Emulsions – Part 3

remarks to: microemulsions

miniemulsions

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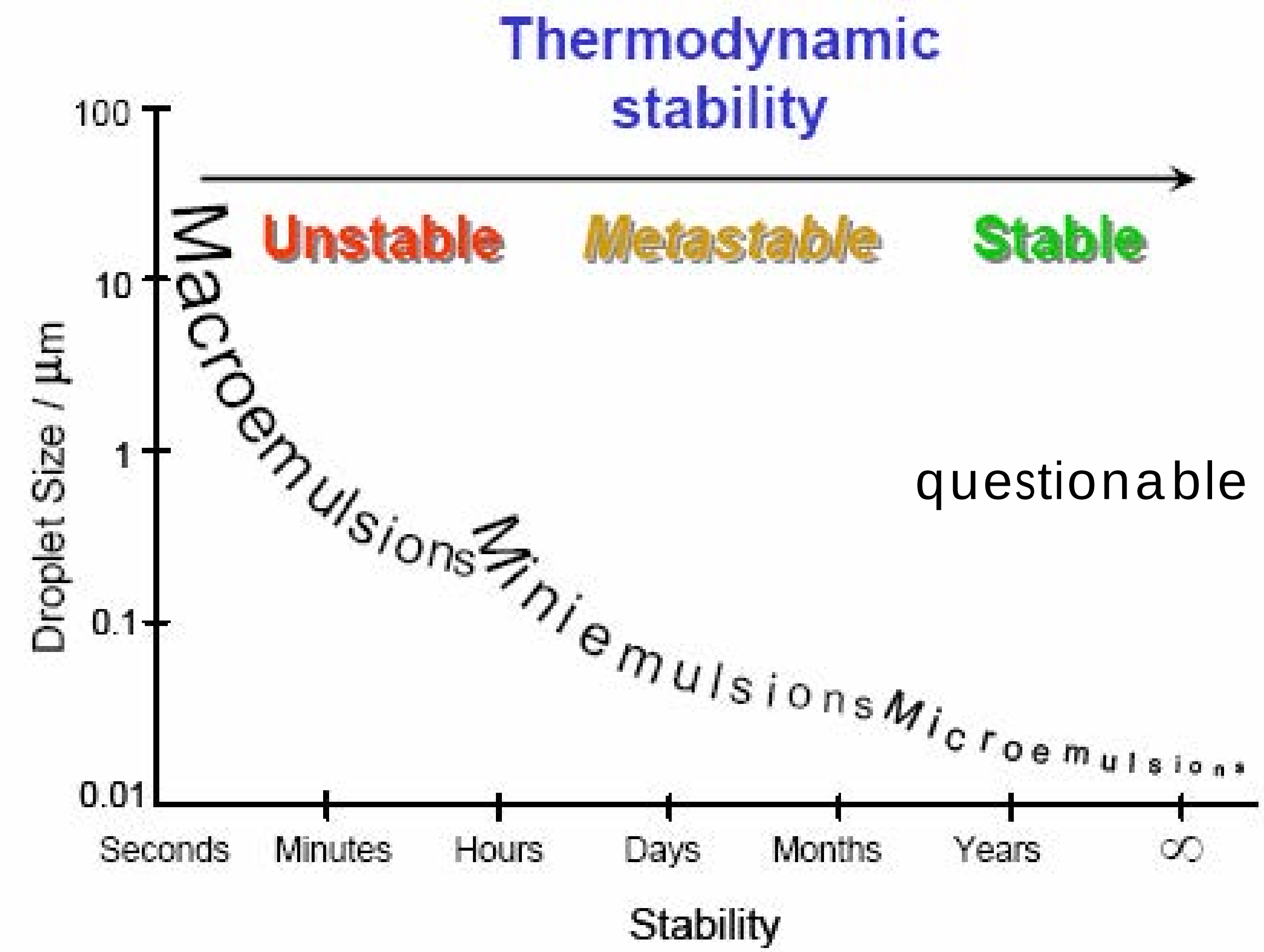
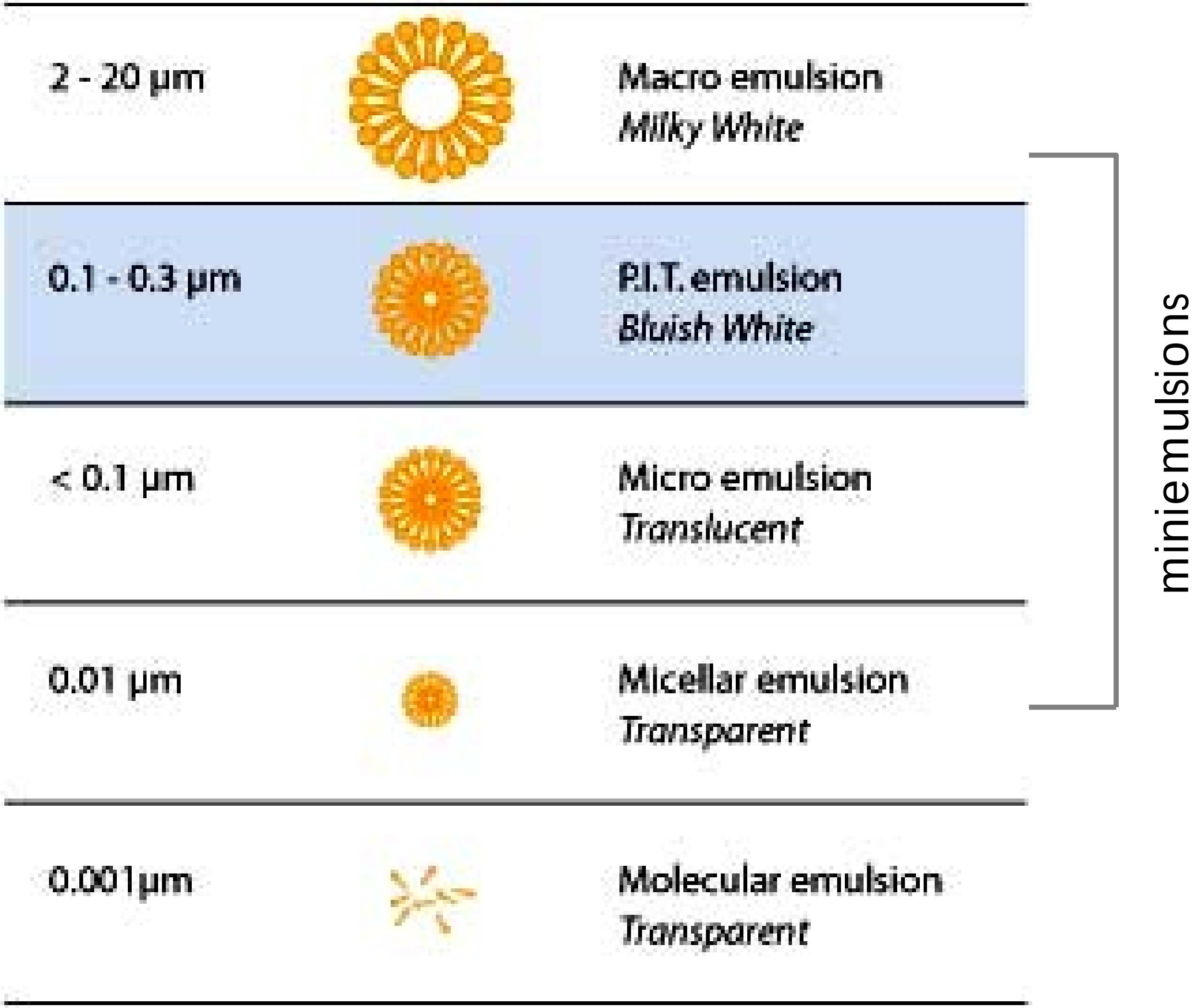
Micro and Miniemulsion – Why Special Emphasis?



questionable graph!!!

M. S. El-Aasser, Lehigh University

droplet size and the appearance of emulsions

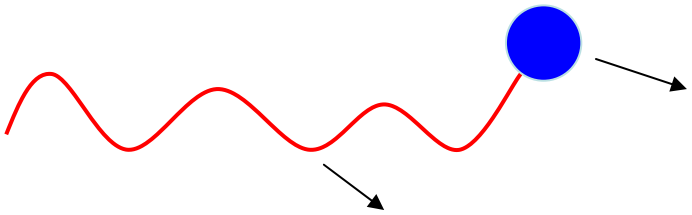


2 - 20 µm	Macro emulsion *Milky White*
0.1 - 0.3 µm	P.I.T. emulsion *Bluish White*
< 0.1 µm	Micro emulsion *Translucent*
0.01 µm	Micellar emulsion *Transparent*
0.001µm	Molecular emulsion *Transparent*

miniemulsions

water and oil do not mix

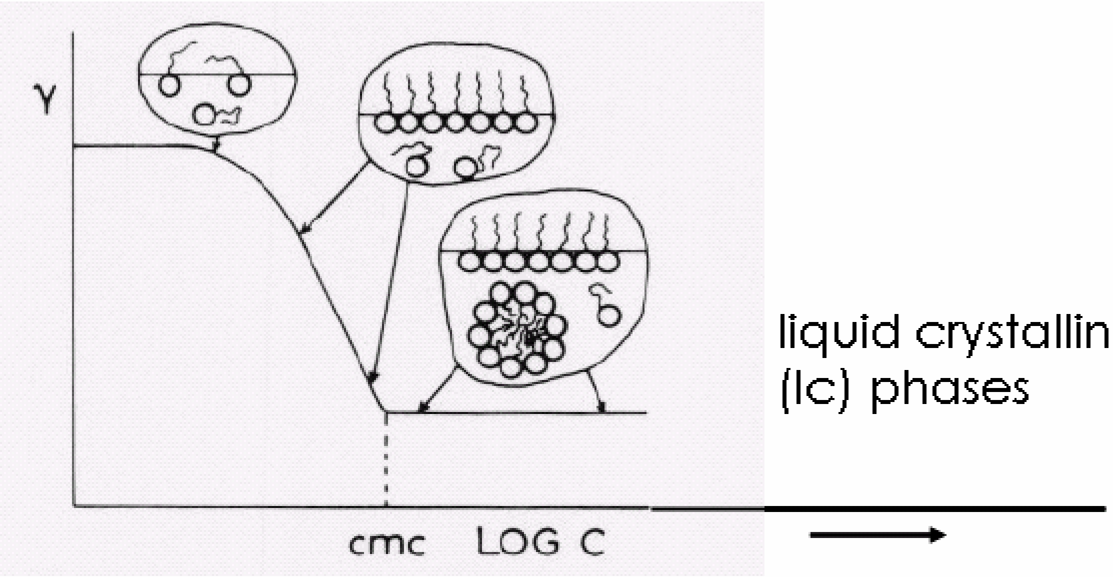
but if some soap is present a small amount of one or the other component is solubilized in soap micelles; which component depends on Bancroft's rule



hydrophilic head

hydrophobic tail

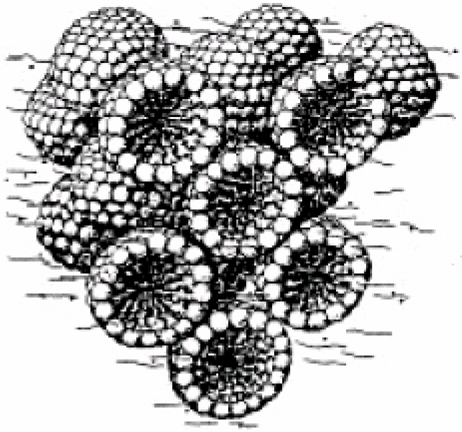
surfactant molecules in water:



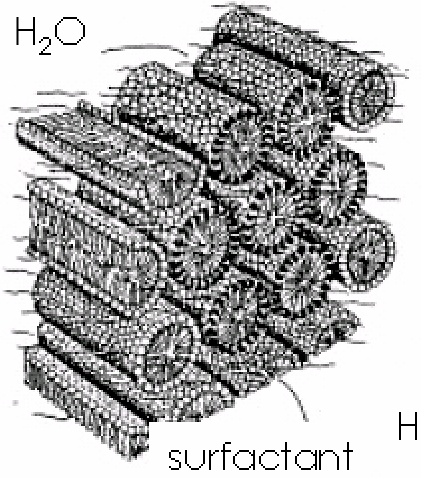
liquid crystalline
(lc) phases

lc phases:

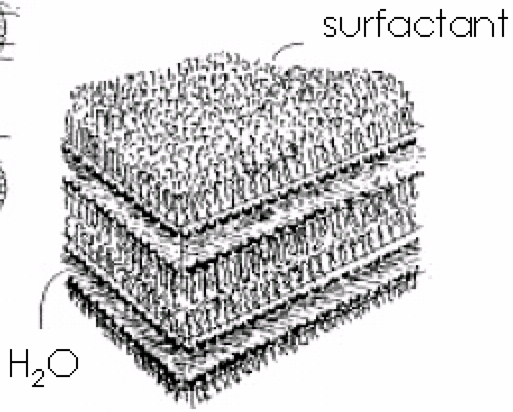
cubic

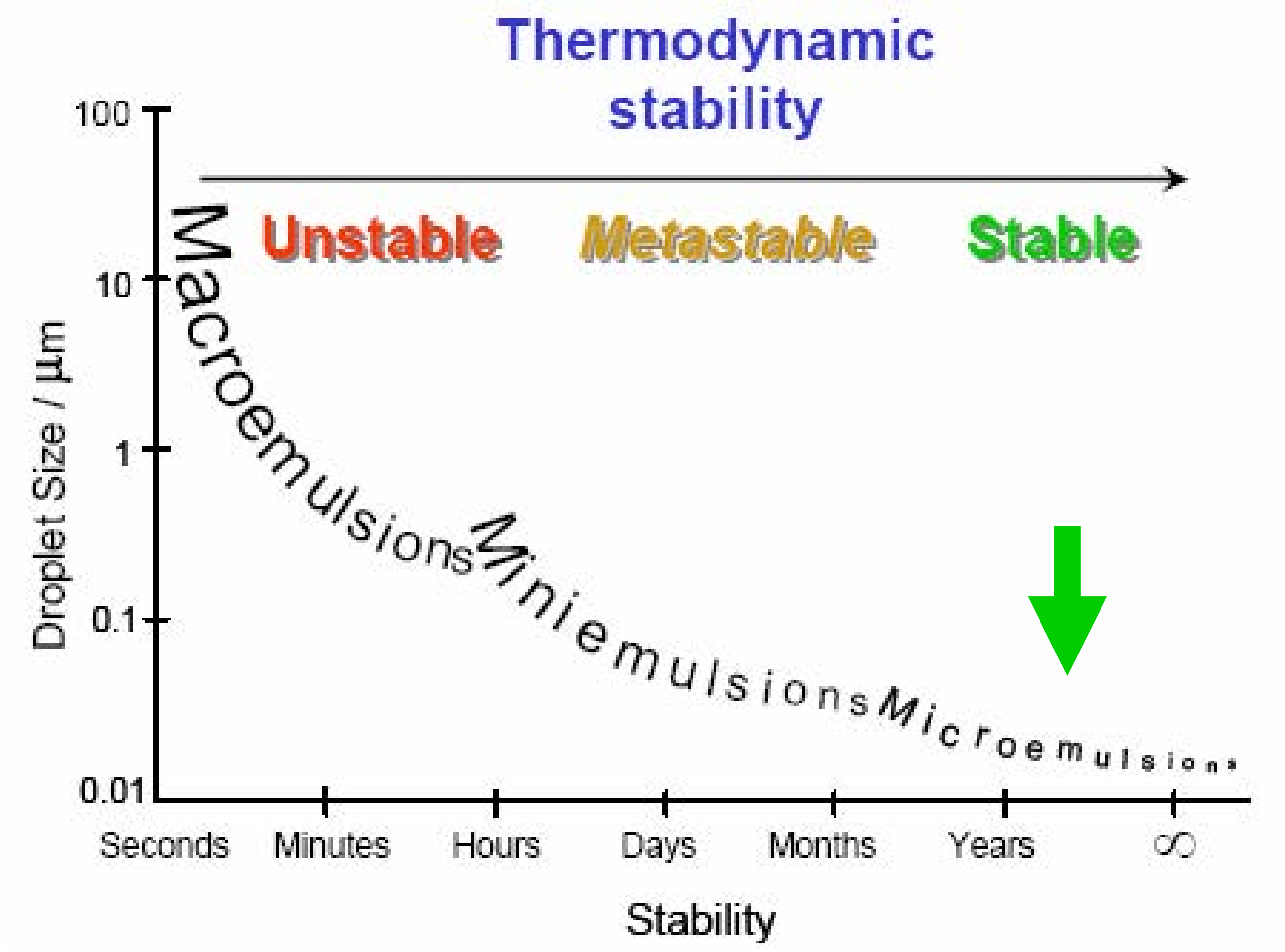


hexagonal



lamellar





M. S. El-Aasser, Lehigh University

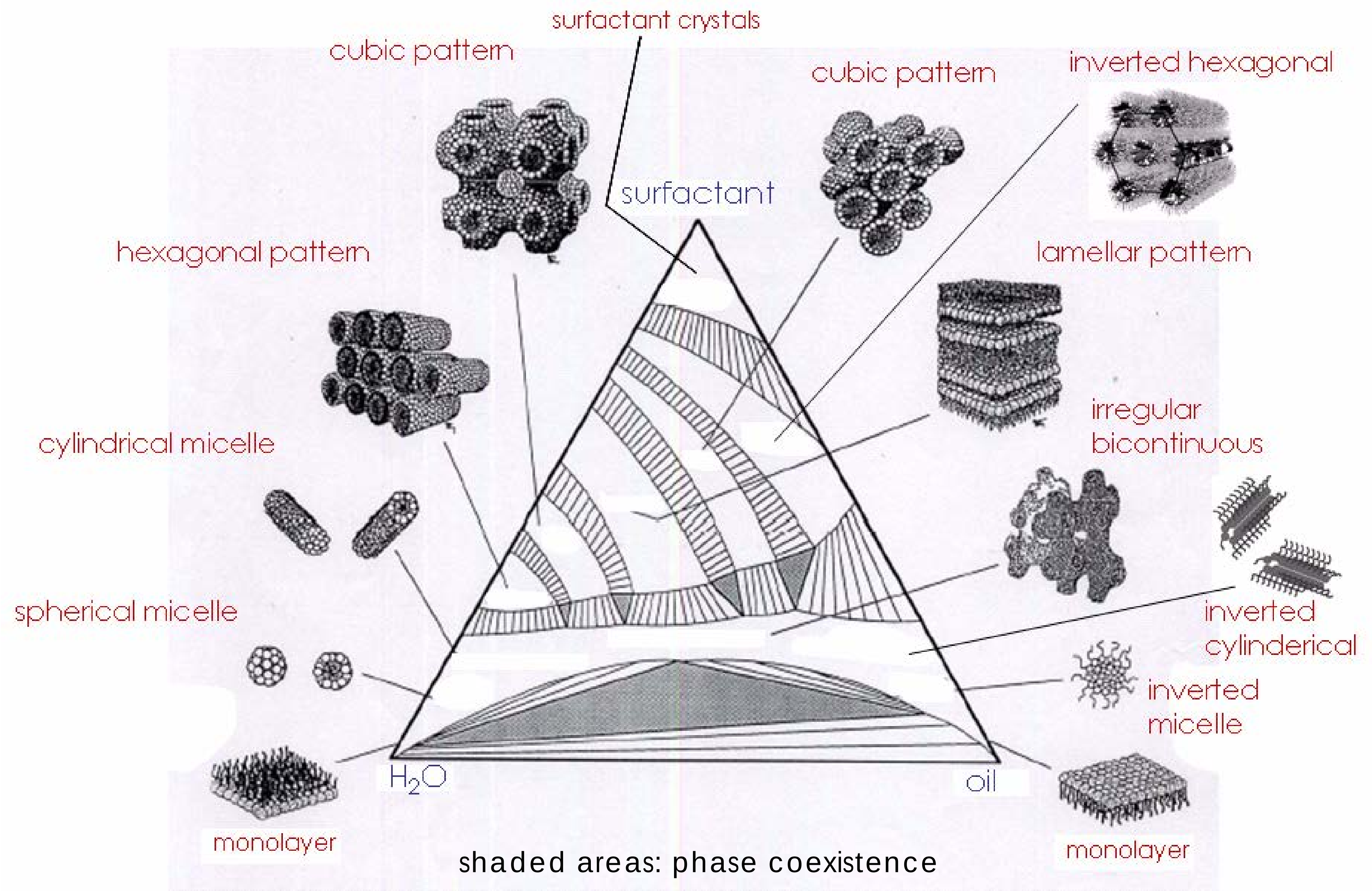
surfactant phases can be swollen with both oil and / or water

hydrophobic tails with oils

hydrophilic heads with water

→ oil + water + surfactant are emulsions

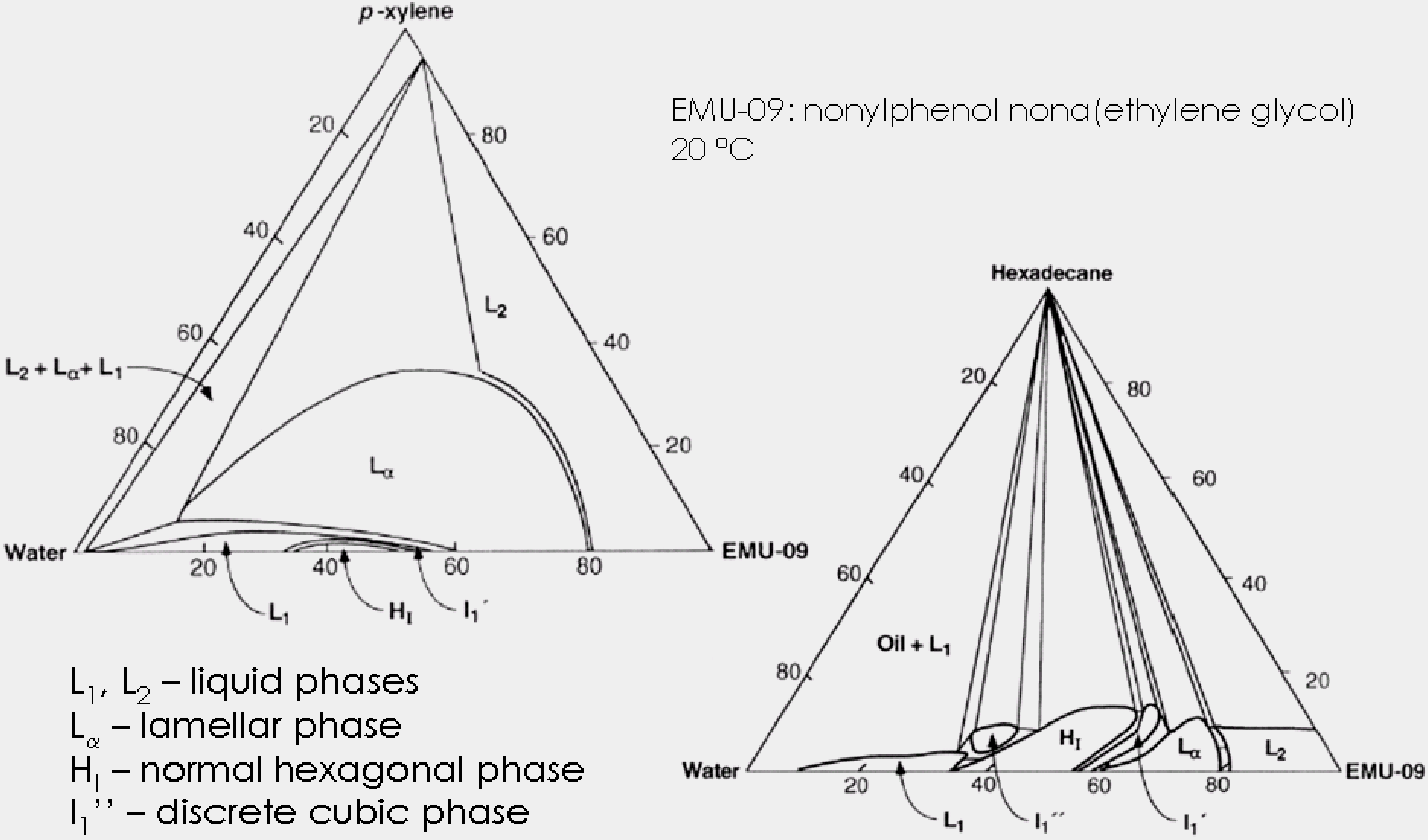
phase diagram: water + oil + surfactant



shaded areas: phase coexistence

ternary phase diagrams

EMU-09: nonylphenol nona(ethylene glycol)
20 °C

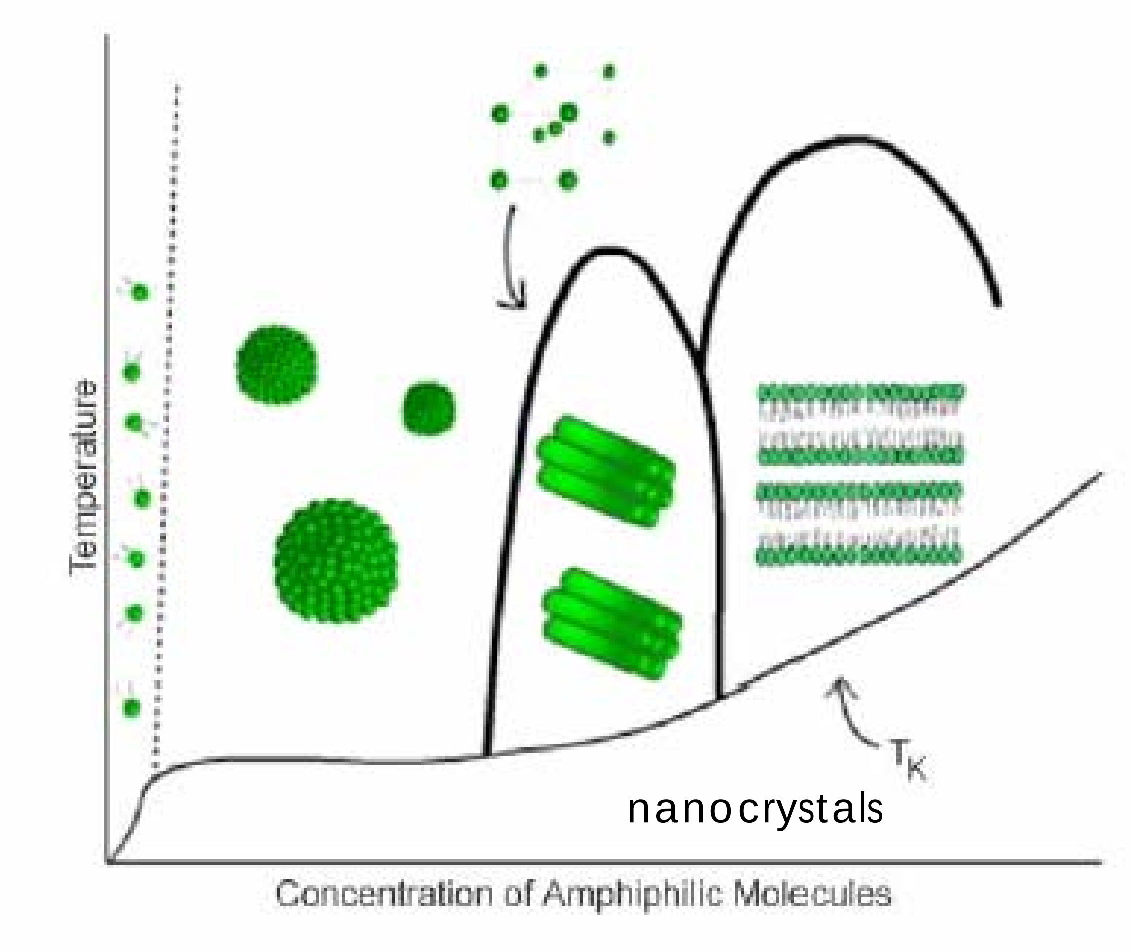


L_1, L_2 – liquid phases
L_α – lamellar phase
H_I – normal hexagonal phase
I_1'' – discrete cubic phase
I_1' – bicontinuous cubic phase

Evans / Wennerström

phase diagrams are multi-dimensional:

surfactant aggregation depends on temperature and other the nature of additives



pseudoternary microemulsion system using Aerosol OT, medium-chain triglycerides with oleic acid (oil phases 1:1), glycerol monooleate (cosurfactant) and water.

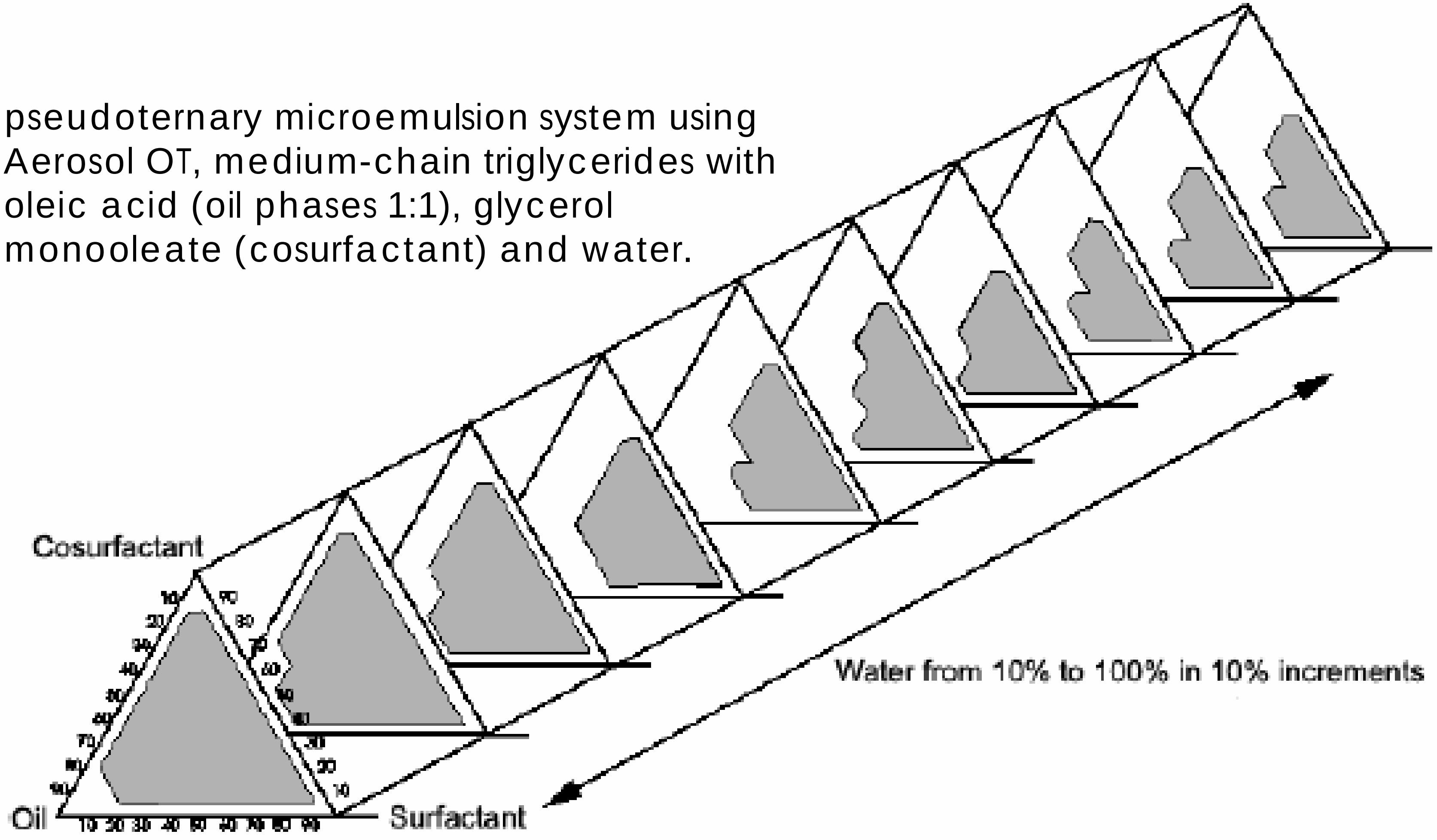


Figure 1. Quaternary phase diagram of aerosol OT microemulsion system.

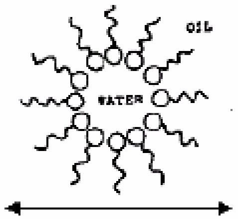
shaded area assigned is fluid, transparent, isotropic, non-birefringent, and stable for more than 3 months; **the unmarked areas indicate multiphase turbid regions**; the microemulsion domain was determined by visual inspection for clarity and fluidity as well as through a cross polarizer for the absence of a liquid crystalline phase

AAPS PharmSciTech 2003; 4 (1) Article 11 (http://www.pharmscitech.org).

What is a Microemulsion?

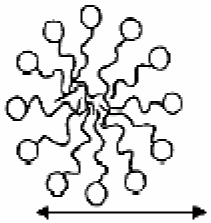
1µm
EMULSION

- will phase separate eventually
- cloudy, milky



100-1000 Å
MICROEMULSION

- thermodynamically stable
- transparent (solution)



50 Å
MICELLE

- colloidal aggregate
- appearance depends on the size

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microemulsions are microstructured, thermodynamically stable mixtures of water, oil and surfactant; in spite of intensive research on microemulsions, a theory of predictive power for microemulsions is still lacking (R. Strey 1999)

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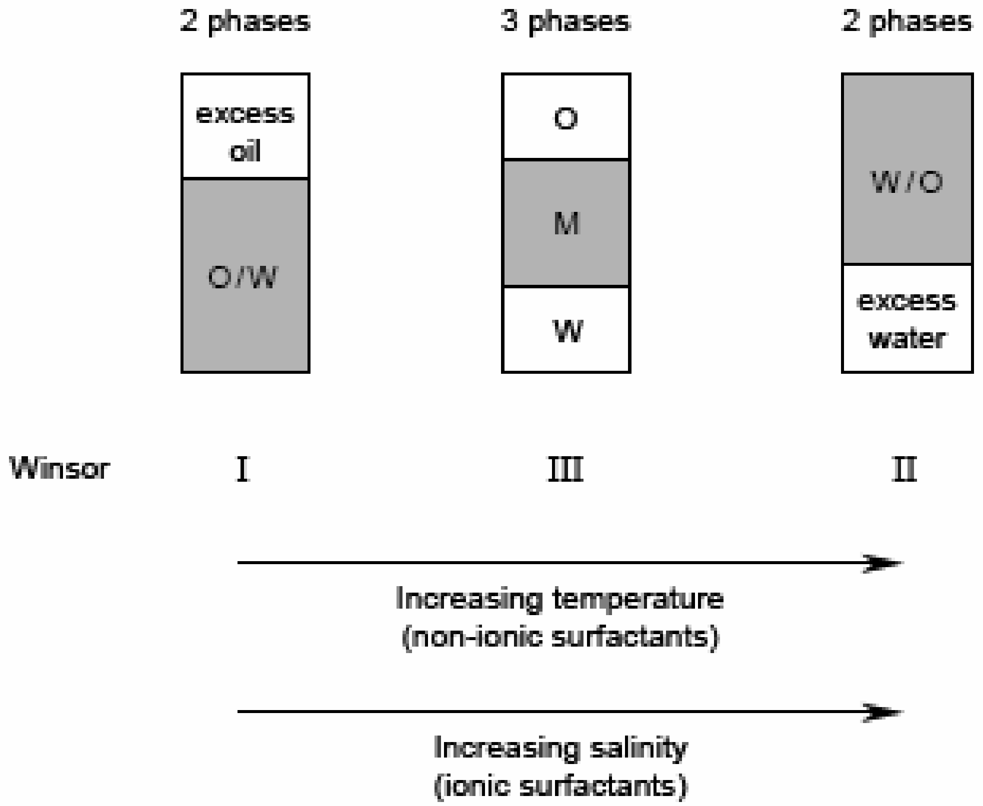
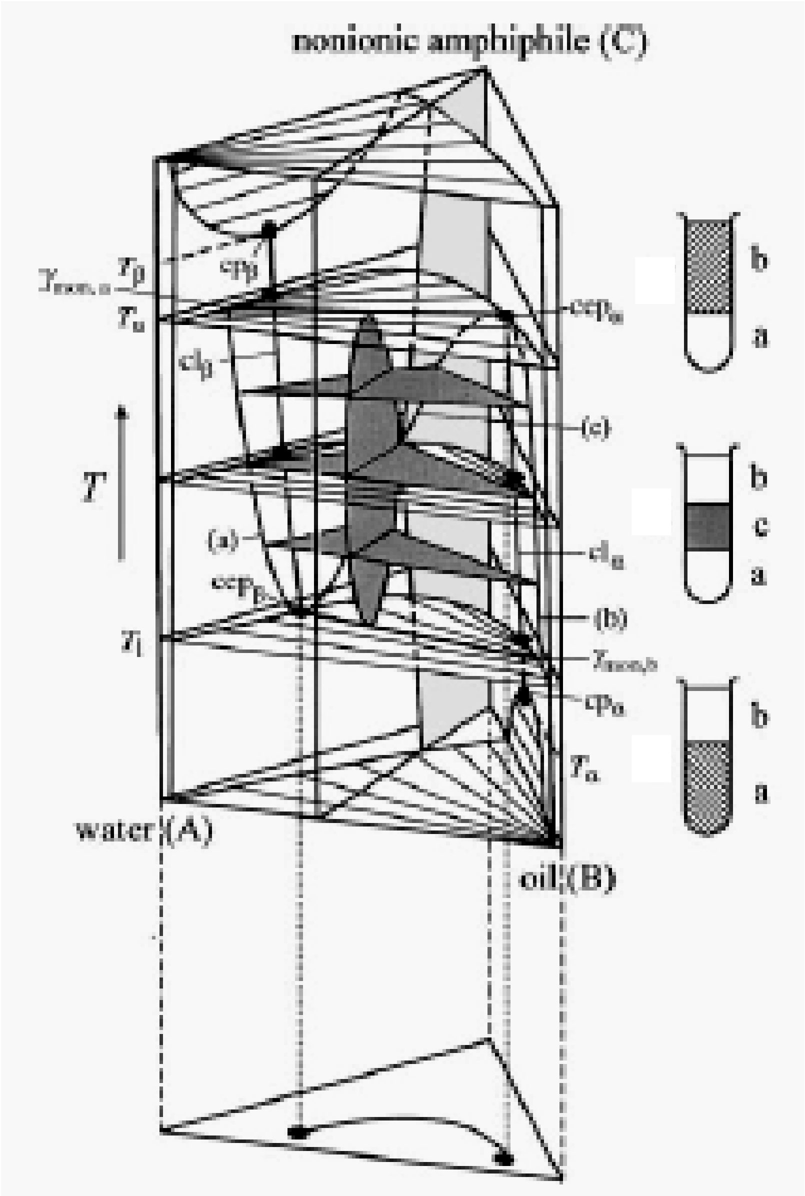
microemulsions are thermodynamically stable isotropic solutions that display a range of self-assembly structures; they can contain spherical drops or bicontinuous structures (Evans, Wennerström 1994)

Figure 3.2 Winsor classification and phase sequence of microemulsions encountered as temperature or salinity is scanned for non-ionic and ionic surfactant respectively. Most of the surfactant resides in the shaded area. In the three-phase system the middle-phase microemulsion (M) is in equilibrium with both excess oil (O) and water (W).



nomenclature:



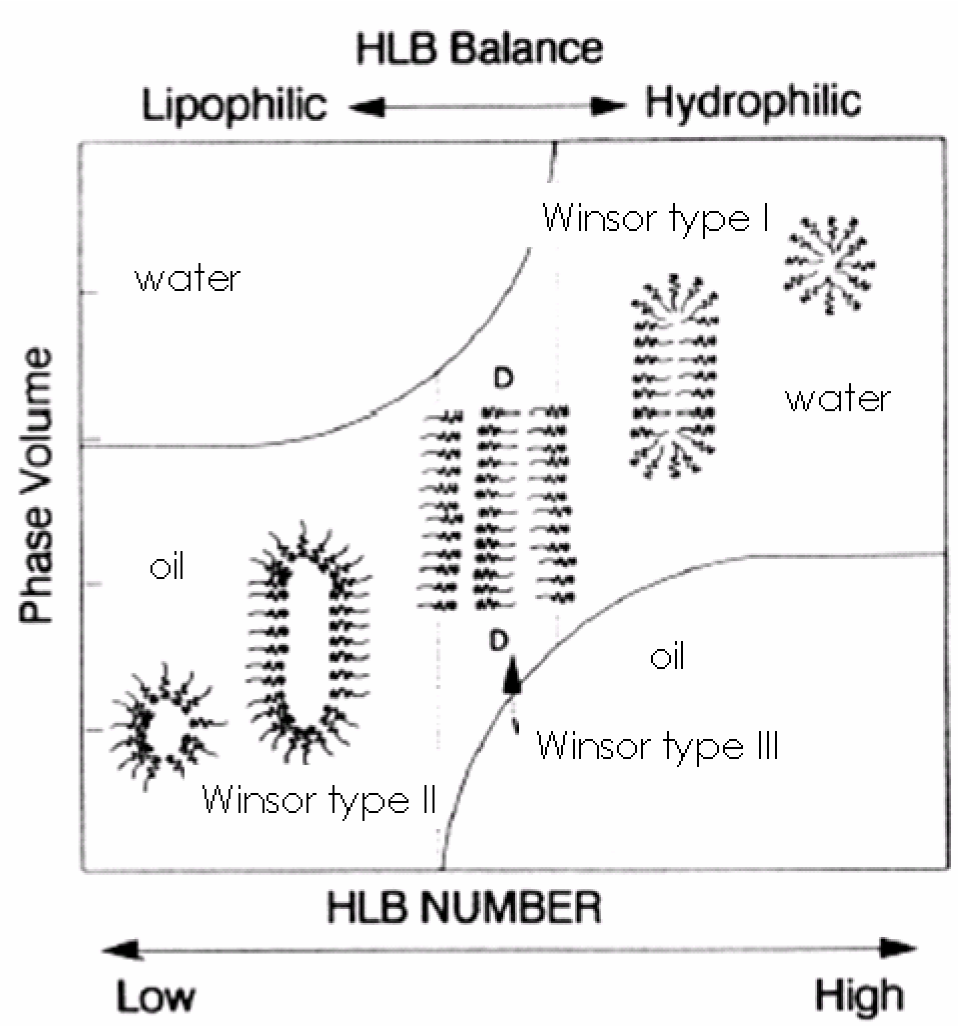
S. Burauer, T. Sachert, T. Sottmann, R. Strey,
Phys. Chem. Chem. Phys., 1999, 1, 4299-4306

$\overline{2}$ Winsor 2

3 Winsor 3

$\underline{2}$ Winsor 1

μ-emulsion tuning-1:

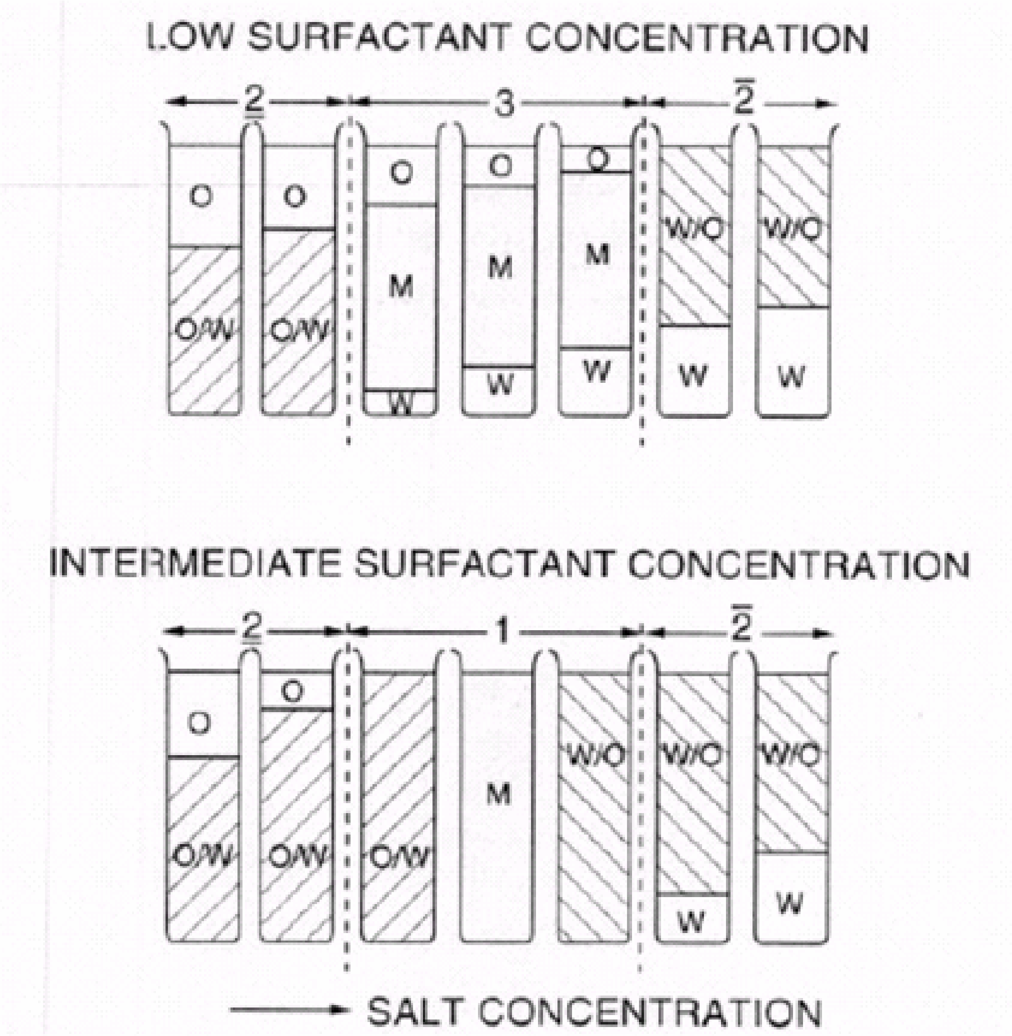


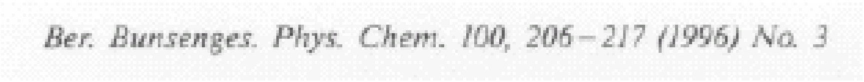
high salinity low

high temperature (non-ionic surf) low

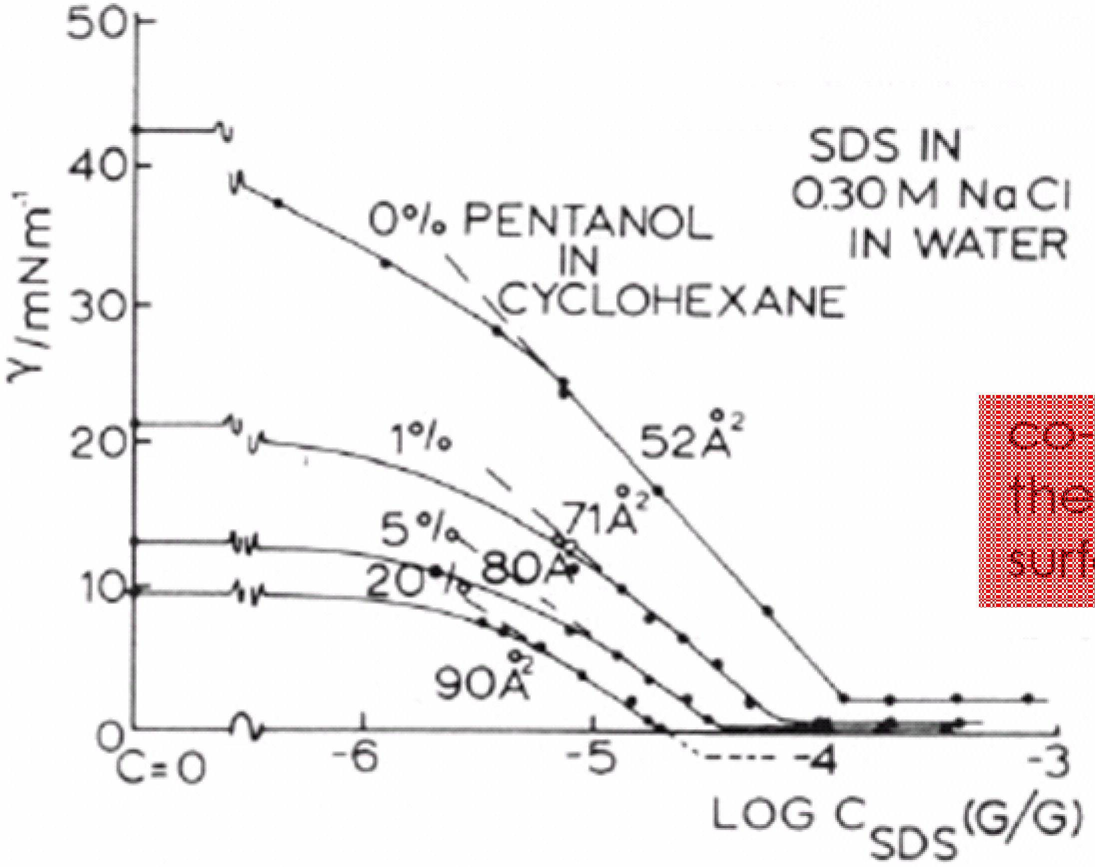
Vol. 32, No. 4—GROUND WATER—July-August 1994

µ-emulsion tuning-2:




Ber. Bunsenges. Phys. Chem. 100, 206–217 (1996) No. 3

SDS – pentanol (the very classical system)

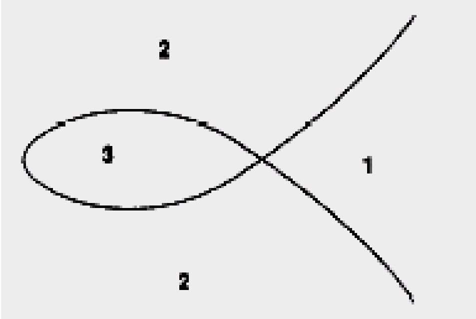


co-surfactant increases the efficiency of the surfactant (a_s increases)

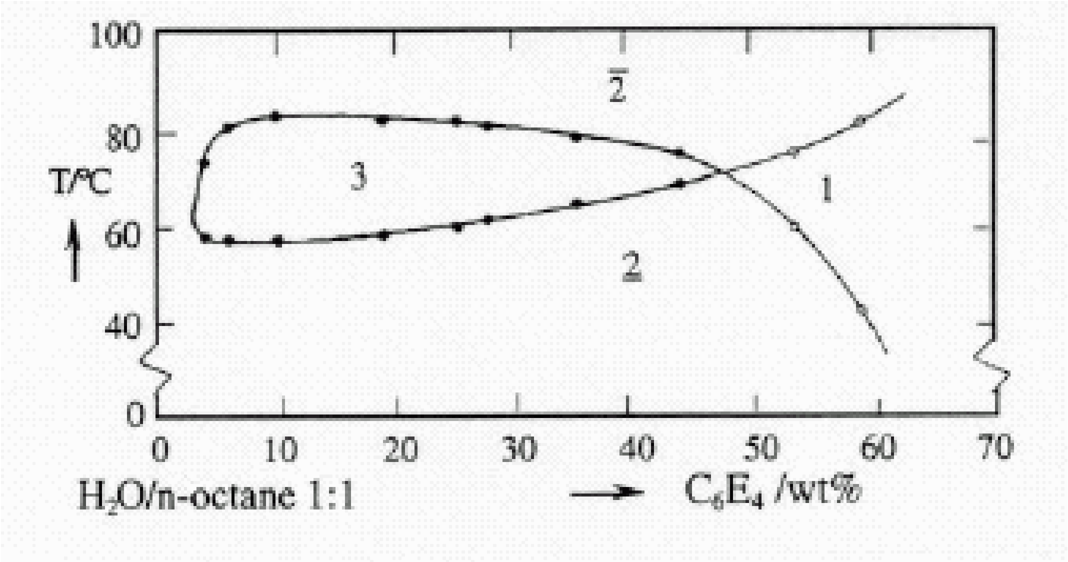
zero interfacial tension is reached before micelles are formed

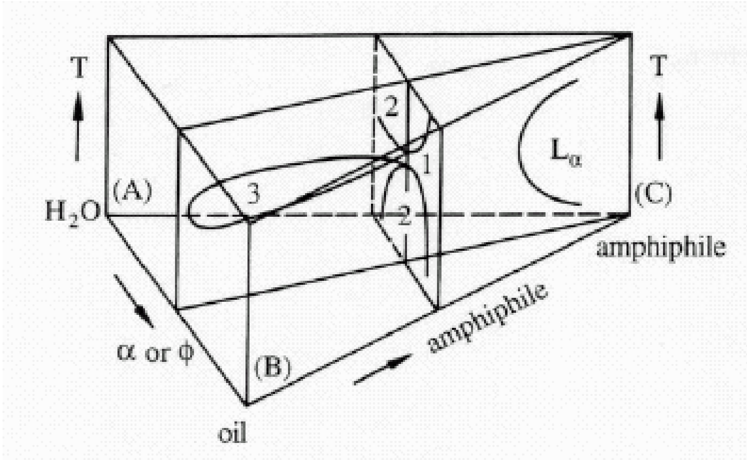
Ber. Bunsenges. Phys. Chem. 100, 206–217 (1996) No. 3

the very classical "fish" with nonionic surfactants:



H_2O – C_8H_{18} – C_6E_4 50 wt-% oil



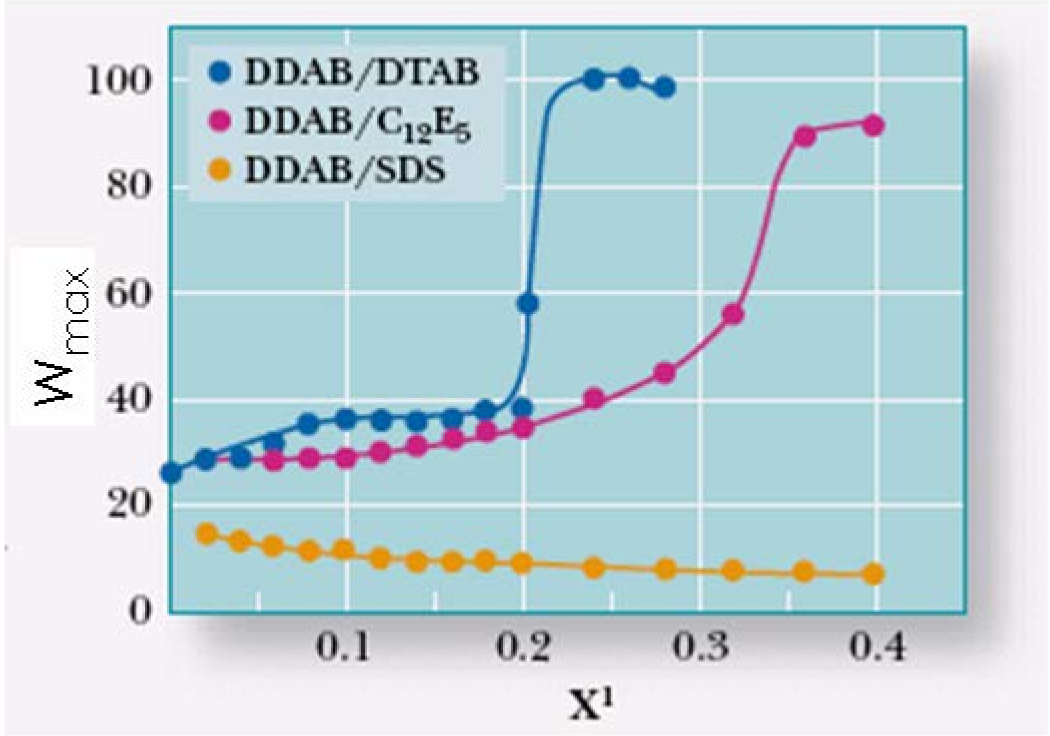



Ber. Bunsenges. Phys. Chem. 100, 190–205 (1996) No. 3

mixed surfactants

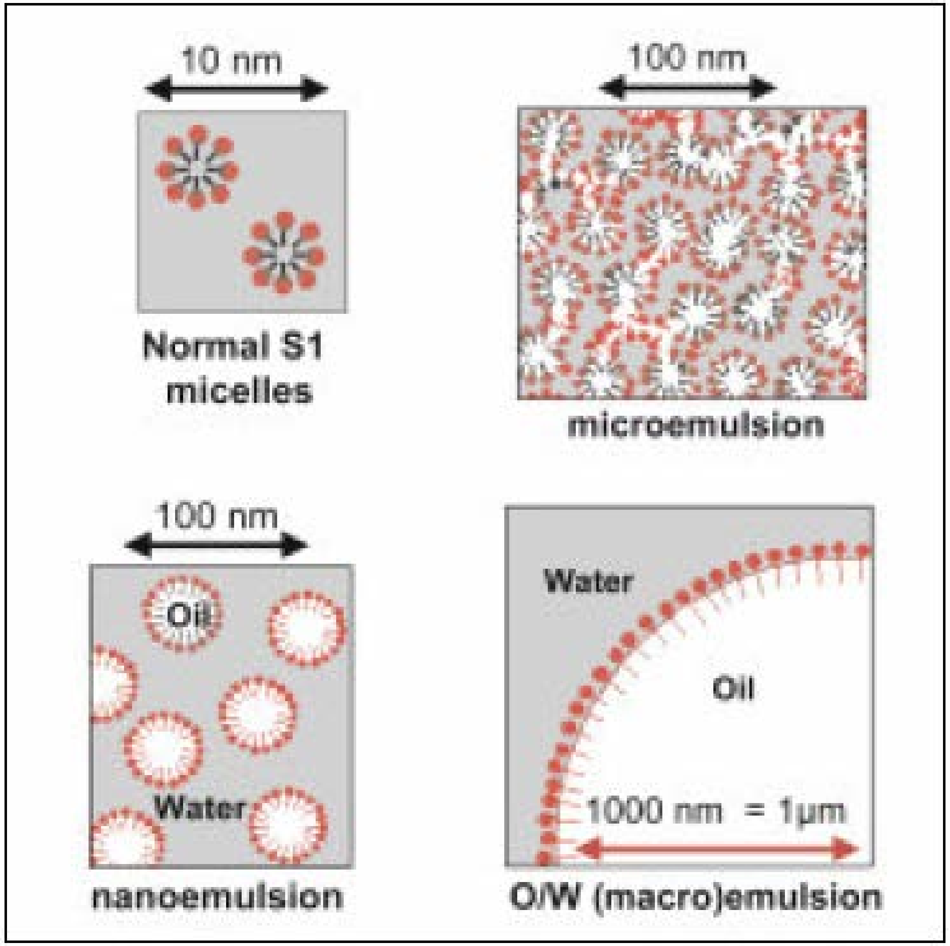
J Eastoe, A Bumajdad (Bristol), R K Heenan (ISIS)

synergistic or antagonistic effects are possible



effect of mixing different single chain surfactants with di-chain DDAB on maximum water uptake (W_{max}) for water-in-heptane µ-emulsions. X^1 is the mole fraction of single chain and the total surfactant concentration is always 0.1M

DDAB – didodecyldimethylammonium bromide; DTAB – dodecyltrimethylammonium bromide; $C_{12}E_5$ – dodecyl penta(ethyleneglycol) ether; SDS – sodium dodecylsulfate



Microemulsions are really single phase systems in which the structure contains fusioned oil balls and fusioned water balls, with no actually dispersed phase.

Microemulsions are flexible **near-zero curvature structures** whose thermodynamic stability implies an ultra low interfacial tension so that interfacial deformation is easy.

In other words a **microemulsion is not an emulsion with small droplets**, but some kind of weaved complex fabric with oil and water interconnected domains.

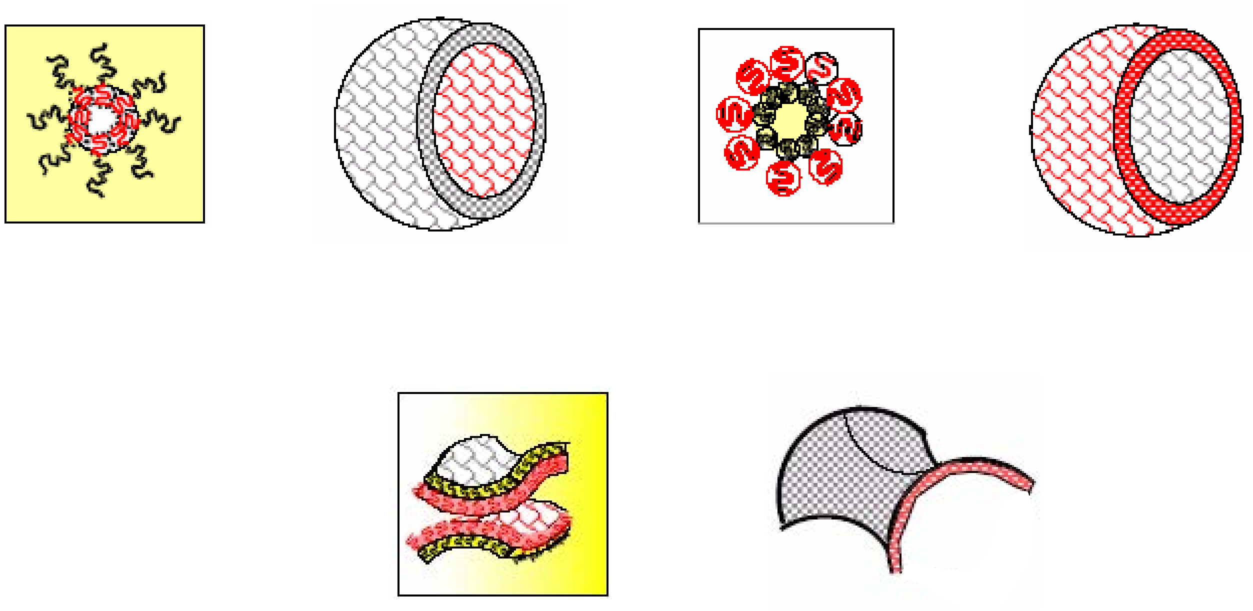
Colloidi TPoint 2/2003; J.-L- Salanger et al.

the shape of microemulsions:

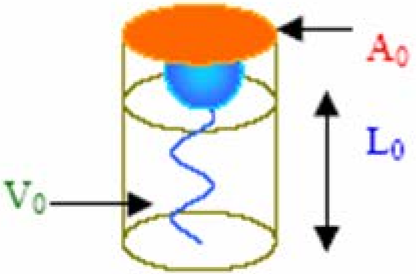
µ-emulsions: swollen surfactant assemblies (?)

determined by the surfactant assembly

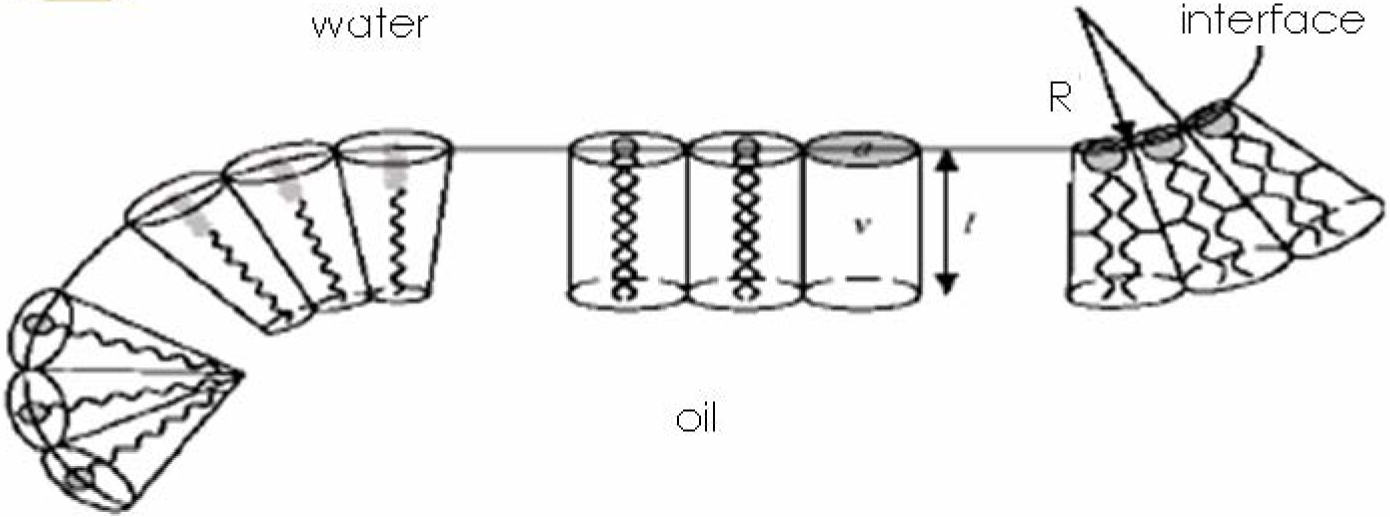
→ variety of shapes (not only spheres) such as:



surfactant's structure and curvature



surfactant parameter $$SP = \frac{V_0}{A_0 \cdot L_0}$$



SP<1/3
sphere

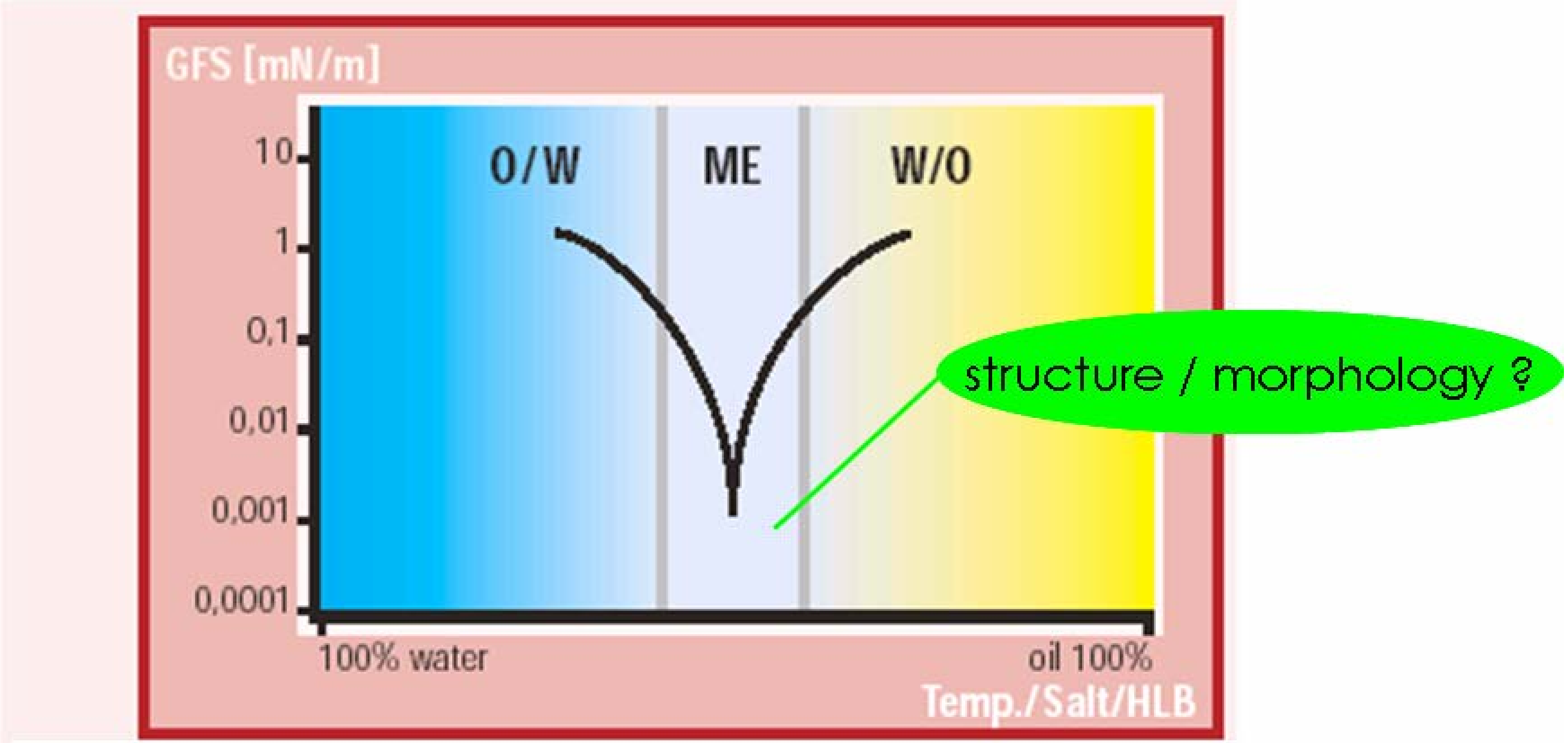
SP: 1/3-1/2
cylinder

SP: 1/2 -1
planar

SP: >1
inverse sphere

curvature of micelles as function of the surfactant

placing oil and water and surfactant(s) in one container



structure / morphology ?

interfacial tension (GFS) between the phases in µ-emulsions
is about 1000 times less than in o/w- or w/o-emulsions

Microemulsions are very interesting systems, because the oil-surfactant-water interface forms a wide variety of structures to avoid the direct oil/water contact.

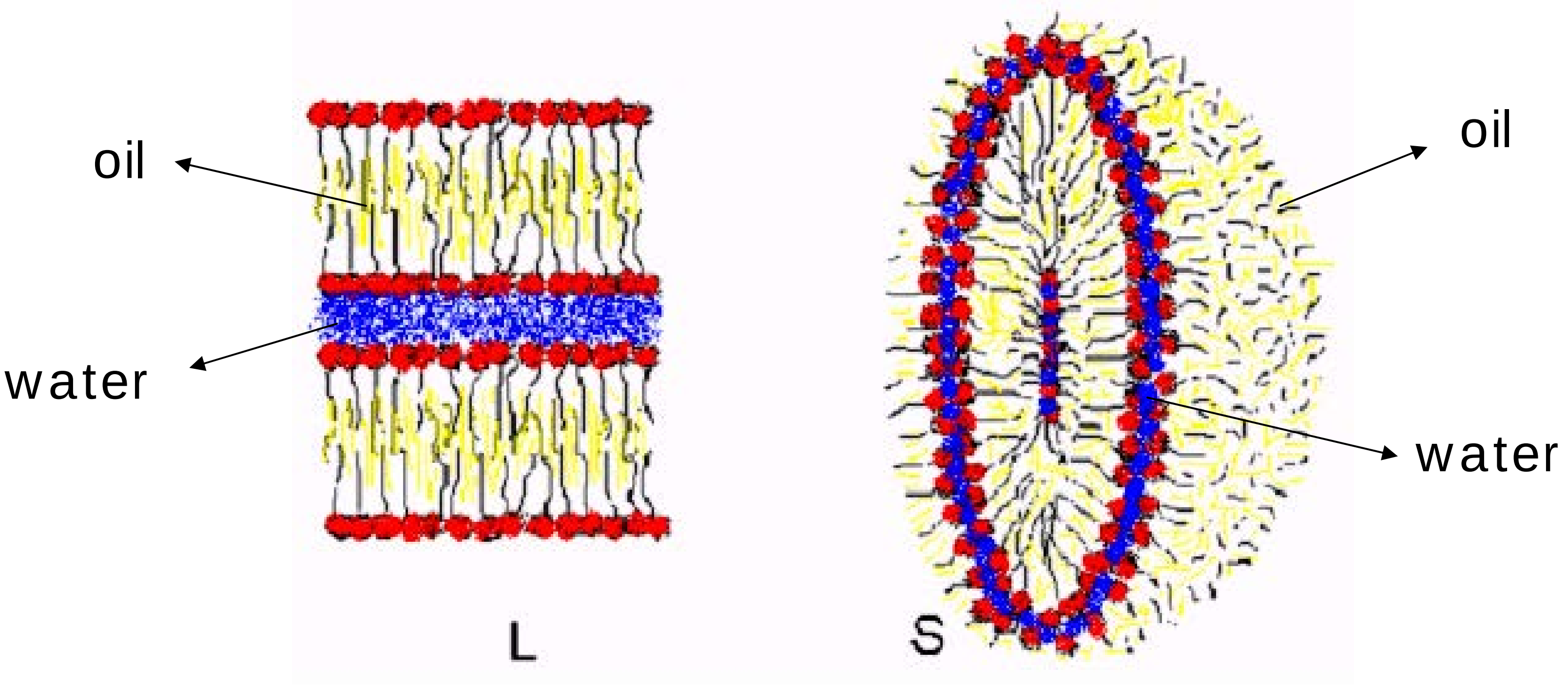
The sizes of these structures are in the range of a few hundreds of nanometers, so the solutions are transparent.

Micelles are the simplest structures: spherical or cylindrical objects formed by surfactant molecules, separating oil and water.

Micelles are like drops of oil in water and reverse micelles are like drops of water in oil.

→ higher interfacial tension stabilizes structures (spheres)

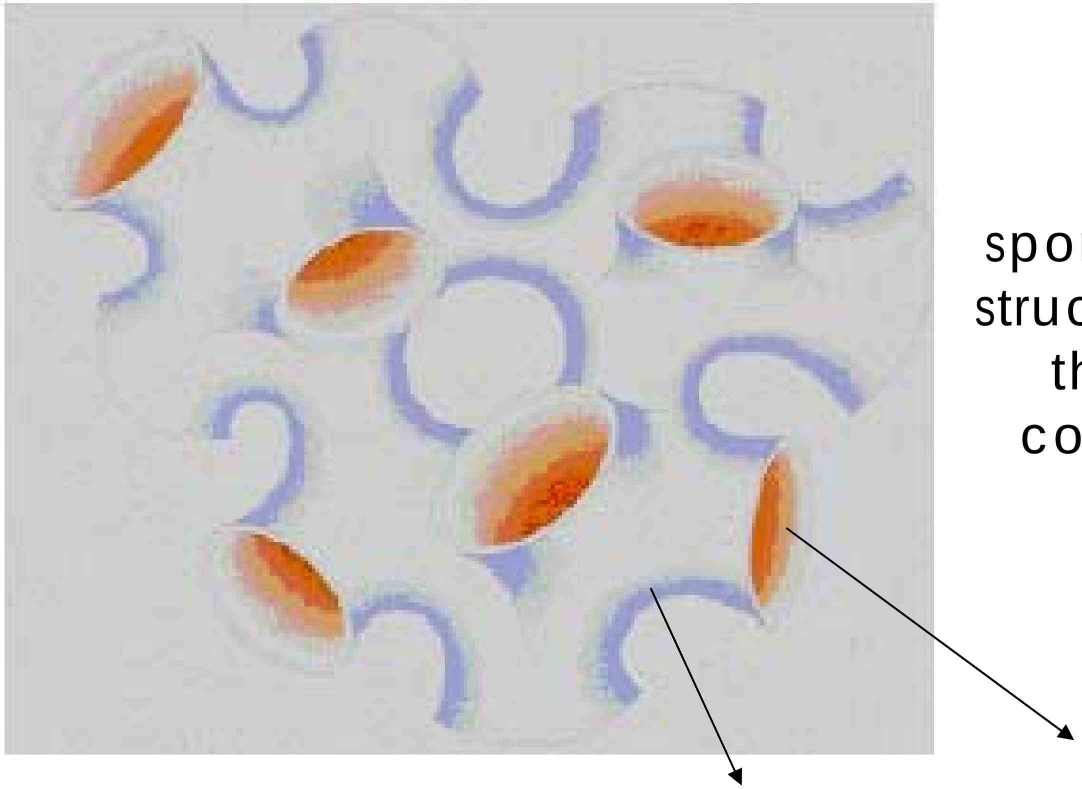
lamellae (L) and spherulite (S) structures:



Another microemulsion structure is the lamellae: water and oil consecutive layers separated by surfactant layers conveniently oriented.

This structure is related with the spherulite structure (onion structure, inverse vesicle). It is possible that spherulites are only out-of-equilibrium transient lamellar phases induced by mechanical work (yet to be proved) or by other stimulus.

bicontinuous structures:



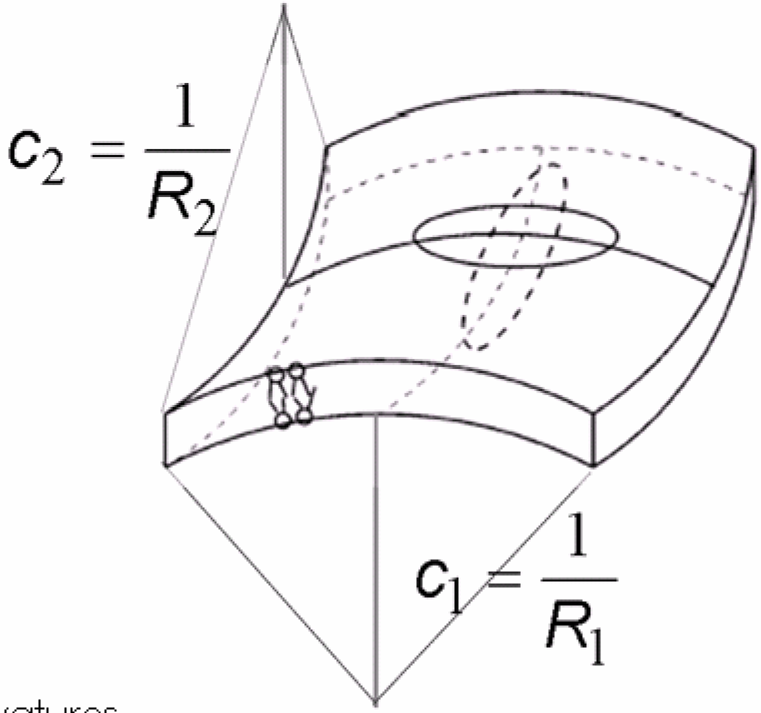
The bicontinuous structure or sponge phase is a quite intricate structure. As its name suggests, in this structure water and oil are continuous phases. The sponge surface is the surfactant.

[M. Daoud and C.E. Williams (Eds.); Soft Matter Physics, Springer-Verlag Berlin, Germany, 1999]

Helfrich free energy:

$$\int dA \left(\frac{\kappa}{2} (c_1 + c_2 - 2c_0)^2 + \bar{\kappa} c_1 c_2 \right)$$

introduced in 1973 by W. Helfrich, explains the thermal interface fluctuations and topological interface changes involving the interface curvatures c_1, c_2 and the spontaneous interface curvature c_0:



c_0 – curvature at which the free energy is minimal

$\kappa, \bar{\kappa}$ -modulus are associated with thermal interface fluctuations and topological interface changes

$$\kappa = \frac{1}{a} \frac{\partial^2 f}{\partial c_1^2}, \qquad \bar{\kappa} = -\kappa + \frac{1}{a} \frac{\partial^2 f}{\partial c_1 \partial c_2}$$

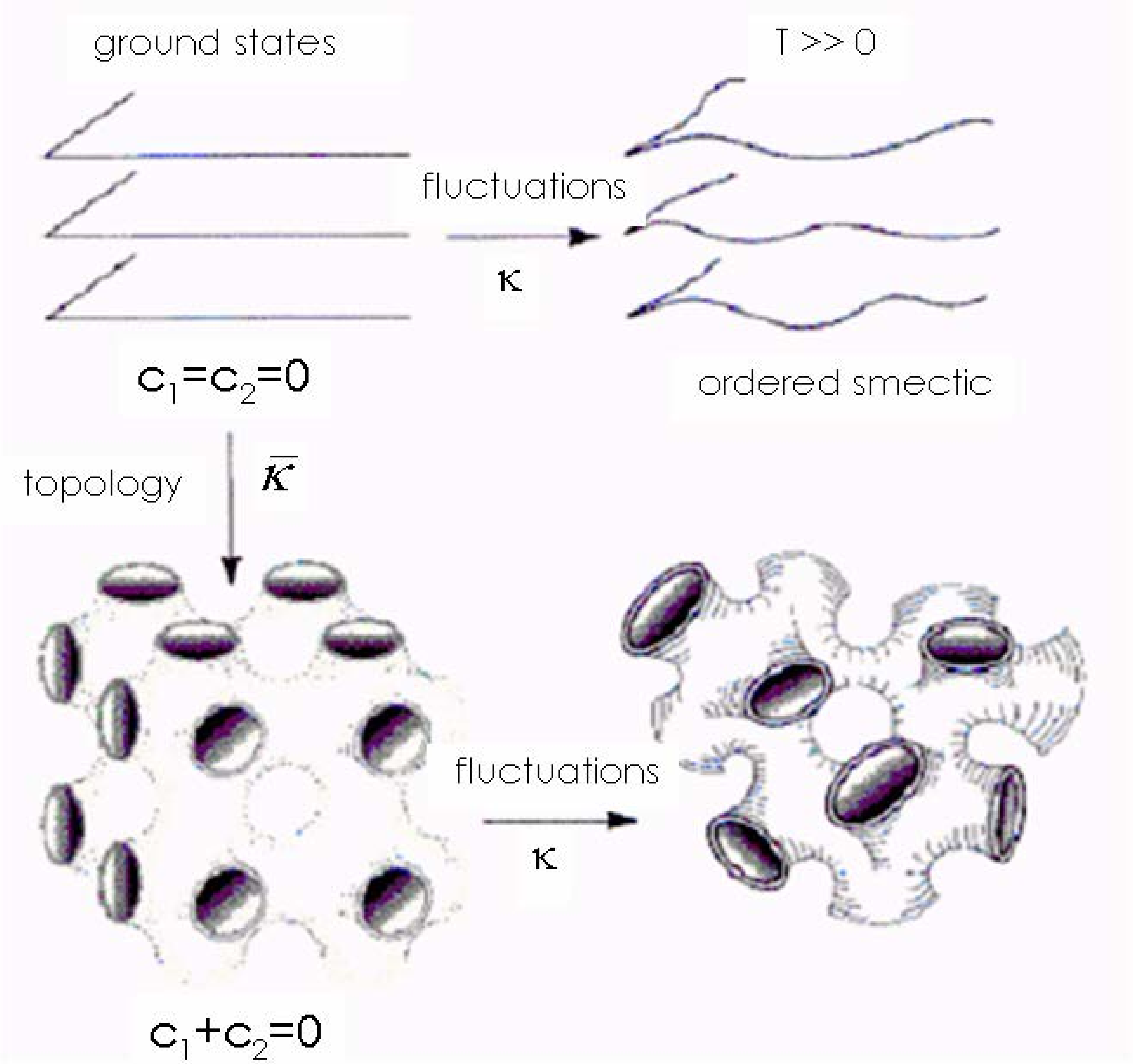
derivatives of the free energy with respect to the curvatures,

$$\mathrm{HFE} = \int \left[\frac{1}{2} \mathrm{K} (c_1 + c_2 - c_0)^2 + \bar{\mathrm{K}} c_1 c_2 \right] \mathrm{d}A$$

For lamellar phases $c_1=c_2=0$ and only thermal fluctuations are possible.

On the other hand, in the bicontinuous phase the saddle splay geometry fixes $c_1 = -c_2$, and the two terms of the HFE become energetically important at room temperatures.

$K, \bar{K}$ determine the interface thermal fluctuations and the interface topology respectively.



ground states

T >> 0

fluctuations

κ

ordered smectic

$c_1=c_2=0$

topology

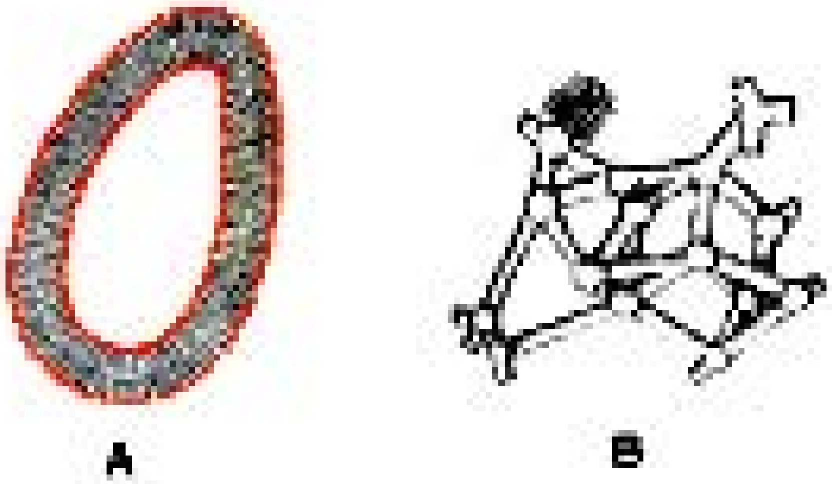
$\bar{\kappa}$

fluctuations

κ

$c_1+c_2=0$

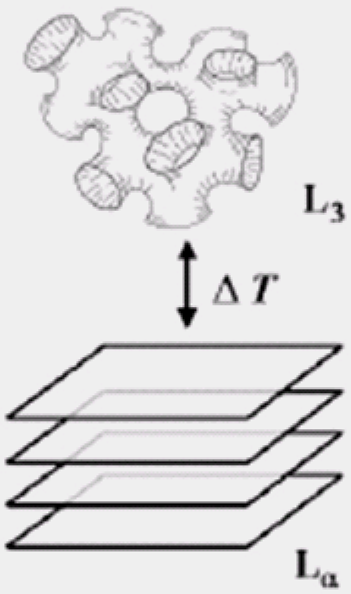
[M. Daoud and C.E. Williams (Eds.); Soft Matter Physics, Springer-Verlag Berlin, Germany, 1999]

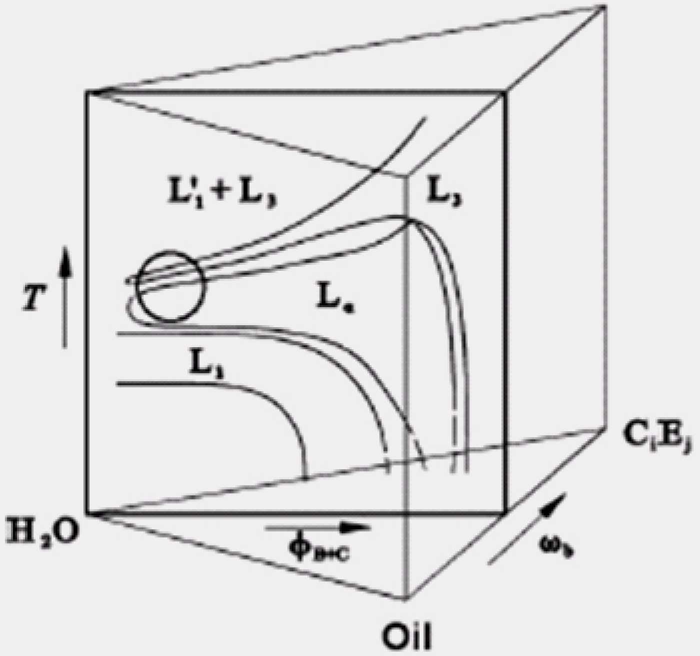


Other microemulsion structures are possible: interconnected rod-like micelles, onions with an inner different structure, vesicles, etc.

It has been found that the principal factors for explaining microemulsion structure changes are surfactant shape, entropic energy terms, as well as solvent properties as ionic force and pH.

[M. Daoud and C.E. Williams (Eds.); Soft Matter Physics, Springer-Verlag Berlin, Germany, 1999]

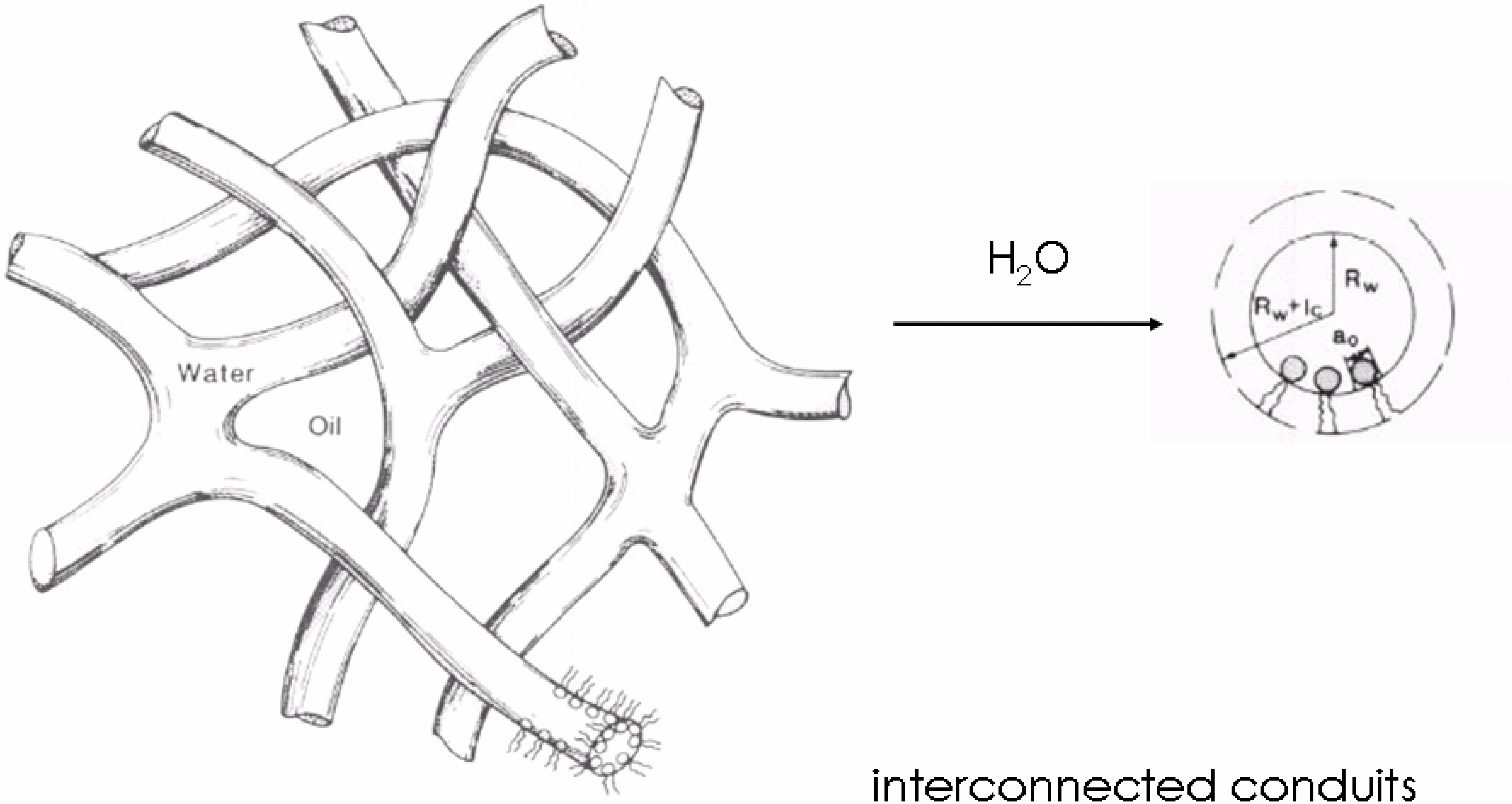




phase transition between the L_3- and L_α-phase in the (D_2O) – oil (*n*-decane) - nonionic surfactant (*n*-odecylpentaoxyethylene; $C_{12}E_5$) system in order to investigate the kinetics and mechanics of passage formation; $\phi_{surf}/\phi_{oil}=0.81$

L_1 – microemulsion
L_3 – micellar cubic
L_α - lamellar

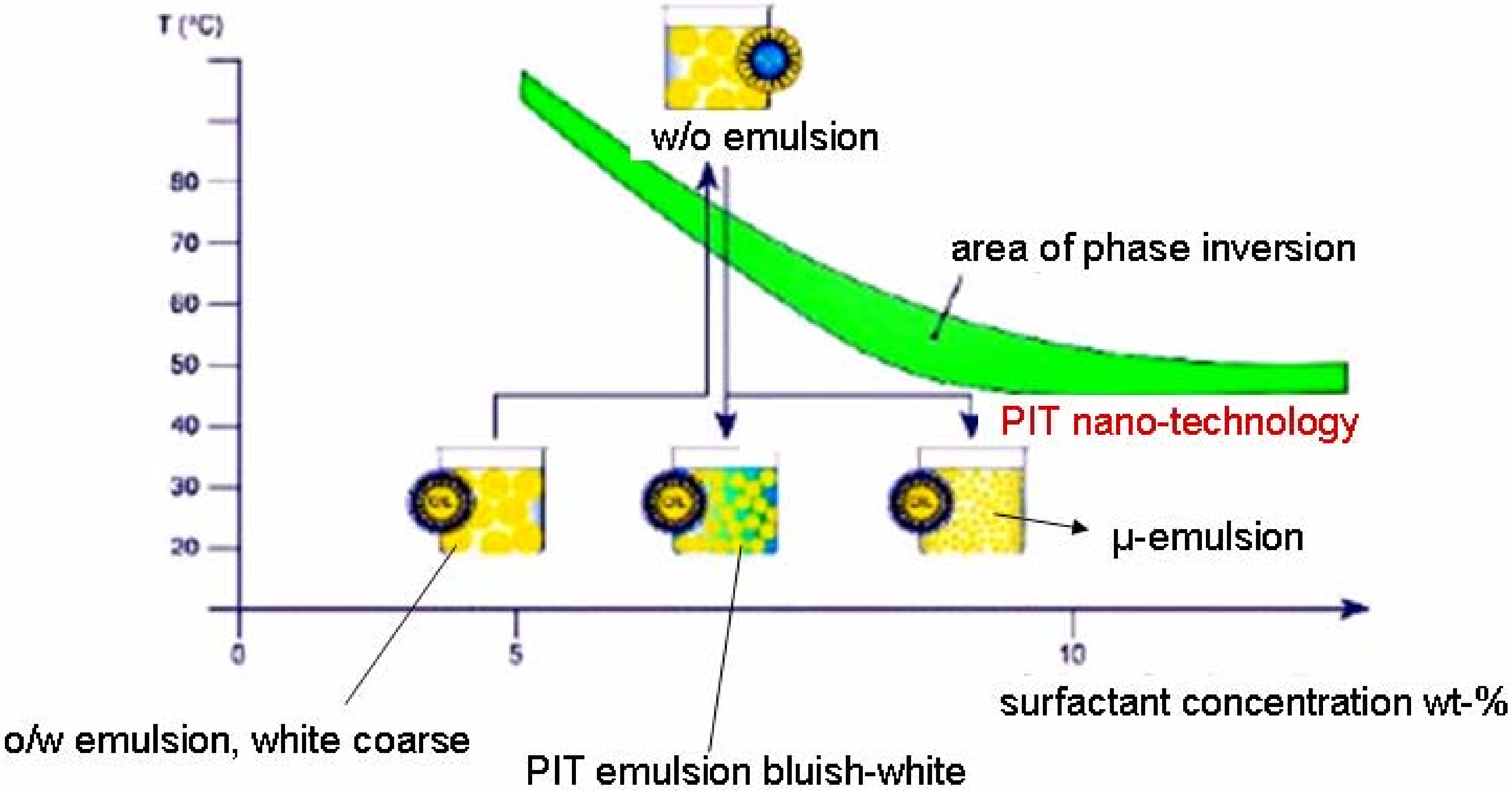
M. S. Leaver, U. Olsson, H. Wennerström, R. Strey and U. Würz, *J. Chem. Soc.*, *Faraday Trans.*, 1995, 91, 4269.



interconnected conduits that comprise the bicontinuous structure in DDAB microemulsions [J. Phys. Chem. 90 (1986) 842]

DDAB – didodecyldimethylammonium bromide
oil - alkanes

Preparation of PIT - Microemulsions and PIT - Emulsions



w/o emulsion

area of phase inversion

PIT nano-technology

μ-emulsion

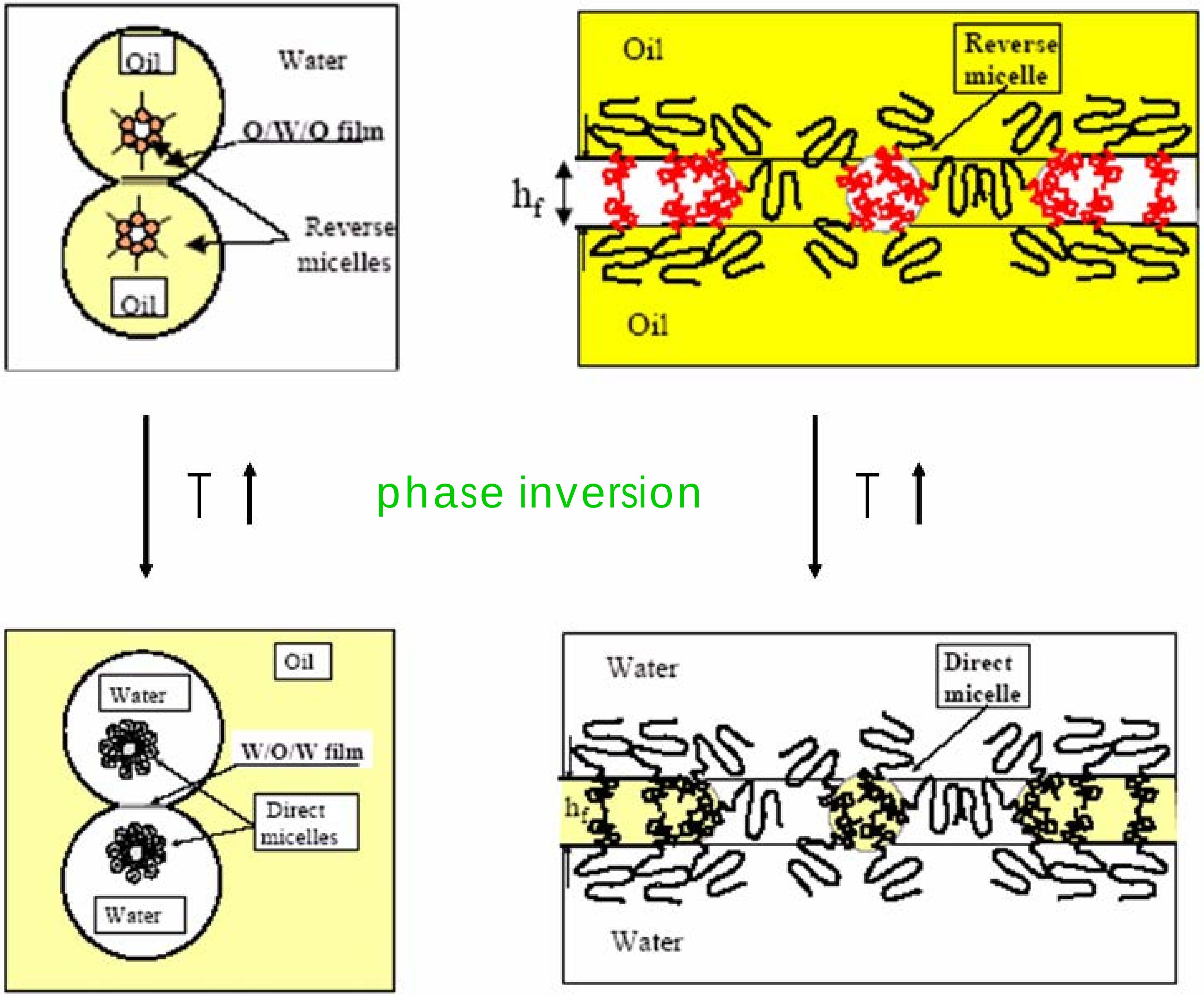
surfactant concentration wt-%

o/w emulsion, white coarse

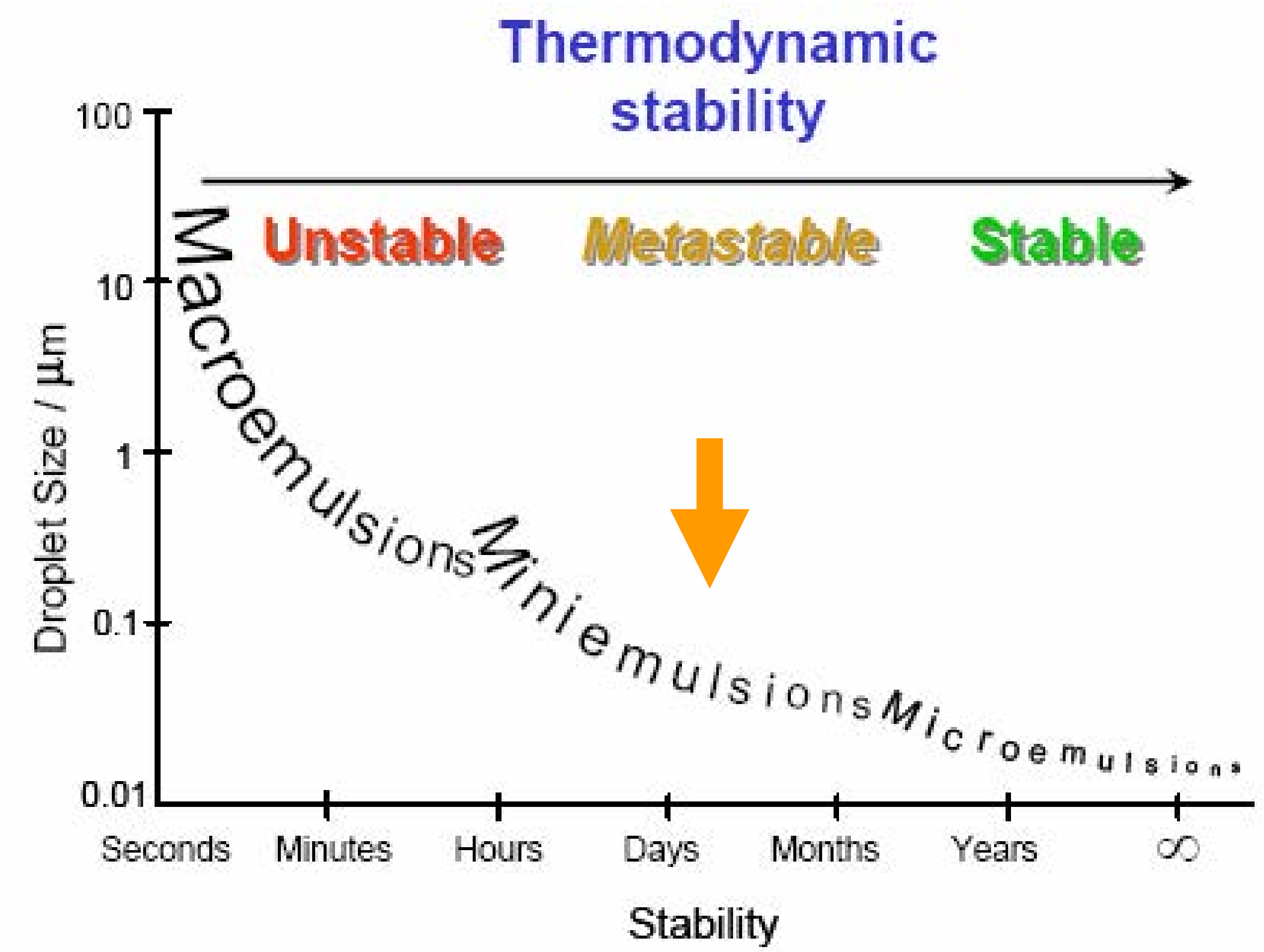
PIT emulsion bluish-white

Beiersdorf AG

emulsion drop-drop contact

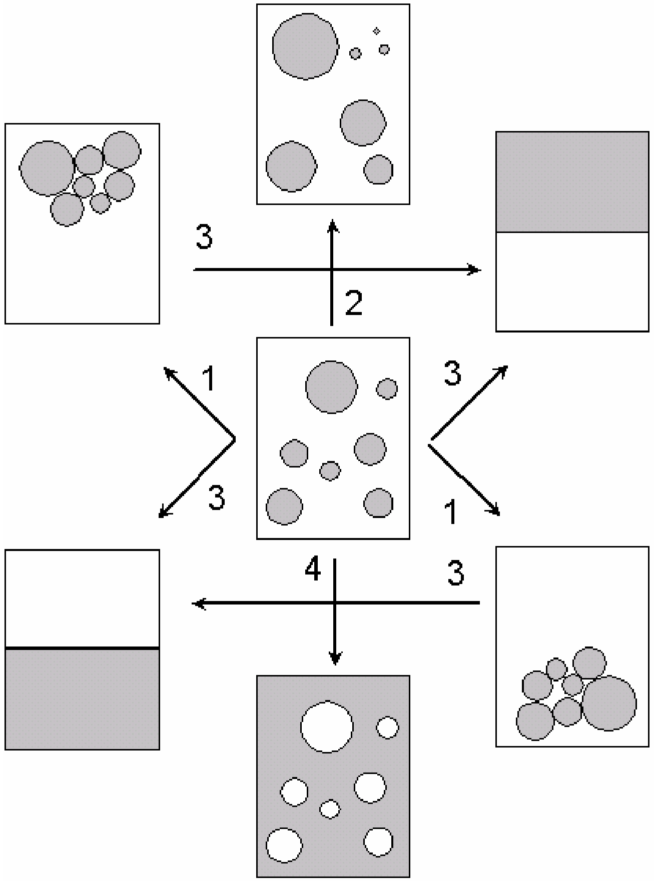


T ↑ phase inversion T ↑



also macro- and miniemulsion can be made stable

understanding emulsion stability



	counter action
1 – phase separation (creaming, sedimentation)	density match
2 – Ostwald ripening	lyophob
3 – aggregation processes (flocculation, coagulation, coalescence)	stabilizers
4 – phase inversion	preserve conditions

understanding emulsion stability-1

$$\mu_{1,r} = \mu_1 - \mu_1^* = \frac{4 \cdot \sigma \cdot v_{m,1}}{D} + RT\ln x_1 \quad (1)$$

The excess chemical potential of monomer emulsion droplets ($\mu_{1,r}$) composed of two components (compound C1 and another compound C2, which has zero solubility in water) as given by equation (1) illustrates the contributions arising from the size (first term on the right hand side leading to an increase in $\mu_{1,r}$) and the droplet composition (second term on the right hand side leading to a decrease in $\mu_{1,r}$).

μ_1 is the chemical potential of the monomer in the droplet of diameter D, μ_1^* is the chemical potential of the pure bulky monomer phase, σ is the interfacial tension between the drop and the continuous phase, $v_{m,1}$ is the molar volume of the monomer, R is the molar gas constant, T is the absolute temperature, and x_1 is the mol fraction of monomer in the drop.

understanding emulsion stability-2

$$\mu_{1,r} = \mu_1 - \mu_1^* = \frac{4 \cdot \sigma \cdot v_{m,1}}{D} + RT\ln\left(1\text{-}x_{2,0} \frac{D_0^3}{D^3} \right) \qquad (2)$$

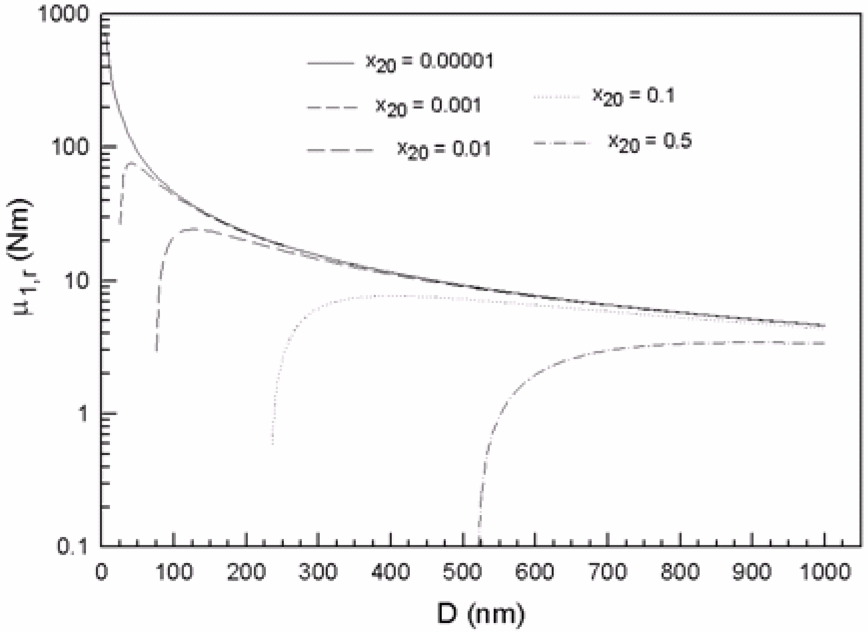
Basically, both D and x_1 are from a practical point of view independent parameters, which can be freely chosen by the experimenter.

However, equation (1) allows to derive a relation showing that for stable droplets of a desired size the composition of the drops cannot be freely chosen.

Assuming spherical drops and allowing that after emulsification the drop sizes are distributed around the initial (or target) value D_0 equation (1) can be transformed into equation (2) where $x_{2,0}$ is the initial (or nominal) mol fraction of the water-insoluble component (C2).

After comminution the drops are not monodisperse but have a drop size distribution (DSD).

understanding emulsion stability-3



D_0 = 100 nm, σ = 10 mNm^{-1}, and different $x_{2,0}$ – values

$$\frac{\partial \mu_{1,r}}{\partial D} > 0 \Rightarrow$$ stable, if for all droplet sizes in the emulsion

$$\frac{\partial \mu_{1,r}}{\partial D} < 0 \Rightarrow$$ equilibrium state is unattainable for the entire range of drop sizes

an emulsion is not stable *per se* unless the droplet size distribution is extremely monodisperse and D_0 and $x_{2,0}$ obey relation (3):

$$x_{0,2} = 1 - \exp\left(-\frac{4 \cdot \sigma \cdot v_{m,1}}{RT \cdot D_0}\right)$$

understanding emulsion stability-4

$$\frac{\partial \mu_{1,r}}{\partial D}(D_0) > 0 \qquad \Rightarrow \qquad x_{2,0} > \frac{4 \cdot \sigma \cdot v_{m,1}}{\left(3 \cdot RT \cdot D_0 + 4 \cdot \sigma \cdot v_{m,1}\right)} \qquad (4)$$

1. A: $C_{\infty,2} = 0 \quad \frac{\partial \mu_{1,r}}{\partial D} > 0$

- the number of drops remains constant
- only C1 diffuses from the smaller to the larger drops leading to a change in the droplet composition that is x_1 and x_2 increases in the larger and smaller drops, respectively
- equilibrium is reached where the chemical potentials of C1 are equal in all drops of different size
- the DSD broadens
- supposing fast enough initiation mainly polymerization inside preformed droplets is possible

1. B: $C_{\infty,2} = 0 \quad \frac{\partial \mu_{1,r}}{\partial D} < 0$

- the experimenter has not met the equilibrium condition [equation (4)]
- no equilibrium due to OR of C1
- smaller drops become richer in x_2 and might reach an equilibrium
- large-size drop fraction continues with OR
- polymerization may be initiated in the fine-drop fraction, which then might be regarded as seed particles where monomer is supplied from the larger drops until they become itself locus of initiation, as they do not completely disappear due to the presence of C2

2. : $C_{\infty,2} > 0$

- C1 and C2 volume fluxes
- reduction factor of OR:

$$F_{RED} = \frac{W_{OR}}{W_{OR2}} = \frac{\tilde{D}_1 \cdot C_{\infty,1} \cdot \varphi_2}{\tilde{D}_2 \cdot C_{\infty,2}}$$

$\tilde{D}_1$ $\tilde{D}_2$ -diffusion coefficients of C_1, C_2

φ 's - volume fractions

$$W_{OR} = \left(\frac{\phi_1}{W_{OR}^1} + \frac{\phi_2}{W_{OR}^2}\right)^{-1}$$

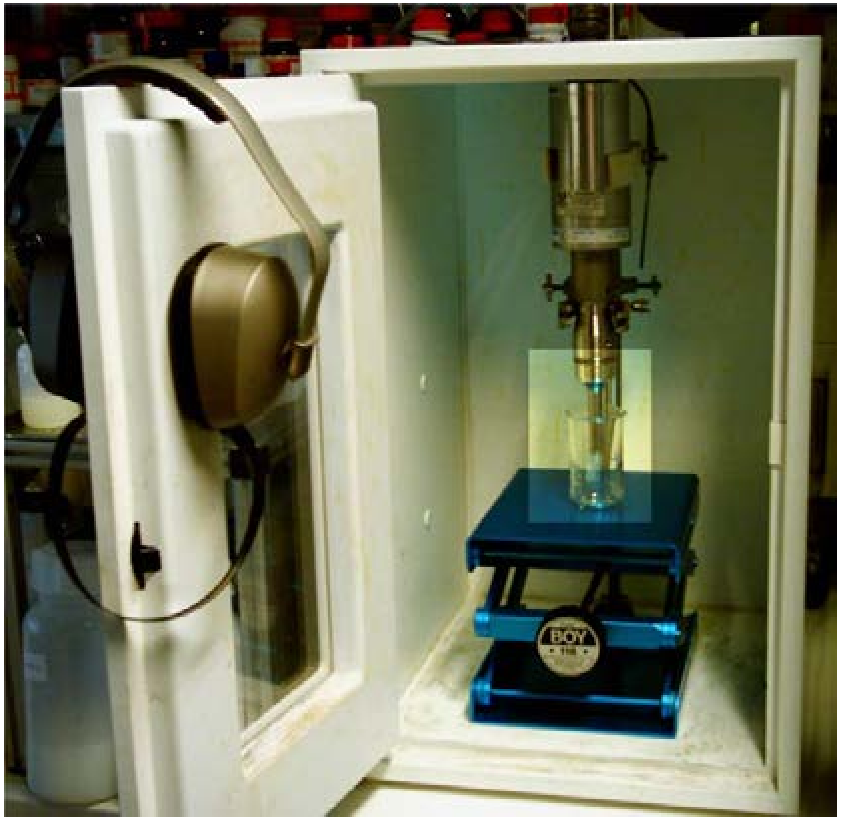
- extremely asymmetric relation: as already small ϕ_2 - values cause a substantial retardation of OR
- large amounts of C1: no influence

W_{OR}^1 W_{OR}^2 - W_{OR} of the pure components

preparing mini-emulsions

premixing oil and water

sonication



standard recipe (lab'pm):

6 g of dispersed phase
24 g of continuous phase
0.25 g of lyophob
3-0.003 g of stabilizer
0.12 g of K-persulfate

stirring

Δt~1min

after stirring

after sonication

Δt~minutes

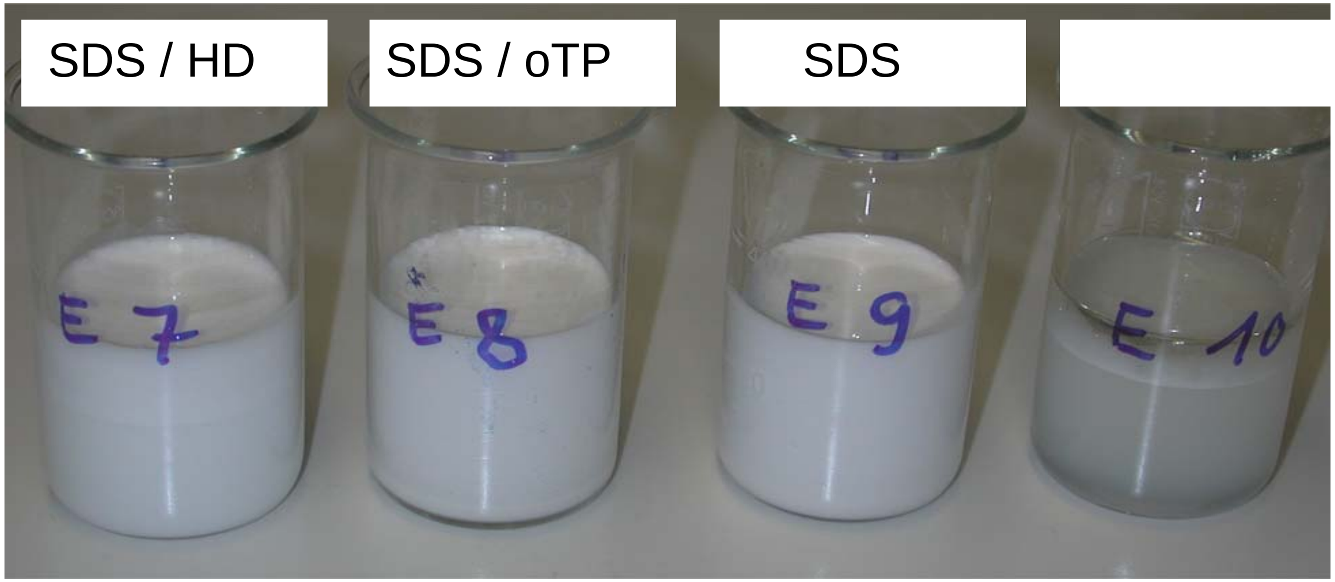
→

Δt~3 day

→

Δt~minutes

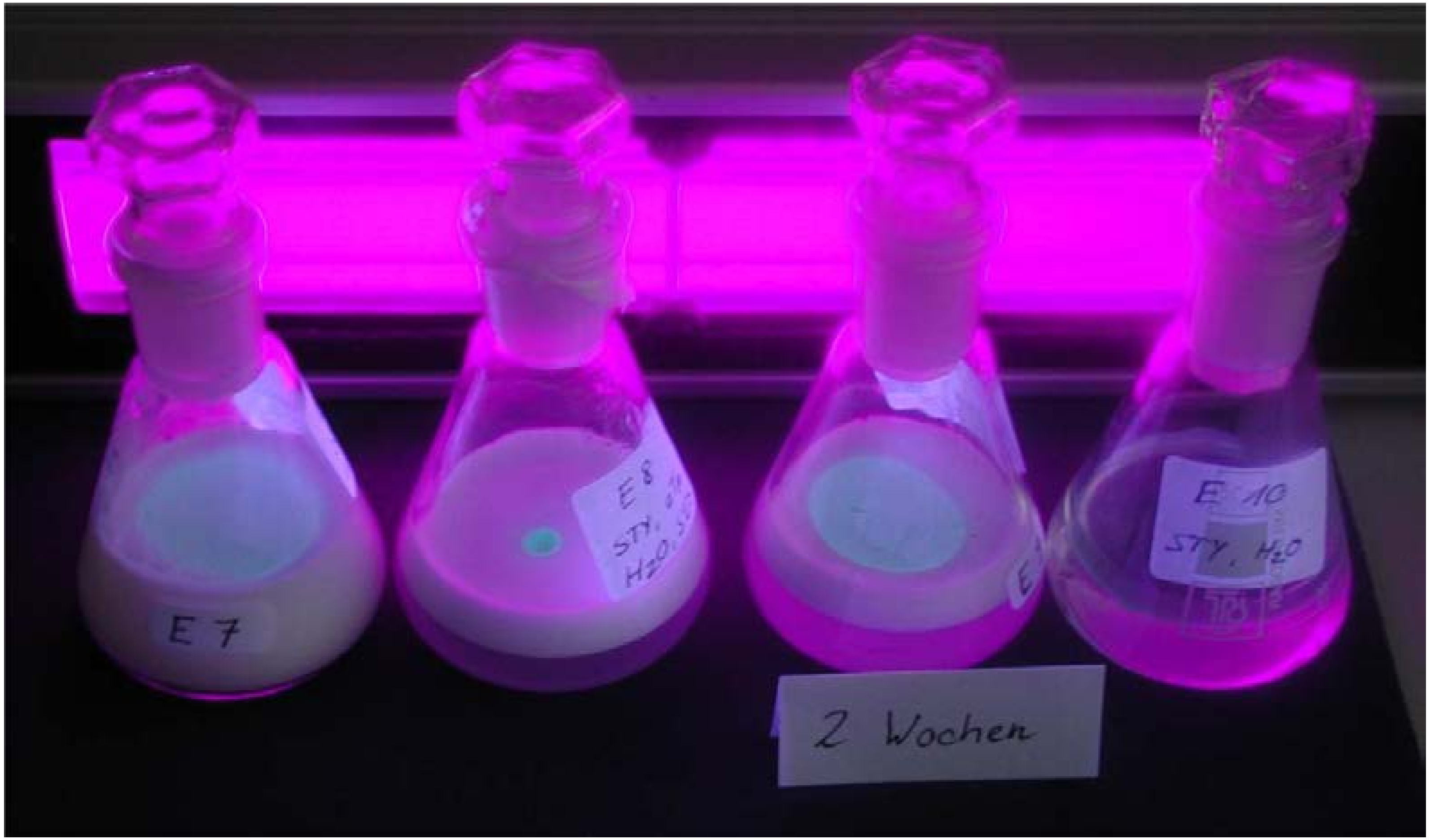
→



Δt~1 week

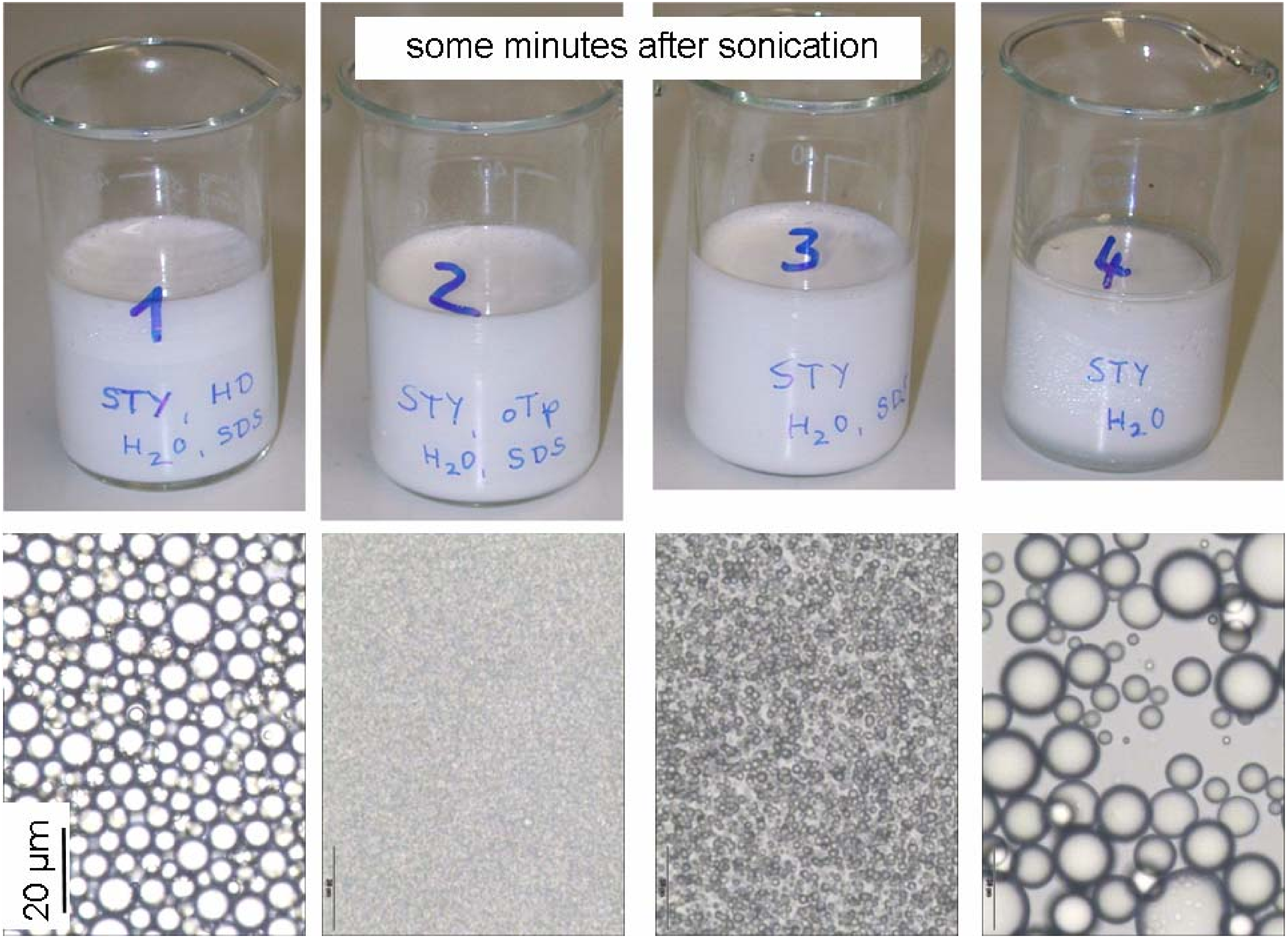
→

+ pyrene



styrene redistributes because
pyrene sucks some of the styrene

some minutes after sonication

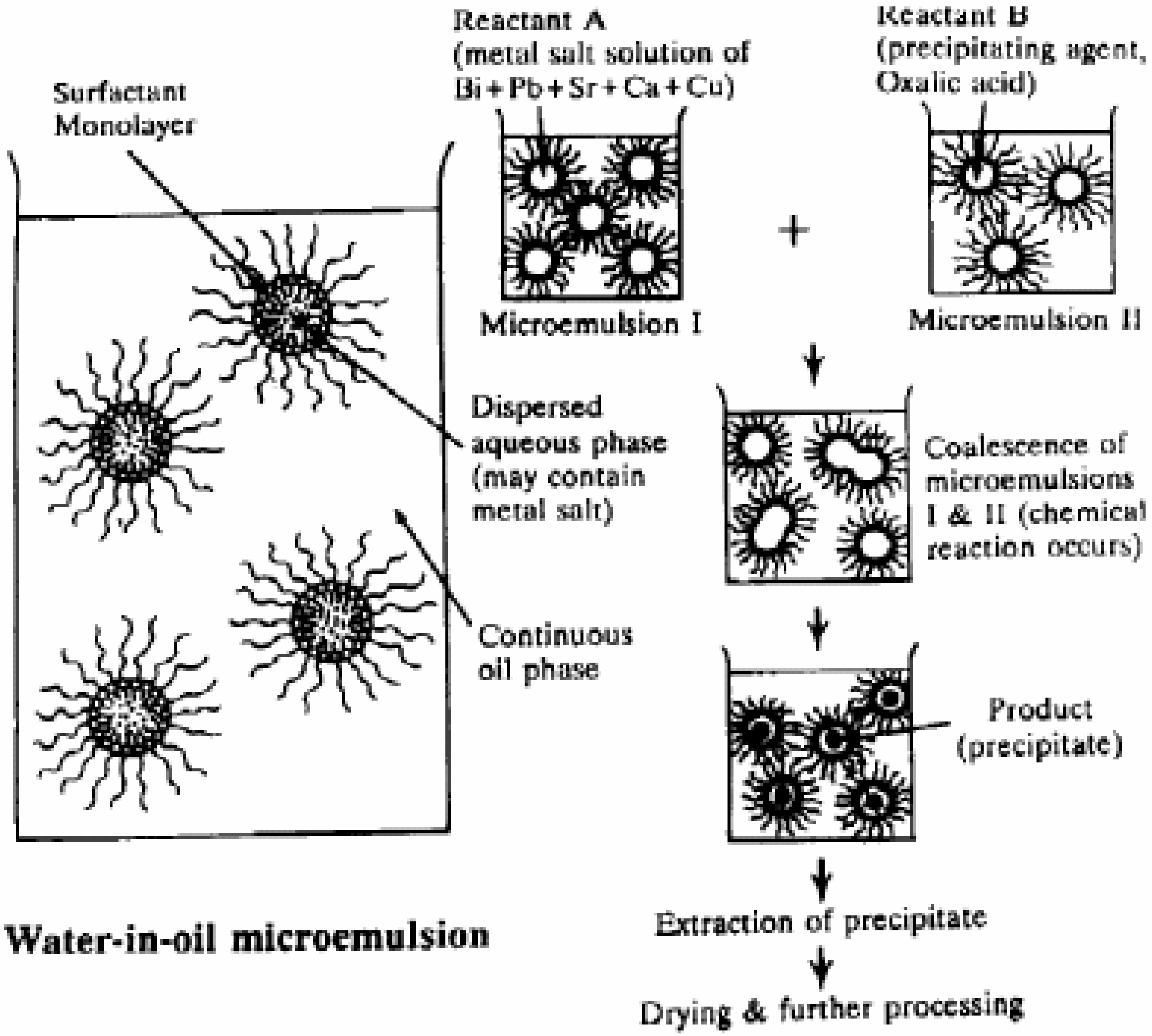


Micro and Miniemulsion – Why Special Emphasis?

nano-reactors

reaction medium

competition with block copolymer micelles



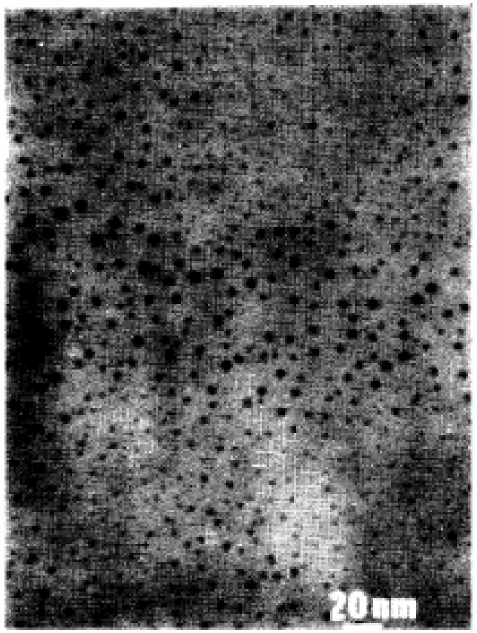
Water-in-oil microemulsion

Reaction in microemulsion media

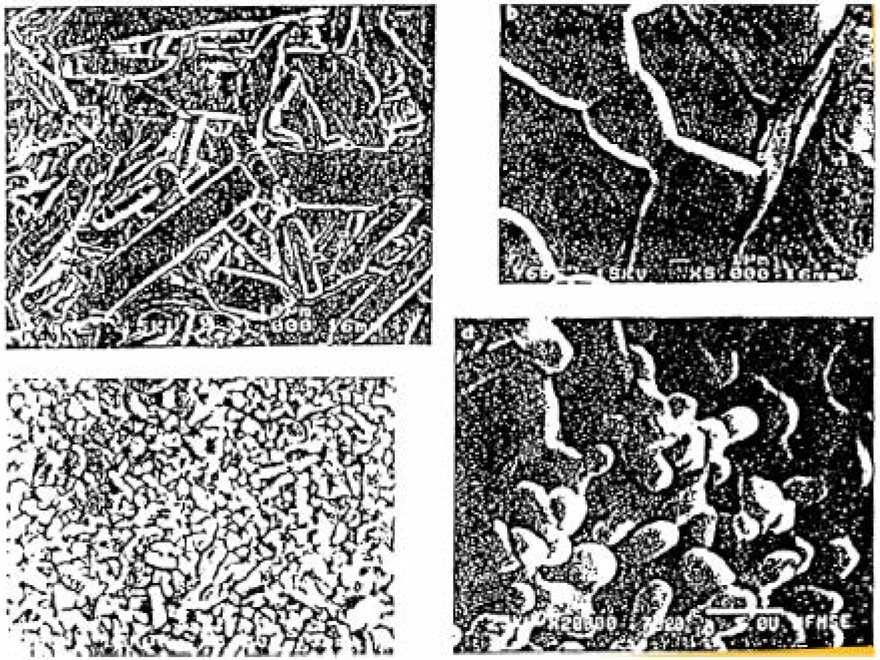
Production of Complex Oxides through microemulsions

- Microemulsions provide a novel vehicle for synthesis of a micro-particulate oxalate precursor which yields very high density sintered pellets of $YBa_2Cu_3O_{7-x}$.
- Steric barrier by surfactant monolayer restricts the growth of precipitated particles and hinders intergrain coagulation.

	Surfactant phase	Hydrocarbon phase	Aqueous phase
Microemulsion I	CTAB + 1-butanol	n-octane	(Y,Ba,Cu) nitrate soln. (0.3 N)
Microemulsion II	CTAB + 1-butanol	n-octane	Ammonium oxalate soln. (0.45 N)
Weight fraction	29.25%	59.42%	11.33%

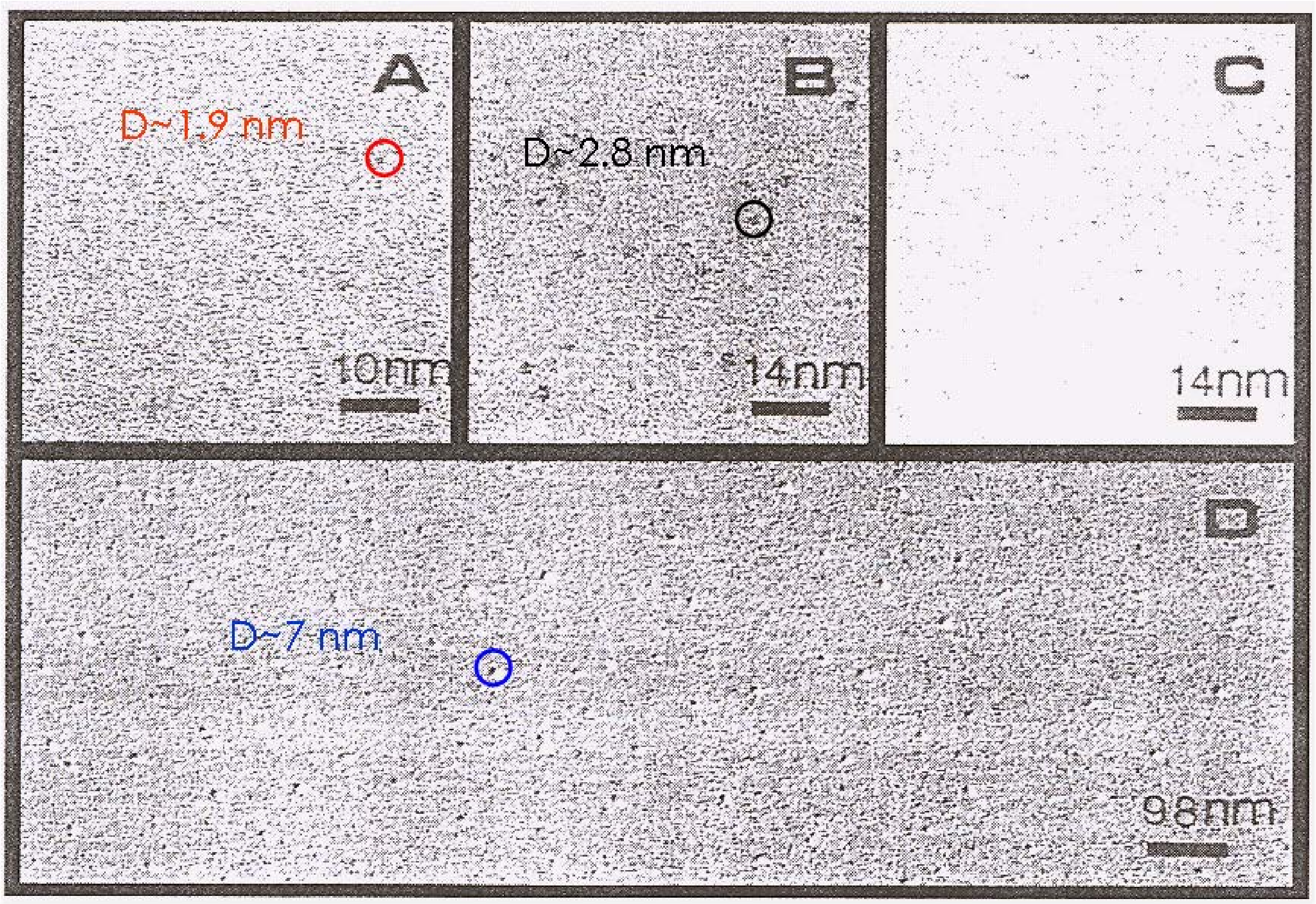


precursor powder



Microstructures of sintered $YBa_2Cu_3O_{7-x}$

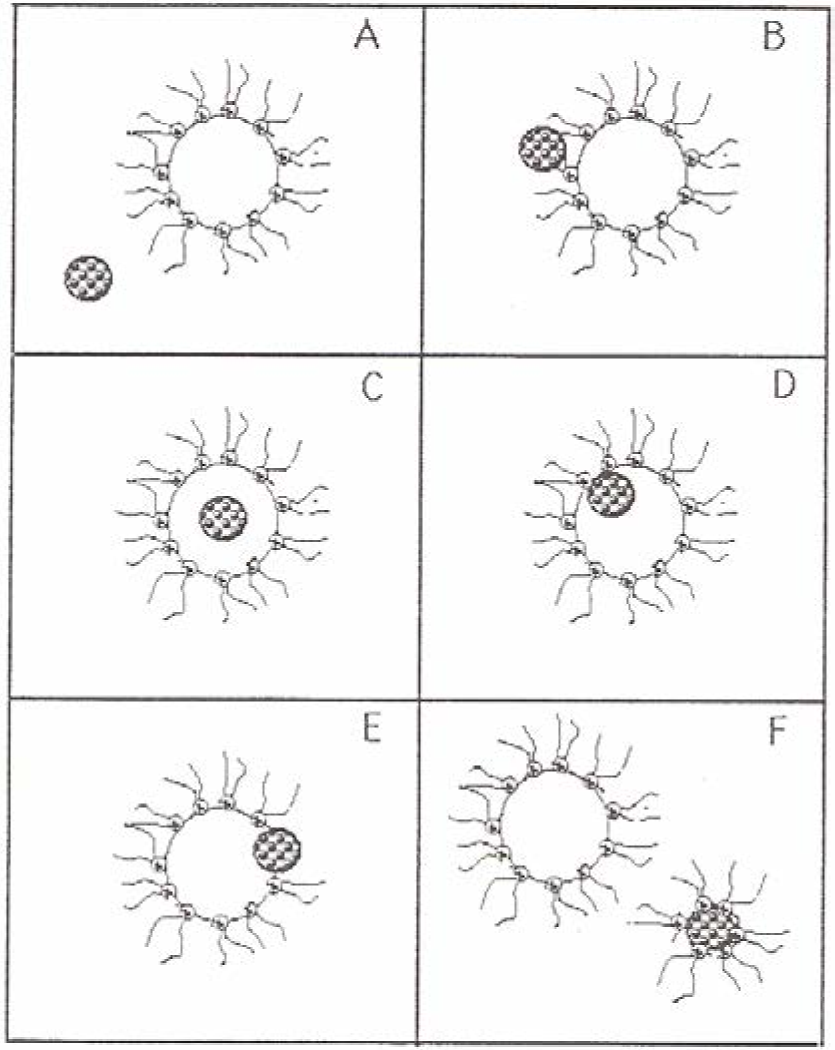
Reactions In Reverse Micelles



polymerization of didecyldimethyl ammonium methacrylate inverse micelles in toluene; w=[H_2O]/[S]; A: w=5, B: w=10, C: w=15, D: w=10; A-C: [S]=0.05M, D: [S]=0.1M, UV irradiation, AIBN,

Langmuir 11 (1995) 3656

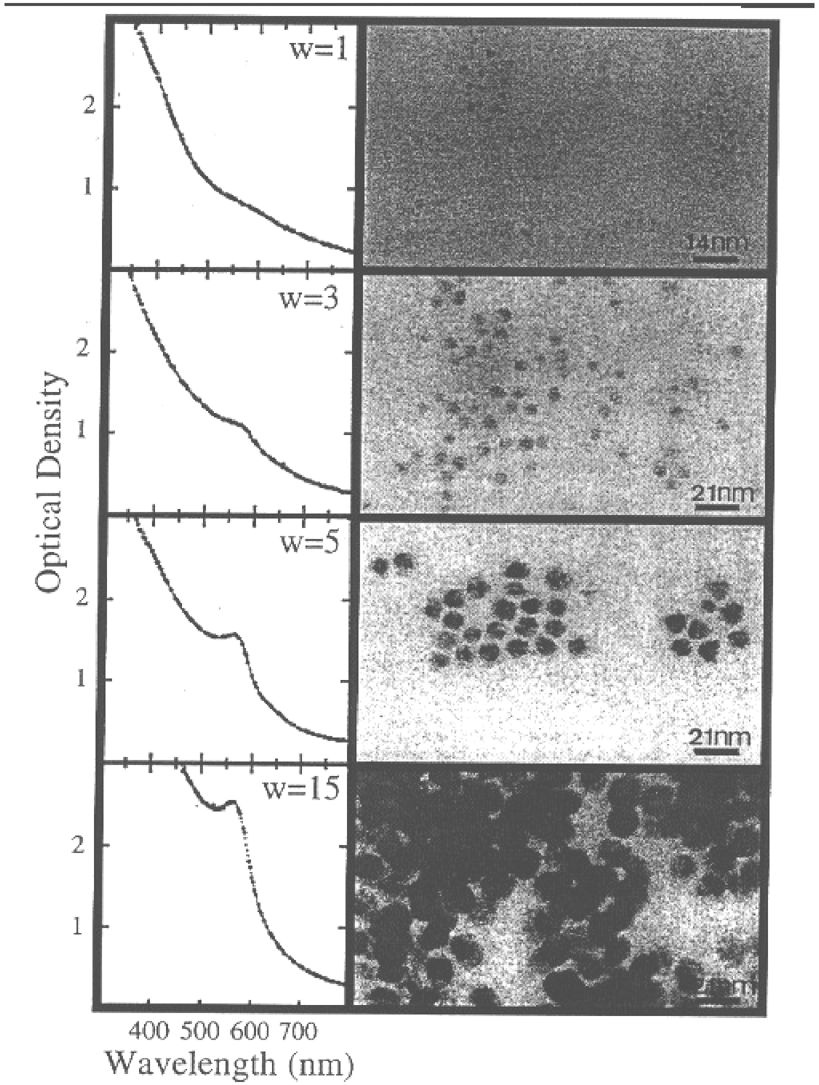
M. P. Pileni in Handbook of Surface and Colloid Chemistry (K. S. Birdi, ed.), CRC 1997



average location of a probe in reverse micelles

micelle properties are influenced

Copper Particles in Reversed Micelles

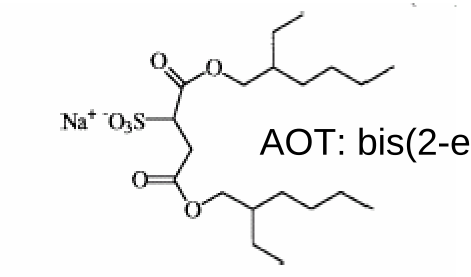


Micelles: NaAOT/$Cu(AOT)_2$ = (8:1)

$Cu(AOT)_2 + N_2H_4$

isocotane as continuous phase

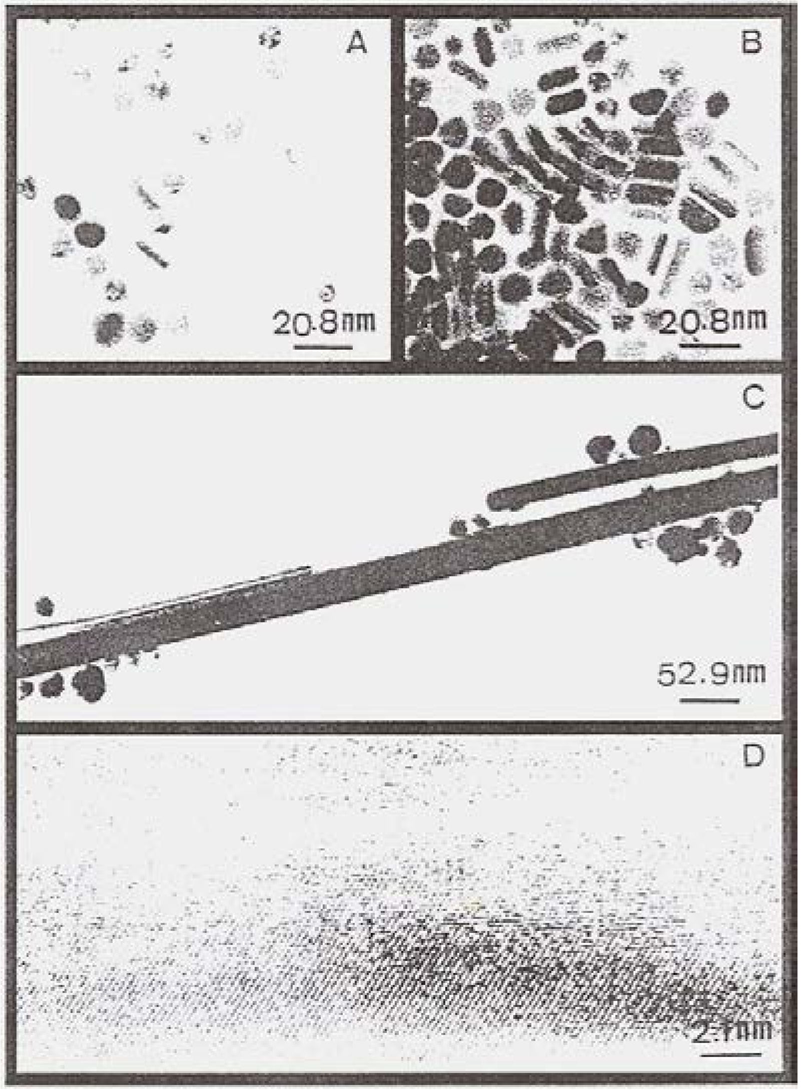
w - molar water surfactant ratio



AOT: bis(2-ethylhexyl)sulfosuccinate

M. P. Pileni in Handbook of Surface and Colloid Chemistry (K. S. Birdi, ed.), CRC 1997

Copper Particles in Different Phases



Micelles: NaAOT/$Cu(AOT)_2$ = (8:1)

$Cu(AOT)_2 + N_2H_4$

A – cylindrical droplets
B – bicontinuous structure
c – lamellar phase

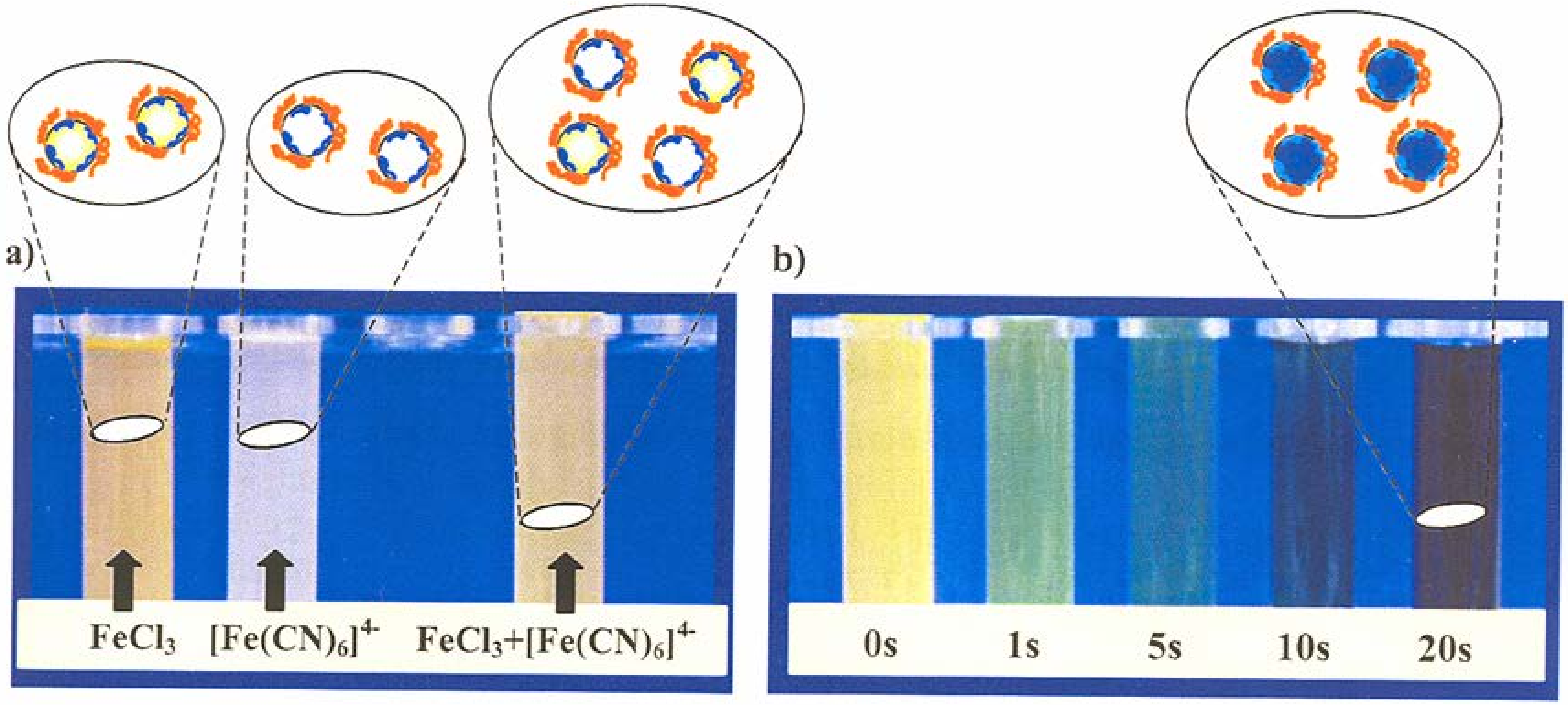
A, B, C different phases

particles with different shapes

D - high resolution TEM of particle prepared in the lamellar phase

M. P. Pileni in Handbook of Surface and Colloid Chemistry (K. S. Birdi, ed.), CRC 1997

stability of miniemulsion droplets



mixing without sonication

sonication

$$nH_2O + 4FeCl_3 + 3K_4[Fe(CN)_6] \longrightarrow Fe_4[Fe(CN)_6]_3\, nH_2O + 12KCl$$

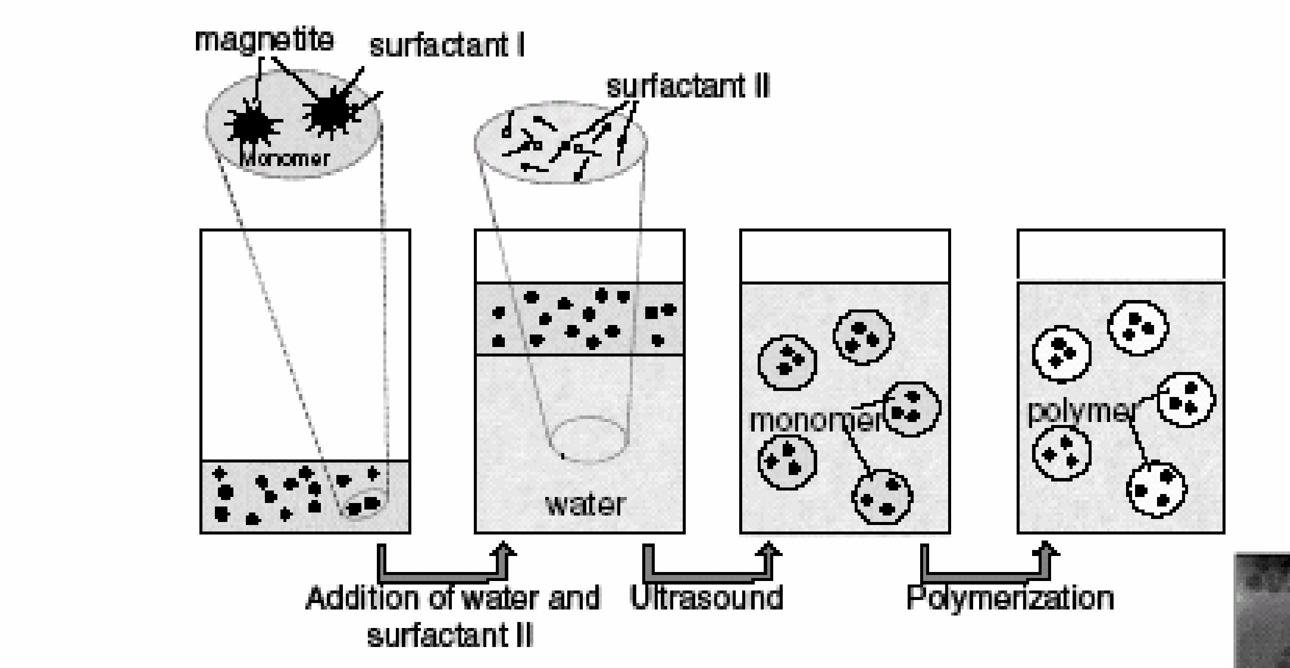
$n \sim 14$

inverse miniemulsions

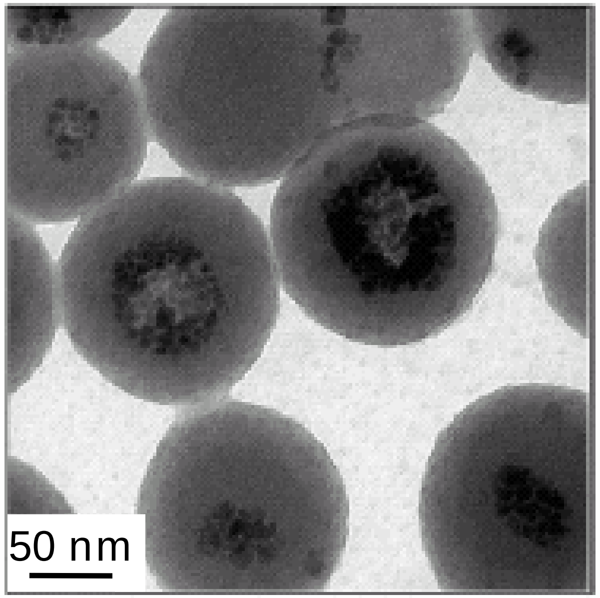
(isopar M / water or cyclohexane / water)

PhD, M. Willert; CHEMPHYSCHEM 2001, 2, 207 ± 210

magnetic composite particles



monomer: styrene

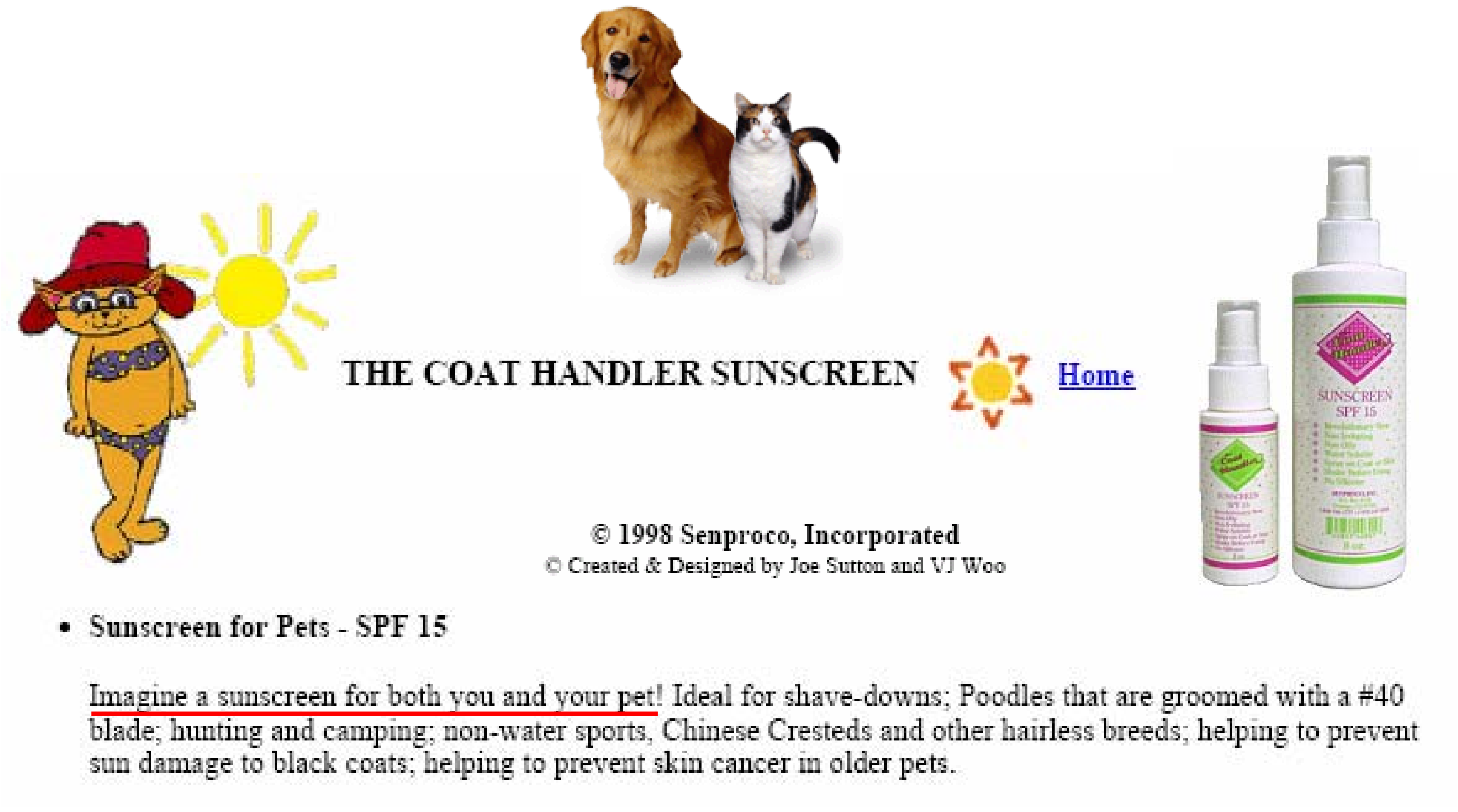


J. Phys.: Condens. Matter **15** (2003) S1345–S1361

Aim and Purpose of Emulsions:

- making money
  (its a good business)
- to contribute to our well-being
  (human vanity / conceitedness is a durable market)
- important part of life-style chemistry
  (humans use emulsion their entire life)

the ultimate emulsion:



THE COAT HANDLER SUNSCREEN

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