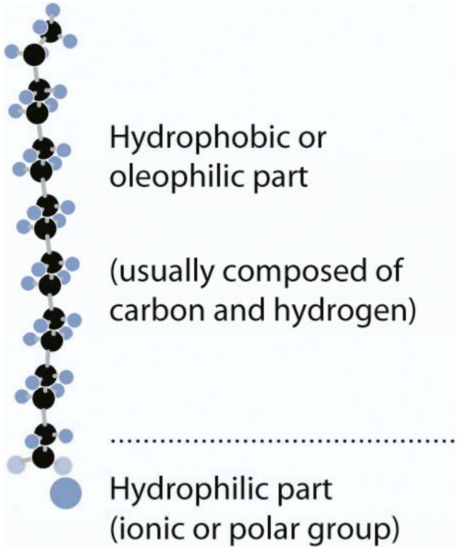
Lecture 12

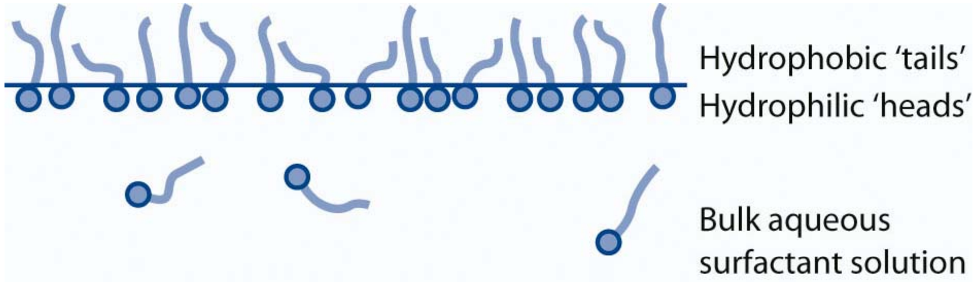
Surfactants and Micelles. Thermodynamics of Micelle Formation.

Absorption of surfactants

- **surfactants** (stands for: surface active agents) belong to a class of **amphiphiles**

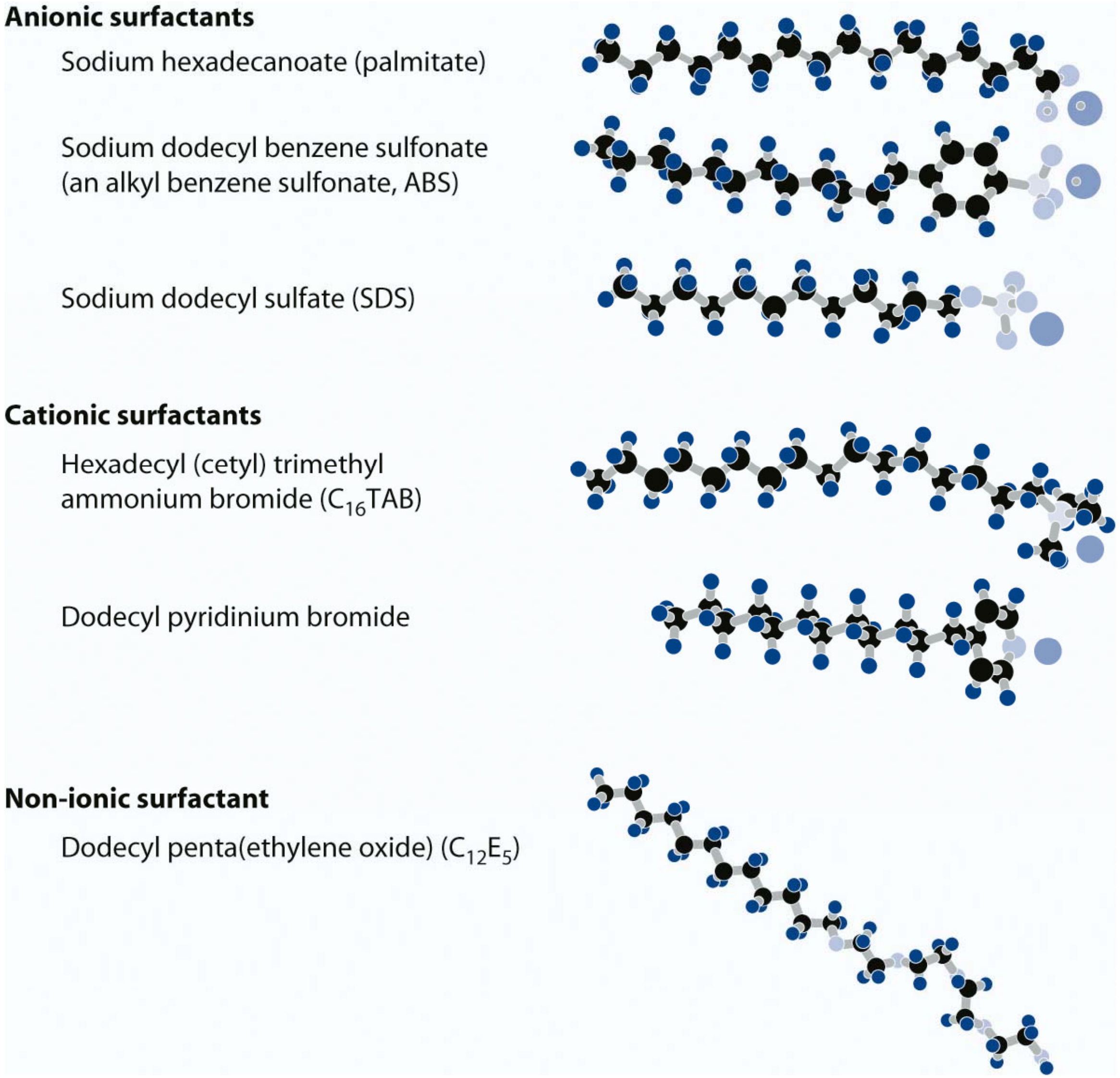


- **Gibbs monolayers**



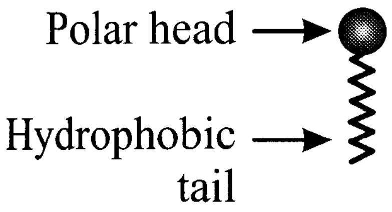
Absorption of surfactants

- Surfactants can be:
  - **anionic** (the most used), bear **negative charge** on the hydrophilic part
  - **cationic**, bear **positive charge** on the hydrophilic part
  - non-ionic, not charged, soluble due to polar groups like polyethylene oxide and sugars
  - zwitterionic

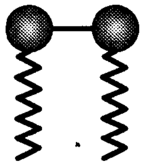


Unconventional surfactants

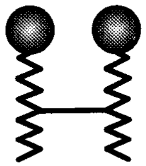
- Surfactants can be designed with more than one of polar and non-polar groups:



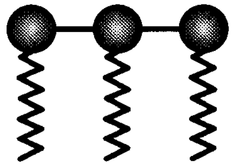
Conventional surfactant



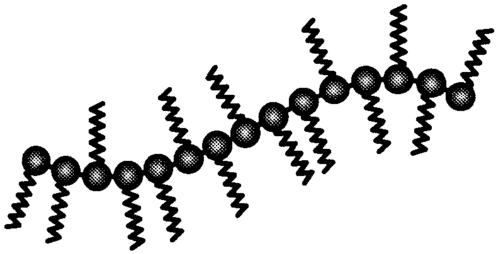
Gemini surfactant



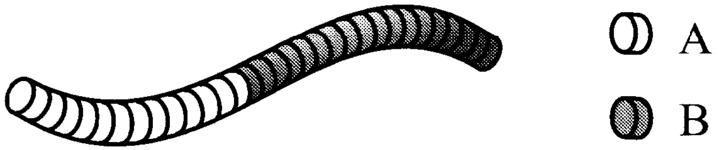
Bolaform surfactant



Trimeric surfactant



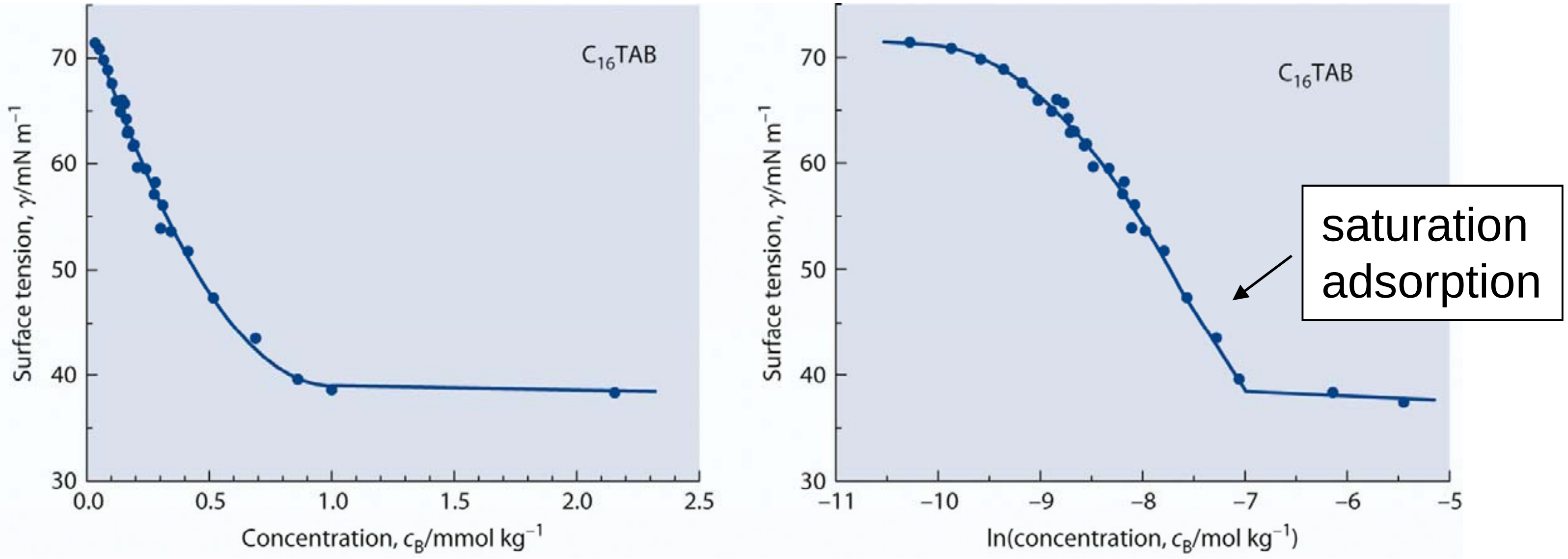
Polymeric surfactant



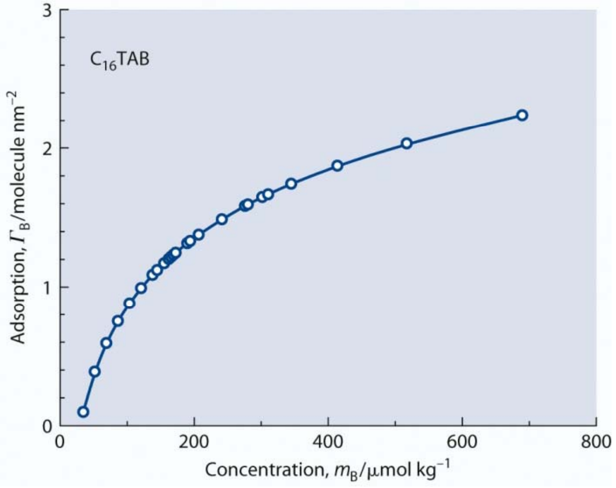
Diblock copolymer

Absorption of surfactants

- Surface tension of surfactant usually falls to a lower limit and becomes a constant after



saturation adsorption



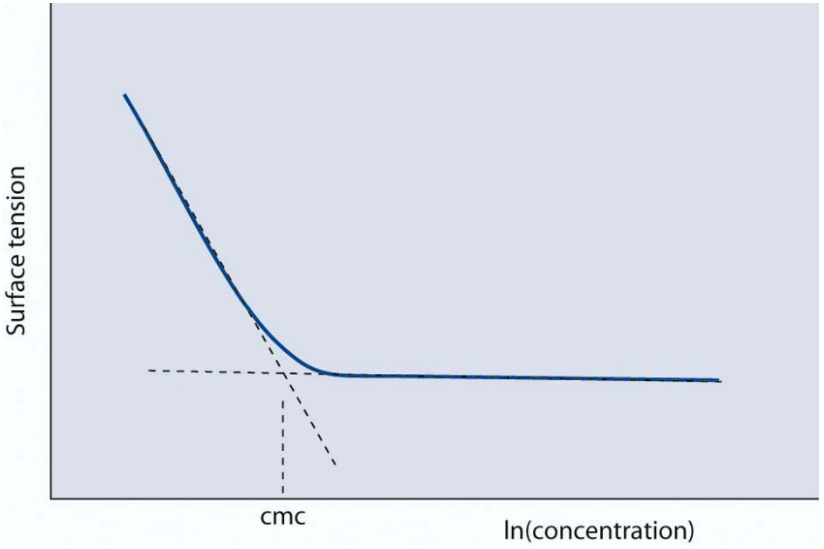
Micelles

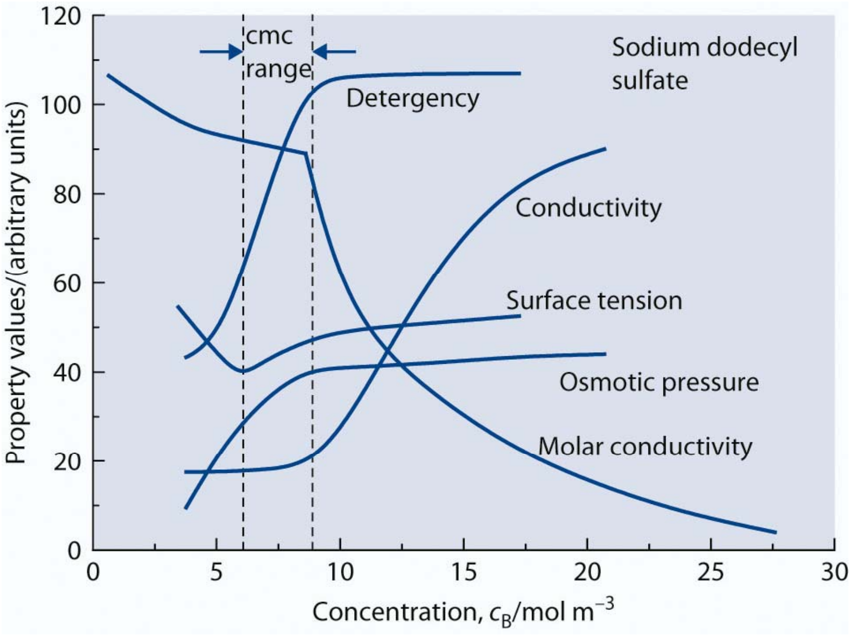
- above certain critical concentration the surface tension becomes independent of concentration: **critical micelle concentration (cmc).**

$$-\frac{d\gamma}{RT} = \Gamma_{X_S}\, d\ln(c_{X_S}) + \Gamma_{X_M}\, d\ln(c_{X_M})$$

not all amphiphiles form micelles.

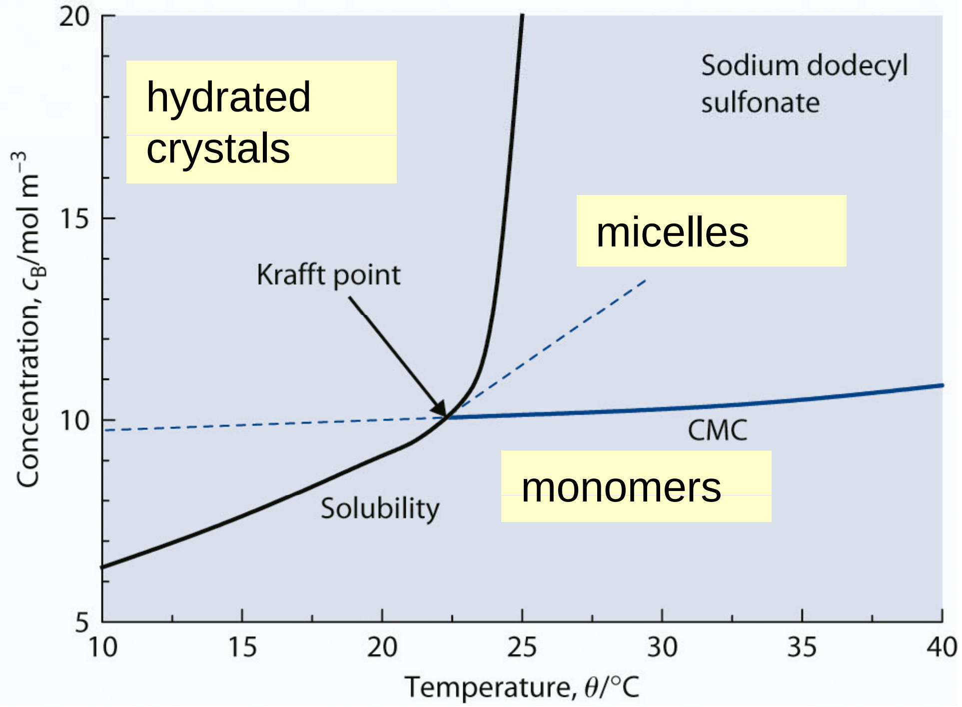
- at **cmc** other properties show distinct changes as well (e.g. osmotic pressure indicate that the number of “solute particles” stays the same above cmc).
- formation of micelles means decrease in G, primarily due to large **increase** in entropy: hydrophobic interaction.





Micelles: influence of temperature

- For **ionic surfactants**:
  - the solubility of surfactants exhibits a sharp rise in above a certain temperature: **Krafft** temperature. Below Krafft temperature solubility is lower than CMC,
  - otherwise, solubility doesn't' depend significantly on temperature bu depends on the ionic strength

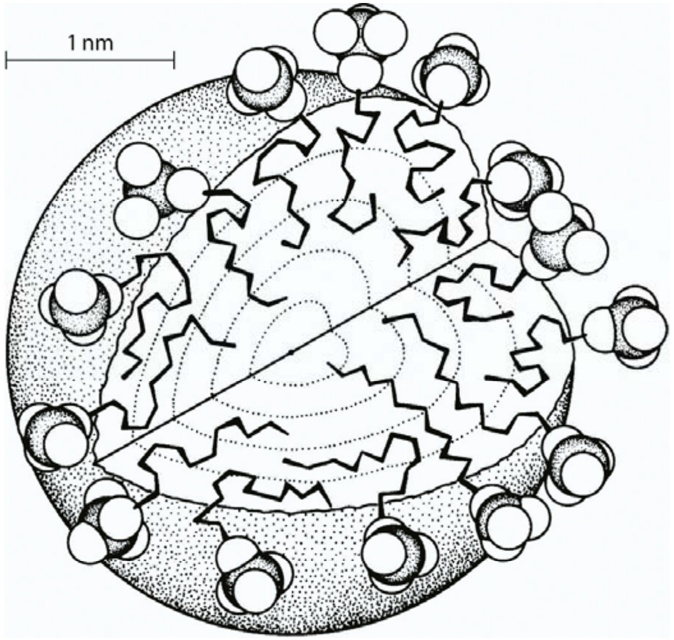


solubility is equal to CMC

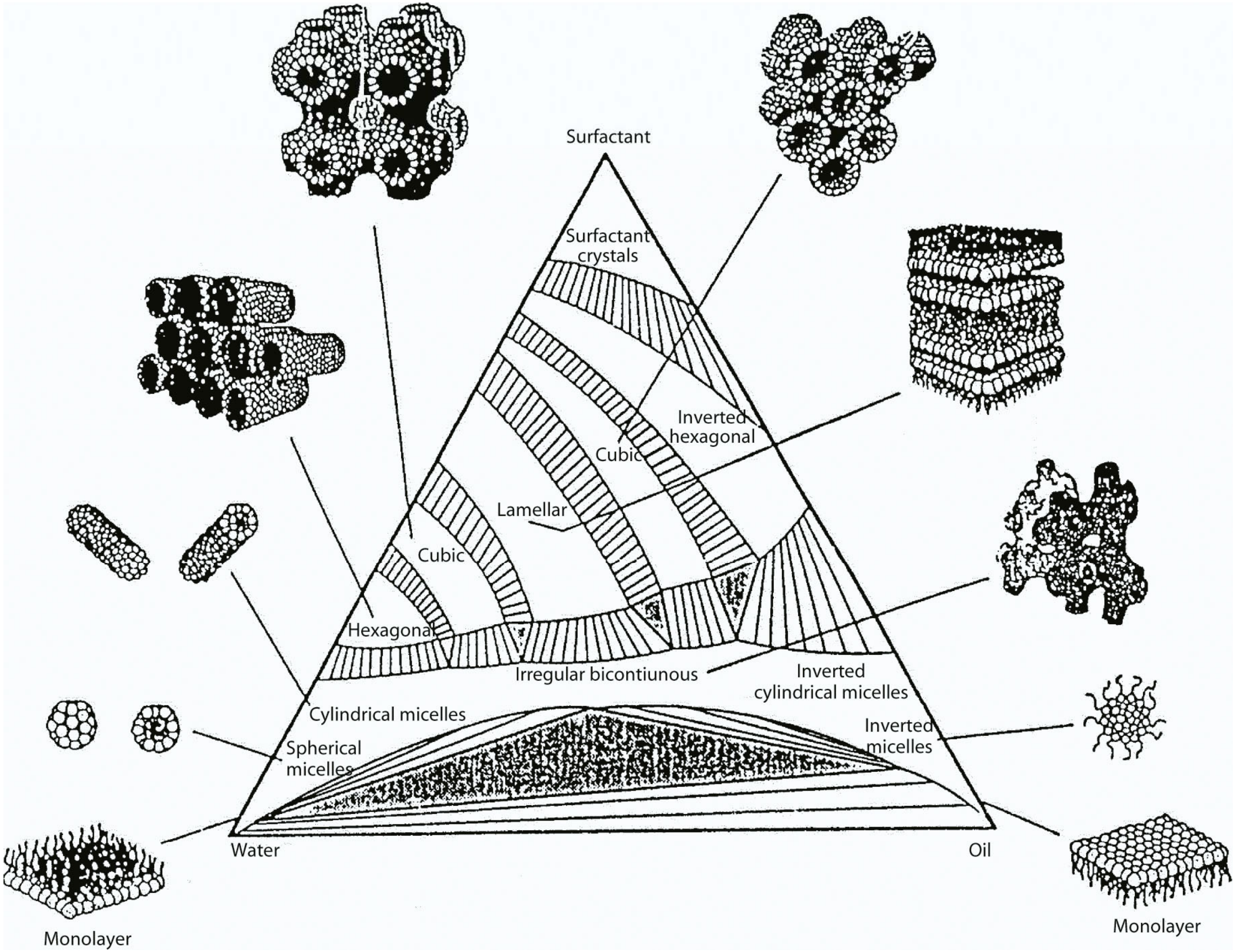
- for **non-ionic surfactants** raising temperature appears to decrease solubility, so above **cloud point** large aggregates of surfactant appear

Micelle structure

- the shape of micelle depends of several factors
- at low concentrations micelles are spherical with diameter slightly less than twice the length of the molecule
- at higher concentration, more complex structures are formed
- if organic solvent are used, **reverse (inverted) micelles** will be formed

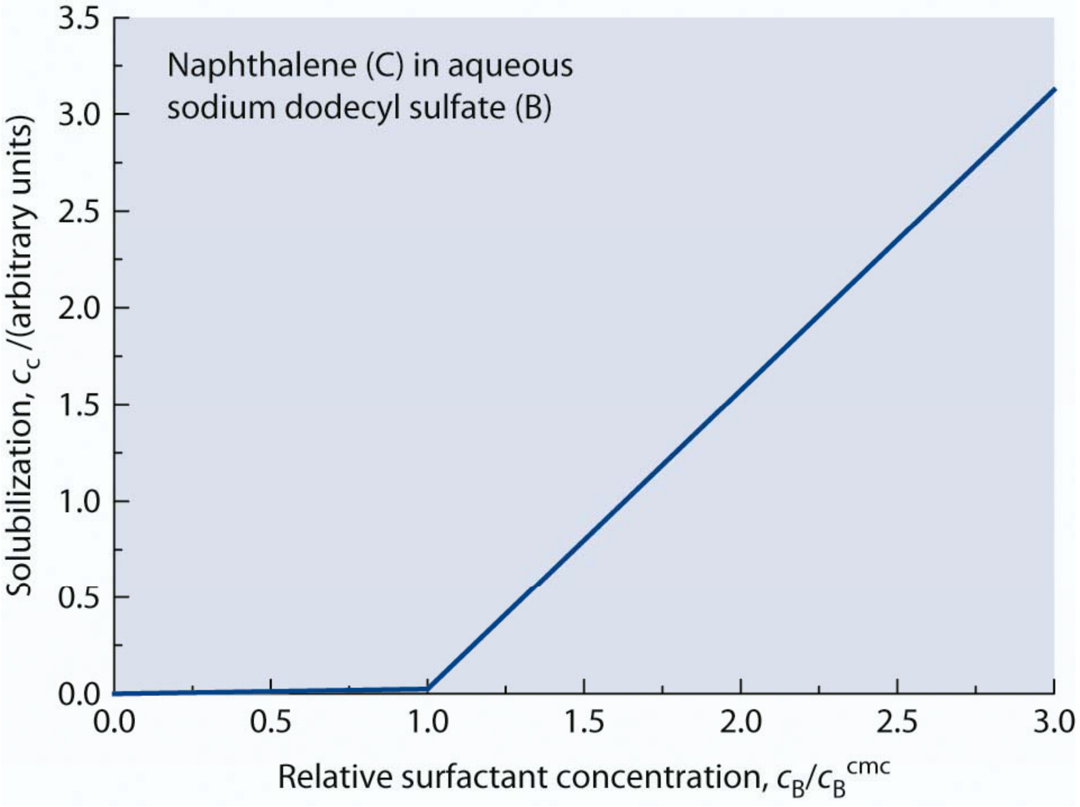


Micelle structure



Solubilization

- micelles can increase solubility of otherwise sparingly soluble substances, as the centre of a micelle is a liquid hydrocarbon



Self-Assembly of Amphiphilic Molecules

- sometimes can be hard and solid, but most of the time are soft and fluid like. Commonly referred as complex fluids.
- usually characterized by size distribution
- most important interactions: ionic repulsion of head groups and hydrophobic interaction of the tails.

Thermodynamics of Self-Assembly

- Let's consider surfactant in the solvent and in the micelle:

$$\mu_{sur}(solvent) = \mu_{sur}^{0} + RT\ln S$$

- at [S]=CMC the chemical potential of the surfactant in micelles and solution is equal:

$$\mu_{sur}(micelle) = \mu_{sur}^{0} + kT\ln CMC$$

- the molar Gibbs energy of micelle formation:

$$\Delta G_m^{micelle} = \mu_{sur}(micelle) - \mu_{sur}^{0} = RT\ln CMC$$

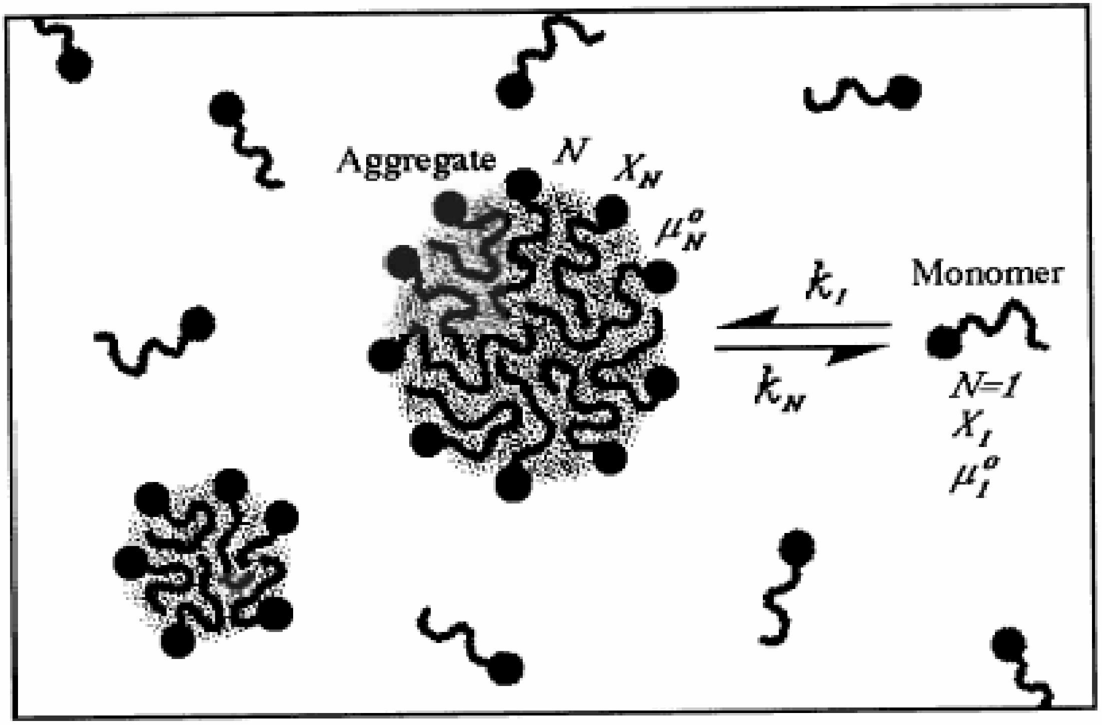
Thermodynamics of Self-Assembly

- If several aggregated structures are in equilibrium than the chemical potential of surfactant molecules in every structure is the same:

$$\mu = \mu_1^0 + kT \ln X_1 = \mu_2^0 + \tfrac{1}{2} kT \ln \tfrac{1}{2} X_2 = \ldots = \mu_N^0 + \tfrac{1}{N} kT \ln \tfrac{1}{N} X_N$$

Thermodynamics of Self-Assembly

- or, from kinetics



$$k_1 X_1^N = k_N \left(X_N / N \right)$$

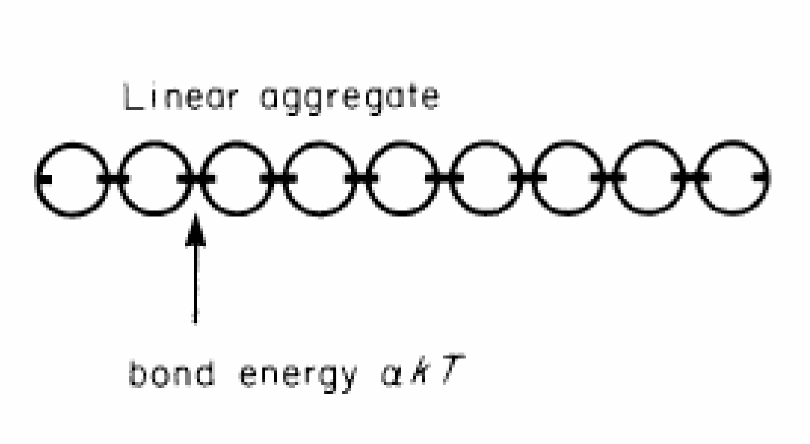
$$K = k_1 / k_N = \exp\left[-N(\mu_N^0 - \mu_1^0) / kT \right]$$

$$X_N = N\left(\left(X_M / M \right) \exp\left[M \left(\mu_M^0 - \mu_N^0 \right) / kT \right] \right)^{N/M}$$

$$X_N = N\left(\left(X_1 \right) \exp\left[\left(\mu_1^0 - \mu_N^0 \right) / kT \right] \right)^{N}$$

Formation of aggregates

- aggregates are formed if $\mu_N^0 < \mu_1^0$
- rod-like aggregates



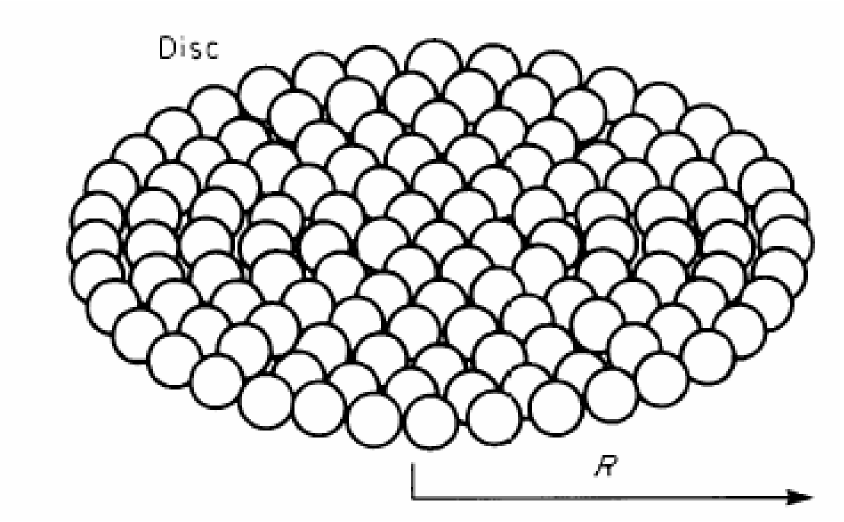
$$N\mu_N^0 = -(N-1)\alpha kT$$

$$\mu_N^0 = \mu_\infty^0 + \alpha kT / N$$

Formation of aggregates

- 2D aggregates

$$\mu_N^0 = \mu_\infty^0 + \alpha kT / N^{1/2}$$



- 3D aggregates

$$\mu_N^0 = \mu_\infty^0 + \alpha kT / N^{1/3}$$

CMC

$$X_N = N\left(X_1 \exp\left[\left(\mu_1^0 - \mu_N^0\right)/kT\right]\right)^N =$$

$$= N\left(X_1 \exp\left[\alpha\left(1 - 1/N^\alpha\right)\right]\right)^N \approx N\left[X_1 e^\alpha\right]^N$$

- as concentrations cannot be larger than 1 $X_1 < e^{-\alpha}$

$$\left(X_1\right)_{crit} = CMC = \exp\left[-\left(\mu_1^0 - \mu_N^0\right)/kT\right] \approx e^{-\alpha}$$

Aggregate distribution above CMC

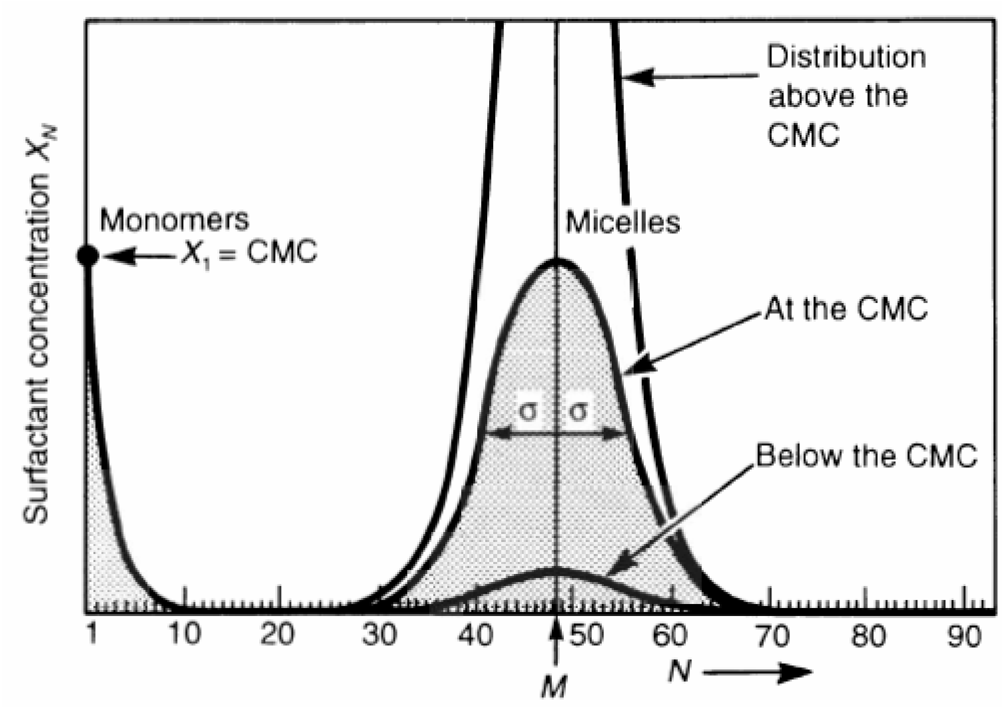
- discs, p=1/2 $$X_N = N\left[X_1 e^{\alpha}\right]^N e^{-\alpha N^{1/2}}$$
- spheres, p=1/3 $$X_N = N\left[X_1 e^{\alpha}\right]^N e^{-\alpha N^{2/3}}$$

- for disks and spheres there are very few aggregates of finate size, the transition goes to an aggregate of infinite size

- rods, p=1 $$X_N = N\left[X_1 e^{\alpha}\right]^N e^{-\alpha}$$

- for rods we expect a polydispersed distribution

Aggregate distribution above CMC



- Mean aggregation number: $N_{\max} = M = \sqrt{Ce^{\alpha}}$

Emulsion stability

- selection of emulsifier determines which type of emulsion will be formed

Bancroft rule: the phase the emulsifier is more soluble in will be the continuous phase

Harkins wedge theory: larger end of the emulsifier lies in the continuous phase

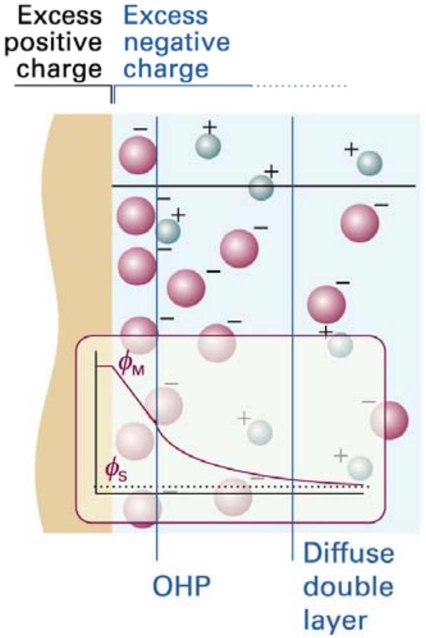
Winsor theory: based on ratio of cohesive energies

$$R = \frac{E_{LO}}{E_{HW}}$$

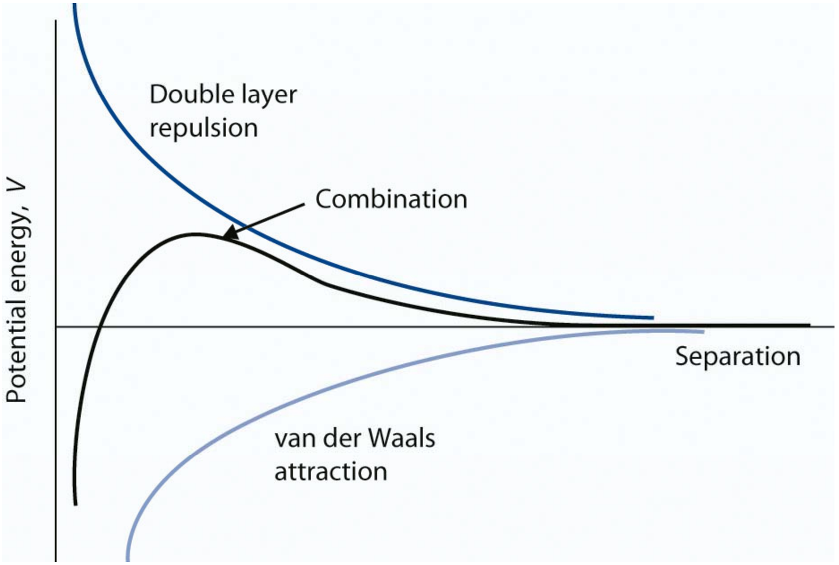
R<1 O/W emulsion is formed
R>1 W/O emulsion is formed

Emulsion stability

- in case of ionic emulsifier, the droplets will interact via **double layers**



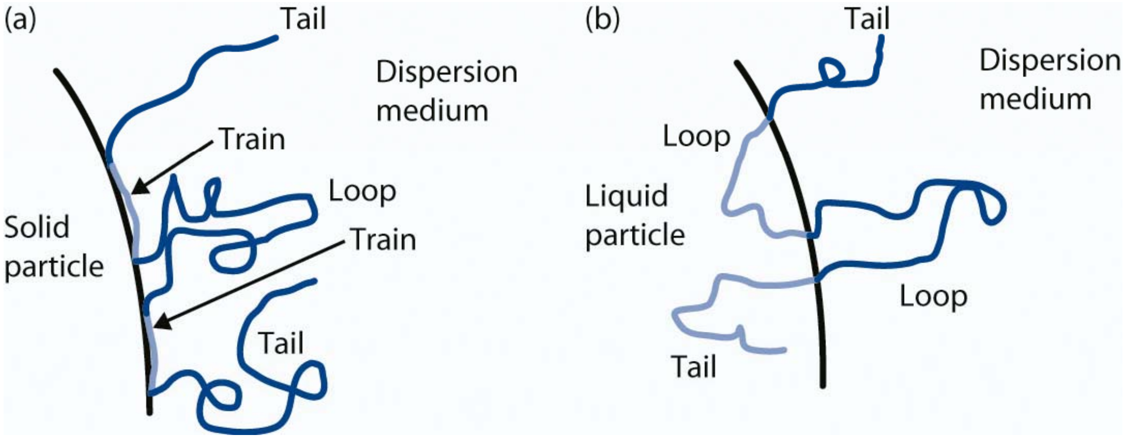
Stern model



- **Example:** stabilization of oil-water emulsions with inorganic electrolytes (e.g. KCNS) due to anions preferably adsorbed in oil

Emulsion stability

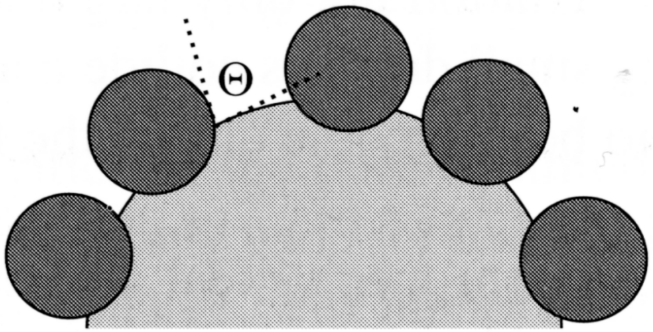
- Steric interaction:
  - loss of configuration entropy due to the excluded volume
  - higher osmotic pressure in the region where absorbed layers overlap
  - changes in the conformation of polymer loops due to approached droplet



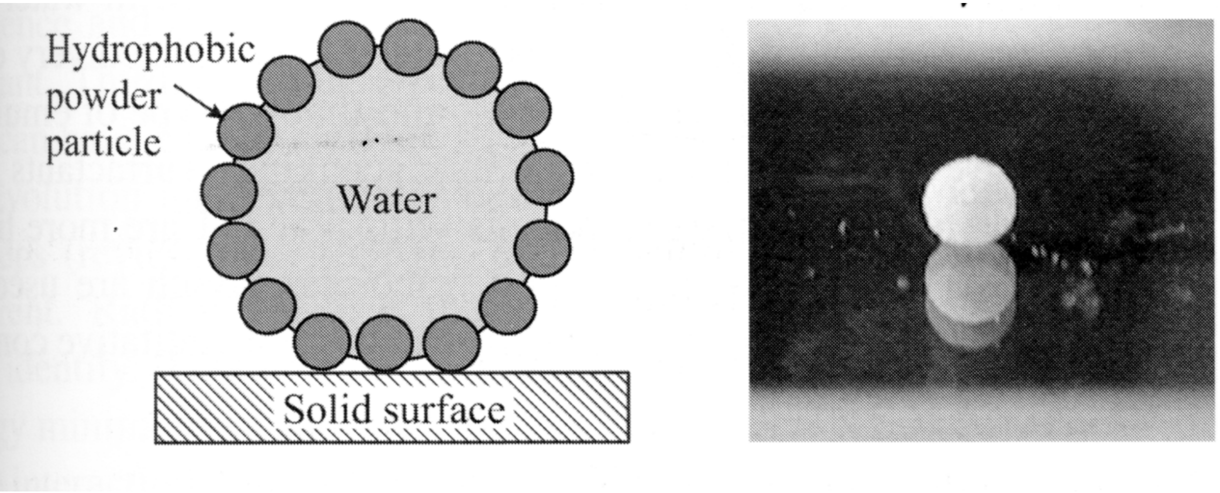
- stabilization by solid particles

Stabilization with solid particles

- For effective stabilization, the particles should assume a stable position on the interface with a non-zero contact angle (Pickering emulsions or solid-stabilized emulsions)

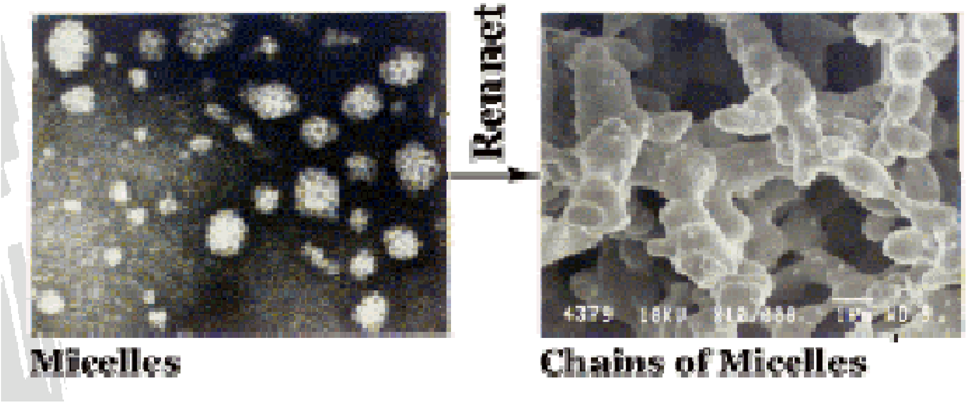


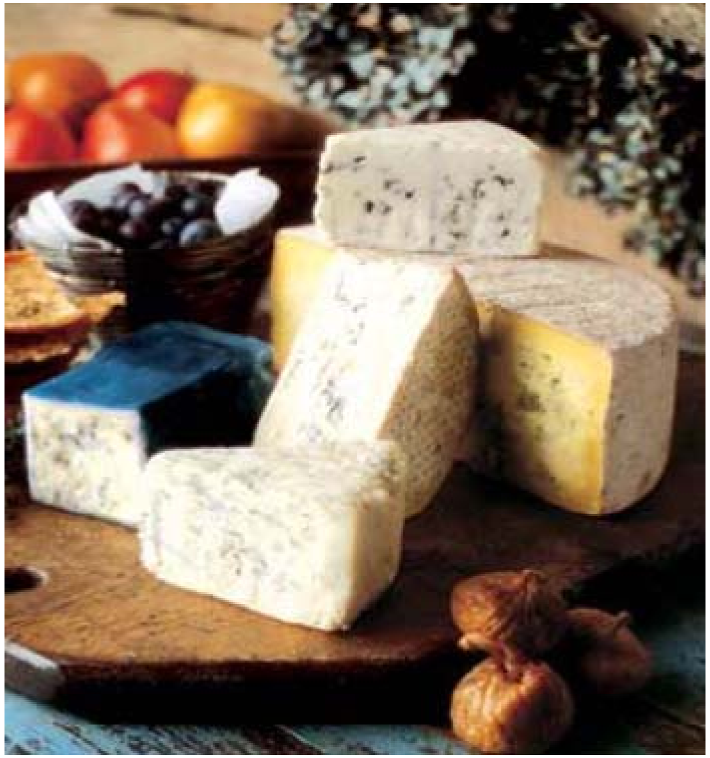
liquid marble on solid surface stabilized with hydrophobic powder



Cheese case

- Casein micelles in milk are sterically stabilized by κ-casein;
- Active enzyme: Proteinase rennin, originally obtained from calf stomach, currently synthesized in bacterial host, e.g. under a name Chymosin.
- Function: cuts the hydrophilic tail of κ-casein, therefore destroying sterical stabilization of casein micelles
- Other substances involved: $CaCl_2$ accelerates aggregation by screening negative charges





Problems

- A surfactant solution of sodium dodecyl sulfonate (SDS) (concentration 1.7 mmol kg^{-1}) is found to have a surface tension of 63 mN m^{-1} at 25ºC. Calculate the adsorption of the surfactant at the air/solution interface and state the two assumptions that are required. The surface tension of pure water at this temperature is 72.0 mN m^{-1}.
- Estimate CMC for Hexane in water. Surface tension of Hexane-Water interface is 51.1mN/m