Self-Assembling Amphiphilic Systems

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Funktionen & Anwendungen

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It‘s the amphiphile content that matters

Low surfactant content, low energy input: emulsions
(usually micrometer size, very instable)

Low surfactant content, high energy input: nanoemulsions
(usually nanometer size, slightly kinetically stable)

High surfactant content, just thermal energy: microemulsions
(lower nanometer size, thermodynamically stable)

Non-amphiphile systems: *e.g.* Pickering emulsions

Microemulsions

thermodynamically stable, macroscopically homogeneous but nano-structured phases of at least 3 components

(A) — (B) — (C)

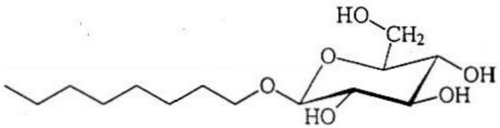
hydrophililic —hydrophobic—amphiphilic component

(A)	(B)	(C)
water glycerol monomers	*n*-alkanes triglycerides, monomers super-critical fluids	non-ionic & ionic surfactants

Binary Water – Surfactant Systems / Surfactant types

non-ionic surfactants

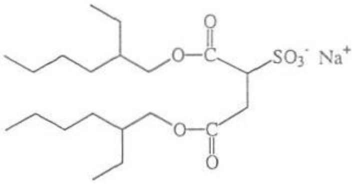
ethylene glycol monoalkyl ether (C_iE_j)



alkylpolyglucoside (C_iG_j)

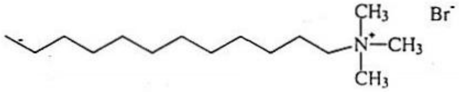
ionic surfactants

anionic



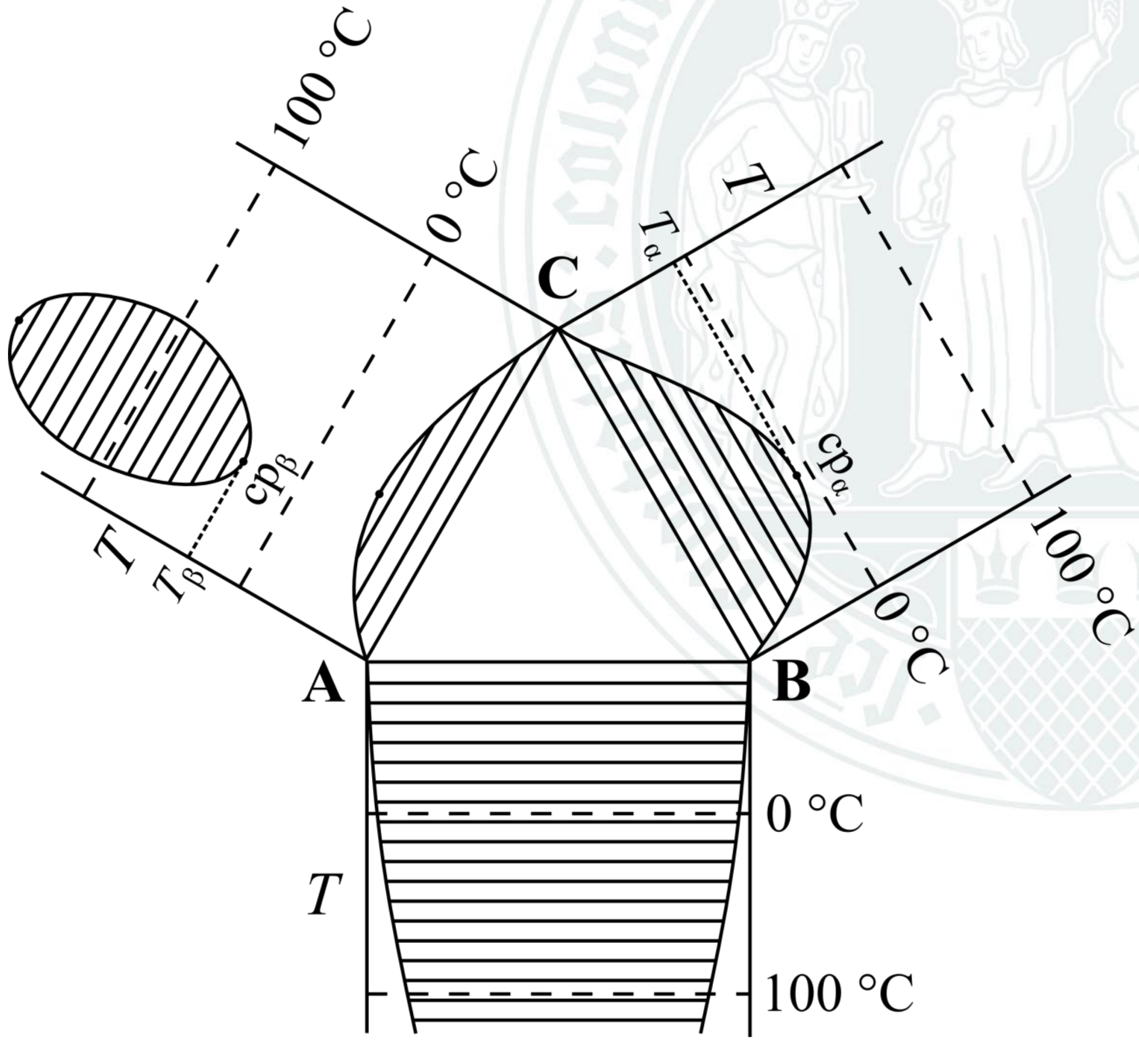
sodium bis(2-ethylhexyl) sulphosuccinate (AOT)

cationic

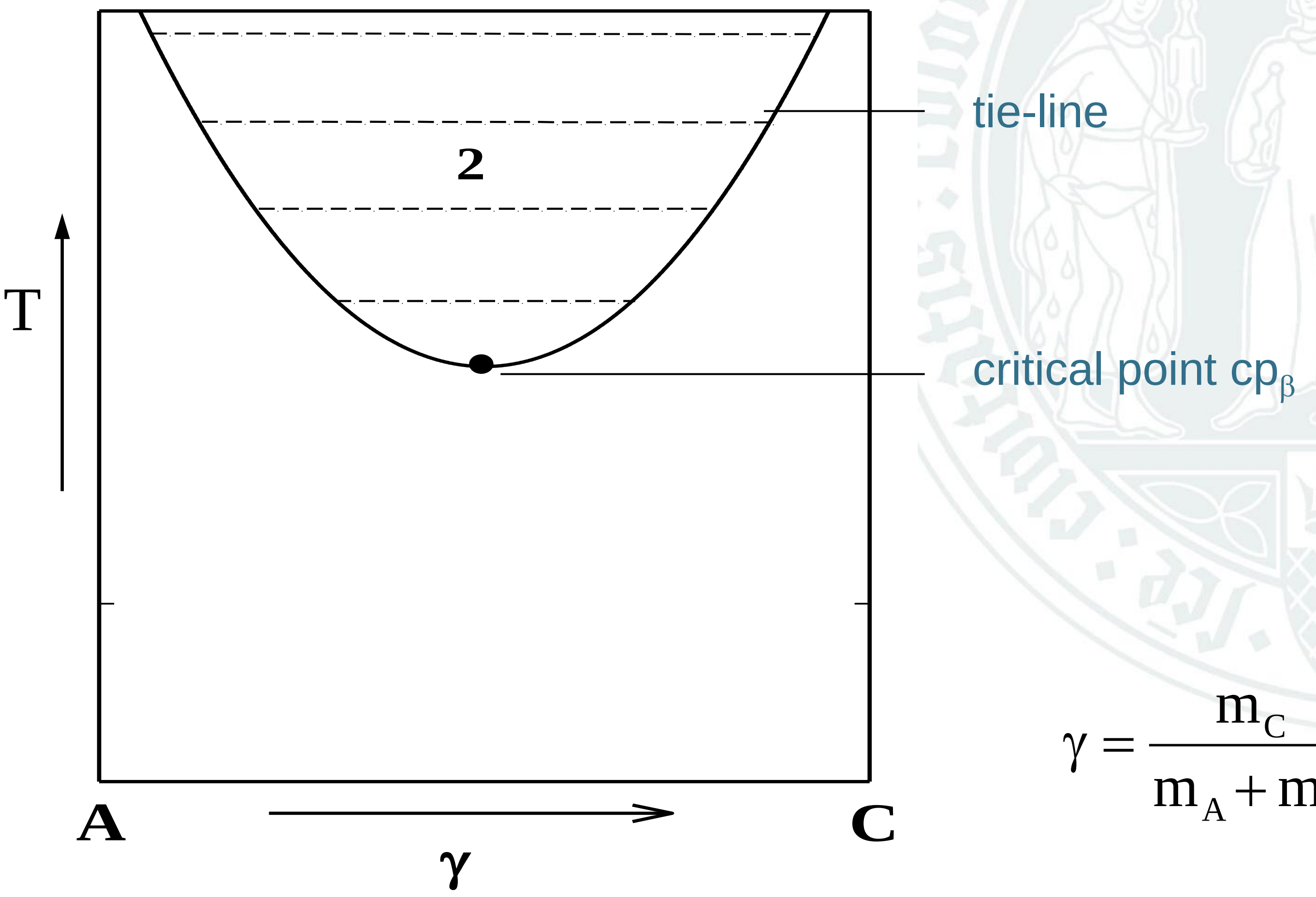


dodecyl trimethylammonium bromide (DTAB)

Binary side-systems

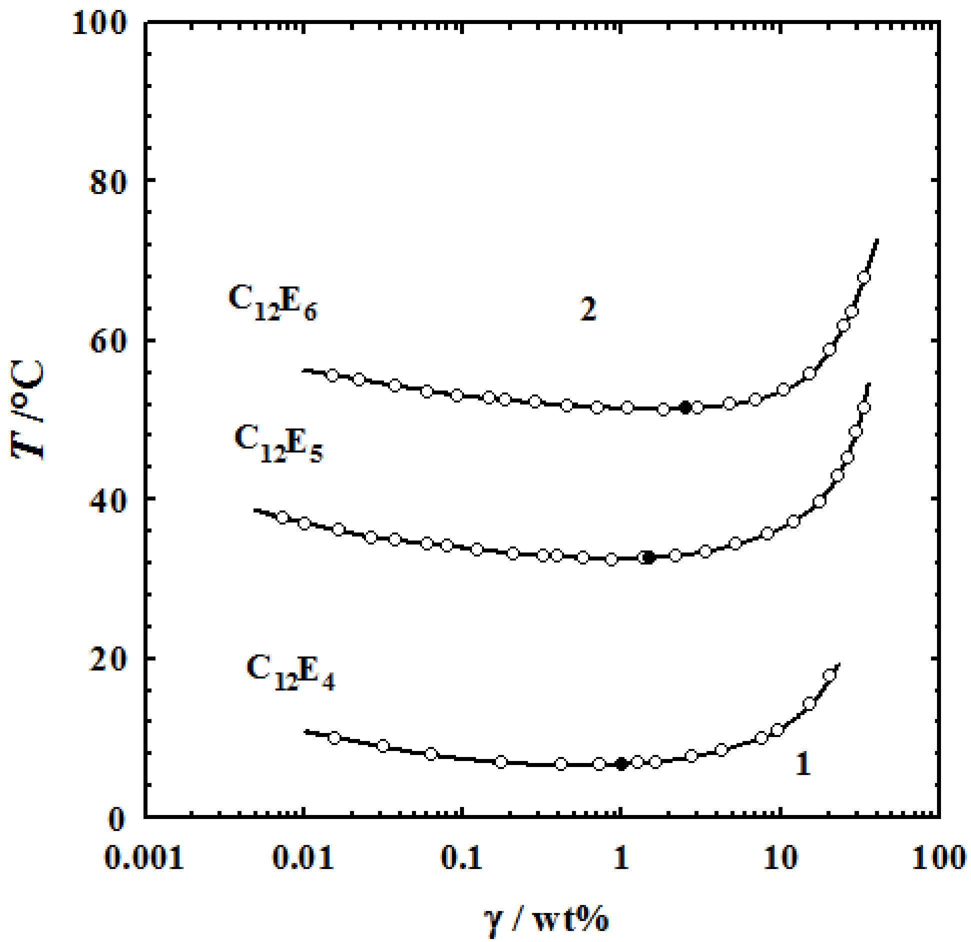


Water (A) – C_iE_j (B) Systems / upper miscibility gap

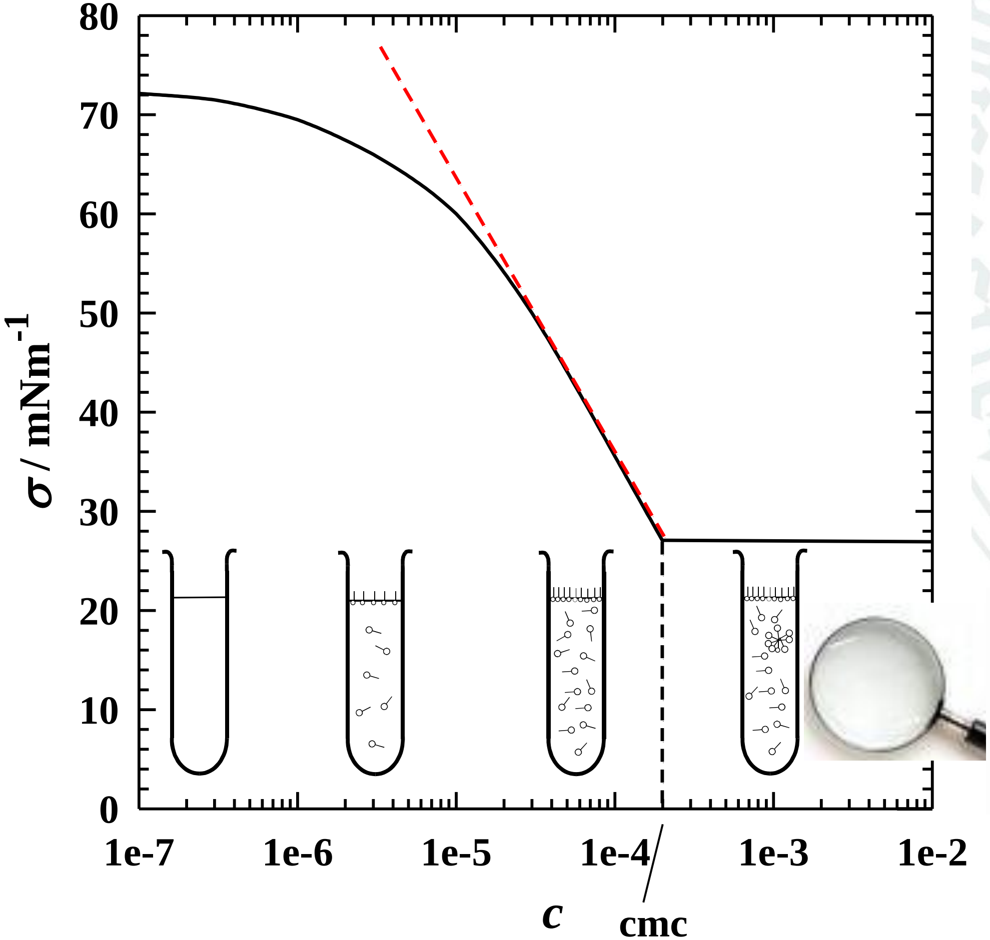


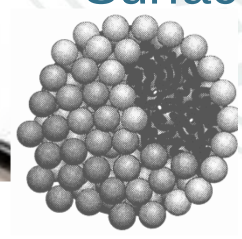
$$\gamma = \frac{m_C}{m_A + m_C}$$

Water (A) – $C_{12}E_j$ (B) / Variation of *j*



Water (A) – C_iE_j (B) / Micelle formation - cmc





Surface tension:

$$\sigma = \left.\frac{dE}{dA}\right|_{p,T}$$

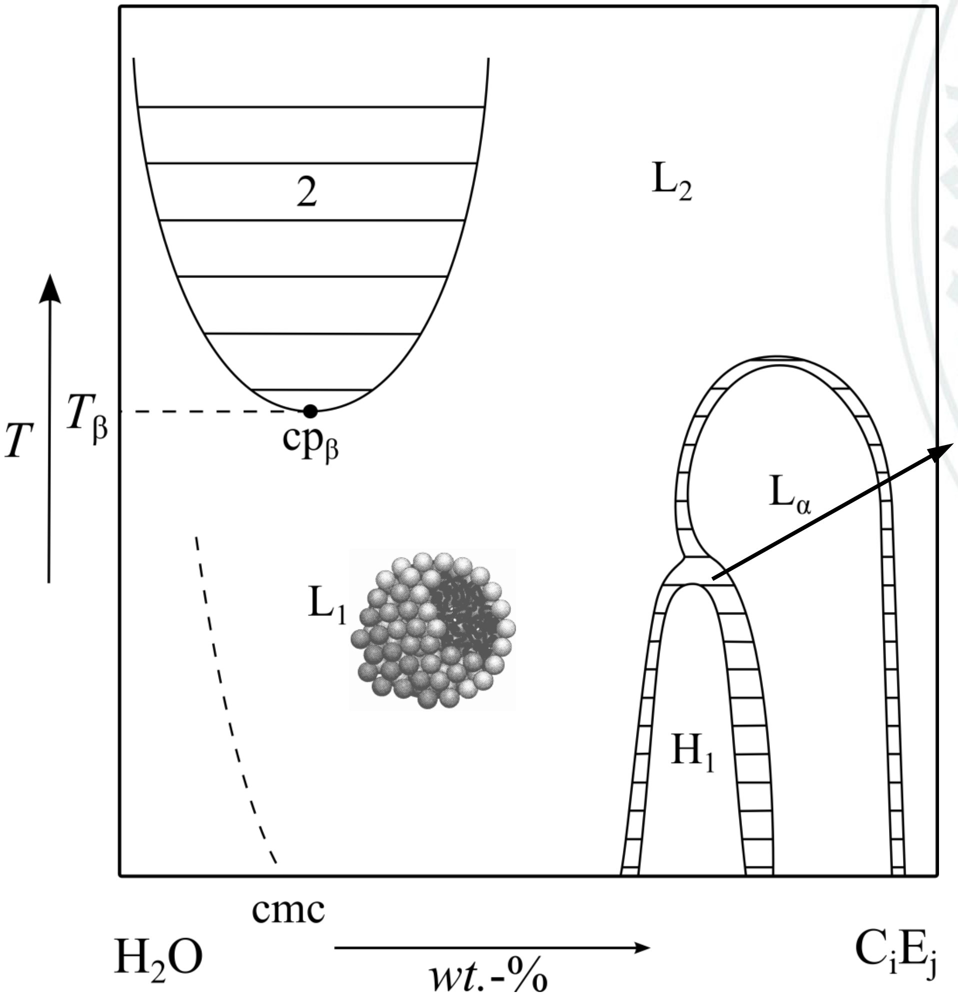
Gibbs adsorptions isotherm:

$$\Gamma = -\frac{1}{RT}\left.\frac{d\sigma}{d\ln c}\right|_{p,T}$$

Surfactant head group area:

$$a = \frac{1}{N_A \Gamma}$$

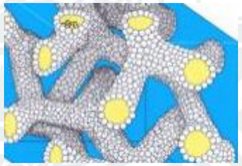
Water – C_iE_j Systems / Liquid crystalline phases



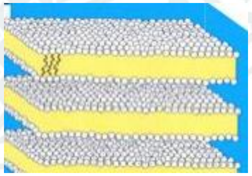
micellar cubic (I_1):

hexagonal (H_1):

bicontinuous cubic (V_1):

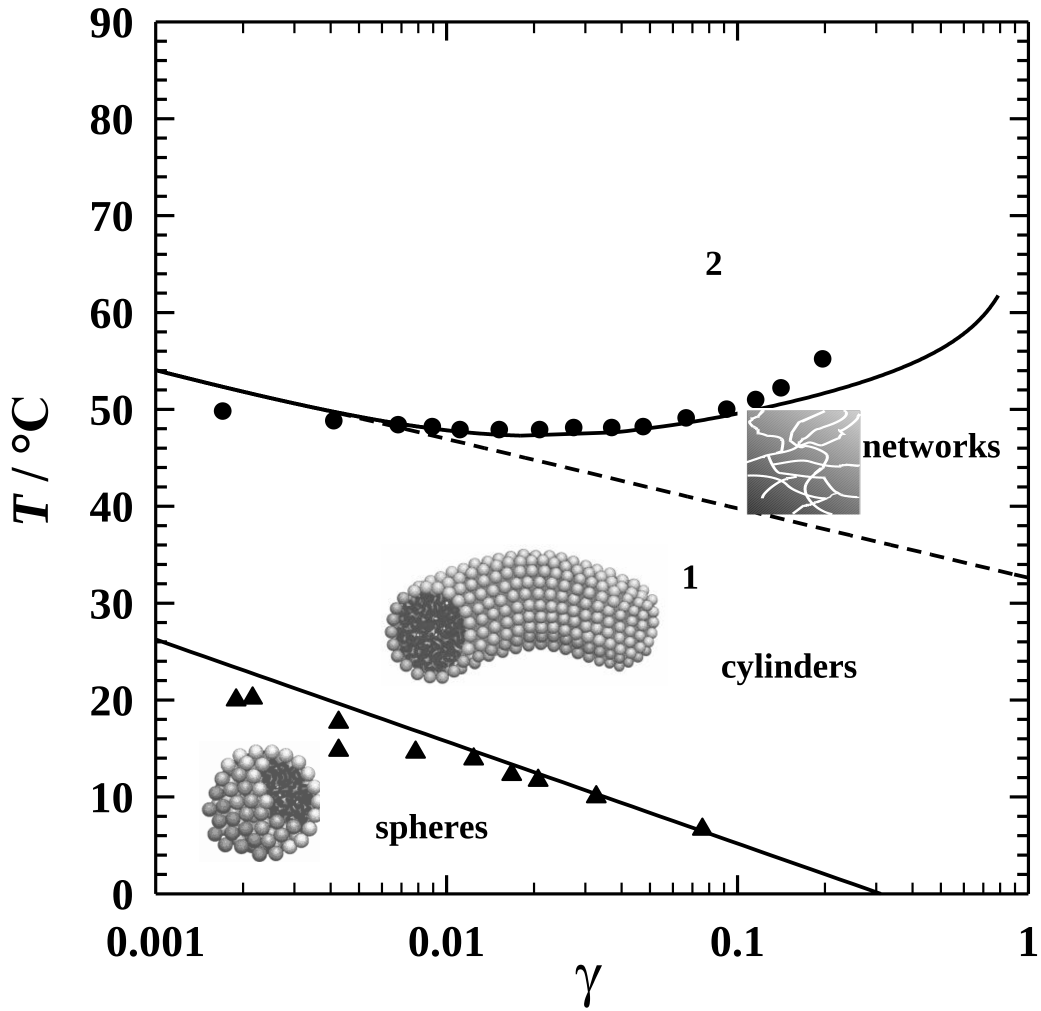


lamellar (L_α):

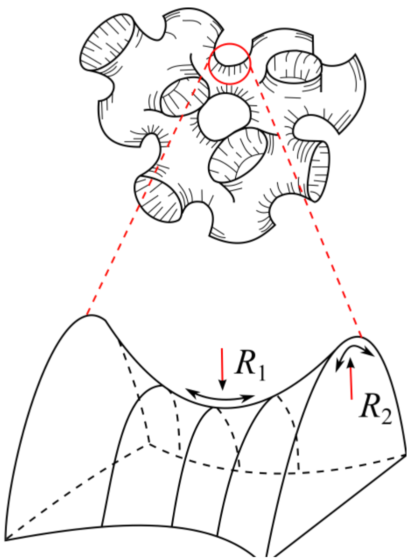


+ inverted liquid crystalline phases: V_2, H_2, I_2

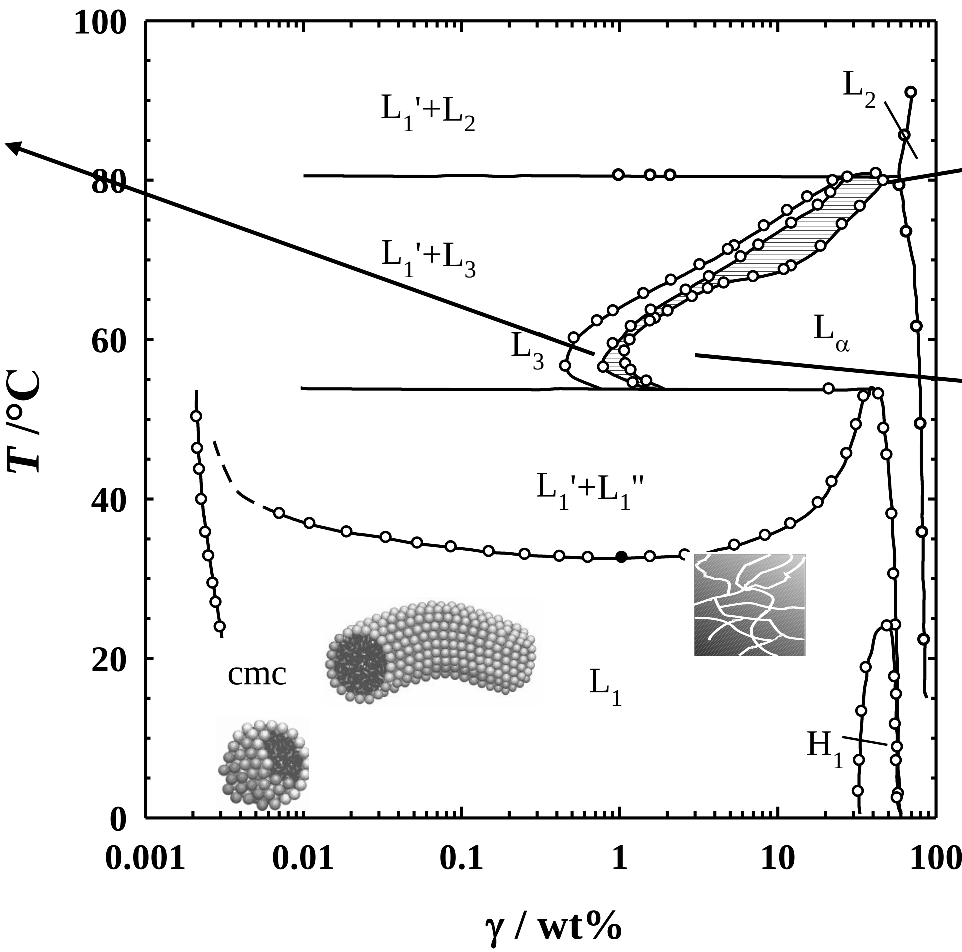
Water – $C_{12}E_6$ / more self-assembly



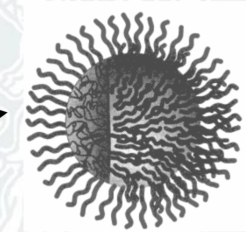
Water – $C_{12}E_5$ System / dilute self-assembled phases



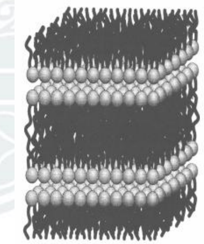
L_3: isotropic bi-layer sponge-phase



L_2: reversed micelles

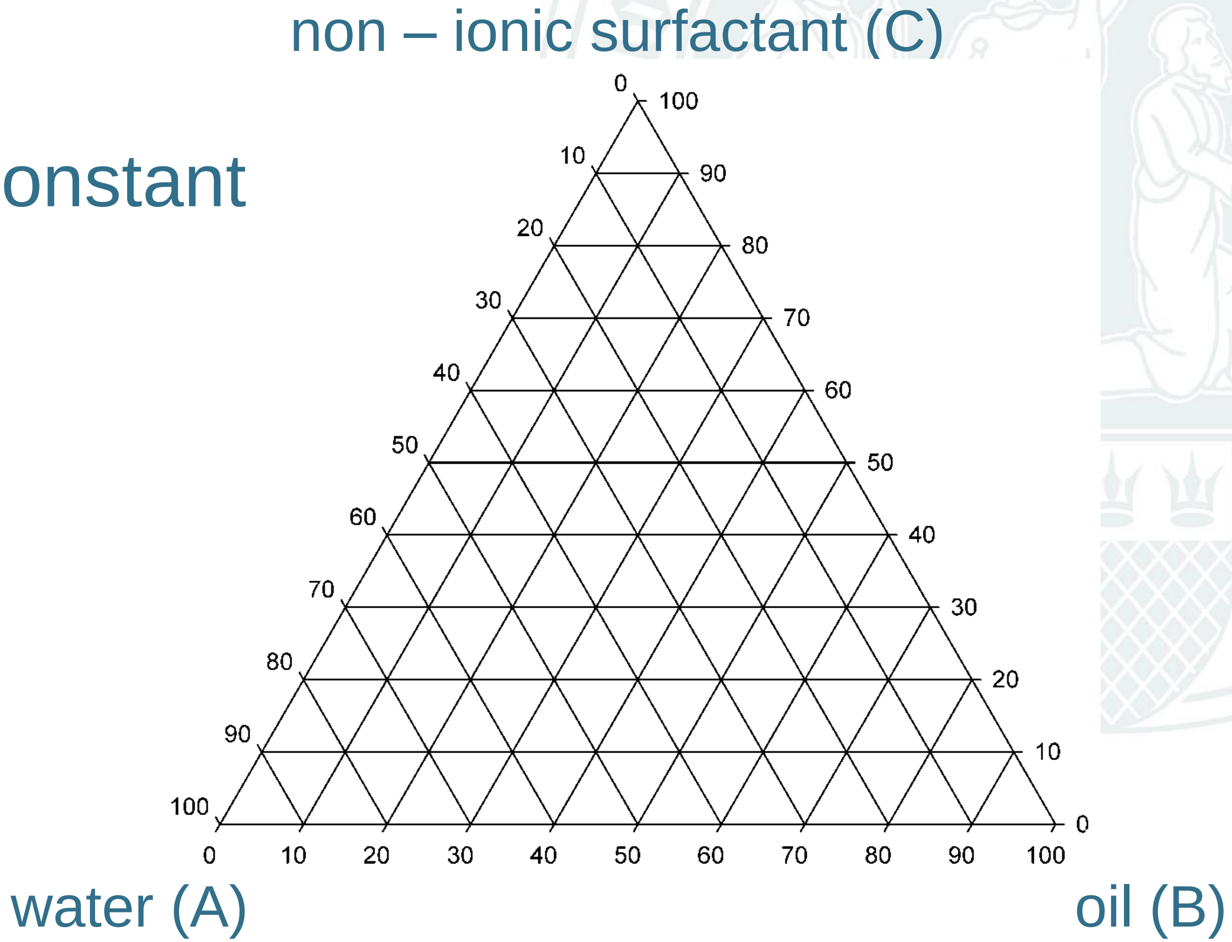


dilute lamellae



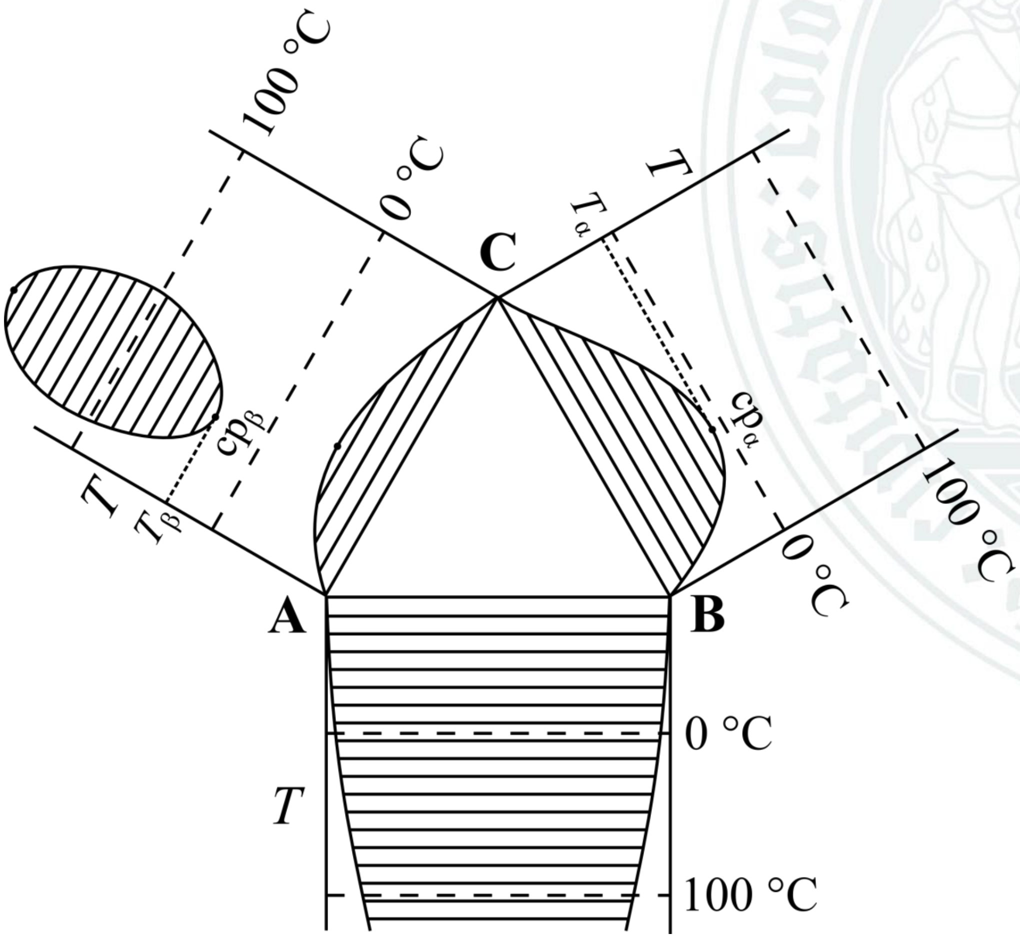
Ternary microemulsion systems / Gibbs phase triangle

T, p = constant

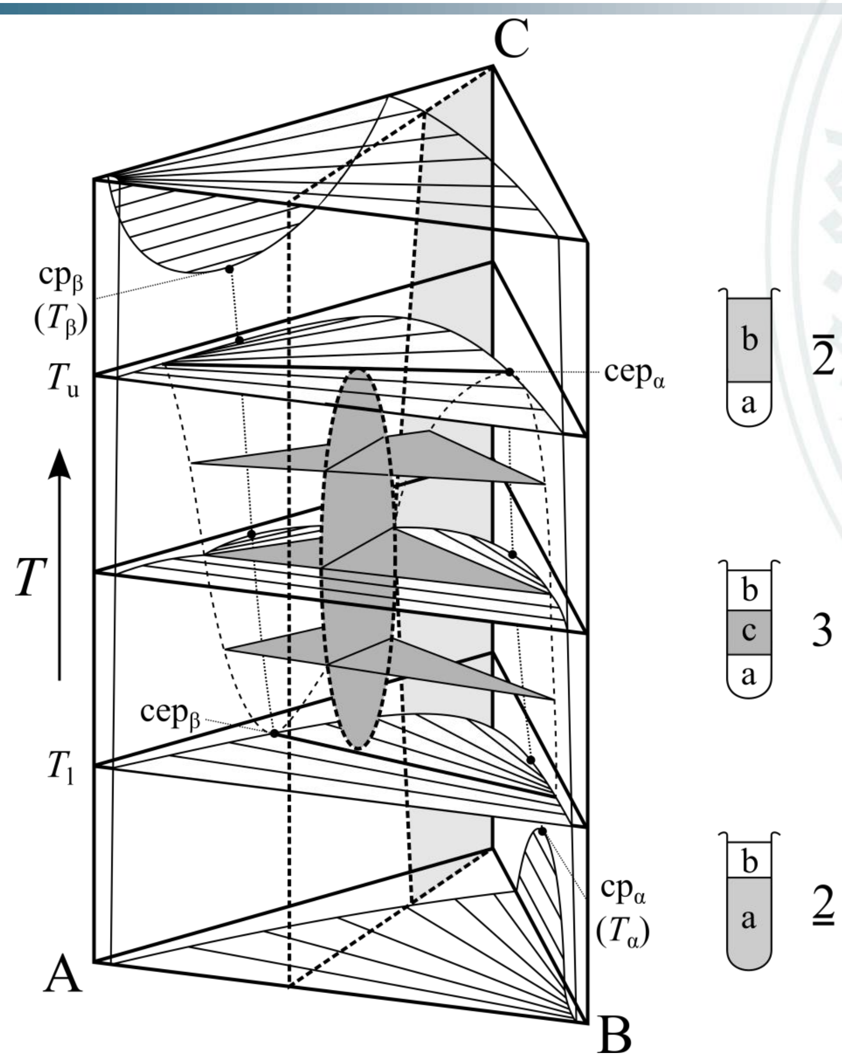


Gibbs phase prism

p = constant



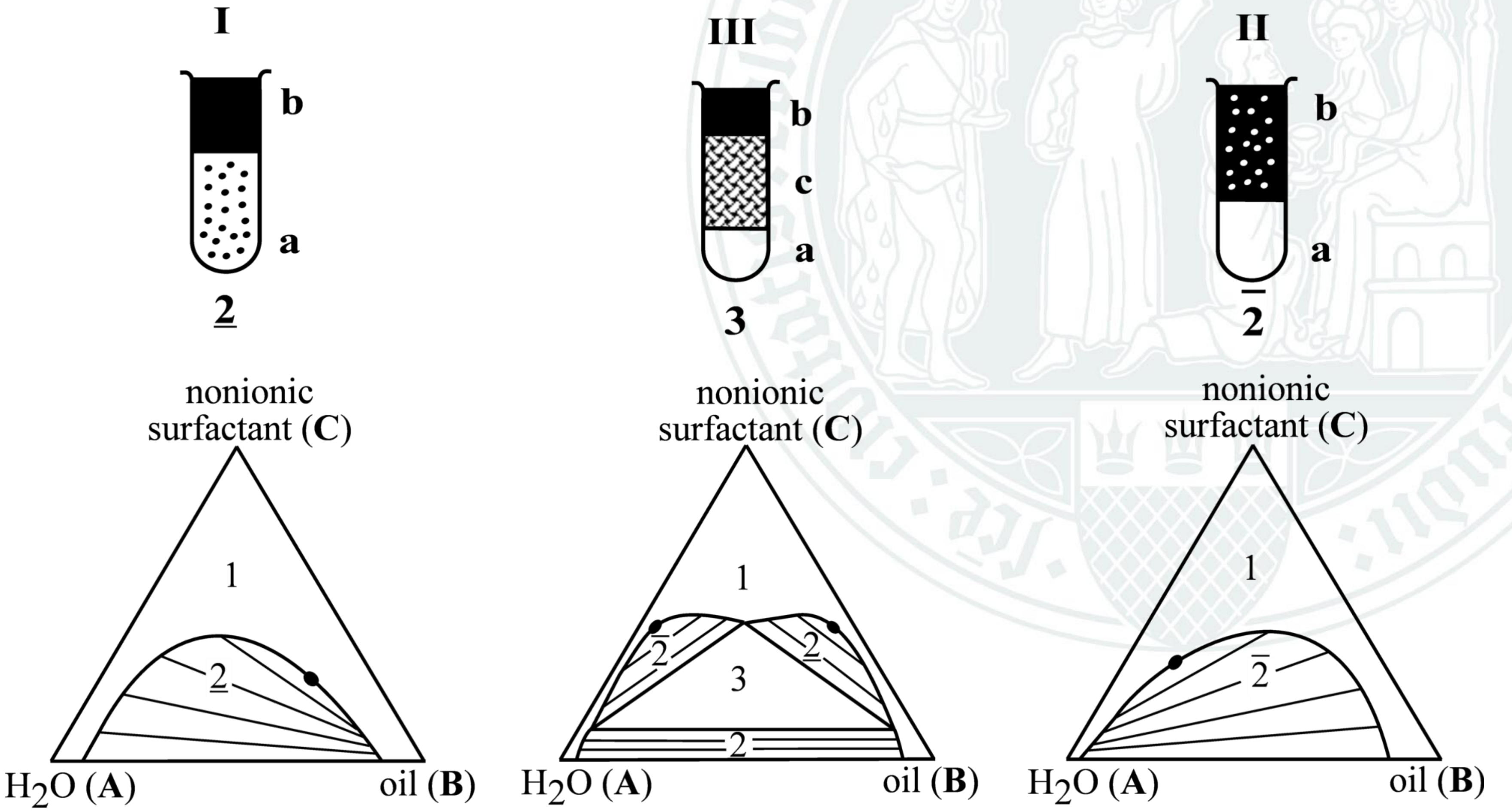
Sections through the phase prism



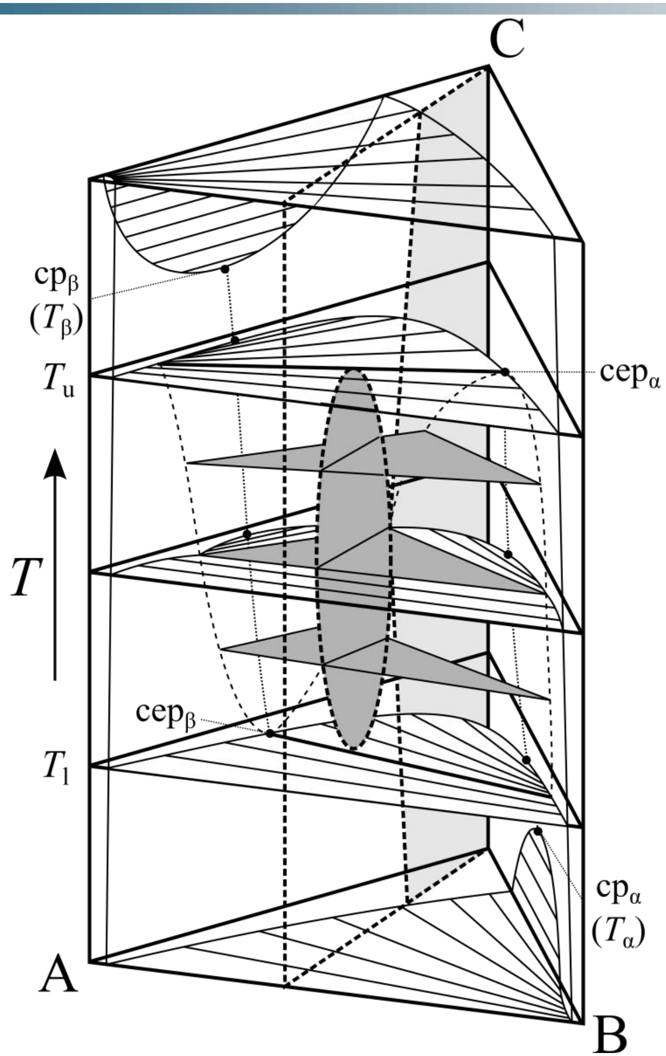
$$\alpha = \frac{m_B}{m_A + m_B}$$

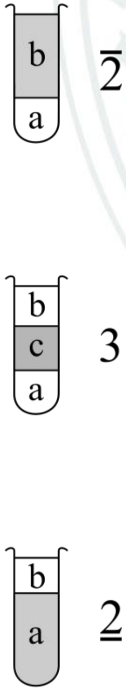
$$\gamma = \frac{m_C}{m_A + m_B + m_C}$$

Isothermal sections - phase inversion



Sections through the phase prism

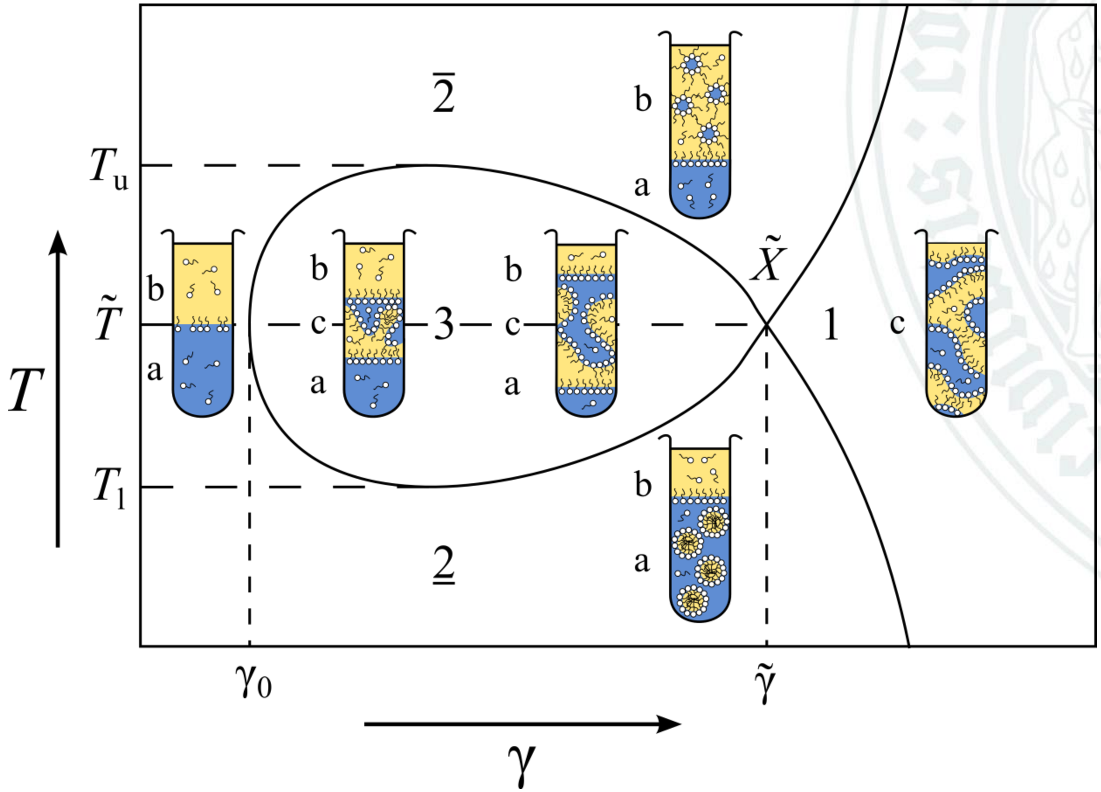




$$\alpha = \frac{m_B}{m_A + m_B}$$

$$\gamma = \frac{m_C}{m_A + m_B + m_C}$$

Isoplethal T(γ)-section I



Measure of

Efficieny: $\tilde{\gamma}$

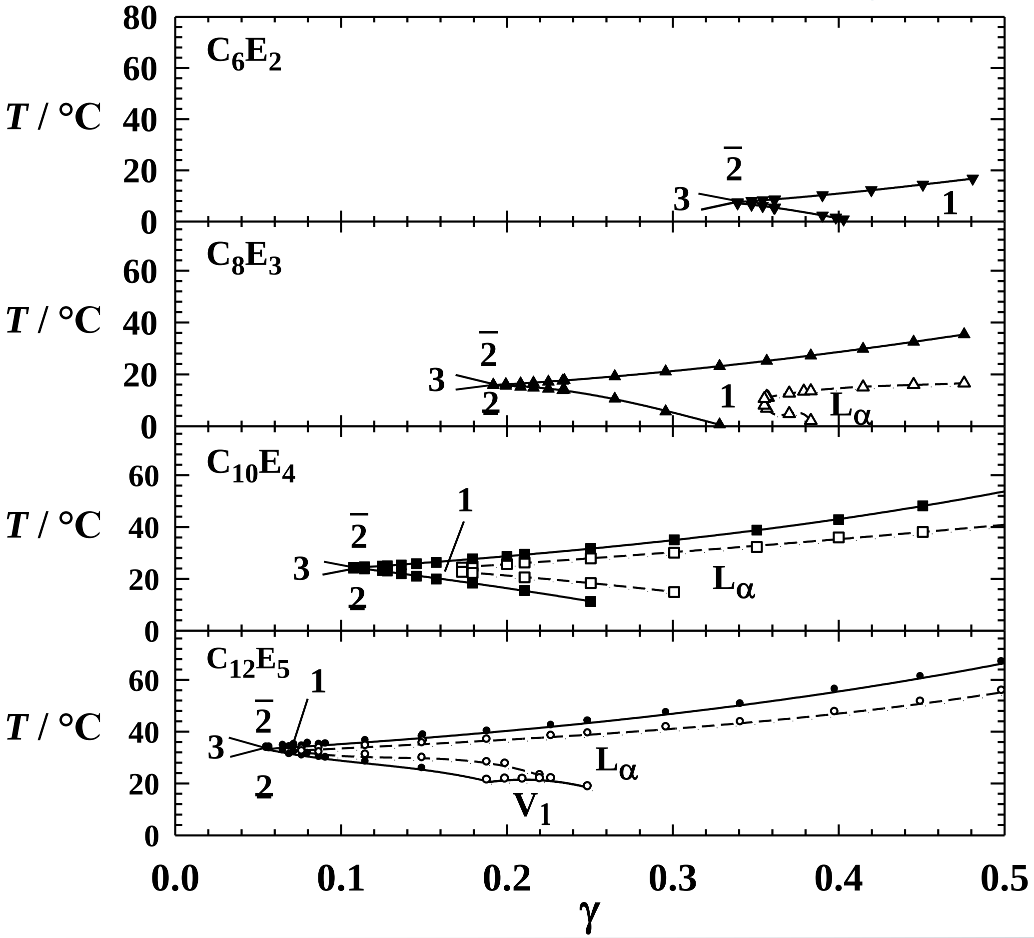
Phase inversion: $\tilde{T}$

Monomeric solubility: γ_0

$\Phi = 0.50 = \text{const.}$

Isoplethal T(γ)-section II

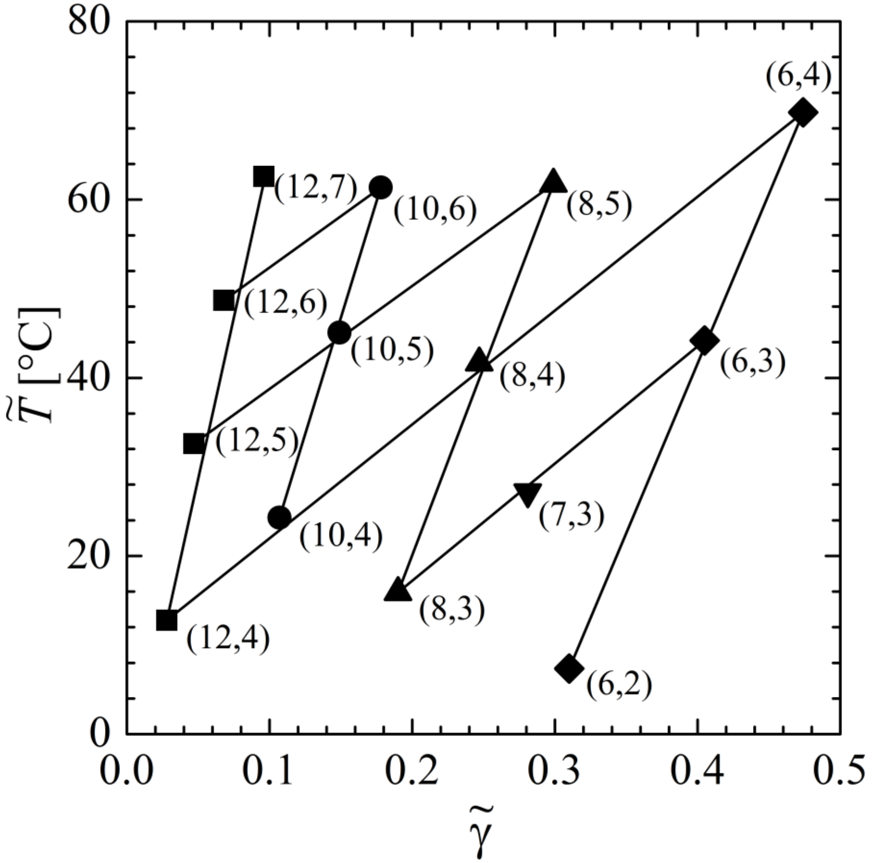
H_2O – *n*-octane – C_iE_j



Φ = 0.50 = const.

Efficiency – Phase inversion temperature

H_2O – *n*-octane – C_iE_j



$\Phi = 0.50 = \text{const.}$

Microstructure

Techniques:

direct: Transmission Electron Microscopy (TEM)

indirect: Scattering Techniques

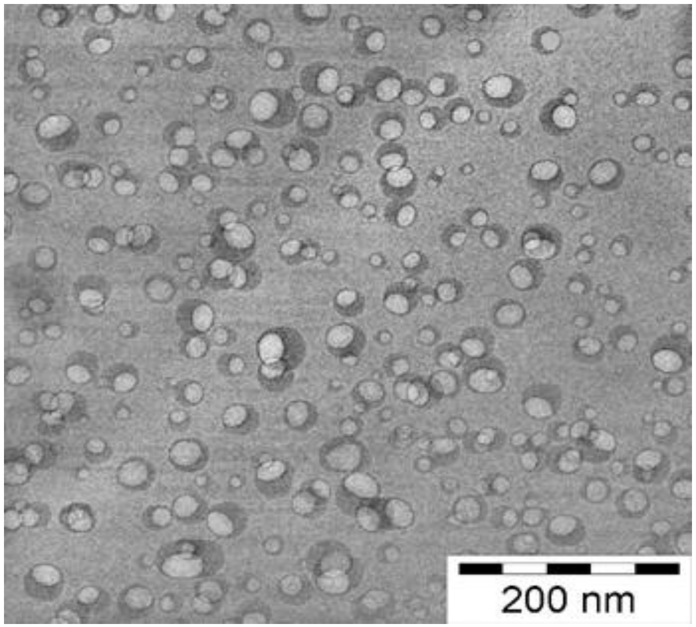
- Small Angle Neutron Scattering (SANS)
- Small Angle X-Ray Scattering
- Dynamic Light Scattering

Diffusion NMR

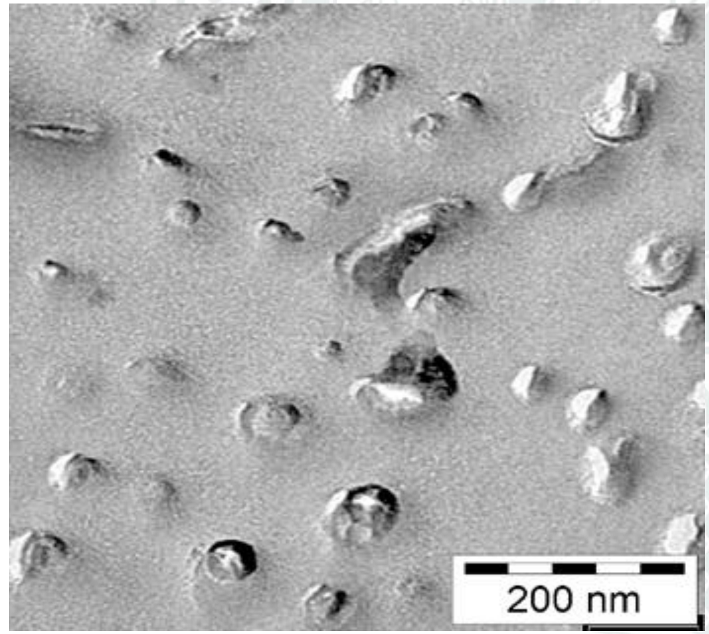
Electric Conductivity

Microstructure – TEM I

H_2O – *n*-octane - $C_{12}E_5$



FFDI



FFEM

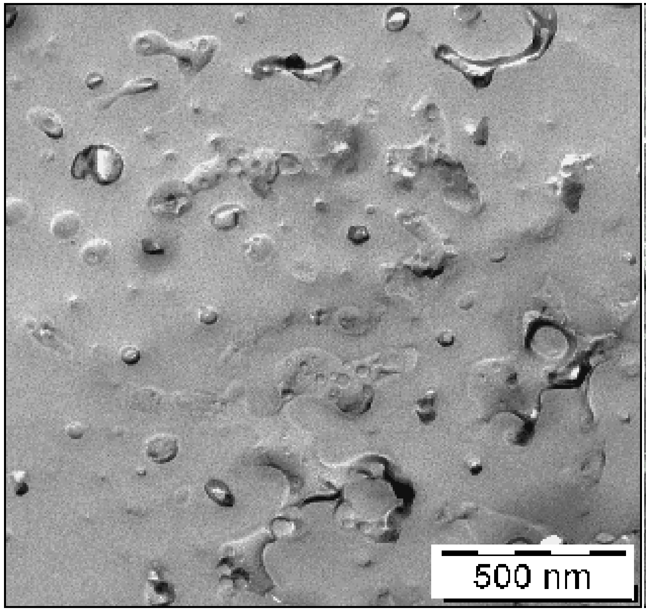
o/w droplets

L. Belkoura, C. Stubenrauch, and R. Strey, Langmuir (2004)

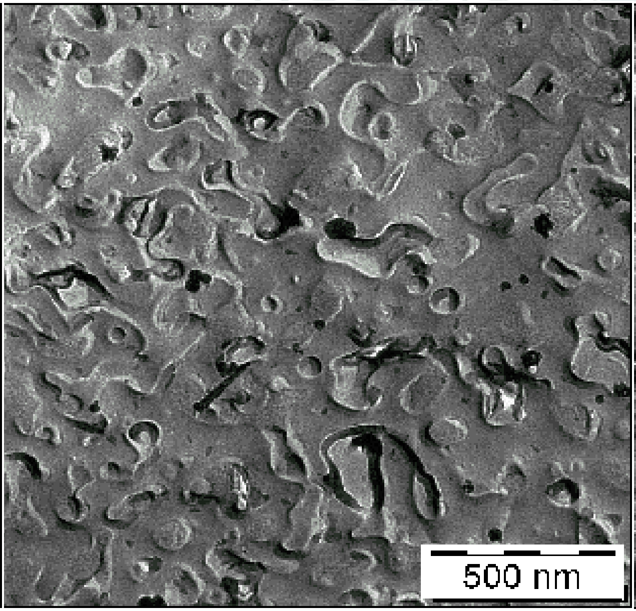
Microstructure – TEM II

From networks to bicontinuous microemulsions

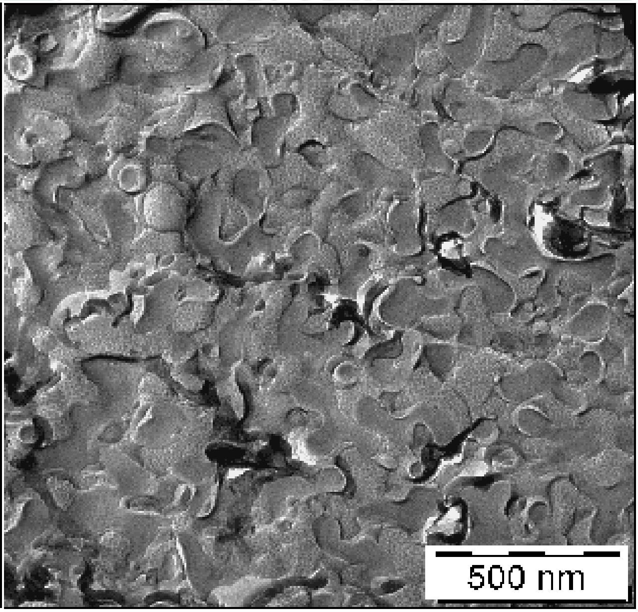
H_2O – *n*-octane - $C_{12}E_5$



T=30.5°C, γ=0.01
ϕ=0.1



T=31.3°C, γ=0.04
ϕ=0.3

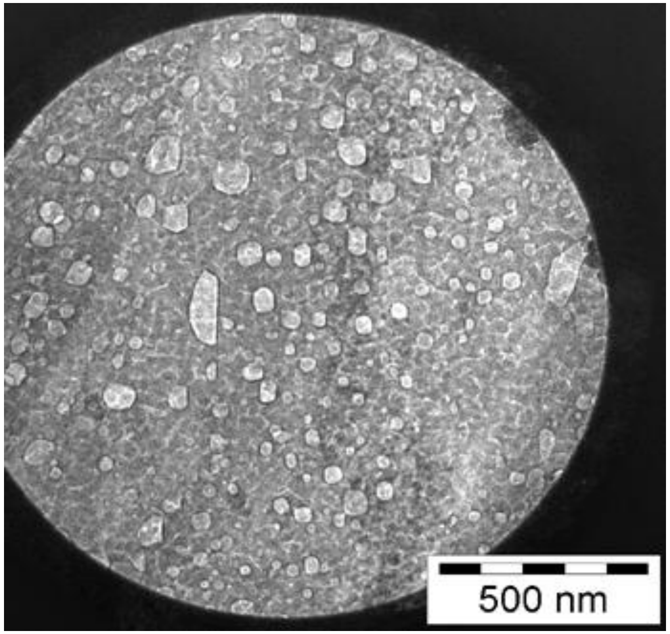


T=32.2°C, γ=0.06
ϕ=0.5

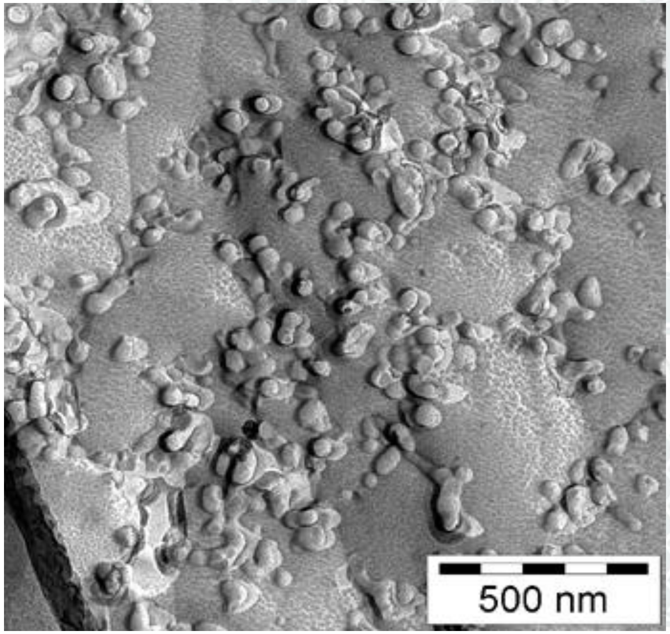
L. Belkoura, private communication

Microstructure – TEM III

H_2O – *n*-octane - $C_{12}E_5$



FFDI

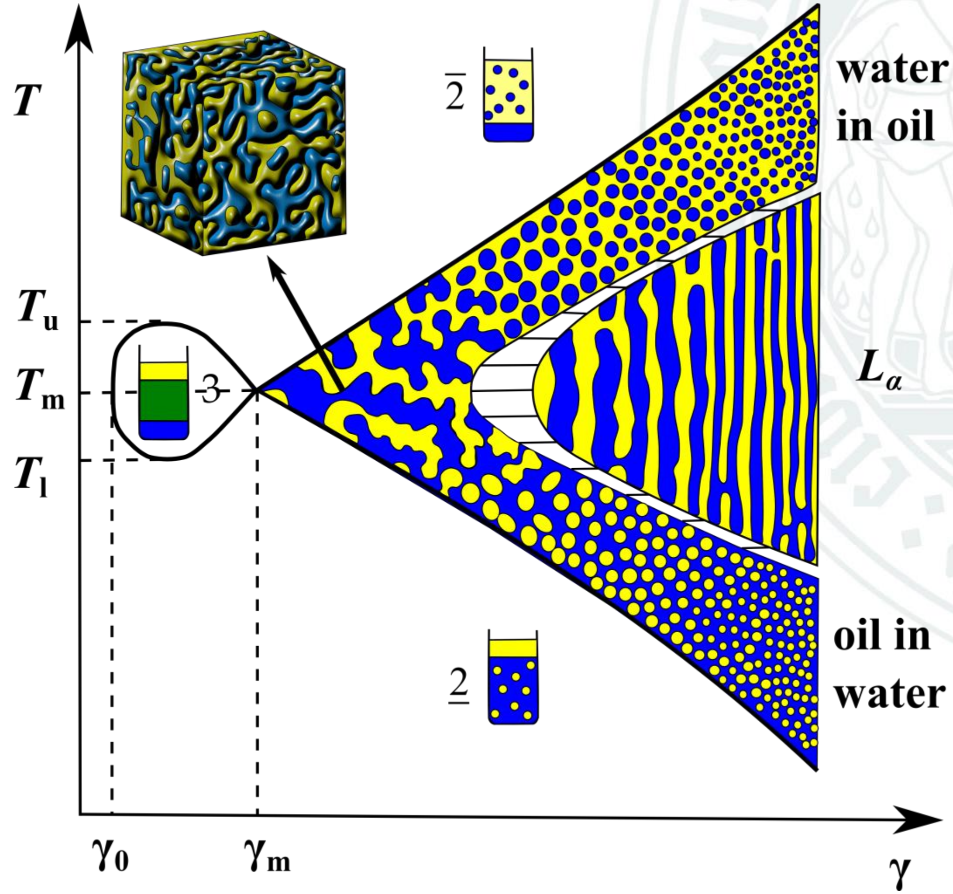


FFEM

w/o droplets

L. Belkoura, C. Stubenrauch, and R. Strey, Langmuir (2004)

Microstructure – Overwiew

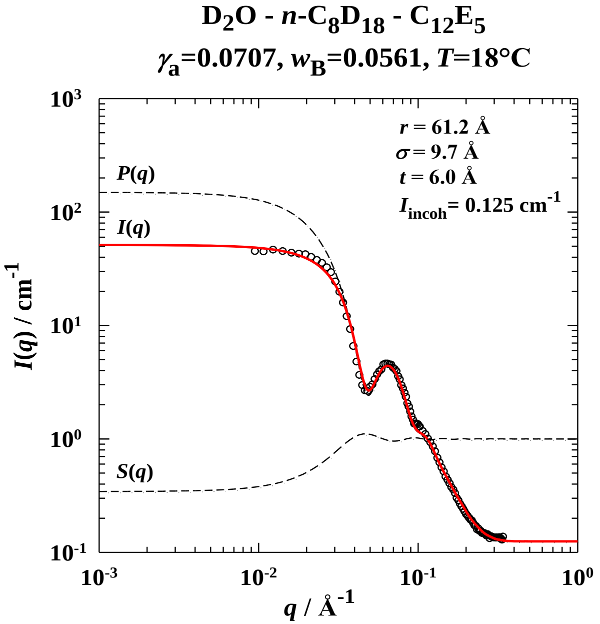


$\Phi = 0.50 = \text{const.}$

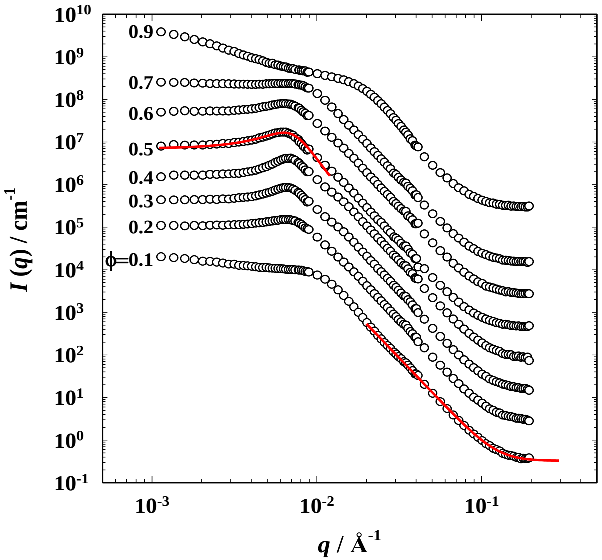
R. Strey, Colloid Polym. Sci., **272** (8), 1005 (1994).

Microstructure – Length Scales I

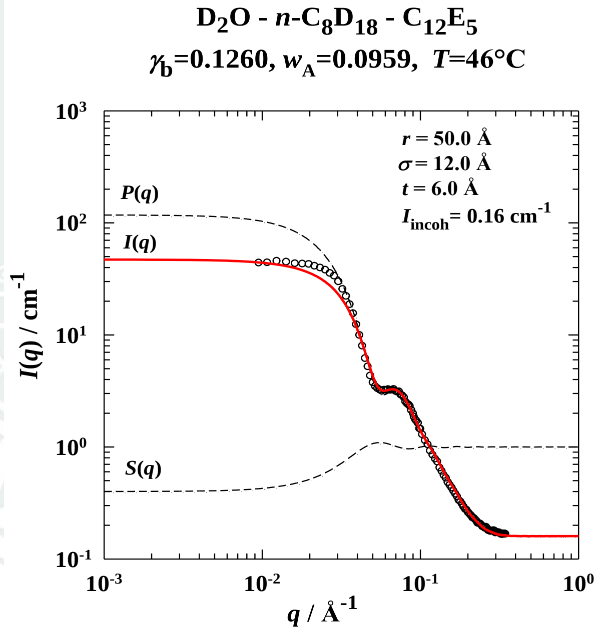
Small angle neutron scattering (SANS)



o/w



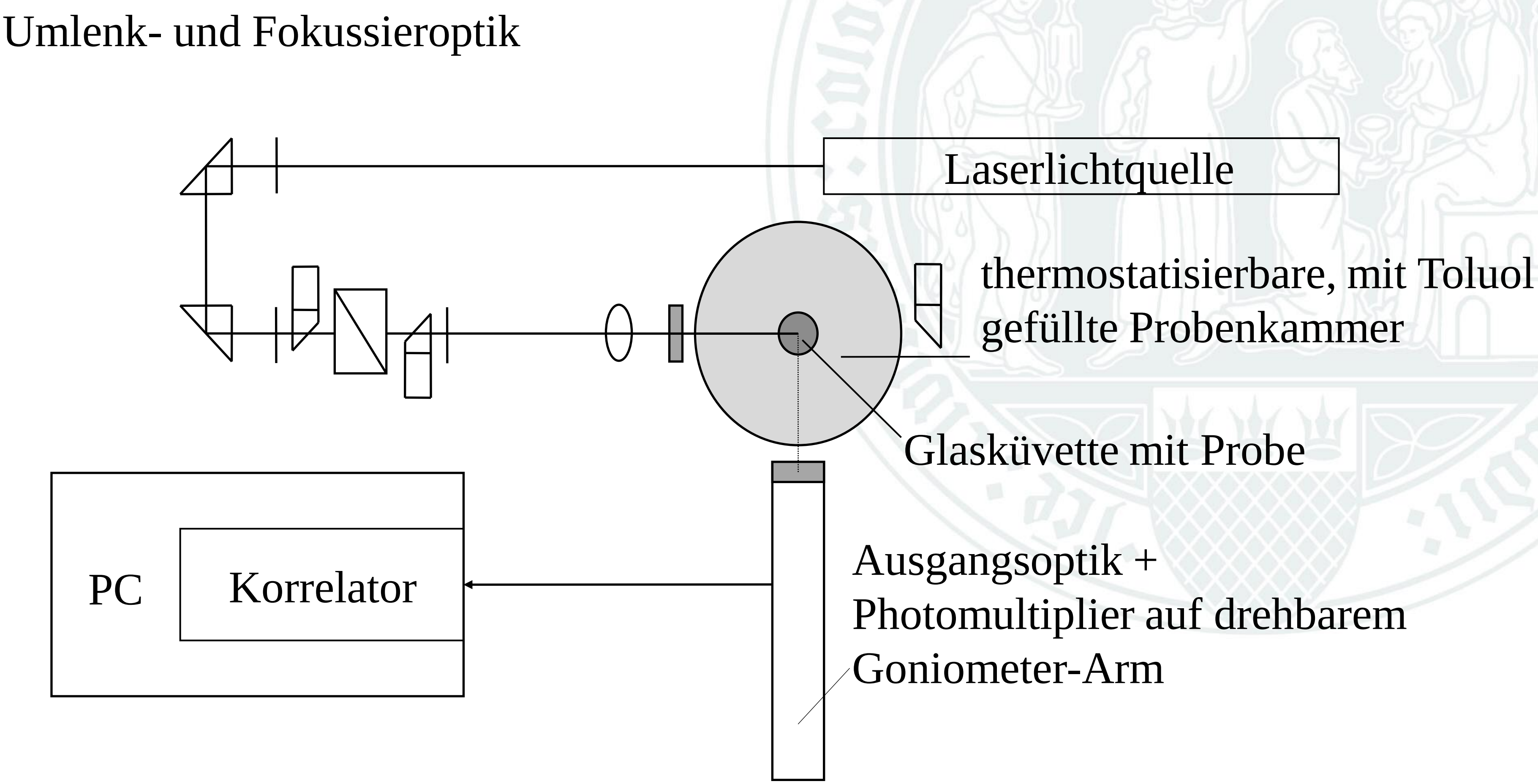
bicontinuous



w/o

M. Gradzielski, D. Langevin, L. Magid, and R. Strey, J. Phys. Chem. 99, 13232 (1995)
M. Teubner and R. Strey, J. Chem. Phys. 87, 3195 (1987)

Lichtstreuung set-up



Lichtstreuung set-up

Lichtquelle: - Laser (P > 70 mW) Vorteile: Strahlen parallel, polarisiert, monochrom, kohärent, Leistung konstant
- Hg-Dampflampe (früher)

Umlenk- und Fokussieroptik: nicht zwingend erforderlich

Probe:
- in zylindrischer Glasküvette (D=10-25 mm)
- Küvette ist in einem Brechungsindex "gematchten" Bad $n_{Toluol} = n_{Glas}$: Vermeidung von Oberflächenreflexion

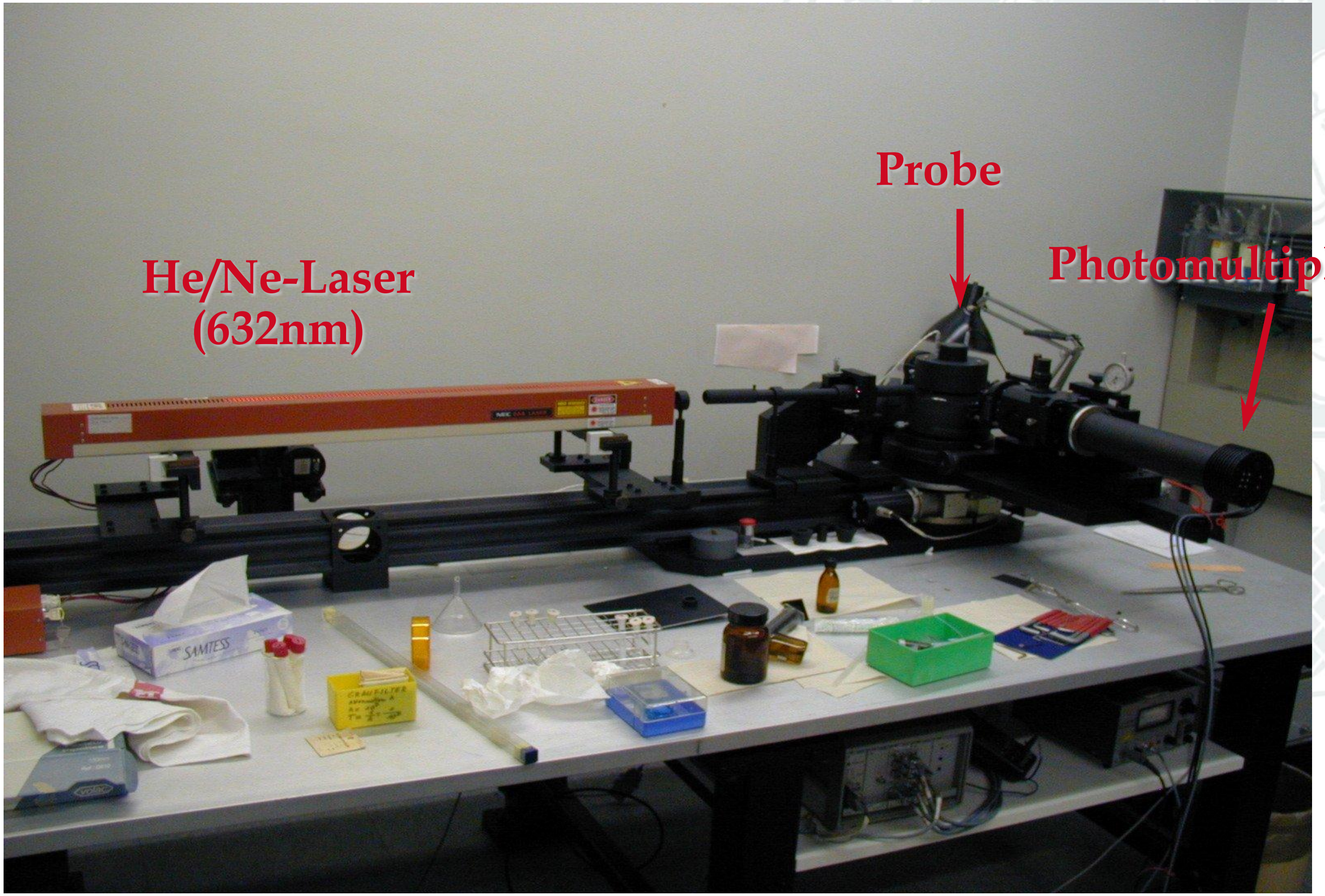
Detektion:
- Photonenmultiplier (IStrom = I Lichtintensität) Spitzenbelastung
- Photodiode

Korrelator: - Für dynamische Lichtstreuung (DLS)

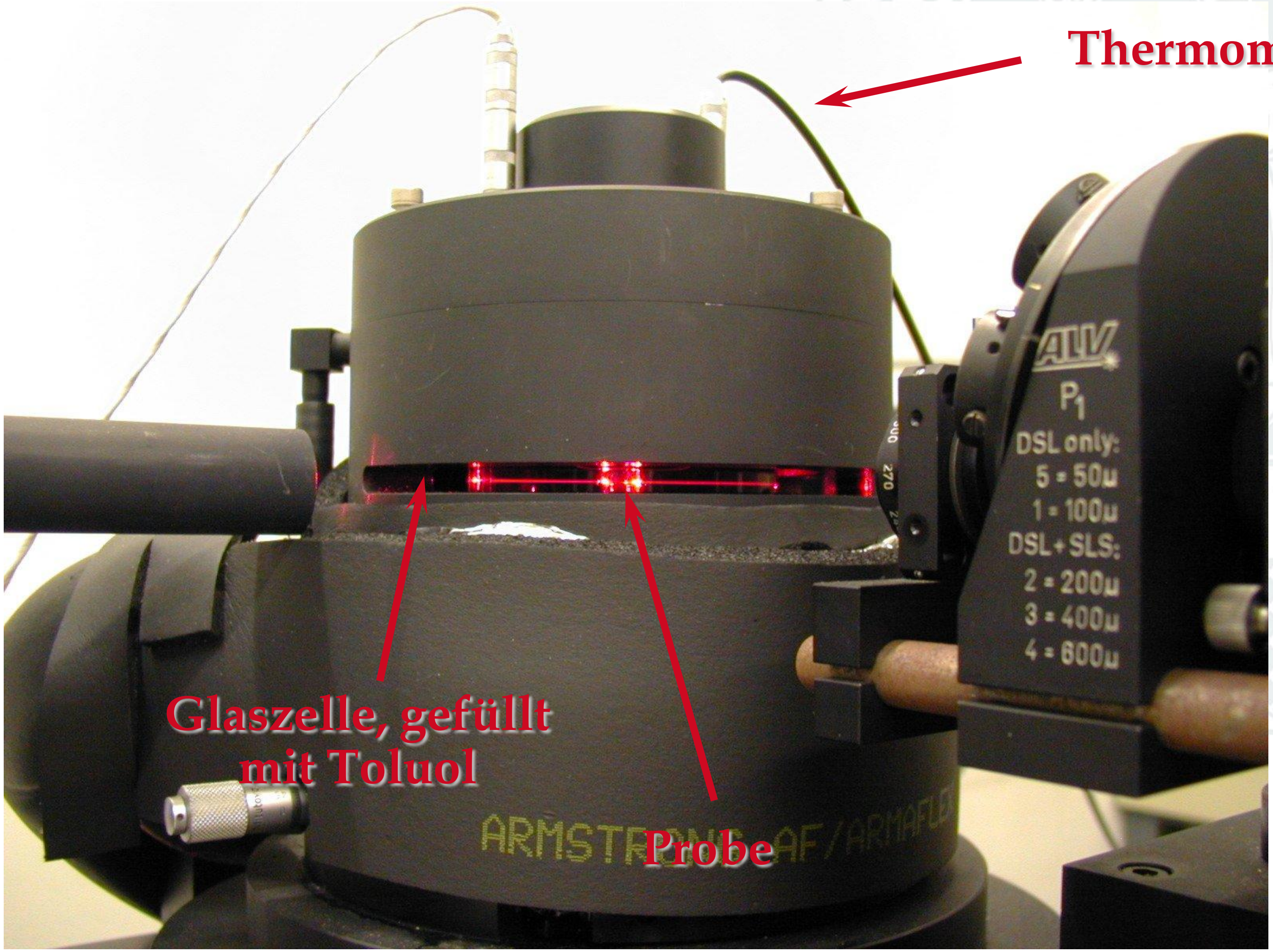
Goniometer: - Küvette und einfallender Strahl genau im Drehmittelpunkt
↓
konstanter Abstand Probe - Detektor *r*, keine Strahlenversetzungen

Ausgangsoptik: nur paralleles Licht wird detektiert

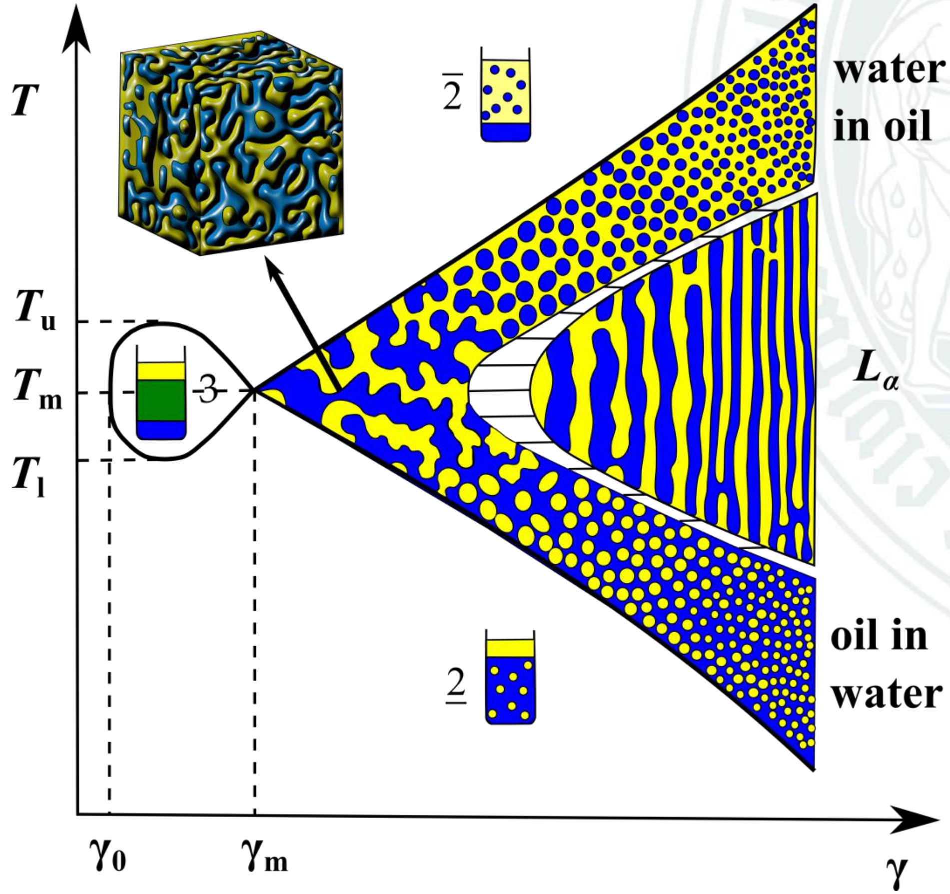
Lichtstreuung set-up



Proben-Umgebung



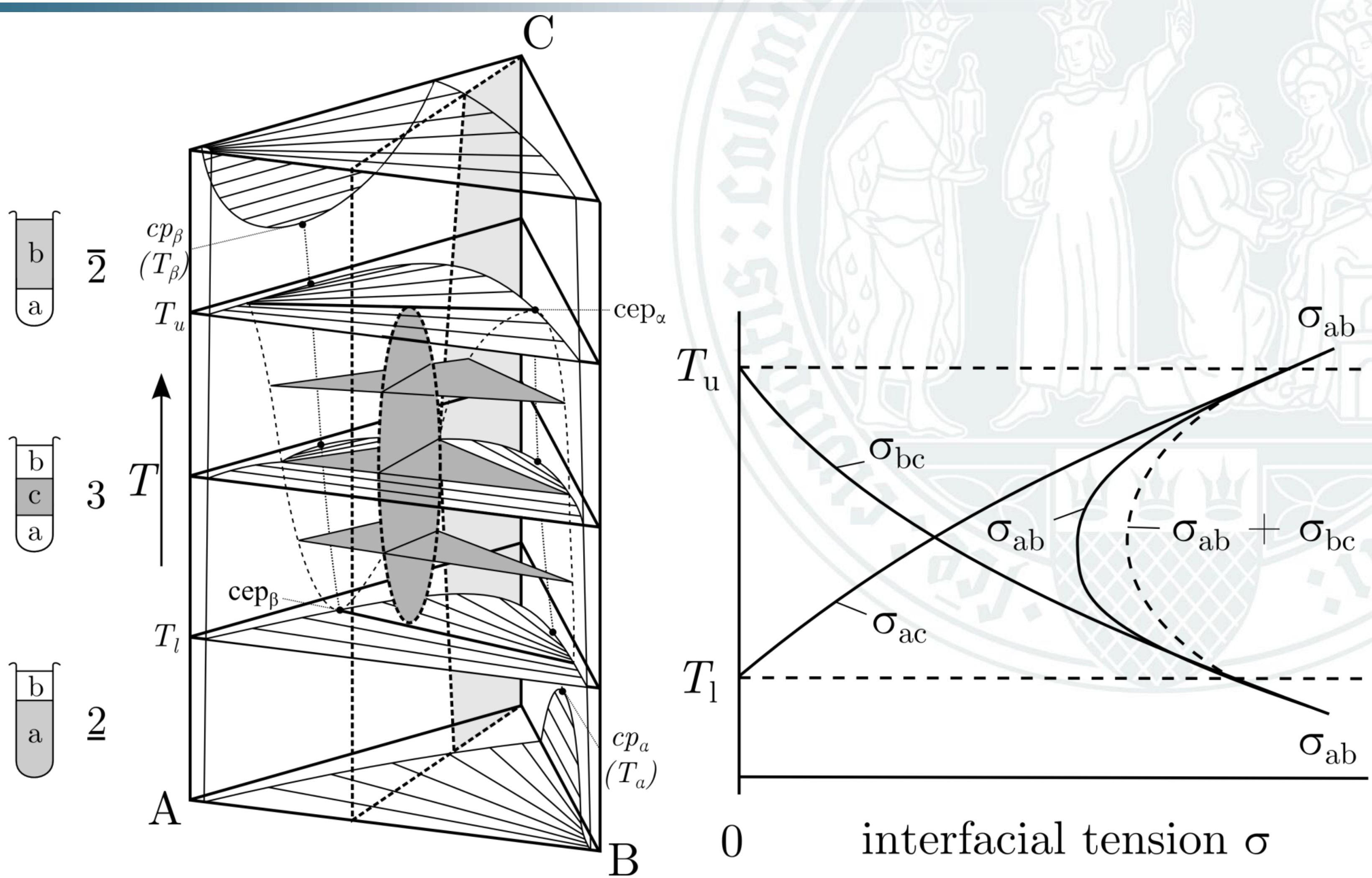
Microstructure – Overwiew



$\Phi = 0.50 = \text{const.}$

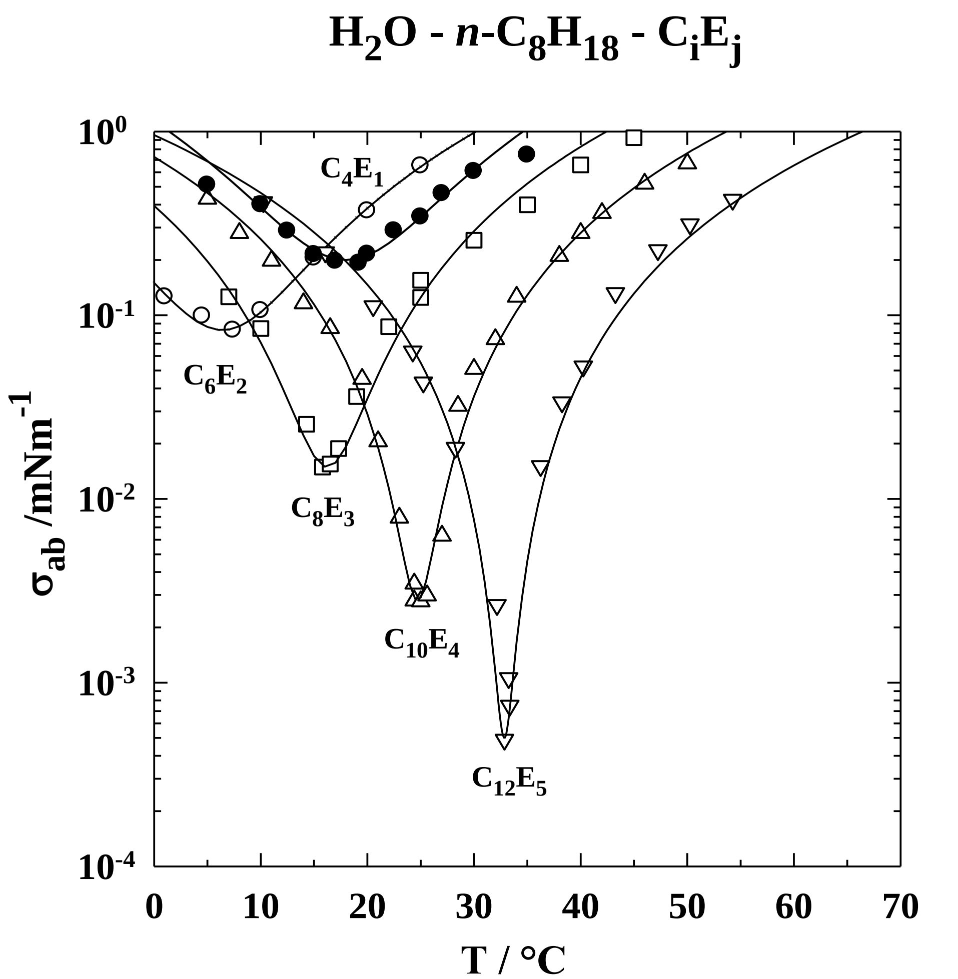
R. Strey, Colloid Polym. Sci., **272** (8), 1005 (1994).

Phase behaviour – Interfacial tensions



Microemulsions, T. Sottmann and R. Strey in Fundamentals of Interface and Colloid Science, Volume V, edited by J. Lyklema, Academic Press (2005)

Variation of oil/water-interfacial tension



T. Sottmann and R. Strey, J. Chem. Phys. 106, 8606 (1997)

Theoretical background

Thermodynamic stability: $k_B T \approx \sigma \xi^2$

Structure size approximation: $\xi \approx a \cdot \frac{\phi(1-\phi)}{S/V}$

Specific internal interface: $S/V = \phi_{c,i} \cdot \frac{a_c}{v_c}$

Droplet radius approximation: $R = 3 \cdot \frac{v_c}{a_c} \cdot \frac{\phi_A}{\phi_{C,i}} = 3 \cdot l_c \cdot \frac{\phi_A}{\phi_{C,i}}$

T. Sottmann and R. Strey, J. Chem. Phys. 106, 8606 (1997)