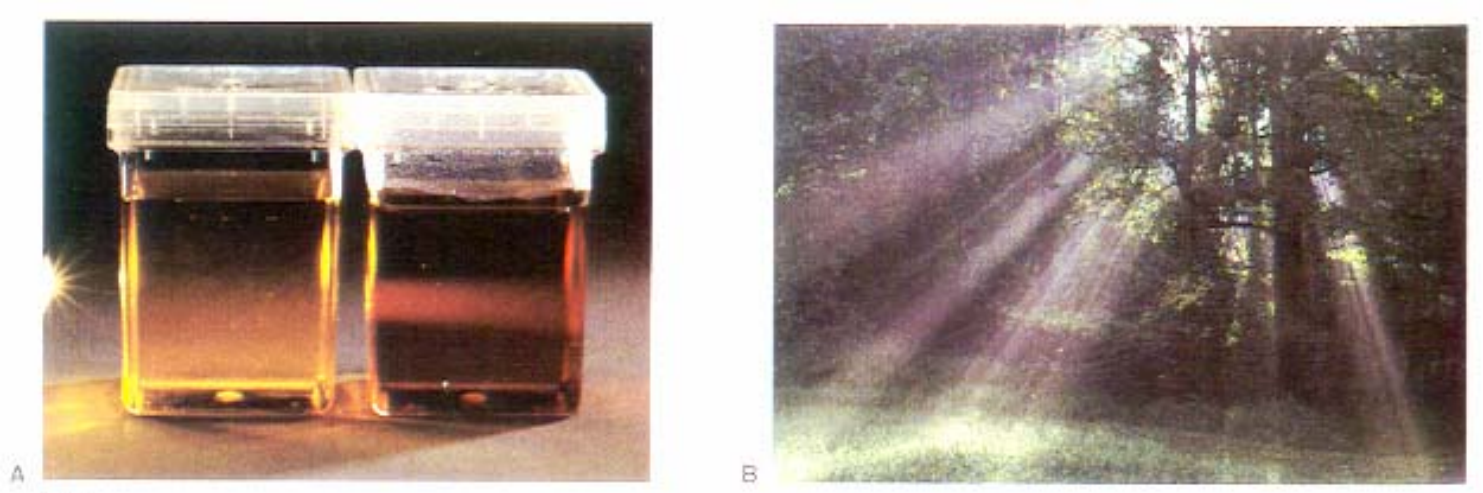
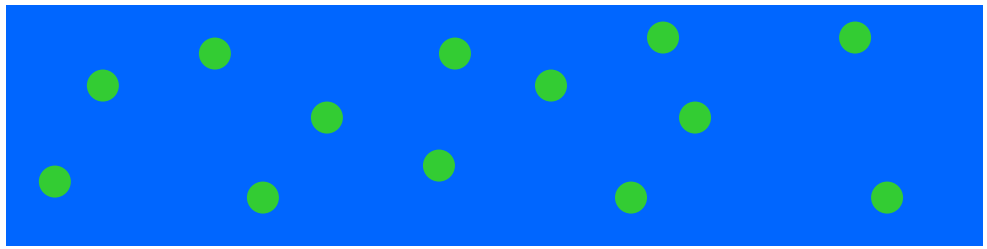
Colloids and Surface Chemistry



- **Simplest: tiny particles dispersed in water**



What is a colloid?

- **Finely-divided dispersion of one phase in another**
- **Size of dispersed (“solute-like”) entity >> ordinary molecules**
- **Example: blood cell in water.**

Solution

homogeneous particles are molecules

Suspension

heterogeneous particles settle out

Colloid

size 1–1000 nm

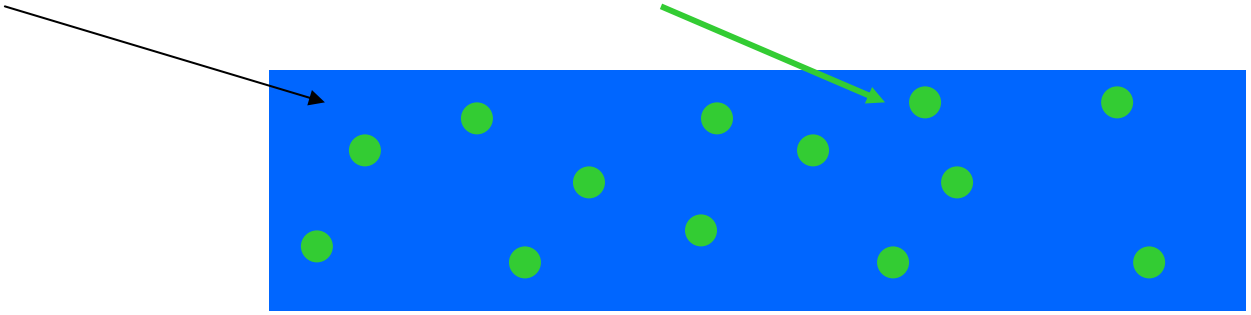
particles remain suspended

Examples

- **Continuous phase is often water.**
- **Wide range of sizes:**
  - **bovine serum albumin: 3 nm**
  - **cells: tens of microns**
- **Classify colloids as hydrophobic (e.g., carbon black) or hydrophilic (e.g., red blood cell).**
- **Stability of colloid: essential part of its function**
  - **whether or not it will coagulate**
- **E.g. blood cells:**
  - **normally colloidally stable, but**
  - **colloidally unstable when they clot**
- **Milk (oil in water emulsion) is on the edge of colloidal stability: it creams (some coalescence).**

Characteristics of colloids

- **Continuous phase and dispersed phase**



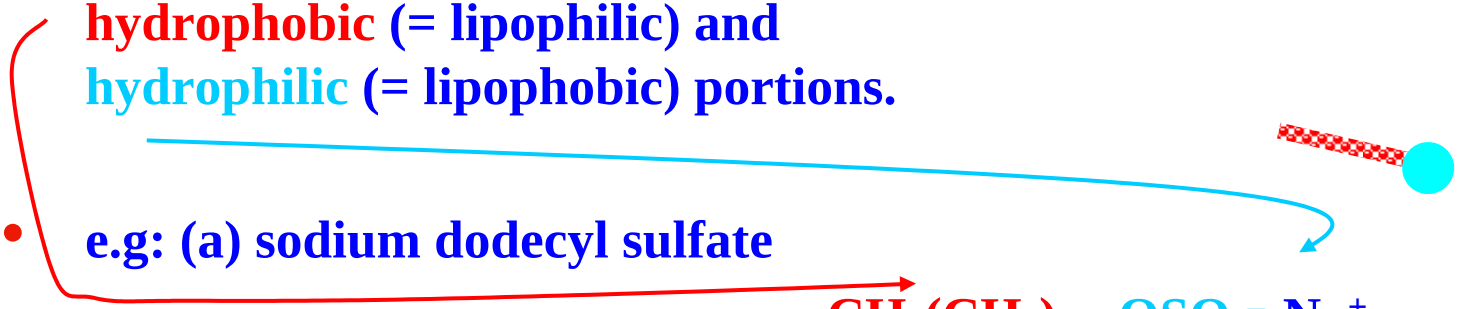
- **Thermodynamically unstable but kinetically stable (i.e. they are stable indefinitely)**
- **Classified in terms of dispersed substance (solid, liquid, gas) in dispersing medium (solid, liquid, gas)**
- **Dispersed phase 10–1000 nm particles:**
  - **Large surface area to volume ratio**
  - **Size appropriate for scattering light**
  - **May have charged surfaces**
- **The name: Greek *kolla* = glue, *eidos*= like**

More examples

continuous phase	dispersed phase	type	example
gas	liquid	aerosol	fog
gas	solid	aerosol	smoke
liquid	gas	foam	whipped cream
liquid	liquid	emulsion	milk
liquid	solid	sol	paint, blood, ink
solid	gas	solid foam	meringue
solid	liquid	solid emulsion	butter
solid	solid	solid sol	opal

Surfactants

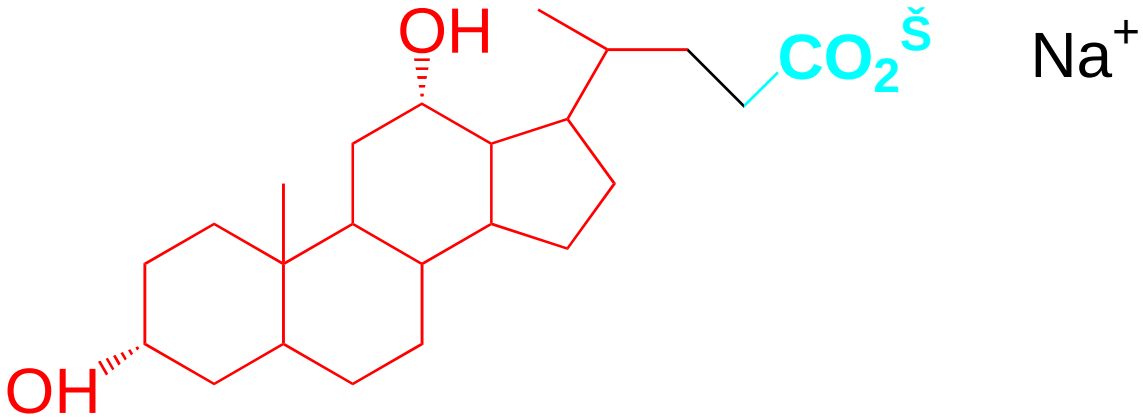
- **Important in colloid and surface chemistry and biology**
- **Surface-active agent: molecule with hydrophobic (= lipophilic) and hydrophilic (= lipophobic) portions.**



- **e.g: (a) sodium dodecyl sulfate**

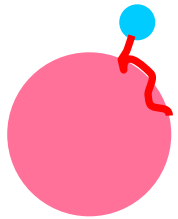
$CH_3(CH_2)_{11}–OSO_3^-\ Na^+$

(b)salts of bile acids – sodium deoxycholate



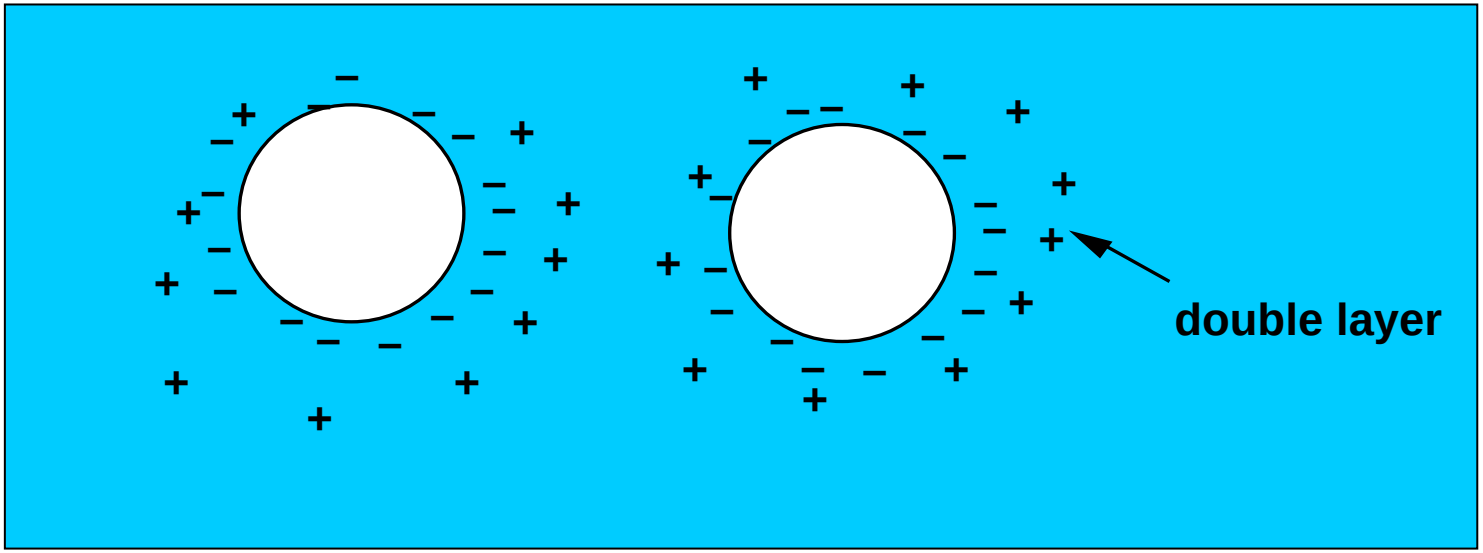
- **Can also be cationic, e.g. $C_{14}H_{29}NH_3^+\ Br^-$ (a common disinfectant)**

Ionic surfactants



- **Ionic surfactants: e.g. sodium dodecyl sulfate**
- **Adsorbs onto a (hydrophobic) colloid: hydrophobic part in/on (organic) colloid, hydrophilic part in water: thermodynamically advantageous.**
- **Colloidal stability through electrostatic repulsion**

Negative charge from adsorbed surfactant attracts opposite charge: double layer
Repulsion between double layers keeps particles apart (colloidal stability)



Micelles

- **Fatty acids: C_{12} = dodecyl, C_{18} = stearic**
- **Ions have long nonpolar tail and polar head**

•Soap solution:

individual fatty acid anions dispersed in water
can group: micelles
hydrophilic part in water, hydrophobic tails with other hydrophobic tails: thermodynamically advantageous

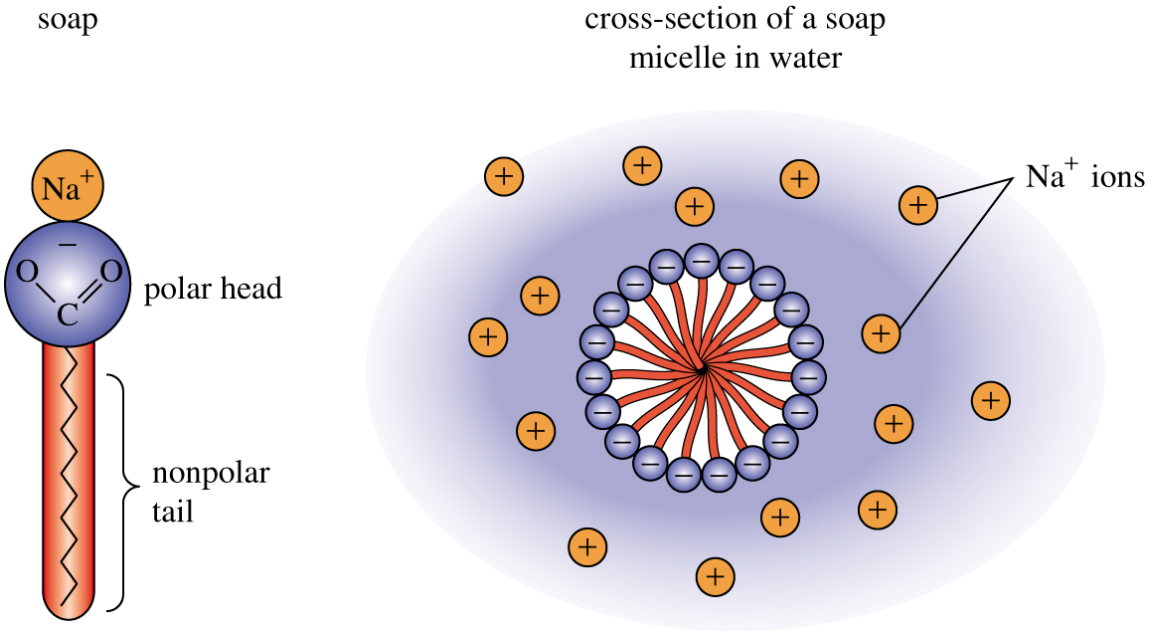


Figure 22.3 Blackman

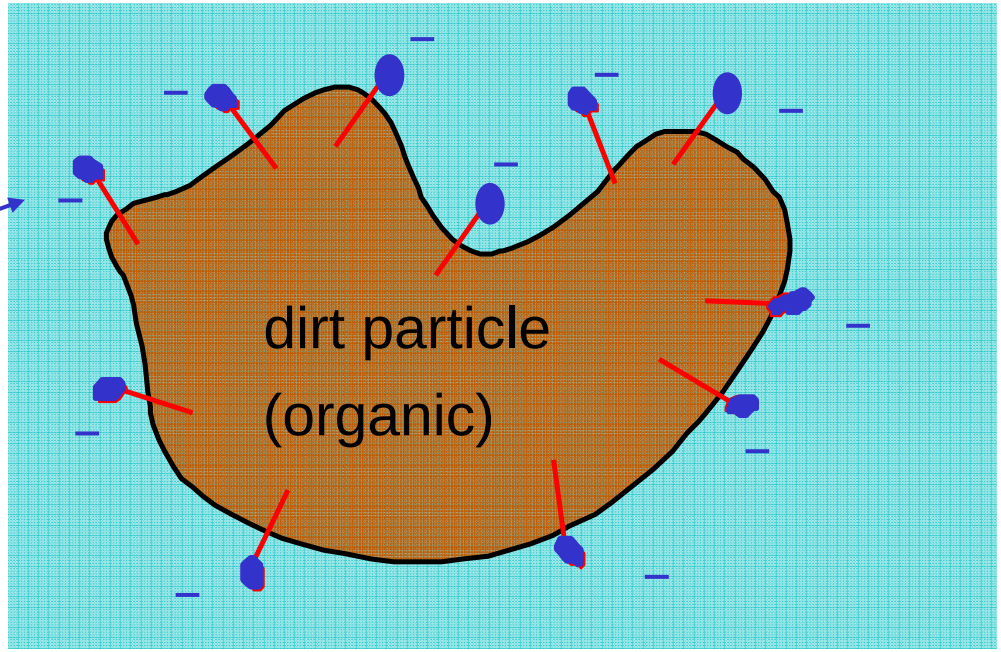
Micelles form above Critical Micelle Concentration (CMC)

- **Soap-water mixture: suspension of micelles in water.**
- **Relatively large micelles scatter light (colloidal) so soapy water looks cloudy**

Surfactants

- "Dirt" is non-polar. Grease = long chain hydrocarbons
- However water is very polar and will not dissolve 'greasy dirt'
- Soaps, detergents (e.g. sodium dodecyl sulfate): emulsifying agent
  - Suspend normally incompatible grease in water

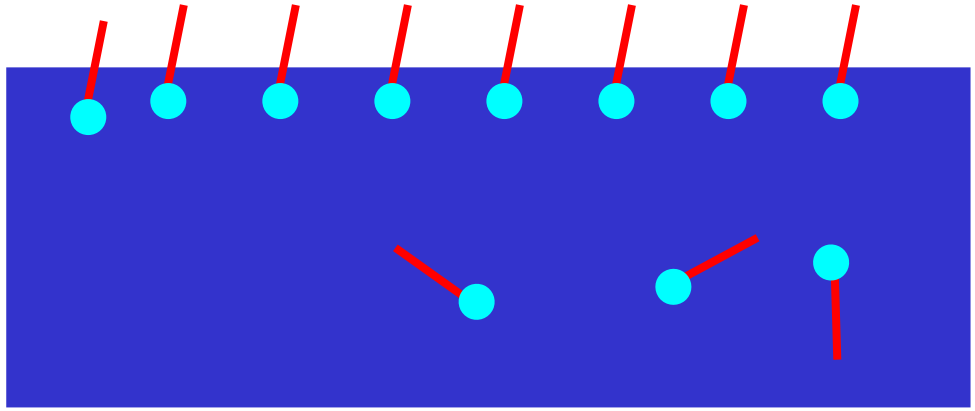
charges on outside from surfactant solubilise particle in water



- Hence called wetting agent or surfactant (= surface-active agent)

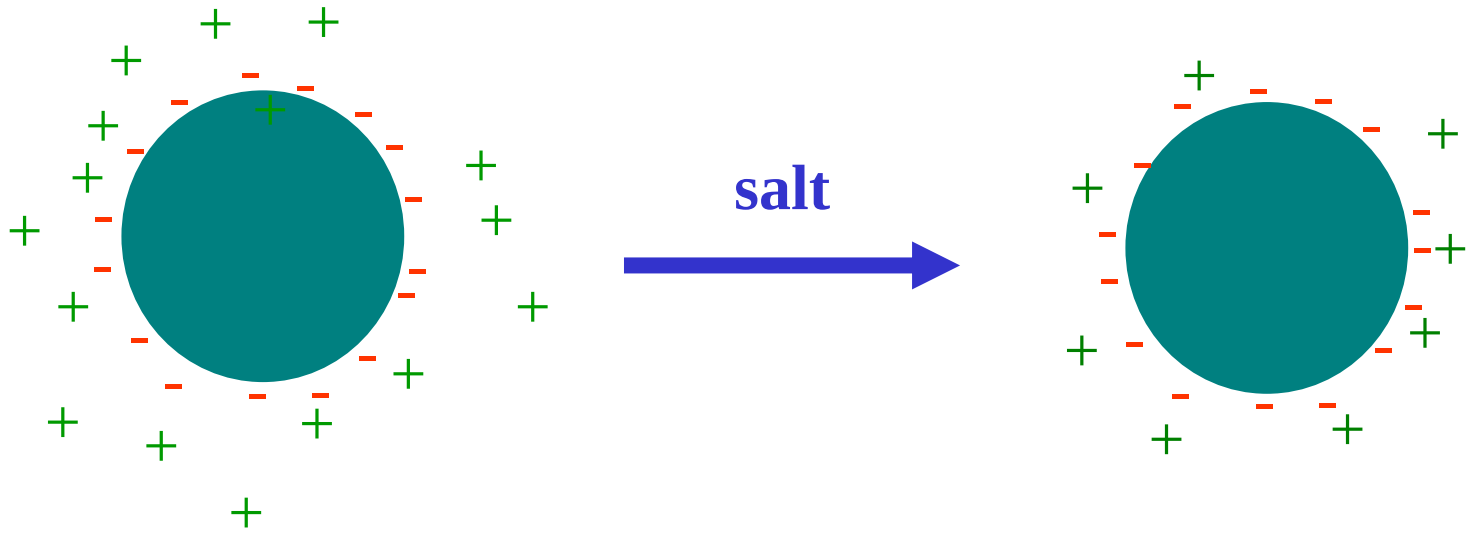
Surfactants at the interface

- **Surfactants have hydrophobic and hydrophilic parts**
- **Hence both parts “happy” in micelles**
  (“happy” = low free energy)
- **Hydrophobic part also makes them accumulate at air-water interface**
  (hydrophobic part is at least out of the water)



Ions and colloidal stability

- **Another effect of ions: they cause perturbation of double layer which gives electrostatically-stabilised colloids their stability**



- **Reduces electrostatic barrier**
- **Can cause coagulation**

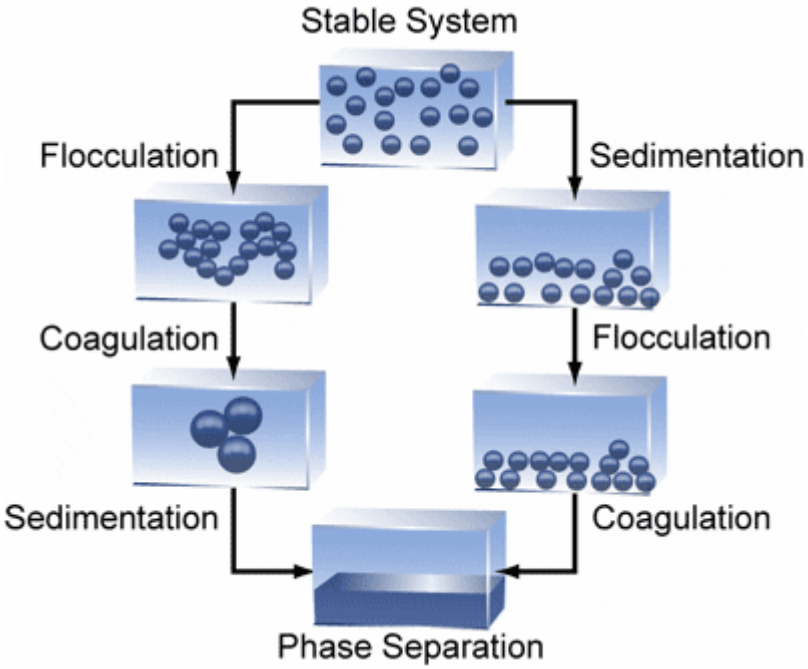
Stabilisation of colloids

- **A stable colloidal system is one in which the particles resist flocculation or aggregation and exhibits a long shelf-life.**

- **Depends upon the balance of the repulsive and attractive forces that exist between particles as they approach one another.**

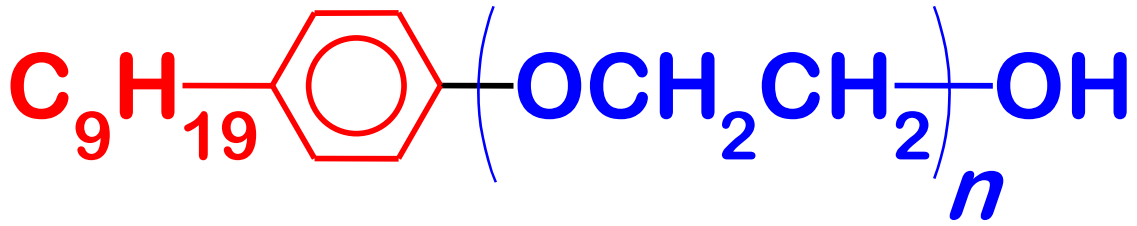
- **If all the particles have a mutual repulsion then the dispersion will remain stable.**

- **If the particles have little or no repulsive force then some instability mechanism will eventually take place e.g. flocculation, aggregation etc.**



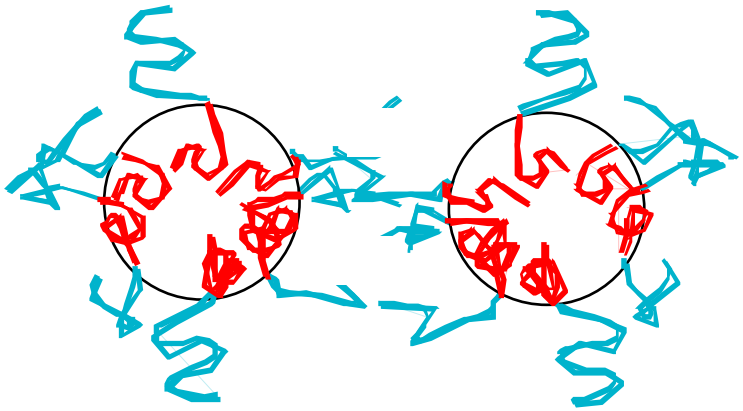
Polymeric surfactants (stabilisers)

- **Polymer with hydrophobic & hydrophilic parts**



***n* is typically 10 – 40**

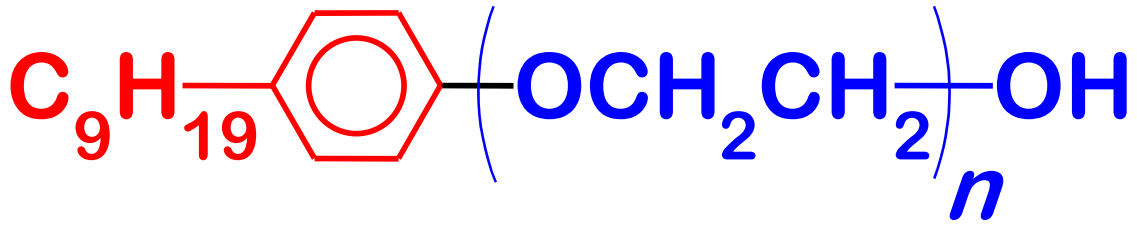
Surrounds particle as "hairy layer"

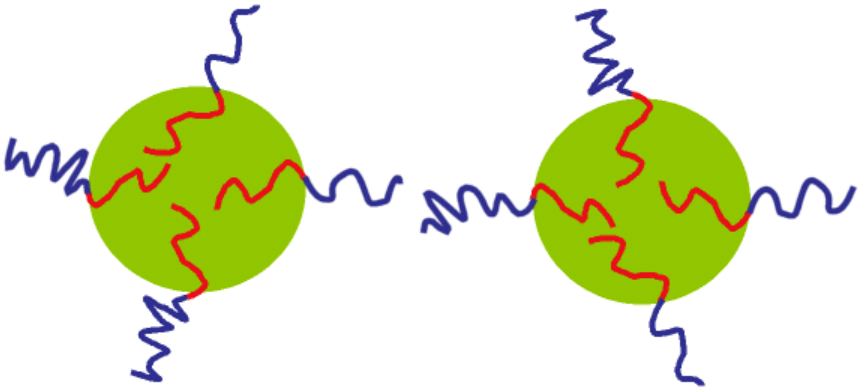


A **steric (or polymeric) stabiliser:**
the *other type of stabiliser*

Polymeric surfactants

- **Polymer with hydrophobic & hydrophilic parts**

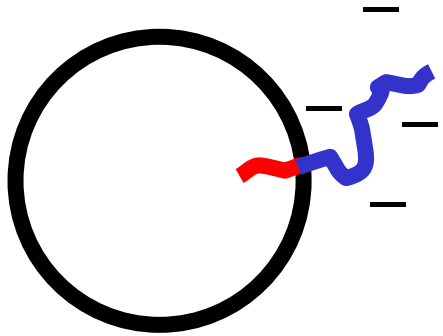




colloidal stability because it is thermodynamically unfavourable to force particles together by compressing chains

Electrosteric stabilisation

- **Some species can function as both electrostatic and steric stabilisers: polymer which can have charge in water phase.**
- **Commonest: proteins**
  - **long polymers.**
  - **both basic and acidic regions**
- **Examples:**
  - **mayonnaise stabilised by egg yolk**
  - **casein: polypeptide with many amino acids, phosphate, polysaccharide (κ-casein): stabilises the fat emulsion droplets in milk**
  - **cells: these colloids are electrosterically stabilized (discussed later)**
  - **paints**



Coagulation

- **Destabilisation of a colloid to form macroscopic lumps...**
- **Can be by:**
  - **Heating: forces particles together and/or changes nature of stabiliser**
  - **Stirring: forces particles together**
  - **Adding salt (electrolyte): shrinks double layer and/or neutralises inherent charge (e.g. on clay)**
  - **Changing pH: can flatten/desorb electrosteric stabilisers**
  - **Adding flocculant (Flocculants, or flocculating agents, are chemicals that promote flocculation by causing colloids and other suspended particles in liquids to aggregate, forming a floc).**
    - **blood clotting is of this type, although it is a complex process**

Lipids

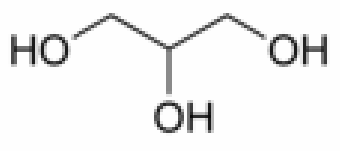
- **Water-insoluble substances:**

  fats

  phospholipids

  waxes

  steroids



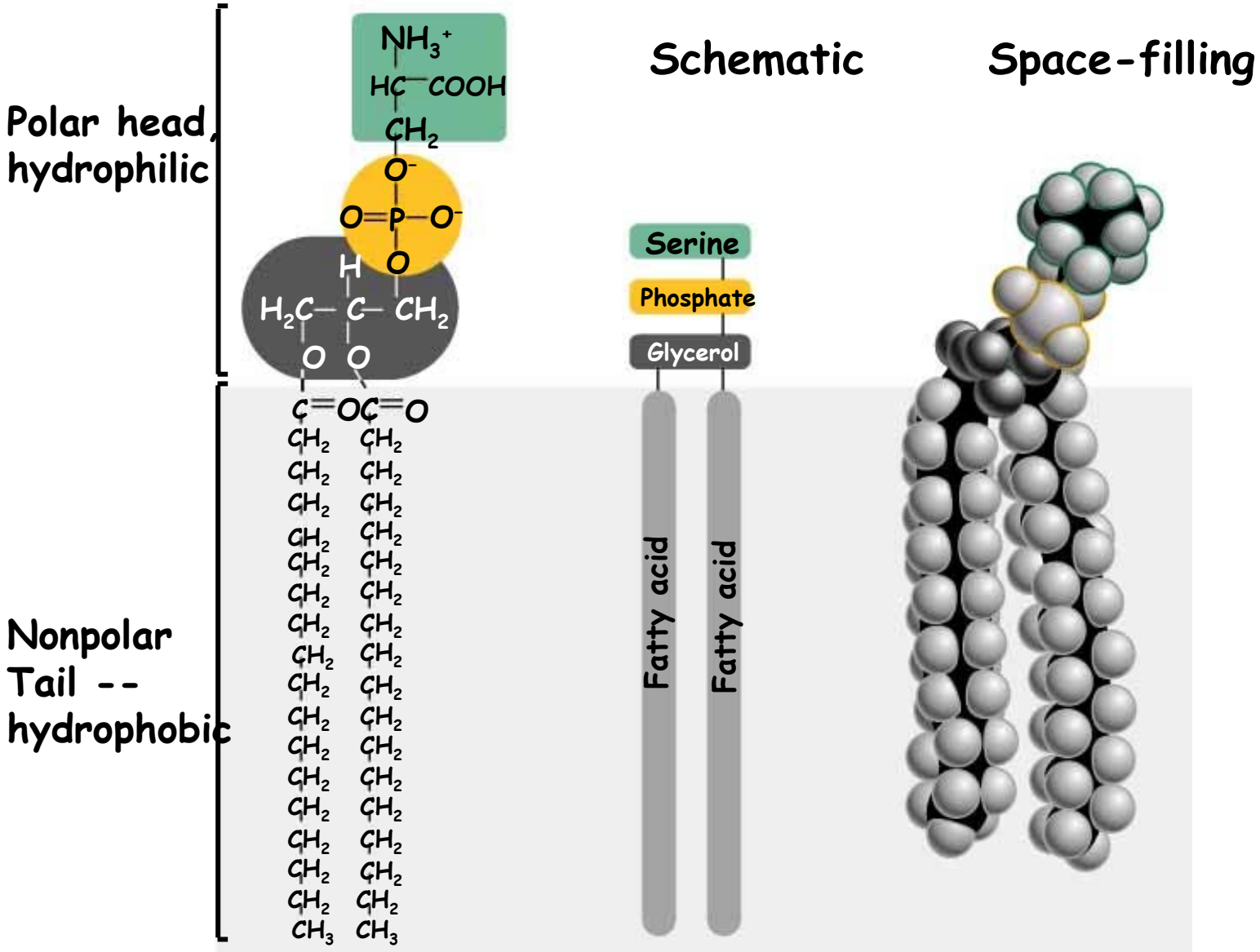
  - **extracted from cells by non-polar organic solvents (benzene…)**

- **Fats = esters of glycerol: triglycerides**

- **Saponification: hydrolysis of triglycerides to glycerol + fatty acids.**
  - **done with NaOH to form carboxylate salts = soaps**

glycerol forms the backbone of triglycerides, it is produced on saponification or transesterification.

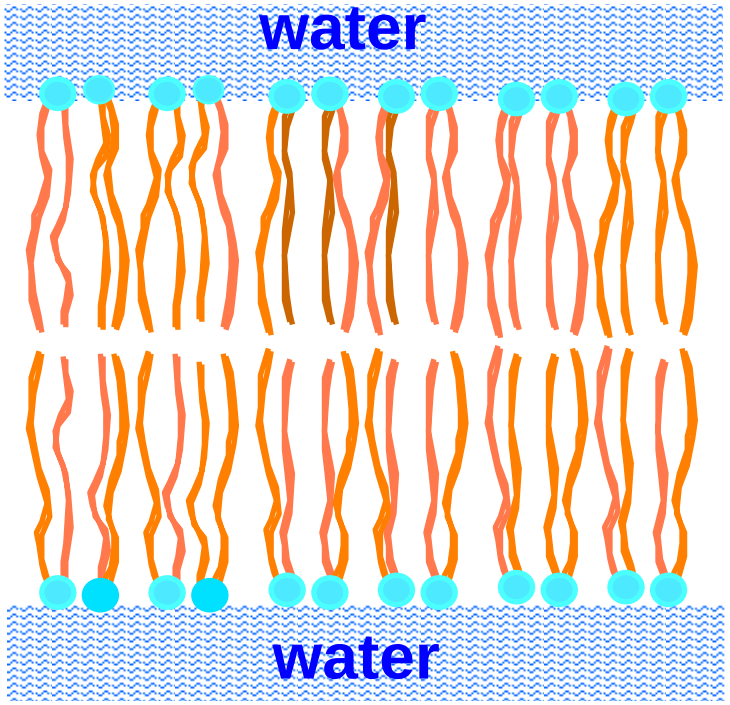
Phospholipids



Phospholipids

- **Similar to fats: esters of glycerol ($CH_2OH–CHOH–CH_2OH$).**
- **Unlike fats: only two fatty acids. 3rd ester linkage involves phosphate group:**
  - **long non-polar tail**
  - **polar substituted phosphate head**

- **Phospholipids tend to form bilayers in aqueous solution:**
  tails in interior, polar heads interfacing
  with polar water molecules



Studying for your exam

- **Examinable part of syllabus and type of exam questions: as given in practice assignments and stated in lectures**
- **Studying for these 9 lectures:**
  - **learn what has been indicated in notes and in lectures**
  - **look at past papers**
  - **some types of assignment questions not suitable for exams: check past papers**
  - **do problems from lectures and assignments again until you can obtain right answer without looking at the notes**
- **Help:**
  - **Duty tutor/ discussion boards over WebCT**

Dr.Chiara Neto's lecture notes are available on

http://notes.chem.usyd.edu.au/course/chiara/CHEM1405.htm