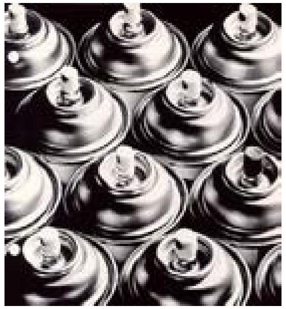
Micelle Formation

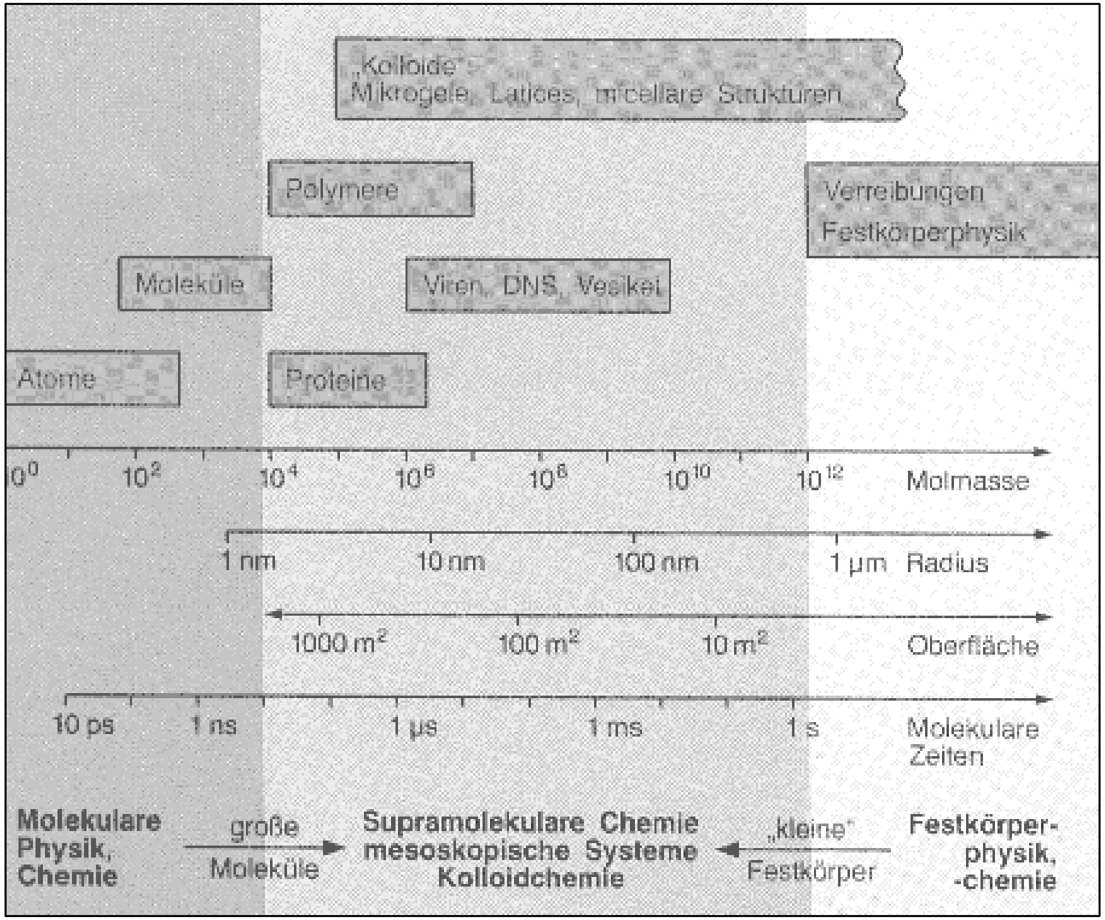
Lecture: Colloidal Phenomena

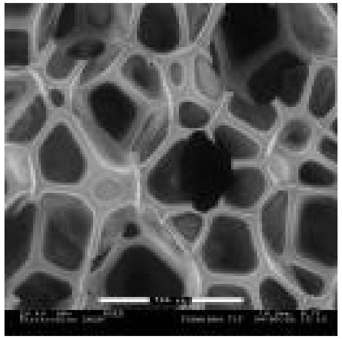
Arne Thomas,
MPI of Colloids and Interfaces, Golm
thomas@mpikg.mpg.de
0331-567 9509

What is a Colloid?

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



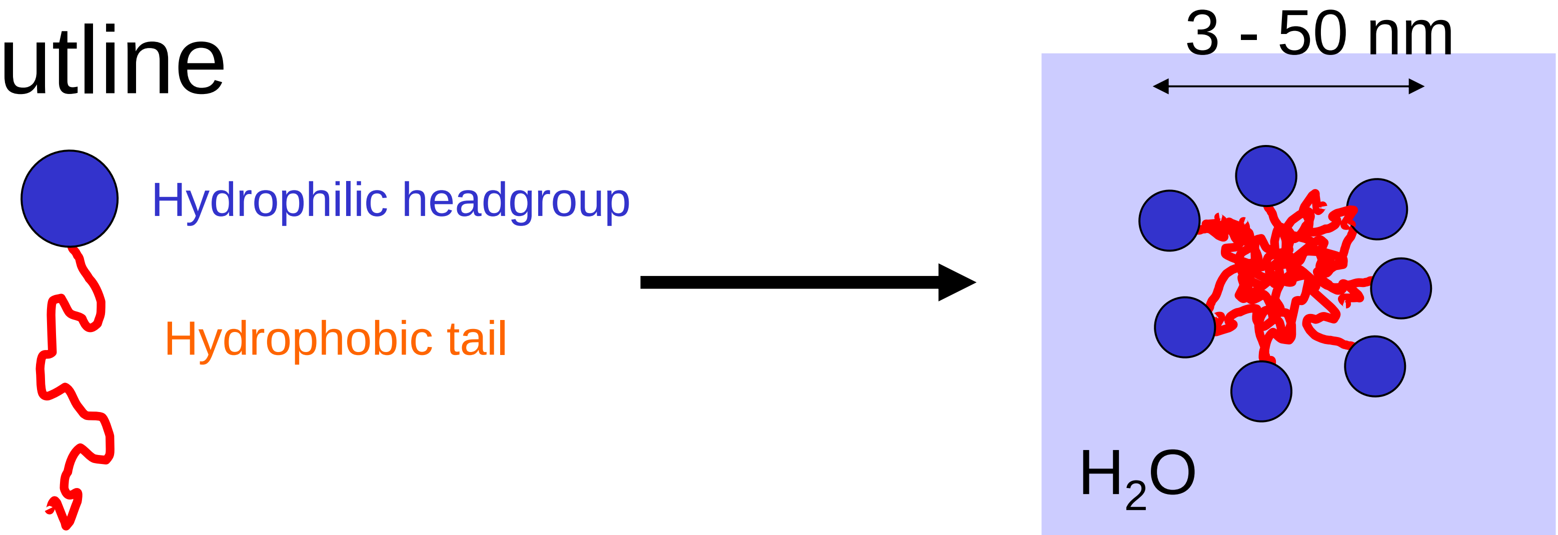




Colloid chemistry is closing the gap between molecular chemistry and solid state properties!

Micelles (“Aggregation colloids”)

Outline



1. Surfactants/Introduction

2. Basics of micellization: characterization and properties

3. Micelle formation mechanism

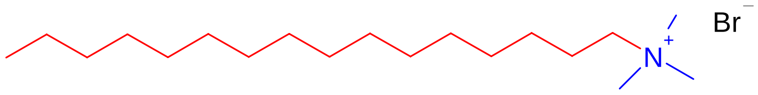
4. Semiquantitative predictive models of micellization

(Tanford, Israelachvili, Ruckenstein, Nagarajan)

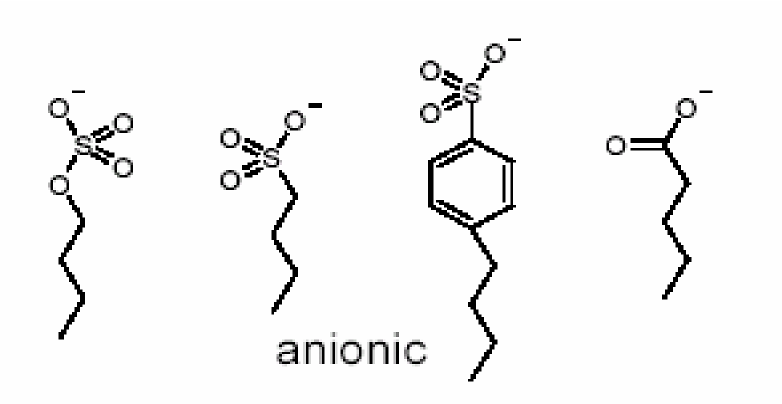
5. What is the “deeper” reason for self-assembly?

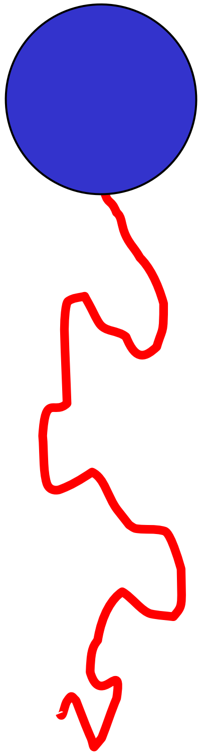
1. Surfactants

Ionic surfactants



cationic

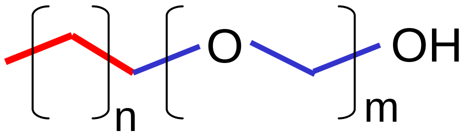




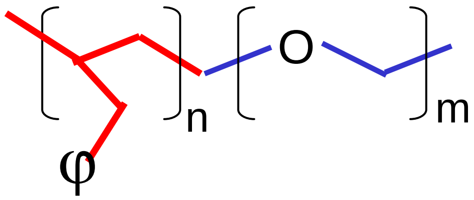
Hydrophilic headgroup
(“loves water”)

Hydrophobic tail
(“hates water”)

Non-ionic surfactants (“Niotenside”)



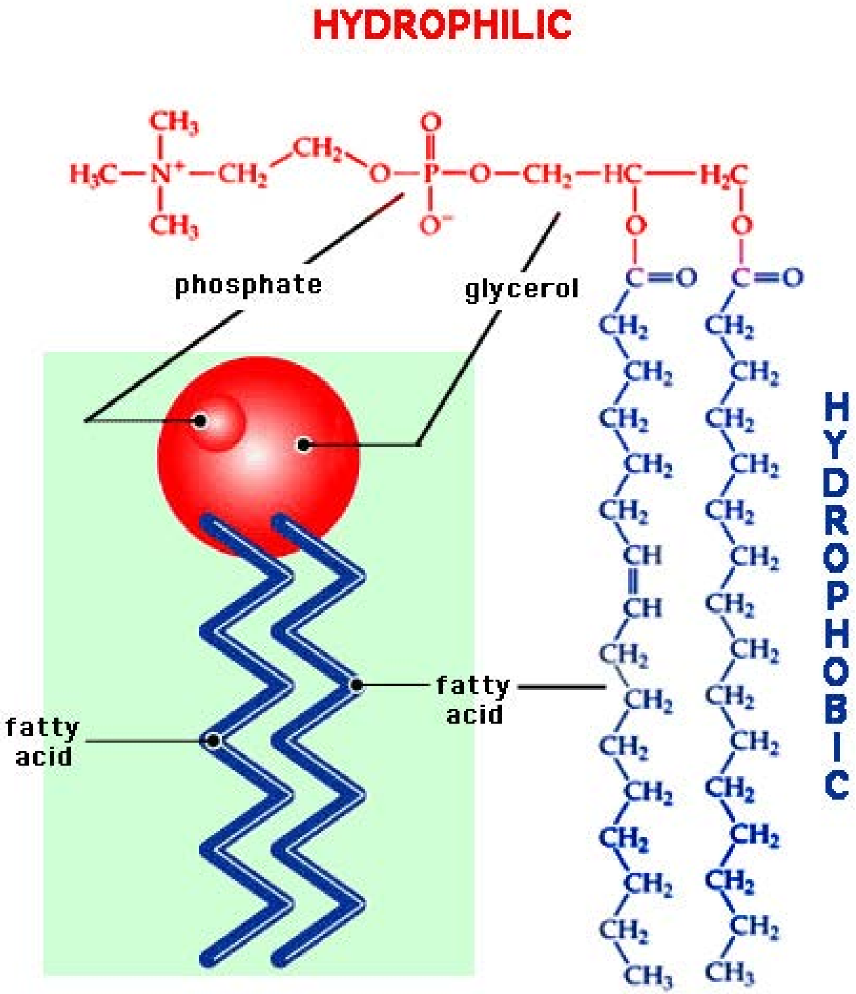
„Brij“



Pluronics: PEO - PPO - PEO

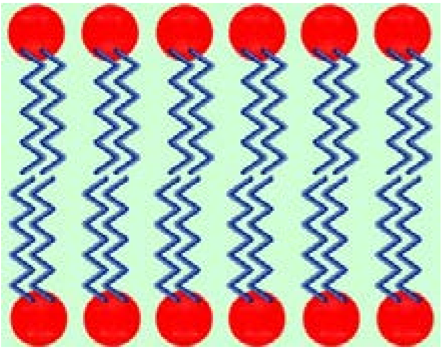
1. Surfactants

Zwitterionic surfactants: Phospholipids



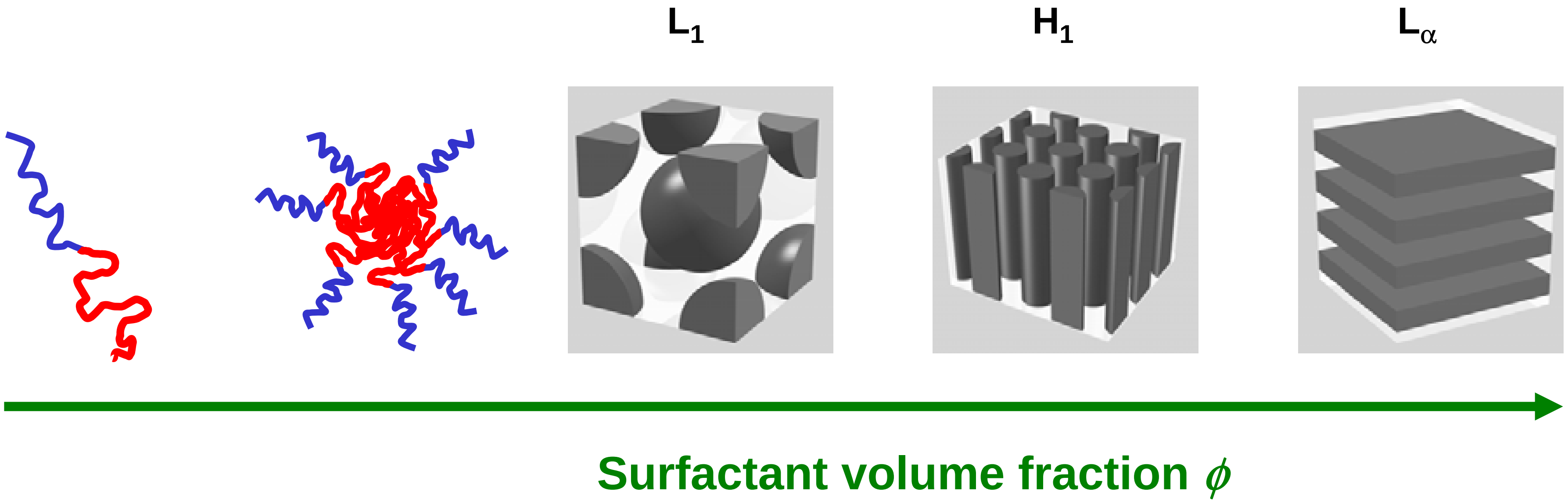
Phosphatidylcholin (Lecithin)

Phospholipids are the building block of biological membranes



Introduction: Self-assembly of surfactants in water

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

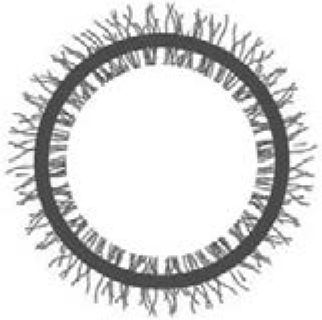


L_1 **H_1** **L_α**

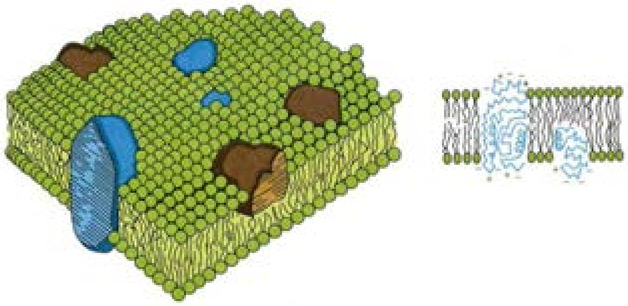
Surfactant volume fraction ϕ

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

1) Living organisms:



Cells = vesicles

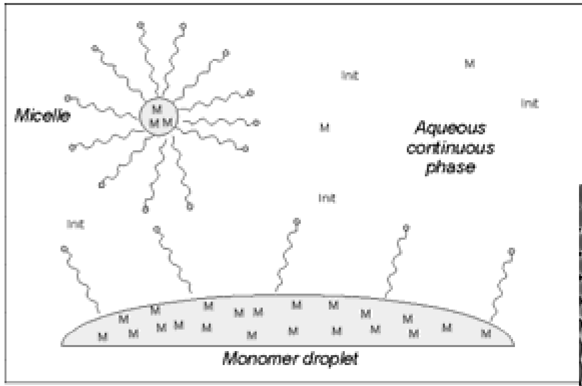


2) Applications of surfactants:

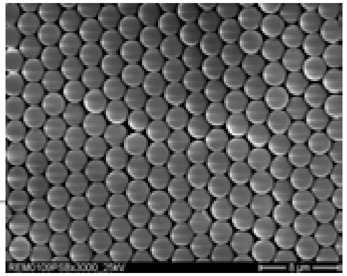
Cleaning/Detergents (40%), Textiles, Cosmetics, Paper Production, Paint, Food, Mining (Flotation)......

Surfactant production per year: ~40 billion tons

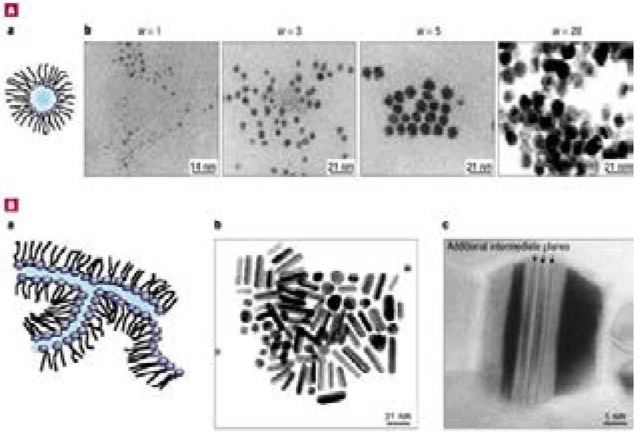
3) Chemical reactions in micelles:



Emulsion polymerisation



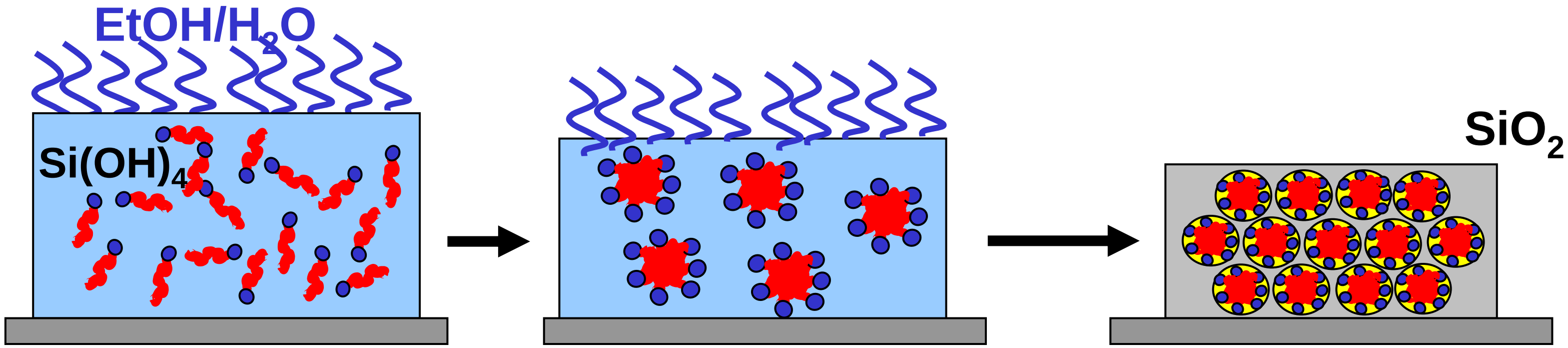
Micelles as „nanoreactors“



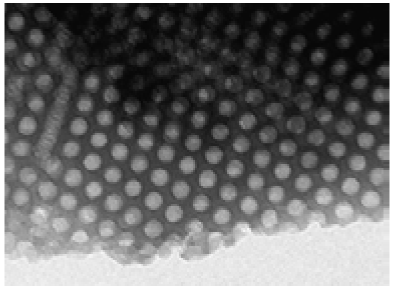
The role of soft colloidal templates in controlling the size and shape of inorganic nanocrystals

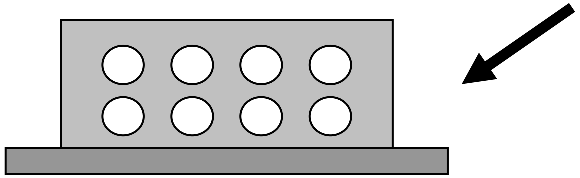
Nature Materials **2,** 145–150 (2003)

4) New materials through templating/casting



Porous material

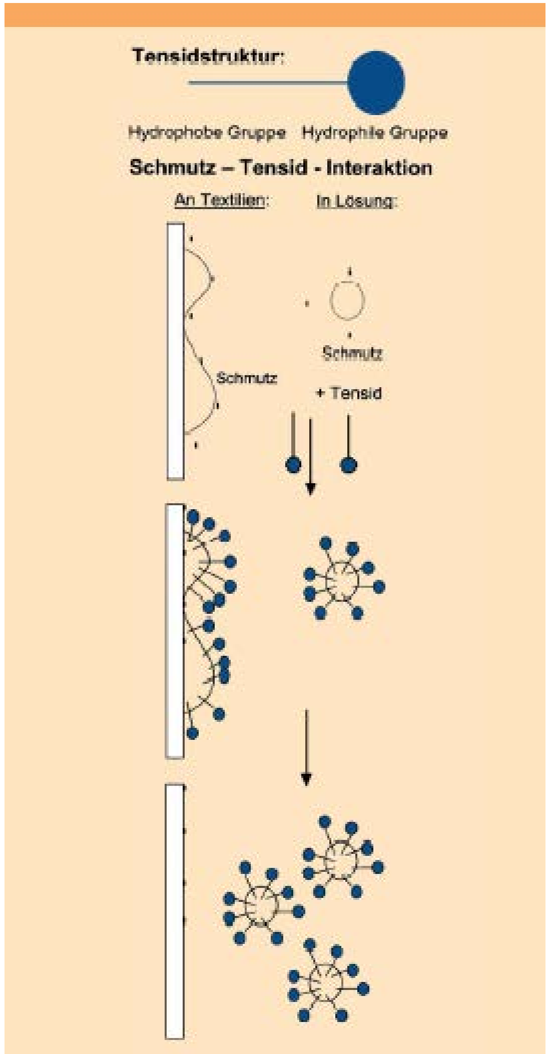




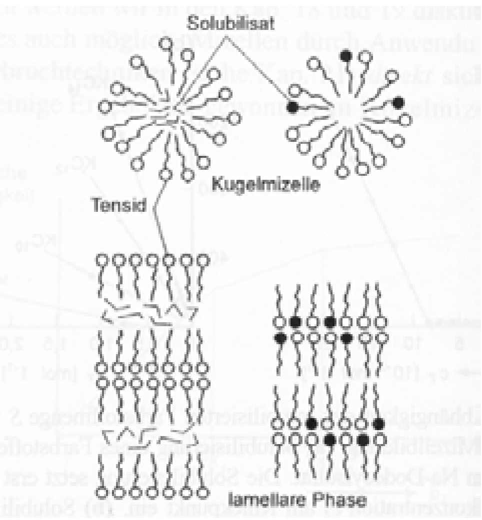
Washing / Solubilization of other substances

Chiuz, 2003

What happens during washing?



Solubilization by micelles

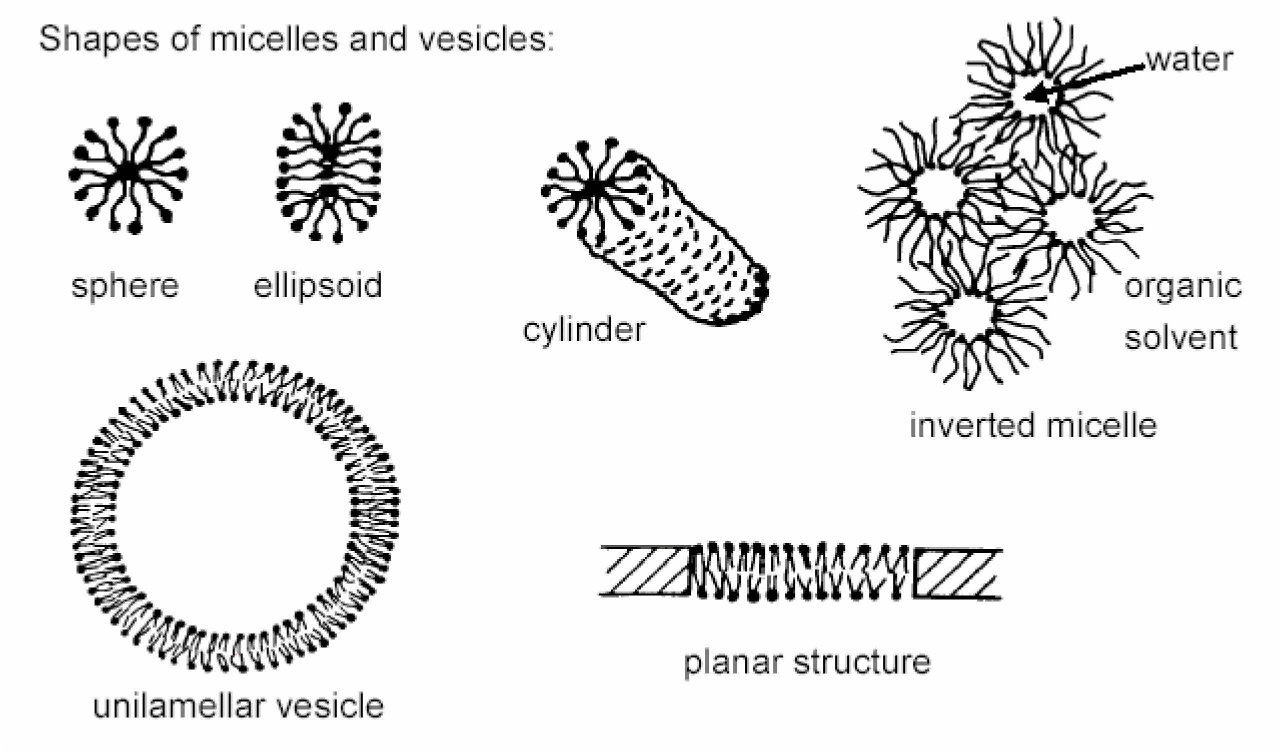


2. Basics of micellization: characterization and properties

Contents of this chapter:

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

Different shapes of micelles

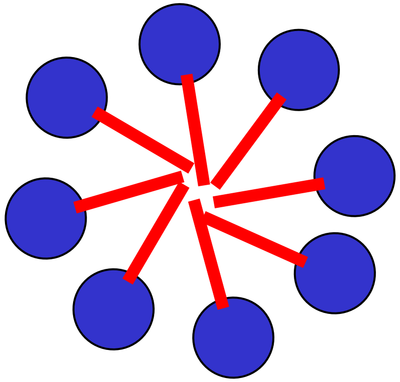


What determines the shape/size of micelles...?

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

A didactic excursion: wrong illustrations of micelles

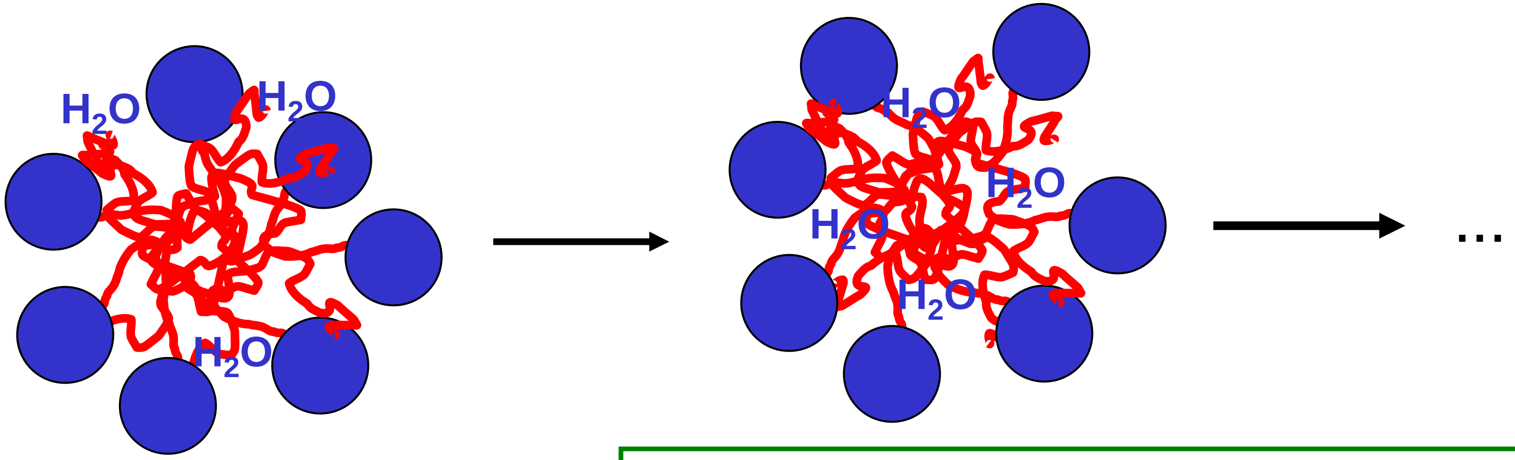
Standard figure seen in textbooks:



Wrong:

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

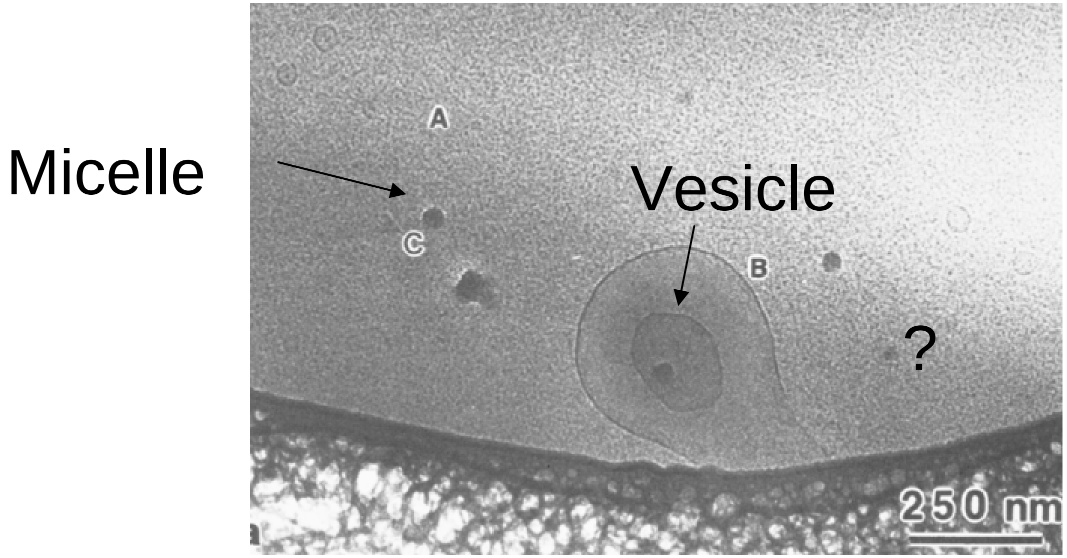
A more realistic illustration of micelles:



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)



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

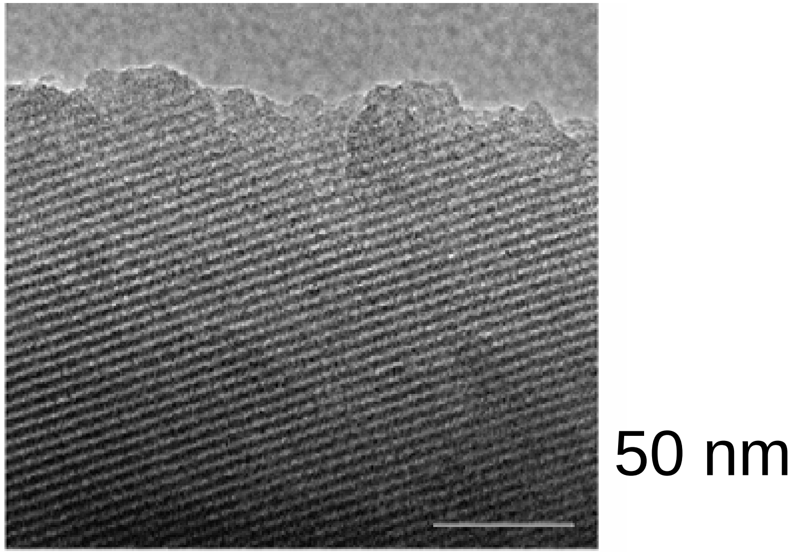
Preparation:

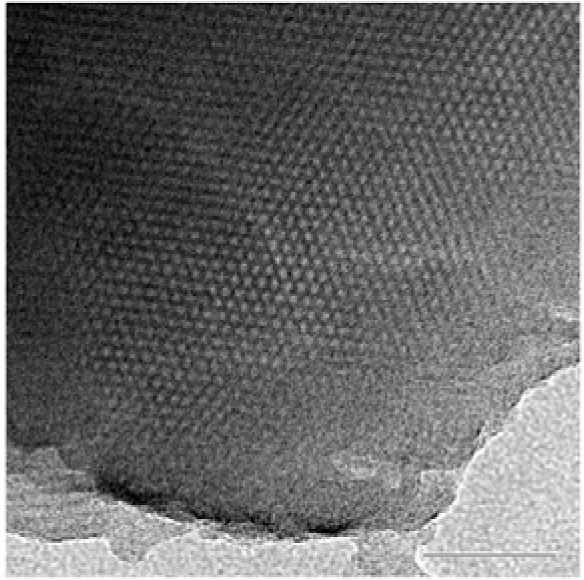
1) Controlled environmental chamber to minimize compositional changes

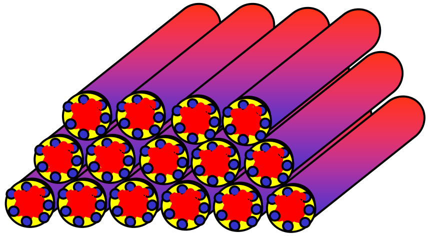
2) rapid thermal quenching of a thin layer of the sample in a liquid ethane slush (formation of vitrified ice).

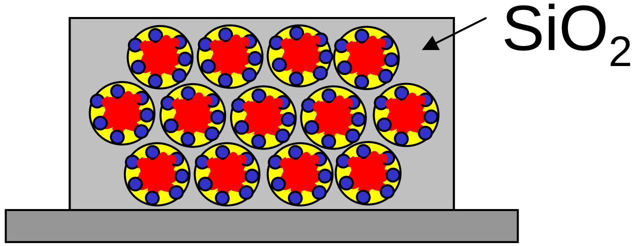
Visualization of self-assembled structures

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



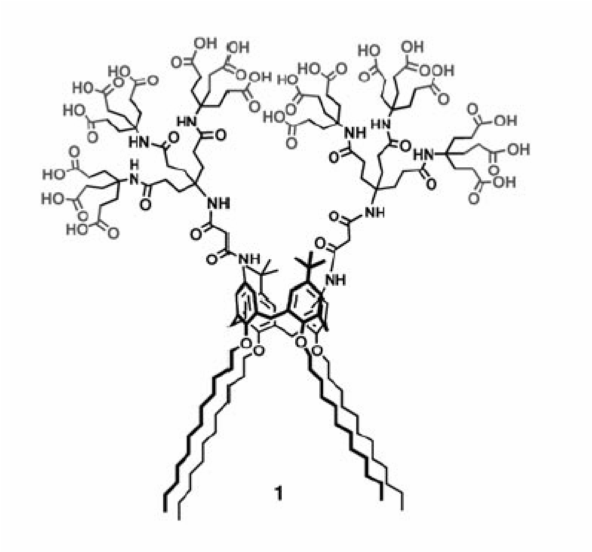






Pore structures can be seen as „cast“ of the micellar structure (Nanocasting)

Shape persistent micelles



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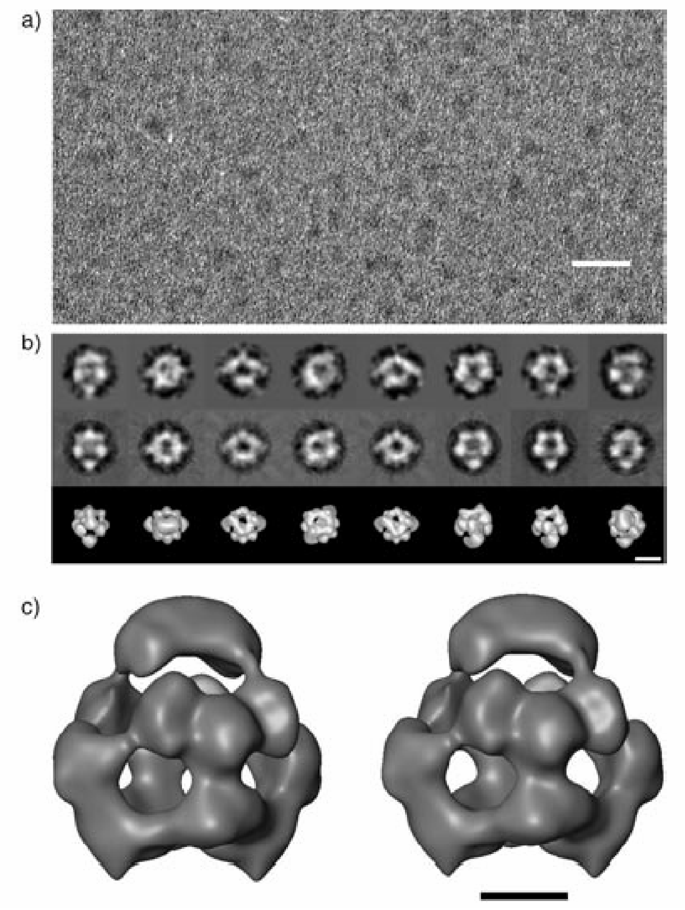
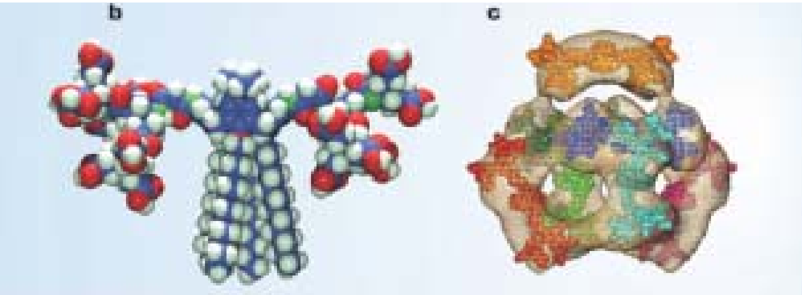
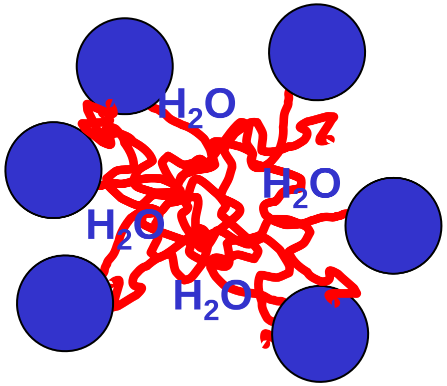
„The first account of a structurally persistent micelle“
Böttcher et al.
Angew. Chemie,
2004, 43, 2959





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

Characterization of micelles



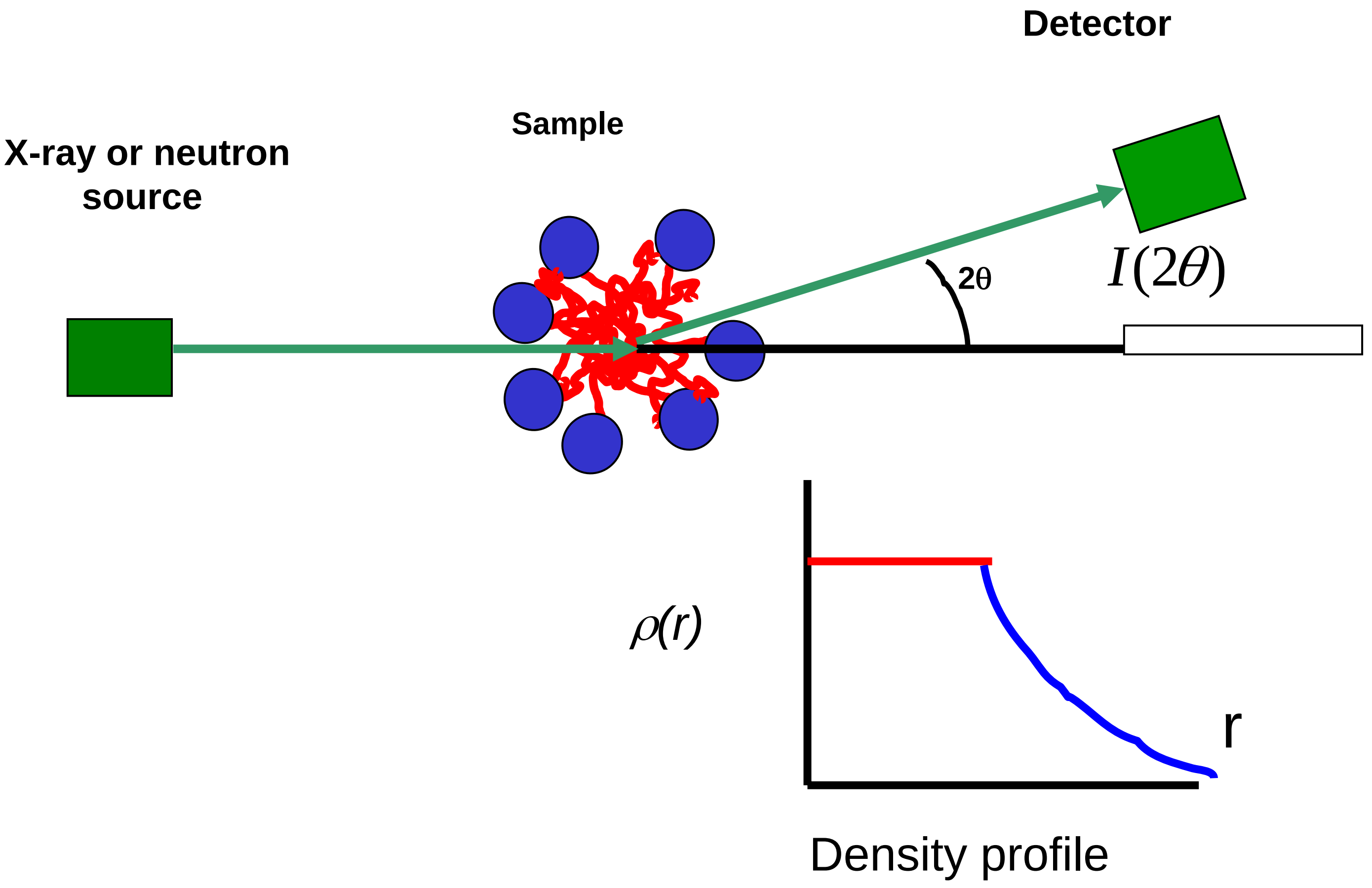
TEM, light scattering, surface tension, spectroscopy, ...

…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



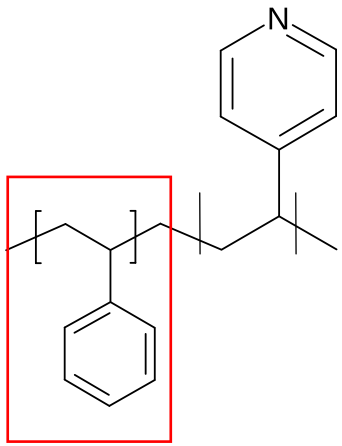
***Coherent* scattering of x-rays or neutrons:**

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

Contrast matching technique for small-angle neutron scattering

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

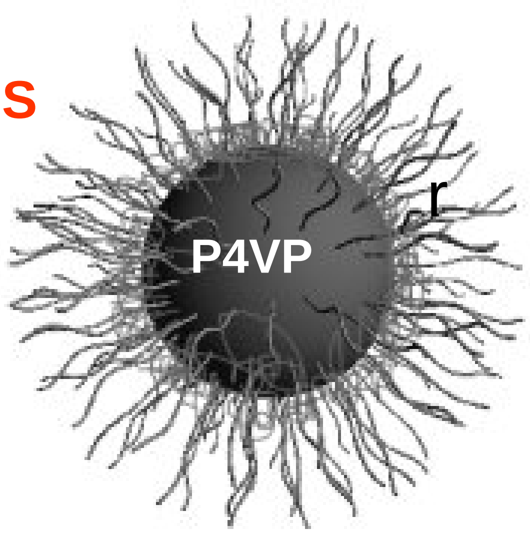
$PS_{120,d8}$-$P4VP_{118}$



deuterated PS

$\xrightarrow{}$

toluene

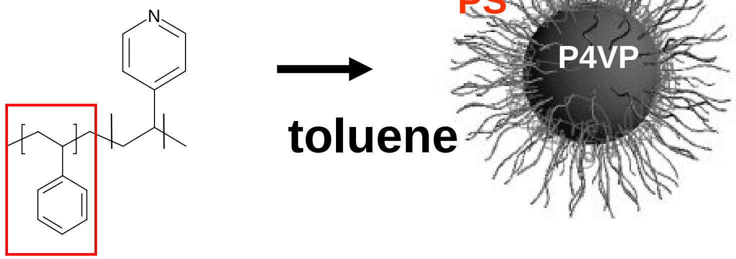


hairy micelles

Contrast matching technique for small-angle neutron scattering

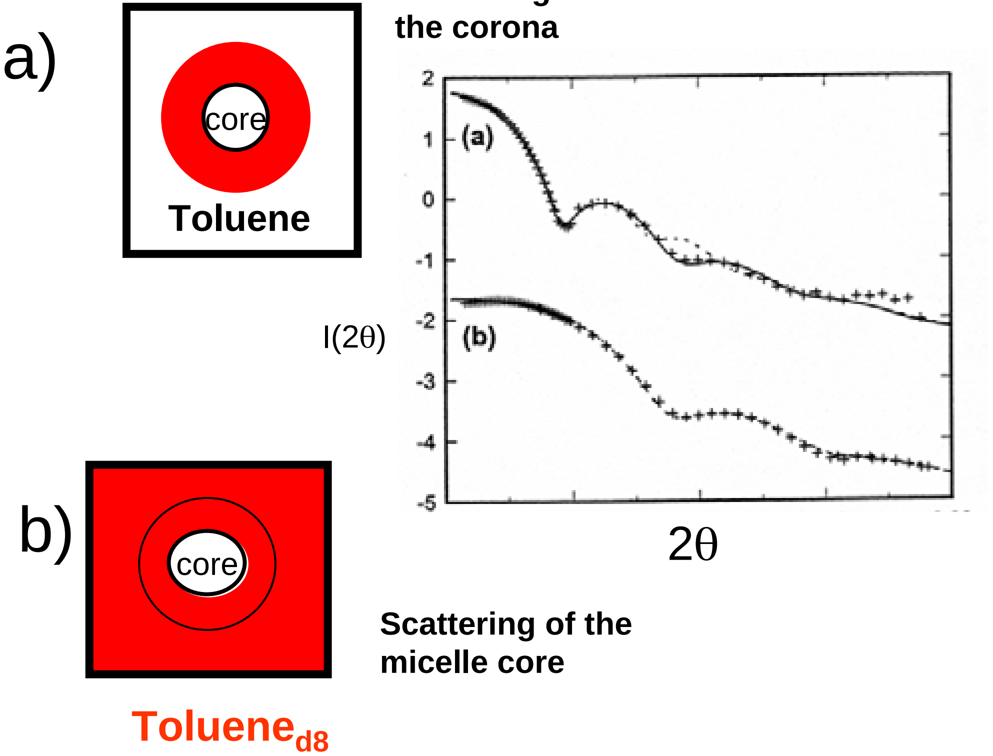
Poly(styrene)-b-poly(4-pyrrolidone) forms inverse micelles in toluene

$PS_{120,d8}$-$P4VP_{118}$



deuterated PS

hairy micelles



Scattering of the corona

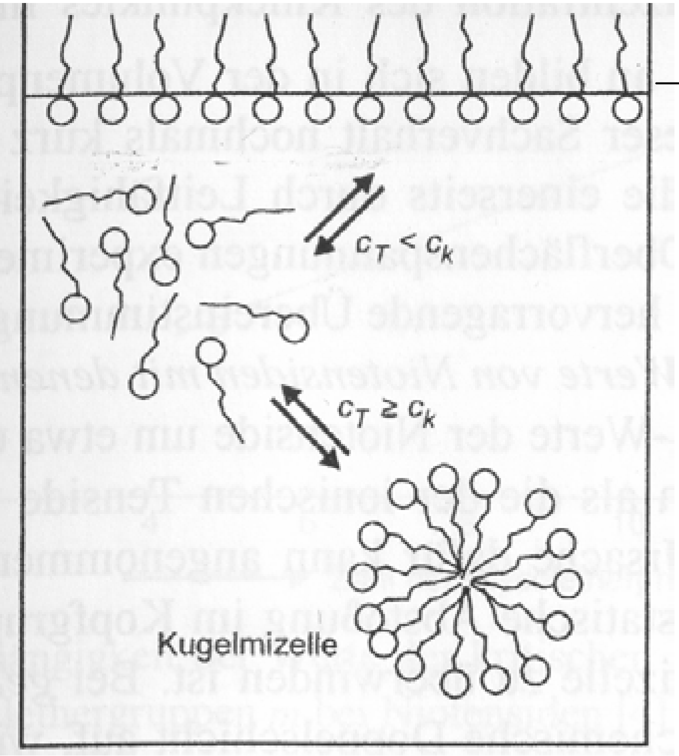
Scattering of the micelle core

Results:

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

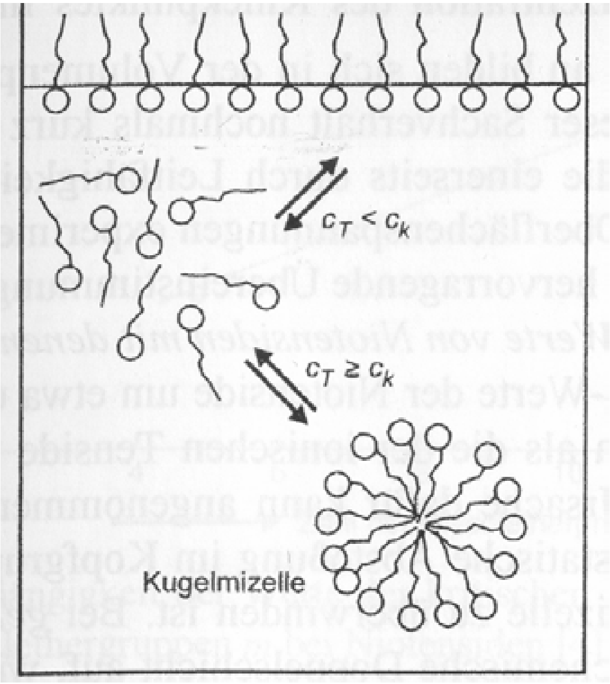
cmc (c_k) = critical micelle concentration:

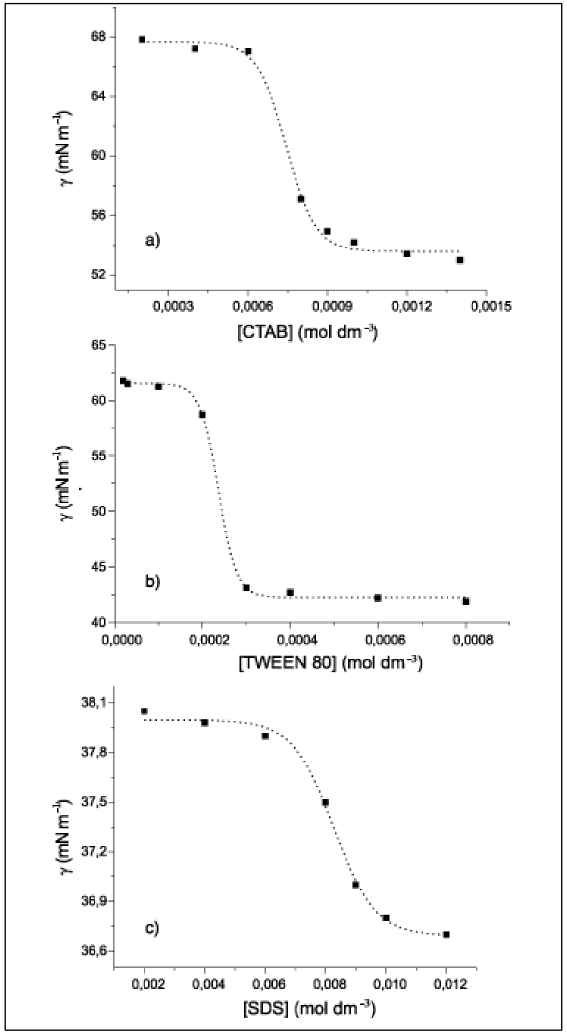
concentration, above which micelles are observed

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

The critical micelle concentration (cmc, c_k)

Surface tension at cmc

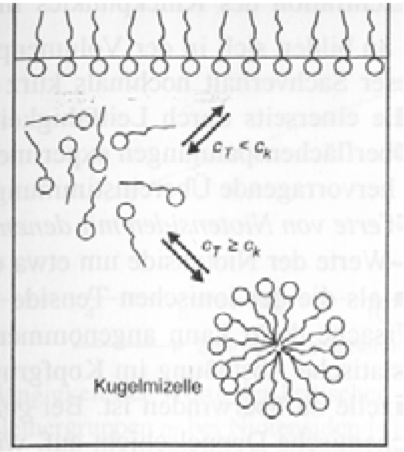


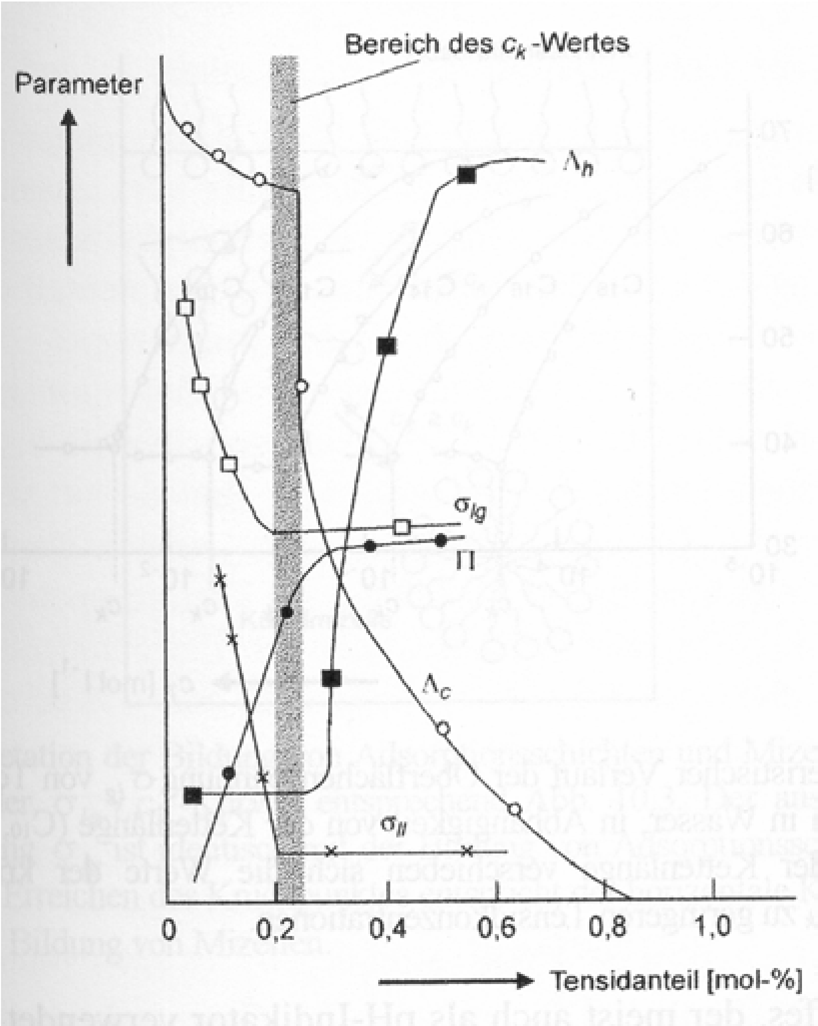


cmc of nonionic surfactants
is generally lower
compared to ionic surfactants

Abrupt changes at the cmc due to micelle formation!

The critical micelle concentration (cmc, c_k)





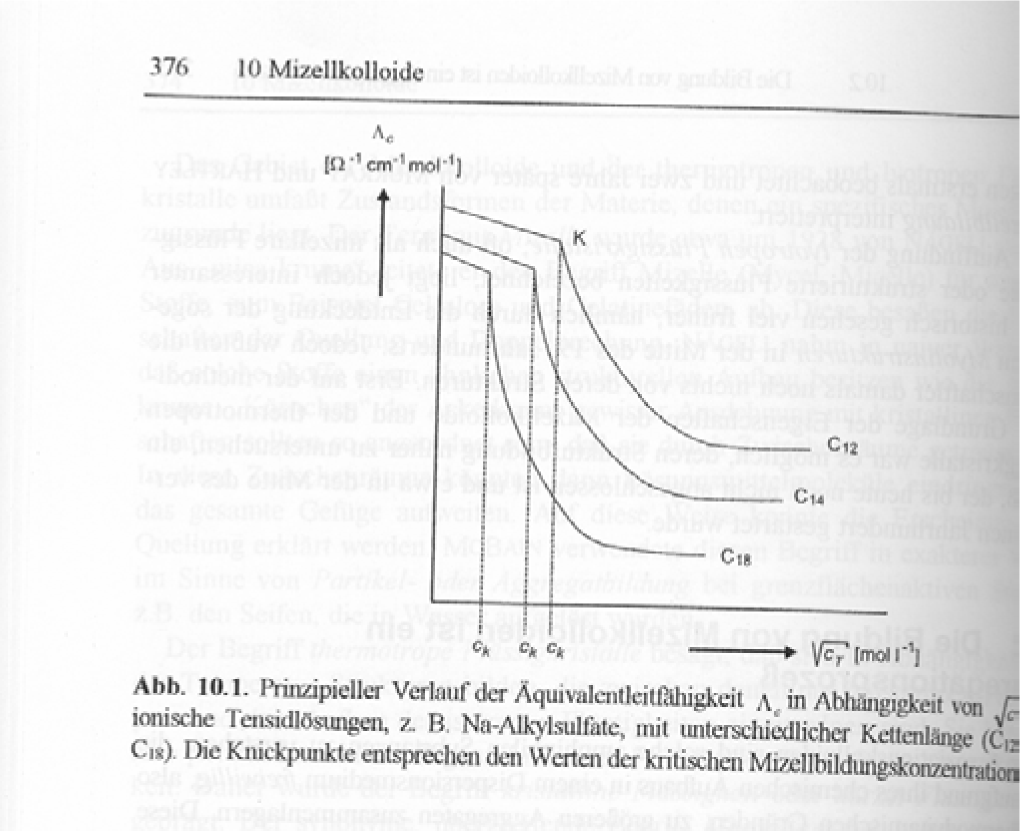
Typical behavior of selected physico-chemical parameters such as the equivalence ***conductivity Λ_c*** or the ***surface tension σ*** on the surfactant concentration

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



376 10 Mizellkolloide

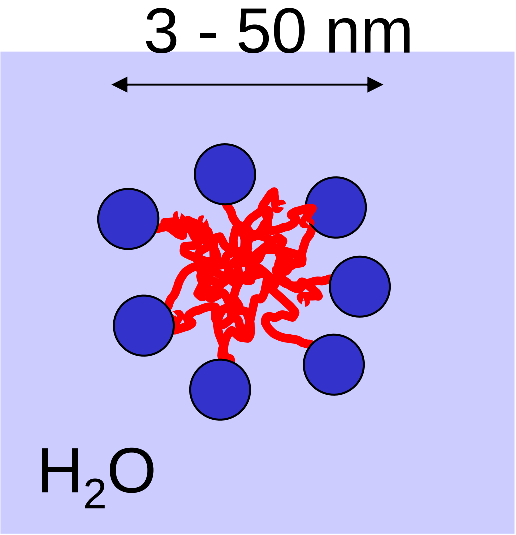
Abb. 10.1. Prinzipieller Verlauf der Äquivalentleitfähigkeit Λ_c in Abhängigkeit von $\sqrt{c}$ ionische Tensidlösungen, z. B. Na-Alkylsulfate, mit unterschiedlicher Kettenlänge (C$_{12}$ C$_{18}$). Die Knickpunkte entsprechen den Werten der kritischen Mizellbildungskonzentration

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

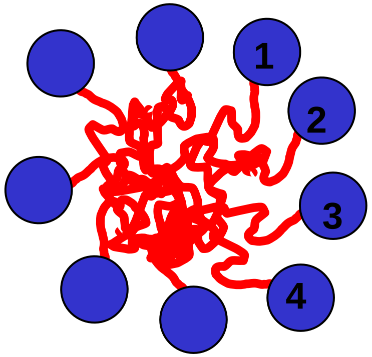
The cmc decreases with increasing tail length because the hydrophobic character increases

Summary: Some values about micelles

Micelle size:



Aggregation number:



Ionic surfactants
z_A = 10-170

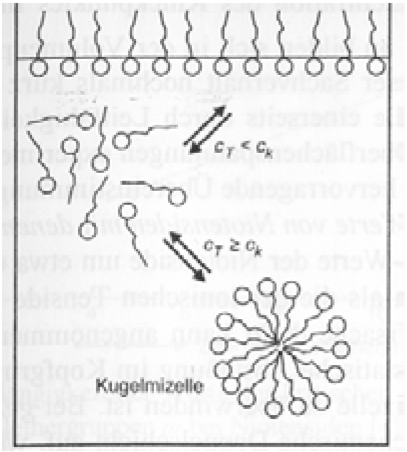
Nonionic surfactants
z_A = 30-10.000

Critical micelle concentrations (CMC):

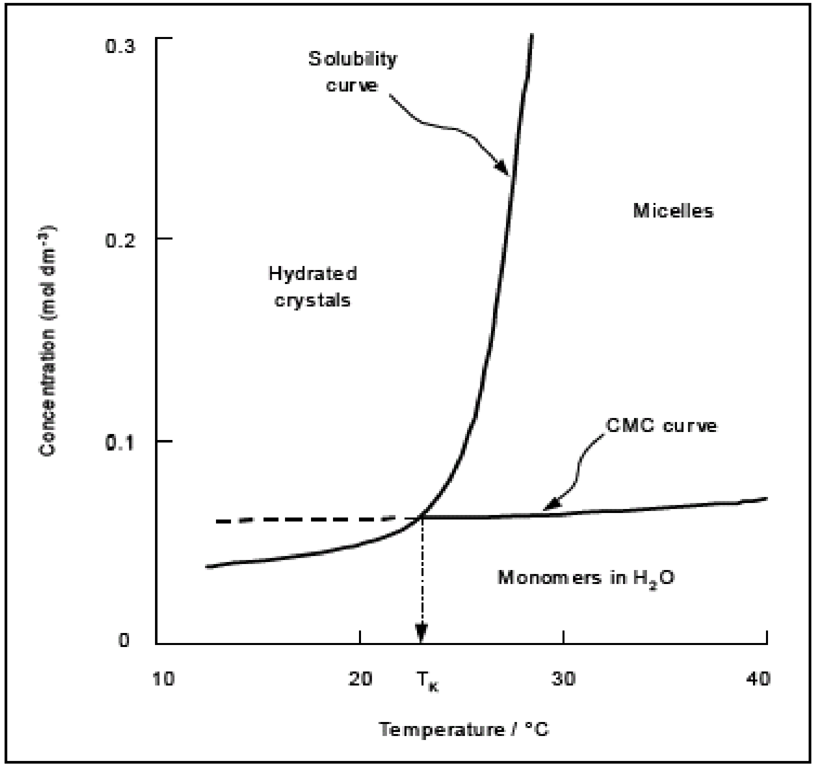
cmc of ionic surfactants
is generally higher
compared to nonionic surfactants

Ionic surfactants
cmc = $10^{-3} – 10^{-2}$ M

Nonionic surfactants
cmc = $10^{-4} – 10^{-3}$ M



Solubility of surfactants-The Krafft temperature



Binary
phase diagram
surfactant/water

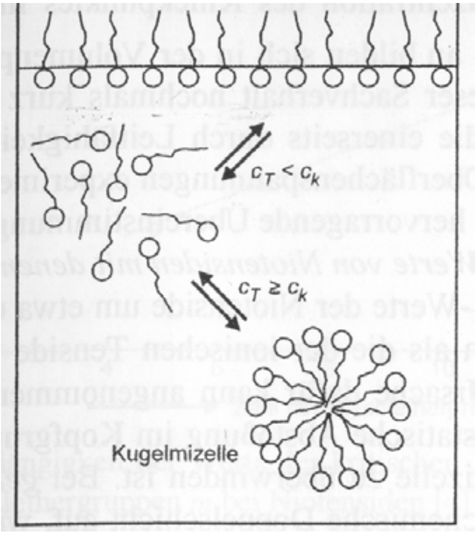
- Solubility of surfactants highly T dependent
- Solubility is usually low at low T, rising rapidly in narrow range
- No micelles possible above a certain temperature
- The point where solubility curve meets CMC curve is the Krafft point, which defines the T_{krafft}..
- The Krafft temperature can be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

3. Micelle formation mechanism

Stepwise growth model (Isodesmic model)

S: surfactant molecule

- $S + (n-1)S \Leftrightarrow S_2 + (n-2)S \Leftrightarrow S_{n-1} + S \Leftrightarrow S_n$
- Aggregation is a continuous process (broad aggregation, no cmc)
- Distribution of species



Not in aggrement with sudden changes at cmc

3. Micelle formation mechanism

Closed aggregation model

$nS \Leftrightarrow Sn$, eq.

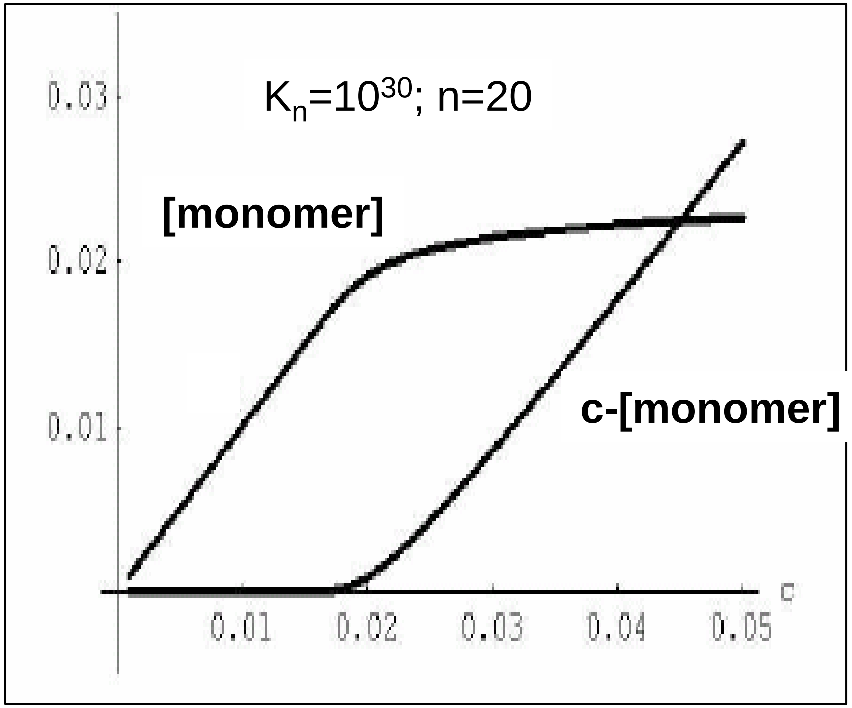
aggregation number n dominates

- (when $n \to \infty$, phase separation model)

→ cooperative phenomenon!

K_n = [micelles]/[monomers]^n = $[S_n]/[S]^n$

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

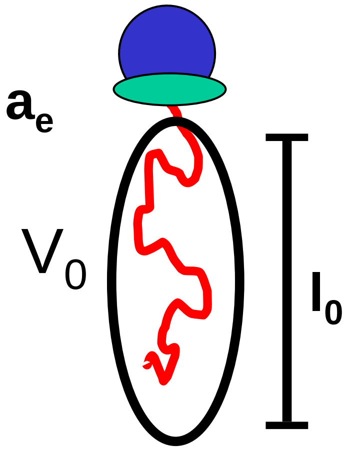


4. Semiquantitative predictive models of micellization

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)

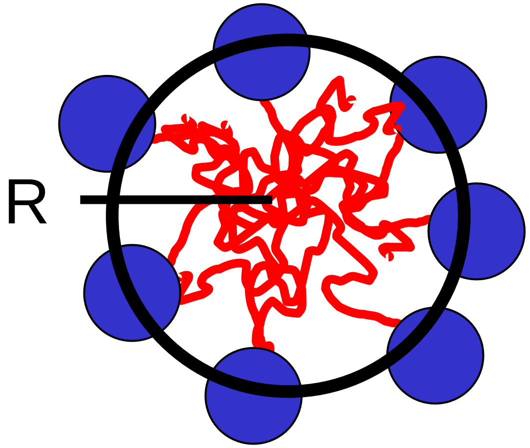


$$P = V_0/(a_e\, l_0)$$

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 = const. = 0.21 nm² (single tail)

Example: Spherical micelle with aggregation number g



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

$$\text{With } R \le l_0 \;\Longrightarrow\; 0 \le V_0/(a_e\, l_0) \le 1/3$$

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

Prediction of the shape of self-assembled structures in solution

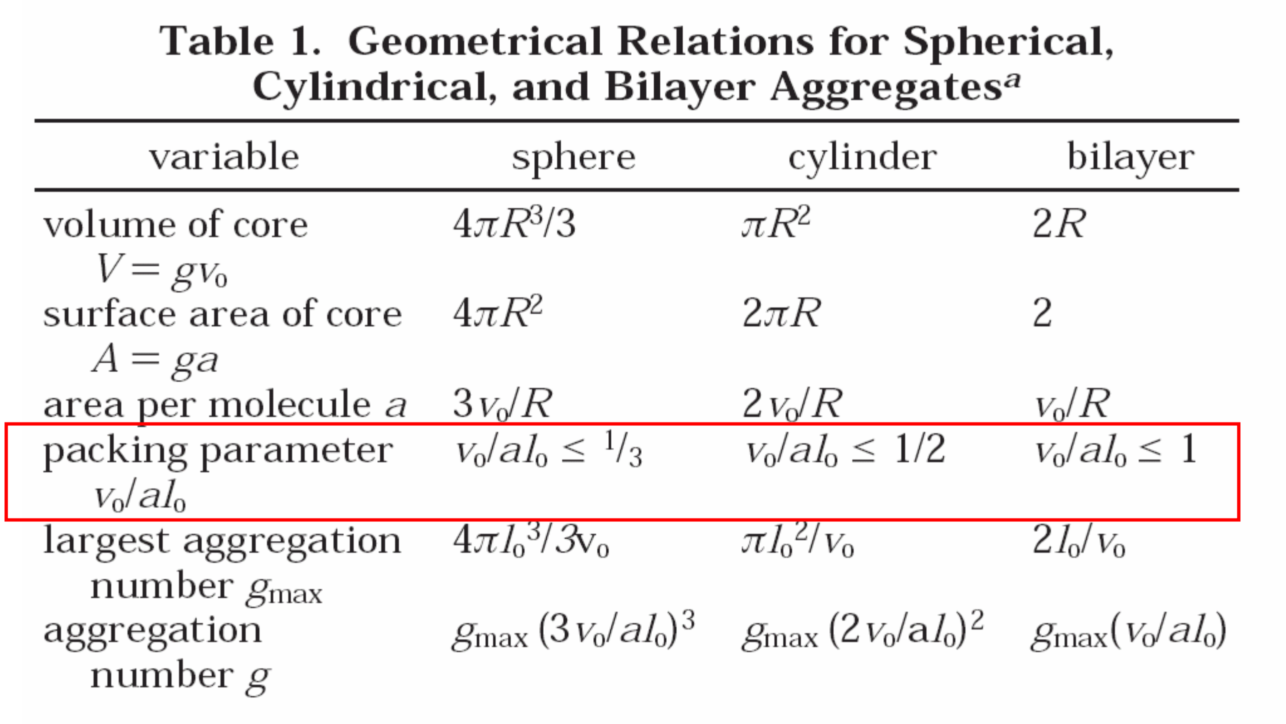


Table 1. Geometrical Relations for Spherical, Cylindrical, and Bilayer Aggregates[a]

variable	sphere	cylinder	bilayer
volume of core $V = g v_0$	$4\pi R^3/3$	πR^2	$2R$
surface area of core $A = ga$	$4\pi R^2$	$2\pi R$	2
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 = const. = 0.21 nm^2
(single tail)

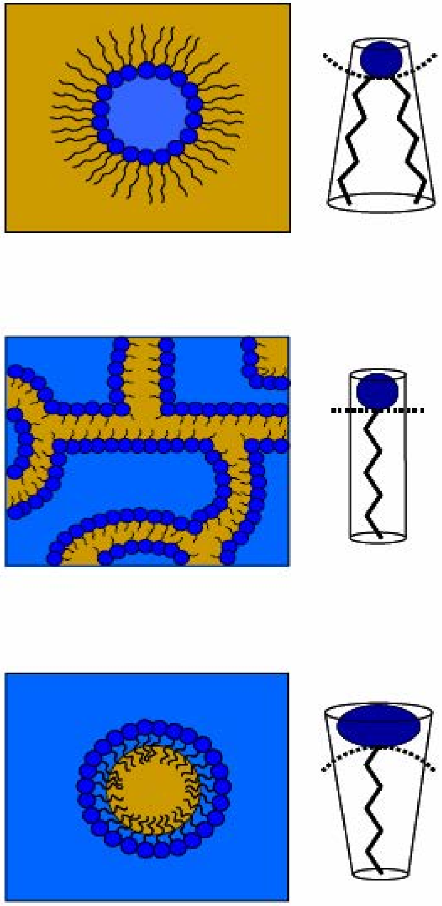
- **Only the headgroup controls the equilibrium aggregate structure via the headgroup area a_e**
- **The tail does not have any influence on the shape and size of the aggregate**

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
0.5 - 1.0	Double-chain surfactants with large head groups and flexible chains	Vesicles and flexible bilayers structures
1.0	Double-chain surfactants with small head groups or rigid, immobile chains	Planar extended bilayers
>1.0	Double-chain surfactants with small head groups, very large and bulky hydrophobic groups	Reversed or inverted micelles

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



Negative or reversed curvature

P > 1

Water-in-oil

Oil-soluble micelles

Zero or planar curvature

P ~ 1

Bicontinuous

Positive or normal curvature

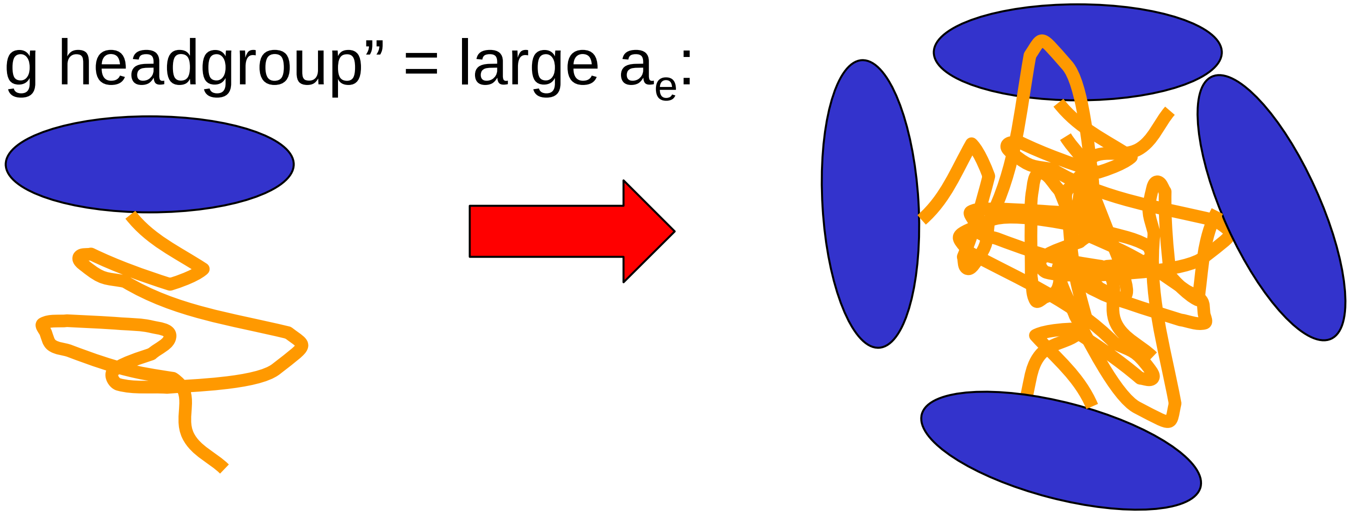
P < 1

Water-soluble micelles

Oil-in-water microemulsions

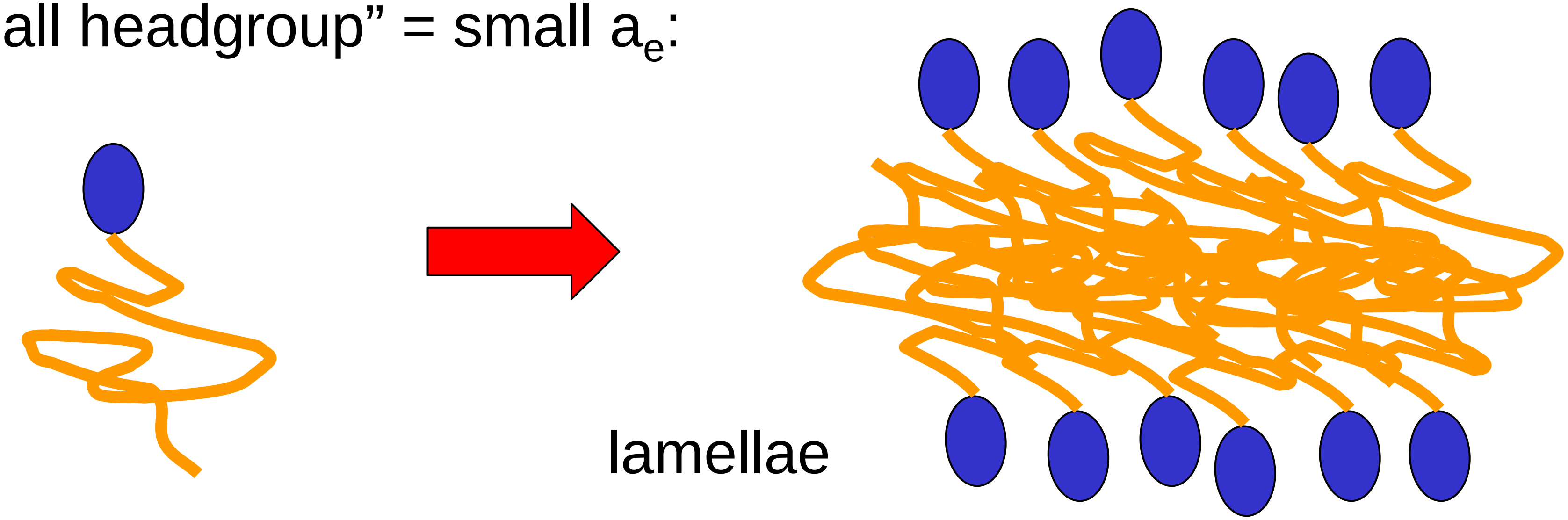
Predictions of the “packing parameter concept”

“Big headgroup” = large a_e:



Spherical micelles

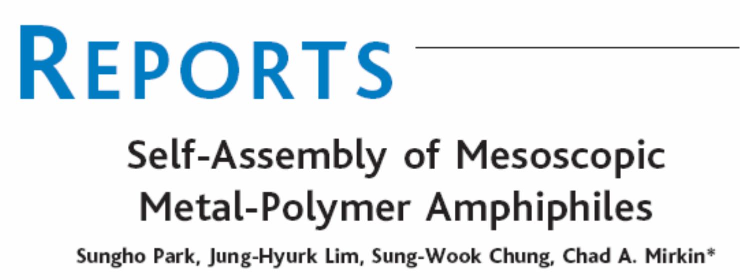
“Small headgroup” = small a_e:



lamellae

Predictions of the “packing parameter concept”

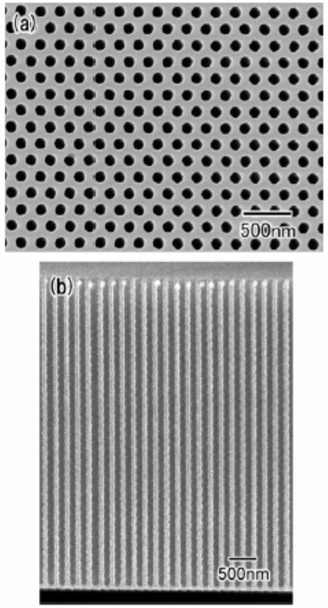
A model surfactant system



REPORTS

Self-Assembly of Mesoscopic Metal-Polymer Amphiphiles

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

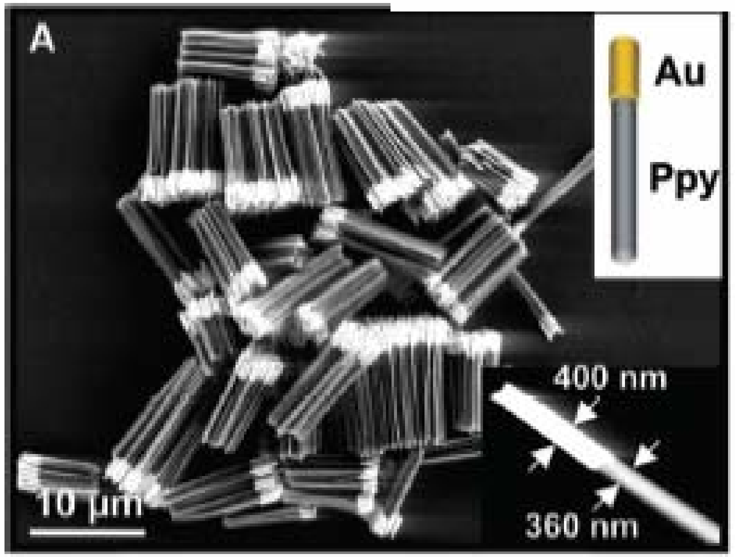


starting from commercial anodic alumina

electro-deposition of gold

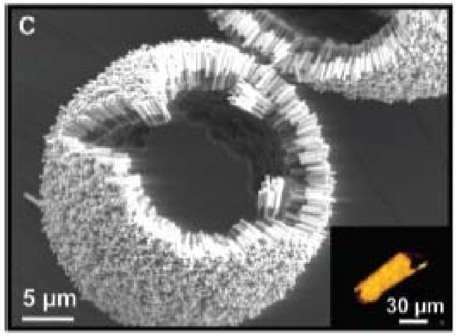
polymerization of polypyrrole

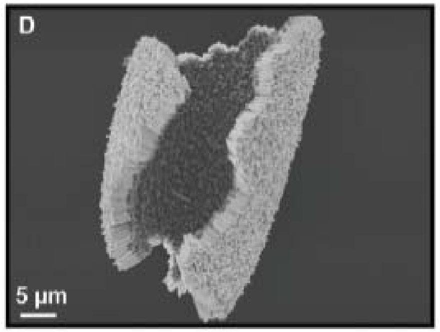
dissolution of the alumina membrane and the silver cathode and backing

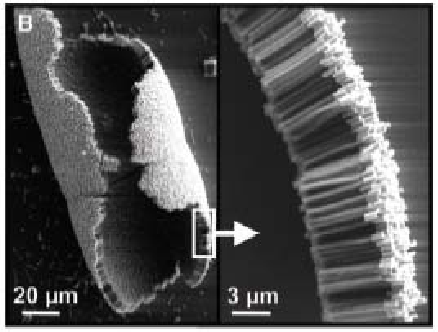


Predictions of the “packing parameter concept”

A model surfactant system

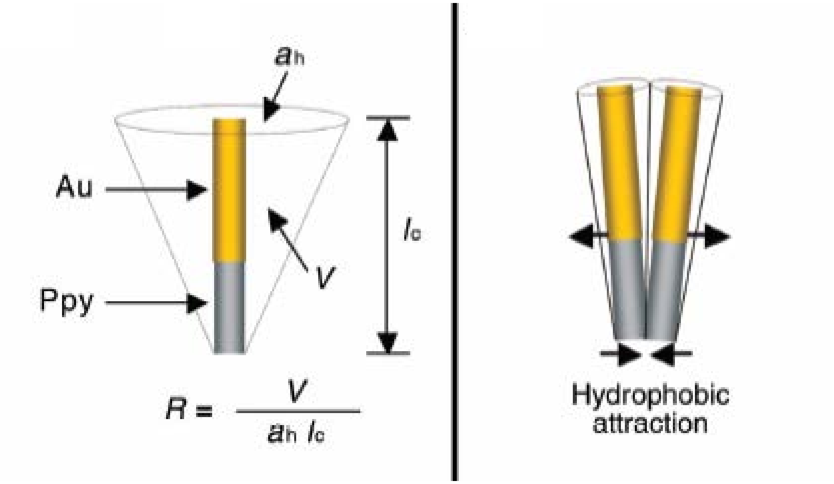






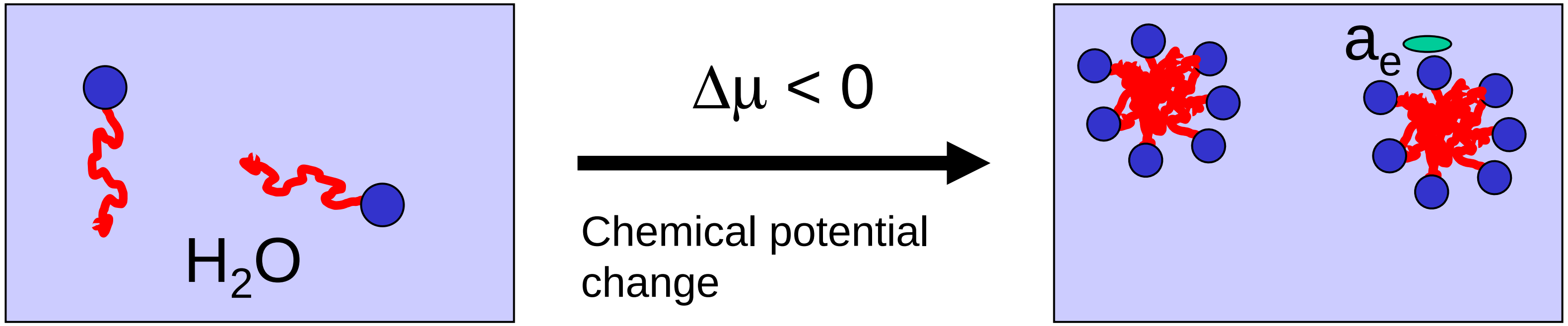
block length ratio (Au/PPy)	3:2	4:1	1:4

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“



$\Delta\mu < 0$

Chemical potential change

Infinitely diluted state

Self-assembled state

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

−

Avoiding the contact between hydrocarbon bails and water

+

Residual contact water – hydrocarbon:

$\sigma \bullet a$

+

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

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

$g \propto 1/a_e$

General aspects:

1) **Tail transfer is responsible for aggregation, no influence on size and shape!**

2) **Residual contact $\propto a_e$ → promotion of the growth of aggregates**

3) **Headgroup repulsion $\propto 1 / a_e$, → limitation of the aggregate size!**

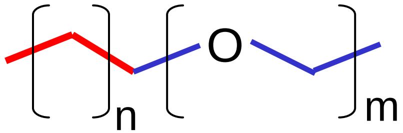
→ Tanford's model explains basic features of micellization!

Some successful predictions of the packing model

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

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

1) Nonionic surfactants with ethylene oxide headgroups



A) m small → α small → a_e small

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

B) m larger … → $V_0/(a_e\ l_0)$ lower → cylindrical micells favored

2) Ionic surfactants:

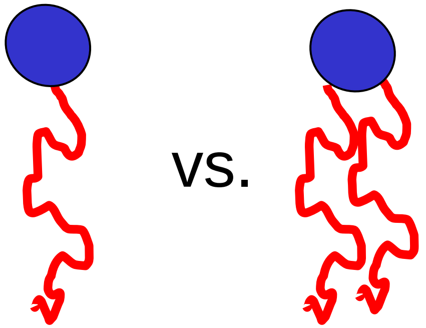
salt addition decreases the repulsion α → decrease in a_e →
increase in $V_0/(a_e\ l_0)$

→ **transition from spherical micelles to cylindrical micelles.**

Some successful predictions of the packing model

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

3) Single tail / double tail surfactants

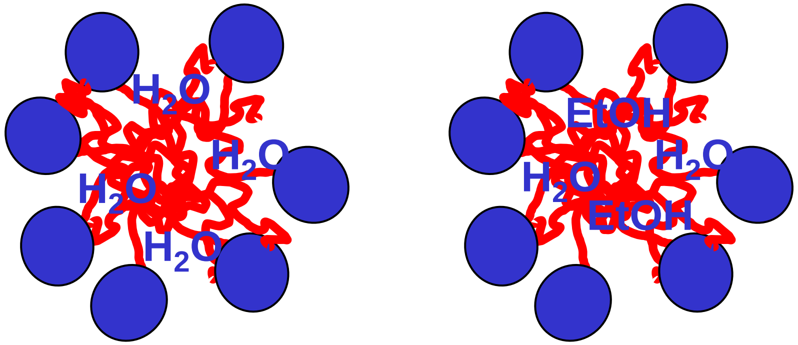


Same equilibrium area a_e

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

→ **bilayers instead of spherical or globular micelles**

4) Influence of solvents



Interfacial tension σ decreases

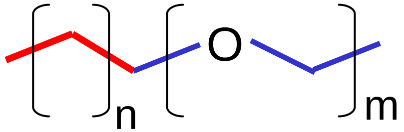
→ **a_e increases** → **$V_0/(a_e\, l_0)$ decreases**

→ bilayer to micelles,
rodlike to spherical micelles

Some successful predictions of the packing model

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

5) Influence of temperature



$\xrightarrow{\Delta T}$ **Increasing the temperature decreases the steric repulsion of PEO headgroup**

→ **α decreases** → **a_e decreases**

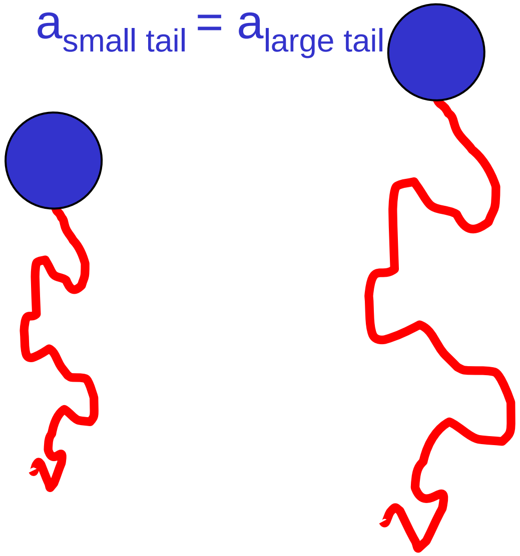
→ **P increases**

→ **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



Geometric head group area

$a_{\text{small tail}} = a_{\text{large tail}}$

Small tail

Large tail

Same aggregation behavior ?

… obviously not!

$$P_{\text{small tail}} = P_{\text{large tail}} \quad ?$$

- **Are the assumptions of the "packing parameter" model incorrect?**

- **How does the tail influence self-assembly ?**

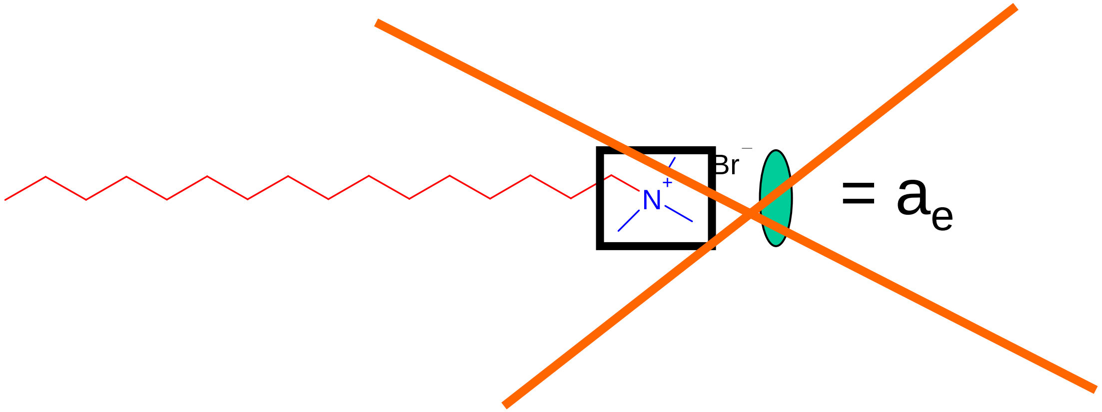
ATTENTION: Neglected role of the surfactant tail!!

- **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…

$P=V_0/(a_e\ l_0)$

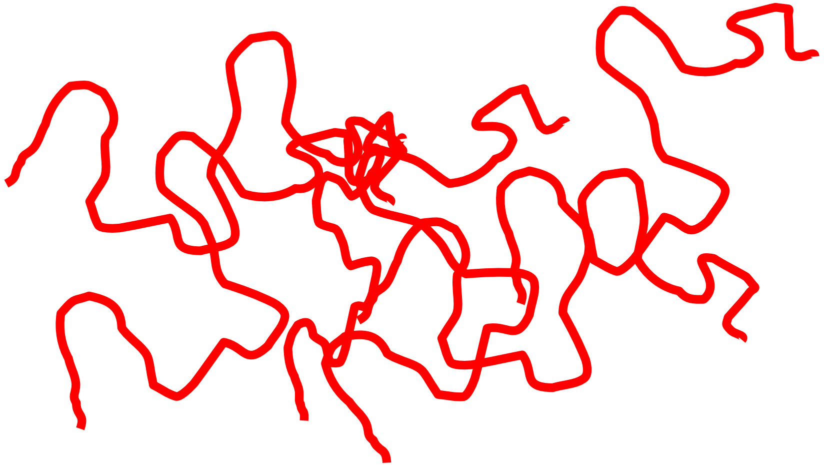
a_e: is an equilibrium parameter, not just a Geometrical surface area!



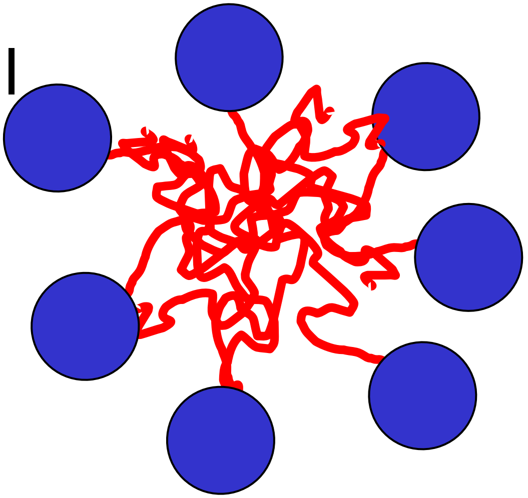
The tail might influence the packing parameter α and thereby the aggregation

Influence of tail packing constraints

Bulk hydrocarbon



Micell



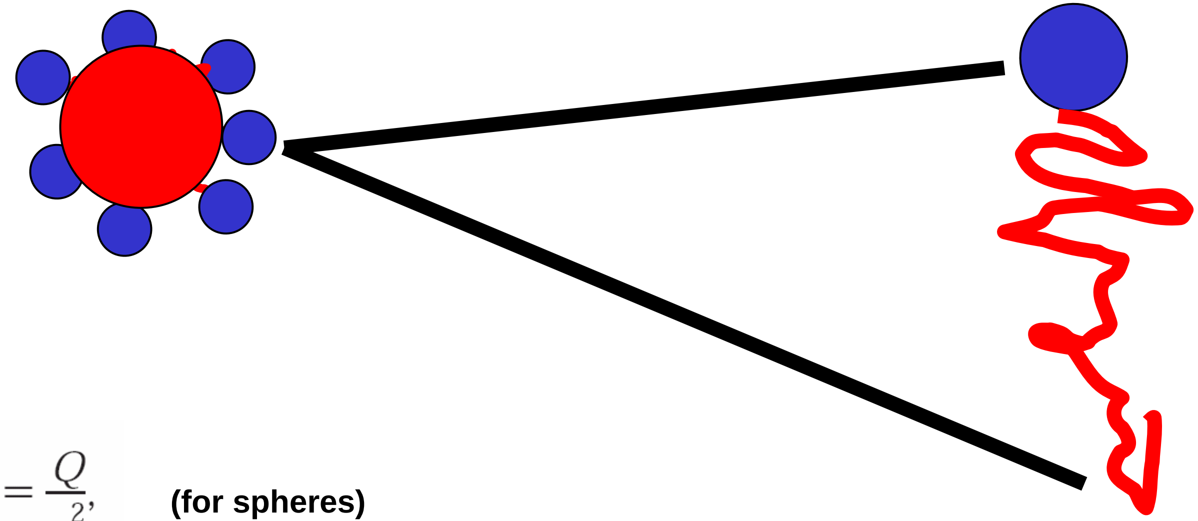
→ **Different packing for the hydrocarbons compared to the bulk: Non-uniform deformation in the micelle!**

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

(Nagarajan, Ruckenstein)

Influence of tail packing constraints – Nagarajan/Ruckenstein

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



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

(for spheres)

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

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

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

$Q \propto L, v_0$

➡ **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

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

Consideration of tail packing constraints

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

	from eq 3		spheres (eq 21)		cylinder (eq 21)		bilayers (eq 21)	
n_C	a_e (Å^2)	$v_0/a_e l_0$	a_e (Å^2)	$v_0/a_e l_0$	a_e (Å^2)	$v_0/a_e l_0$	a_e (Å^2)	$v_0/a_e l_0$
For $\sigma/kT = 0.12$ Å^{-2}, $\alpha/kT = 300$ Å^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

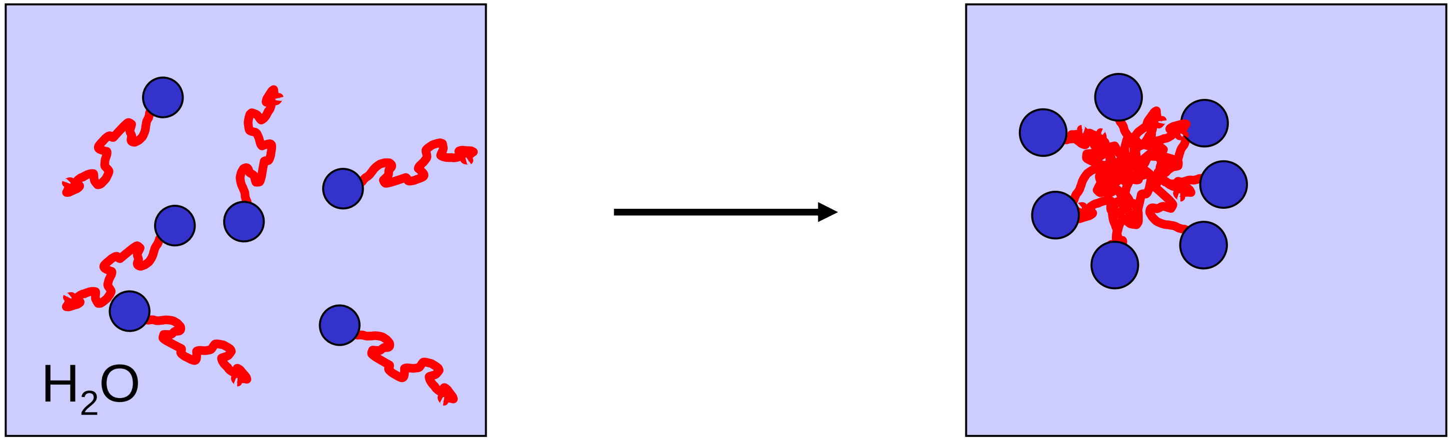
Spherical micelles possible!!

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

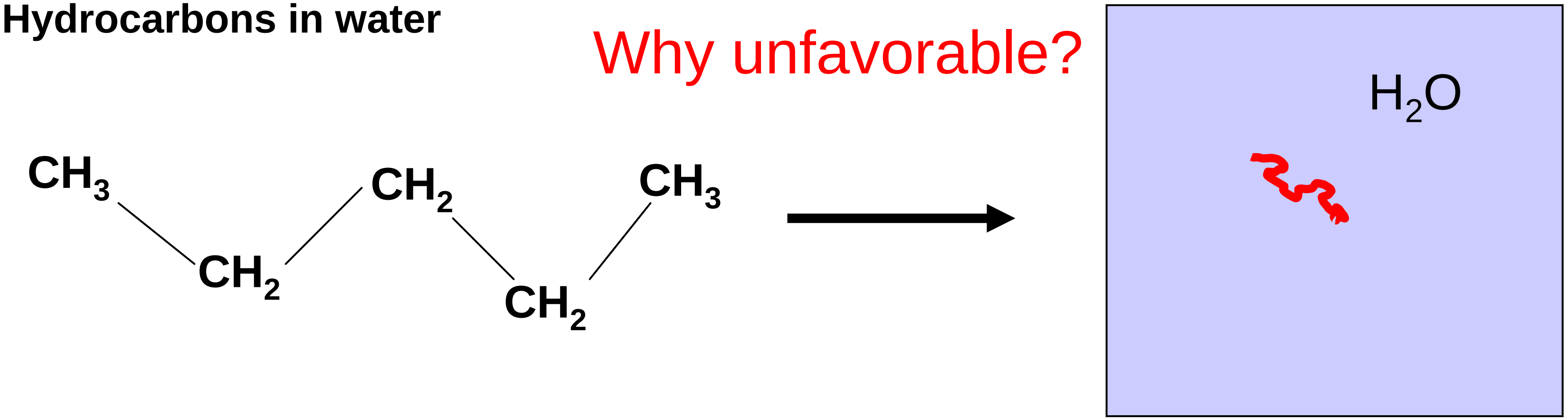
5. What is the “deeper” reason for self-assembly?

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

1) Micellization



2) Hydrocarbons in water



Why unfavorable?

Entropie/enthalpy of micellization

$$\boxed{\Delta G = \Delta H - T\,\Delta S}$$

Low-molecular weight surfactants:

- Δ H ca. + 1-2 kJ/mol
  Micellization is unfavorable with respect to the enthalpy!!

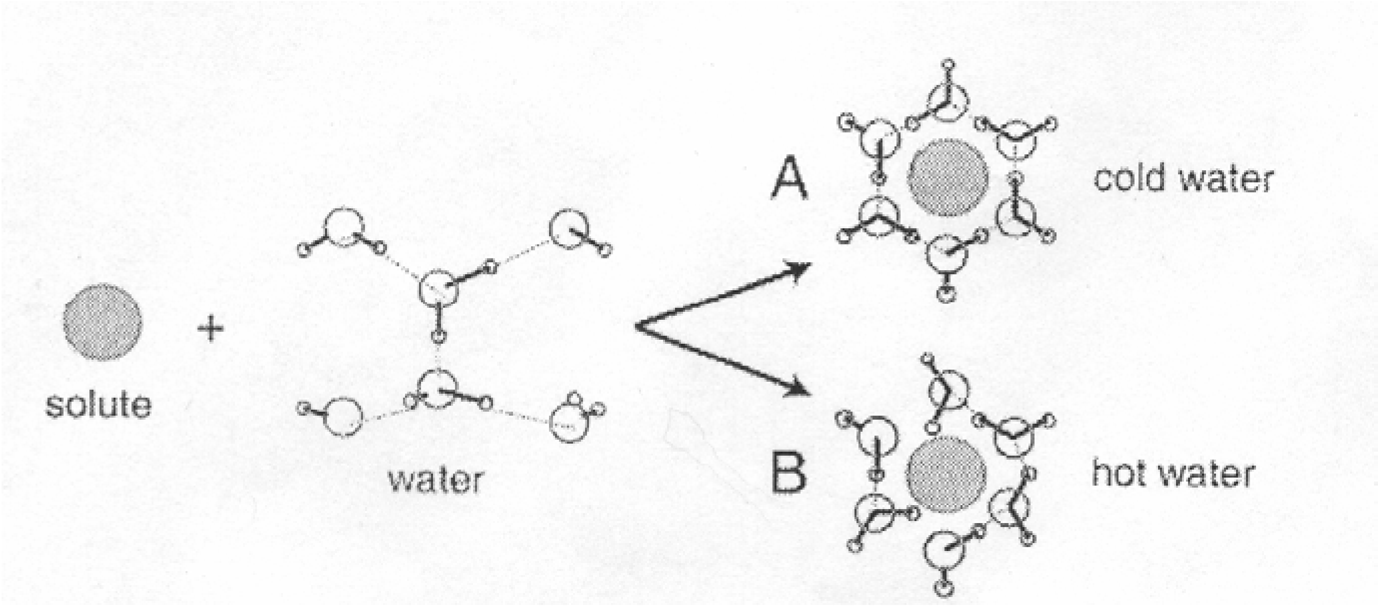
- Δ S ca. + 140 J /K: The entropy of micellization is POSITIVE

➡ 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”

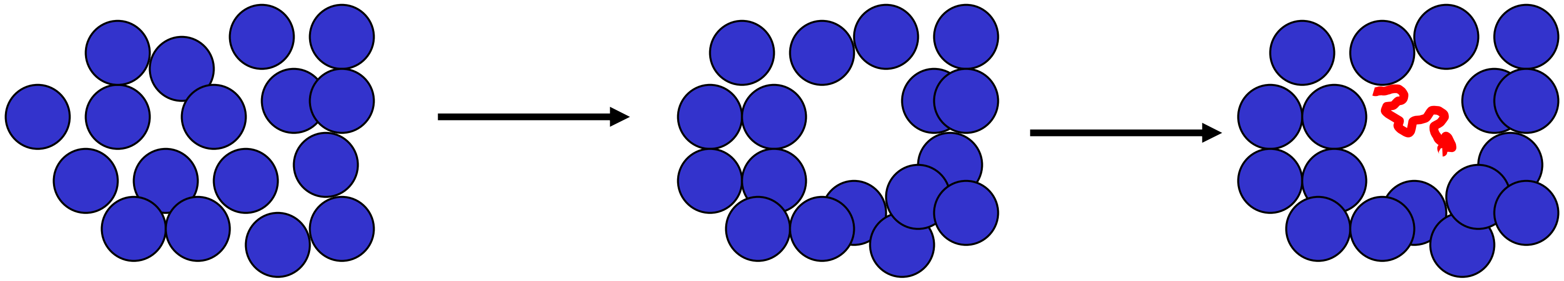
Frank, Evans, ***J. Chem. Phys.*** **1945,** *13(11),* **507.**

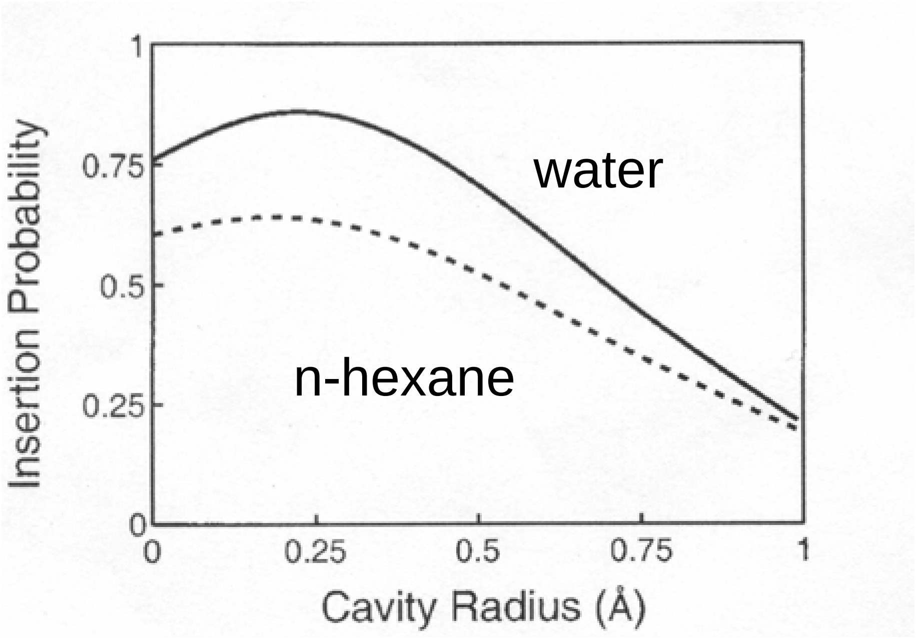


A) **Nonpolar solutes create a clathrate-like cage of first-shell waters around the solute.**
B) **Large entropic cost to order the hydrogen bonds into a more open “iceberg”-like structure (low temperature).**
C) **High-Temperatures break hydrogen bonds to gain entropy, at the cost of the enthalpy.**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