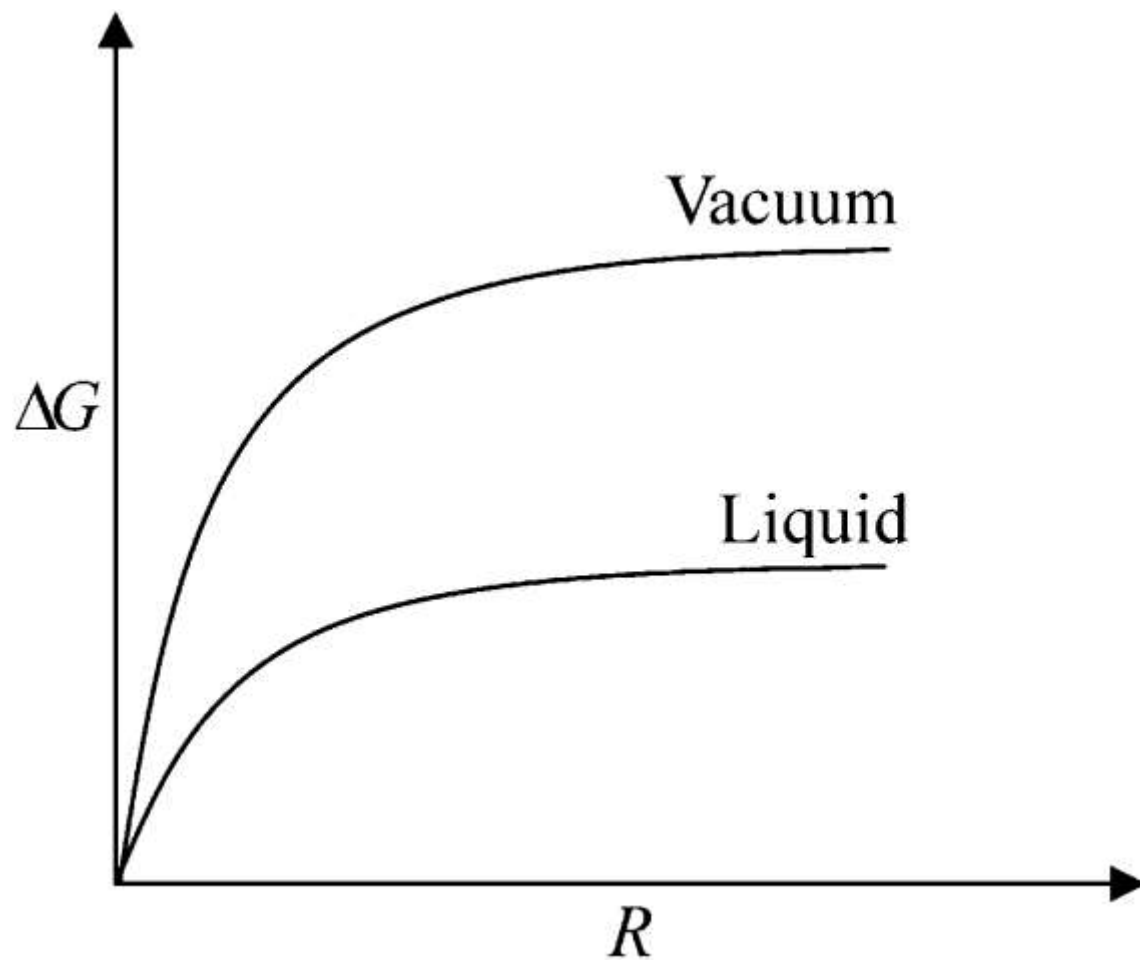
Concept of Free Energy

- Free energy of a body is a measure of its ability to do work.
- A body always tends to attain the state of lower energy by releasing 'free energy'
- In order to understand the meaning of surface free energy, consider that a cylinder with cross section 'A' and length '2l' is cut into two equal pieces.
- Work has to be done in order to break the cylinder into two pieces and separate them by a distance R .



- Energy increases as the distance between the two pieces increases.
- The two pieces keep on attracting each other due to intermolecular forces at the broken interface. Therefore, more and more energy has to be supplied in order to separate them.



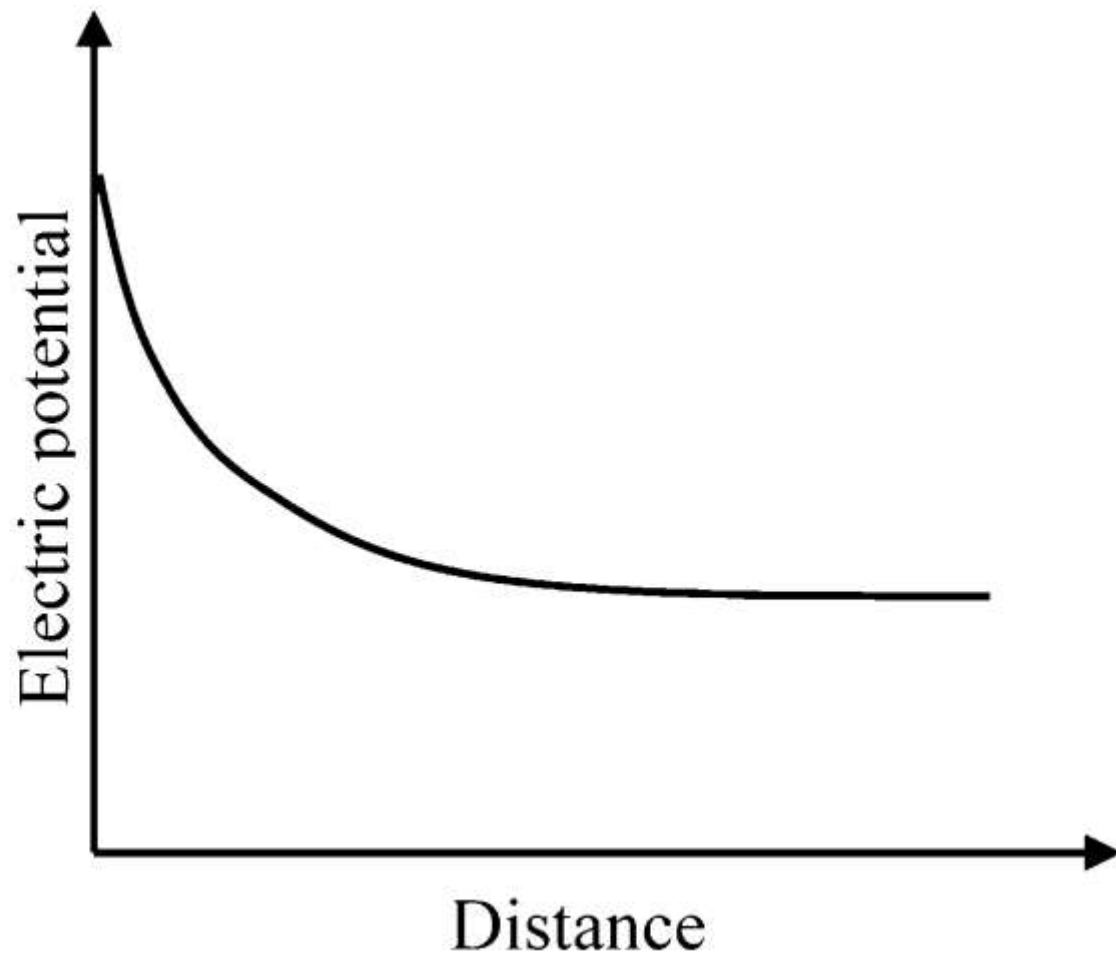
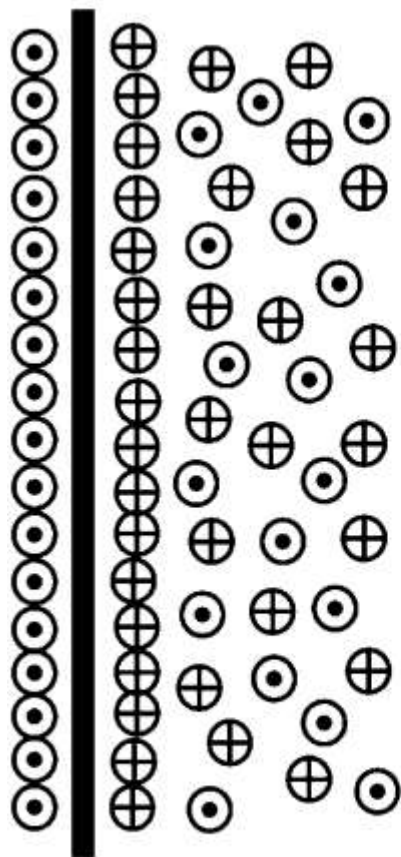


- The force of attraction would increase in vacuum but in a liquid medium the force of attraction would reduce in general.
- With the help of this experiment, we understand the interaction of colloidal particles with the medium.

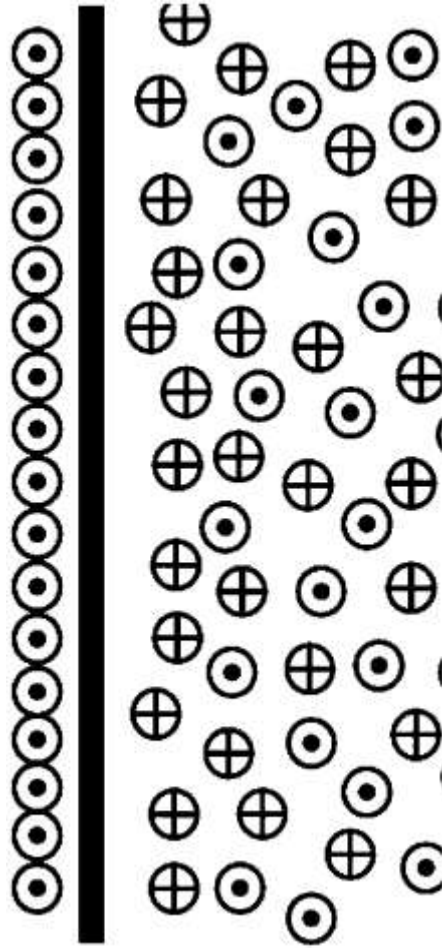
Effect of Charges on Colloids

- Colloids in liquid may be positively charged, negatively charged or even neutral. But in most of the cases they are charged.
- There are various sources for colloids by which they acquire charges on their surfaces viz. through composition of colloidal material, properties of dispersing medium including the type and concentration of dissolved ions in the solution.

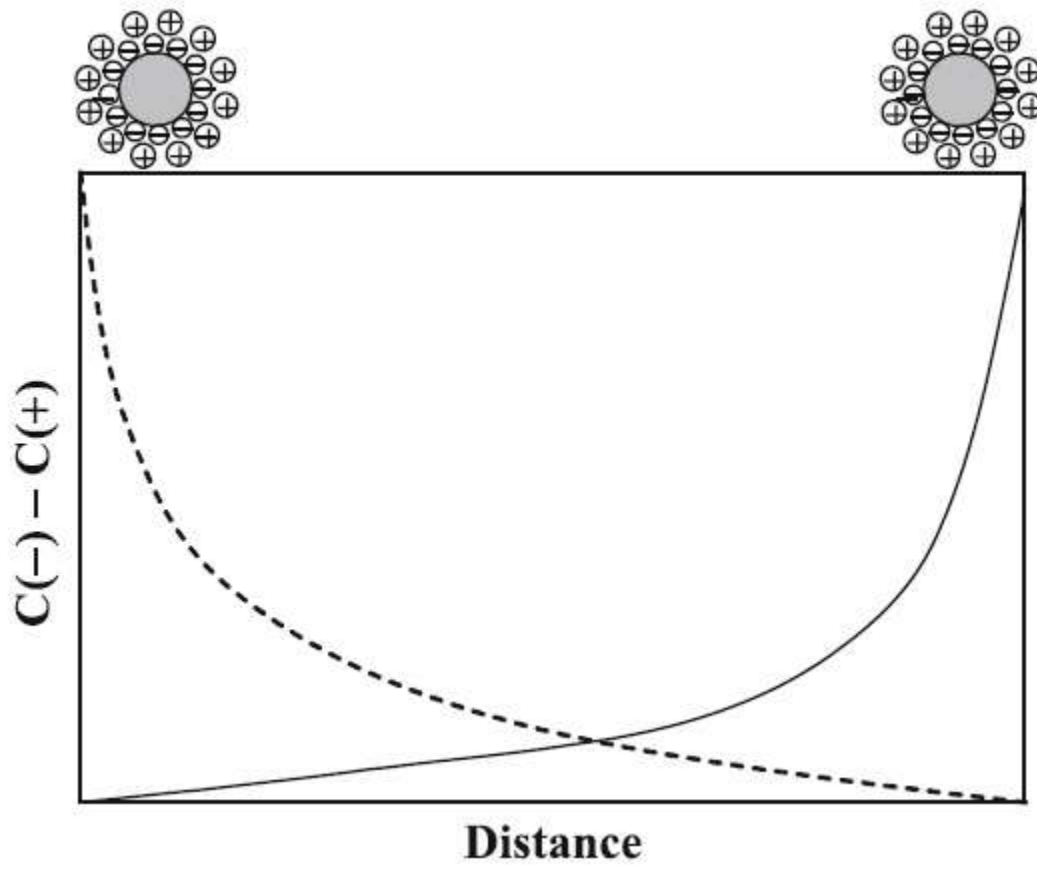
- In any case as soon as there are some charges on particles, ions of opposite charges accumulate around them.
- Oppositely charged ions are known as *Counter ions*. This accumulation of counter ions leads to formation of an Electric double layer.



- Helmholtz considered that the situation is like that in a parallel plate condenser, where there are opposite charges separated through a medium.
- Due to their Brownian motion, counter ions are not fixed nor are colloidal particles at rest. They execute their own Brownian motion and form a dynamic double layer around them

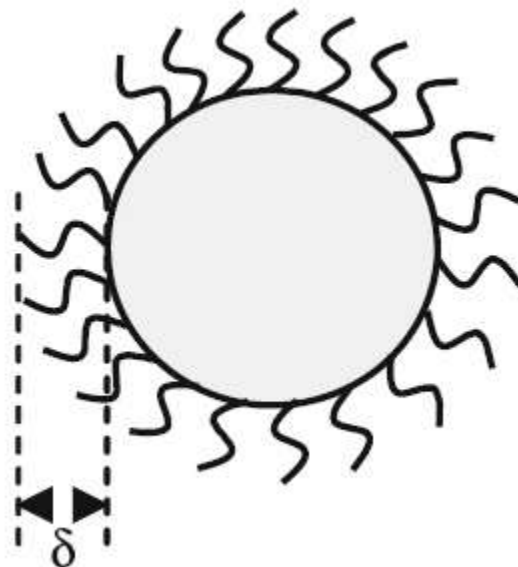
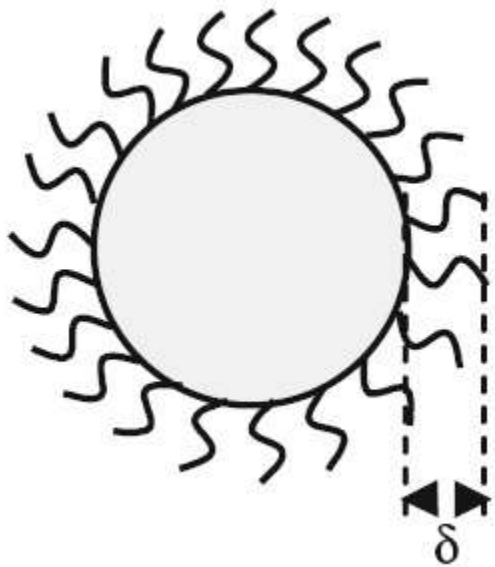


- Consider now a situation in which two charged colloidal particles come closer with their electric double charge layers.
- As they approach each other, force of repulsion increases. It is easy to see that the difference in concentrations of double layer charges would play an important role.



Stearic Repulsion

- Stability of colloids can be increased by creating Stearic hindrance or repulsion.
- By adsorbing some layers of a different material on colloidal particles e.g. polymer or organic molecules on inorganic colloidal particles, it is possible to reduce the attractive forces between them.



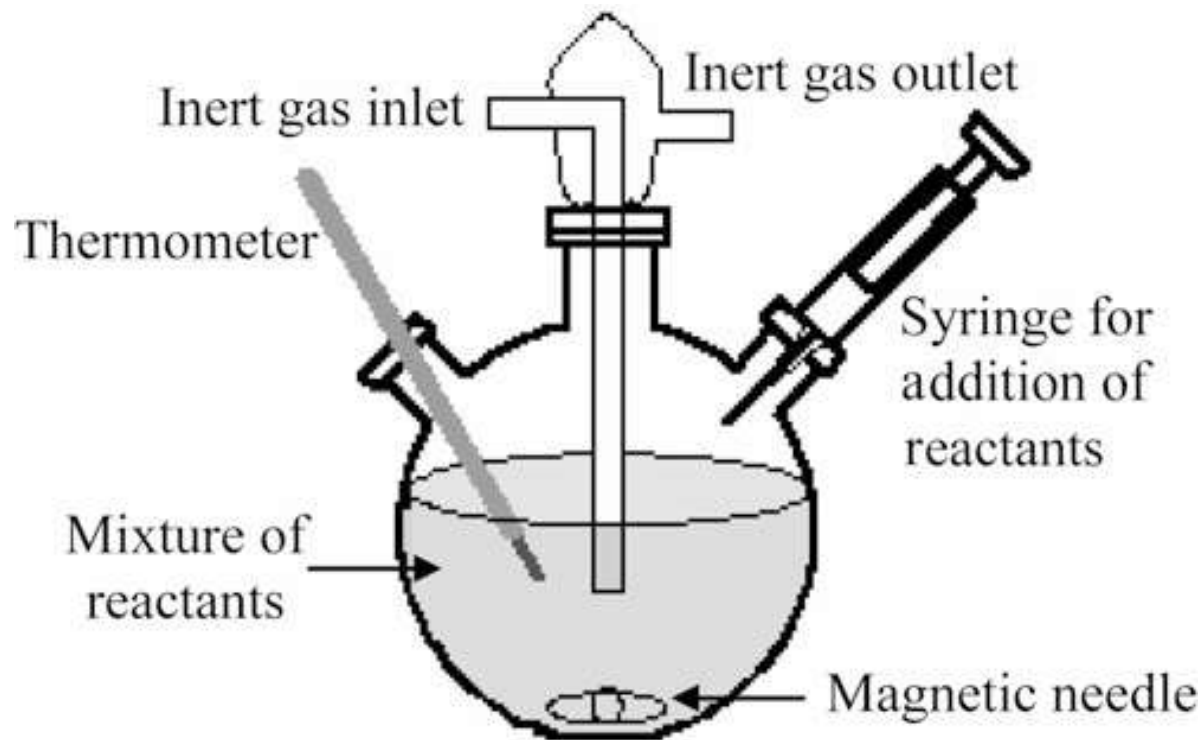
- Addition of adsorbants would change the sizes of the particles which helps them to stay at a longer distance from each other, reducing the attractive interaction.
- If the coating material is similar in properties to that of the solvent, the effect of coating would be negligible.

- Thus colloids interact with each other dynamically and are affected by van der Waals forces, colloid-colloid interaction mediated through dispersing medium, electric double layer and Steraic interactions.
- If the repulsive forces are strong enough, colloids would be stabilized. Otherwise ripening, coagulation, or network formation may take place.

1. Synthesis of Colloids

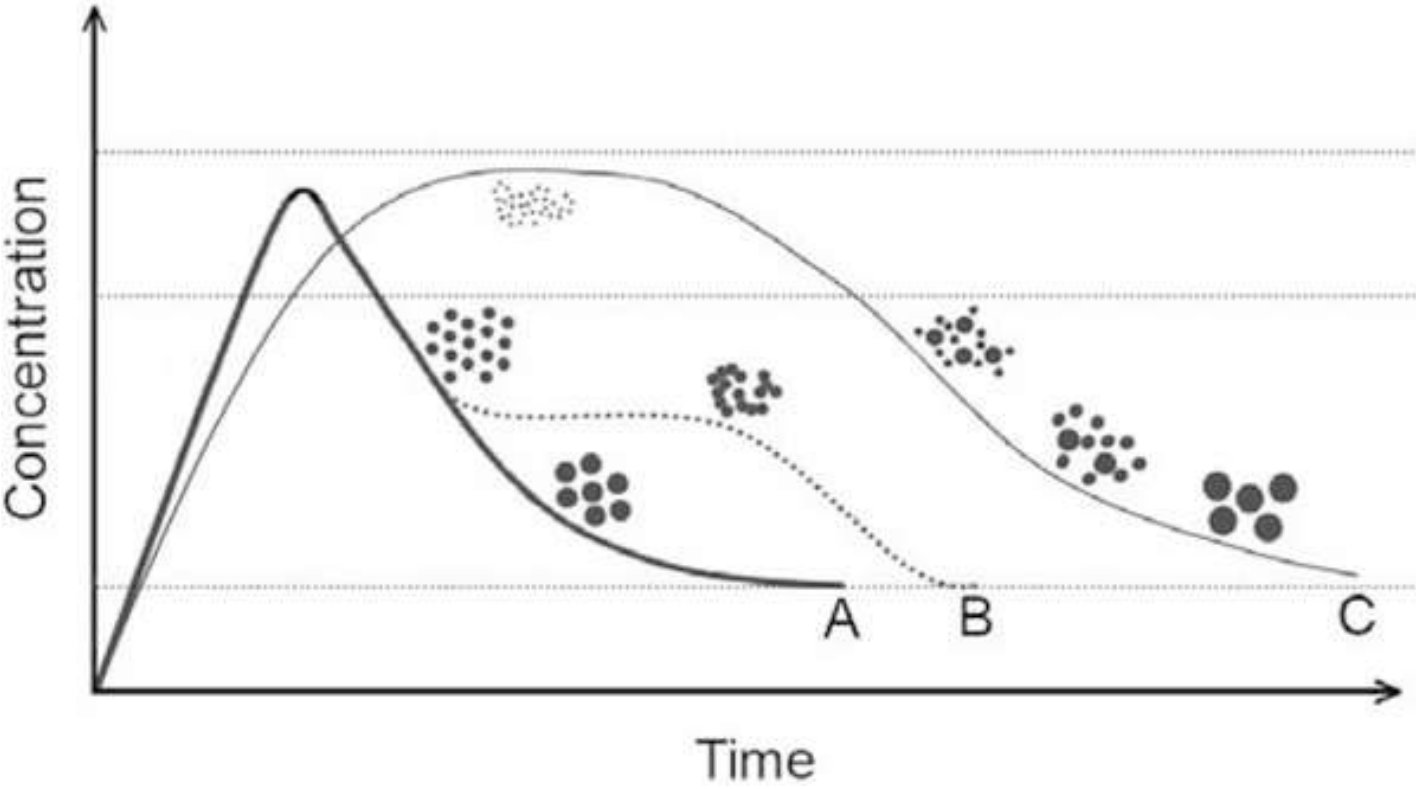
- Synthesis of colloids is a very old method.
- Making nanoparticles using colloidal route goes back to 19th century when M. Faraday synthesized gold nanoparticles by wet chemical route.
- The particles are so stable that even today the colloidal solution made by him can be seen in the British Museum in London.

- Chemical reactions in which colloidal particles are obtained are carried out in some glass reactor of suitable size.
- Glass reactor usually has a provision to introduce some precursors, gases as well as measure temperature and pH during the reaction. It is usually possible to remove the products at suitable time intervals.



- Reaction is usually carried out under inert atmosphere like argon or nitrogen gas so as to avoid any uncontrolled oxidation of the products.
- There is also a provision made to stir the reactants during the reaction by using teflon-coated magnetic needle.

Bottom-Up Process of Nucleation

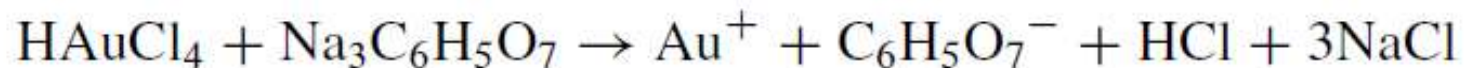


- A = Homogenous Nucleation. Fast nucleation takes place as the solute concentration approaches a super saturation stage.
- B = Heterogeneous Nucleation. Aggregates without uniformity
- C = Ostwald ripening process. Larger particles tend to grow at the expense of smaller ones thus becoming even larger.

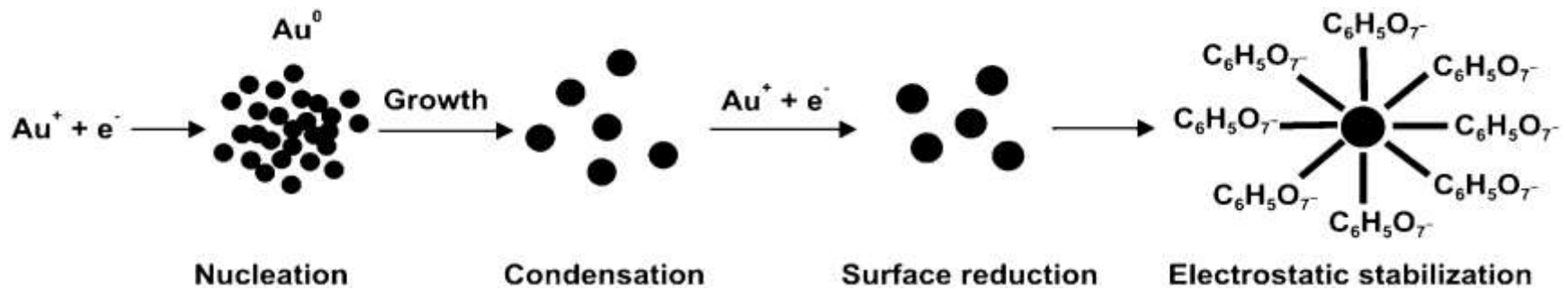
- Heterogeneous nucleation lowers the energy necessary for the nucleation of a particle.
- Consequently the critical size of the particles is smaller in heterogeneous nucleation than that for homogeneous nucleation.

2a. Synthesis of Metal Nanoparticles by Colloidal Route

- Colloidal metal nanoparticles are often synthesized by reduction of some metal salt or acid.
- Example: Highly stable Gold particles can be obtained by reducing Chloroauric acid Trisodium Citrate.



Stabilization by Electrochemical double layer formation



- Metal gold nanoparticles exhibit intense red, magenta and other colors, depending upon the particle size.
- Gold nanoparticles discussed above are stabilized by repulsive Coulombic interactions.
- It is also possible to stabilize gold nanoparticles using thiol or some other capping molecules.

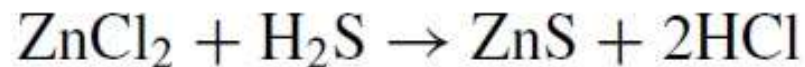
- In a similar manner, silver, palladium, copper and other metal nanoparticles can be synthesized using appropriate precursors, temperature, pH, duration of synthesis etc.

2b. Synthesis of Semiconductor Nanoparticles by Colloidal Route

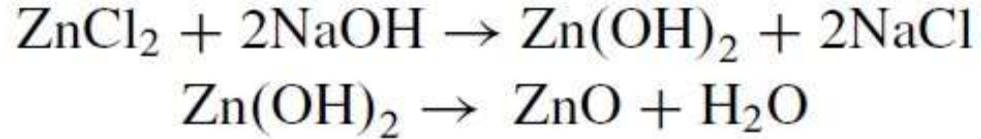
- Compound semiconductor nanoparticles can be synthesized by wet chemical route using appropriate salts.
- Sulphide semiconductors like CdS and ZnS can be synthesized as nano-particles simply by coprecipitation.

Examples

- To obtain ZnS nanoparticles any zinc salt like zinc sulphate (ZnSO_4), zinc chloride (ZnCl_2), zinc nitrate (ZnNO_3) or zinc acetate ($\text{Zn}[\text{CH}_3\text{COO}]_2$) can be dissolved in aqueous medium and Na_2S is added to the solution. (One can even dissolve H_2S gas in the Zn salt solution).



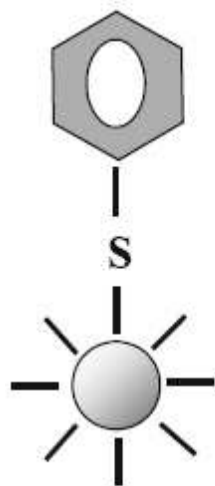
- To obtain zinc oxide particles, we can use NaOH.



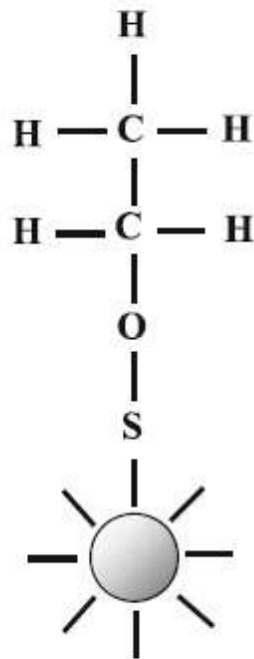
- Once we get our desired nanoparticles, they need to be surface passivated as colloids formed in liquids have a tendency to coagulate or ripen due to attractive forces existing between them.
- This is often known as ‘Chemical capping’.
- Advantage with this chemical route is that, one can get stable particles of variety of materials not only in the solution, but even after drying off the liquid.

- The coating, however, has to be stable and noninteractive with the particle itself except at the surface.
- Chemical capping can be carried out at high or low temperature depending on the reactants.
- In high temperature reactions, cold organometallic reactants are injected in some solvent like trioctylphosphineoxide (TOPO) held at a temperature of 300–400 °C.

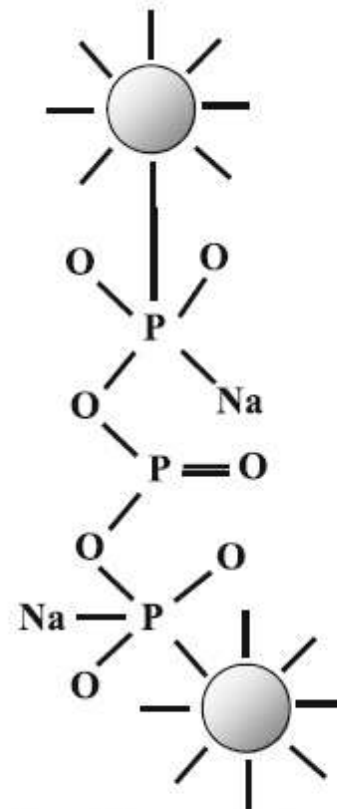
- For example when dimethyl cadmium [$\text{Cd}(\text{CH}_3)_2$] and Se powder were injected in TOPO, CdSe nanoparticles capped with PO_4 groups were obtained.
- Although, this is a very good route of synthesizing the nanoparticles, most of the organo-metallic compounds are prohibitively expensive.
- Besides they are also toxic and difficult to handle.



Thiophenol
(C_6H_5SH)



Mercaptoethanol
(C_2H_5OSH)



Sodium Hexametaphosphate
($NaPO_3$)₆

Size Selective Precipitation

- In order to selectively obtain nanoparticles with uniform sizes, one needs to use a proper pair of solvent-nonsolvent liquids.
- Some of the solvent-nonsolvent pairs are pyridine-hexane, chloroform-methanol or dimethyl sulphoxide-diethyl ether.

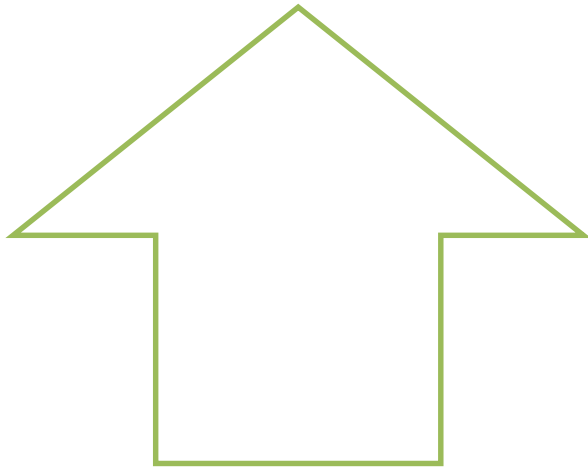
- The nanoparticles are dispersed in a solvent so as to get an optically clear solution.
- Nonsolvent solution is then added so that flocculation occurs.
- Supernatant and flocculate are separated by centrifugation.

- Precipitate has larger particles and can be separated. Bigger particles, therefore, are first separated from smaller particles and again dispersed in the solvent solution.
- The process is continued until no change in the size distribution is observed by repeating the procedure.

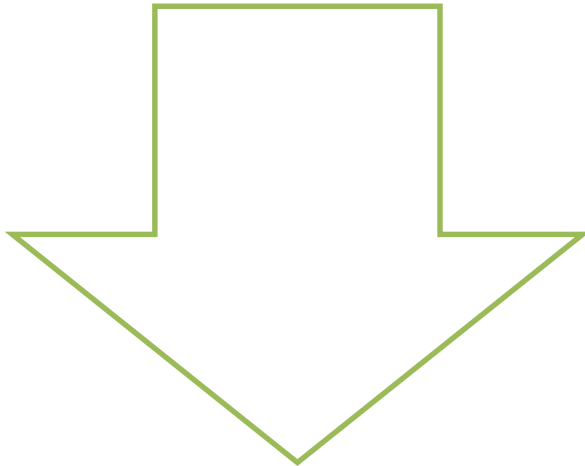
Langmuir-Blodgett (LB) Method

- This technique to transfer organic overlayers at air-liquid interface onto solid substrates is known for nearly 70 years.
- The technique was developed by two scientists Langmuir and Blodgett.
- In this technique, one uses amphiphilic long chain molecules like that in fatty acids.

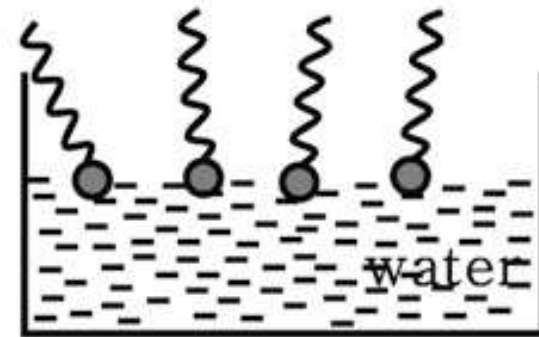
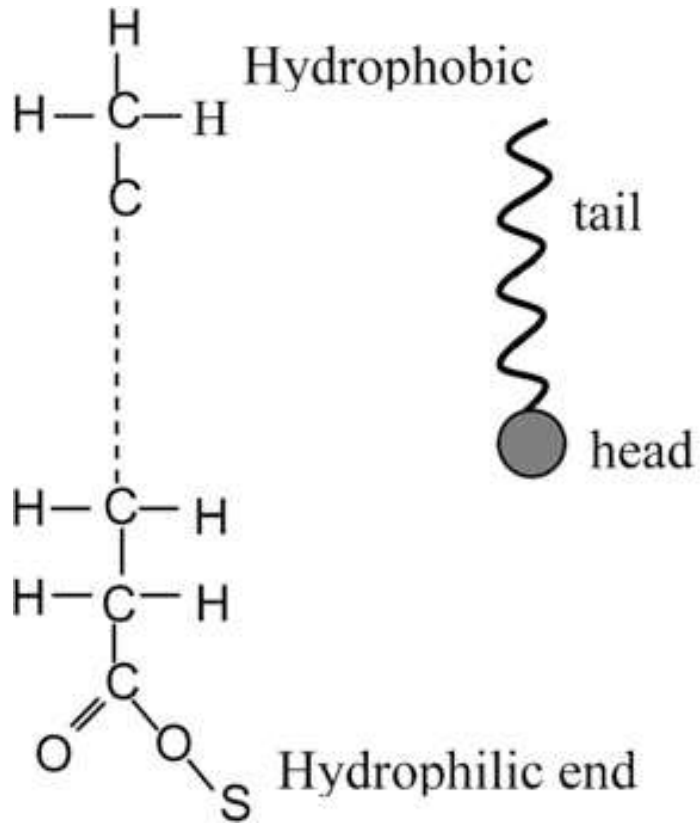
Amphiphilic Structure



**Hydrophobic
group**

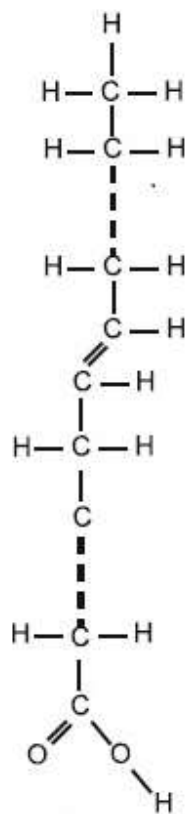


**Hydrophilic
group**

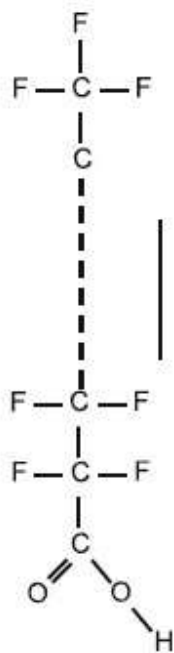


- For Example, consider the molecule of arachidic acid, which has a chemical formula $[\text{CH}_3(\text{CH}_2)_{16}\text{COOH}]$.
- There are many such long organic chains with
- general chemical formula $[\text{CH}_3(\text{CH}_2)_n\text{COOH}]$ where n is a positive integer.
- In this case $-\text{CH}_3$ is hydrophobic and $-\text{COOH}$ is hydrophilic in nature.
- Usually molecules with $n > 14$ are candidates to form L-B films

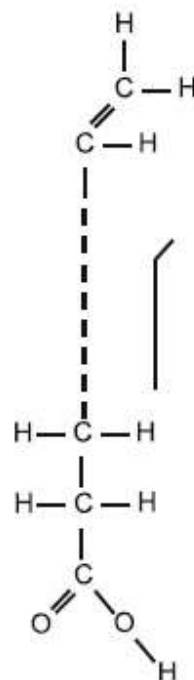
Modified hydrophobic tail



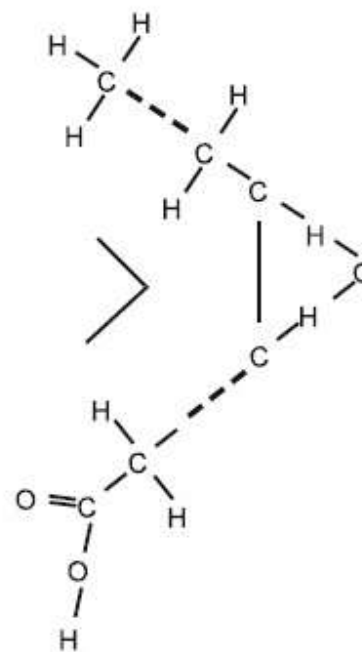
Elaidic acid
 $C_nH_{2n-1}COOH$



$C_nF_{2n+1}COOH$



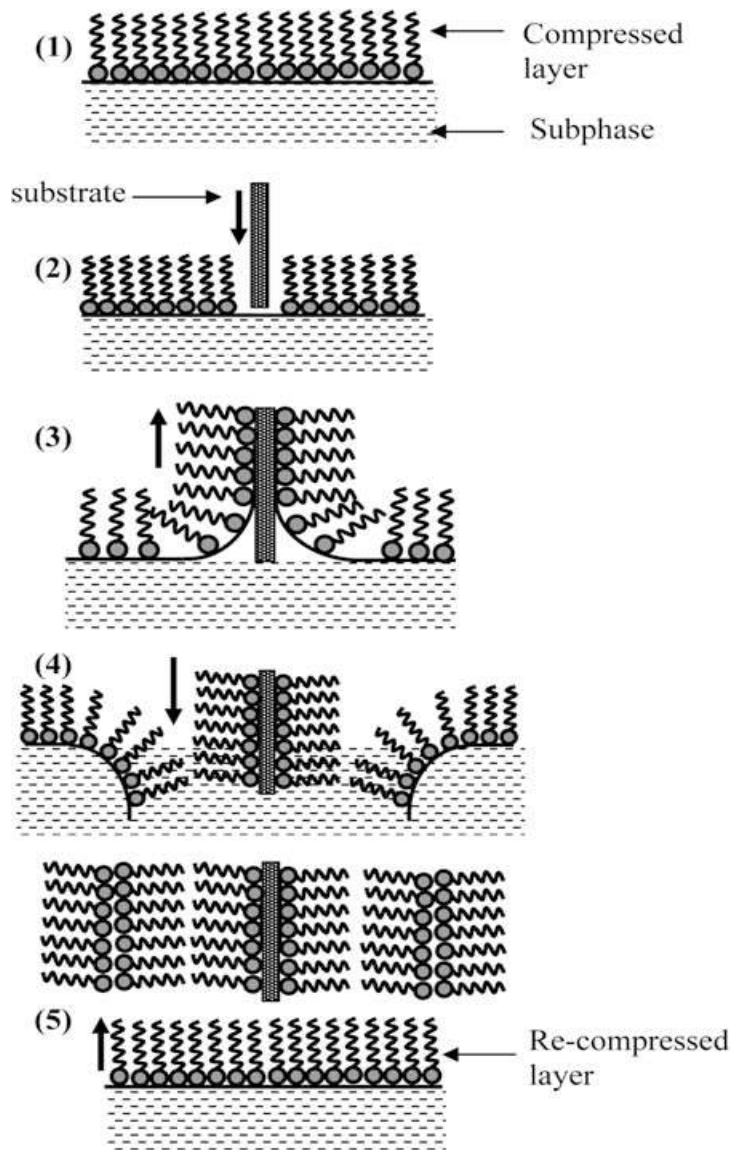
Omega-3 fatty acid



Oleic
epoxide

- When such molecules are put in water, the molecules spread themselves on surface of water in such a way that their hydrophilic ends, often called as 'heads' are immersed in water, whereas the hydrophobic ends called as 'tails' remain in air.
- They are also surface active agents or surfactants.

- Using a movable barrier, it is possible to compress these molecules to come closer together to form a 'monolayer' and align the tails.
- Such monolayers are two dimensionally ordered and can be transferred on some suitable solid substrates like glass, silicon etc.
- This is done simply by dipping the solid substrate inside the liquid in which ordered organic molecular monolayer is already formed.



- Depending upon the nature of substrate material i.e. whether hydrophobic or hydrophilic, layers are transferred on the solid substrates.
- A glass slide when dipped in the solution becomes wet with water. Therefore, while it is withdrawn from the liquid the head groups can be easily attached to glass surface.
- As a result the whole monolayer gets transferred in a manner as if a carpet is pulled.

- Now the glass substrate has tail groups, which are hydrophobic on outer side.
- Therefore as it is dipped in the liquid again, it acquires a second layer with tail – tail coming closer together and while it is pulled back to air, another monolayer of molecules with head-head groups coming together is pulled.

- The process of dipping and pulling the substrate can be repeated several times to obtain ordered multilayers of molecules. However to keep ordered layers available on water surface, it is necessary to keep constant pressure on the molecules.

Types of L-B Films

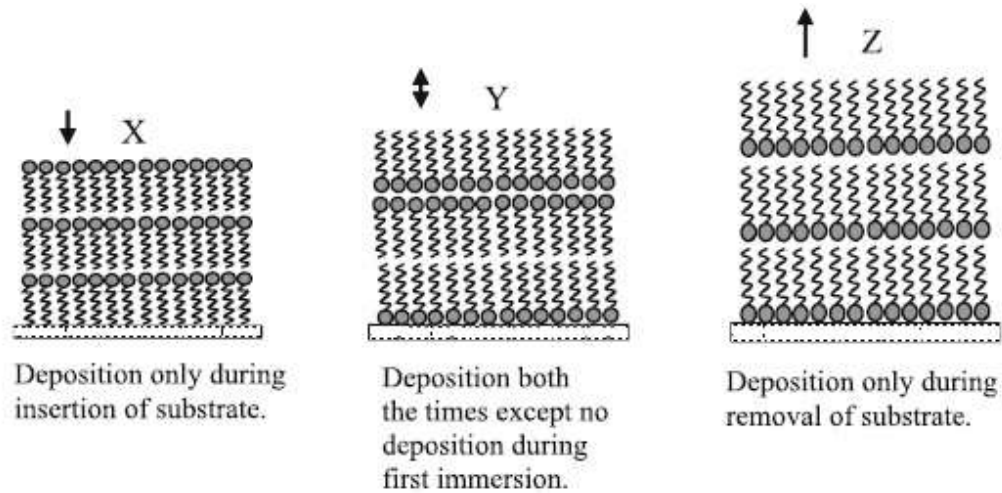


Fig. 4.22 X, Y and Z type L-B films

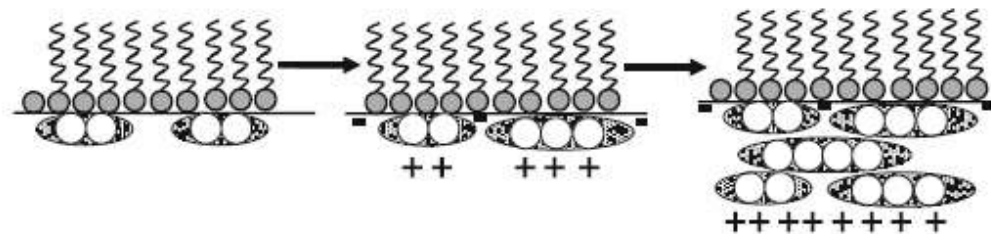


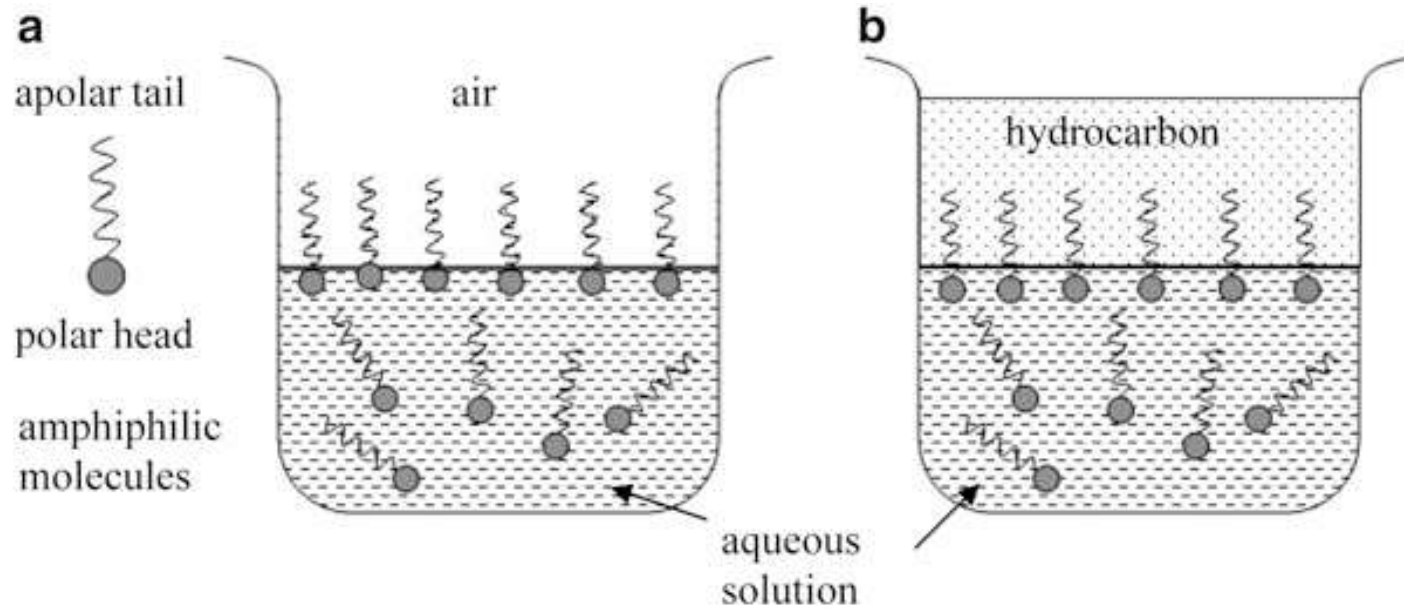
Fig. 4.23 Metal sulphide nanoparticles obtained under the monolayers at water-air interface. The time of hydrogen sulphide treatment increases from top to bottom

Microemulsions

- Whenever two immiscible liquids are mechanically agitated or stirred together, they are known to form an 'emulsion'.
- The tendency of the liquids is such that the liquid in smaller quantity tries to form small droplets, coagulated droplets or layers so that they are all separated from the rest of the liquid in large quantity (for example droplets of fat in milk).

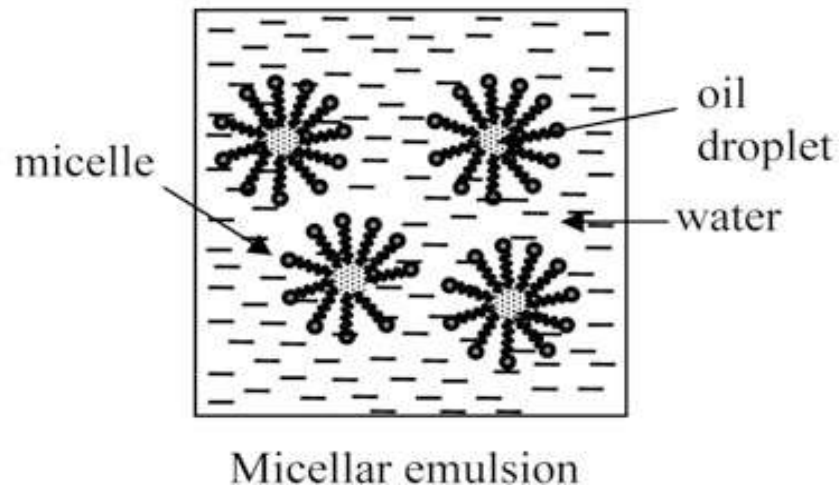
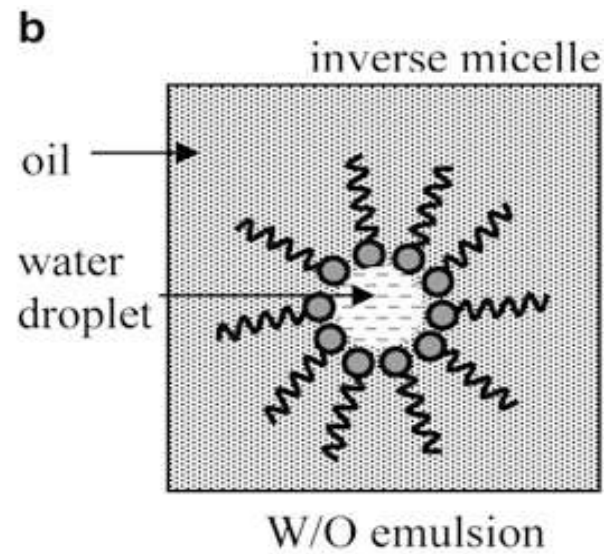
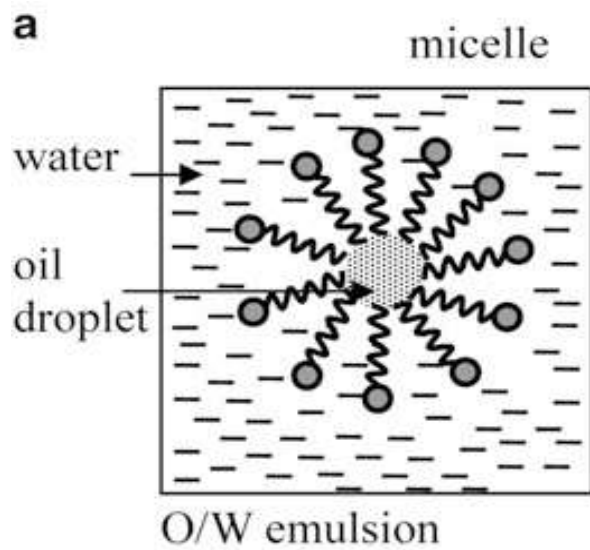
- The droplet sizes in emulsions are usually larger than 100 nm upto even few mm.
- Emulsions are usually turbid in appearance.
- On the other hand there is another class of immiscible liquids, known as **Microemulsions** which are transparent and the droplets are in the range of 1–100 nm.

- Advantage of this method is the biocompatibility and biodegradability of synthesized materials.
- Biocompatibility is useful in novel applications like drug delivery of nanomaterials and biodegradability is useful to avoid environmental pollution.

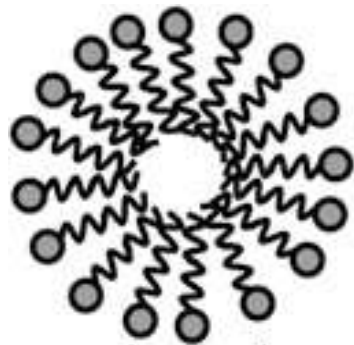


Micelles

- Microemulsions are stabilized using surfactants (surface stabilized active agents).
- When an organic liquid or oil (O), water (W) and surfactant (T) are mixed together, under some critical concentration, 'micelles' or 'inverse micelles' are formed, depending upon the concentrations of water and organic liquid.



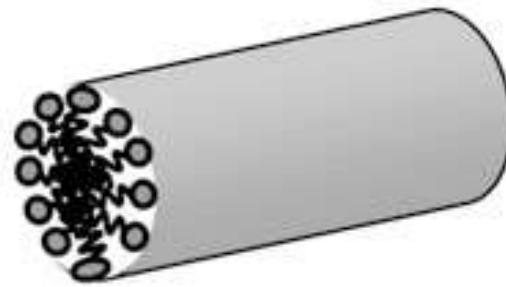
- Micelles are formed with excess water and inverse micelles are formed in excess of organic liquid or oil.
- They can be formed in various shapes as well.



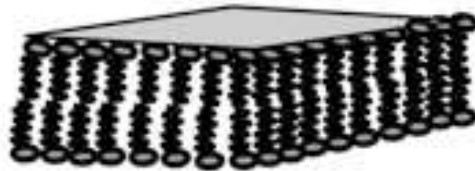
spherical



disc-like



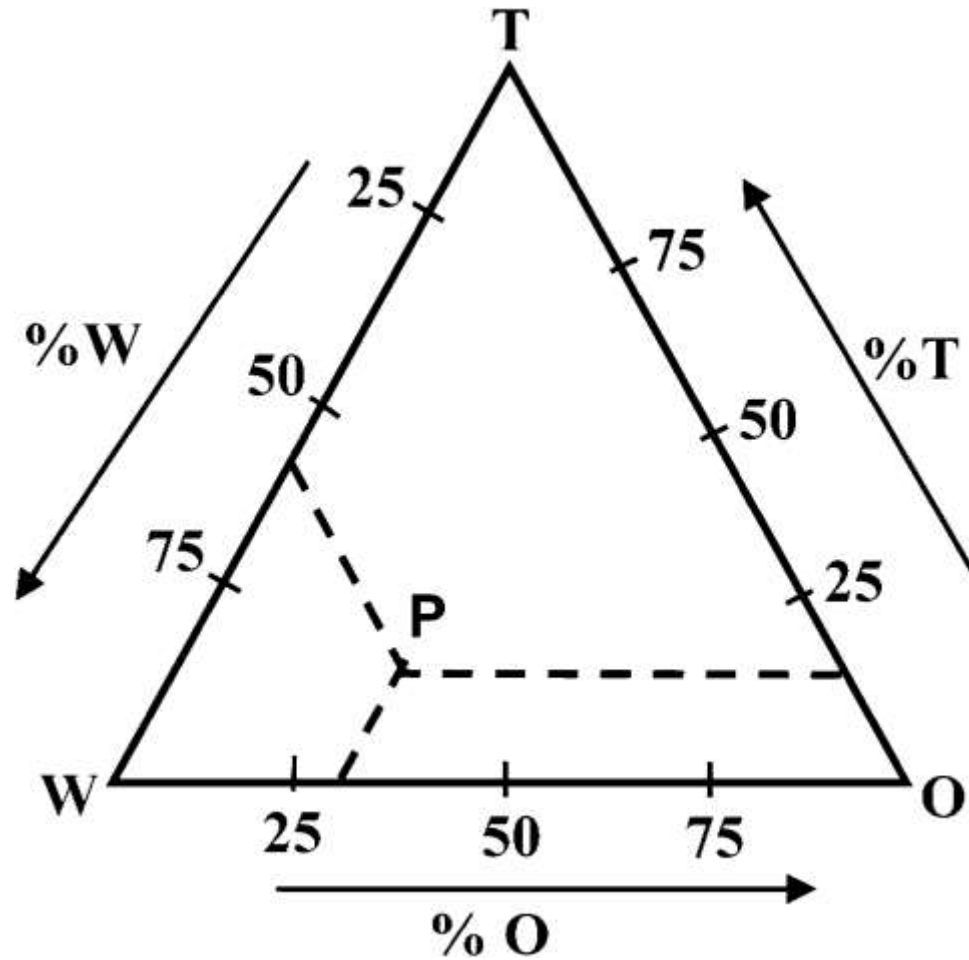
cylindrical



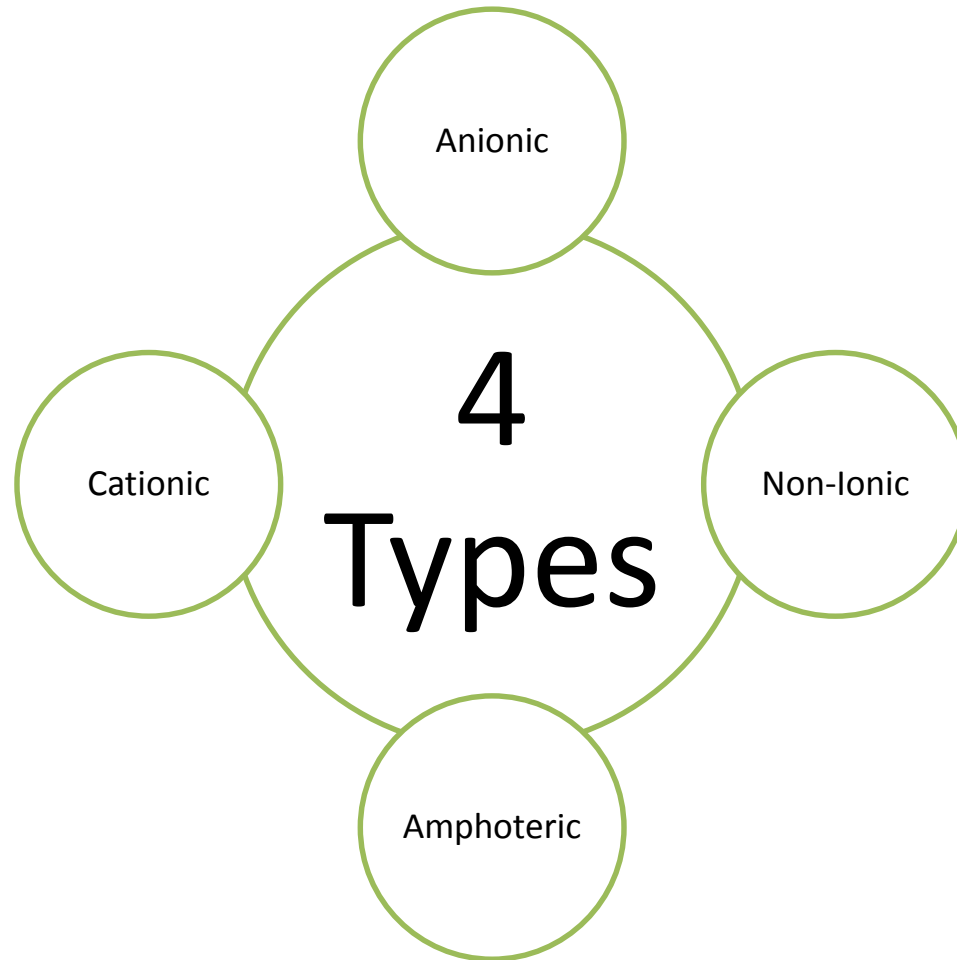
Lamellar

- The ratio of water (W), oil (O) and surfactant (T) is important to decide which type of micelle will be formed and can be represented in a ternary phase diagram
- Composition can be determined by drawing lines parallel to all three sides of the triangle

$P = 60\%$ water, 26% oil and 14% surfactant.



Types of Surfactants



- A large number of nanoparticles (metals, semiconductors and insulators) of cobalt, copper, CaCO_3 , BaSO_4 , CdS or ZnS have been synthesized using microemulsions or inverse micelles.
- Consider the synthesis of Co nanoparticles by using sodium bis (2-ethylhexyl)sulfosuccinate or $\text{Na}(\text{AOT})_2$ as a surfactant.

- A reverse micelle solution of water and oil can be stabilized using a monolayer of surfactant like Na(AOT)_2
- The droplet diameter is controlled simply by controlling the amount of water.
- Two micelle solutions having same diameter of droplets can be formed.

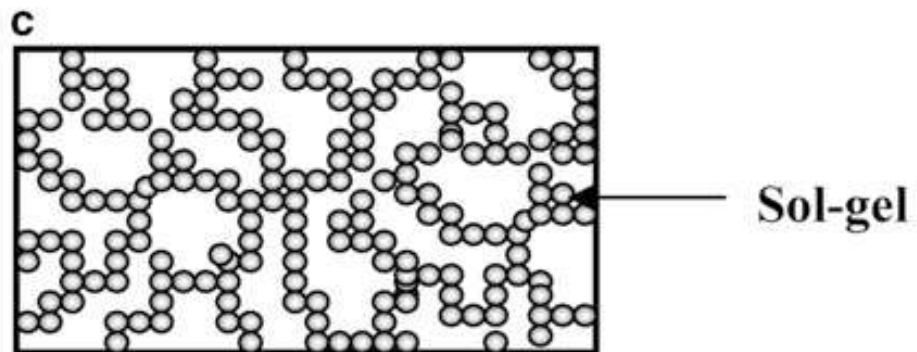
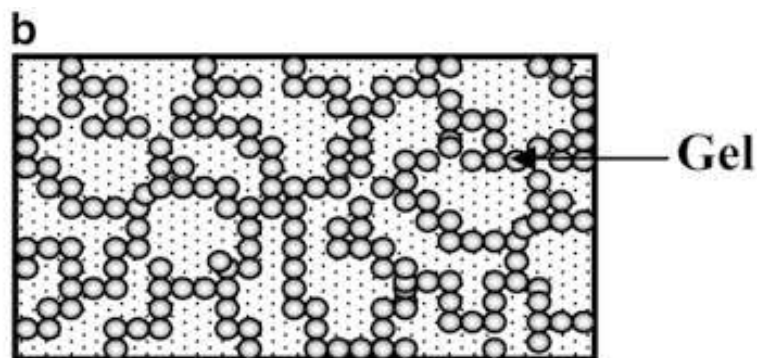
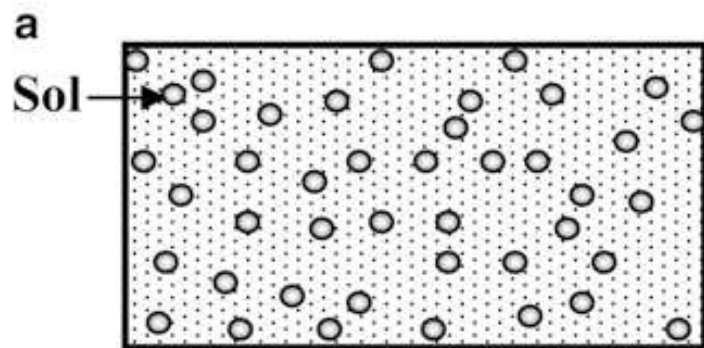
- Thus one solution should have $\text{Co}(\text{AOT})_2$ i.e. cobalt bis (2-ethylhexyl) sulfosuccinate and the other should have sodium tetrahydroborate (NaBH_4 i.e. sodium borohydride).
- When two solutions are mixed together the resultant solution appears clear but the color changes from pink to black.

- One can find by electron microscopy or some other analysis that cobalt nanoparticles are formed.

Sol – Gel Method

- Sol gels are known since the time when M. Ebelman synthesized them in 1845.
- As the name suggests sol gel involves two types of materials or components, 'sol' and 'gel'.
- Sols are solid particles in a liquid. They are thus a subclass of colloids.

- Gels are nothing but a continuous network of particles with pores filled with liquid (or polymers containing liquid).
- A sol gel process involves formation of 'sols' in a liquid and then connecting the sol particles to form a network.
- By evaporating the liquid, it is possible to obtain powders, thin films or even monolithic solid



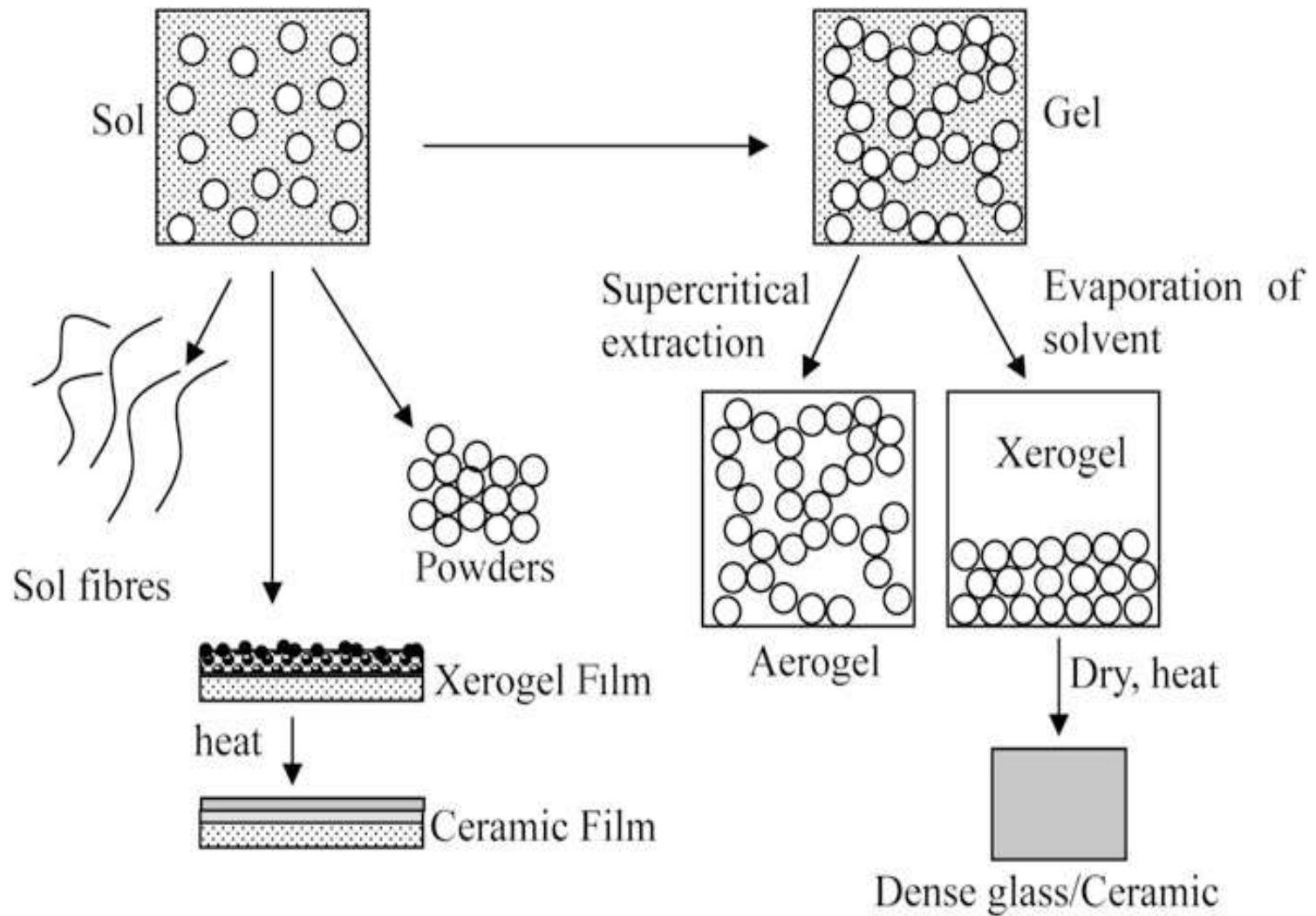
- Sol gel method is particularly useful to synthesize ceramics or metal oxides although sulphides, borides and nitrides also are possible.

Advantages

- Sol gel formation is usually a low temperature process. This means less energy consumption and less pollution too.
- It competes with other processes like CVD or metalloorganic vapours derived ceramics.
- It is also possible to synthesize nanoparticles, nanorods or nanotubes using sol-gel

Synthesis

- Synthesis of sol-gel in general involves hydrolysis of precursors, condensation followed by polycondensation to form particles, gelation and drying process.
- Precursors (starting chemicals) are to be chosen so that they have a tendency to form gels.
- Both Alkoxides or metal salts can be used.



- Alkoxides have a general formula $M(\text{ROH})_n$, where M is a cation and R is an alcohol group, n is the number of (ROH) groups with each cation.
- For example (ROH) can be methanol (CH_3OH), ethanol ($\text{C}_2\text{H}_5\text{OH}$), propanol ($\text{C}_3\text{H}_7\text{OH}$) etc. bonded to a cation like Al or Si .
- Salts are denoted as MX , in which M is a cation and X is an anion like in CdCl_2 , Cd is a cation and Cl is an anion.

- By polycondensation process (i.e. many hydrolyzed units coming together by removal of some atoms from small molecules like OH), sols are nucleated and ultimately sol-gel is formed.

Other Methods

- Hydrothermal Synthesis
- Sonochemical Synthesis
- Microwave Synthesis
- Synthesis Using Micro-reactor or Lab-On-Chip

Thank You