

Micelle Formation

Lecture: Colloidal Phenomena



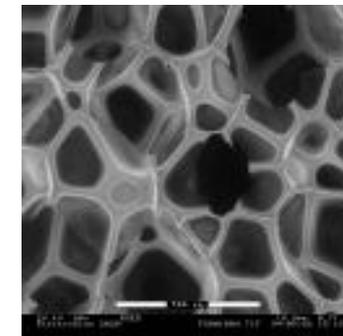
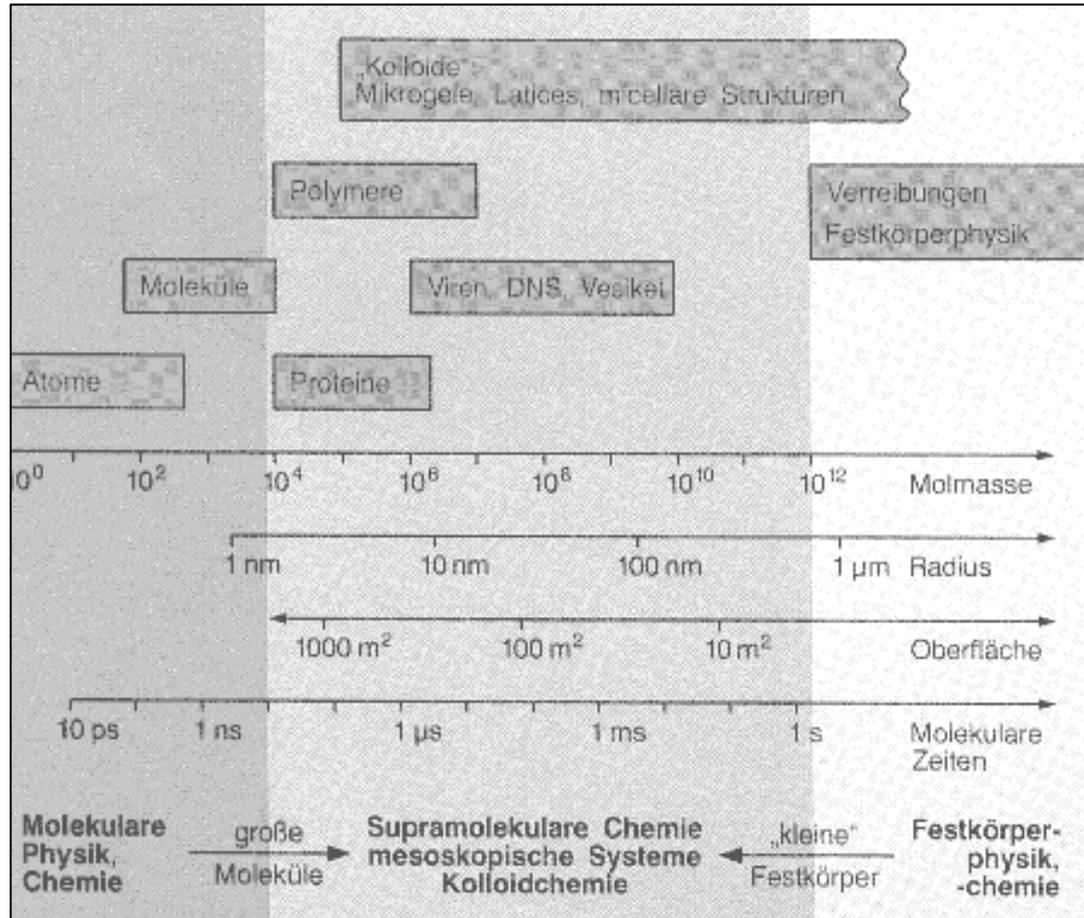
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0331-567 9509

What is a Colloid?

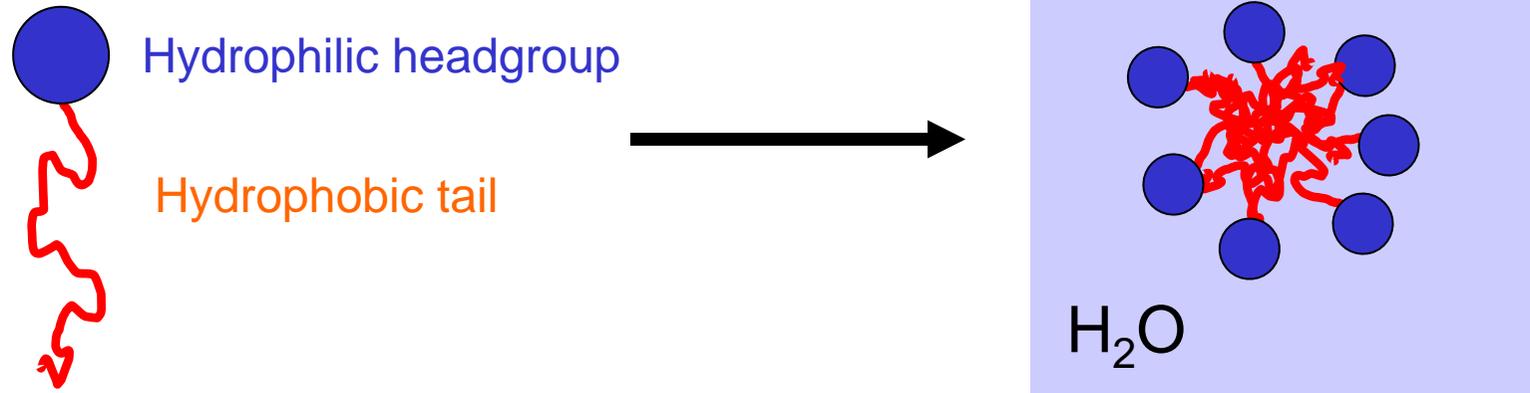
Colloid science is the study of systems involving small particles of one substance suspended in another



→ Colloid chemistry is closing the gap between molecular chemistry and solid state properties!

Micelles (“Aggregation colloids”)

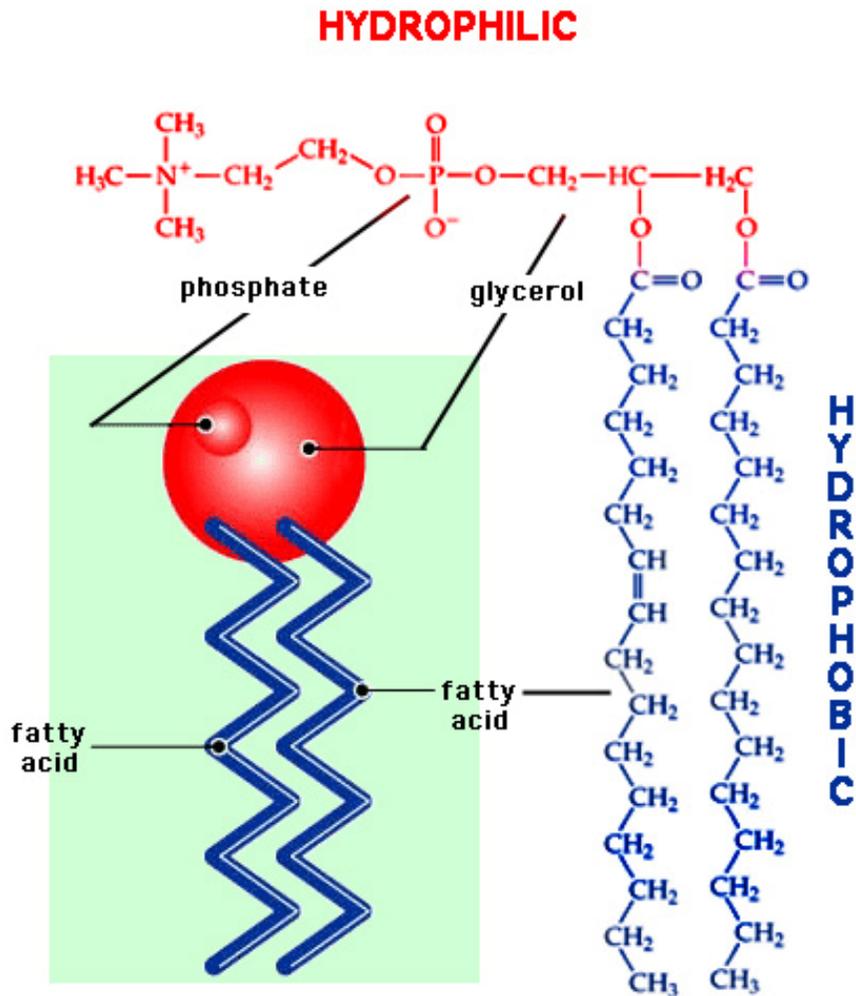
Outline



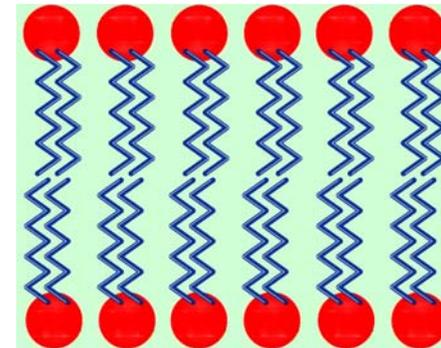
1. Surfactants/Introduction
2. Basics of micellization: characterization and properties
3. Micelle formation mechanism
4. Semiquantitative predictive models of micellization
(Tanford, Israelachvili, Ruckenstein, Nagarajan)
5. What is the “deeper” reason for self-assembly?

1. Surfactants

Zwitterionic surfactants: Phospholipids



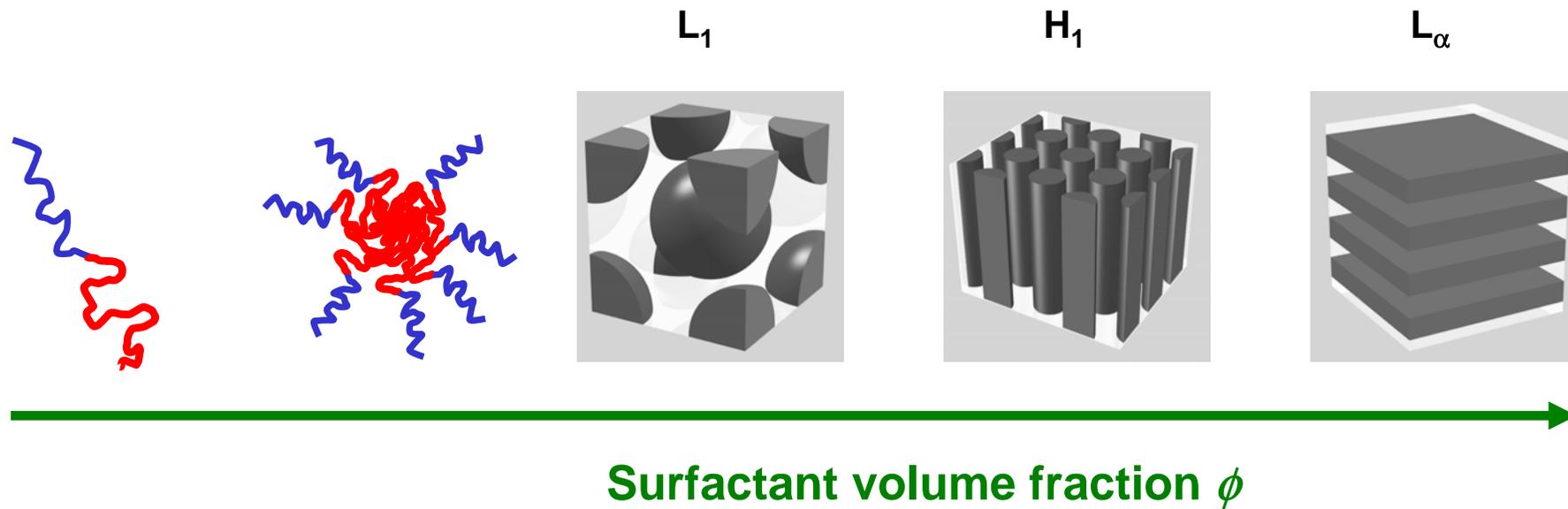
Phospholipids are the building block of biological membranes



Phosphatidylcholin (Lecithin)

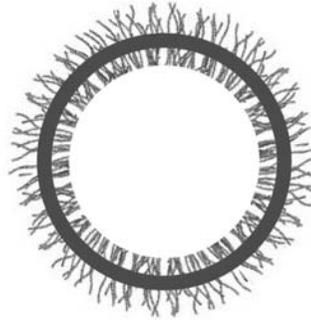
Introduction: Self-assembly of surfactants in water

Formation of liquid crystals („lyotropic mesophases“) upon increase in the surfactant concentration

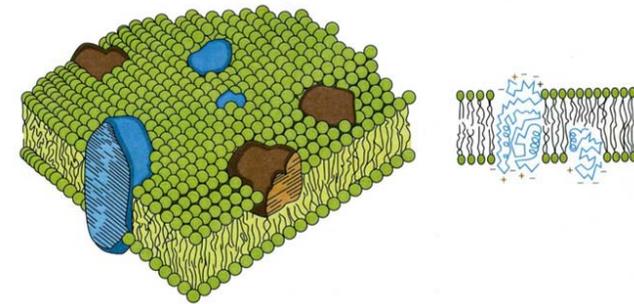


Why are micelles/self-assembled structures of interest at all?

1) Living organisms:



Cells = vesicles



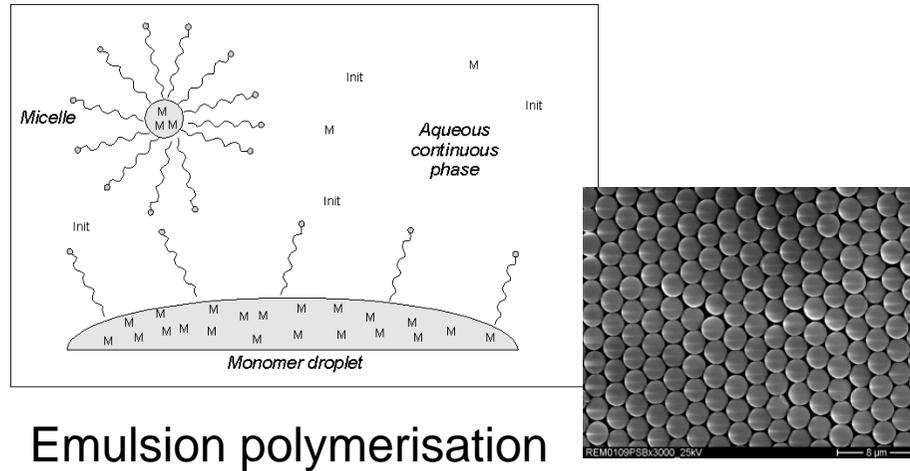
2) Applications of surfactants:

Cleaning/Detergents (40%), Textiles, Cosmetics, Paper Production, Paint, Food, Mining (Flotation).....



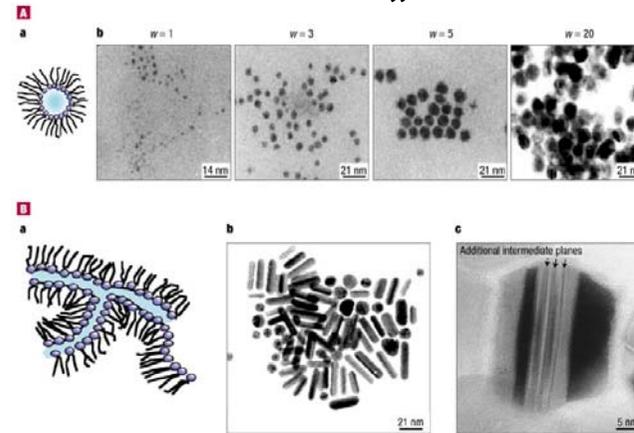
Surfactant production per year: ~40 billion tons

3) Chemical reactions in micelles:



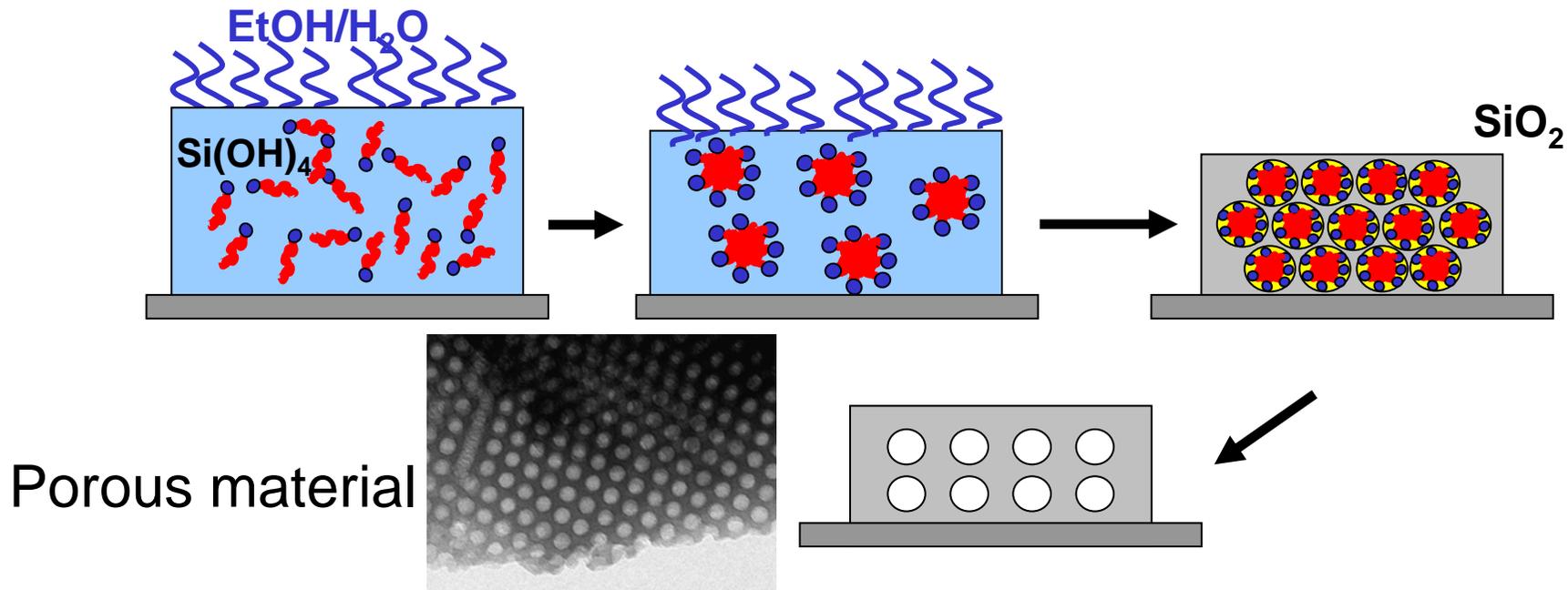
Emulsion polymerisation

Micelles as „nanoreactors“



The role of soft colloidal templates in controlling the size and shape of inorganic nanocrystals
Nature Materials 2, 145–150 (2003)

4) New materials through templating/casting



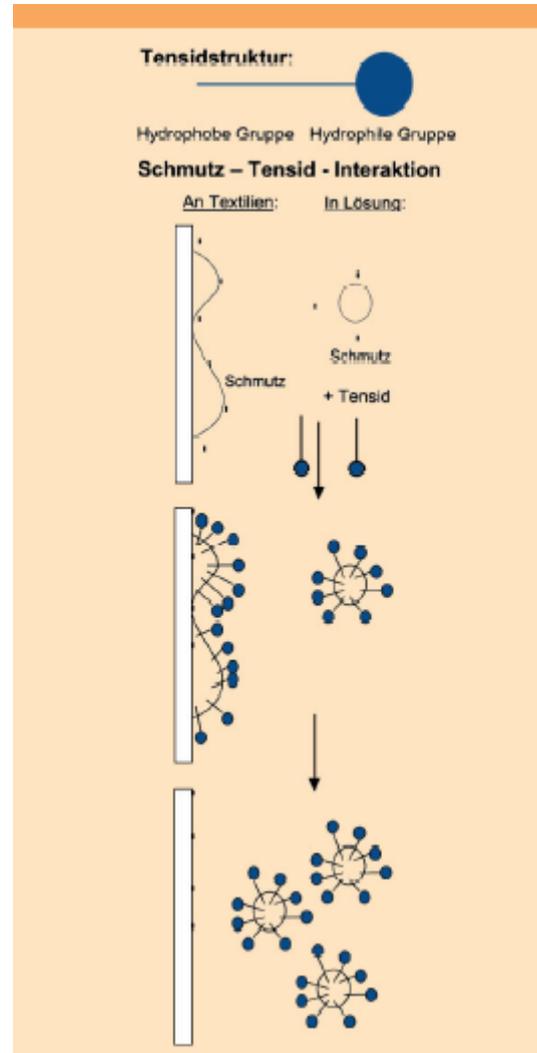
Porous material

Washing / Solubilization of other substances

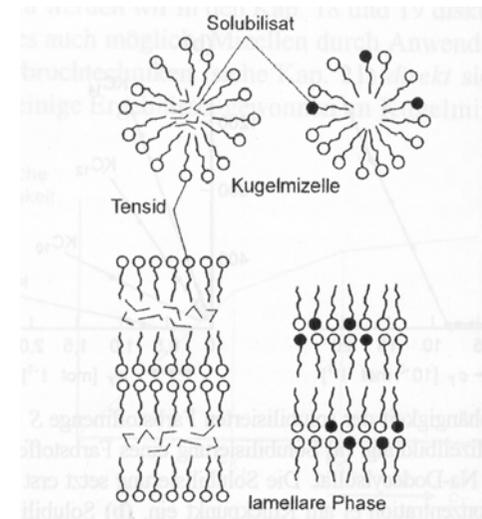


Chiuz, 2003

What happens during washing?



Solubilization by micelles



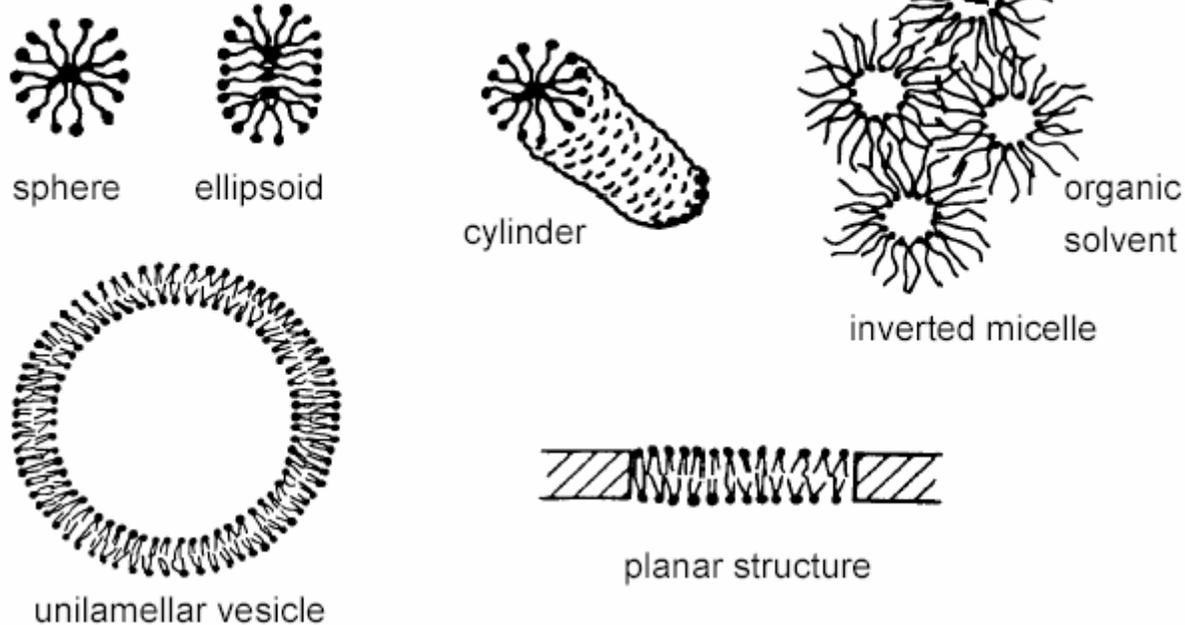
2. Basics of micellization: characterization and properties

Contents of this chapter:

- Characterization of micelles
- Basic properties of micelles
- The critical micelle concentration
- The Krafft temperature

Different shapes of micelles

Shapes of micelles and vesicles:

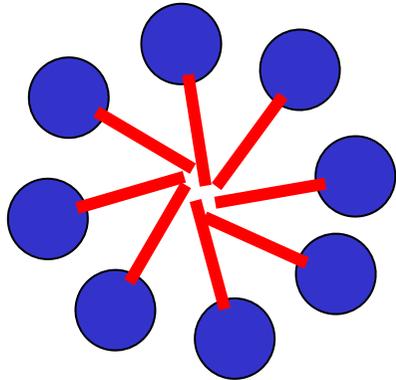


What determines the shape/size of micelles...?

- Head group size ?
- ionic strength ?
- Hydrophobic tail?

A didactic excursion: wrong illustrations of micelles

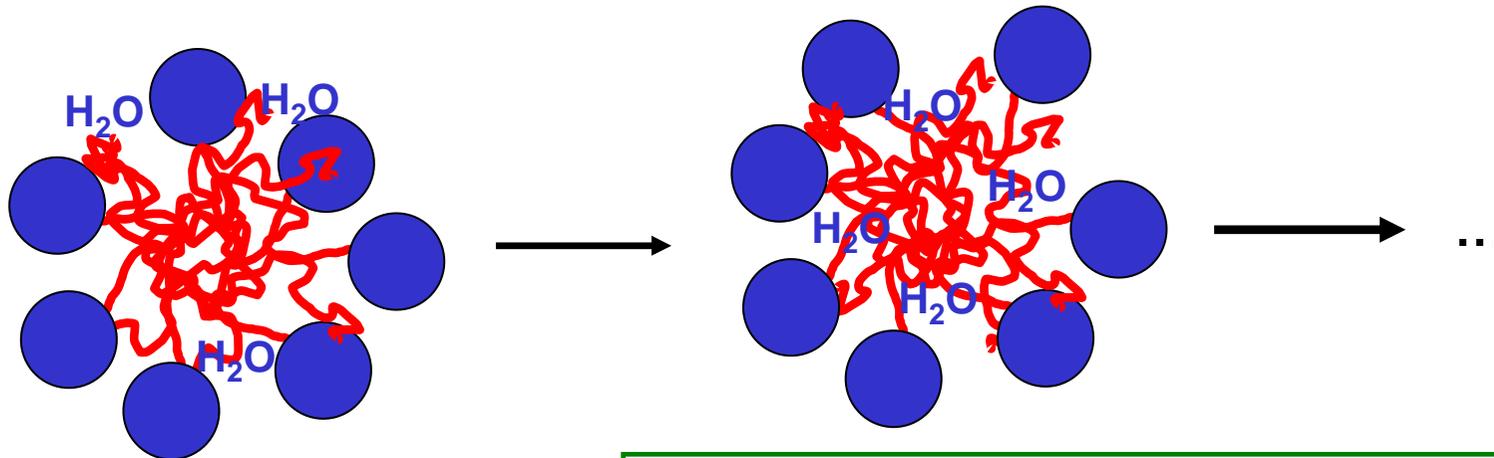
Standard figure seen in textbooks:



Wrong:

1. There is no denser core!
2. The heads are not so perfectly arranged
3. For normal surfactants, micelles are not shape-persistent

A more realistic illustration of micelles:

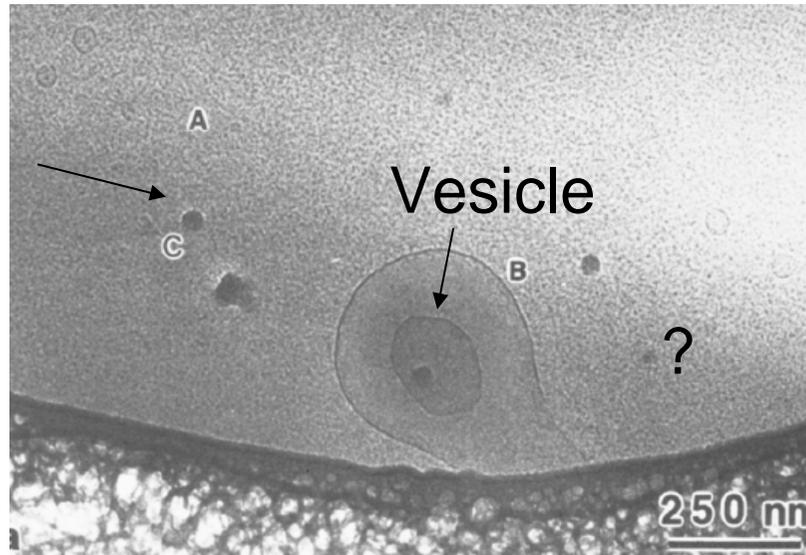


Pluronics: up to 30% of the core is water

Can micelles be seen by microscopic techniques ?

Special preparation techniques necessary:
„Cryo Transmission Electron microscopy“ (Cryo-TEM)

Micelle



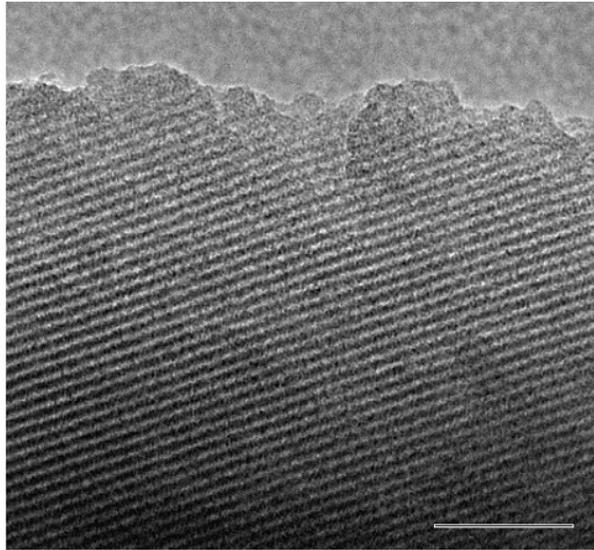
Evans, *Langmuir*,
1988, 34,1066.

Preparation:

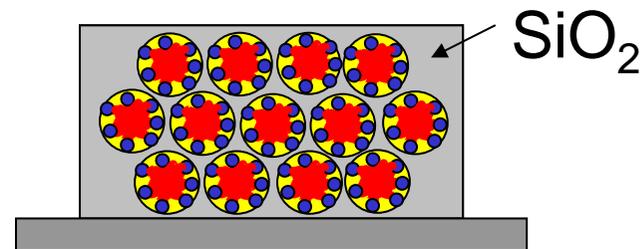
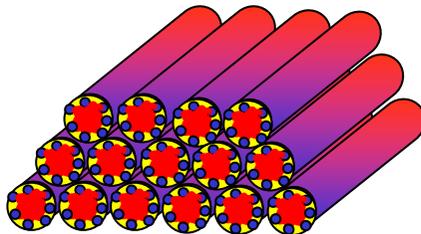
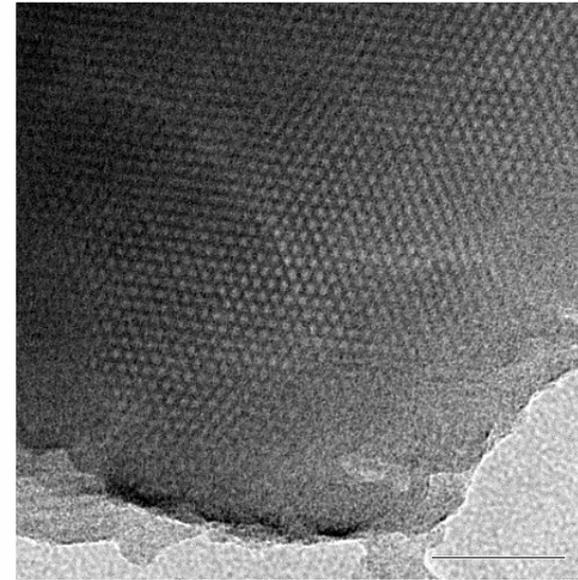
- 1) Controlled environmental chamber to minimize compositional changes
- 2) rapid thermal quenching of a thin layer of the sample in a liquid ethane slush (formation of vitrified ice).

Visualization of self-assembled structures

Cylindrical micelles forming a stable 2D hexagonal lattice in a SiO_2 matrix

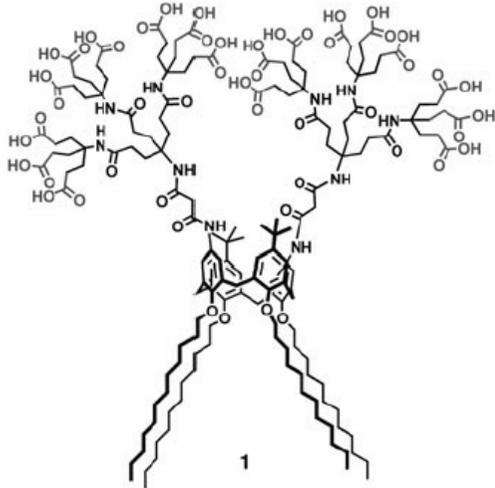


50 nm

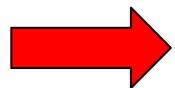
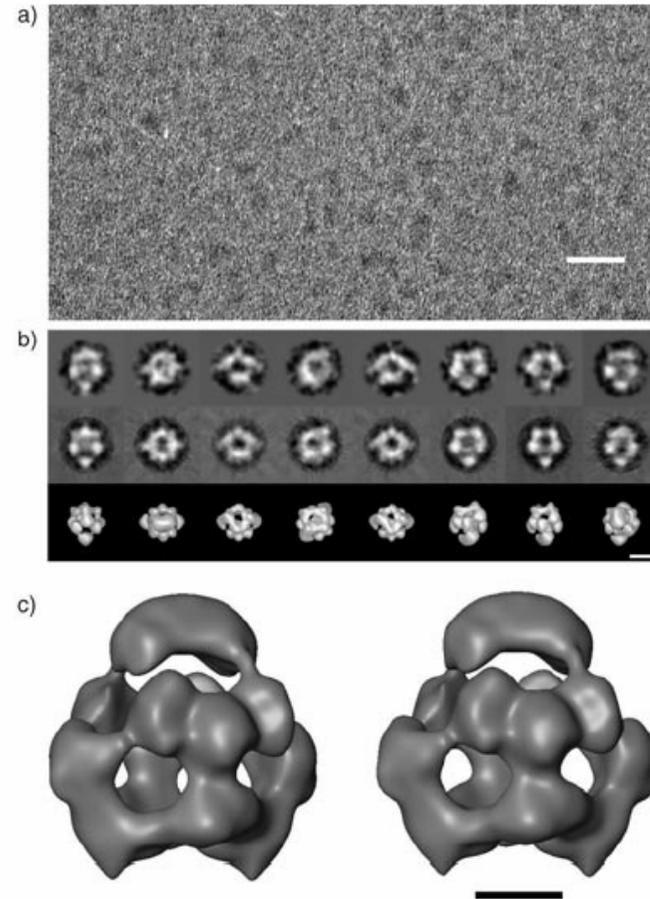
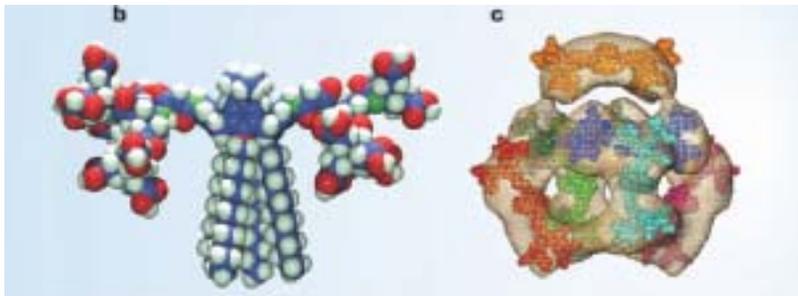


Pore structures can be seen as „cast“ of the micellar structure (Nanocasting)

Shape persistent micelles

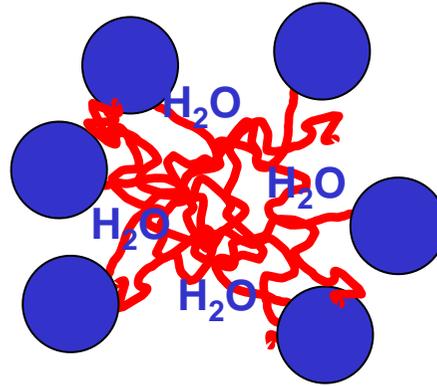


„The first account
of a structurally
persistent micelle“
Böttcher et al.
Angew. Chemie,
2004, 43, 2959



Specific interactions / covalent linkages can lead to micelles, which do not change their size/shape!

Characterization of micelles



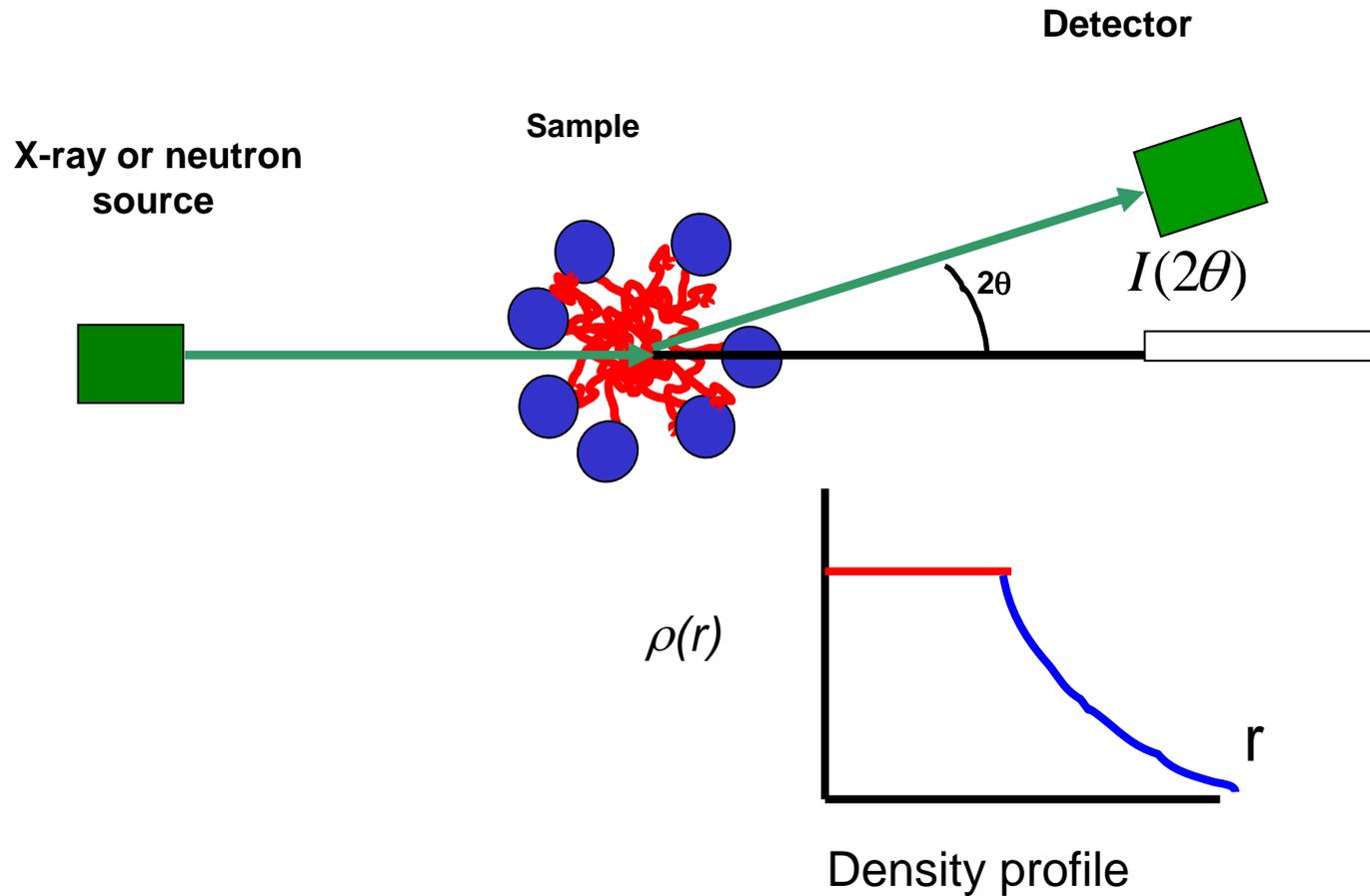
TEM, light scattering, surface tension, spectroscopy, ...

➔ ...but, just informations about the size, shape ...
of the overall micelle

What evidence does exist that the general core-shell picture
of micelles is correct?

➔ A non-invasive technique with nanometer resolution
is needed

Small-angle scattering of micellar objects



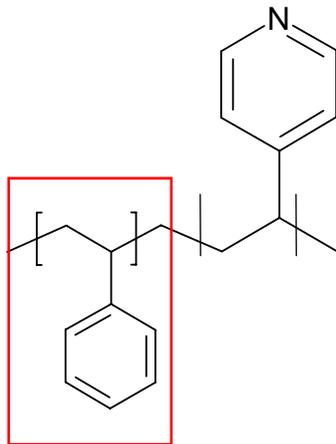
Coherent scattering of x-rays or neutrons:

$$I(2\theta) = \text{function}(\rho(r))$$

Contrast matching technique for small-angle neutron scattering

Poly(styrene)-*b*-poly(4-pyrrolidone) forms inverse micelles in toluene

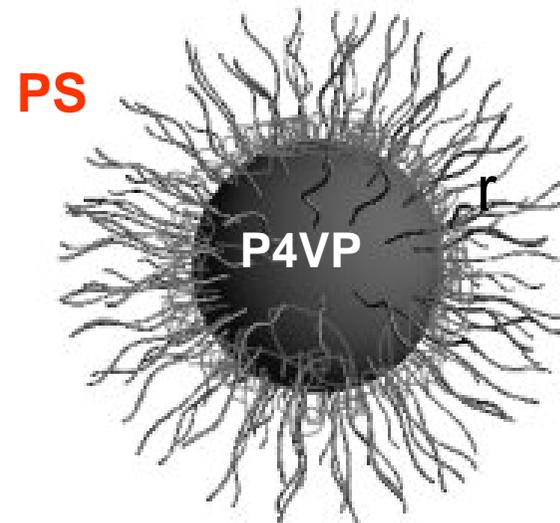
PS_{120,d8}-P4VP₁₁₈



deuterated PS



toluene

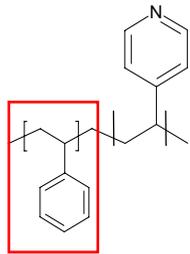


hairy micelles

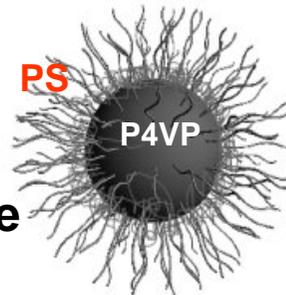
Contrast matching technique for small-angle neutron scattering

Poly(styrene)-b-poly(4-pyrrolidone) forms inverse micelles in toluene

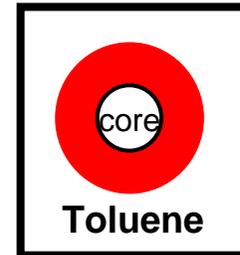
PS_{120,d8}-P4VP₁₁₈



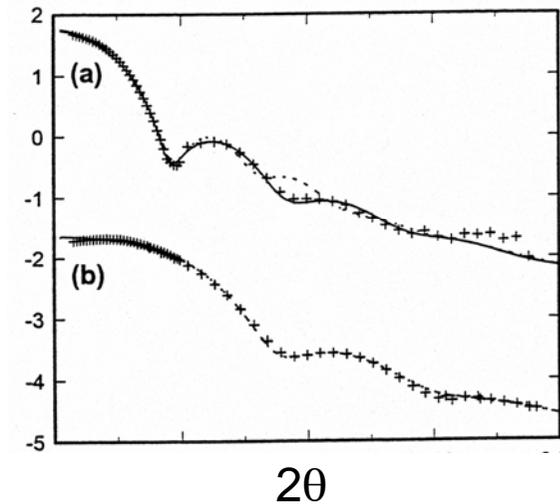
toluene



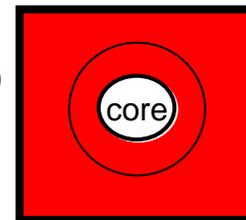
a)



Scattering of the corona



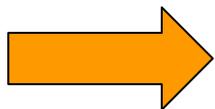
b)



Scattering of the micelle core

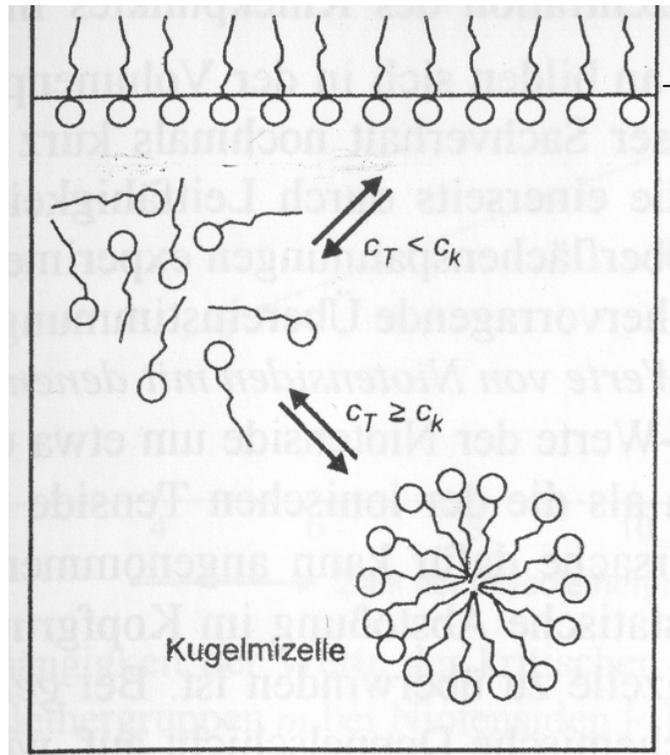
Results:

$$R_{\text{Core}} = 12 \text{ nm}, R_{\text{micelle}} = 36 \text{ nm}$$



Parameters such as the radius, core/shell size, density profile, shape

The critical micelle concentration (cmc, c_k)



Air
Water

1. Small c : Adsorption of surfactants at the air-water interface
2. $c > cmc$: formation of micelles

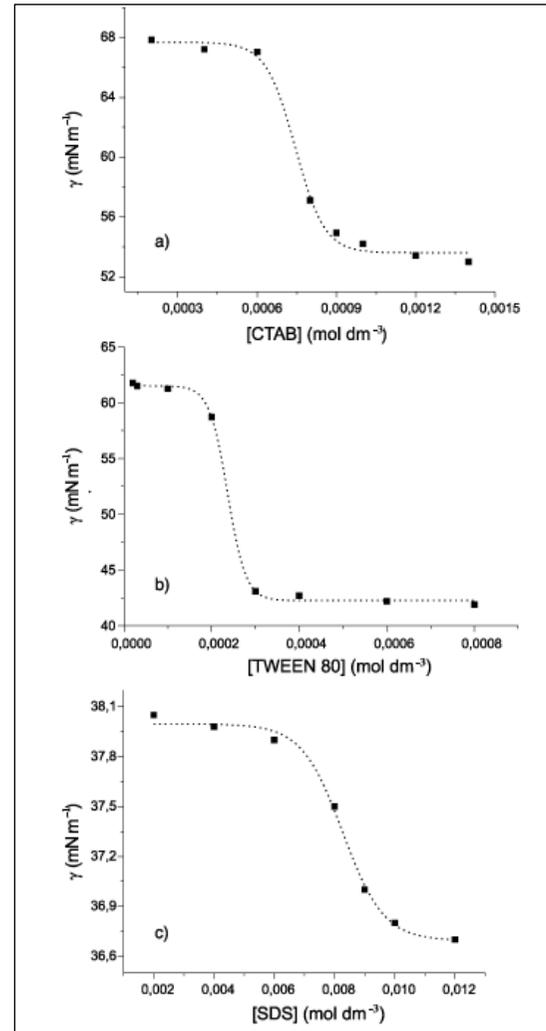
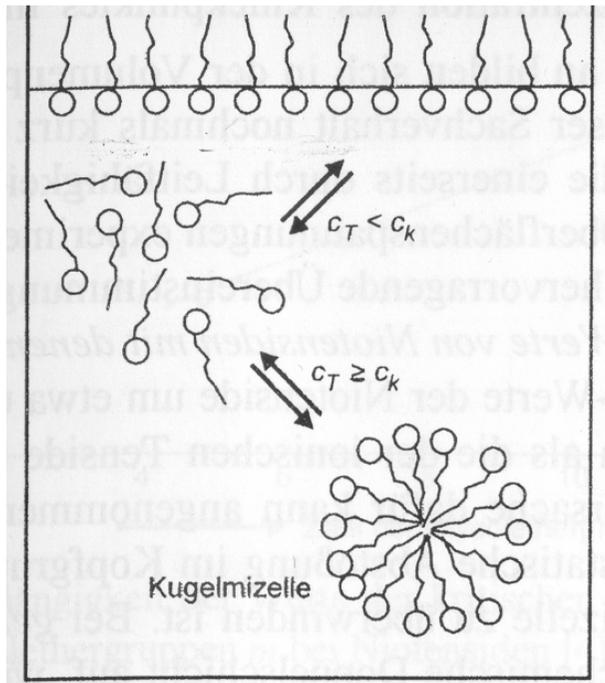
$cmc (c_k)$ = critical micelle concentration:

concentration, above which micelles are observed

$$\Delta G^\circ_{mic} = \mu^\circ_{mic} - \mu^\circ_{solv} = RT \ln (cmc)$$

The critical micelle concentration (cmc, c_k)

Surface tension at cmc

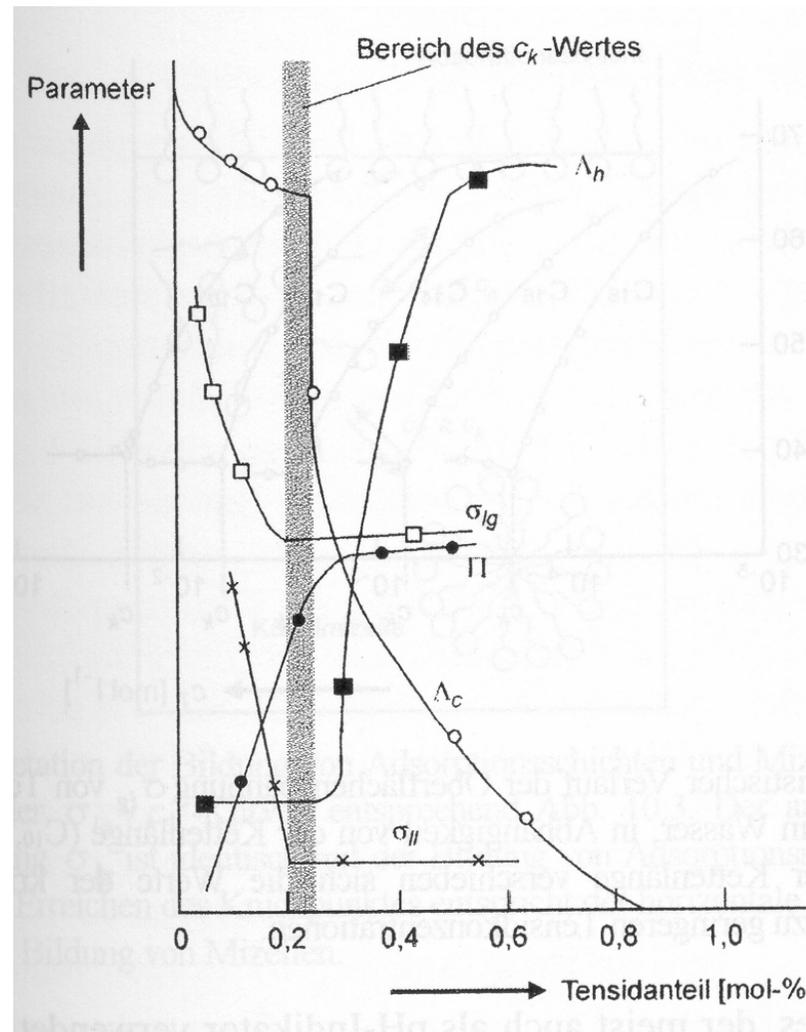
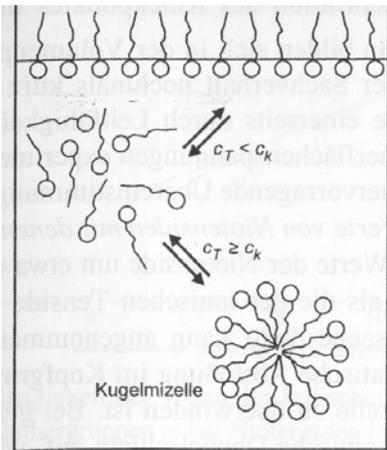


cmc of **nonionic** surfactants is generally **lower** compared to ionic surfactants



Abrupt changes at the cmc due to micelle formation!

The critical micelle concentration (cmc, c_k)

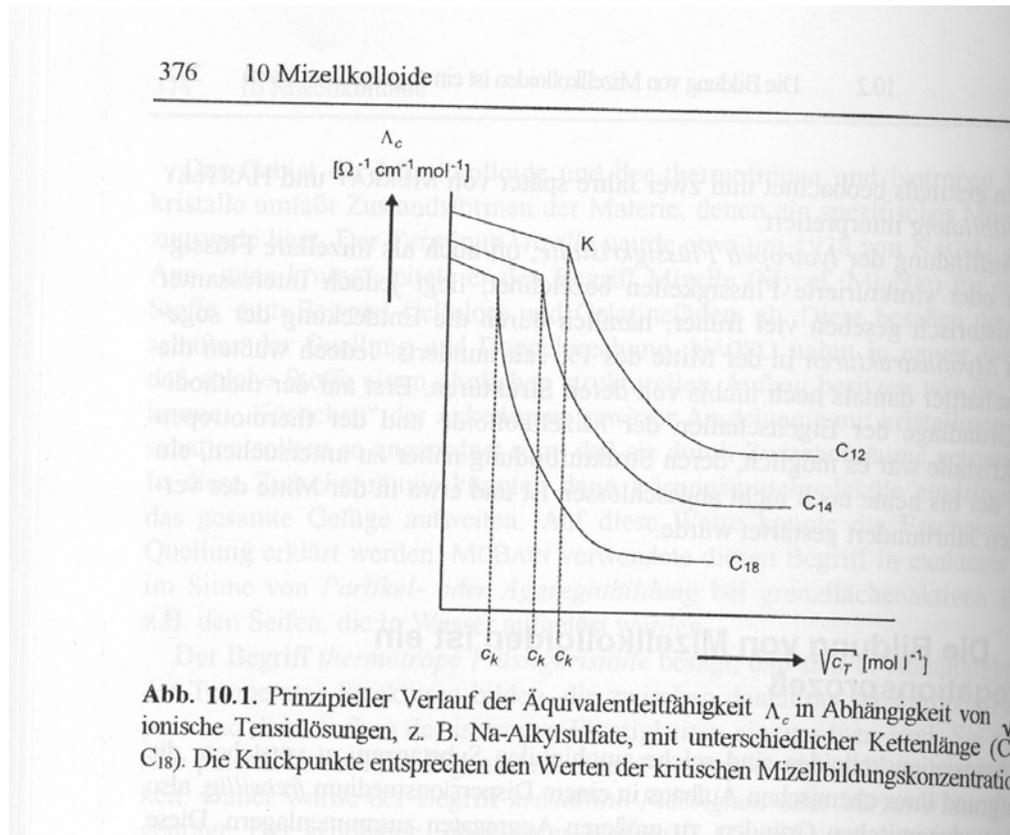


Typical behavior of selected physico-chemical parameters such as the equivalence **conductivity Λ_c** or the **surface tension σ** on the surfactant concentration

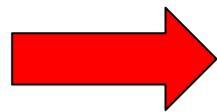
Ionic surfactants
Conductivity:
 $\Lambda_c \approx \mu$ (mobility)

 Abrupt changes at the cmc due to micelle formation!

Influence of the surfactant structure on the cmc: tail length



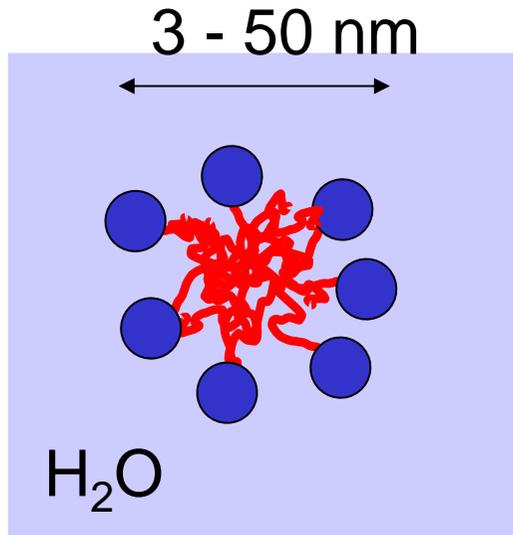
Ionic surfactants
Conductivity:
 $\Lambda_c \approx \mu$ (mobility)



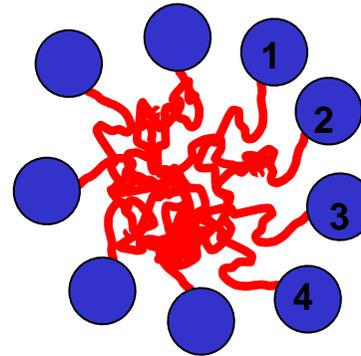
The cmc decreases with increasing tail length because the hydrophobic character increases

Summary: Some values about micelles

Micelle size:



Aggregation number:



Ionic surfactants

$$z_A = 10-170$$

Nonionic surfactants

$$z_A = 30-10.000$$

Critical micelle concentrations (CMC):

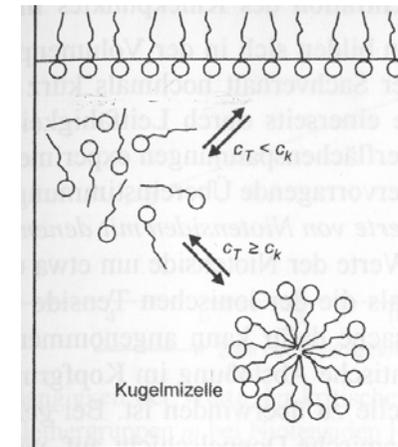
cmc of **ionic** surfactants
is generally **higher**
compared to nonionic surfactants

Ionic surfactants

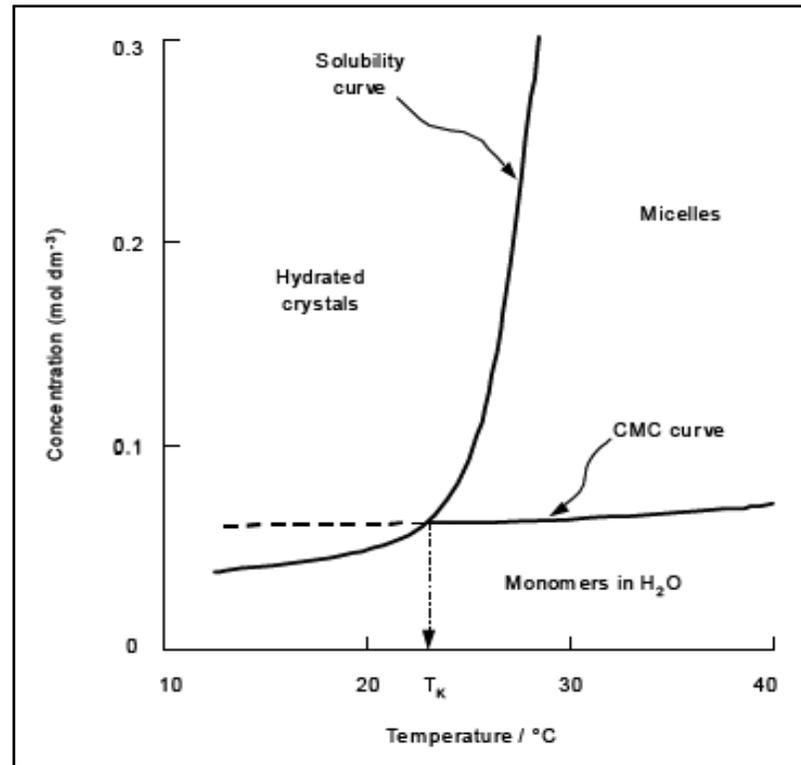
$$\text{cmc} = 10^{-3} - 10^{-2} \text{ M}$$

Nonionic surfactants

$$\text{cmc} = 10^{-4} - 10^{-3} \text{ M}$$



Solubility of surfactants-The Krafft temperature



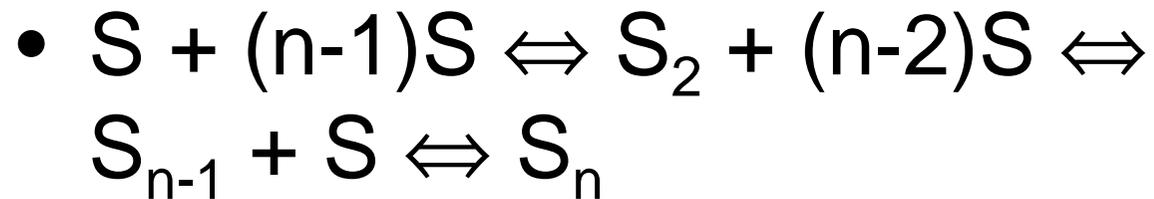
Binary
phase diagram
surfactant/water

- Solubility of surfactants highly T dependent
- Solubility is usually low at low T, rising rapidly in narrow range
- No micelles possible above a certain temperature
- The point where solubility curve meets CMC curve is the Krafft point, which defines the T_{krafft} .
- The Krafft temperature can be regarded as a „melting point“

3. Micelle formation mechanism

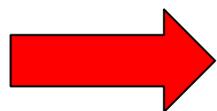
Stepwise growth model (Isodesmic model)

S: surfactant molecule

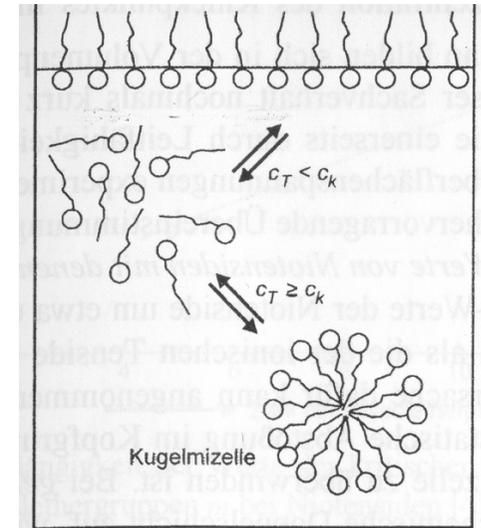


- Aggregation is a continuous process (broad aggregation, no cmc)

- Distribution of species



Not in agreement with sudden changes at cmc



3. Micelle formation mechanism

Closed aggregation model

aggregation number n dominates

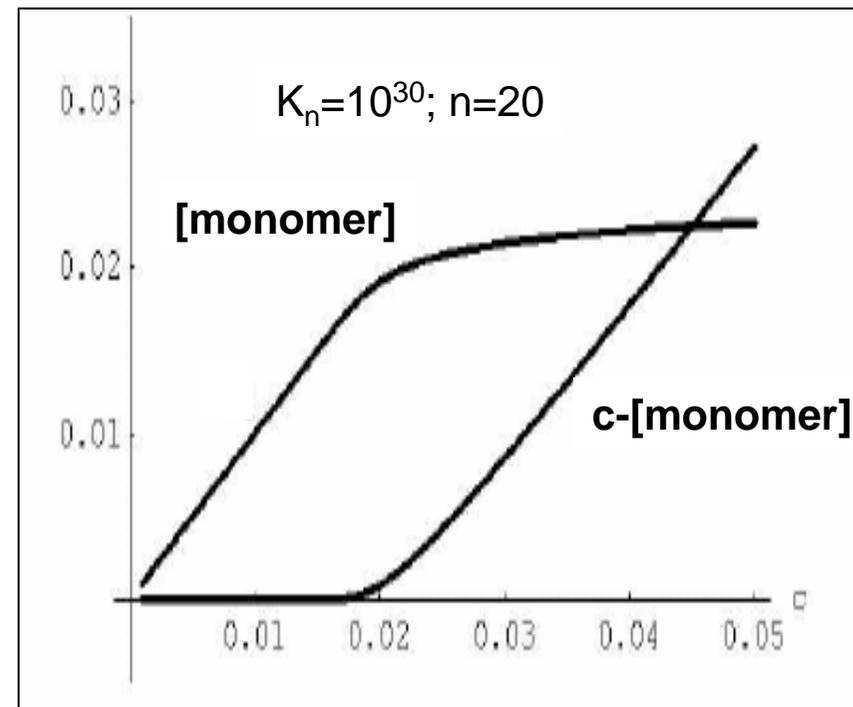
– (when $n \rightarrow \infty$, phase separation model)



→ cooperative phenomenon!

$$K_n = [\text{micelles}]/[\text{monomers}]^n = [S_n]/[S]^n$$

$$\text{CMC} = (nK_n)^{-1/n}$$

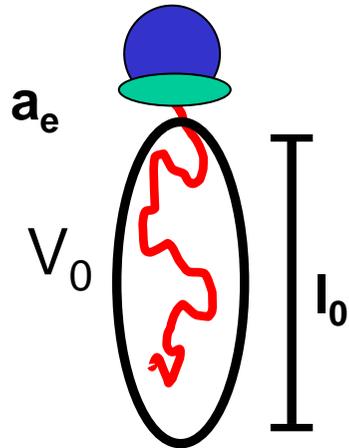


4. Semiquantitative predictive models of micellization

Contents of this chapter:

- Concept of the packing parameter (Israelachvili, 1976)
for the prediction of micelle shapes and sizes
- Which energetic contributions determine the micellization?
(Tanford-modell + extention by Nagarajan and Ruckenstein)
- Application to basic features of micellization

The concept of the “packing parameter P” (Israelachvili, 1976)

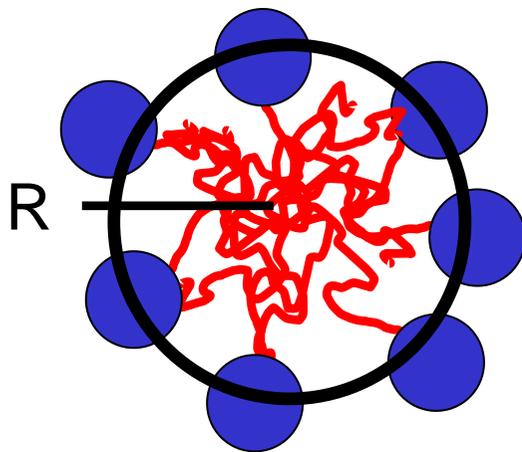


$$P = V_0 / (a_e l_0)$$

V_0 surfactant tail volume
 a_e **equilibrium** area per molecule at the aggregate interface
 l_0 tail length

Common surfactants:
 $v_0/l_0 = \text{const.} = 0.21 \text{ nm}^2$ (single tail)

Example: Spherical micelle with aggregation number g



$$\left. \begin{aligned} V_{\text{core}} &= g V_0 = 4\pi R^3/3 \\ A &= g a_e = 4\pi R^2 \end{aligned} \right\} R = 3 V_0 / a_e$$

With $R \leq l_0$ ➔ $0 \leq V_0 / (a_e l_0) \leq 1/3$

The concept of the “packing parameter P” (Israelachvili)

Prediction of the shape of self-assembled structures in solution

Table 1. Geometrical Relations for Spherical, Cylindrical, and Bilayer Aggregates^a

variable	sphere	cylinder	bilayer
volume of core $V = gv_0$	$4\pi R^3/3$	$\pi R^2 l_0$	$2Rl_0$
surface area of core $A = ga$	$4\pi R^2$	$2\pi Rl_0$	$2l_0$
area per molecule a	$3v_0/R$	$2v_0/R$	v_0/R
packing parameter v_0/al_0	$v_0/al_0 \leq 1/3$	$v_0/al_0 \leq 1/2$	$v_0/al_0 \leq 1$
largest aggregation number g_{\max}	$4\pi l_0^3/3v_0$	$\pi l_0^2/v_0$	$2l_0/v_0$
aggregation number g	$g_{\max} (3v_0/al_0)^3$	$g_{\max} (2v_0/al_0)^2$	$g_{\max}(v_0/al_0)$

**Common surfactants:
 $v_0/l_0 = \text{const.} = 0.21 \text{ nm}^2$
(single tail)**



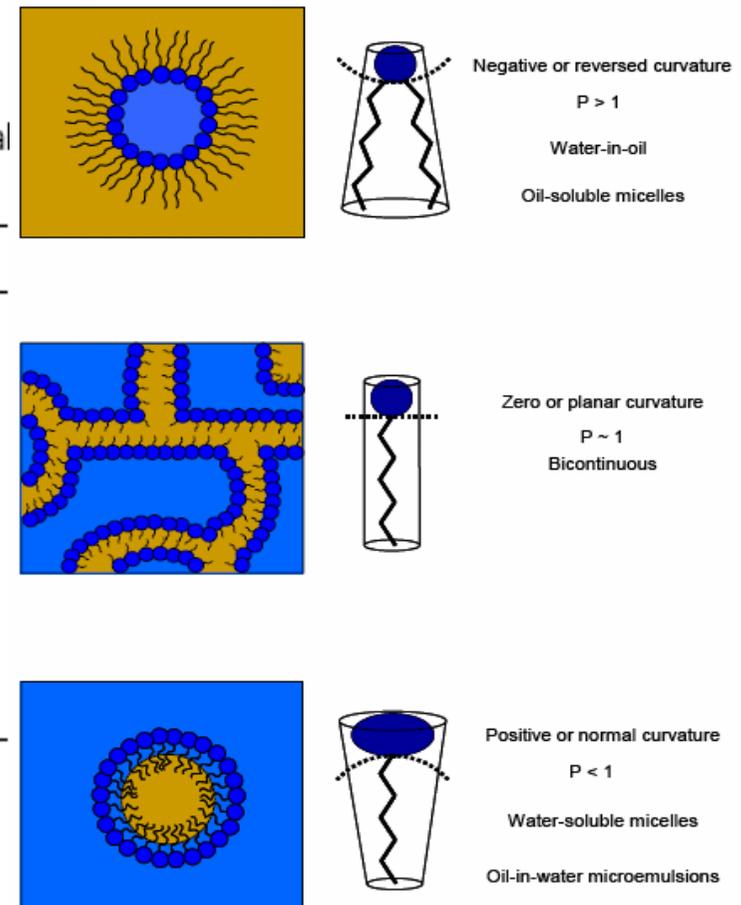
- Only the headgroup controls the equilibrium aggregate structure via the headgroup area a_e
- The tail does not have any influence on the shape and size of the aggregate

The concept of the “packing parameter P” (Israelachvili)

Table 2.1 Expected aggregate characteristics in relation to surfactant critical packing parameter, $P_c = v/a_0 l_c$

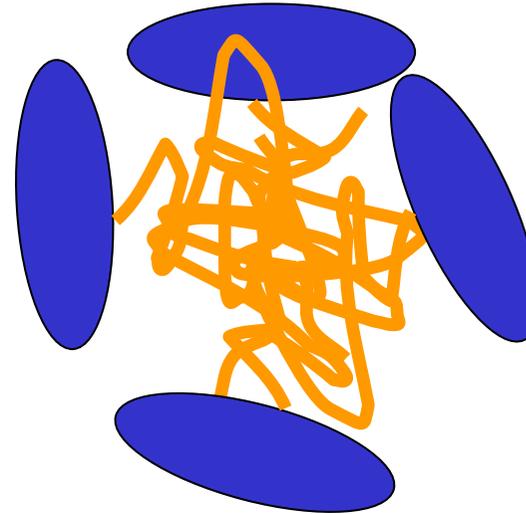
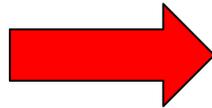
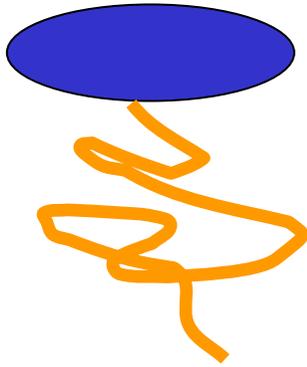
P_c	General Surfactant type	Expected Aggregate Structure
< 0.33	Single-chain surfactants with large head groups	Spherical or ellipsoidal micelles
0.33 - 0.5	Single-chain surfactants with small head groups, or ionics in the presence of large amounts of electrolyte	Large cylindrical or rod-shaped micelles Vesicles and flexible bilayers structures
0.5 - 1.0	Double-chain surfactants with large head groups and flexible chains	Planar extended bilayers
1.0	Double-chain surfactants with small head groups or rigid, immobile chains	Reversed or inverted micelles
> 1.0	Double-chain surfactants with small head groups, very large and bulky hydrophobic groups	

Figure 2.6 Changes in the critical packing parameters (P_c) of surfactant molecules give rise to different aggregation structures.



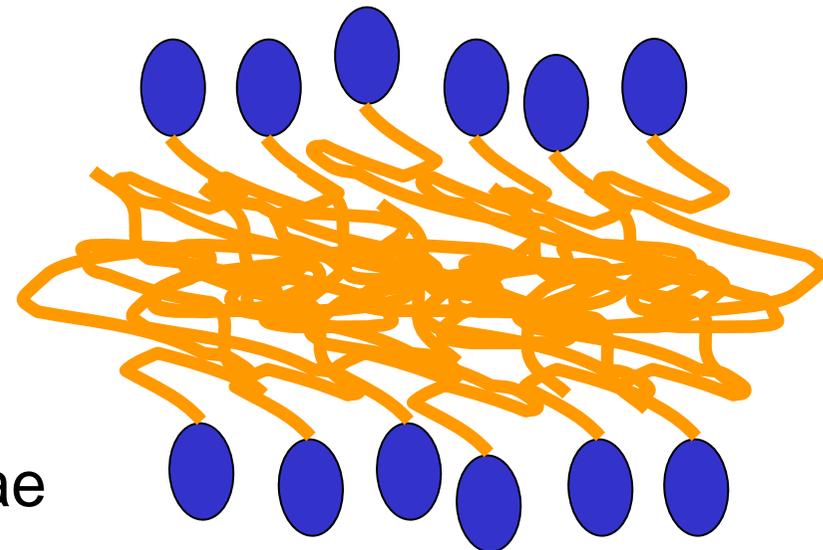
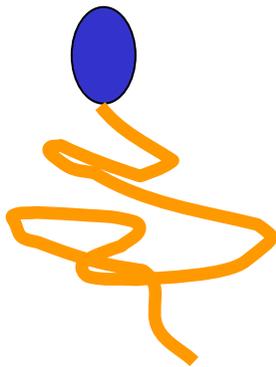
Predictions of the “packing parameter concept”

“Big headgroup” = large a_e :



Spherical
micelles

“Small headgroup” = small a_e :



lamellae

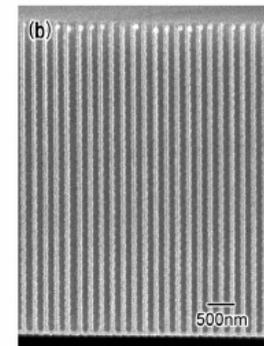
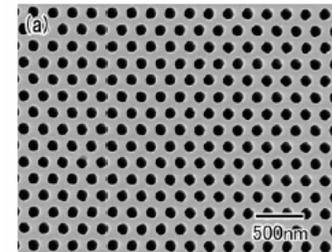
Predictions of the “packing parameter concept”

A model surfactant system

REPORTS

Self-Assembly of Mesoscopic Metal-Polymer Amphiphiles

Sungho Park, Jung-Hyurk Lim, Sung-Wook Chung, Chad A. Mirkin*



starting from commercial anodic alumina



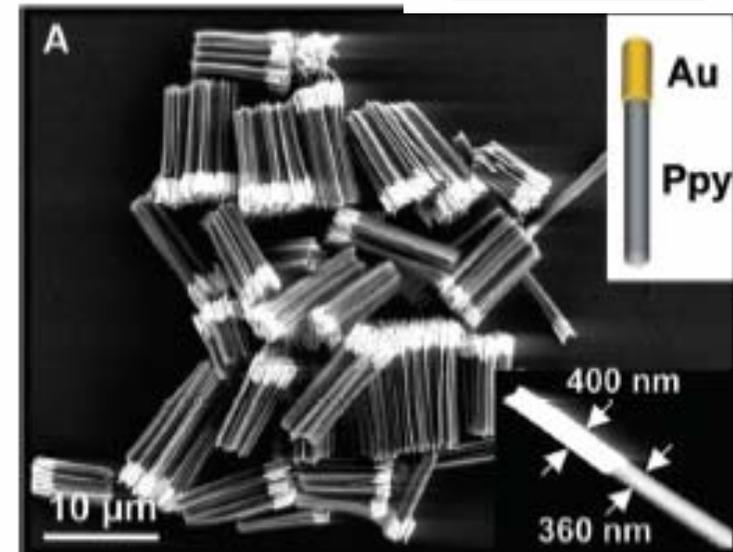
electro-deposition of gold



polymerization of polypyrrole

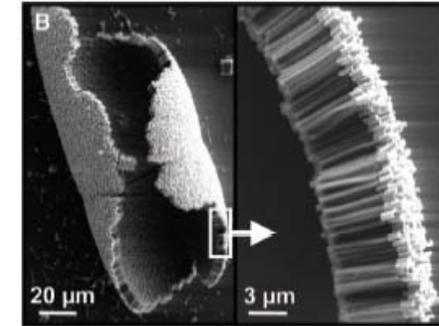
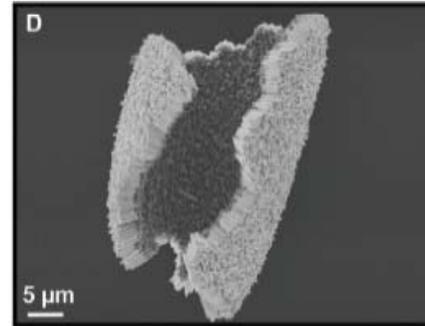
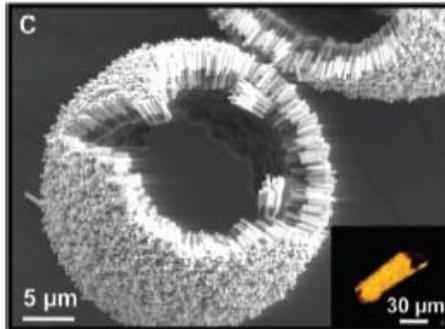


dissolution of the alumina membrane and the silver cathode and backing



Predictions of the “packing parameter concept”

A model surfactant system



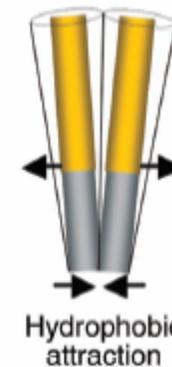
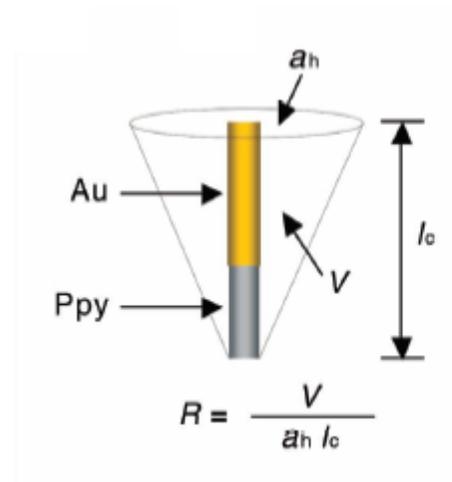
block length
ratio (Au/PPy)

3:2

4:1

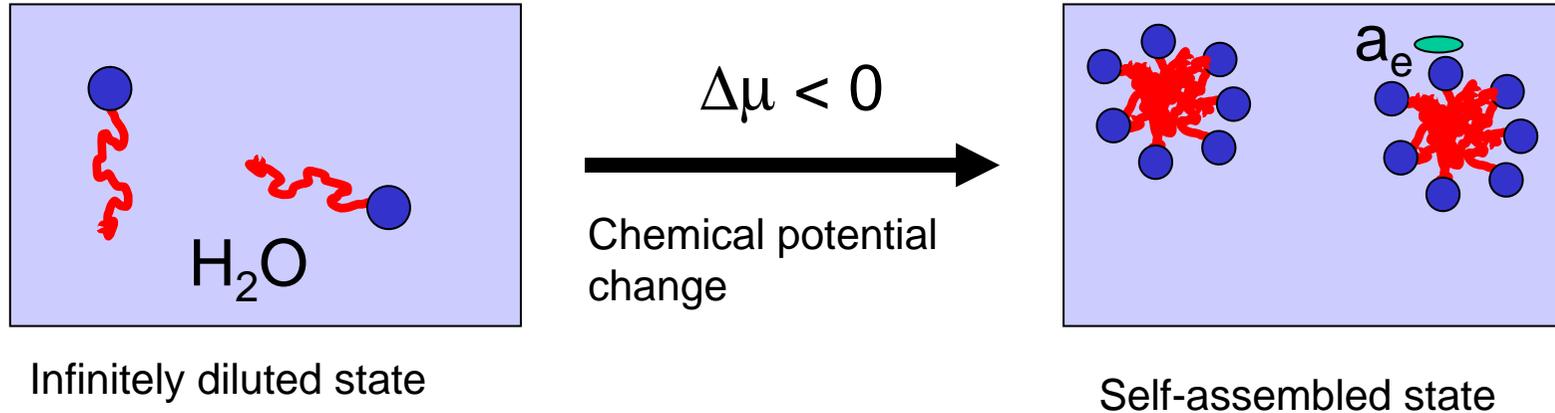
1:4

explanation of the self-assembly
by use of the concept of the packing
parameter



The free energy model by Tanford

„Phase separation model“: micelles are „microphase“



$$\left(\frac{\Delta\mu_g^0}{kT}\right) = \left(\frac{\Delta\mu_g^0}{kT}\right)_{\text{Transfer}} + \left(\frac{\Delta\mu_g^0}{kT}\right)_{\text{Interface}} + \left(\frac{\Delta\mu_g^0}{kT}\right)_{\text{Head}}$$



Avoiding the contact
between hydrocarbon
bails and water



Residual contact
water – hydrocarbon:
 $\sigma \cdot a$



Head group repulsion:
 α / a

The free energy model by Tanford and the equilibrium headgroup area a_e

Micelles in thermodynamic equilibrium:

$$\frac{\partial}{\partial a} \left(\frac{\Delta\mu_g^\circ}{kT} \right) = 0 \Rightarrow \left(\frac{\sigma}{kT} \right) - \left(\frac{\alpha}{kT} \right) \frac{1}{a^2} = 0 \text{ at } a = a_e \Rightarrow$$

σ : interfacial tension
 α : headgroup repulsion parameter

$$a_e = \left(\frac{\alpha}{\sigma} \right)^{1/2} \quad g \propto 1/a_e$$

General aspects:

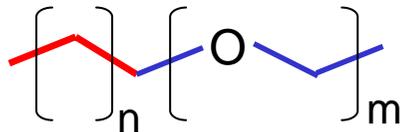
- 1) **Tail transfer** is responsible for aggregation, no influence on size and shape!
- 2) **Residual contact** $\propto a_e$ \longrightarrow promotion of the growth of aggregates
- 3) **Headgroup repulsion** $\propto 1/a_e$, \longrightarrow limitation of the aggregate size!

 Tanford's model explains basic features of micellization!

Some successful predictions of the packing model

$$a_e = \left(\frac{\alpha}{\sigma}\right)^{1/2} \quad P = V_0 / (a_e l_0)$$

1) Nonionic surfactants with ethylene oxide headgroups



A) m small \longrightarrow α small \longrightarrow a_e small

$V_0 / (a_e l_0)$ large \longrightarrow bilayers/lamellae favored

B) m larger ... \longrightarrow $V_0 / (a_e l_0)$ lower \longrightarrow cylindrical micells favored

2) Ionic surfactants:

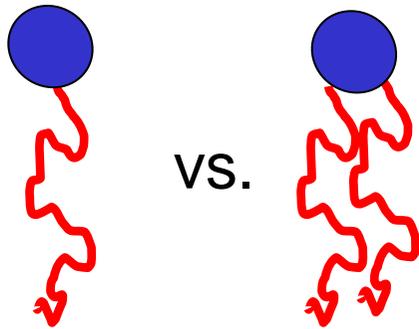
salt addition decreases the repulsion $\alpha \longrightarrow$ decrease in $a_e \longrightarrow$
increase in $V_0 / (a_e l_0)$

\longrightarrow transition from spherical micelles to cylindrical micelles.

Some successful predictions of the packing model

$$a_e = \left(\frac{\alpha}{\sigma}\right)^{1/2} \quad P = V_0 / (a_e l_0)$$

3) Single tail / double tail surfactants



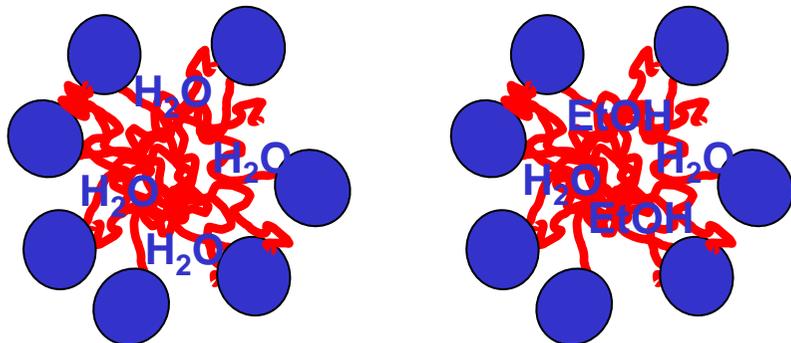
vs.

Same equilibrium area a_e

→ $V_0 / (a_e l_0)$ twice as large for double tail

→ bilayers instead of spherical or globular micelles

4) Influence of solvents



Interfacial tension σ decreases

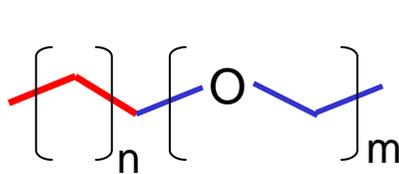
→ a_e increases → $V_0 / (a_e l_0)$ decreases

→ bilayer to micelles,
rodlike to spherical micelles

Some successful predictions of the packing model

$$a_e = \left(\frac{\alpha}{\sigma}\right)^{1/2} \quad P = V_0 / (a_e l_0)$$

5) Influence of temperature



Increasing the temperature decreases the steric repulsion of PEO headgroup

$\longrightarrow \alpha$ decreases $\longrightarrow a_e$ decreases

$\longrightarrow P$ increases

\longrightarrow transition from spherical micelles to cylindrical micelles.

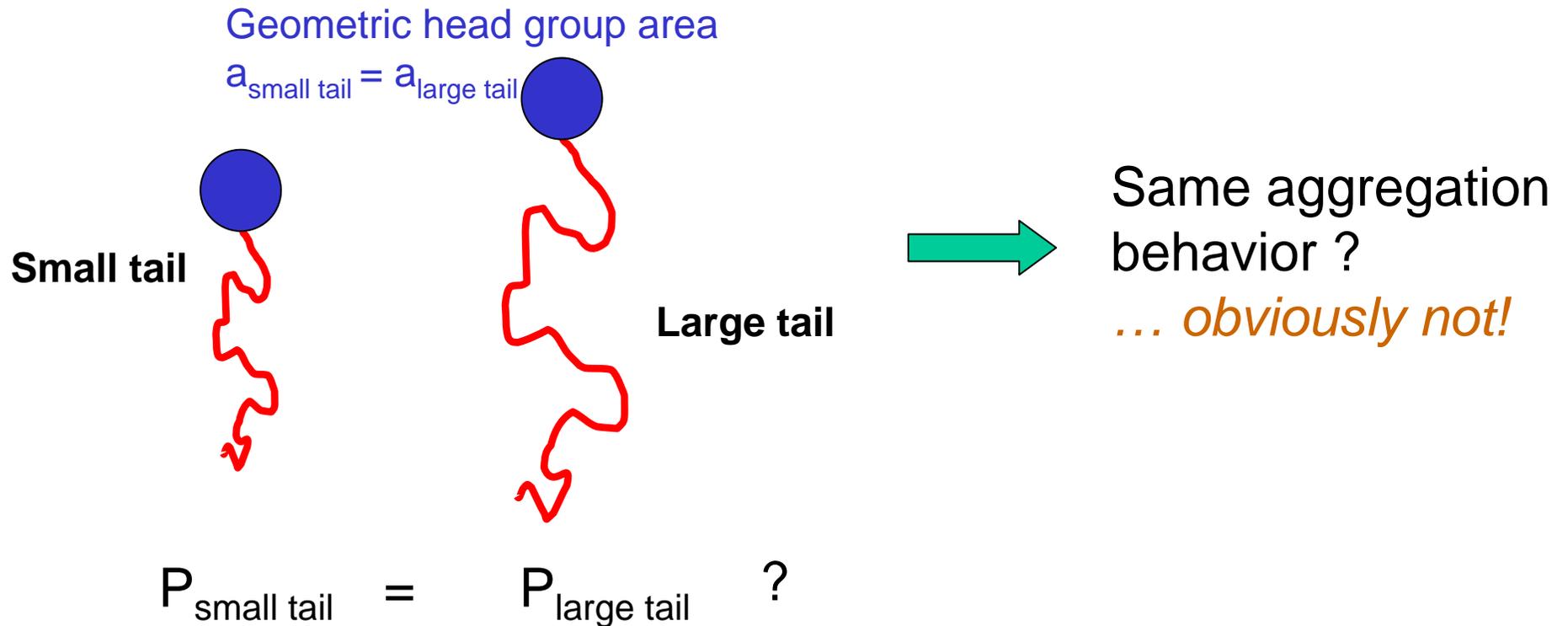


The Tanford model predicts various experimental findings and supports the “packing parameter” concept!



Attention! Possible misinterpretation of the packing parameter P

Straightforward interpretation of the molecular packing concept



→ • Are the assumptions of the “packing parameter” model incorrect?

• How does the tail influence self-assembly ?

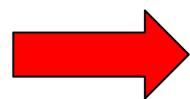
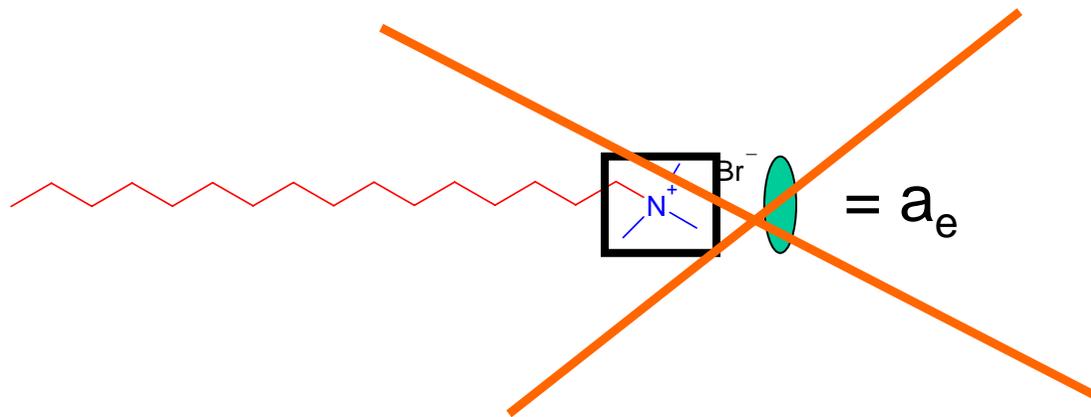
ATTENTION: Neglected role of the surfactant tail!!

- What is the role of the tail?
- Is there a misinterpretation of the Tanford model?

... Let's have a closer look on the model again...

$$P = V_0 / (a_e l_0)$$

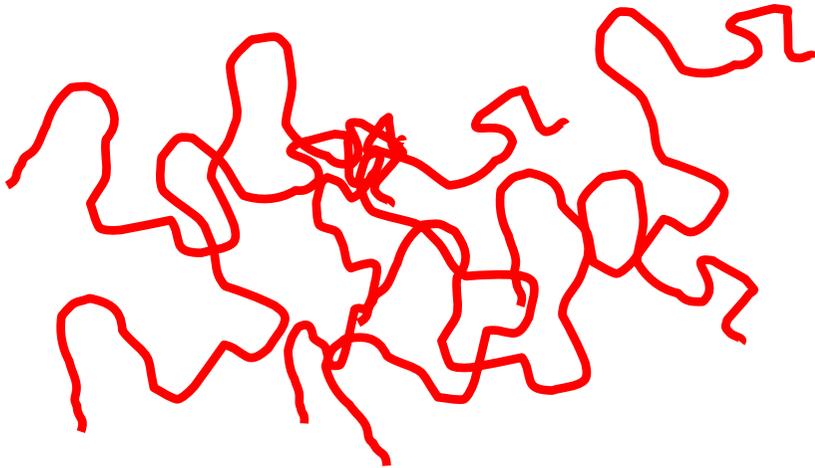
a_e : is an equilibrium parameter, not just a Geometrical surface area!



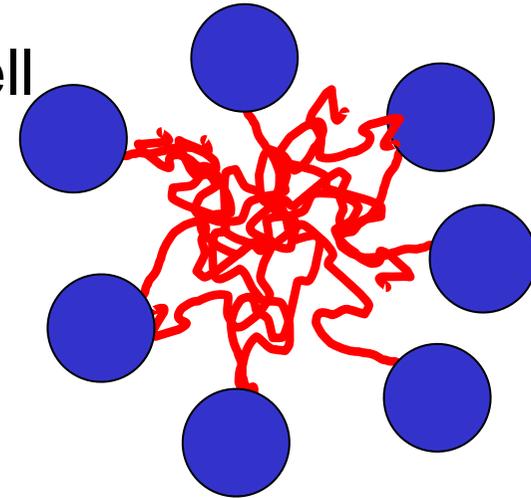
The tail might influence the packing parameter α and thereby the aggregation

Influence of tail packing constraints

Bulk hydrocarbon



Micell



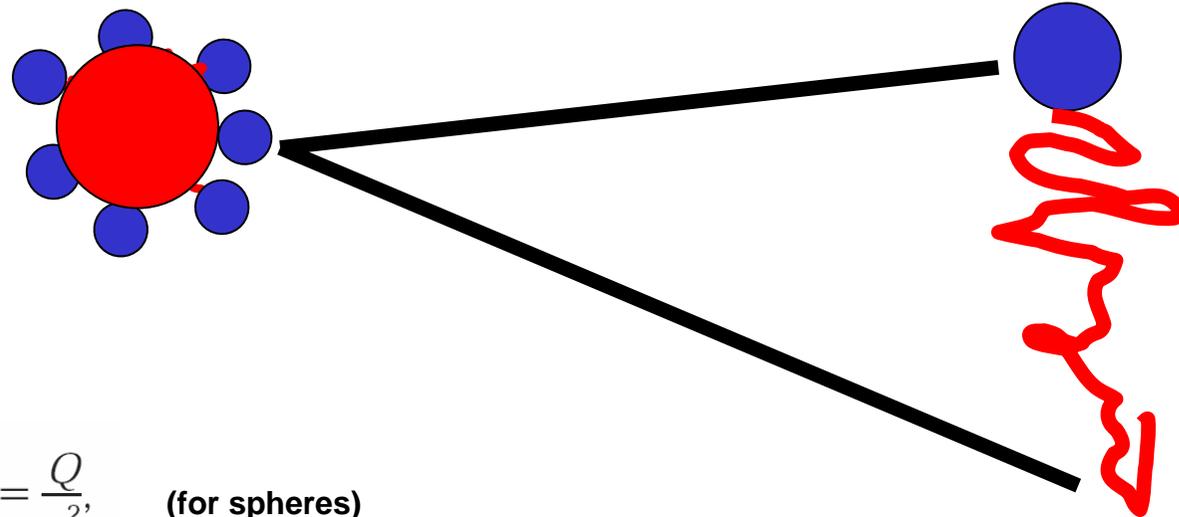
➔ Different packing for the hydrocarbons compared to the bulk:
Non-uniform deformation in the micelle!

$$\left(\frac{\Delta\mu_g^\circ}{kT}\right) = \left(\frac{\Delta\mu_g^\circ}{kT}\right)_{\text{Transfer}} + \left(\frac{\Delta\mu_g^\circ}{kT}\right)_{\text{Interface}} + \left(\frac{\Delta\mu_g^\circ}{kT}\right)_{\text{Head}} + \left(\frac{\Delta\mu_g^\circ}{kT}\right)_{\text{Packing}}$$

(Nagarajan, Ruckenstein)

Influence of tail packing constraints – Nagarajan/Ruckenstein

The hydrocarbon chains have to deform non-uniformly to fill the core with uniform density.



$$\left(\frac{\Delta\mu_g^\circ}{kT}\right)_{\text{Packing}} = \left(\frac{3\pi^2}{80}\right)\frac{R^2}{NL^2}, = \frac{Q}{a^2}, \quad (\text{for spheres})$$

$$\frac{\partial}{\partial a}\left(\frac{\Delta\mu_g^\circ}{kT}\right) = 0 \Rightarrow \left(\frac{\sigma}{kT}\right) - \left(\frac{\alpha}{kT}\right)\frac{1}{a^2} - \frac{2Q}{a^3} = 0$$

$$\text{at } a = a_e \Rightarrow a_e = \left(\frac{\alpha}{\sigma} + \frac{2Q/a_e}{\sigma/kT}\right)^{1/2} \quad Q \propto L, V_0$$

L = characteristic segment length
N = number of segments
R = radius of micelle

➔ The equilibrium head group area (a_e) is dependent on the length of the hydrophobic tail!!

➔ Shape transitions possible with varying tail length!

Influence of tail packing constraints - simulations

“classical” packing model

Consideration of tail packing constraints

$$a_e = \left(\frac{\alpha}{\sigma}\right)^{1/2}$$

$$a_e = \left(\frac{\alpha}{\sigma} + \frac{2Q/a_e}{\sigma/kT}\right)^{1/2}$$

n_C	from eq 3		spheres (eq 21)		cylinder (eq 21)		bilayers (eq 21)	
	a_e (Å ²)	$v_0/a_e l_0$						
For $\sigma/kT = 0.12 \text{ \AA}^{-2}$, $\alpha/kT = 300 \text{ \AA}^2$								
8	50	0.42	(59.6)	(0.352)	57.5	0.365	(54.1)	(0.388)
12	50	0.42	62.9	0.334	60.1	0.349	(55.7)	(0.377)
16	50	0.42	65.7	0.320	62.5	0.336	(57.2)	(0.367)

Cylindrical micelles

Spherical micelles possible!!

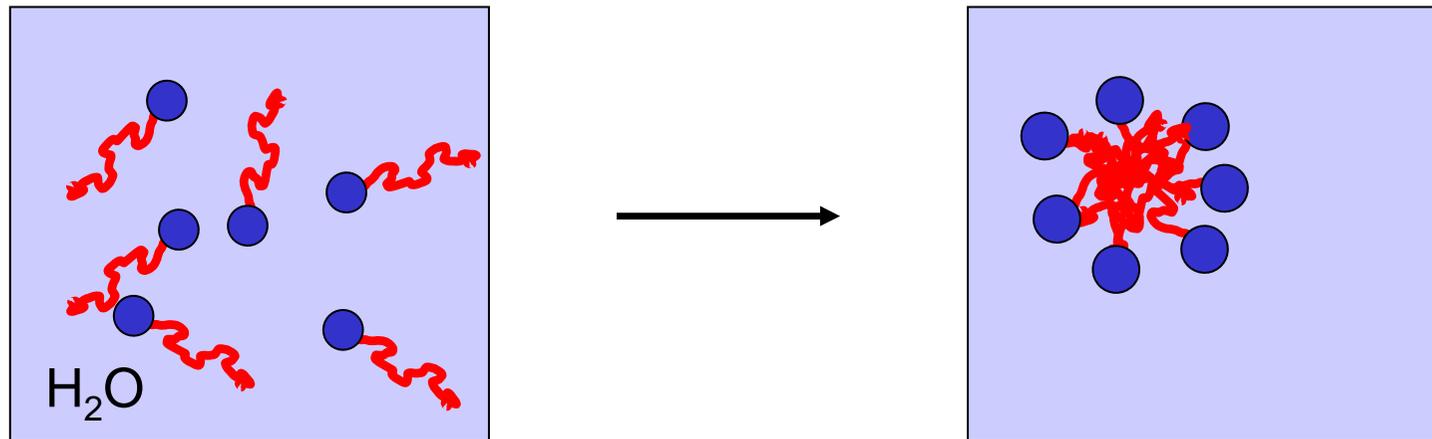


The tail length influences the head group area and thereby the shape!

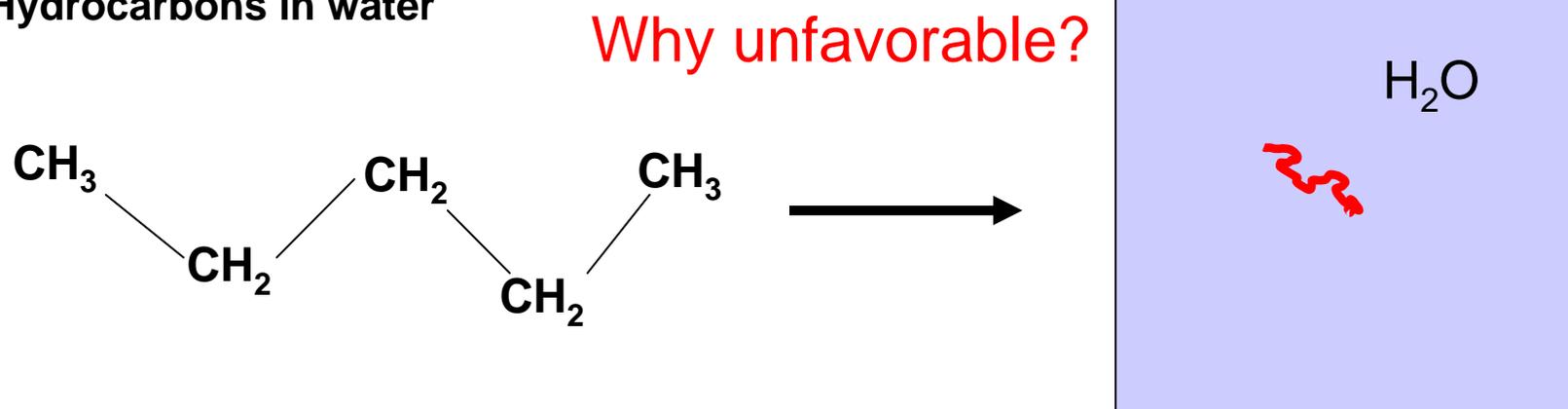
5. What is the “deeper” reason for self-assembly?

Why don't oil and water mix? The “hydrophobic effect”

1) Micellization



2) Hydrocarbons in water



Entropie/enthalpy of micellization

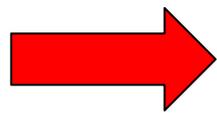
$$\Delta G = \Delta H - T \Delta S$$

Low-molecular weight surfactants:

- ΔH ca. + 1-2 kJ/mol

Micellization is unfavorable with respect to the enthalpy!!

- ΔS ca. + 140 J /K: The entropy of micellization is POSITIVE

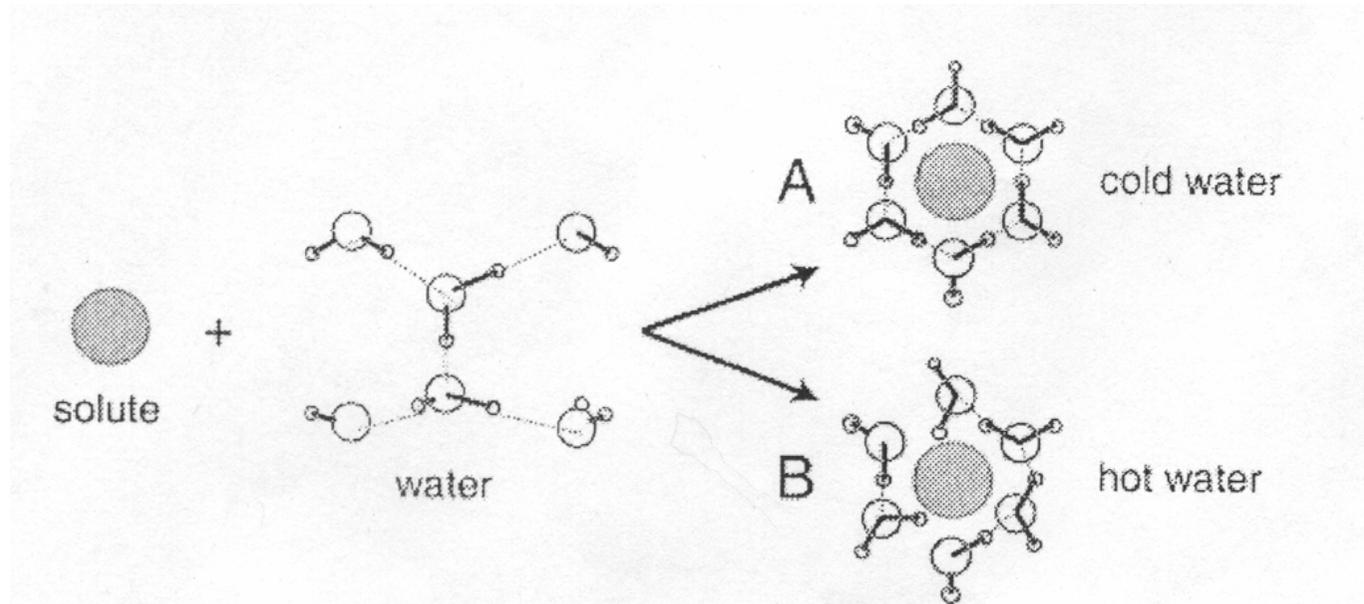


Specific features of the solvent (water) enable micellization!

- * High surface tension,
- * very high cohesion energy,
- * high dielectric constant, high boiling point, etc etc

Water is not a normal liquid! The “iceberg model”

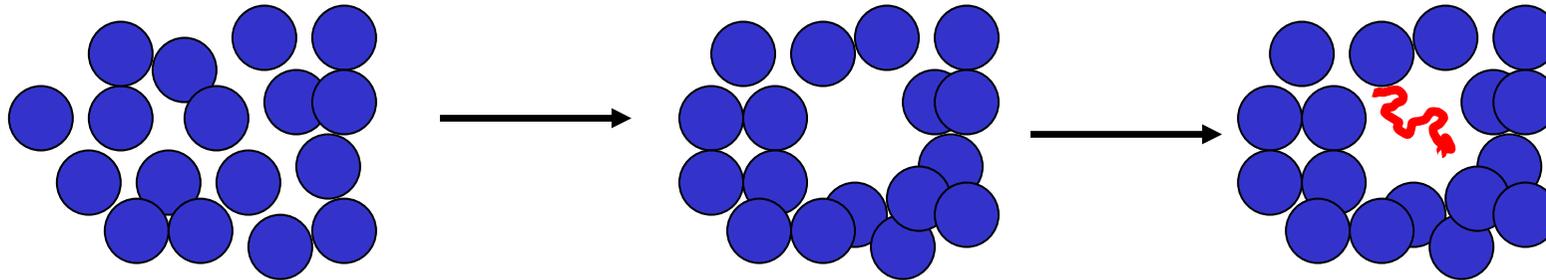
Frank, Evans, *J. Chem. Phys.* 1945, 13(11), 507.



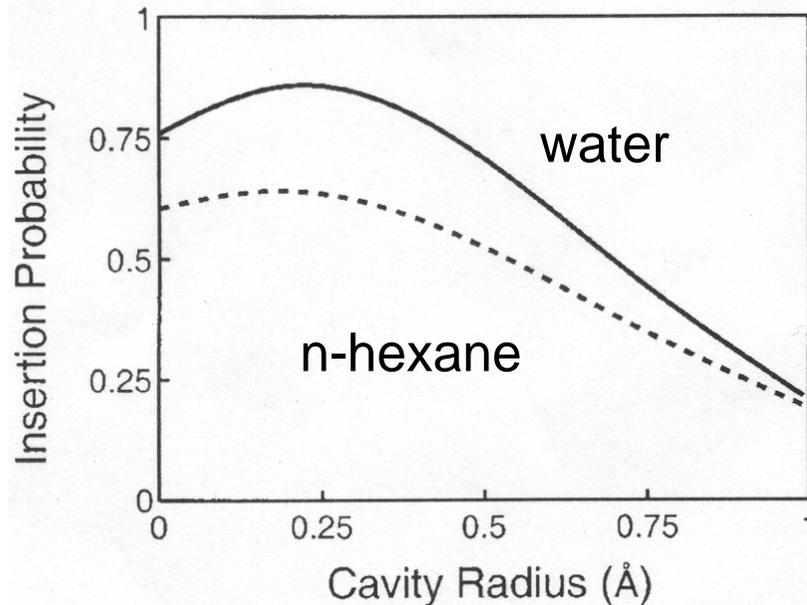
- A) Nonpolar solutes create a clathrate-like cage of first-shell waters around the solute.
- B) Large entropic cost to order the hydrogen bonds into a more open “iceberg”-like structure (low temperature).
- C) High-Temperatures break hydrogen bonds to gain entropy, at the cost of the enthalpy.
- D) Analogy: Clathrate formation of rare gases in water.

Small-Size Model: Is the disaffinity of oil for water due to water's small size?

The high cost in free energy comes from the difficulty of finding an appropriate cavity in water, due to the small size of water molecules.



Free-volume distribution of a simple liquid (n-hexane) and water



Literature:

Thermodynamics:

- Nagarajan, R. and Ganesh, K.
Block copolymer self-assembly in selected solvents,
J. Chem. Phys. 1989, p. 5843.
- Nagarajan, R. *Langmuir* 2002, 18, 31.

Visualization of micelles:

- Evans et al., *Langmuir*, **1988**, 34,1066.
- Böttcher et al., *Angew. Chemie*, **2004**, early view.

Washing/surfactants:

Chiuz, 2003, 37, 336.

Hydrophobic effect:

Southall et al., *J. Phys. Chem. B*, 2002, 106, 521.



Thank you!!