

Modern Aspects of Colloid Science

MICELLES

critical micelle concentration (CMC)

micellar shape

determination of critical micelle concentration

purity of surfactants

Krafft temperature

micellar equilibria

micelles as reaction partners

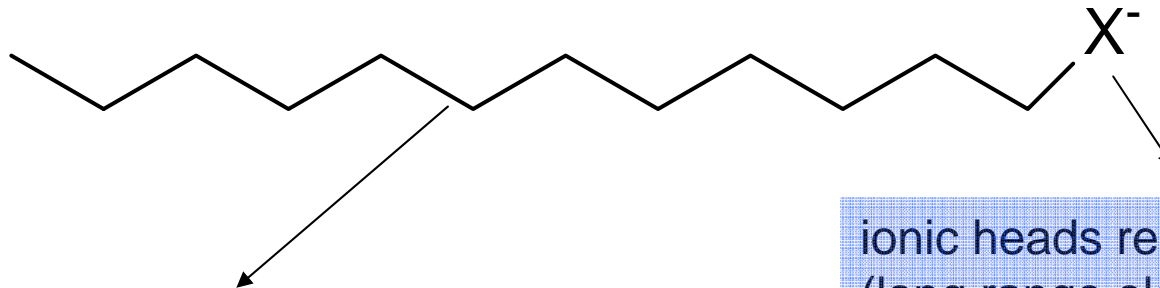
surfactants - block copolymers - particles

amphiphilic molecules

lyophilic and lyophobic parts combined in one molecule

reference state water: e.g. paraffin chain ions

water: high cohesive forces (hydrogen bonding) &
high dielectric constant



hydrocarbon chains attract
each other
(short range van der Waals forces)
promoting micelle formation

ionic heads repel each other
(long range electrical forces)
counteracting micelle formation

micelle is a self-assembled structure of amphiphilic molecules and consists of core and shell

lyophobic core

lyophilic shell

shapes of micelles

water outside



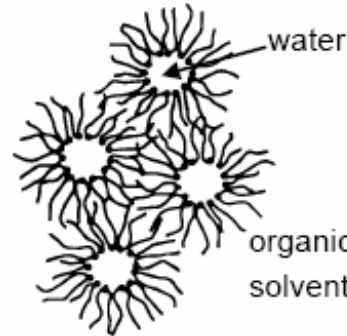
sphere



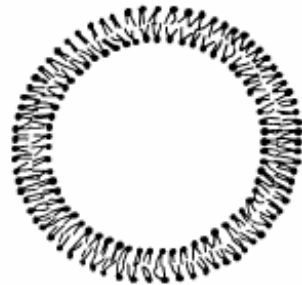
ellipsoid



cylinder



inverted micelle



unilamellar vesicle



planar structure

transition from a solution to a colloidal dispersion

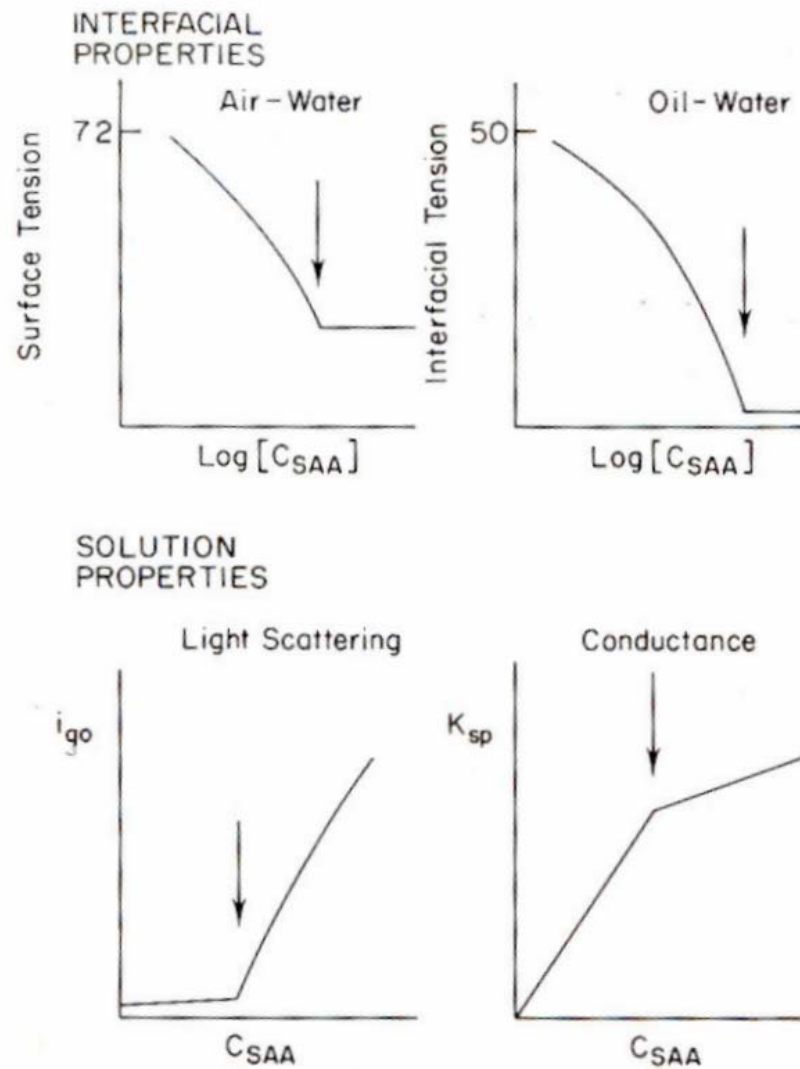
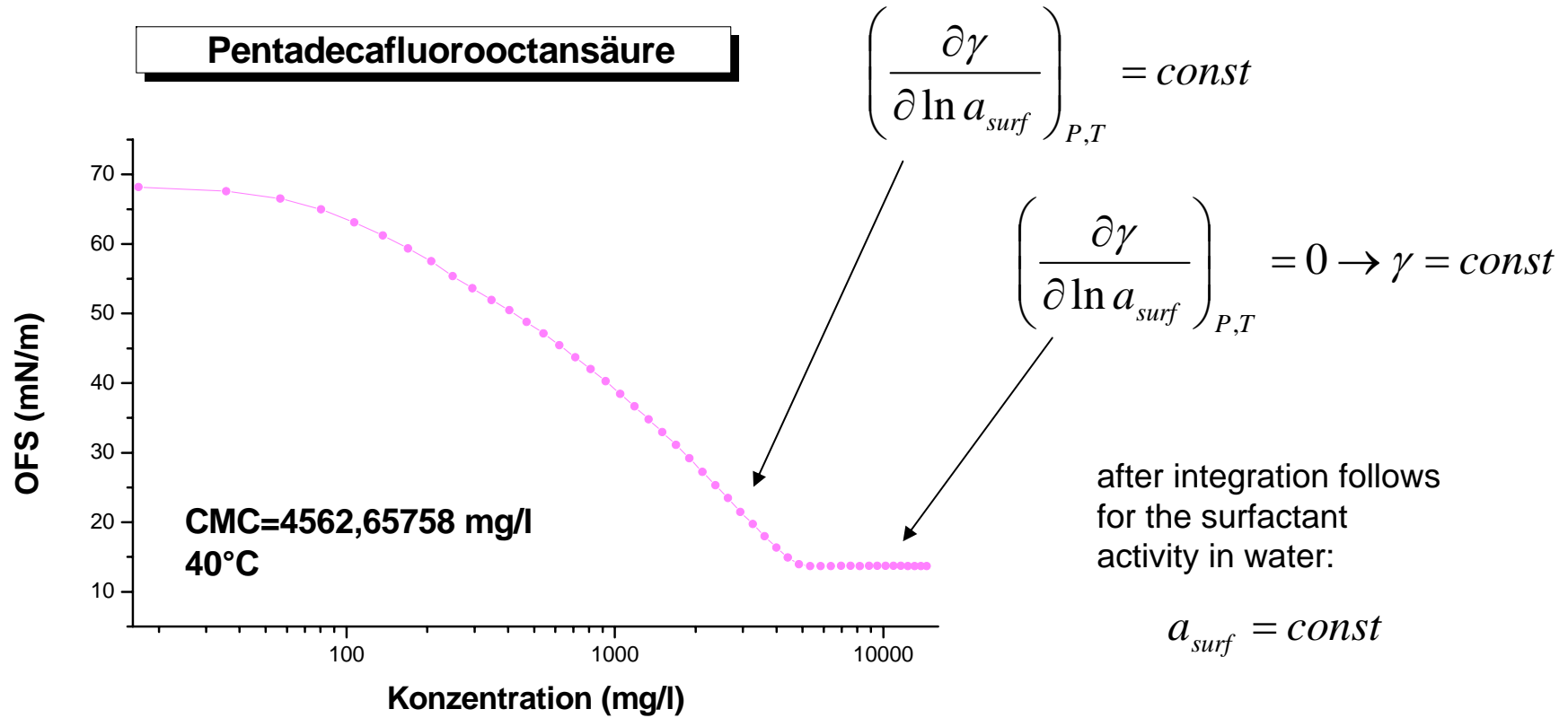
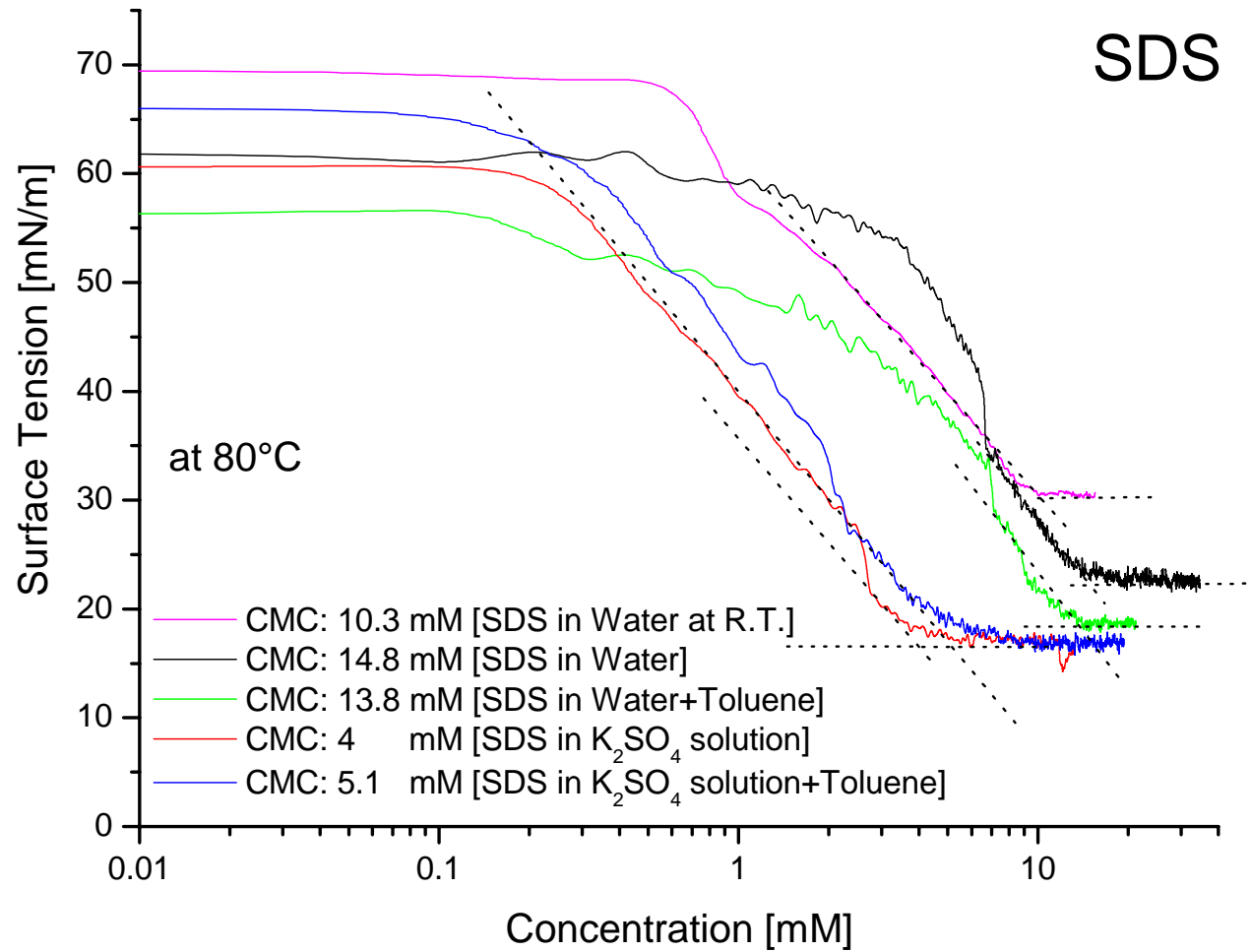


Fig. 2. Interfacial and solution properties of surface active agents:- (a) air-water tension versus log concentration, (b) oil-water interfacial tension versus log concentration, (c) scattered light intensity versus concentration, (d) specific conductance versus concentration.

practical example



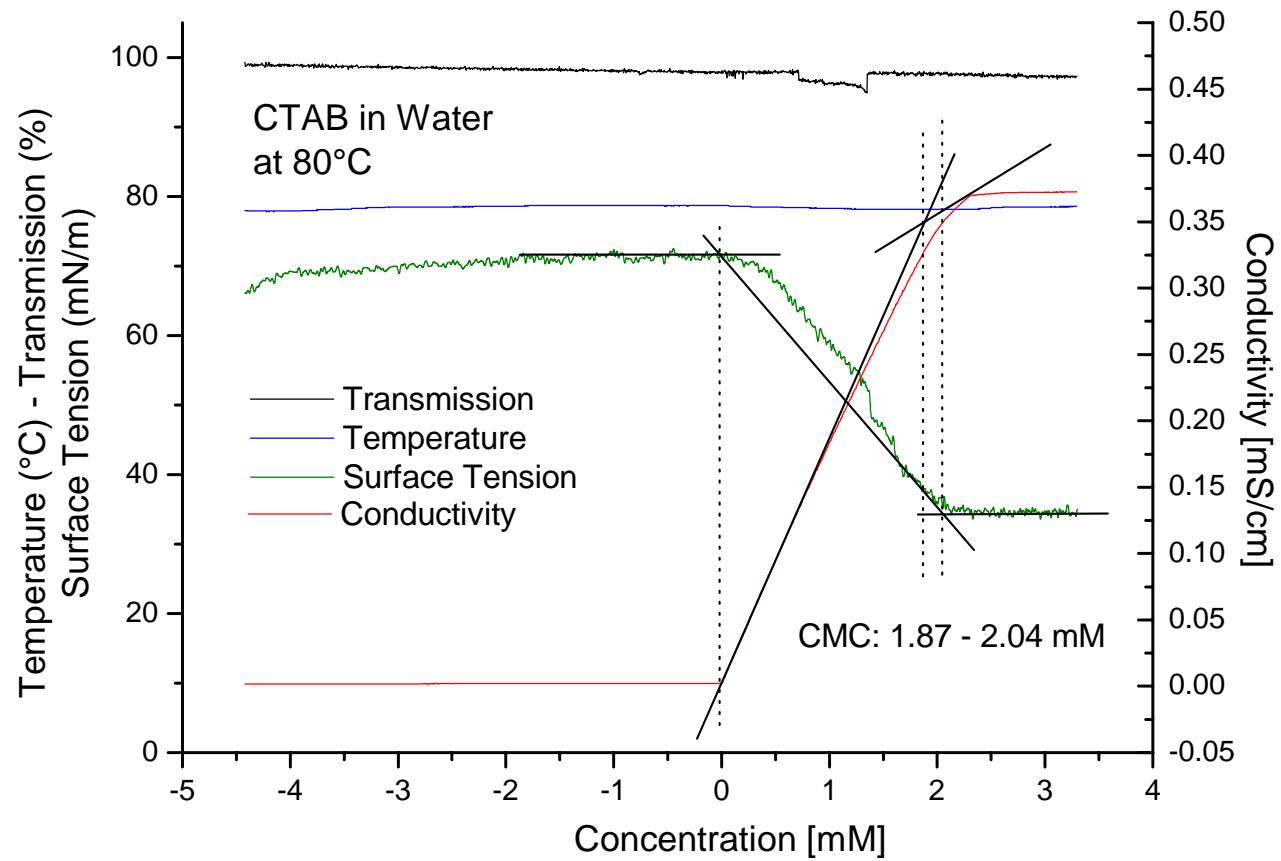
CMC depends on temperature, ionic strength, solvency

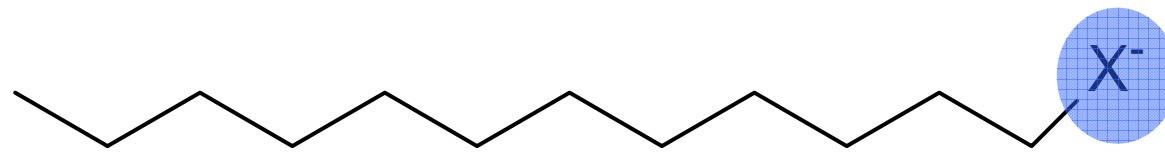


very easy: bubble tensiometer

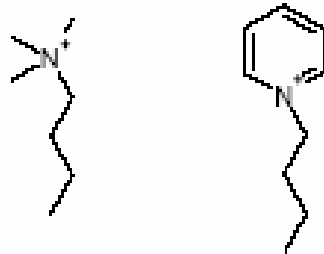
combination of methods

CTAB

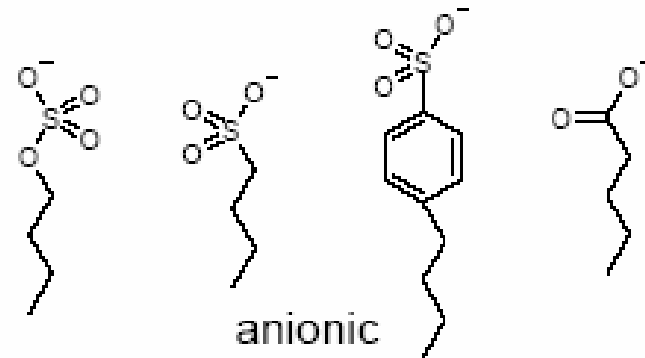




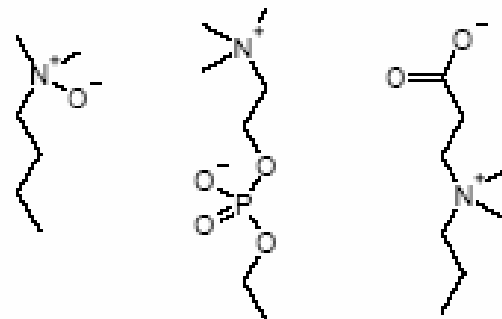
Examples of polar headgroups:



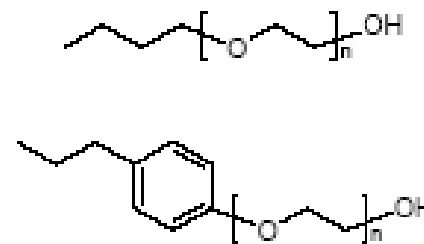
cationic



anionic



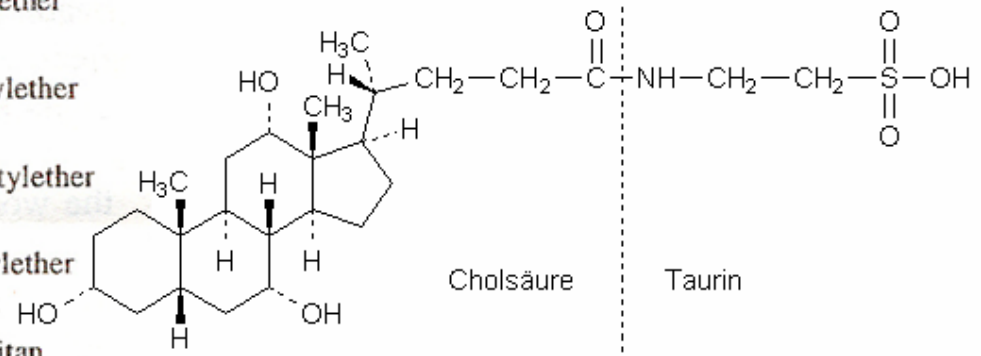
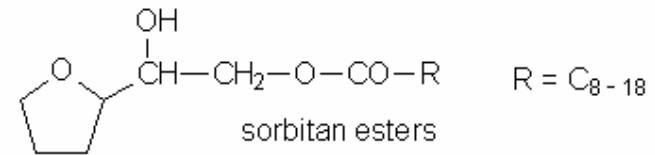
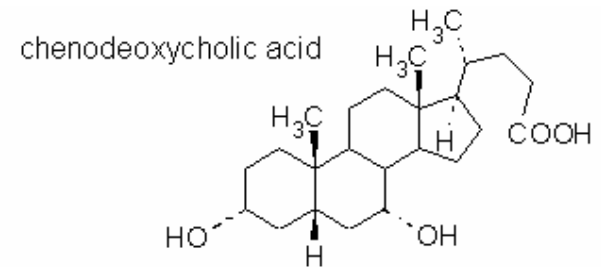
zwitterionic



non-ionic

some surfactants:

Ionics	Nonionics
Sodium palmitate	Polyethylene glycol tertocetyl phenyl ether (Triton × 100)
Sodium oleate	Sorbitan monolaurate (Span 20)
Sodium decyl sulphate (NaDes)	Sorbitan monopalmitate (Span 40)
Sodium dodecyl sulphate (SDS)	Sorbitan monostearate (Span 60)
Sodium dodecyl sulphonate	Sorbitan monooleate (Span 80)
Sodium dodecyl benzene sulphonate (SDBS)	Polyoxyethylene (4) laurylether (Brij 30)
Sodium cholate (NaC)	Polyoxyethylene (23) laurylether (Brij 35)
Sodium deoxycholate (NaDC)	Polyoxyethylene (9) palmitylether (Brij 56)
Sodium chenodeoxycholate (NaDC)	Polyoxyethylene (9) stearylether (Brij 76)
Sodium taurochenodeoxycholate (NaTCDC)	Polyoxyethylene (20) sorbitan monolaurate (Tween 20)
Sodium bis ethyl hexyl sulfo-succinate (AOT)	Polyoxyethylene (20) sorbitan monopalmitate (Tween 40)
Dodecyltrimethyl ammonium bromide (DTAB)	Polyoxyethylene (20) sorbitan monostearate (Tween 60)
Tetradecyltrimethyl ammonium bromide (TTAB)	Polyoxyethylene (20) sorbitan monooleate (Tween 80)
Hexadecyl (or cetyl) trimethyl ammonium bromide (CTAB)	Octylmethyl sulphoxide
Hexadecyl (or cetyl) pyridinium chloride (CPC)	Tetradecyl <i>N</i> betaine



fatty acids:

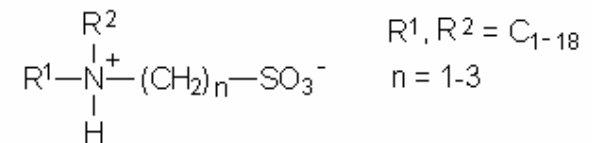
C_{12} – lauric acid

C_{16} – cetylic or palmitic acid

C_{18} – stearic acid

cis-9-octadecanoate: oleic acid

$CH_3(CH_2)_7CH=CH(CH_2)_7C(O)OPEG$ $(H_3C)_3N^+ - CH_2 - COO^-$



betaine & sulfobetaine

Table 2. Physicochemical properties of some typical surfactants

Surfactant ^a	CMC/m mol dm ⁻³	Aggregation number	% Counterion bound
SDeS ⁴⁰	41.0	30	40
SDS ²⁵	8.0	50	60
AOT ²⁵	3.0	15	10
NaC ²⁰	12.0	2	—
NaDC ²⁰	5.0	4	—
NaTC ²⁰	10.0	4	—
DTAB ³⁰	16.0	48	77
TTAB ³⁰	3.1	55	73
CTAB ³⁰	0.8	55	85
CPC ³⁰	0.83	—	58
Triton X-100 ²⁵	0.03	134	—
Tween 20 ²⁵	0.05	86	—
Tween 40 ²⁵	0.023	92	—
Tween 60 ²⁵	0.021	112	—
Tween 80 ²⁵	0.01	124	—

^a Superscripts refer to the temperature in °C. Abbreviations as in Table 1.

micellar shape and surfactant geometry:

Factors governing micellar shape:

- optimal headgroup area: a_0
- volume of the alkyl chains: $V (= 27.4 + 26.9n_c [\text{Å}^3])$
- critical chain length: $L_c (= 1.54 + 1.26n_c [\text{Å}])$

For a spherical micelle with N surfactants:

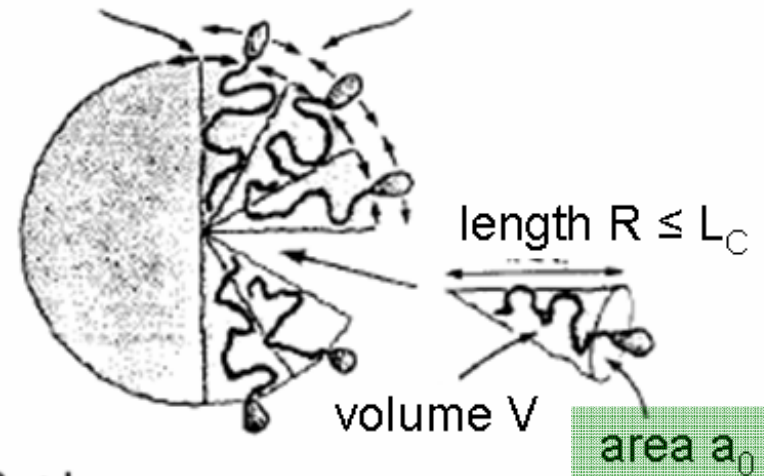
volume = $NV = (4\pi/3)R^3$
 outer area = $Na_0 = 4\pi R^2$

So: $R = 3NV/Na_0 = 3V/a_0$

Spherical packing is allowed when:

So: critical packing parameter:

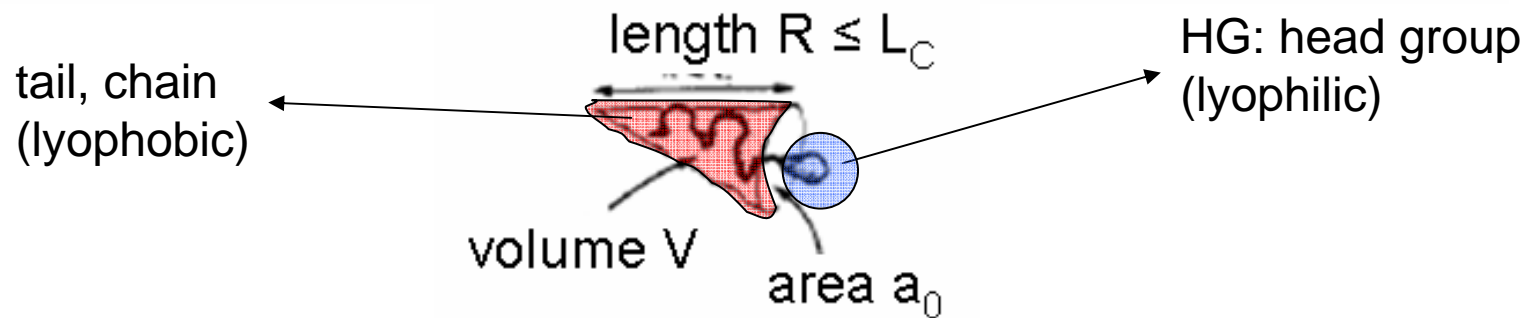
$R < L_c$
 $V/a_0L_c < 1/3$



not a geometrical area but an effective area including head group repulsion

micellar shapes:

V/a_0L_c	surfactant	aggregate
< 0.33	single chain, large HG	spherical/ellipsoidal
$0.33 - 0.5$	single chain, small HG	cylindrical/rod
$0.5 - 1.0$	double, flexible chains, large headgroup	vesicles, flexible bilayers (1.0: planar bilayer)
> 1.0	double, rigid, bulky chains, small HG	reversed/inverted micelles

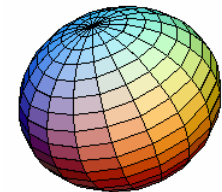


micelles of paraffin chain mono-salts in solution:

- interior of the micelle consists of hydrocarbon chains
- polar groups are spaced on the surface
- chains are in unordered arrangement (liquid state)
- there cannot be an open space in the interior

L_C cannot be the same for all chains

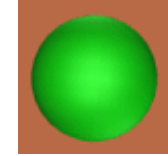
with this limitation, the simplest geometric form having the least area for the volume is that of sphere or an oblate spheroid



oblate spheroid
(earth – like)

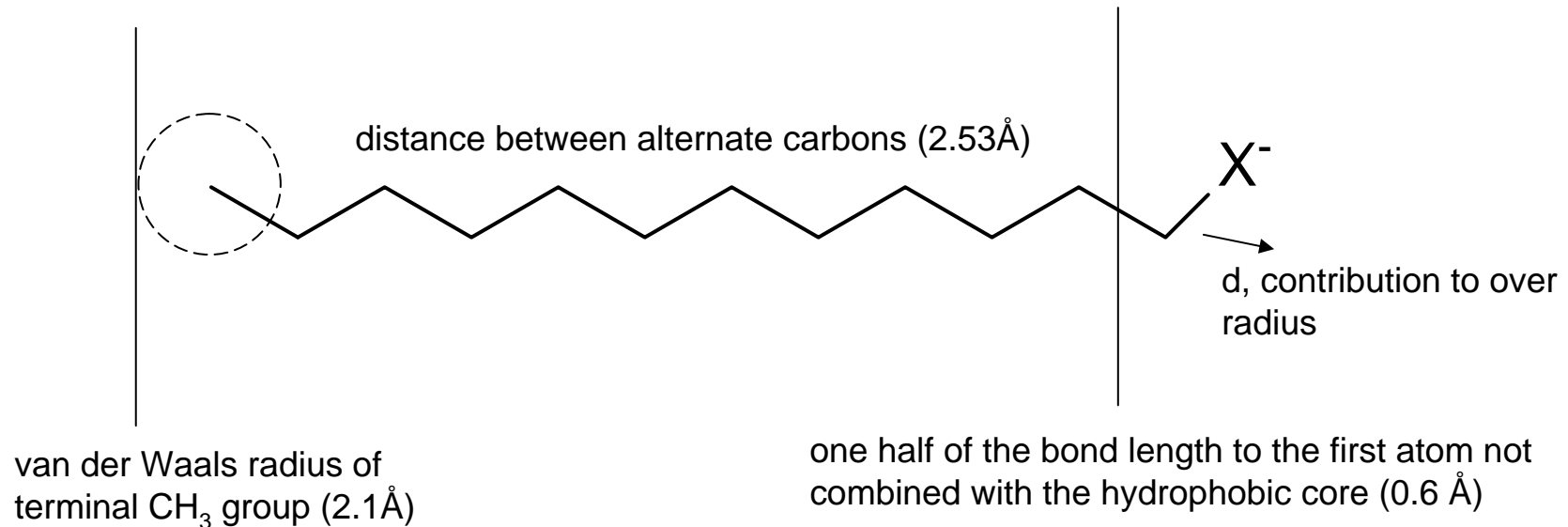
the shape of a micelle may vary from spherical depending upon the chain length (chain length distribution) and the area occupied per head group

estimate shape of micelles:



$$L_C = 1.5 + 1.265n_C \quad V_C = 27.4 + 26.9n_C \quad V_M = \frac{4\pi}{3} \cdot R_C^3$$


$$S = 4\pi \cdot (R_C + d)^2 \quad m = \frac{V_M}{V_C}$$



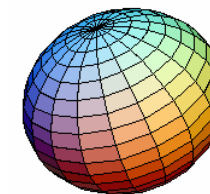
n_C	$L_C(\text{Å})$	$V_C (\text{Å}^3)$	$V_M (\text{Å}^3)$	m	$S/m (\text{Å}^2)$
6	9.1	189	3150	17	92.7
8	11.6	243	6570	27	86.0
10	14.2	296	11870	40	81.9
12	16.7	350	19440	56	79.0
14	19.2	404	26690	74	76.9
16	21.7	458	43040	94	75.3
18	24.3	512	59880	117	74.1
20	26.8	565	80630	143	73.1

experimental value SDS: $m \sim 62$ (absence of salt) and 126 (in 0.5 M NaCl)

the calculated n_C - values are too small

 distortion in the spherical shape to incorporate a larger number of molecules

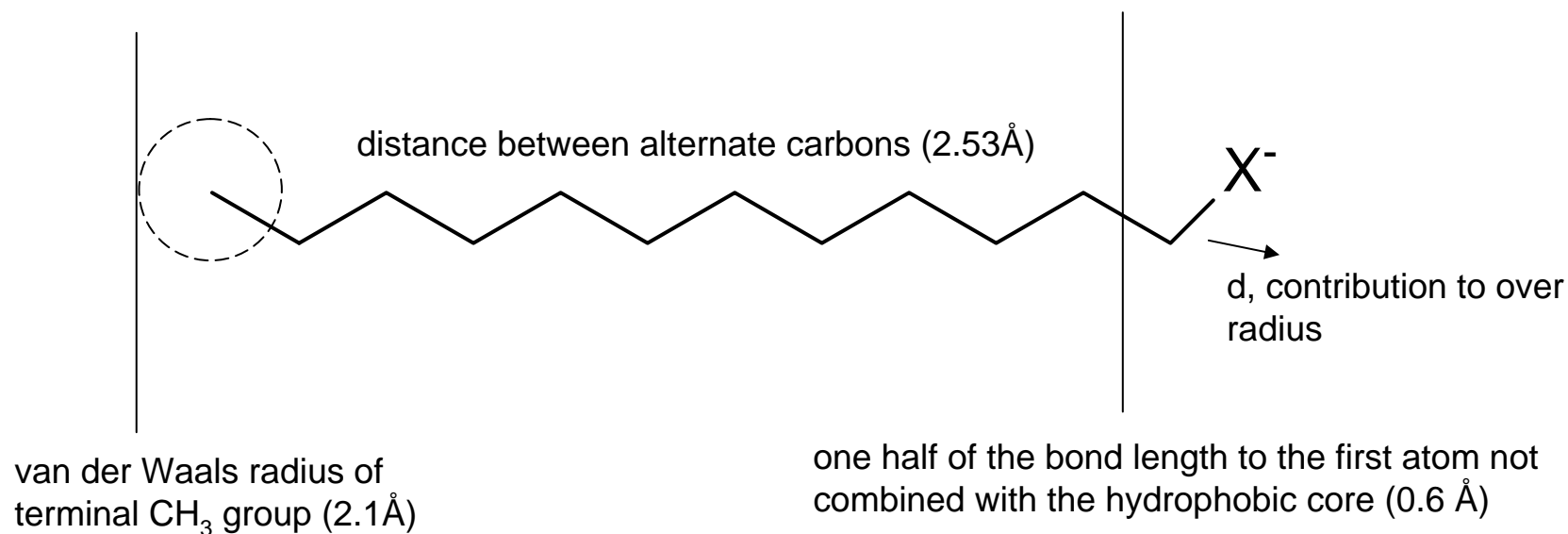
from a sphere to an oblate spheroid:



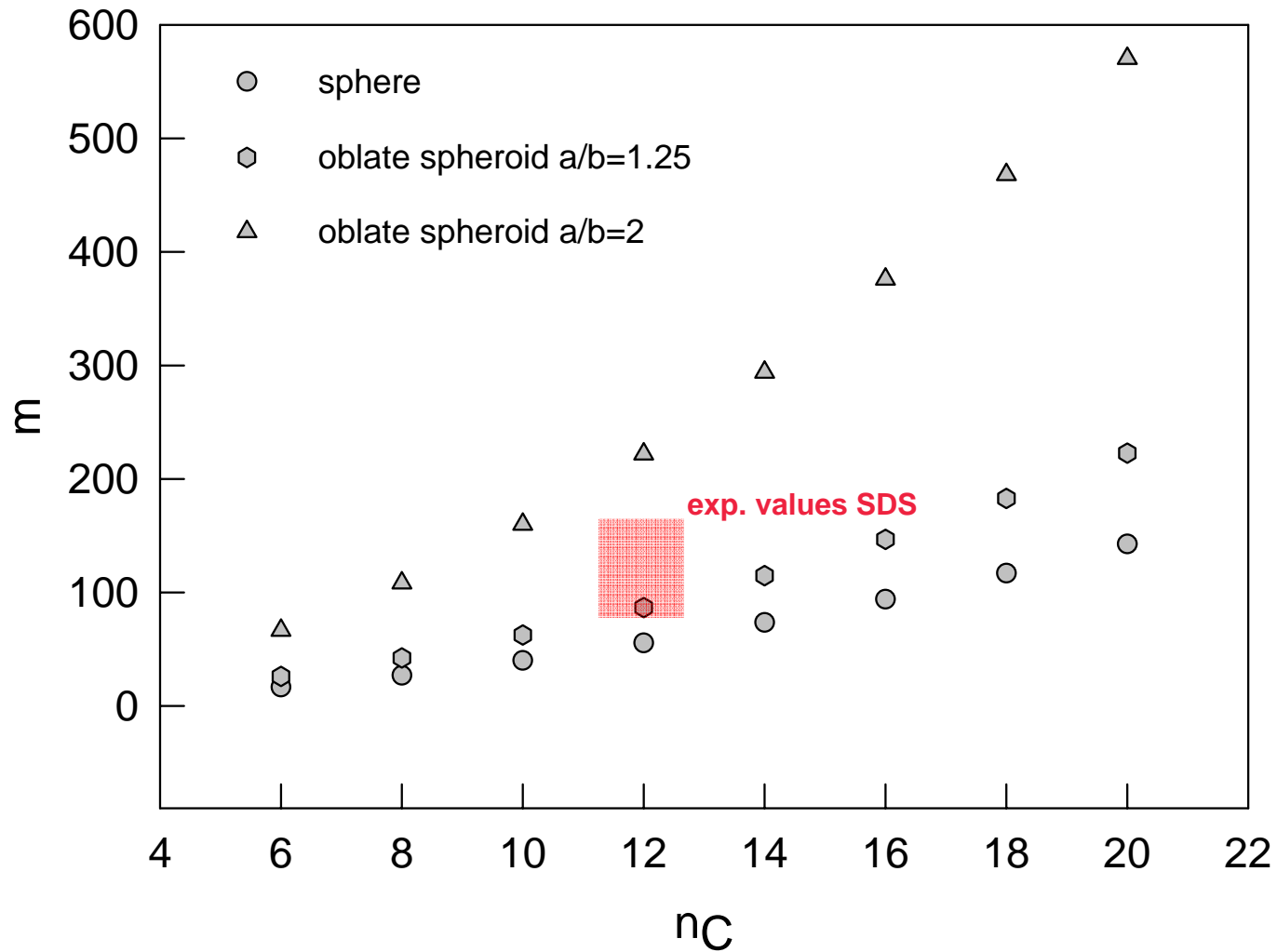
$$L_C = 1.5 + 1.265n_C \quad V_C = 27.4 + 26.9n_C \quad V_{M,obl} = \frac{4\pi}{3} \cdot a_0^2 \cdot b_0$$

$$S_{obl} = 2\pi \cdot a_0^2 + \pi \frac{b_0^2}{e} \ln \frac{1+e}{1-e} \quad e = \sqrt{\frac{(a_0^2 - b_0^2)}{a_0^2}} \quad m = \frac{V_{M,obl}}{V_C}$$

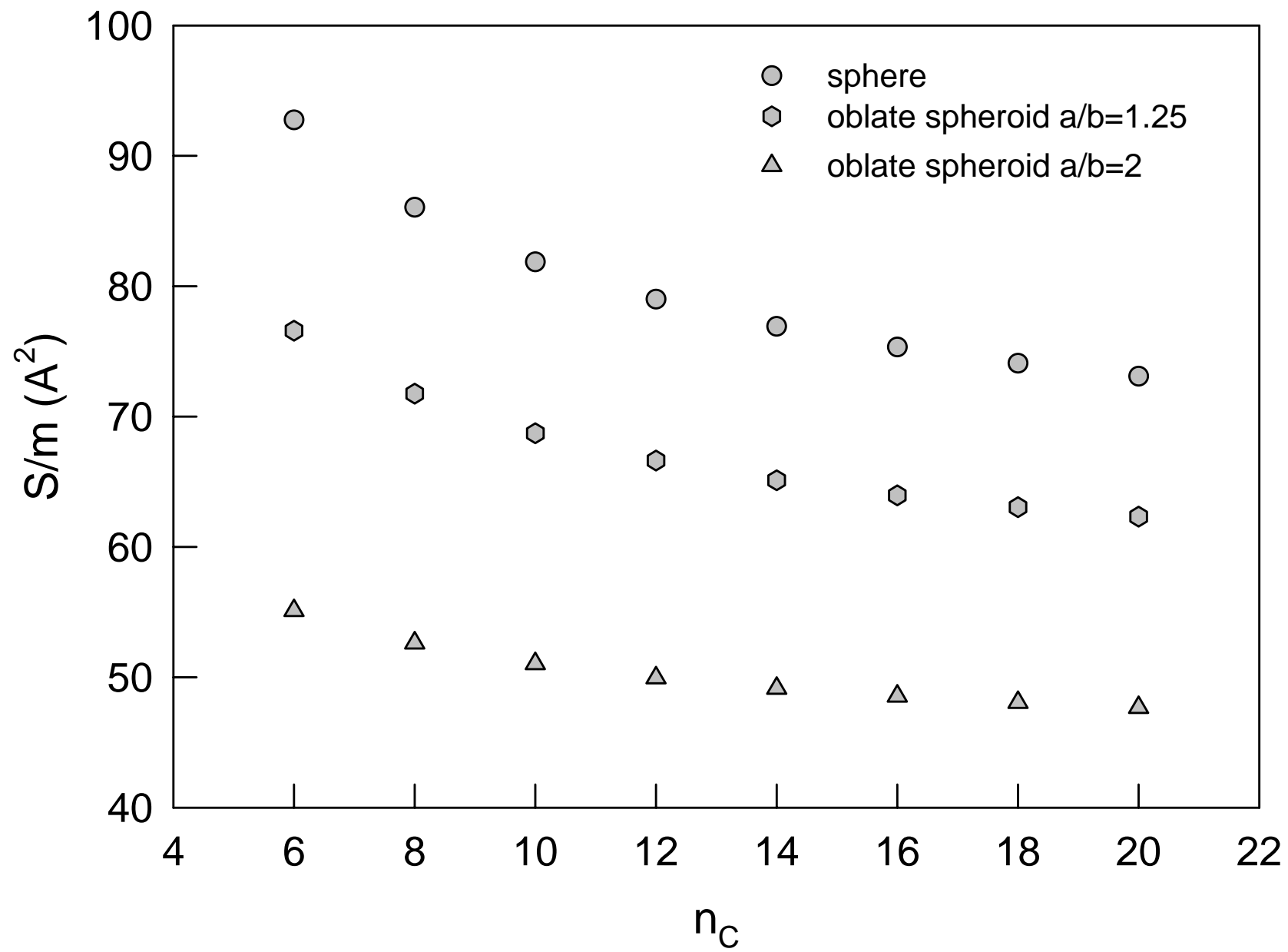
eccentricity



from a sphere to an oblate spheroid:



the stronger the deviation from a sphere the larger the aggregation number

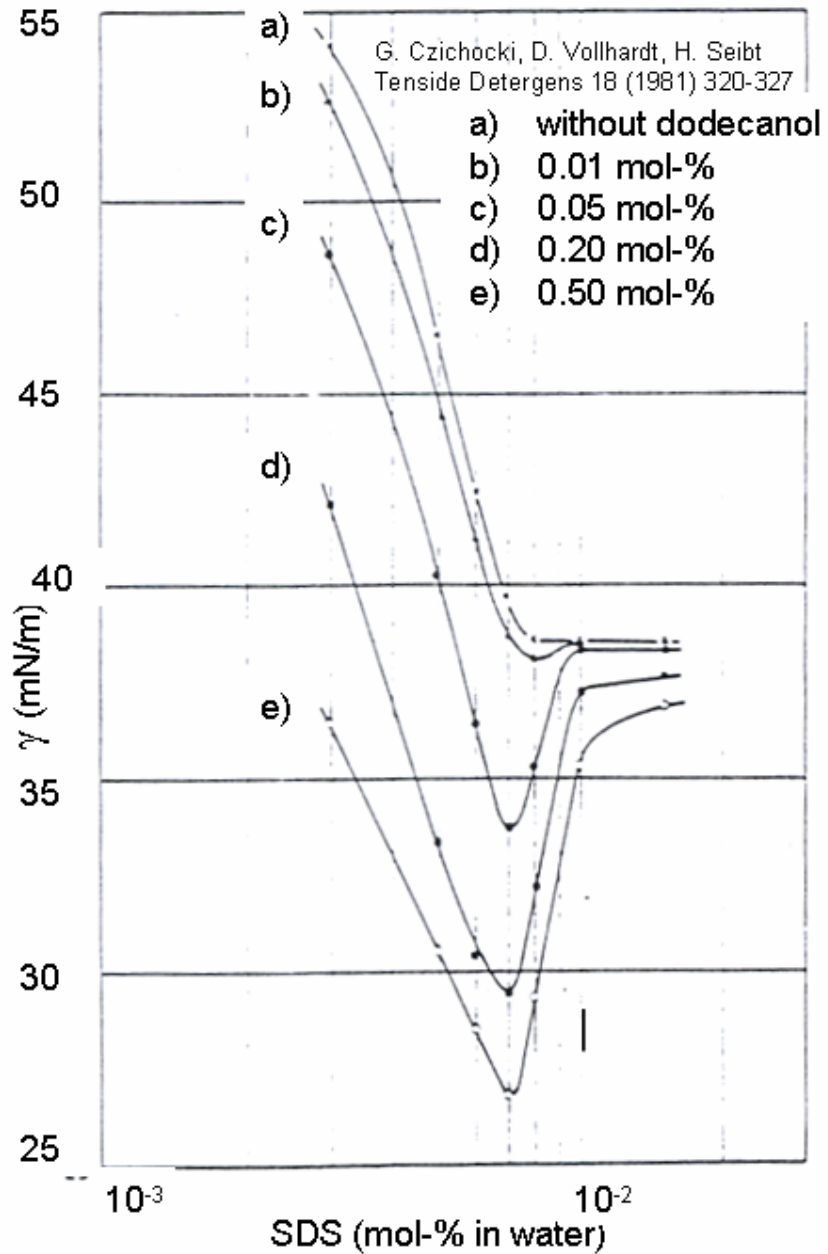


- distortion is accompanied by an increase in the total surface but the increase is less than the increase in volume
- the surface area per hydrocarbon chain is diminished
- S/m is the surface area per surfactant molecule or the area per head group, which is an important quantity because it measures the distance between polar head groups
- the decrease in S/m with increasing chain length reflects the increasing attraction at constant repulsion
- if S/m becomes larger there will be necessarily contact between water molecules and the core surface, and a consequent pressure to reduce S/m

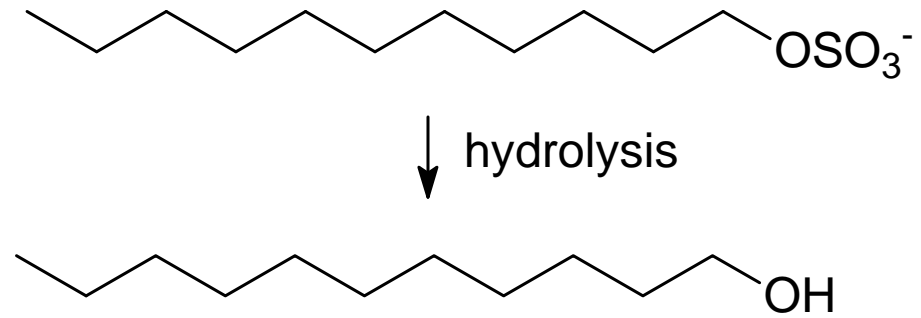
➤ all theory is based on pure substances

➤ monodisperse chain length

➤ for surfactants purity is always an issue



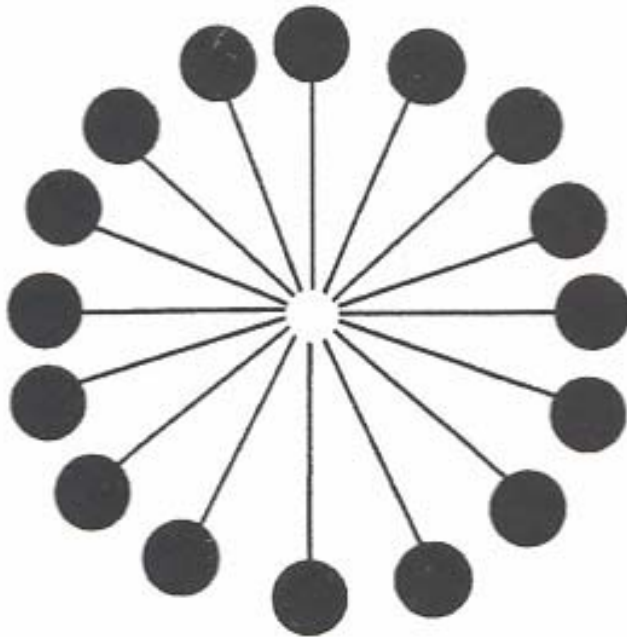
dodecanol has higher surface activity and adsorbs first



the corresponding alcohol is always an admixture in alkylsulfates

the very classical spherical shape

spokes – of – a – wheel structure



Hartley - micelle

G. S. Hartley disclaimed:

“The symmetrical asterisk form ... has no physical basis and is drawn for no other reason than the human mind is an organizing instrument and finds unorganized processes uncongenial.”

(G. S. Hartley *Aqueous Solutions of Paraffin-Chain Salts. A Study of Micelle Formation*; Herman, Paris 1936, Fig.11A and discussion)

in fact a micelle is a highly disorganized structure with multiple bent chains, cavities, hydrocarbon – water contact, and deviations from an exact spherical shape (JACS 108 (1986) 1297, Langmuir 9 (1993) 9, J. Phys. Chem. 89 (1985) 153)

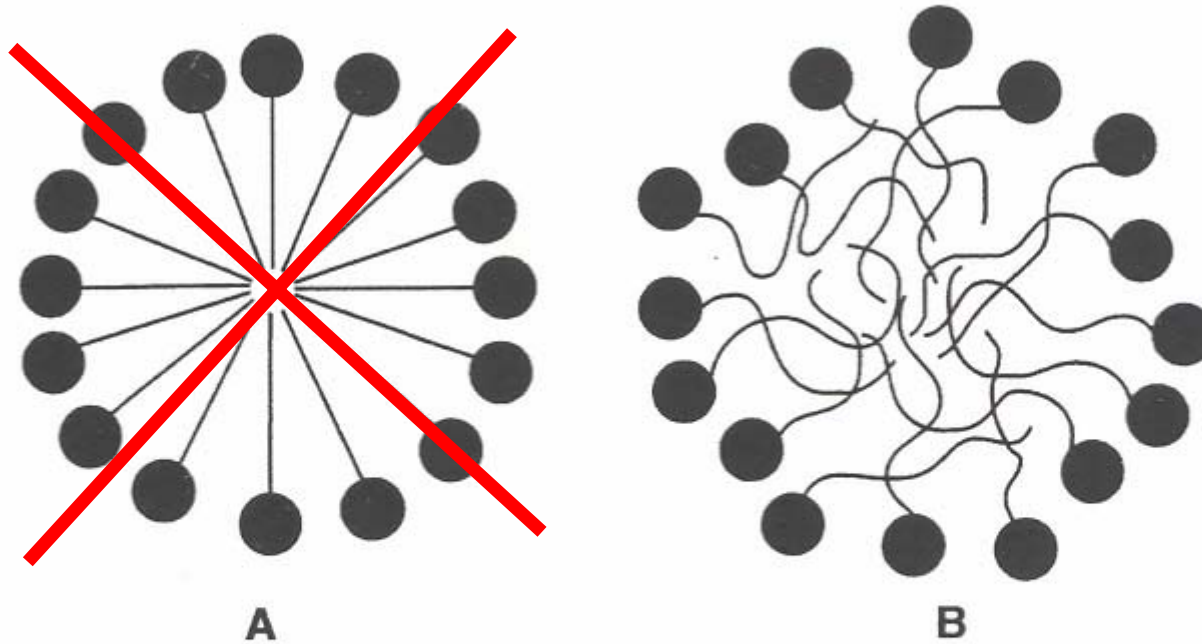
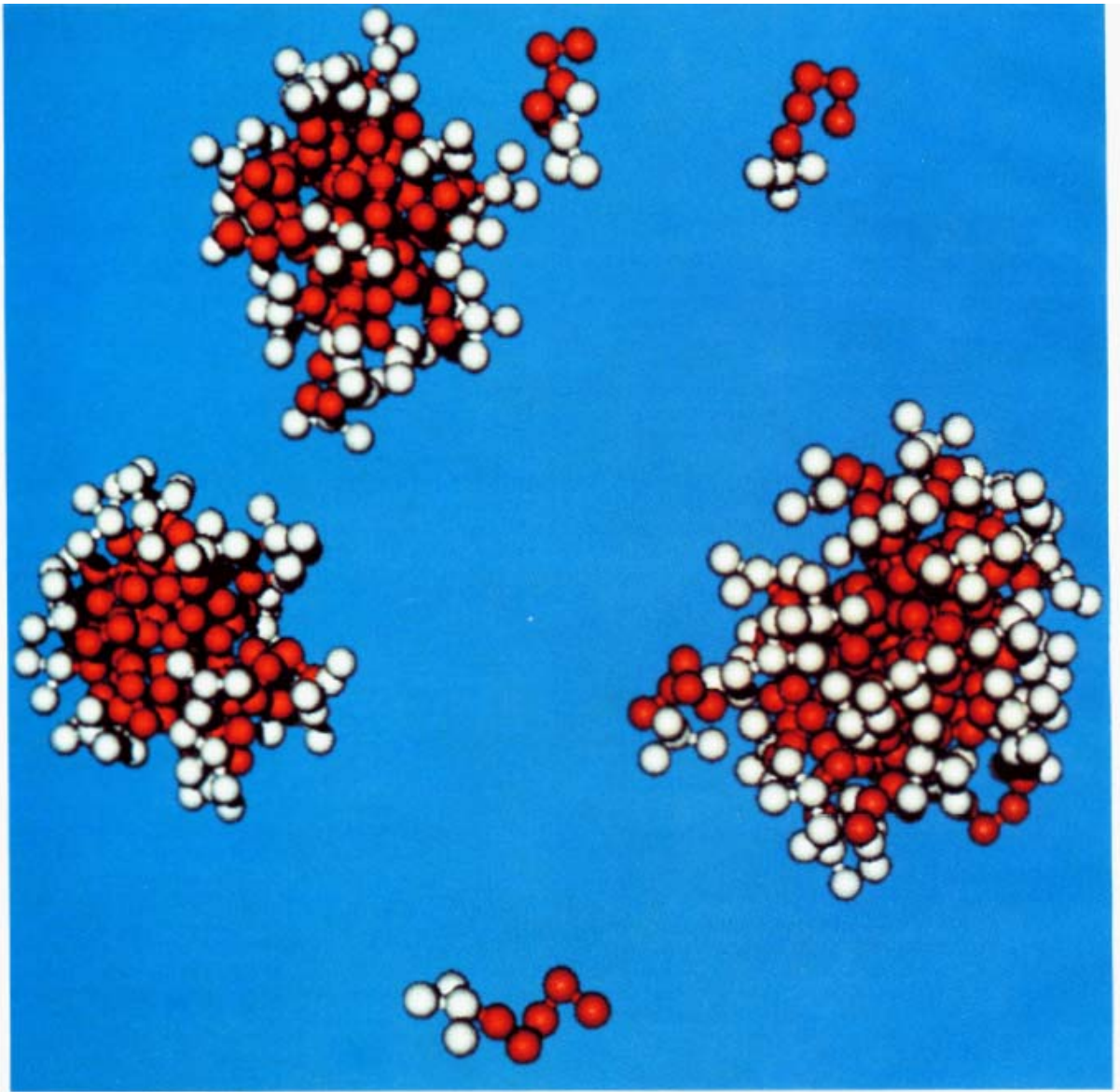
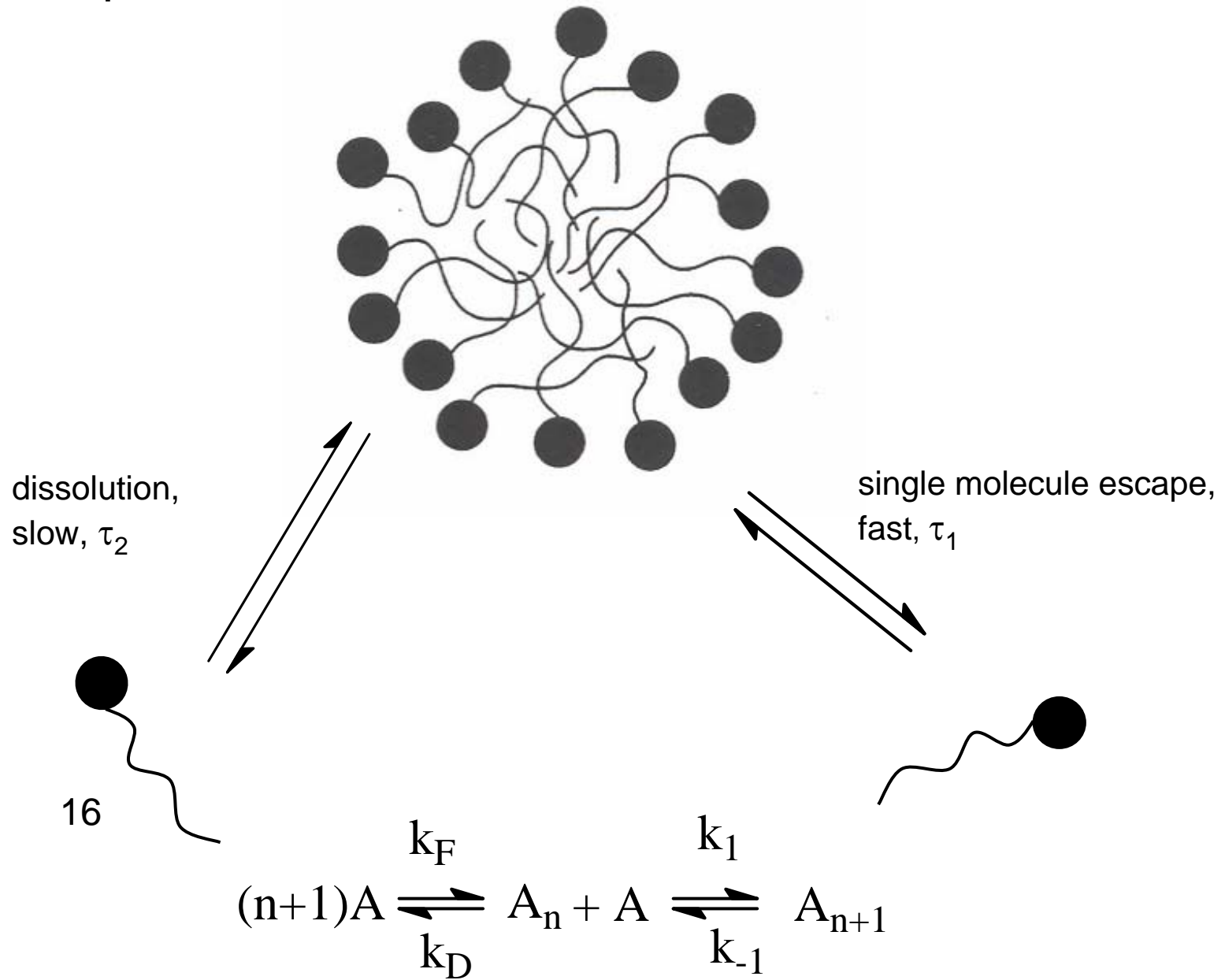


Figure 1. A: the misnamed “Hartley” micelle as portrayed in most modern chemistry and biochemistry texts. B: a more realistic schematic attempting to depict the disordered and fluid nature of the micelle interior.



Snapshot of a small part of the system. For clarity only the surfactants are shown; the white spheres are the hydrophilic segments, the red spheres the hydrophobic.

micellar equilibria:



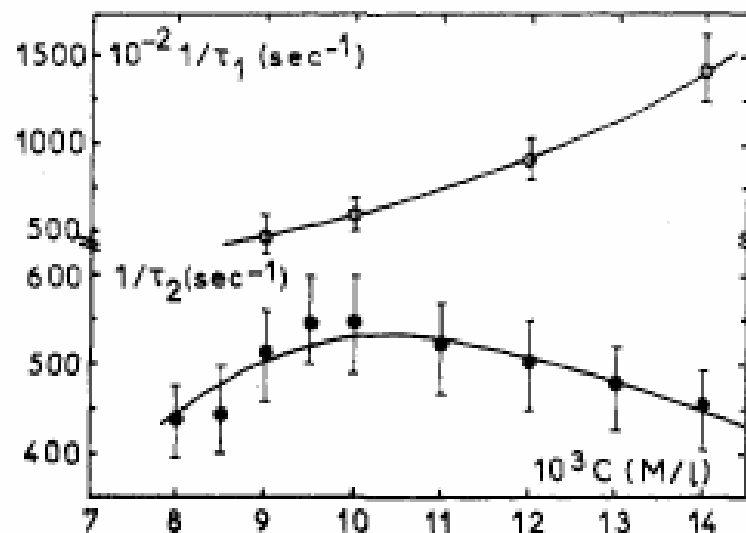


Figure 2. Variation of $1/\tau_1$ (shock tube) and $1/\tau_2$ (P jump) with NaLS concentration at 20° and without added salt.

SDS
 τ_1 : 29 μ s
 τ_2 : 2.3 ms

TABLE I: Values of the Relaxation Times at $C = \text{cmc}$

	NaLS ^a	LPI ^b	LPBr ^b
τ_1 , μ SEC	29	12	<5
τ_2 , msec	2.3	>100	0.4

^a Results at 20°. ^b Results at 25°.

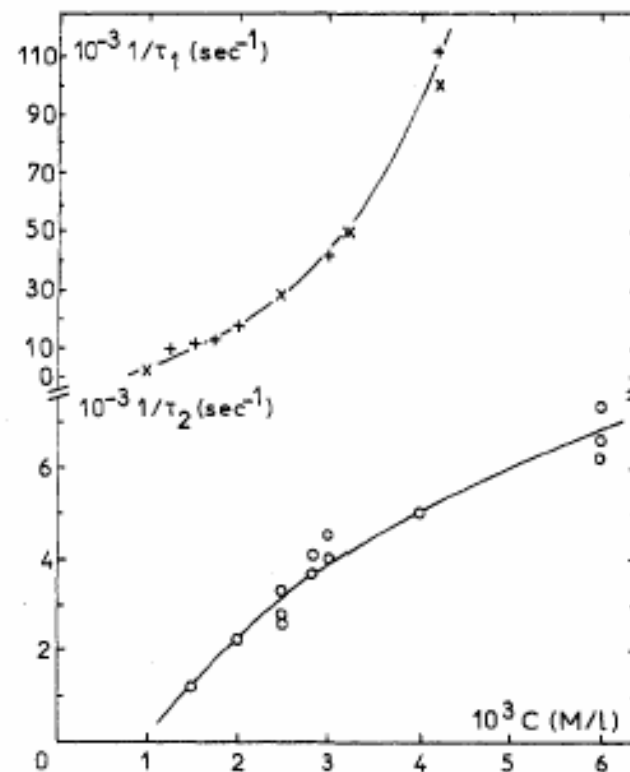


Figure 3. Variation of $1/\tau_1$ and $1/\tau_2$ with C for LPI solutions in 0.05 M KI at 25°: (+) shock-tube experiments; (O,X) T-jump experiments (λ 342 nm).

micellar phase as sorbent phase:



latex particles as sorbent phase:



Photograph of the neat 100 nm latex (right) particles and the particles after dyeing by sorption with the hydrophobic pigment Sudan IV (left).

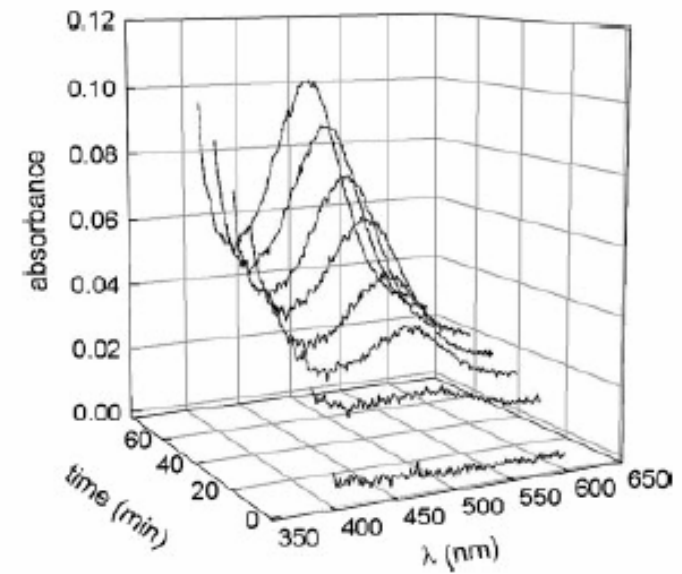
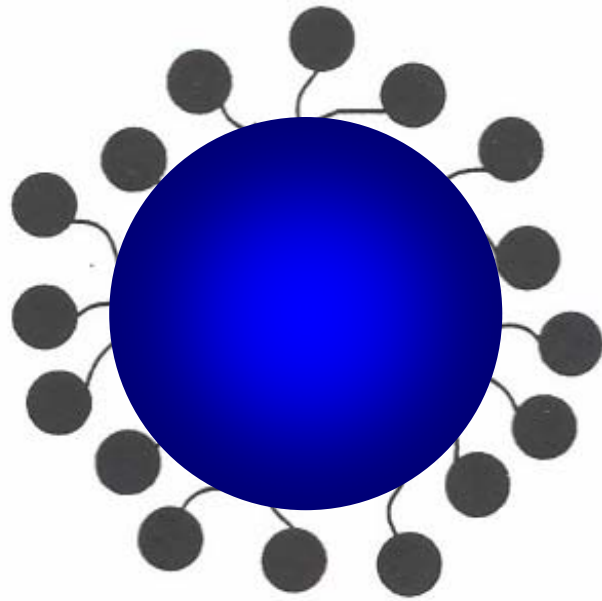


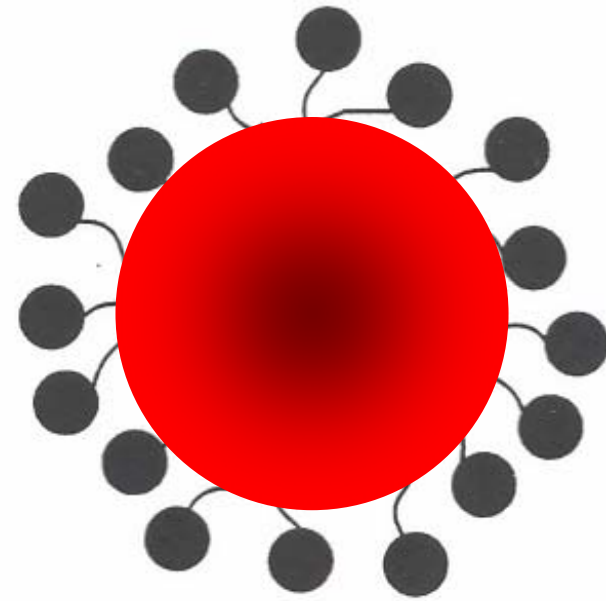
Figure 1. Absorption spectra acquired during the sorption of a BDB in styrene solution into PS-seed particles.

micelles as containers:

swollen SDS micelles

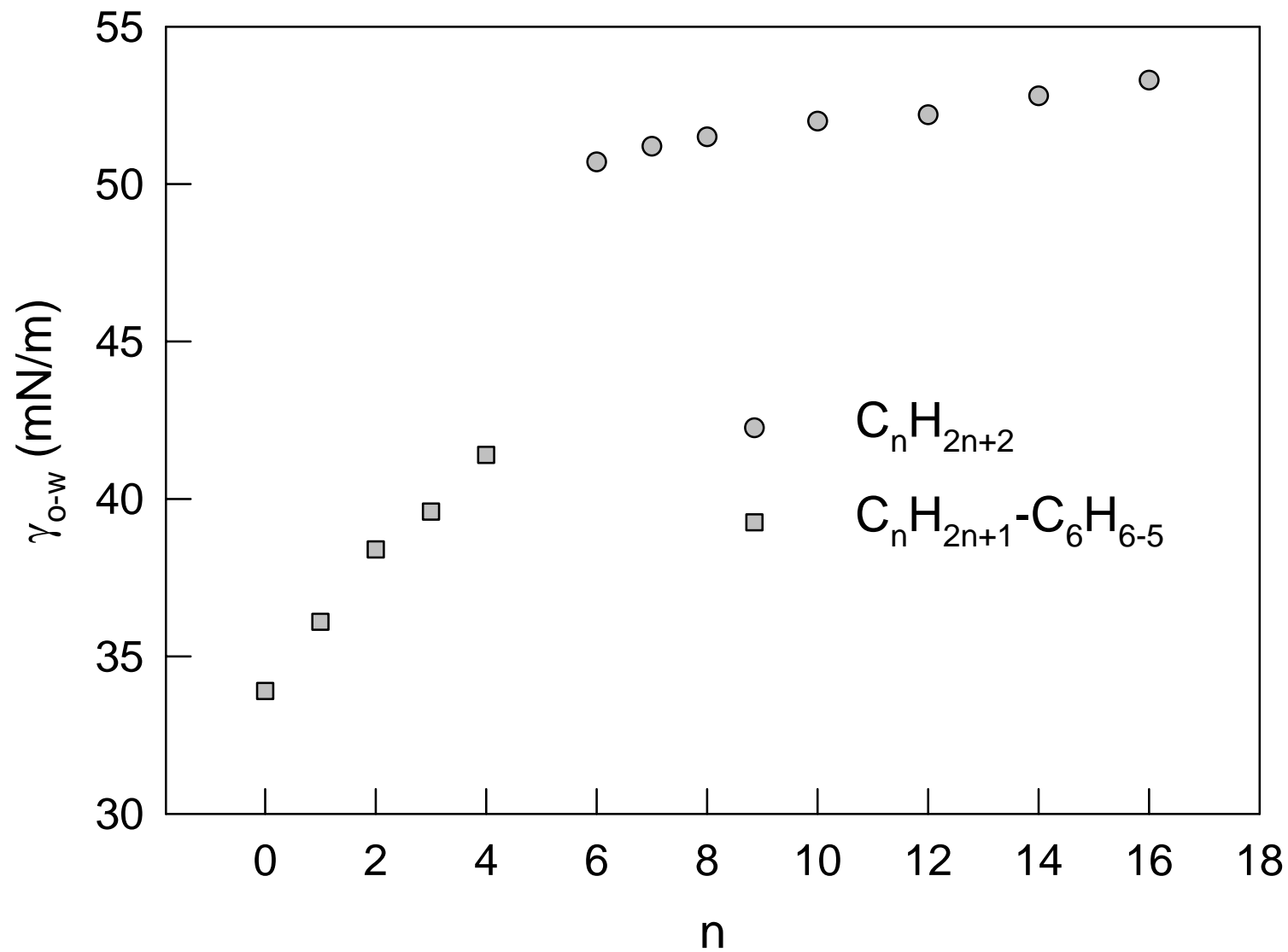


styrene

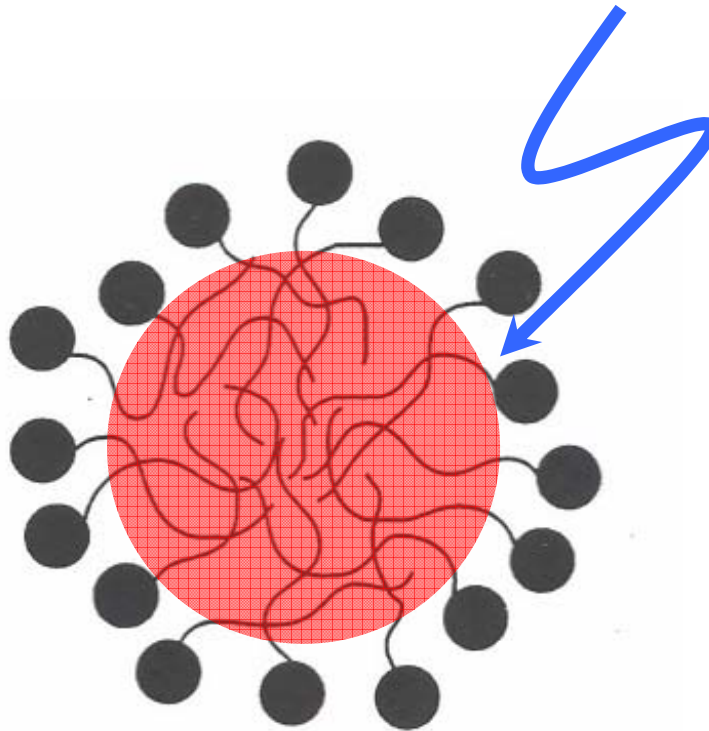


octane

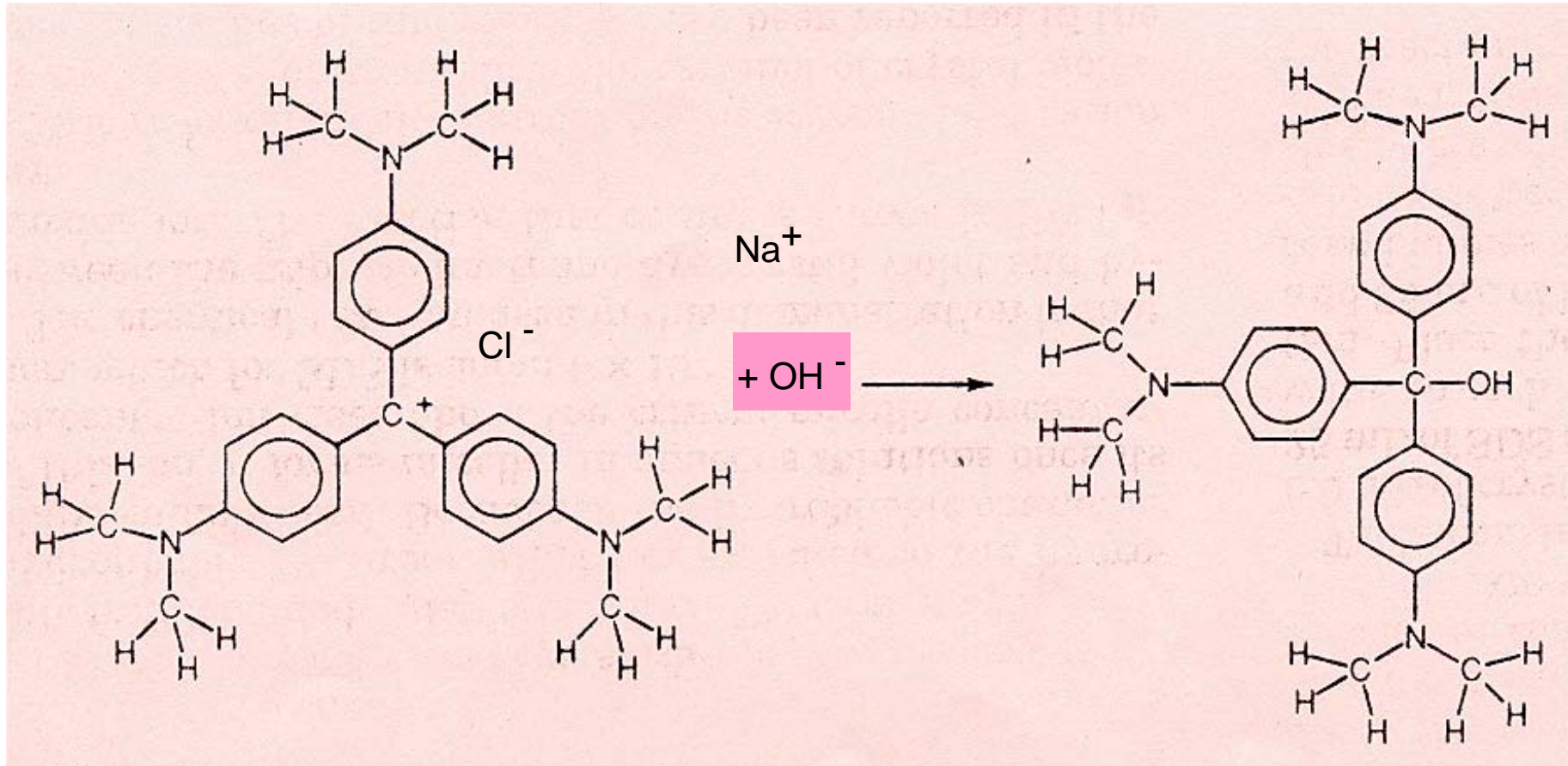
styrene or benzene and alkanes have a different spatial distribution inside micelles



Is the micellar core a safe place?



degradation of crystal violet (CV):



Can SDS - micelles protect CV against degradation?



it's a surprising result

Krafft temperature or point:

- unusual solubility behavior of surfactants
- solubility increases drastically above a certain T
- behavior changes from hydrophobic to hydrophilic

$\text{C}_{18}\text{—SO}_3\text{Na}$ is absolutely hydrophobic at room temperature

SDS

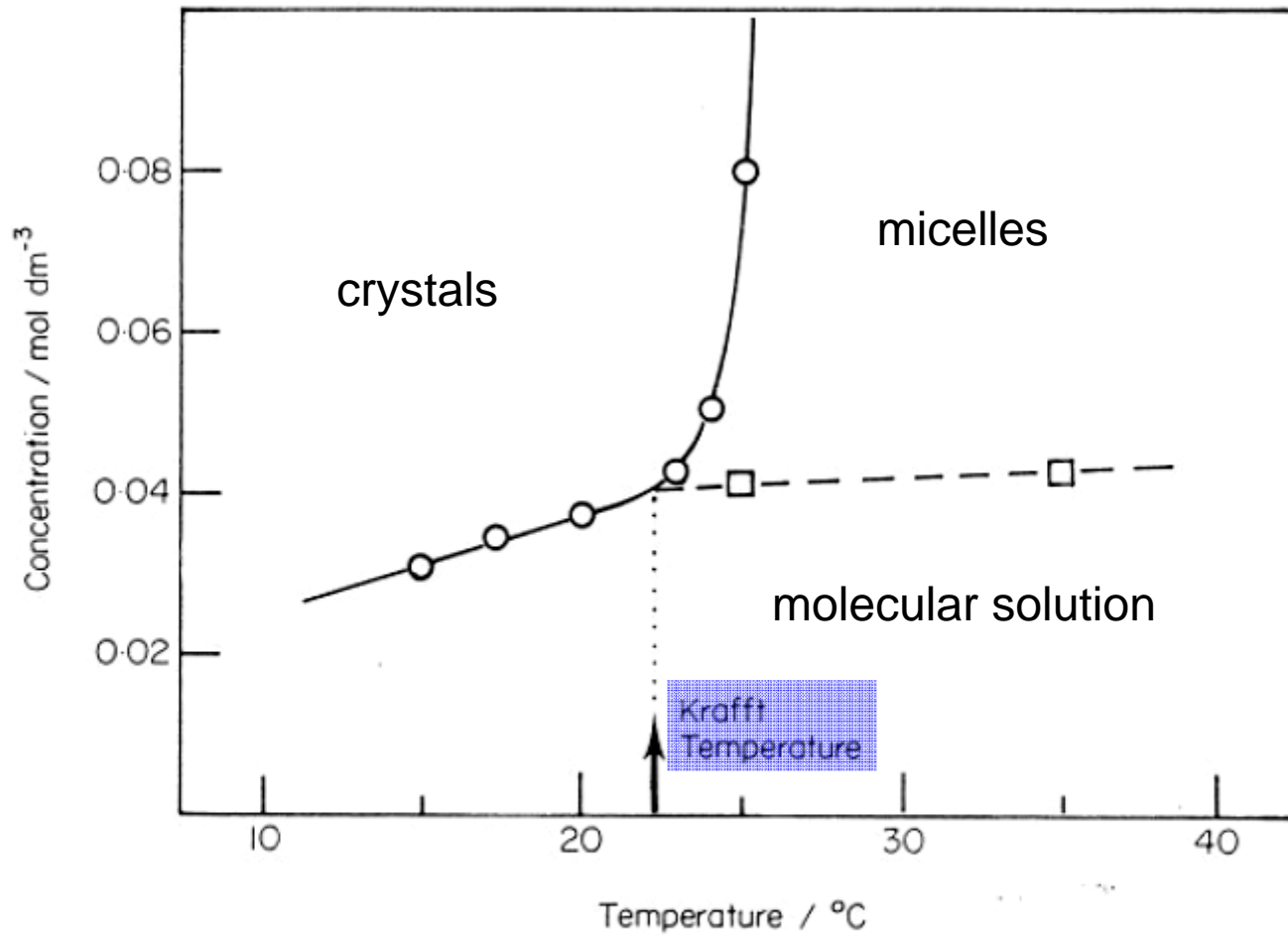
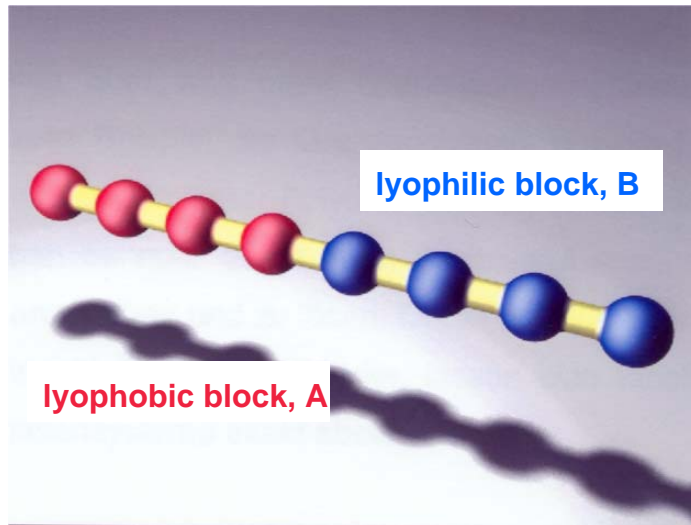


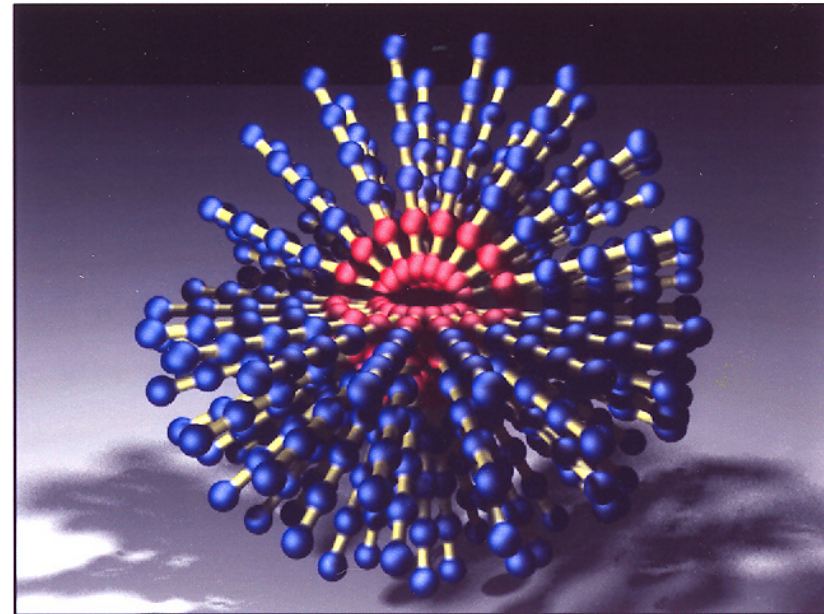
Fig. 4. Solubility versus temperature for sodium decylsulphate in water showing location of the Krafft point (after Shinoda, 1974); -o-, solubility data; -□-, c.m.c. values.

diblock copolymer

molecule



micelle



$$m = N_A^\alpha N_B^\beta$$

$$\alpha > 0$$

$$\beta < 0$$

block copolymer micelles:

Binary Surfactant - Water Phase Diagram

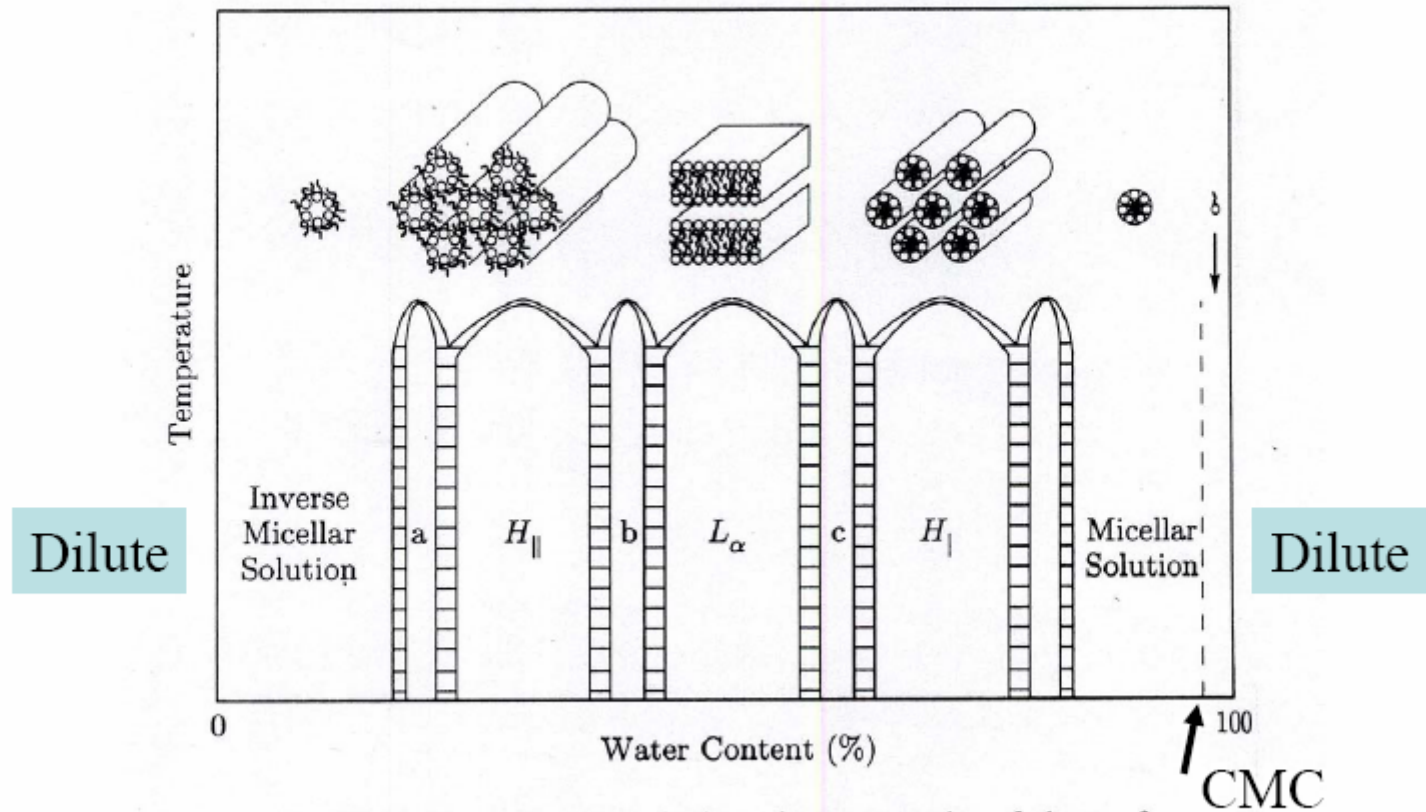
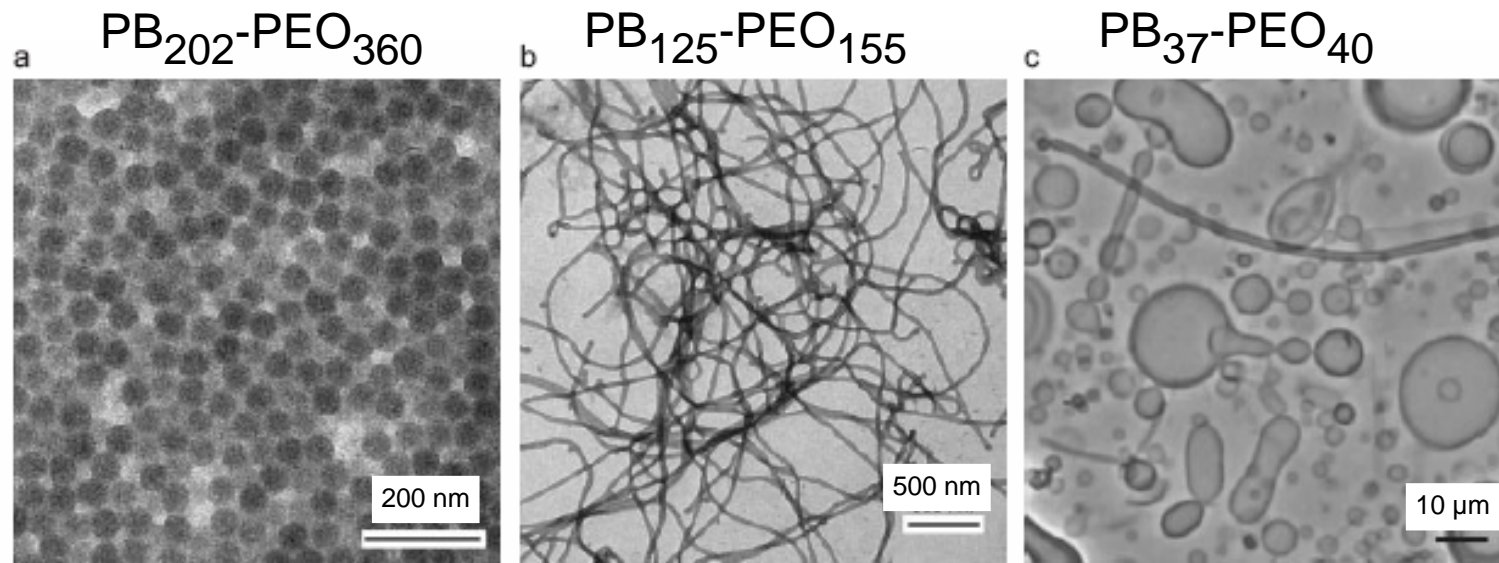


Fig. 2.7.14. Phase diagram and schematic representation of phases of aliphatic chains in water showing micellar solutions, lamellar (L_{α}), and hexagonal columnar H_{II} and H_I phases [courtesy S. Gruner].

block copolymer micelles: morphology is chain length dependent



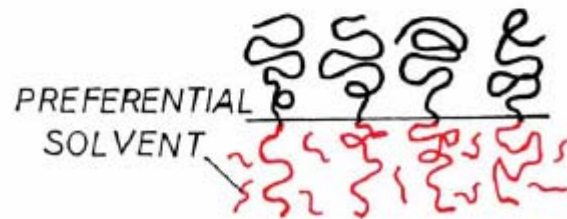
TEM images (a, b) and optical micrograph (c) of aggregates for a series of PB-PEO block copolymers

block copolymer micelles: ways to change morphology



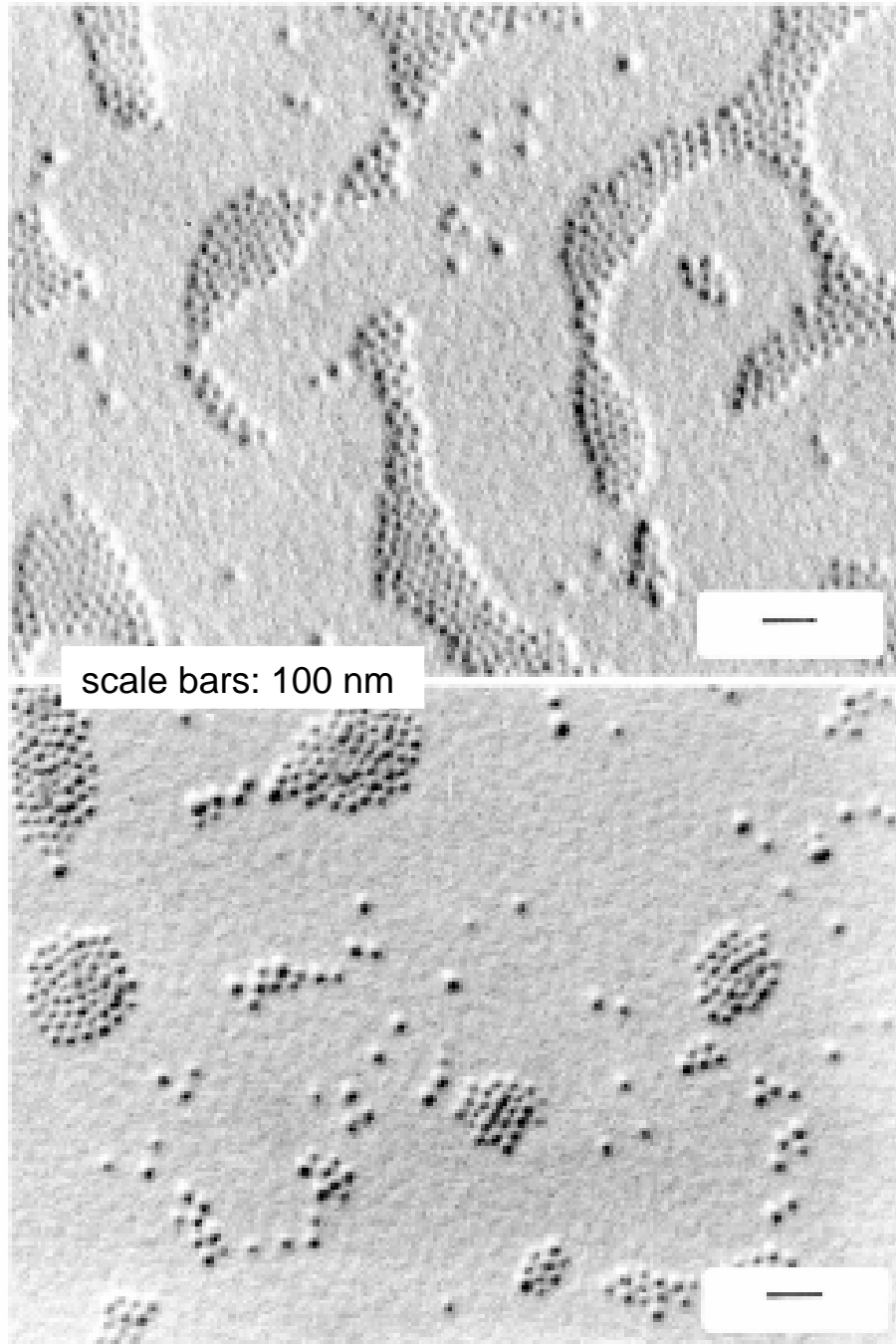
Compositional Asymmetry

PREFERRED INTERFACE
CURVATURE



Preferred Swelling

block copolymer micelles



PS(45)-b-P4VP(122)

$D_h = 11.4 \text{ nm}$

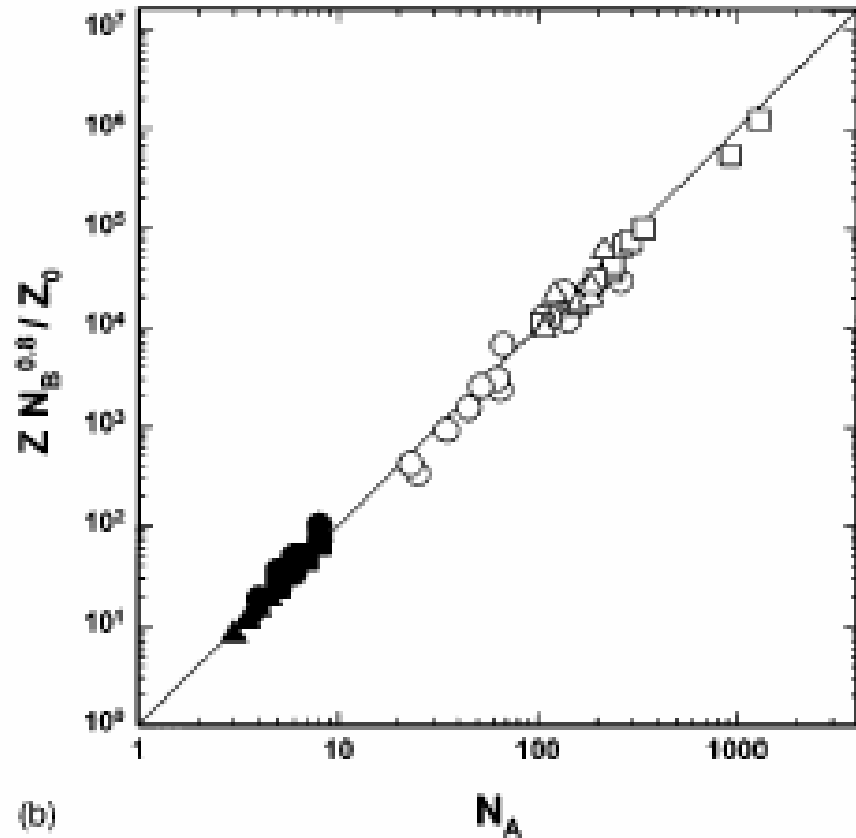
$Z = 54$

PS(63)-b-P4VP(122)

$D_h = 13.5 \text{ nm}$

$Z = 123$

aggregation numbers Z as function of N_A and N_B for:



PS-P4/VP (open circles),
 PS-PMAc (open squares)
 PMAc-PS-PMAc (open triangles)
 C_xE_y (filled circles)
 $RN^+(CH_3)_3Br^-$ (filled squares)
 $ROSO_3^-$ (filled triangles up)
 RSO_3^- (filled triangles down)

influence of the corona block size is compensated by the factor $N_B^{0.8}$

additionally is compensated for the monomer volume v_0 and interchain distance b_0 , which are specific for each system; both parameters are absorbed into the quantity $Z_0 = 36\pi v_0^2 / b_0^6$ (packing parameter at the core – corona interface)

block copolymers
(Eisenberg)

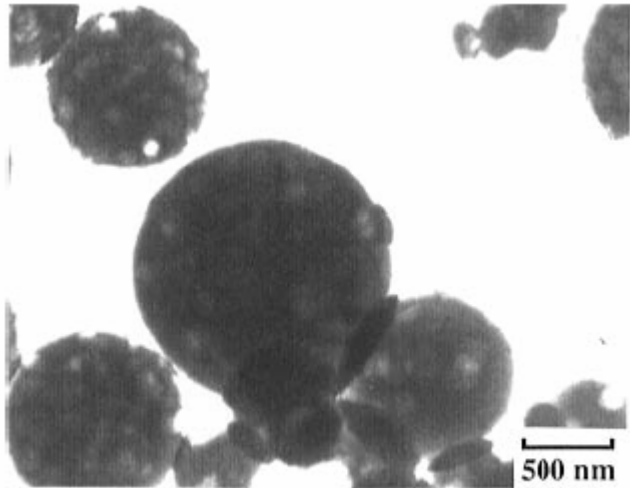
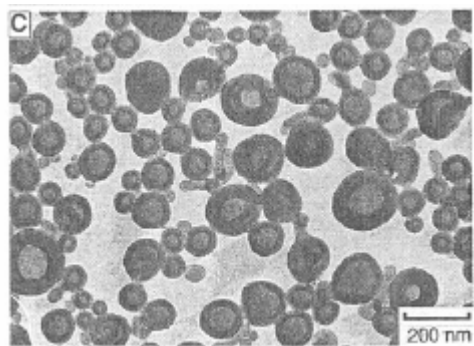
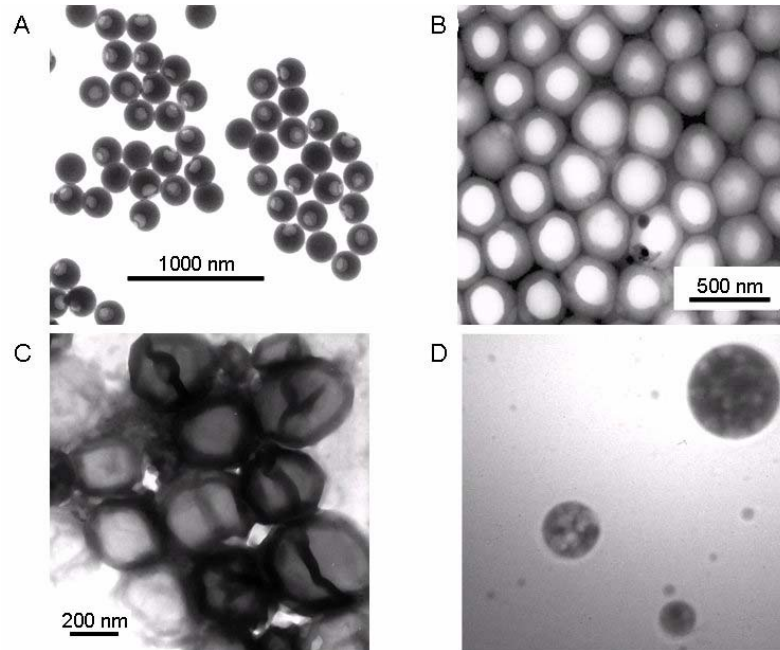


Figure 3. Porous spheres made from PS(240)-b-PEO(45).



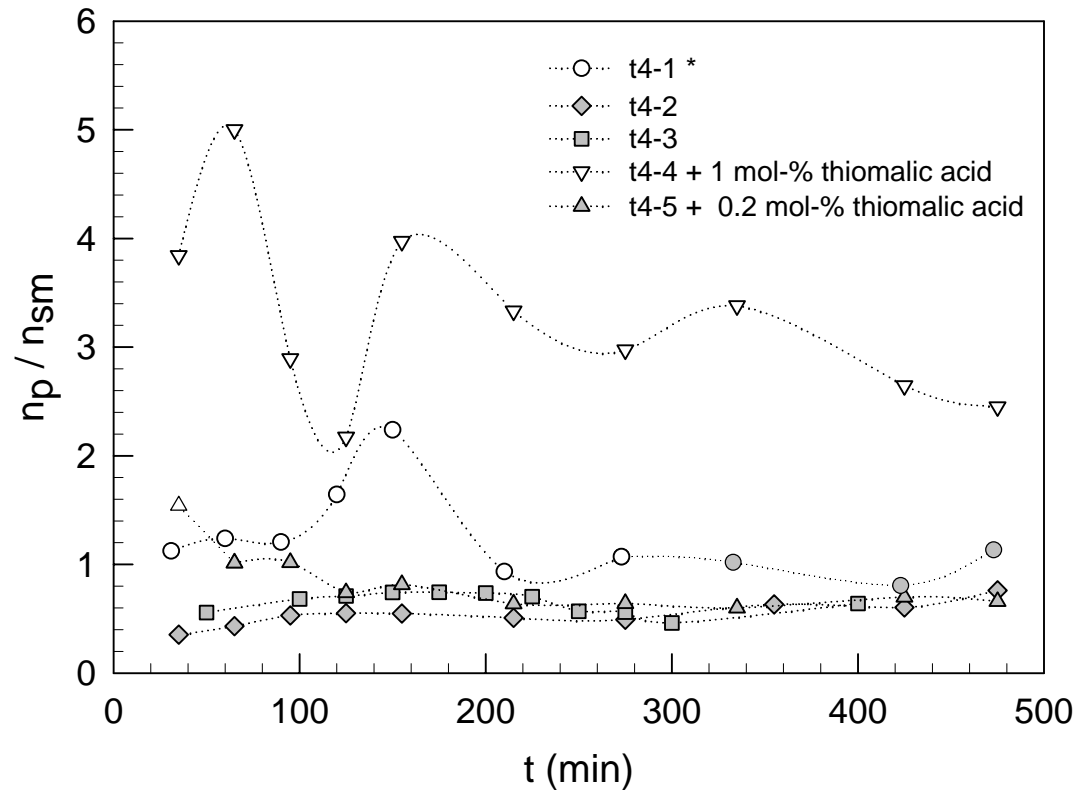
PS(410)-b-PAA(25)

latex particles



TEM images (A – C) and X-ray absorption microscopy image (D) of polystyrene particles showing various morphological features
A – polystyrene particles prepared by surfactant-free emulsion polymerization with potassium peroxodisulfate as initiator

2000 ml water, 91.1 g styrene monomer, 0.021 g sodium hydrogen carbonate buffer, and if necessary the thiomalic acid chain-transfer agent (either 1 or 0.2 mol % relative to styrene monomer); 70 °C, 1.872 g KPS



$n_p > n_{sm}$ more engroups than surface area and consequently phase separation inside the particles

$$n_{sm} = \frac{\pi \cdot D^2}{a_s}$$

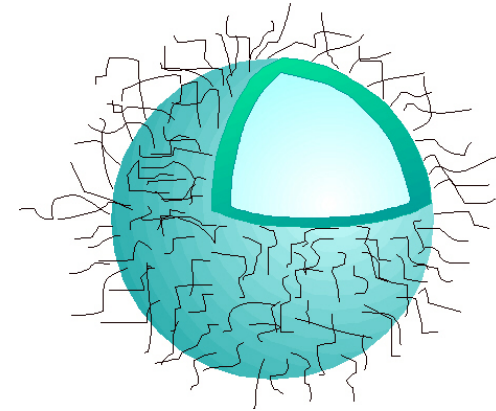
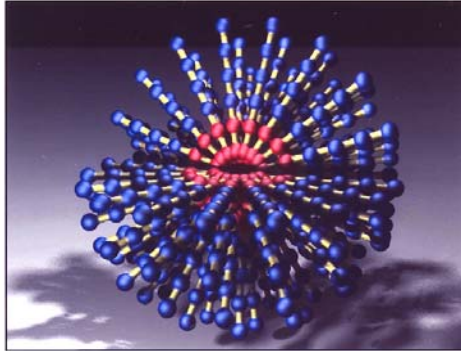
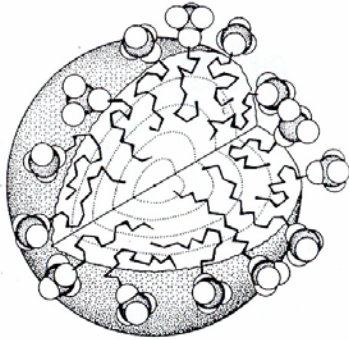
n_{sm} - number of chains per particle if the surface is saturated with lyophilic groups

$$n_p = \frac{m_p \cdot N_A}{M_n}$$

n_p - number of chains per particles

surfactants - block copolymers - particles

self-assembled colloidal objects in a selective solvent



common properties:

- stabilization
- swelling, sorbent phases
- nanoreactors
- morphology
- etc etc