Self-Assembly

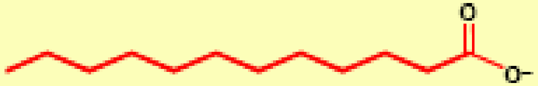
Lecture 3

Surfactants Self-Assembly

Anionic surfactants

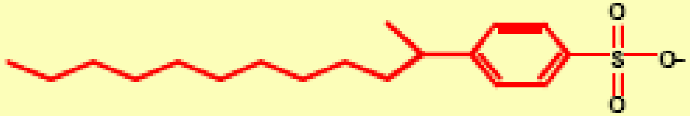
- **Largest group of surfactants** *(~65% world market)*
- **Sensitive to electrolytes (salt and Ca^{2+})**
- **Sulphates hydrolyse at low pH, otherwise chemically stable**
- **Soaps still important (foam and washing)**
- **Alkylether sulphates, lower cmc, compatible low pH and high hardness.**
- **Phosphate esters; good wetting agents, corrosion inhibitors, antistatic properties**

Biodegradable under aerobic conditions
Shampoos, handsoaps, laundry detergents

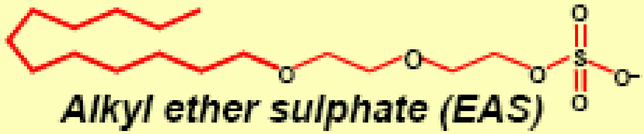


soap

Na lauryl sulphate (SDS)



Linear alkyl benzene sulphonate (LABS)



Alkyl ether sulphate (EAS)

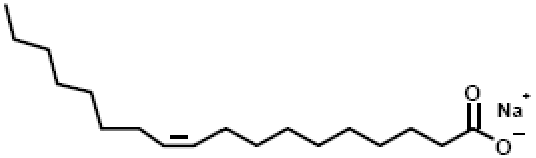
Phosphate ester

unsaturated

fatty acids

saturated

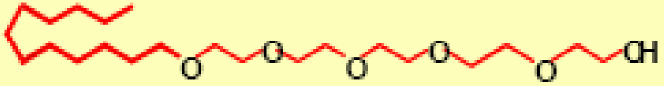
omega-3 – 3rd carbon from the metyl end has double bond



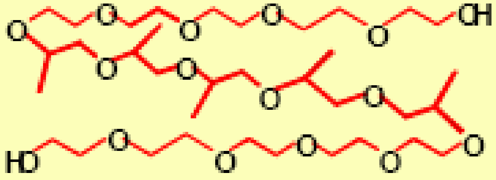
Non-ionic surfactants

- **Second largest group of surfactants** (~25% world market)
- **Dominated by polyoxyethylene products**
- **Not sensitive to salts (e.g. Ca^{2+})**
- **Temperature sensitive: water solubility reduced at higher T**
- **Much lower cmc than anionic surfactants; efficient at low concentrations**

Alkyl ethoxylate (AE, CxEy)



EO-PO blockpolymer



(Joy dish soap)

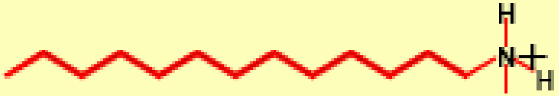
Spans (Sorbitan Esters)
Tweens (Polyoxyethylene Sorbitan Esters)

Smooth rinsing (no water spots)
Dish soaps, window washers, insecticides

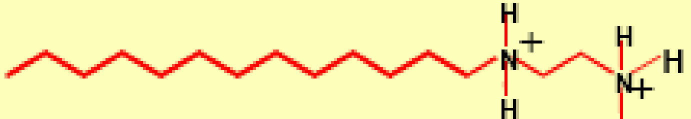
Cationic surfactants

- Composed of a quaternary amino group as cationic head
- Not compatible with anionic surfactants
- Adsorbs strongly to many surfaces
- Used to modify surface properties:
  - Textile softener
  - Adhesion promoter
  - Corrosion inhibitor
  - Anticaking agent
  - Mineral flotation
  - Desinfectant

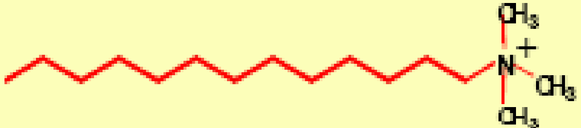
- Counter ions: halides (Cl^-, Br^-) or organic ($MeSO_4^-$)
  - More toxic than anionic surfactants



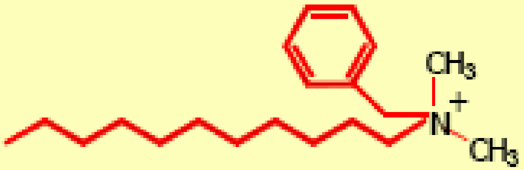
Alkyl amine salt



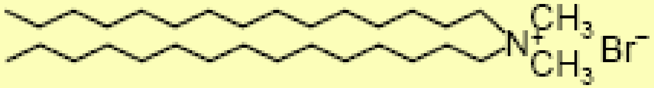
Alkyl diamine salt



Alkyl trimethyl ammonium salt (Quat)



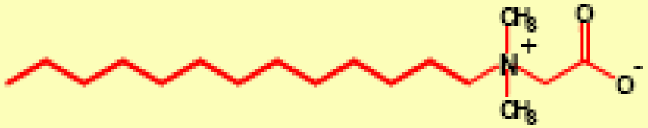
Benzalkonium salt



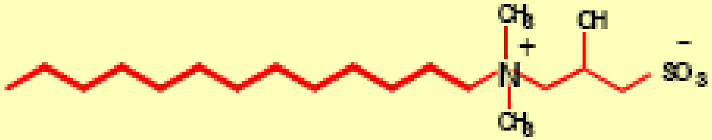
(Downey fabric softener)

Zwitterionic surfactants

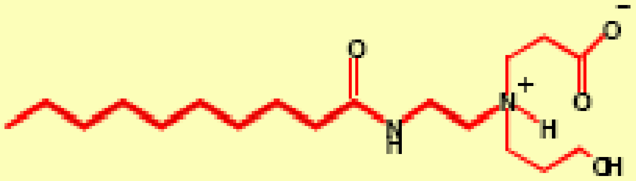
- Smallest group of surfactants
- Usually composed of a quaternary aminogroup and a sulphonic or carboxylic acid
- Charge depends on pH
- Very mild and low irritation, used in shampoos etc.
- Generally stable in acids and alkali



Alkyl betaine

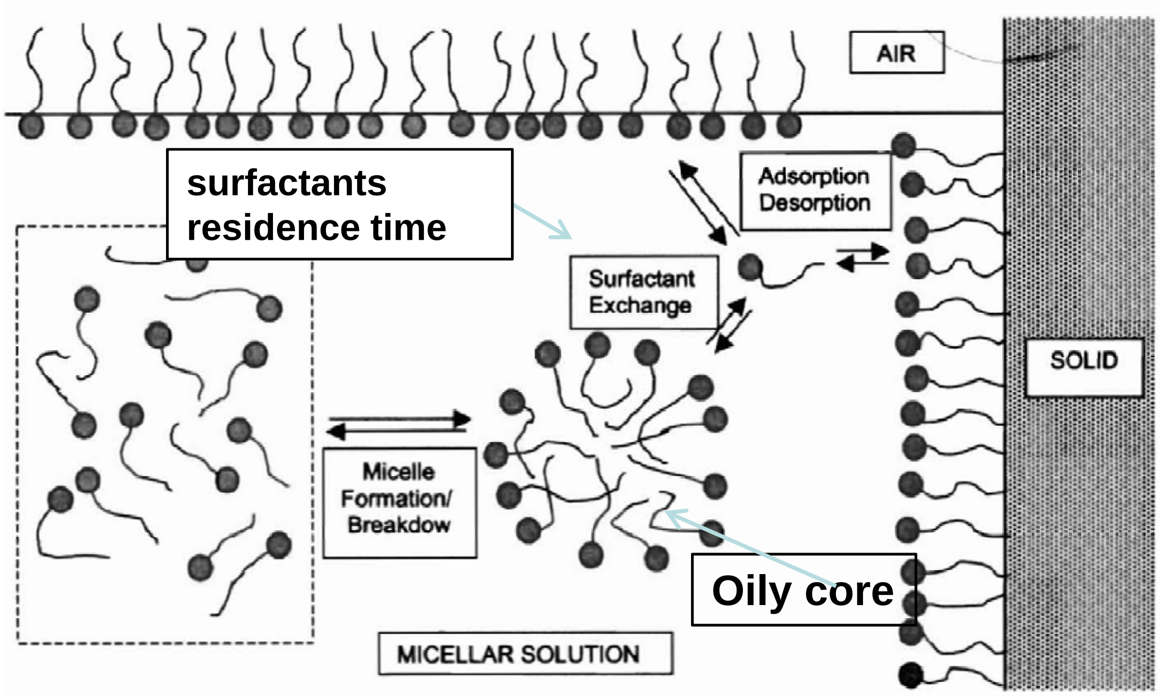


Alkyl sulphobetaine



Alkyl imidazoline

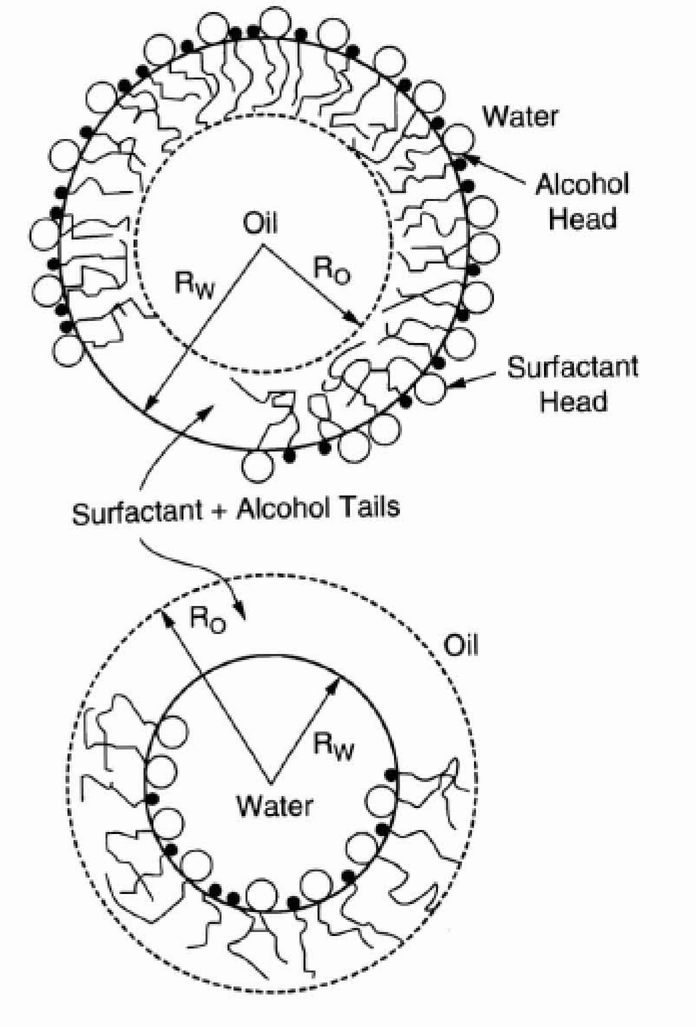
Surfactant self-assembly



- At low concentrations surfactants form adsorbed layers of air/solution and solid/solution interfaces
- At ***critical micellization concentration*** (cmc) the surfactant starts self-assembling into micelles
  - – driven by hydrophobic interaction
  - – spontaneous and reversible cooperative transition

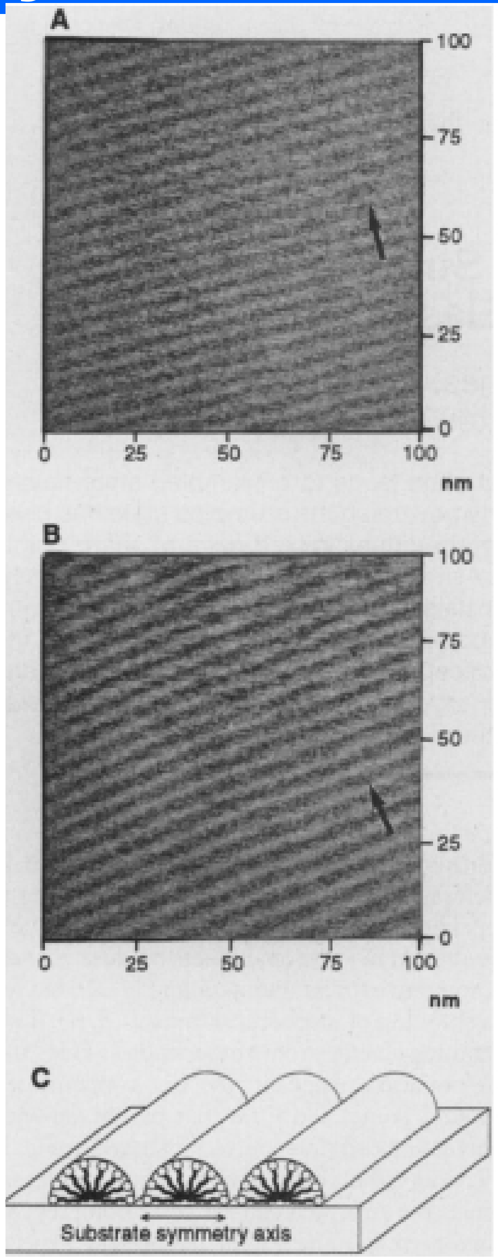
Surfactant self-assembly

- Compounds that are sparingly soluble in water can dissolve in oily core above cmc yielding **solubilized systems**
- Addition of co-surfactants (usually alcohols) to an emulsion can lead to formation of a termodynamically stable **microemulsion**
- Some surfactants self-assembling into **vesicles** (called **liposomes** in case of phospholipids)
- At high concentrations surfactants forrm **liquid crystalline phases**



Adsorbed surfactant layers

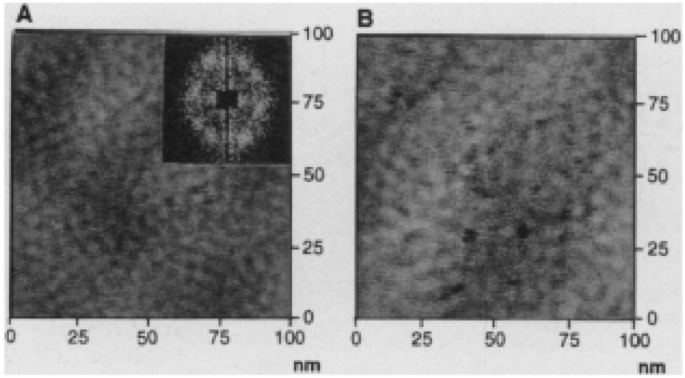
- Surfactant in contact with clean adsorbs onto the surface
- Hydrophobic surfaces:
  - surfactant contacts surface via tail forming progressively more compact monolayers
  - at higher coverage the morphology was observed to form hemi-cylindrical aggregates irrespective of the nature of surfactants



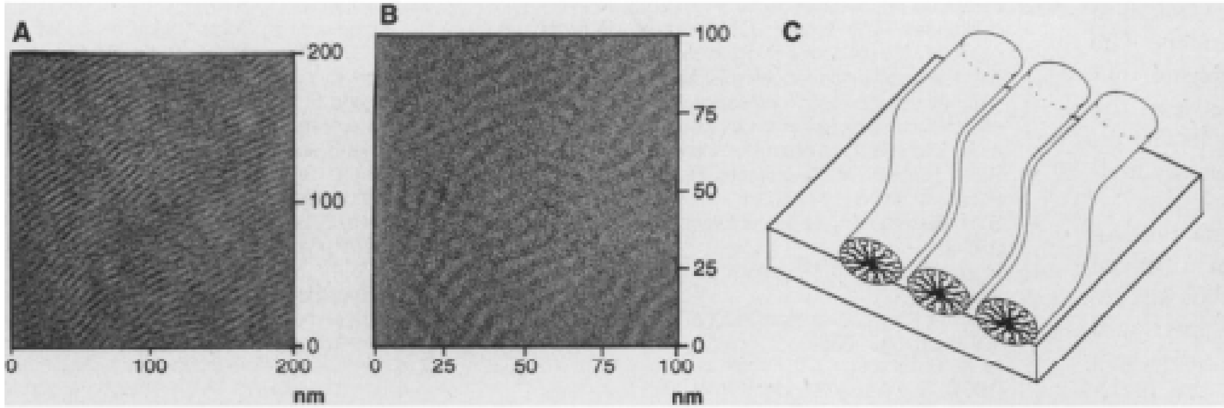
S.Manne and H.Gaub, Science 270, 1480 (1995)

Adsorbed surfactant layers

- Hydrophilic surfaces:
    - surfactant is attracted to the surface via ion-exchange step
    - then, surface aggregates are formed in a cooperative process
    - the morphology depends on the surfactant geometry, could be bilayer, sperical or cylindrical aggregates



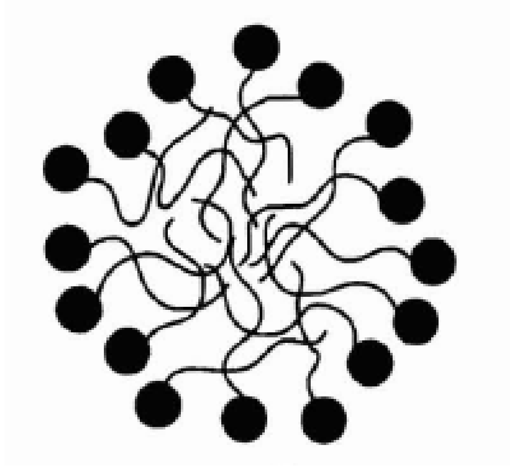
C_{14}TAB on silica 7mM. Sperical micelles, (A) pH 6.3; (B) pH=2.9



C_{14}TAB on mica 7mM. cylindrical micelles

S.Manne and H.Gaub, Science 270, 1480 (1995)

Micelles

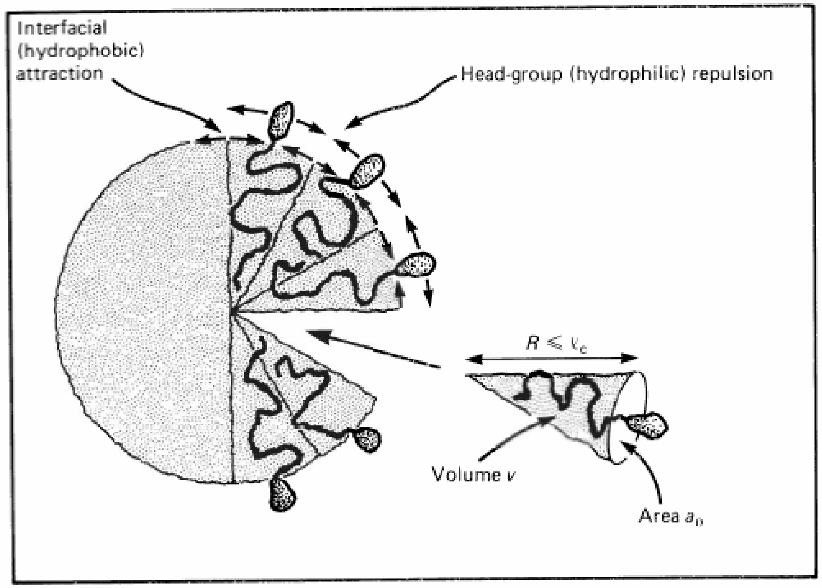


- The balance between the attractive and repulsive interaction in a micelles results in a micelles of finite size
- Micelles are spherical near CMC
- The aggregation number of a spherical micelle can be estimated as

$$N_S = \frac{4\pi l^3}{3v}$$

$$l \approx \left(0.154 + 0.1265 \cdot n\right) nm$$

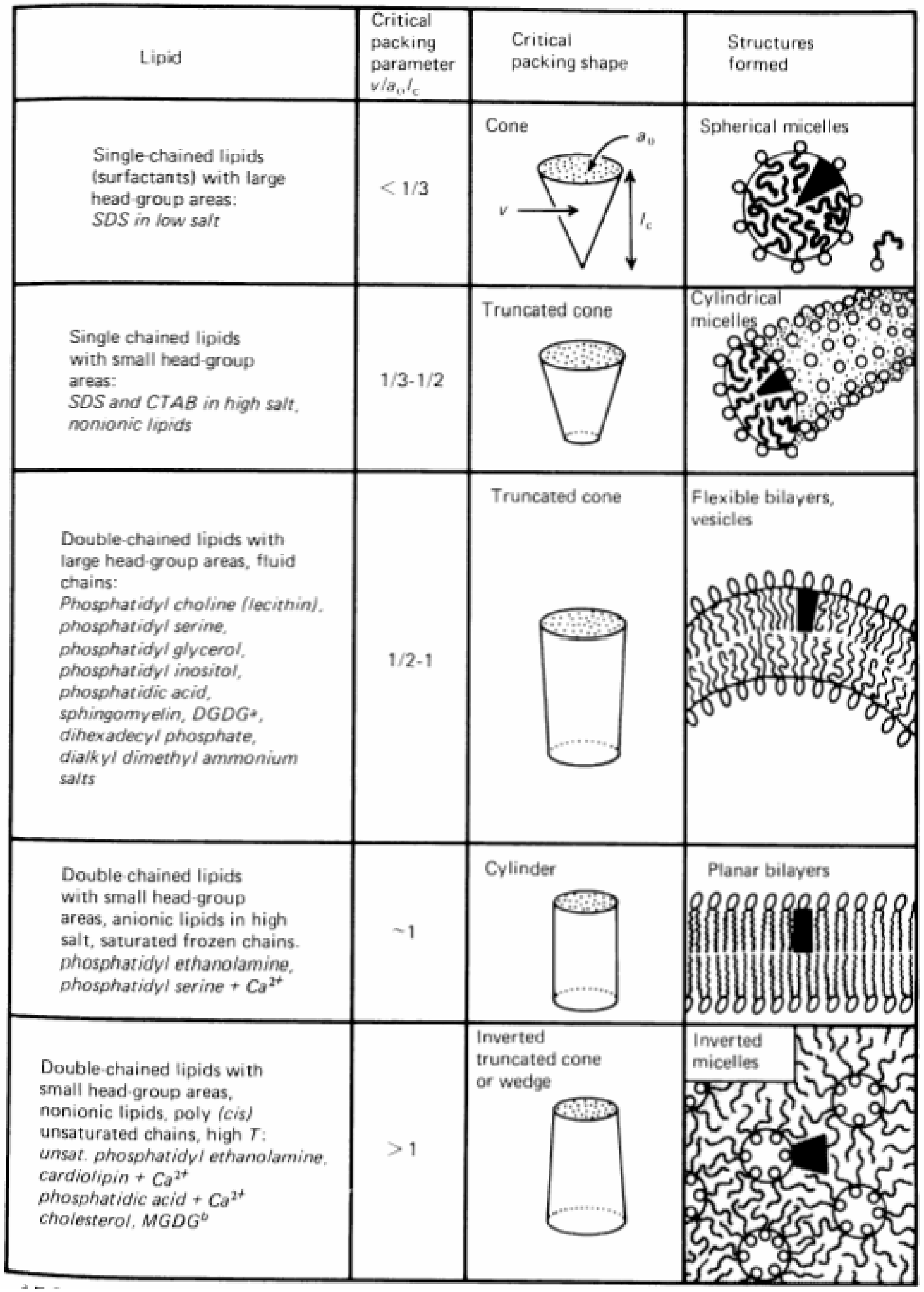
$$v \approx \left(27.4 + 26.9 \cdot n\right) \times 10^{-3} nm^3$$



Micelles

- At higher concentration the micellar shape is governed by the surfactant packing parameter

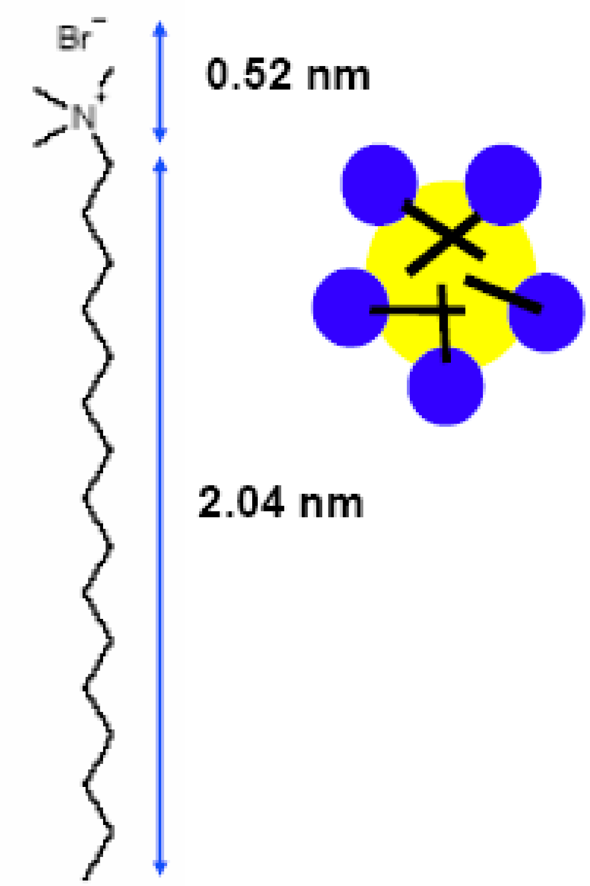
$$P = \frac{v}{a_0 l_c}$$



Lipid	Critical packing parameter $v/a_0 l_c$	Critical packing shape	Structures formed
Single-chained lipids (surfactants) with large head-group areas: *SDS in low salt*	< 1/3	Cone	Spherical micelles
Single chained lipids with small head-group areas: *SDS and CTAB in high salt, nonionic lipids*	1/3-1/2	Truncated cone	Cylindrical micelles
Double-chained lipids with large head-group areas, fluid chains: *Phosphatidyl choline (lecithin), phosphatidyl serine, phosphatidyl glycerol, phosphatidyl inositol, phosphatidic acid, sphingomyelin,* DGDG^a, *dihexadecyl phosphate, dialkyl dimethyl ammonium salts*	1/2-1	Truncated cone	Flexible bilayers, vesicles
Double-chained lipids with small head-group areas, anionic lipids in high salt, saturated frozen chains. *phosphatidyl ethanolamine, phosphatidyl serine +* Ca^{2+}	~1	Cylinder	Planar bilayers
Double-chained lipids with small head-group areas, nonionic lipids, poly *(cis)* unsaturated chains, high T: *unsat. phosphatidyl ethanolamine, cardiolipin +* Ca^{2+} *phosphatidic acid +* Ca^{2+} *cholesterol,* MGDG^b	> 1	Inverted truncated cone or wedge	Inverted micelles

Micelles

Hydrophobic core, little penetration by water
Electrical double layer shell



CTAB volume: 35 nm³

Area per headgroup determined by:

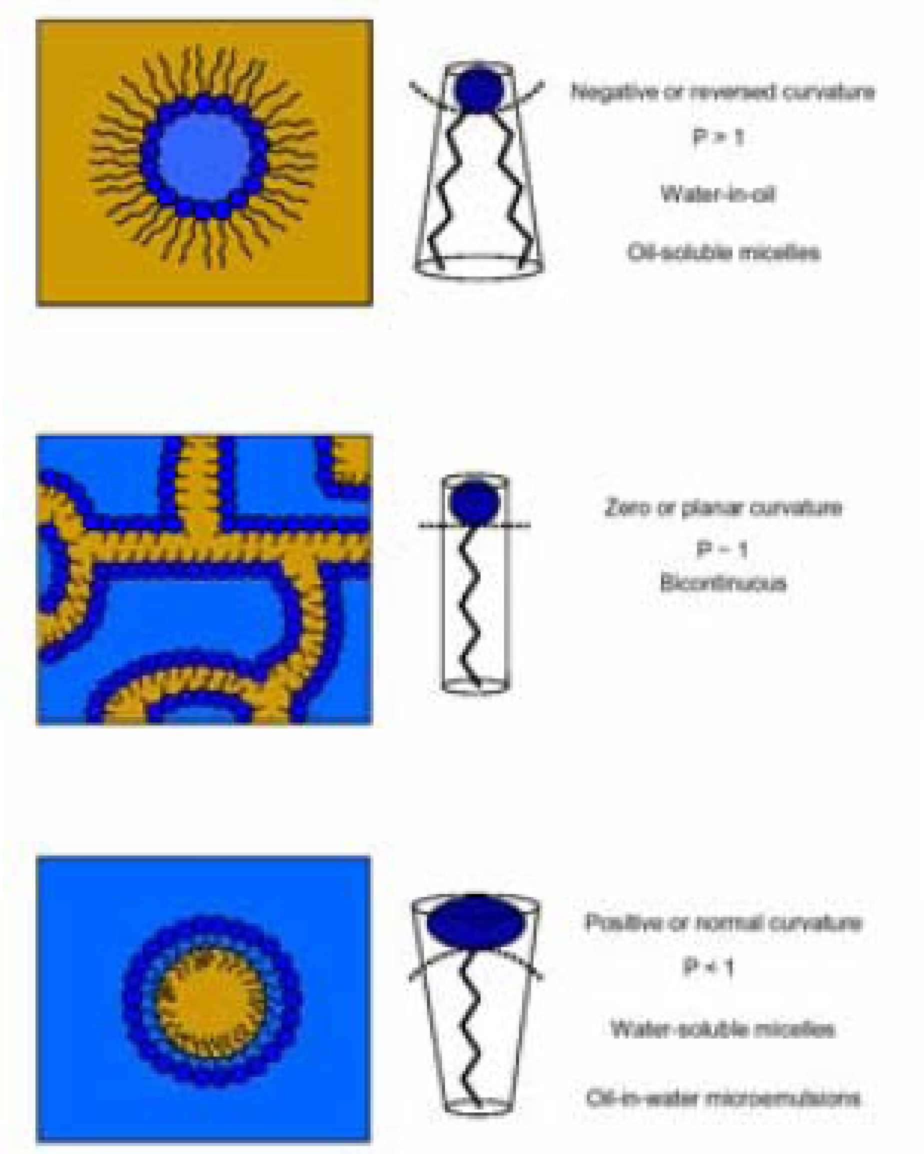
- surface tension: reduction by small area per headgroup
- electrostatic repulsion & chain packing: larger area per headgroup

Optimal headgroup area a_0, dependent on:

- amphiphile
- ionic strength
- temperature, pressure
- solvent

But independent on chain length !
(but shape differences possible)

Micelles



Factors affecting the surfactant parameter a_0

- Size of polar group
- Solvation (temperature)
- Salt concentration

Factors affecting the surfactant parameter v/l_c

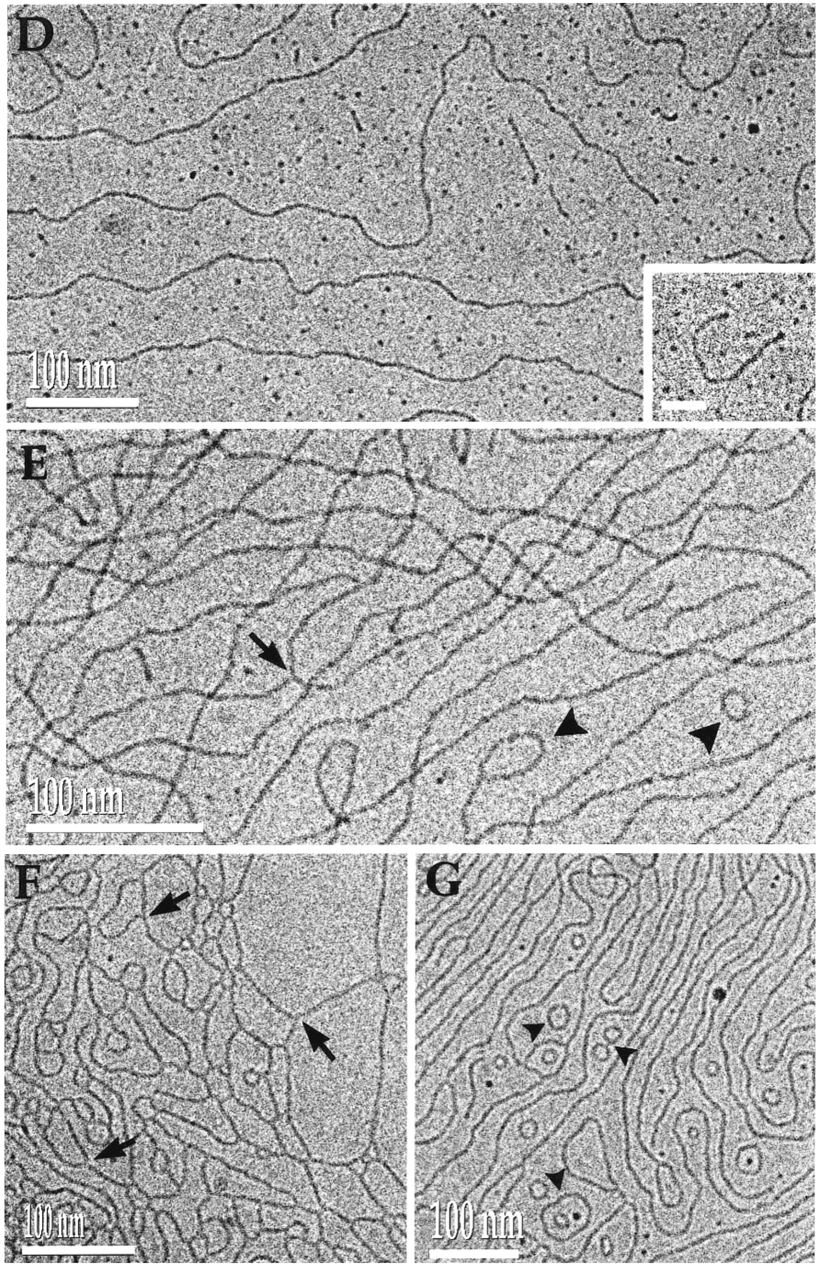
- Number of carbon atoms in chain
- Structure and mobility of chain
- Number of chains

Micelles

- The micelle oily core is in a quasi-liquid state
- very rapid movement of the chain
- very low viscosity
- extensive chain looping
- rapid fluctuation of micellar shape (10^{-3} – 10^{-10} s)

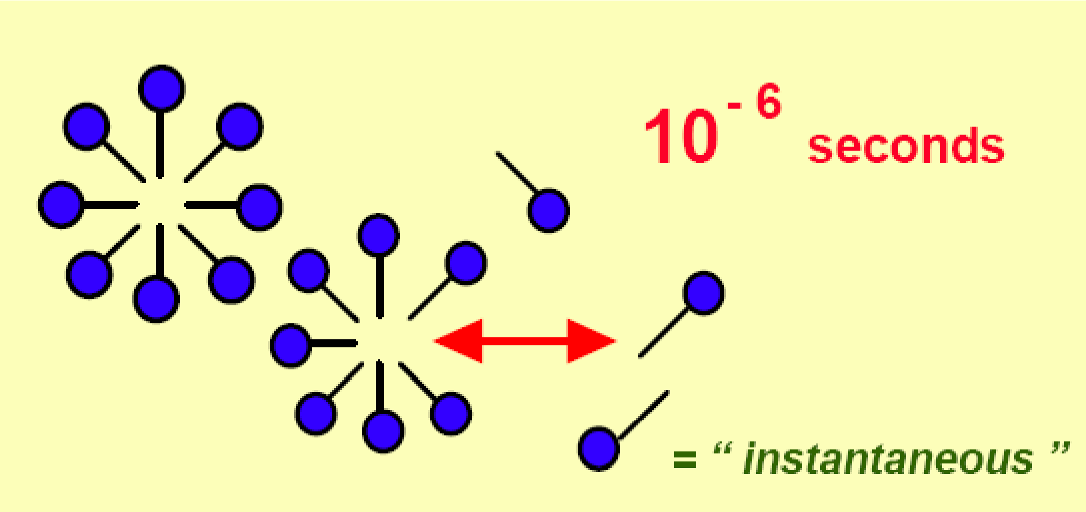
Micelles

- Formation of giant thread-like micelles in gemini surfactant 12-2-12 solution observed by cryo-SEM, the concentration 0.74 wt% (D), 1wt% (E) and 1.5wt% (F and G)

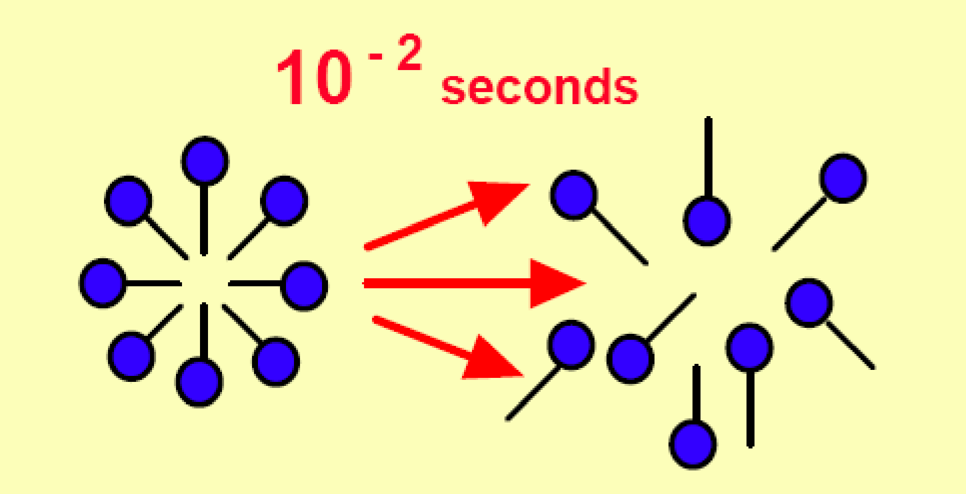


Micelle is a dynamic object

- Molecular Relaxation time (exchange)



- Relaxation Time for Aggregate Dissolution



CMC

- CMC value slightly depends on the experimental technique used
- Mainly determined by the nature of surfactant and the length of the chain
- Decreases exponentially with the chain length increase

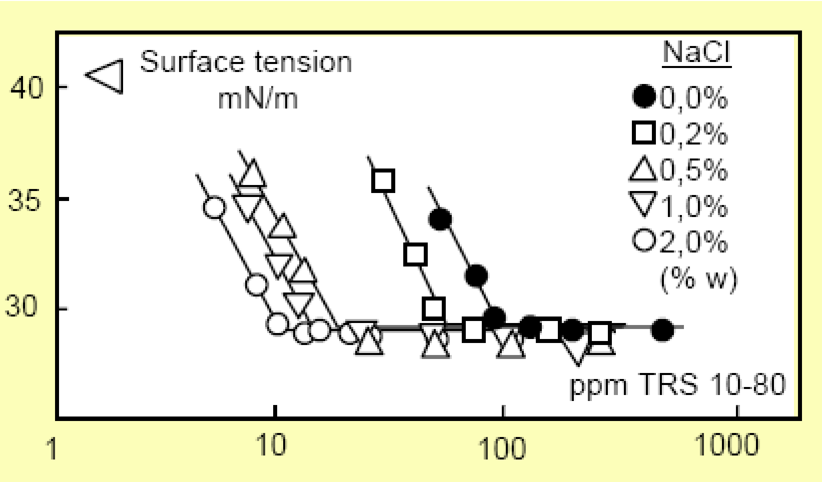
$$\log cmc = b - a \cdot m$$

- CMC is increased with branching (increased solubility)

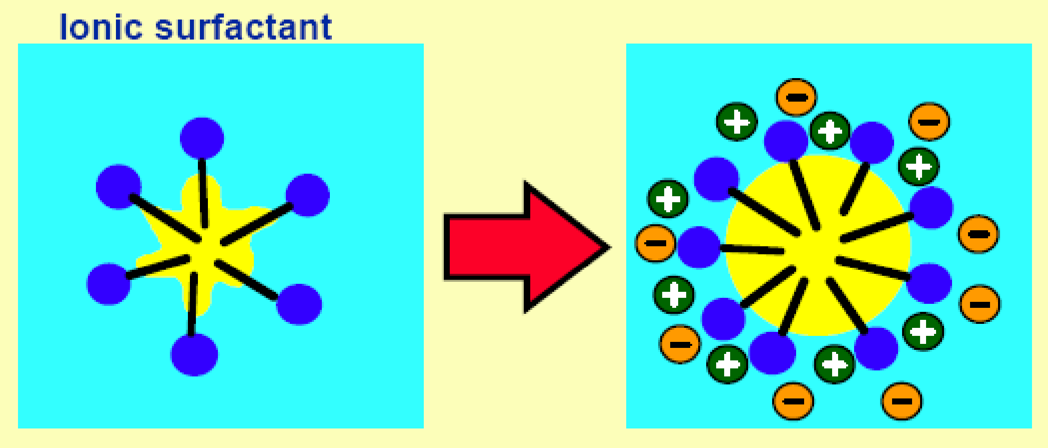
CMC

- CMC Decreases upon increasing concentration of an added electrolyte that has a common ion with surfactant

$$\log cmc = A - B \cdot \log(cmc_0 + C_0)$$



- Explanation:
  Ions produce electrostatic screening. This allow the head groups to get closer



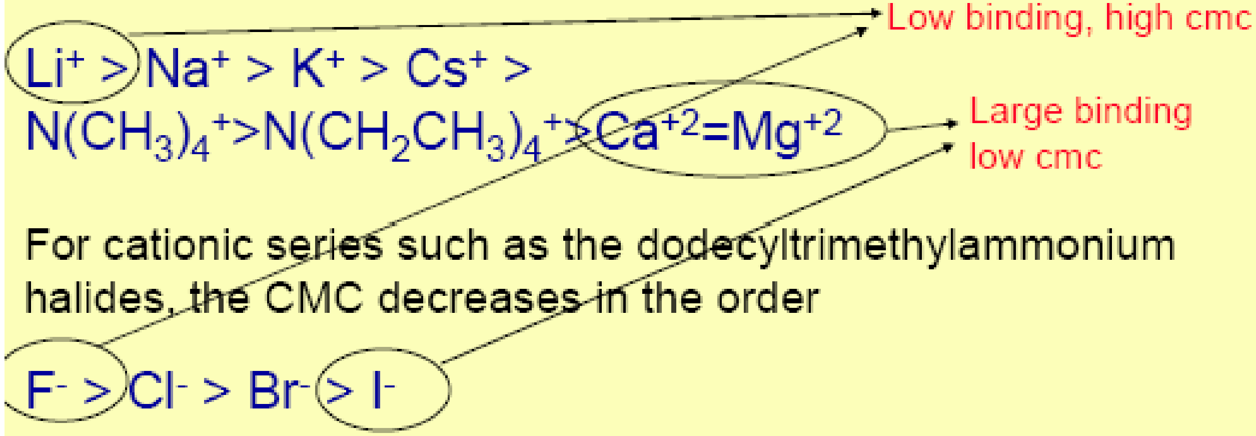
CMC

- Effect of counter ion

	mmol/L
Li Dodecyl sufate	9
K Dodecyl sufate	8
Ca Dodecyl sufate	3
Tetrabutyl-ammonium Dodecyl sufate	1

Increase in the degree of ion binding decrease the CMC.

For a given hydrophobic tail and anionic head group, the CMC decreases as:



$Li^+ > Na^+ > K^+ > Cs^+ >$
$N(CH_3)_4^+ > N(CH_2CH_3)_4^+ > Ca^{+2} = Mg^{+2}$

Low binding, high cmc

Large binding
low cmc

For cationic series such as the dodecyltrimethylammonium halides, the CMC decreases in the order

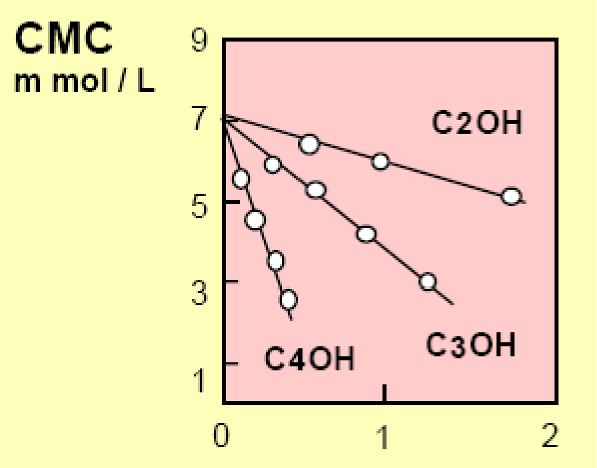
$F^- > Cl^- > Br^- > I^-$

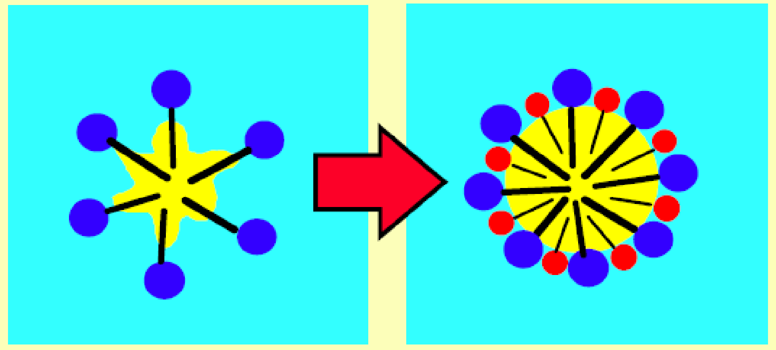
Note that varying counterion valency produces a significant effect.

Solubilized systems

- Generally, all said about micelles holds for solubilized systems

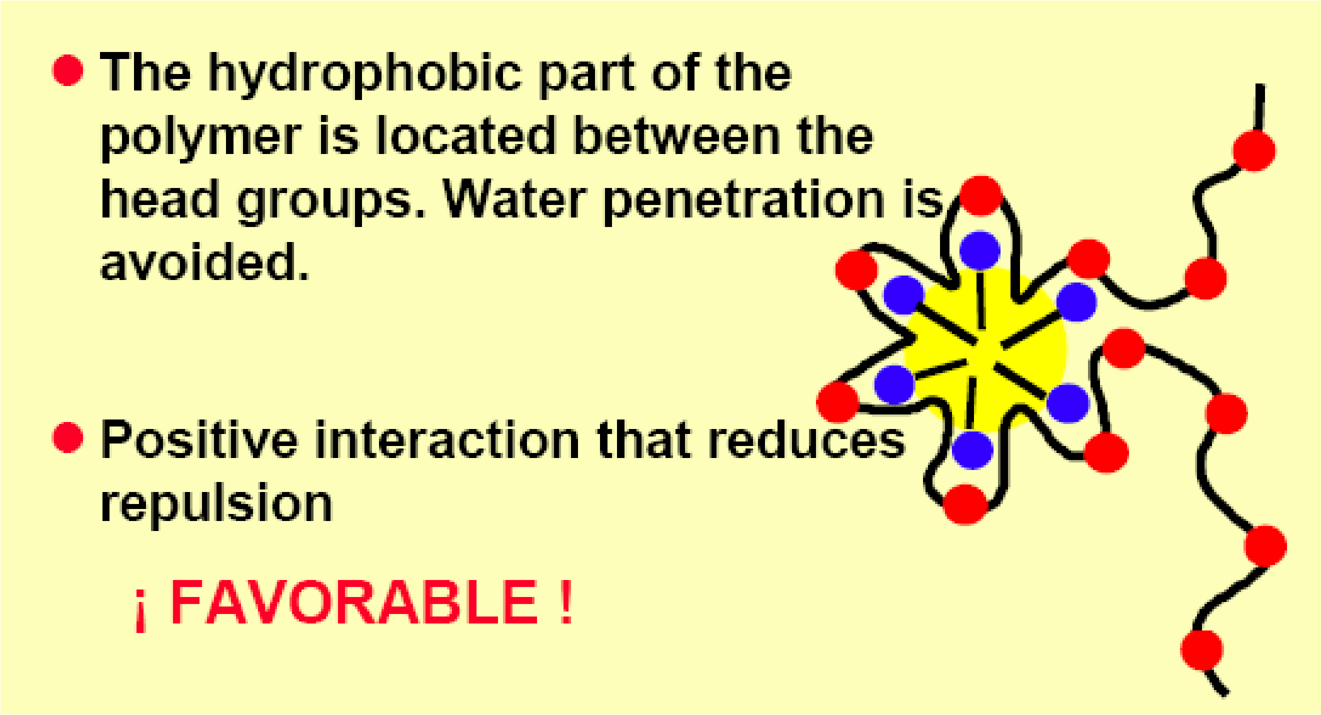
- Short chain alcohols (methanol – propanol) reduce micelle size and transform them into spherical ones
- Medium chain alcohols (butanol-hexanol) reduce micelle size at lower concentration and increase at high concentration
- High chain alcohols increase the size of the micelles and change the shape





Water soluble polymers/surfactant system

- Water-soluble polymers lower CMC and aggregation number
- form “necklace bearing beads”



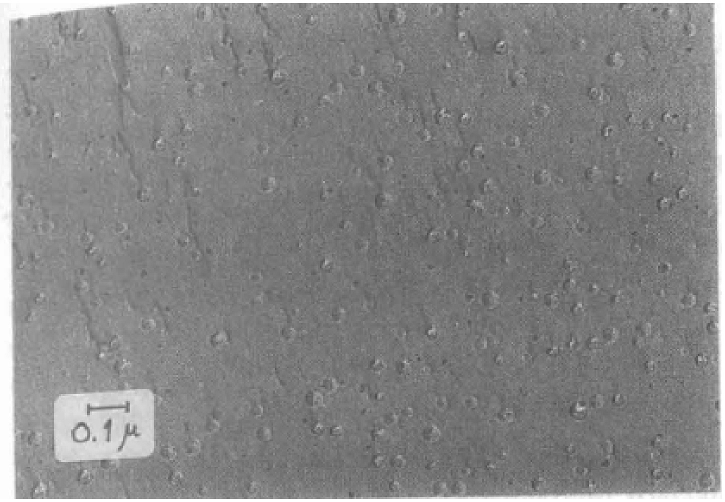
- The hydrophobic part of the polymer is located between the head groups. Water penetration is avoided.
- Positive interaction that reduces repulsion

¡ FAVORABLE !

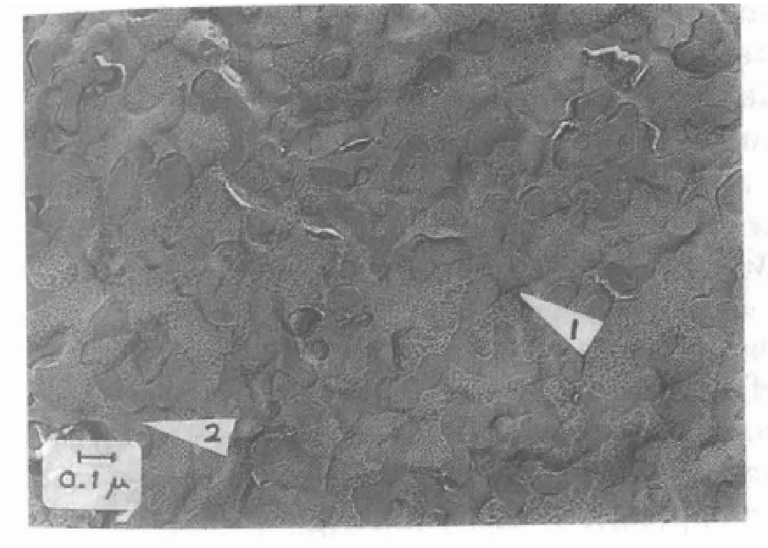
Microemulsions

- First discovered by Hoar and Schulman in 1943: they found that is alcohol is added to benzene emulsion the system is clarified
- Significant interest after oil crisis in 1975 in attempt to improve iol recovery
- Surface tension at oil-water interface can be reduced down to 10^{-4} mN/m^2

water/n-octane/$C_{12}E_5$ microemusion



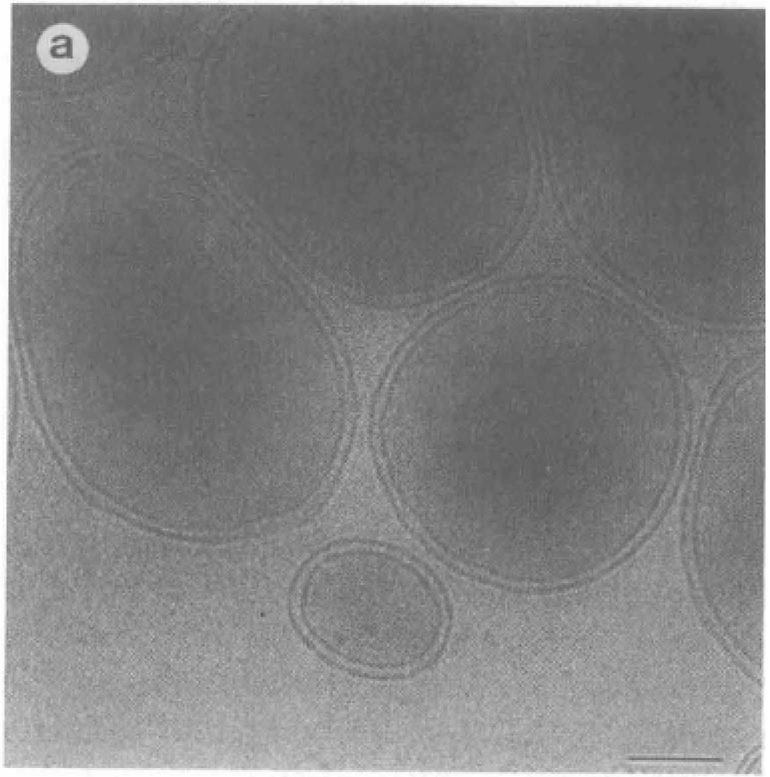
spherical micelles



bicontinuous phase

Vesicles

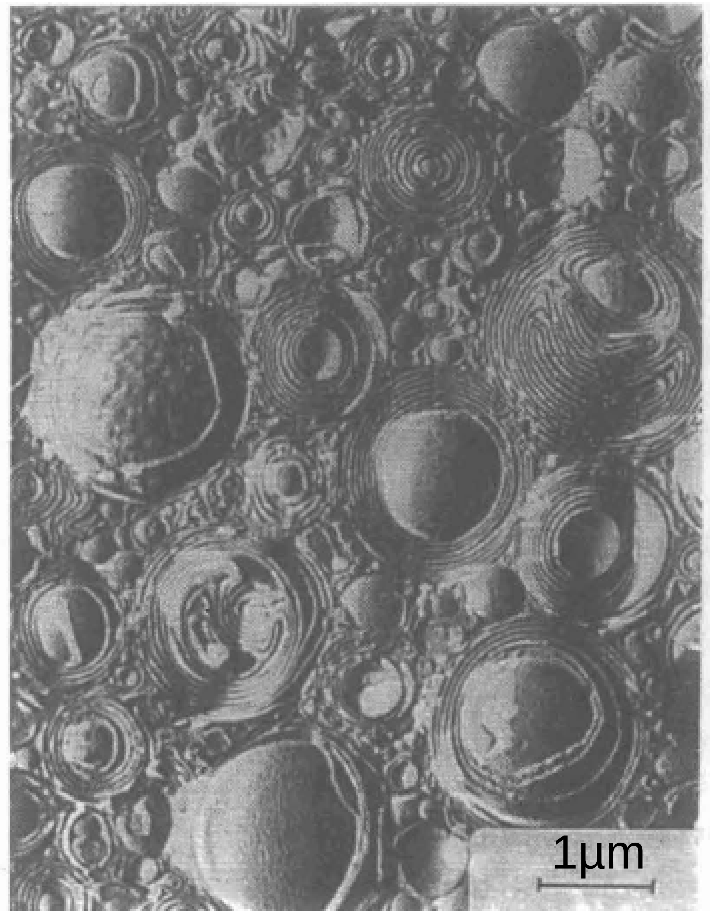
- Vesicles in water are commonly observed with phospholipids and other two chain surfactants with 10 or more carbons
- Commonly prepared by:
  - solubilizing the amphiphile in organic solvent
  - evoporating the solution on glas surface
  - exposing the film to water
  - sonification, extrusion etc further used to reduce the vesicles into unilamellar
  - usually unstable
- Stable vesicles can be prepared by mixing two surfactants



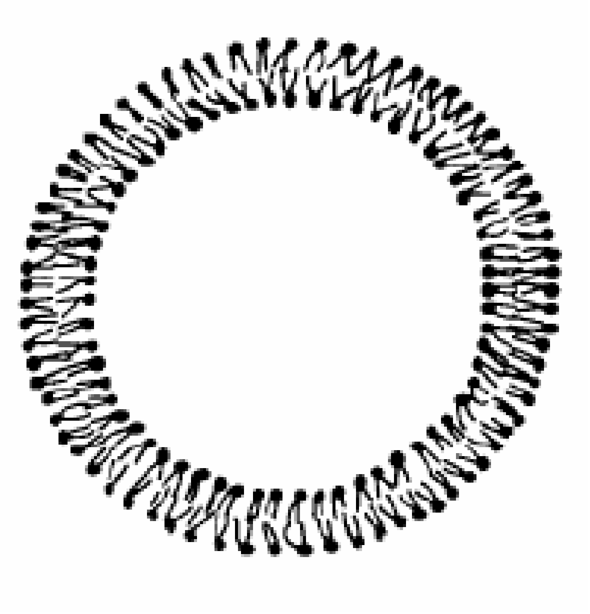
vesicles in 12-20-12 gemini surfactant

Vesicles

- ”Onion phase” (multilamellar vesicles)



Vesicles



Bilayer structures:

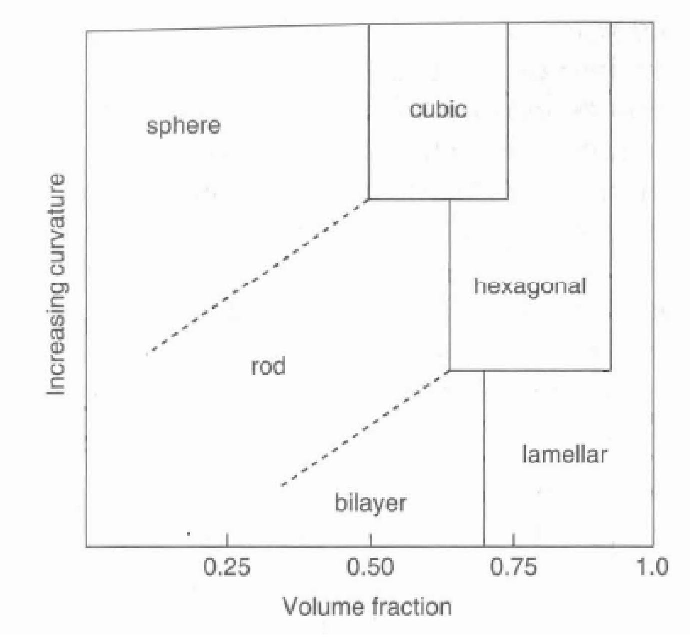
- preparation difficult because solubility of monomers is extremely low
- strong, closed structures
- slow dynamics
- compartmentization

Detection:

- DSC (differential scanning calorimetry)
- freeze fracture electron microscopy
- fluorescence spectroscopy

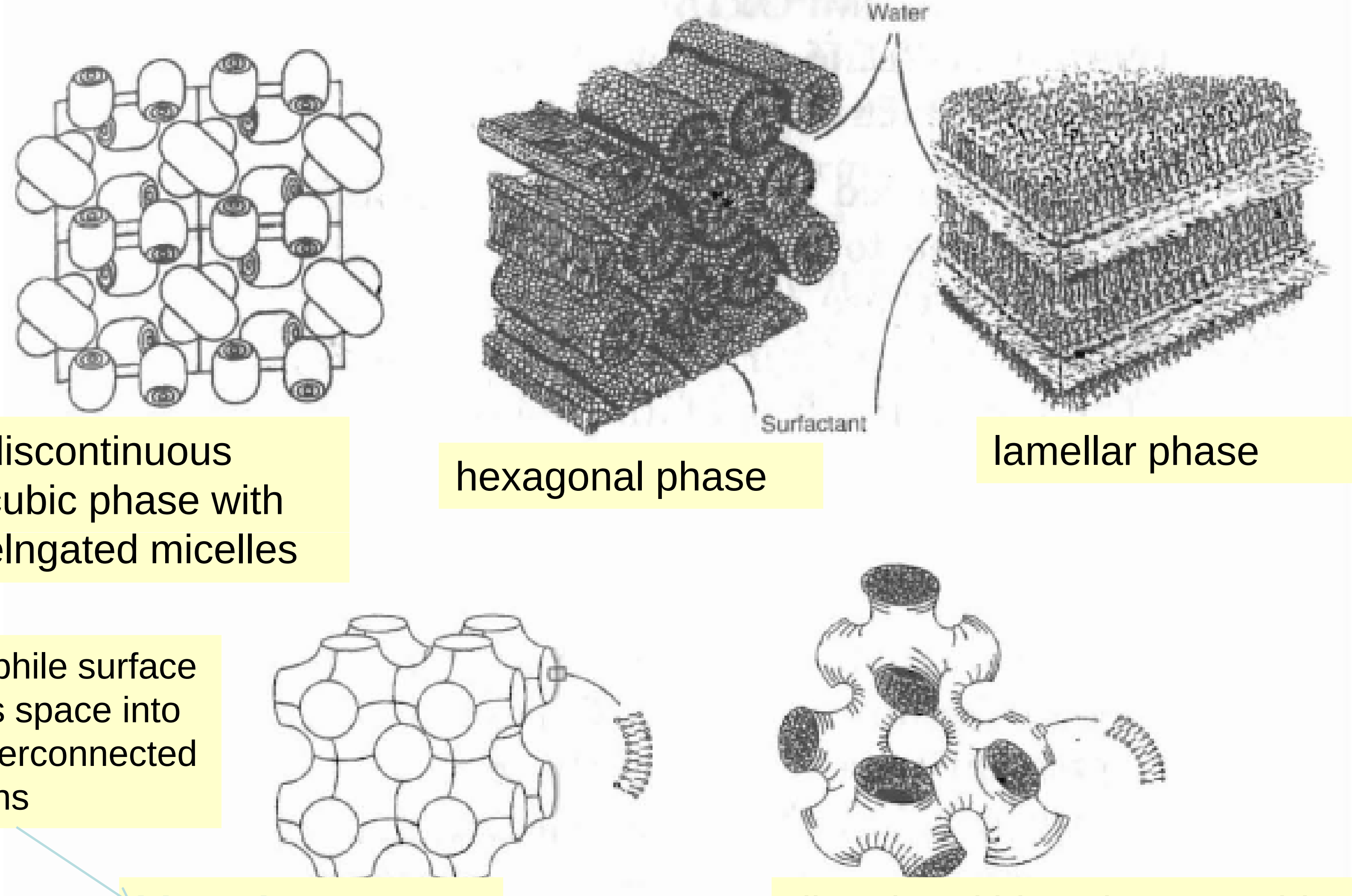
Liquid crystal phases

- As the surfactant concentration increases, repulsive intermicelle interaction induce micelle ordering
- For spherical micelles (P<1/3) :
  Sperical micelles →cubic phase → hexagona phase → lamellar phase
- For elongated (1/3<P<1/2) or disklike (1/2<P<1)
  Disordered elongated micelles→ hexagonal phase → lamellar phase
  Disordered disklike micelles→ lamellar phase
- As the system tries to keep intermicelle distance as large as possible, the micelle might coarsened before:
  Sperical micelles →cubic phase → hexagonal phase → lamellar phase
  Disordered elongated micelles→ hexagonal phase → lamellar phase



Liquid crystal phases

- Commonly encountered mesophases



discontinuous cubic phase with elngated micelles

hexagonal phase

lamellar phase

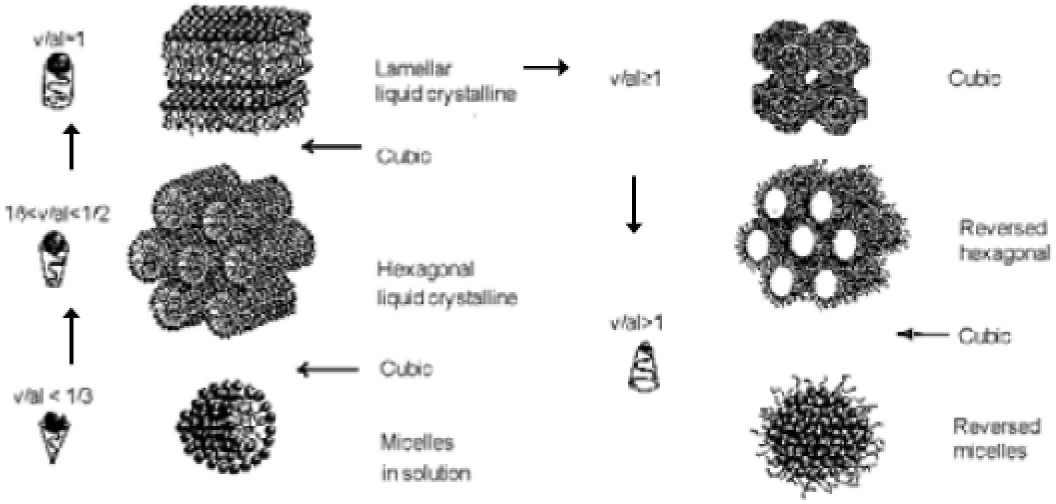
amphiphile surface divides space into two interconnected domains

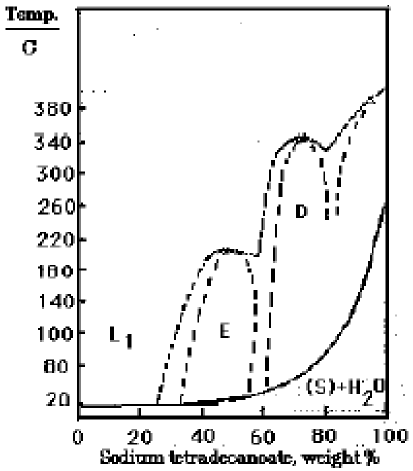
bicontinuous cubic phase

disordered bicontinuous cubic phase (L_3)

Liquid crystal phases

- Dependence between the phase structure and the structure of surfactant





Phase diagram for sodium tetradecanoate (myristate)/water system

L1 = micellar solution,
S = solid,
E = hexagonal,
D = lamellar liquid crystalline phase.