Microemulsions: Basic Theory and Structure Kinetics

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MN-C-WP/c

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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

water
glycerol
monomers

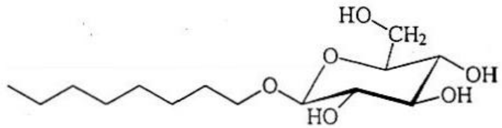
n-alkanes
triglycerides, monomers
super-critical fluids

non-ionic
& ionic
surfactants

Binary Water – Surfactant Systems / Surfactant types

non-ionic surfactants

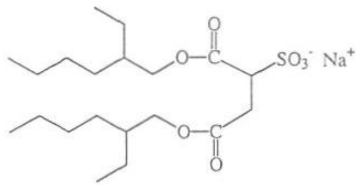
ethylene glycol monoalkyl ether (C_iE_j)



alkylpolyglucoside (C_iG_j)

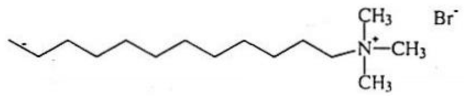
ionic surfactants

anionic



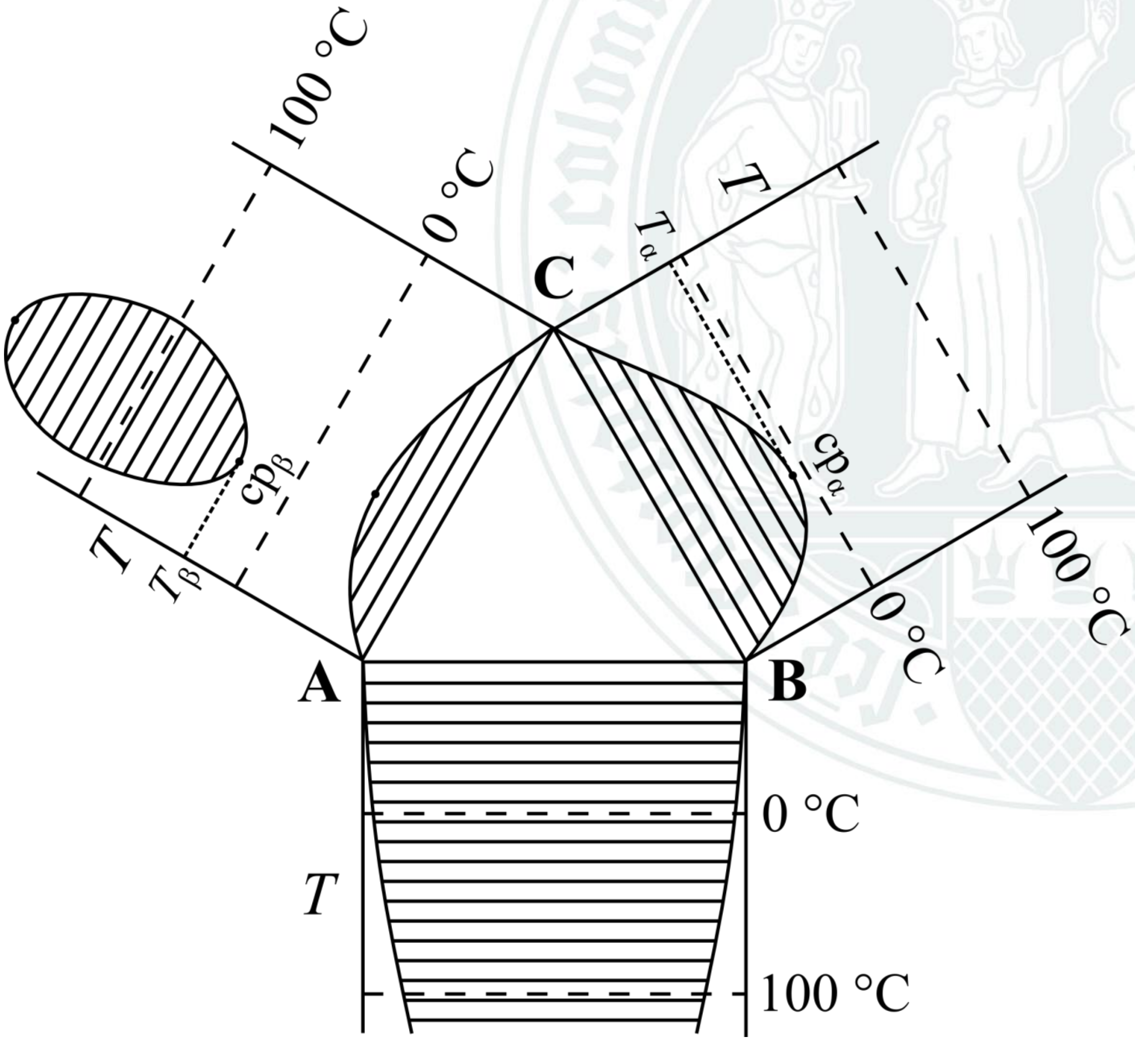
sodium bis(2-ethylhexyl) sulphosuccinate (AOT)

cationic

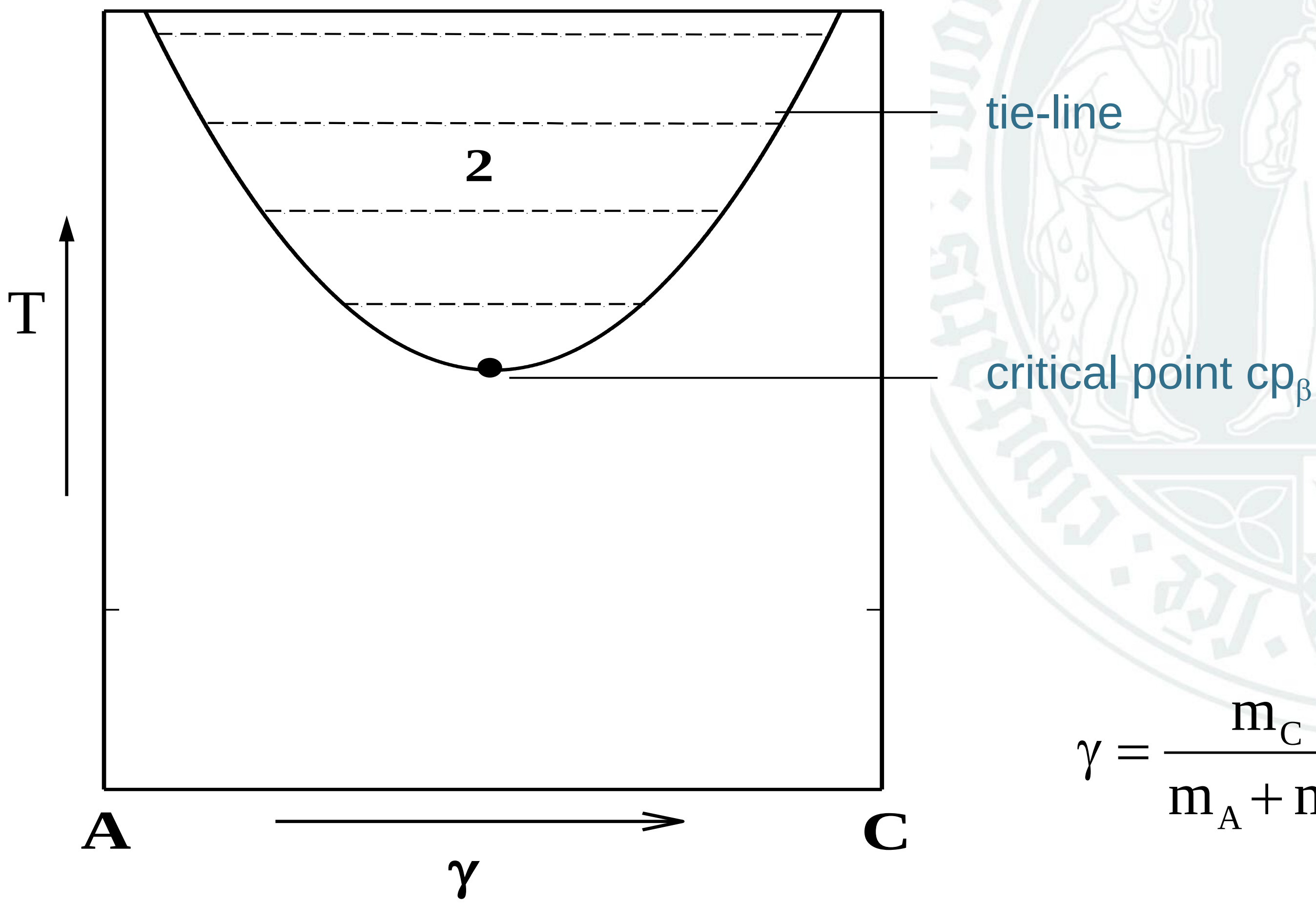


dodecyl trimethylammonium bromide (DTAB)

Binary side-systems

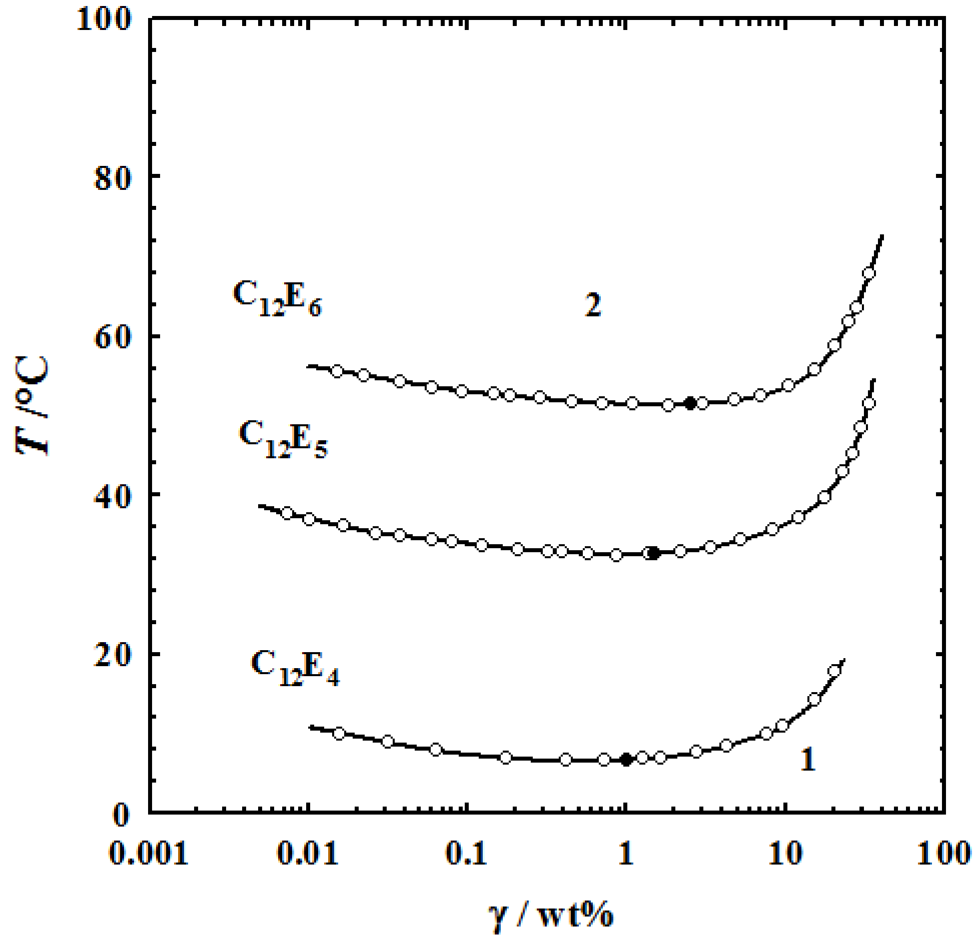


Water (A) – C_iE_j (B) Systems / upper miscibility gap

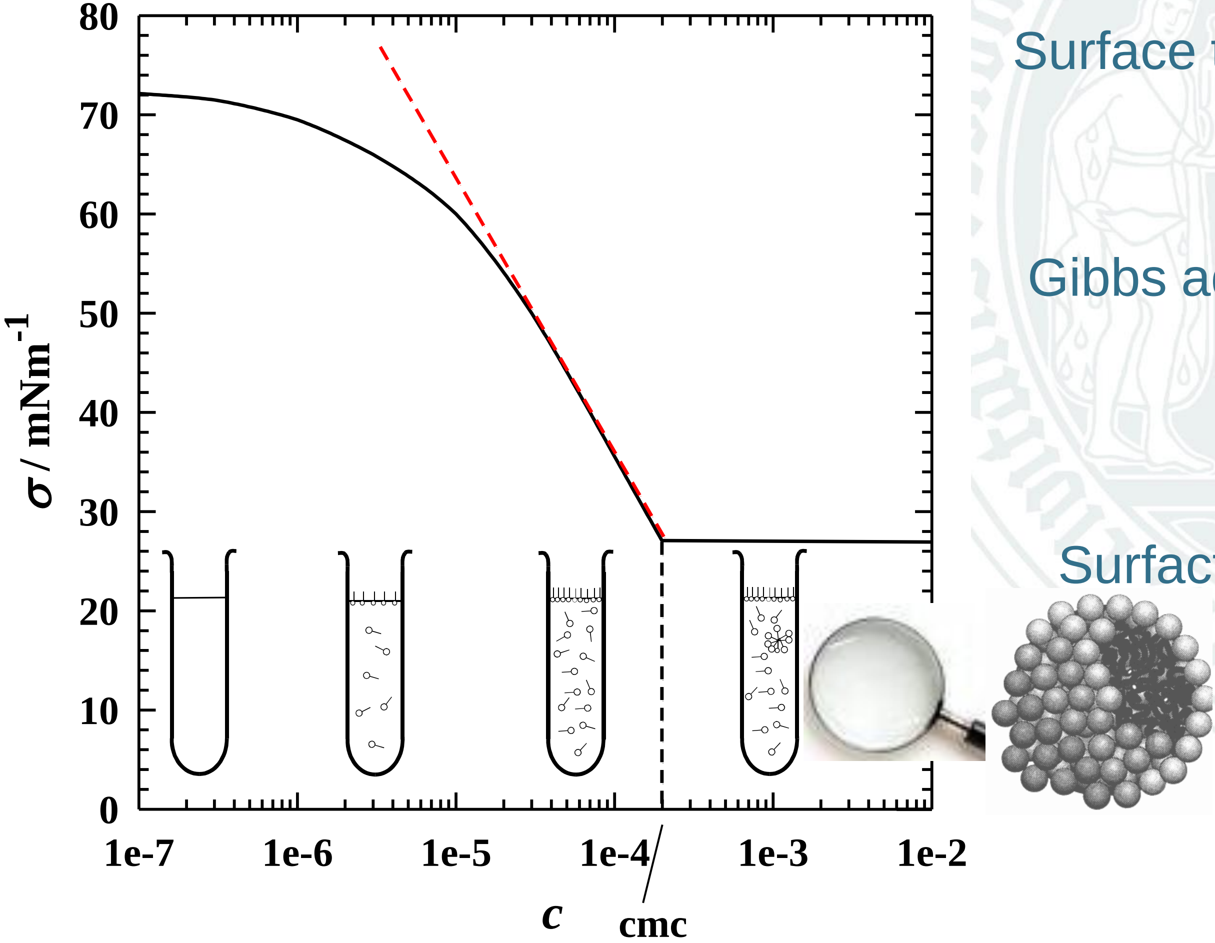


$$\gamma = \frac{m_C}{m_A + m_C}$$

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



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



Surface tension:

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

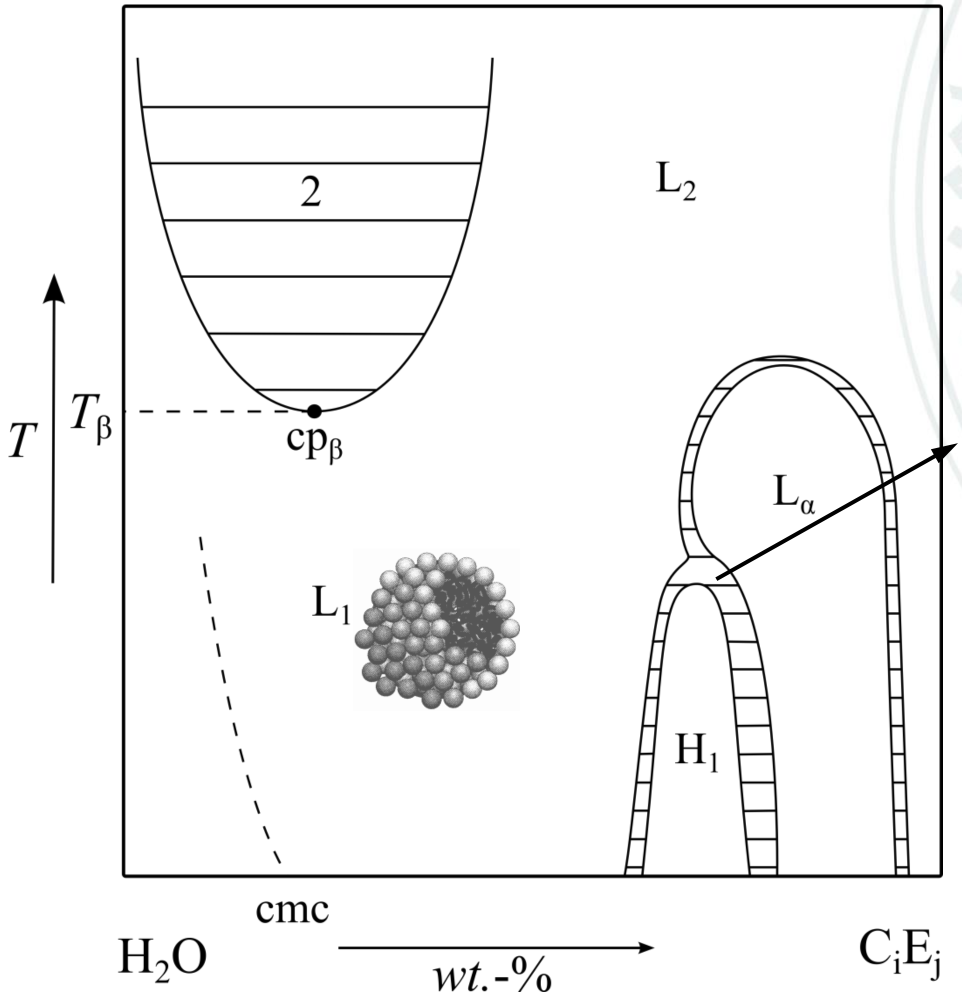
Gibbs adsorptions isotherm:

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

Surfactant head group area:

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

Water – C_iE_j Systems / Liquid crystalline phases

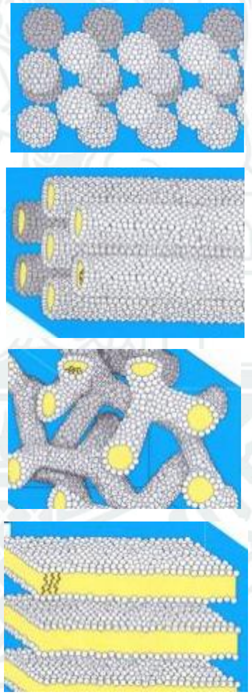


micellar cubic (I_1):

hexagonal (H_1):

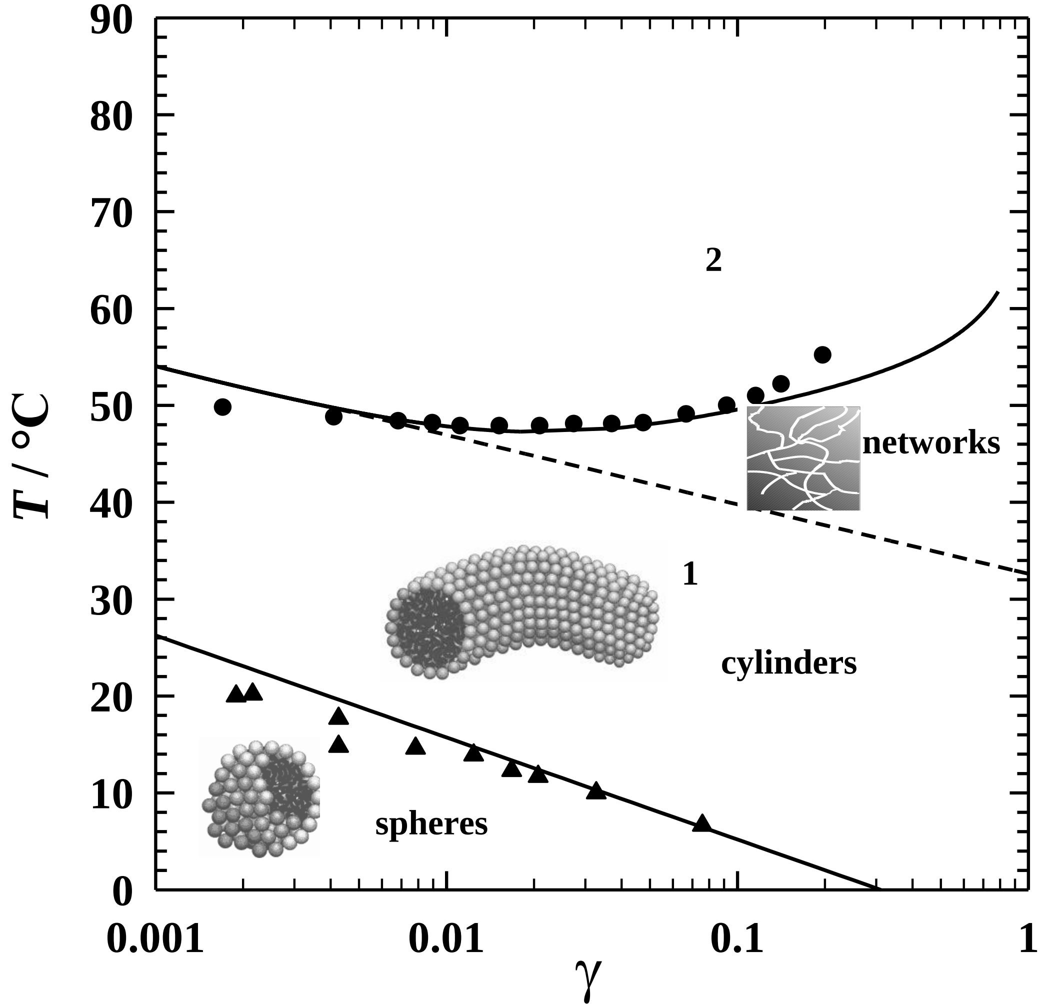
bicontinuous cubic (V_1):

lamellar (L_α):

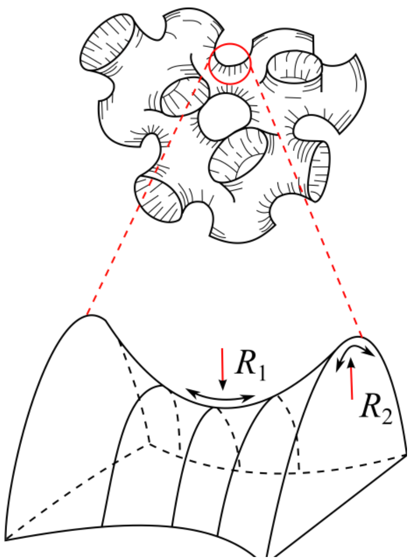


+ inverted liquid crystalline phases: V_2, H_2, I_2

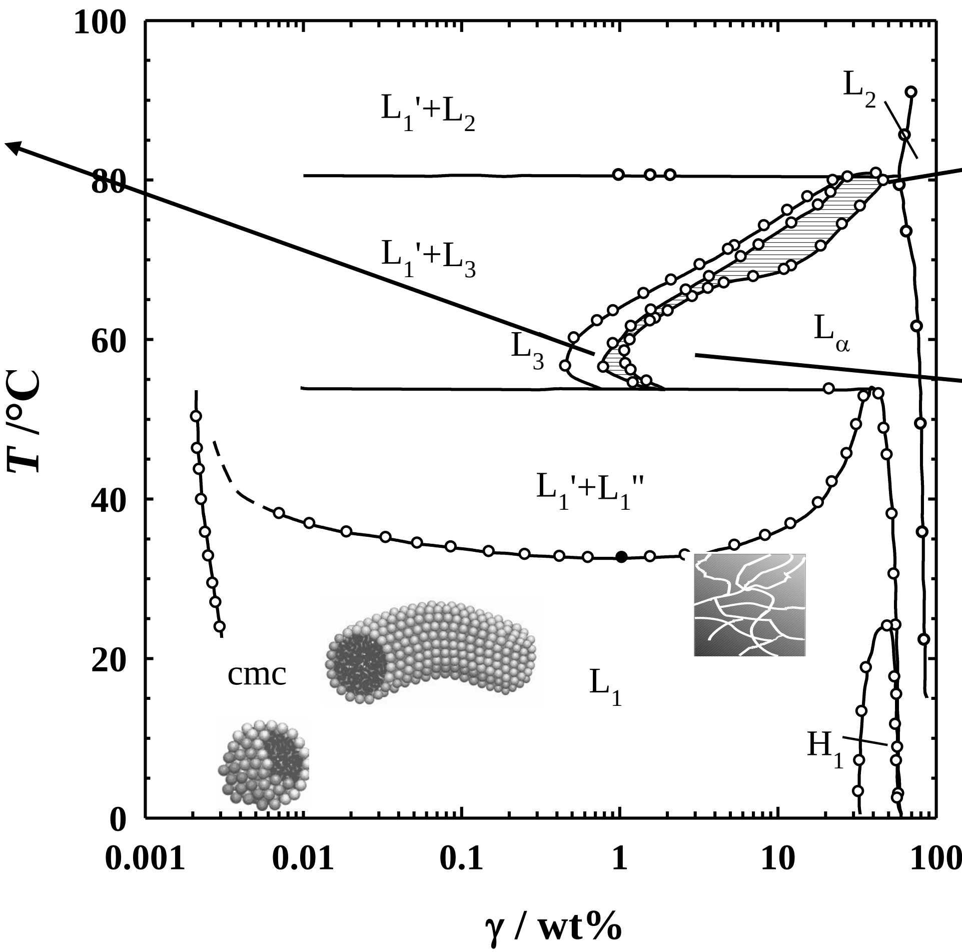
Water – $C_{12}E_6$ / more self-assembly



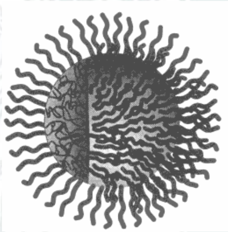
Water – $C_{12}E_5$ System / dilute self-assembled phases



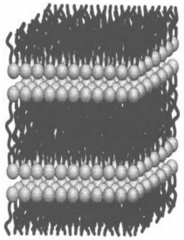
L_3: isotropic bi-layer sponge-phase



L_2: reversed micelles

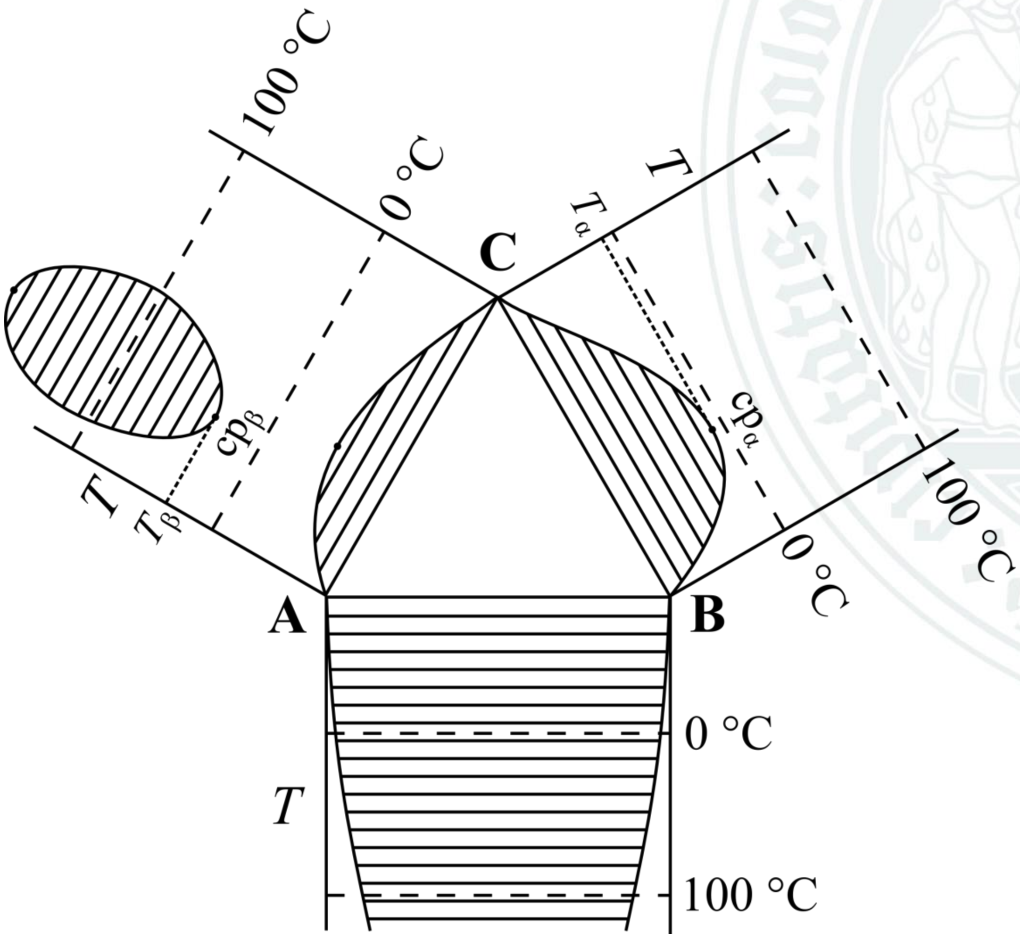


dilute lamellae

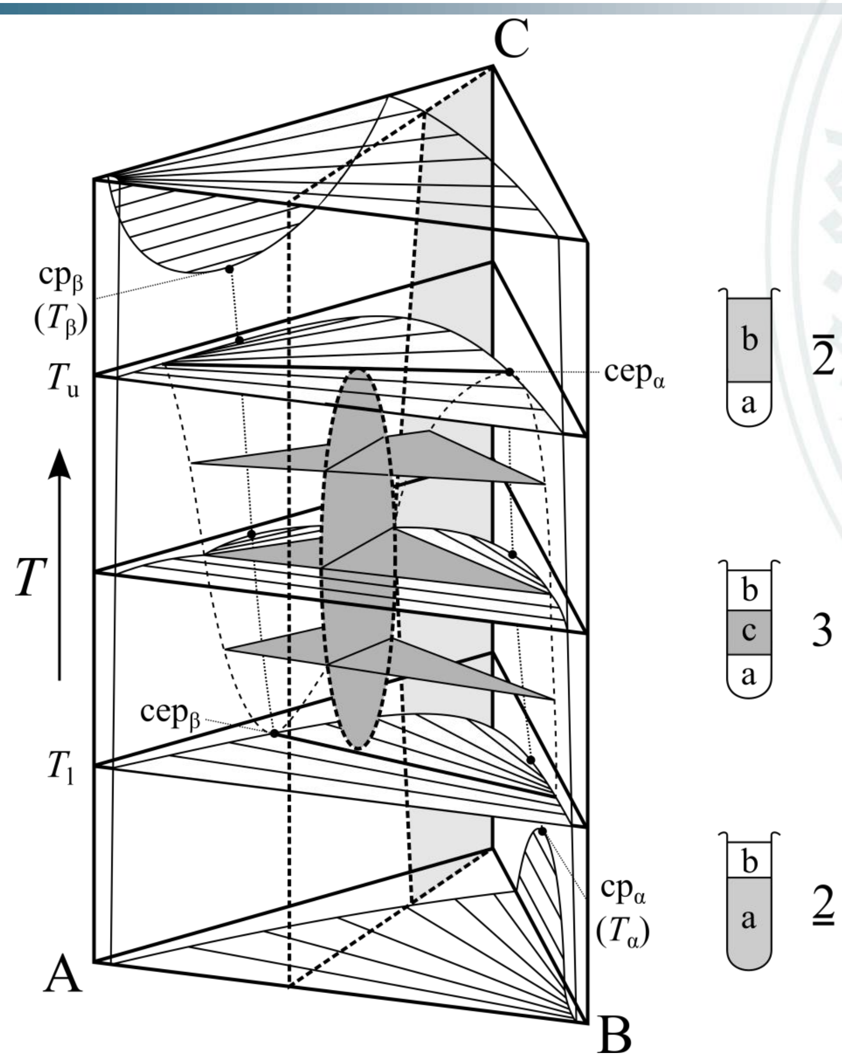


Gibbs phase prism

p = constant



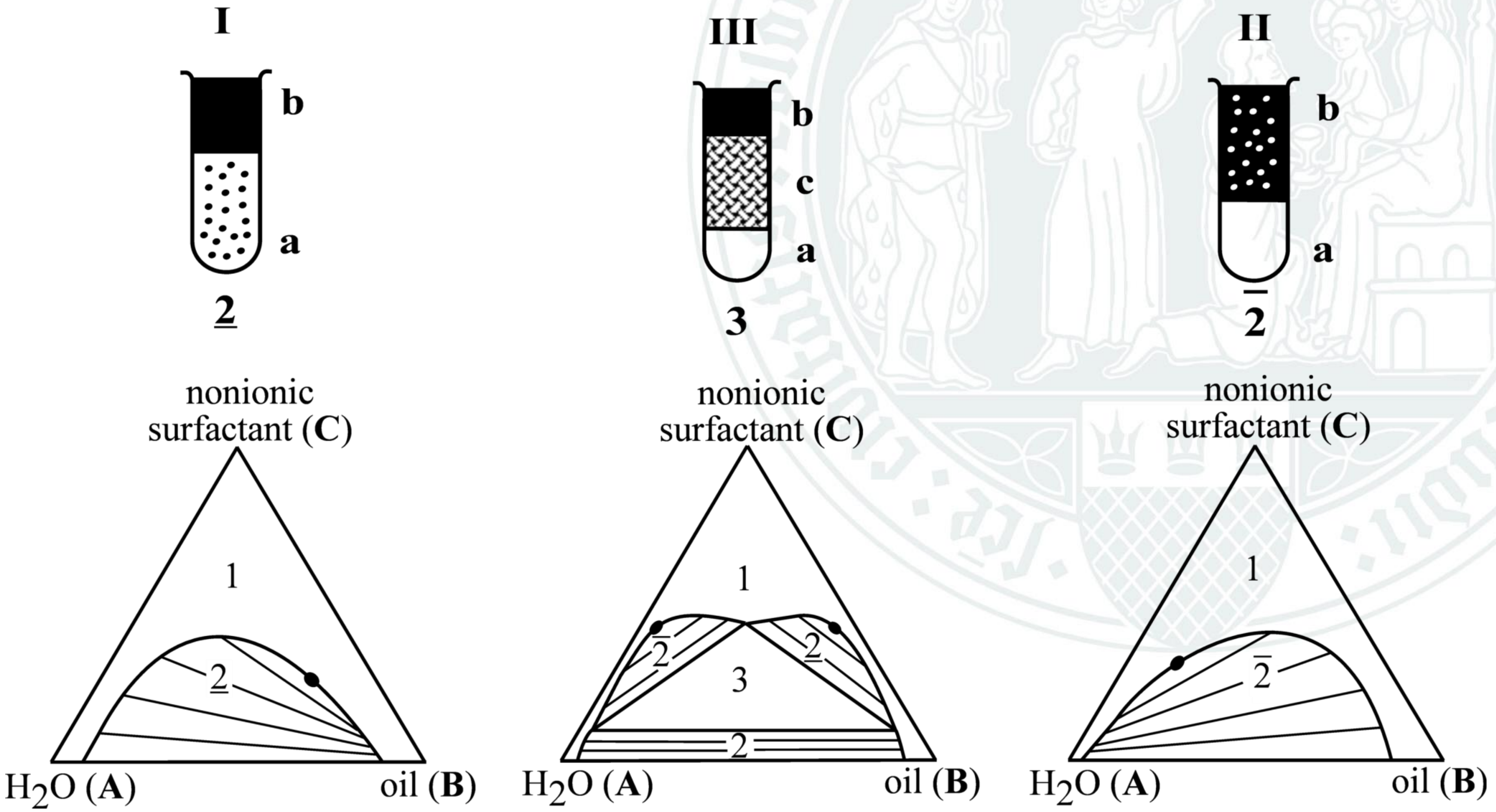
Sections through the phase prism



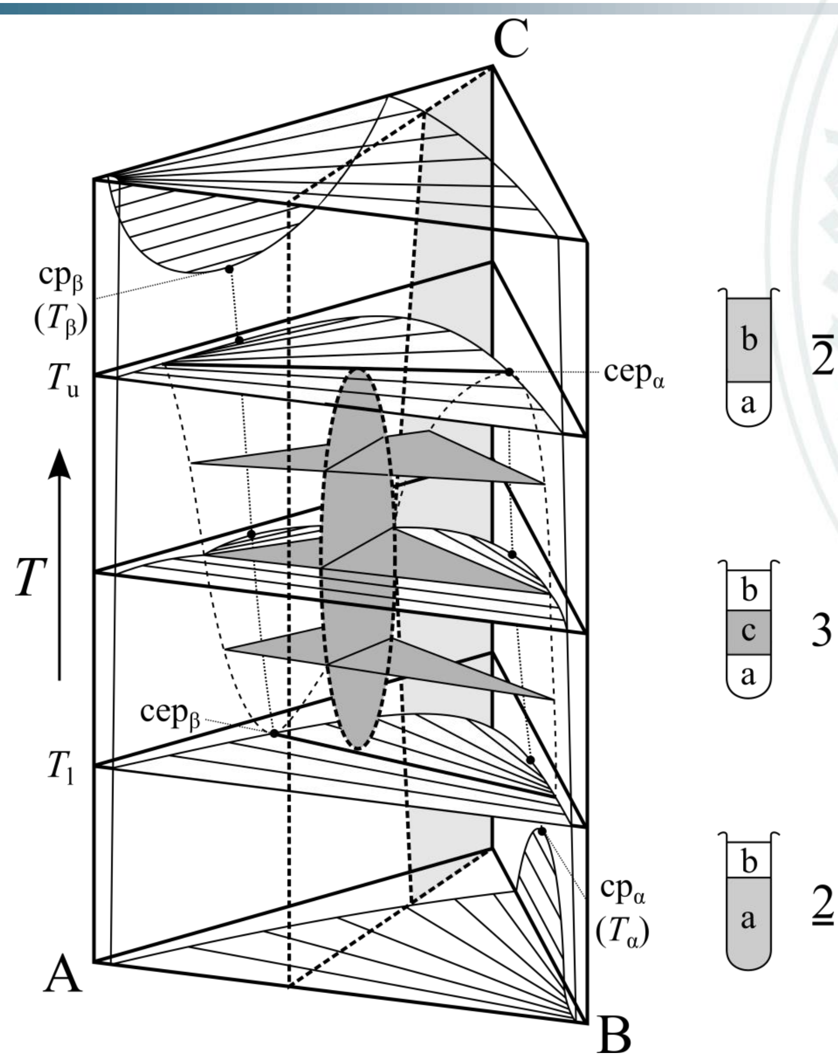
$$\alpha = \frac{m_B}{m_A + m_B}$$

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

Isothermal sections - phase inversion



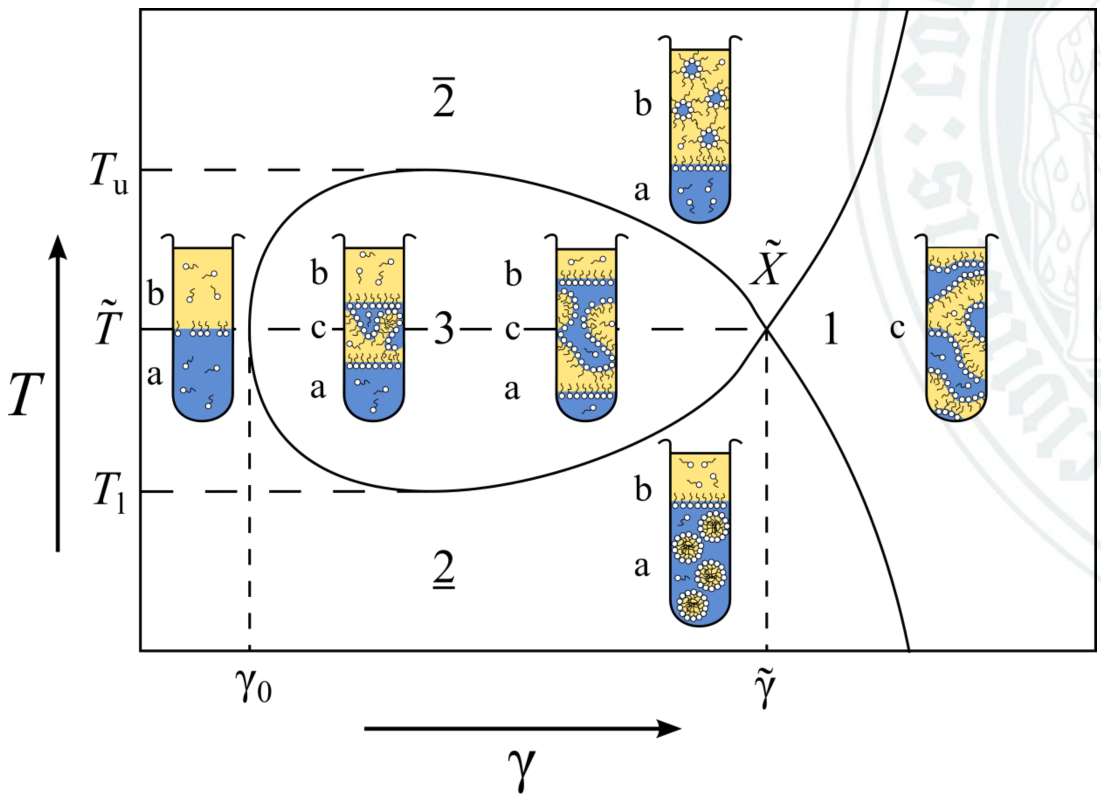
Sections through the phase prism



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

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

Isoplethal T(γ)-section I



Measure of

Efficieny: $\tilde{\gamma}$

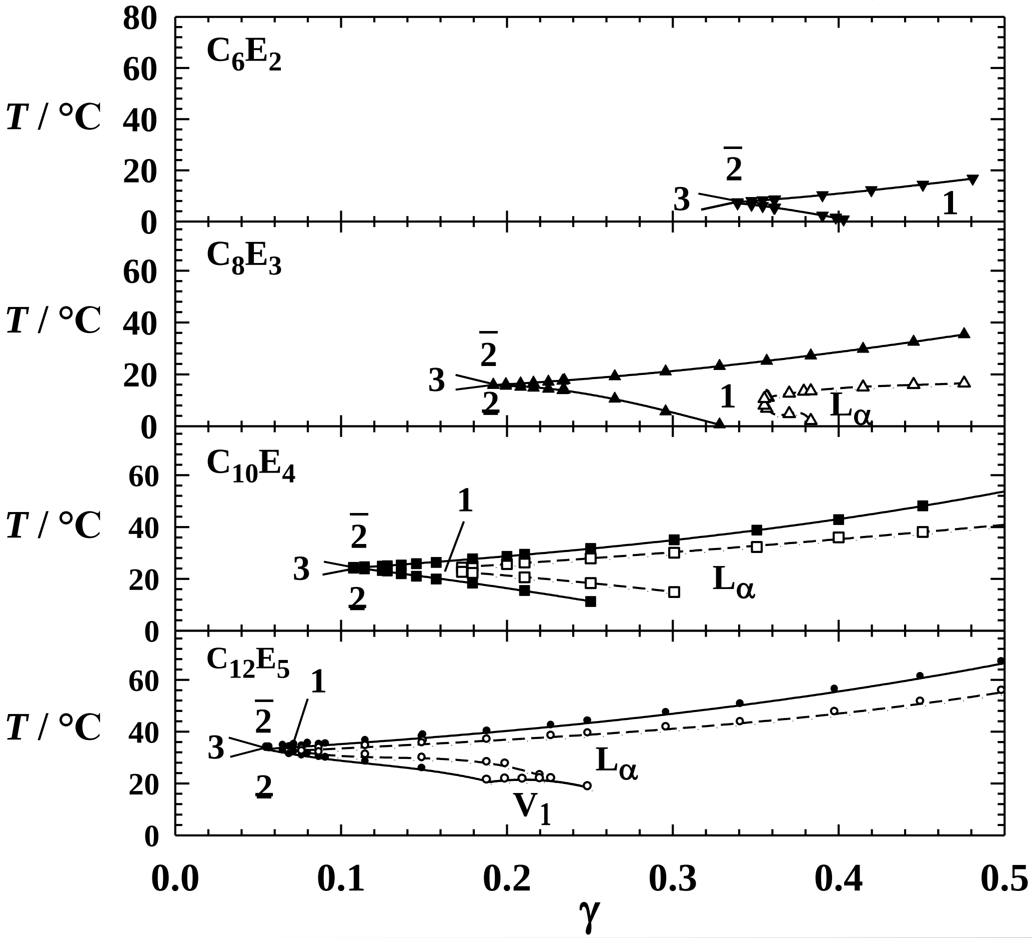
Phase inversion: $\tilde{T}$

Monomeric solubility: γ_0

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

Isoplethal T(γ)-section II

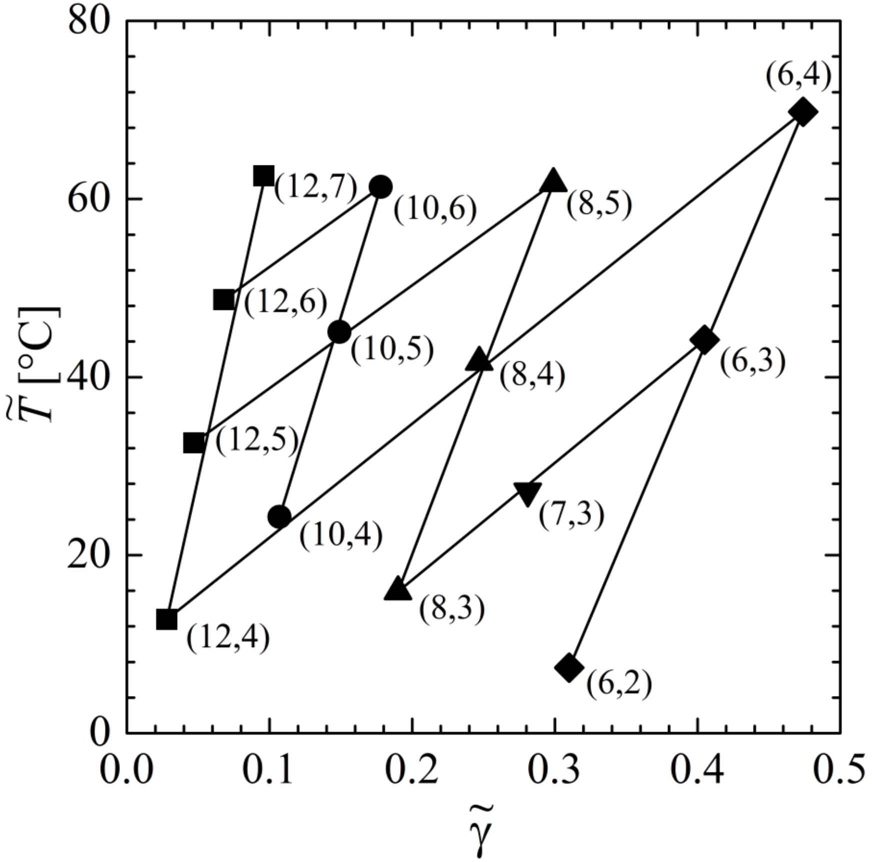
H_2O – *n*-octane – C_iE_j



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

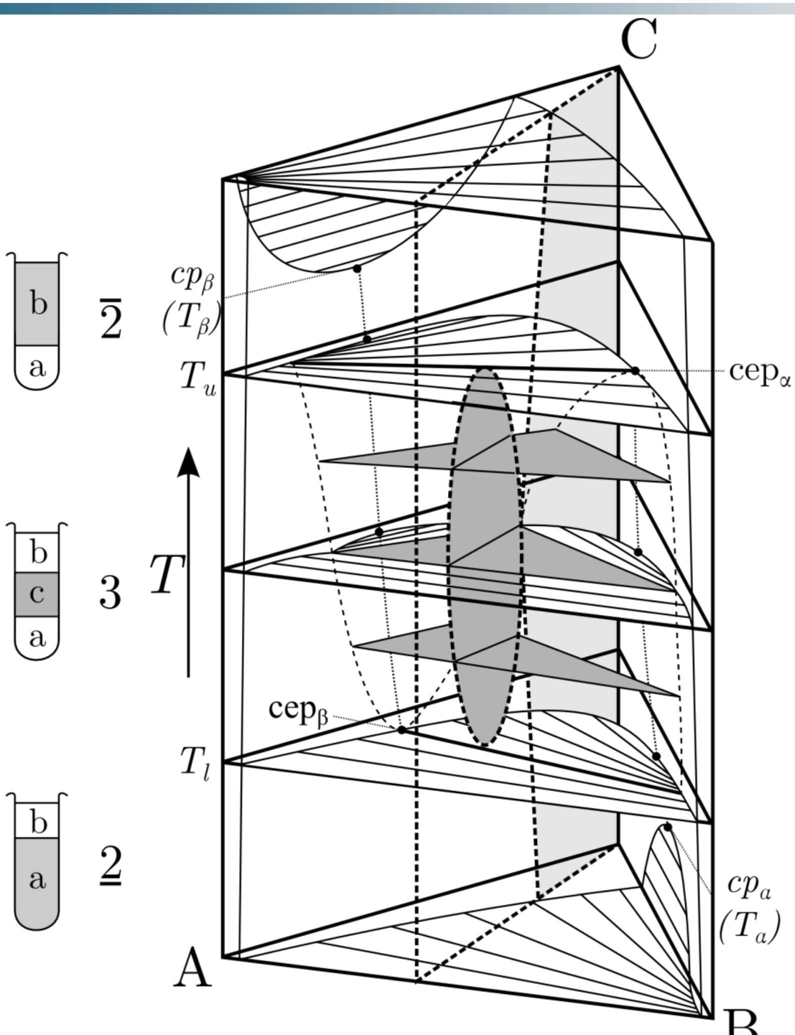
Efficiency – Phase inversion temperature

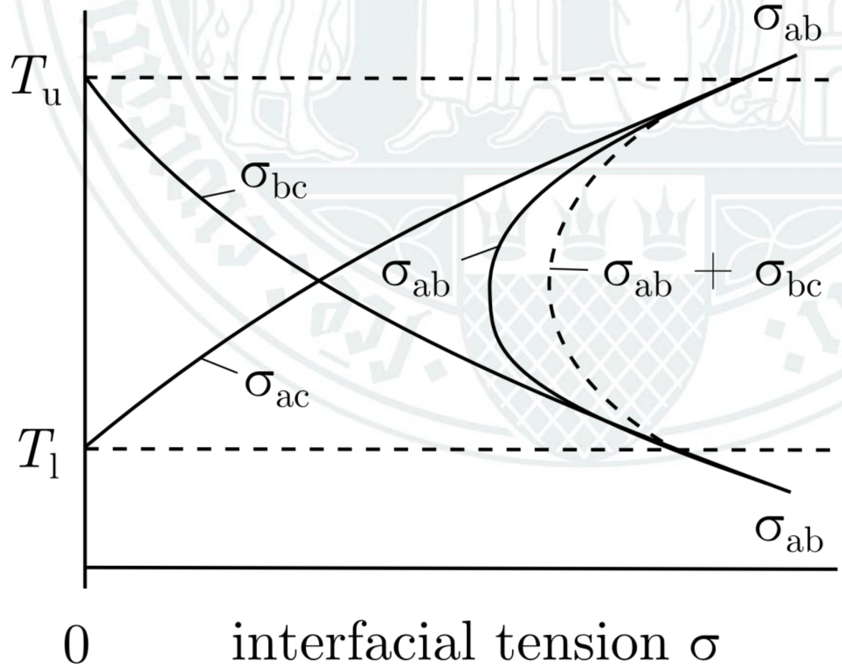
H_2O – *n*-octane – C_iE_j



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

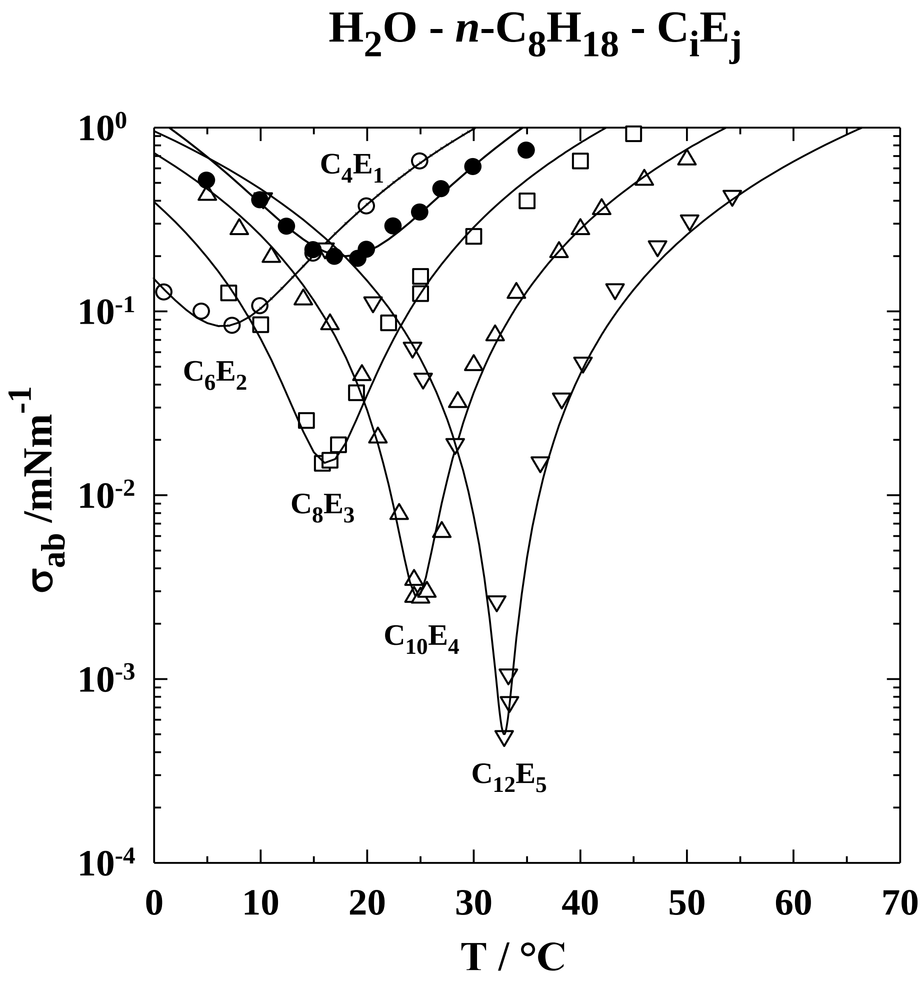
Phase behaviour – Interfacial tensions





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)

Microstructure

Techniques:

direct: Transmission Electron Microscopy (TEM)

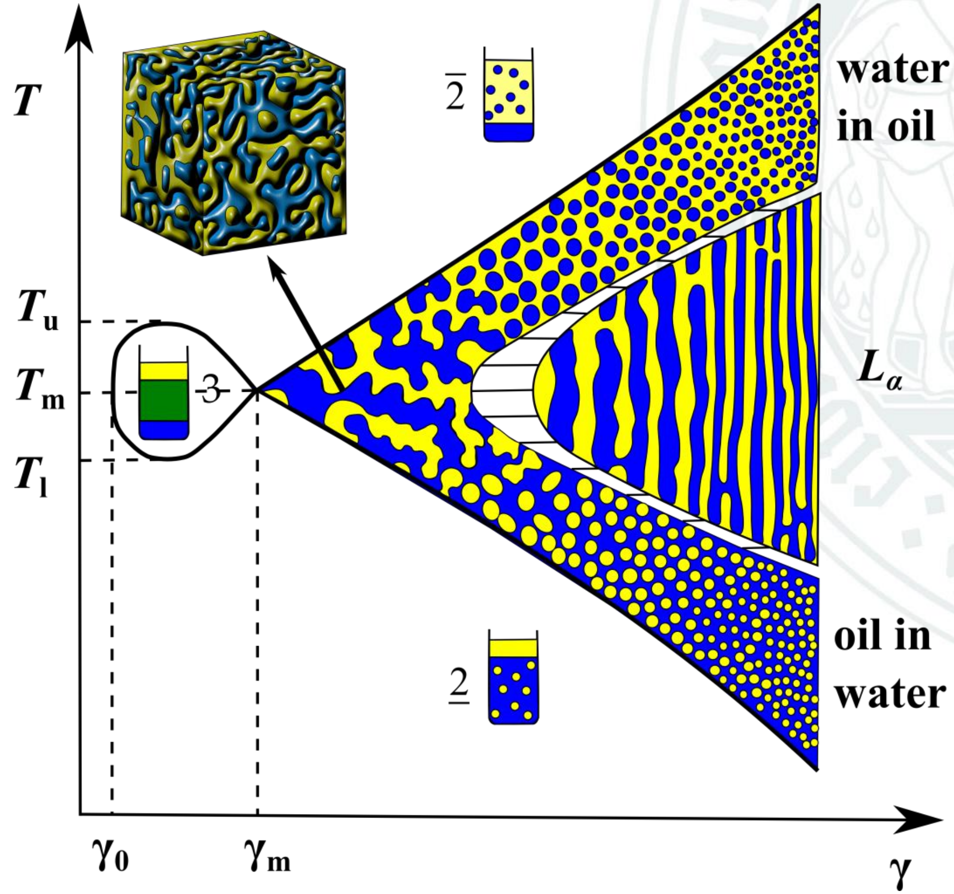
indirect: Scattering Techniques

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

Diffusion NMR

Electric Conductivity

Microstructure

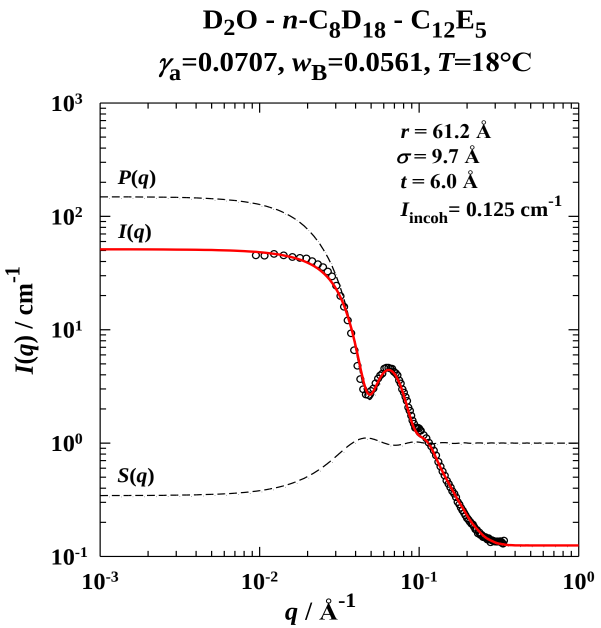


$\Phi = 0.50 = \text{const.}$

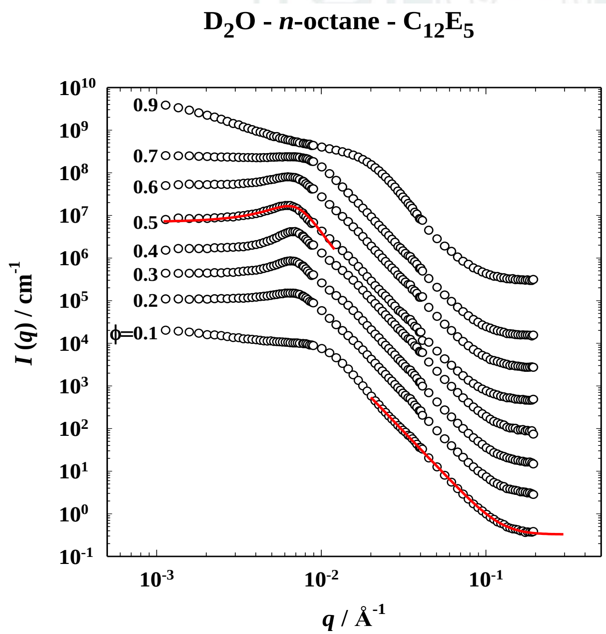
R. Strey, Colloid Polym. Sci., **272** (8), 1005 (1994).

Microstructure – Length Scales

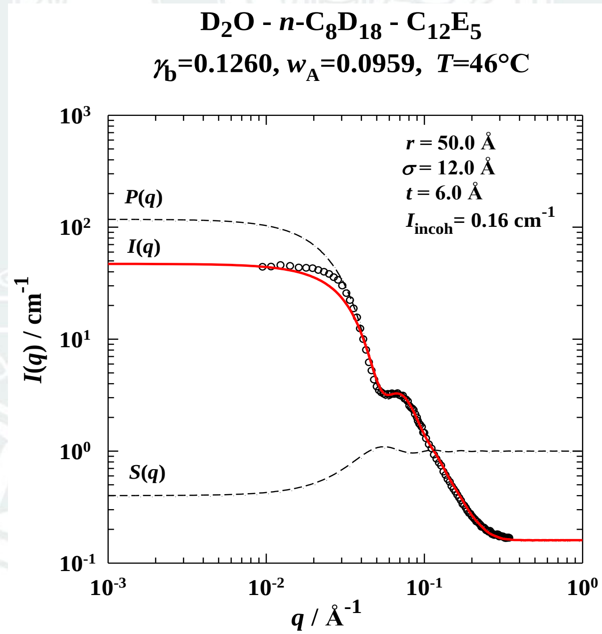
Small angle neutron scattering (SANS)



o/w



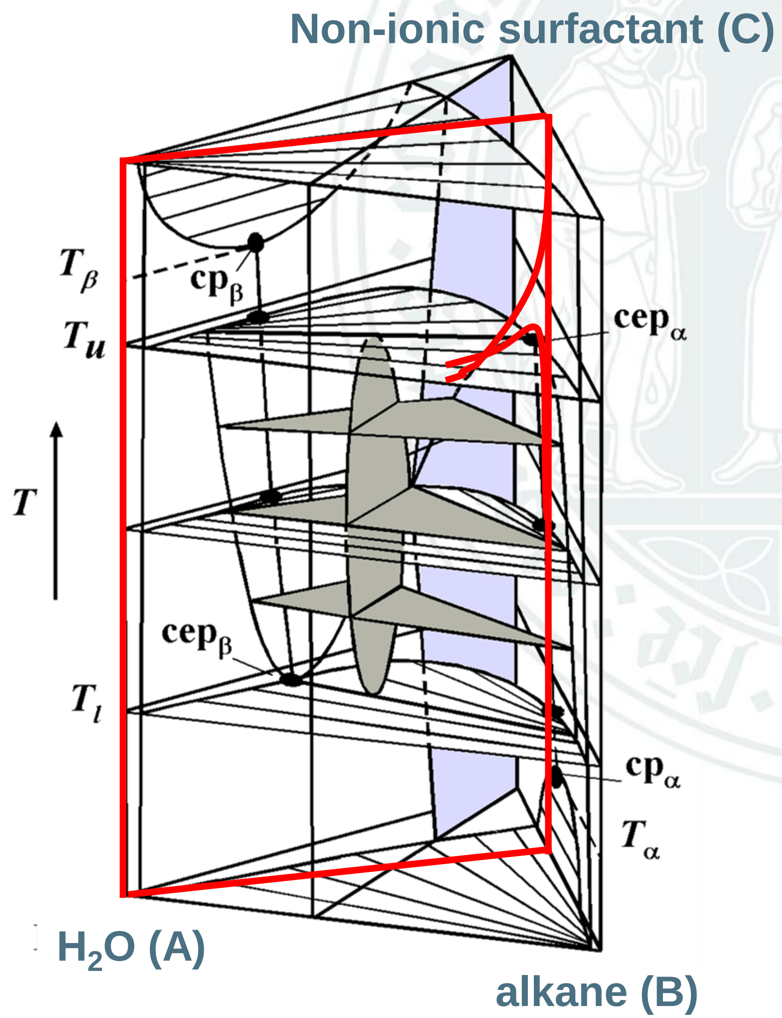
bicontinuous



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)

Sections through the phase prism



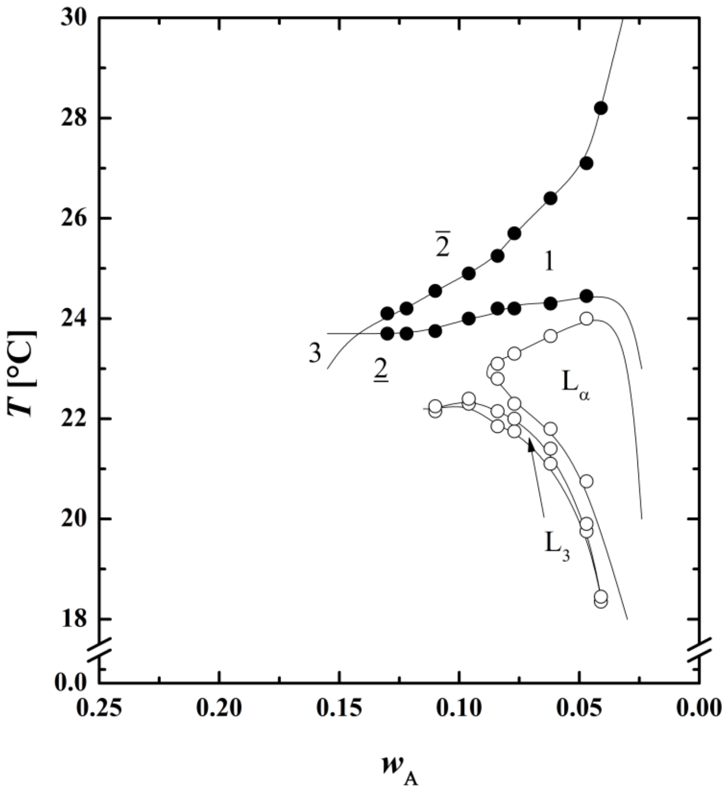
$$\gamma_b = \frac{m_C}{m_B + m_C}$$

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

Redrawn from:
Strey, R., *Colloid Polym. Sci.*, **1994**, 272 (8), 1005.
Gompper, G., Kroll, D. M., *Phys. Rev. Lett.*, **1998**, 81, 2284.

The $T(w_A)$-Cut

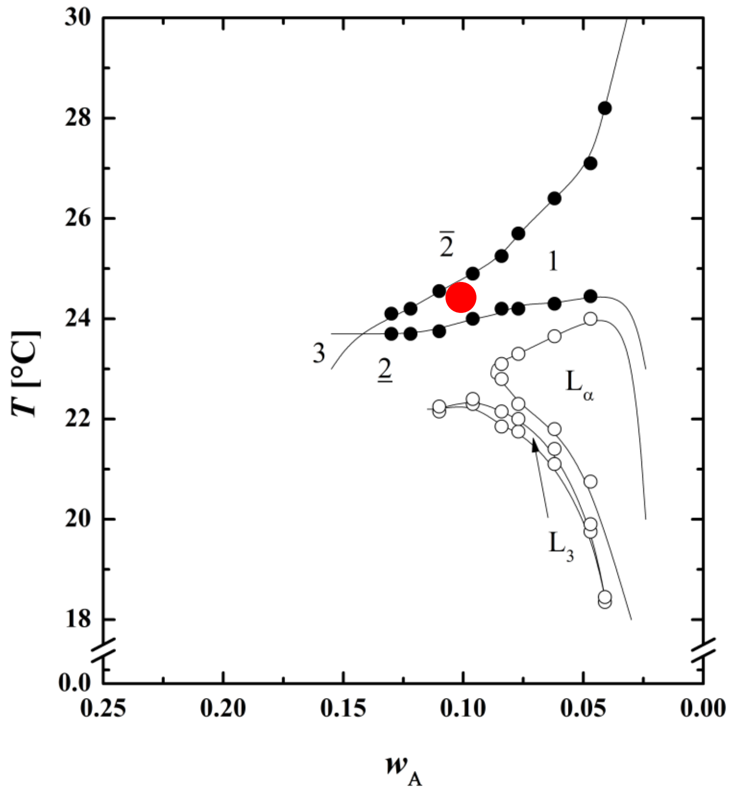
D_2O/NaCl – cyclohexane-h12 – $C_{10}E_5$
ε = 0.001, γ_b=0.05, T=24.50°C

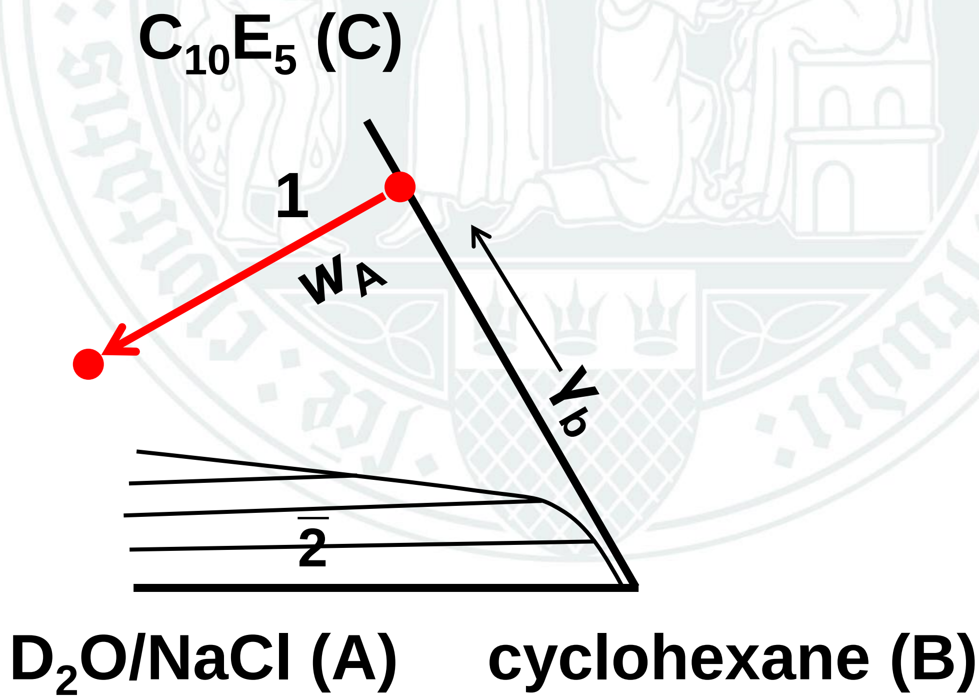


$$w_A = \frac{m_A}{m_{total}} \quad \gamma_b = \frac{m_C}{m_B + m_C} \quad \varepsilon = \frac{m_{NaCl}}{m_A}$$

The Mixing Pathway

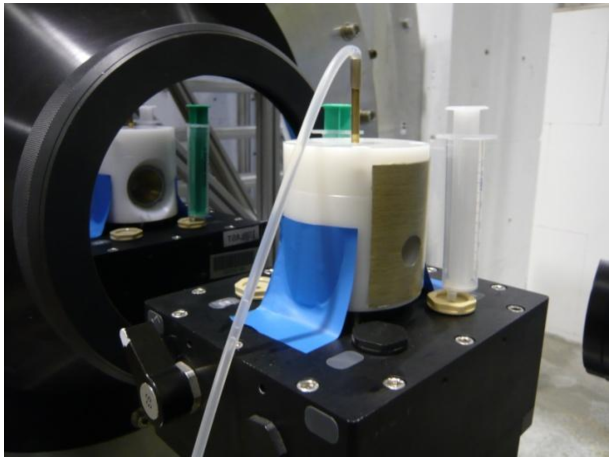
D_2O/NaCl – cyclohexane-h12 – $C_{10}E_5$
ε = 0.001, γ_b=0.05, *T*=24.50°C

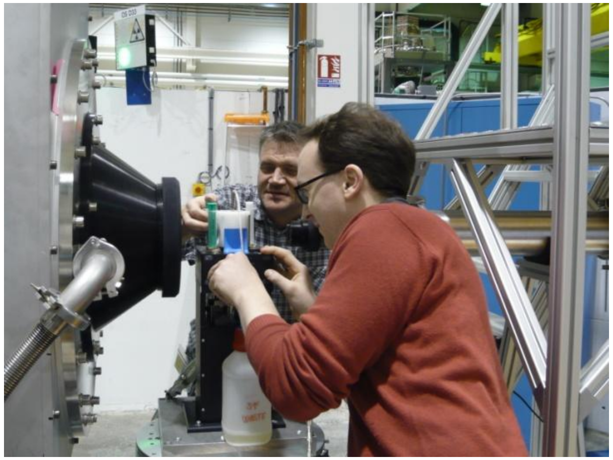




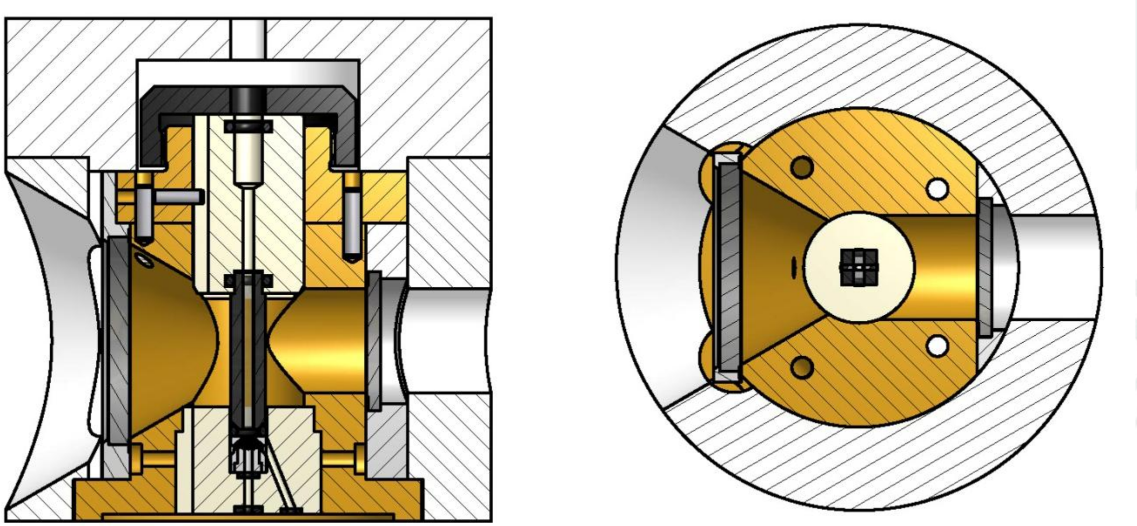
$$w_A = \frac{m_A}{m_{total}} \qquad \gamma_b = \frac{m_C}{m_B + m_C} \qquad \varepsilon = \frac{m_{NaCl}}{m_A}$$

The Experimental Setup





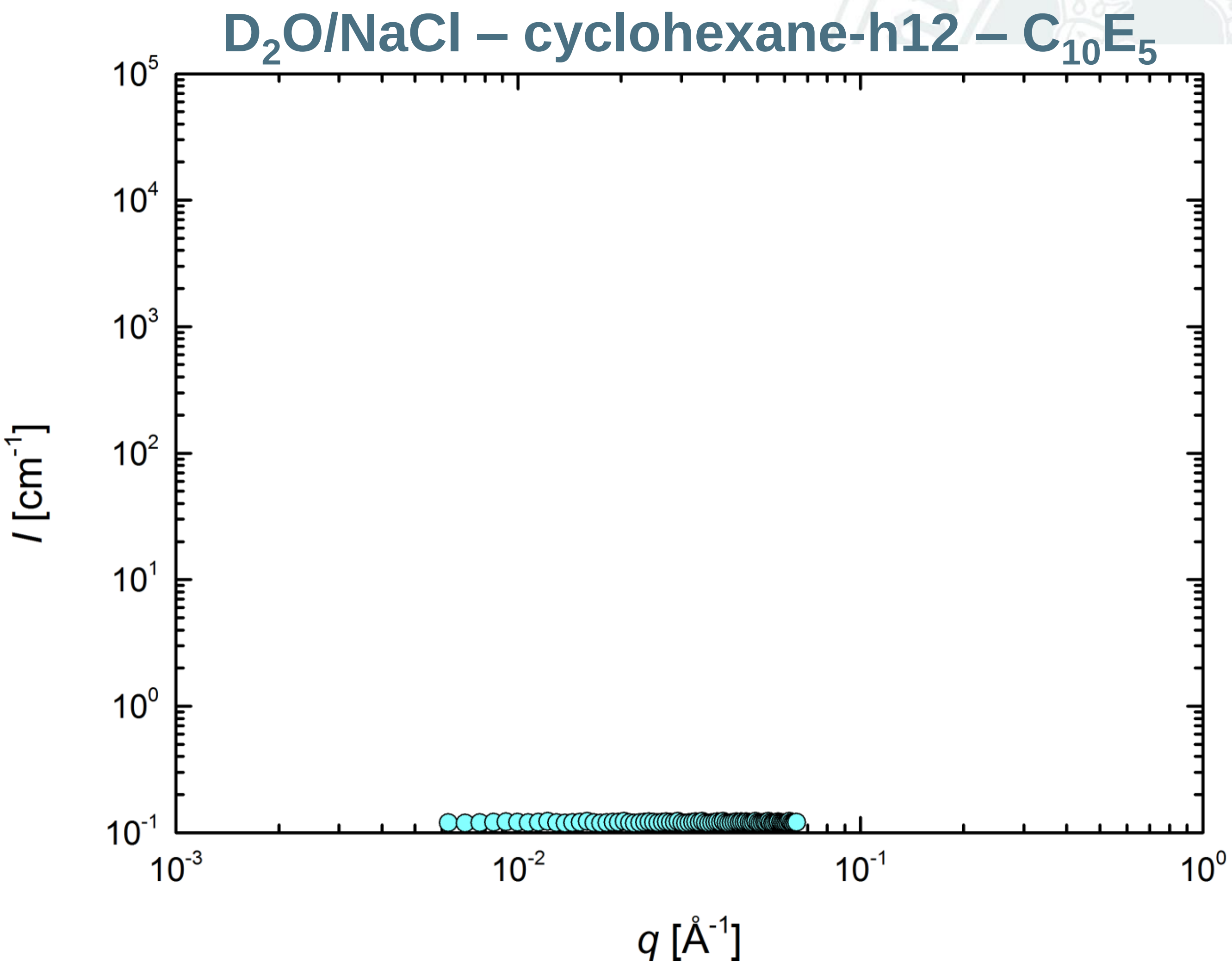
BioLogic stopped flow combined with:



High temperature stability:

$\Delta T \leq 0.1$ K for 273 K $\leq T \leq$ 343 K

Microemulsion Formation Kinetics



$\gamma_b = 0.05$

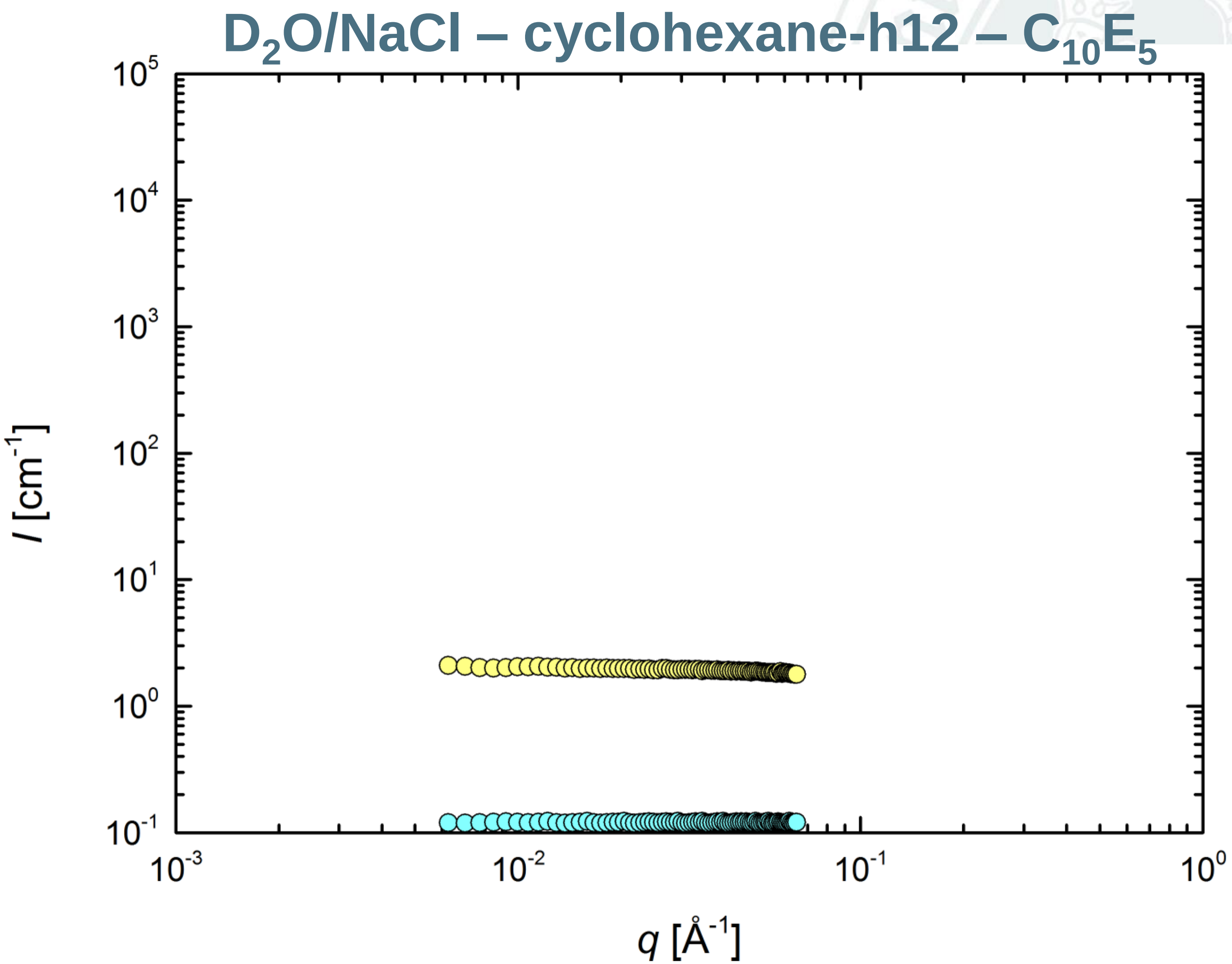
$\varepsilon = 0.001$

$T = 24.50$°C

$w_A = 0.11$

● D_2O/NaCl

Microemulsion Formation Kinetics



$\gamma_b = 0.05$

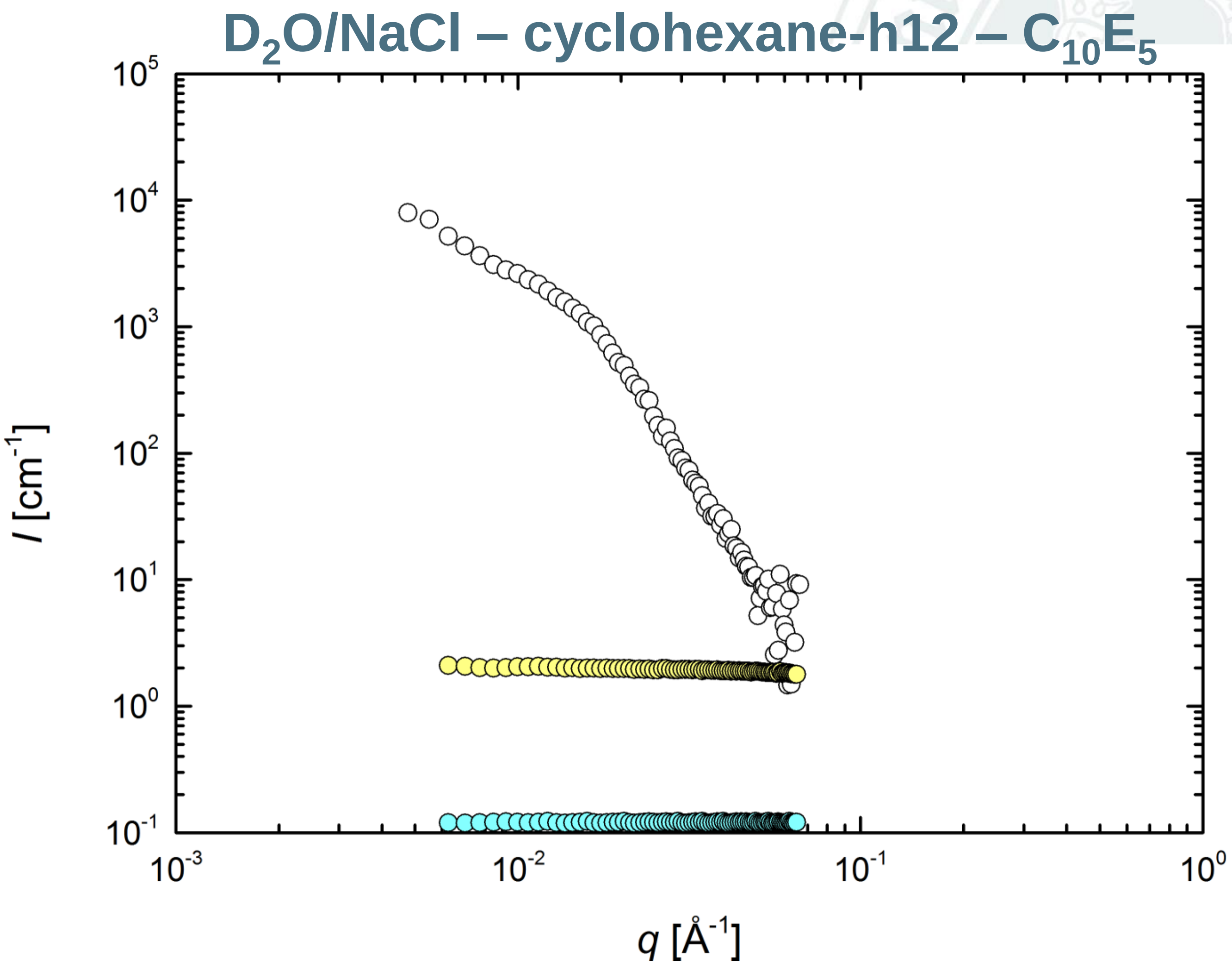
$\varepsilon = 0.001$

$T = 24.50°C$

$w_A = 0.11$

- D_2O/NaCl
- c-B_6/$C_{10}E_5$

Microemulsion Formation Kinetics



$\gamma_b = 0.05$

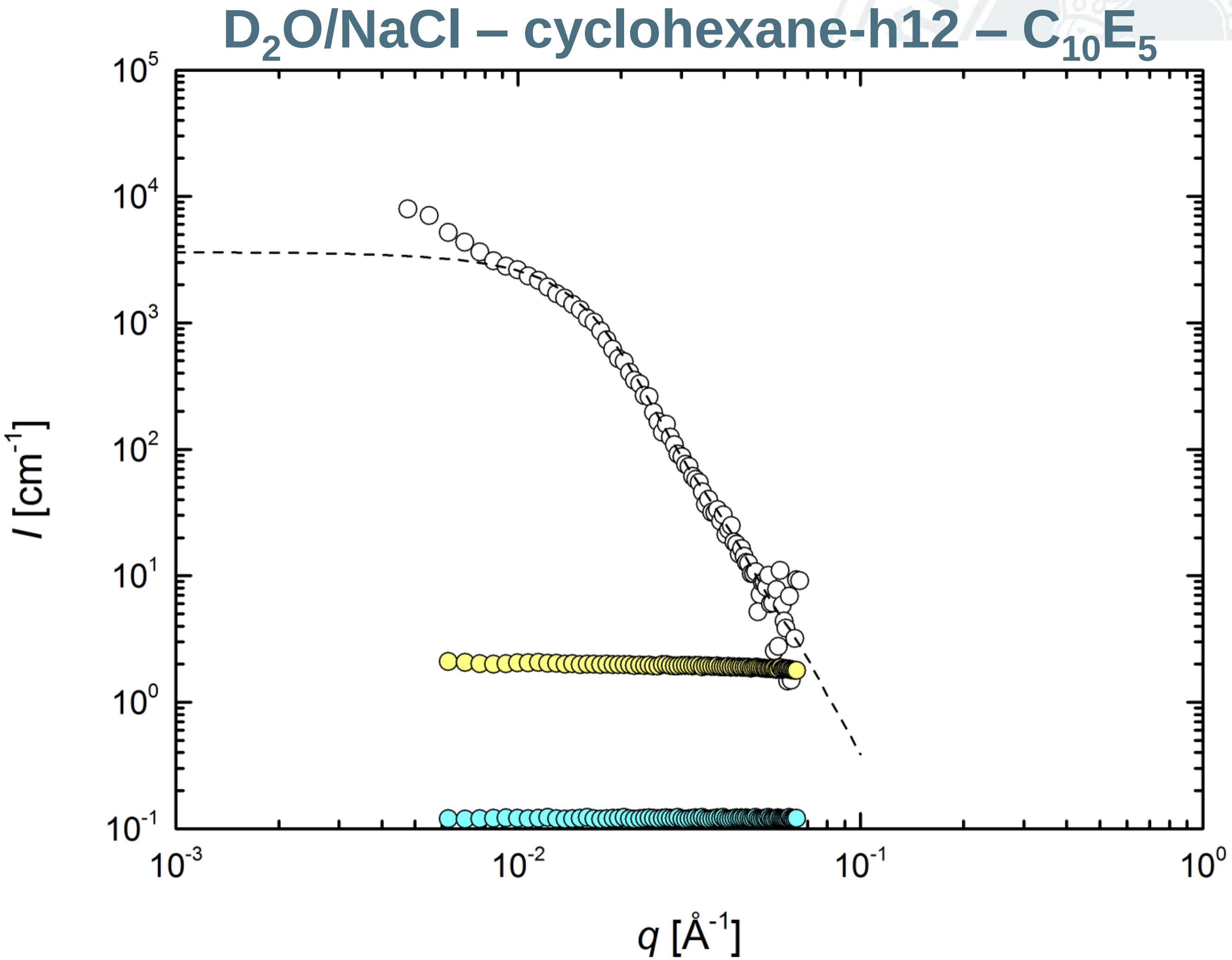
$\varepsilon = 0.001$

$T = 24.50°C$

$w_A = 0.11$

- D_2O/NaCl
- c-$B_6/C_{10}E_5$
- t = 22 ms

Microemulsion Formation Kinetics



$\gamma_b = 0.05$

$\varepsilon = 0.001$

$T = 24.50°C$

$w_A = 0.11$

- $D_2O/NaCl$
- $c\text{-}B_6/C_{10}E_5$
- t = 22 ms

J. S. Pedersen, J Appl Crystallogr, 1994, 27, 595-608.
M. Kotlarchyk, S. H. Chen and J. S. Huang, Phys Rev A, 1983, 28, 508-511.
M. Gradzielski, D. Langevin, L. Magid and R. Strey, J Phys Chem-Us, 1995, 99, 13232-13238.
T. Foster, T. Sottmann, R. Schweins and R. Strey, J Chem Phys, 2008, 128.
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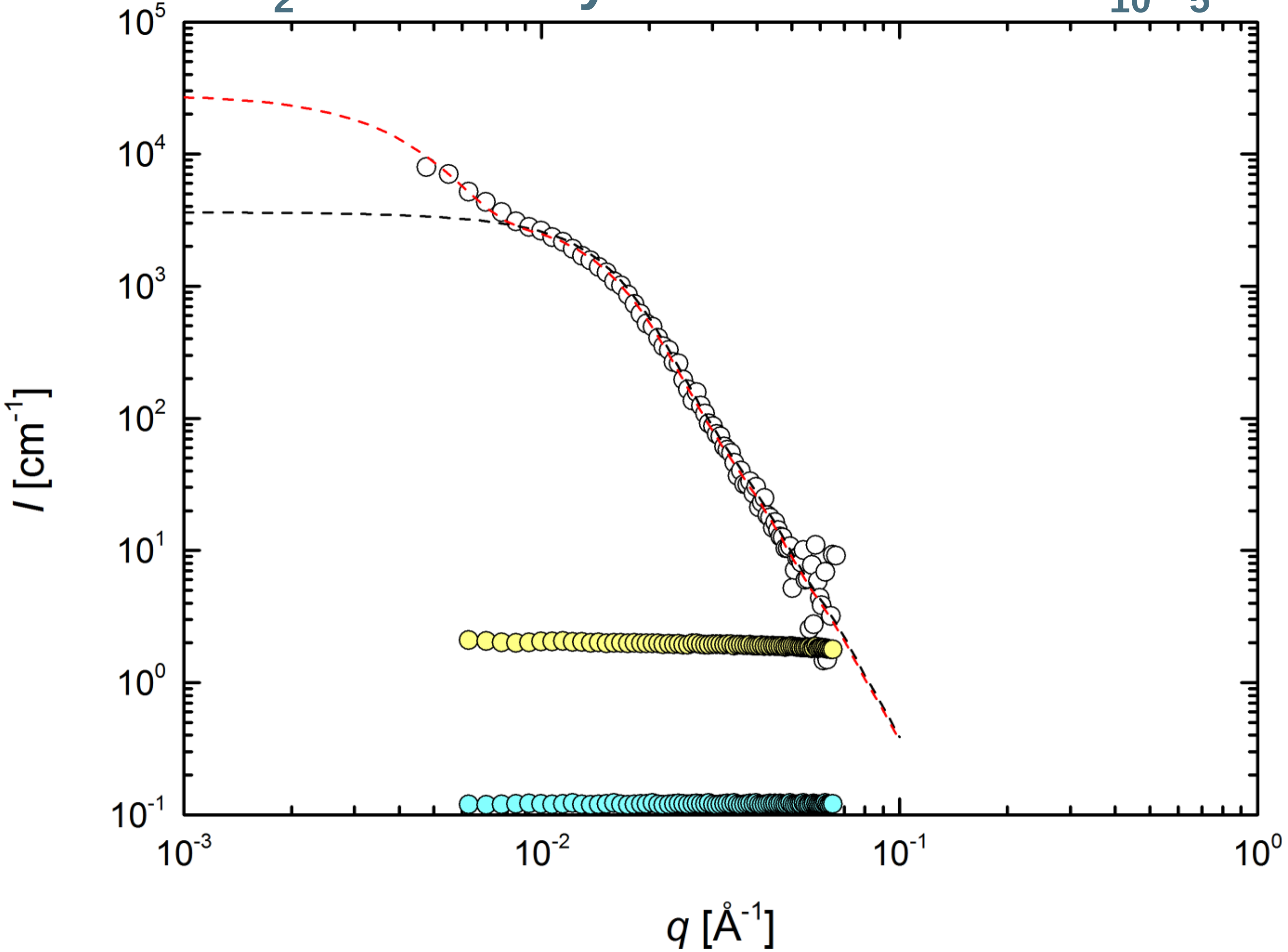
Microemulsion Formation Kinetics

D_2O/NaCl – cyclohexane-h12 – $C_{10}E_5$



$\gamma_b = 0.05$

$\varepsilon = 0.001$

$T = 24.50°C$

$w_A = 0.11$

- D_2O/NaCl
- c-$B_6/C_{10}E_5$
- t = 22 ms

J. S. Pedersen, J Appl Crystallogr, 1994, 27, 595-608.
M. Kotlarchyk, S. H. Chen and J. S. Huang, Phys Rev A, 1983, 28, 508-511.
M. Gradzielski, D. Langevin, L. Magid and R. Strey, J Phys Chem-Us, 1995, 99, 13232-13238.
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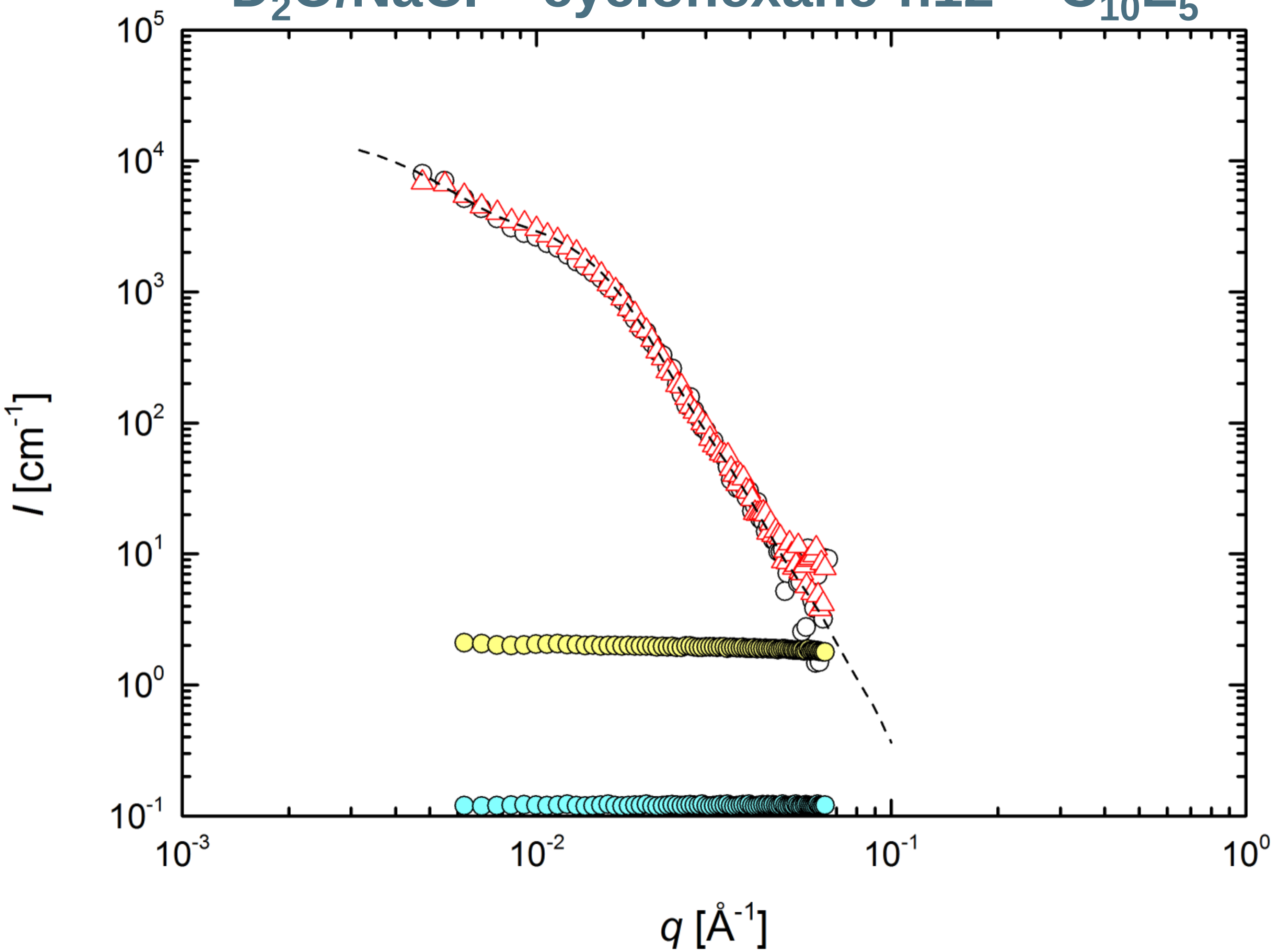
Microemulsion Formation Kinetics

D_2O/NaCl – cyclohexane-h12 – $C_{10}E_5$



$\gamma_b = 0.05$

$\varepsilon = 0.001$

$T = 24.50°C$

$w_A = 0.11$

- D_2O/NaCl
- c-$B_6/C_{10}E_5$
- t = 22 ms
- t = 134 ms

J. S. Pedersen, J Appl Crystallogr, 1994, 27, 595-608.
M. Kotlarchyk, S. H. Chen and J. S. Huang, Phys Rev A, 1983, 28, 508-511.
M. Gradzielski, D. Langevin, L. Magid and R. Strey, J Phys Chem-Us, 1995, 99, 13232-13238.
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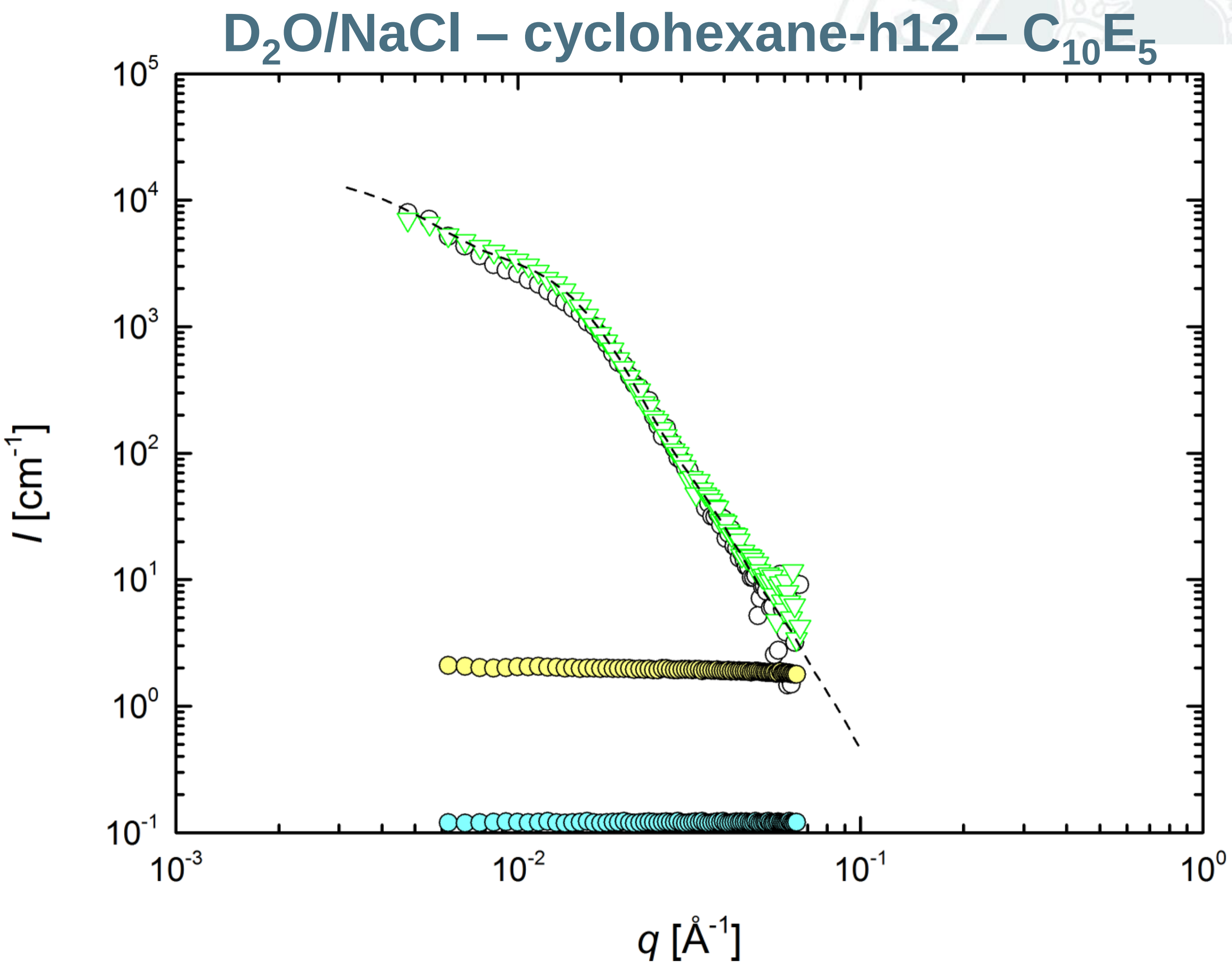
Microemulsion Formation Kinetics



$\gamma_b = 0.05$
$\varepsilon = 0.001$
$T = 24.50°C$
$w_A = 0.11$

- $D_2O/NaCl$
- c-$B_6/C_{10}E_5$
- t = 22 ms
- t = 539 ms

J. S. Pedersen, J Appl Crystallogr, 1994, 27, 595-608.
M. Kotlarchyk, S. H. Chen and J. S. Huang, Phys Rev A, 1983, 28, 508-511.
M. Gradzielski, D. Langevin, L. Magid and R. Strey, J Phys Chem-Us, 1995, 99, 13232-13238.
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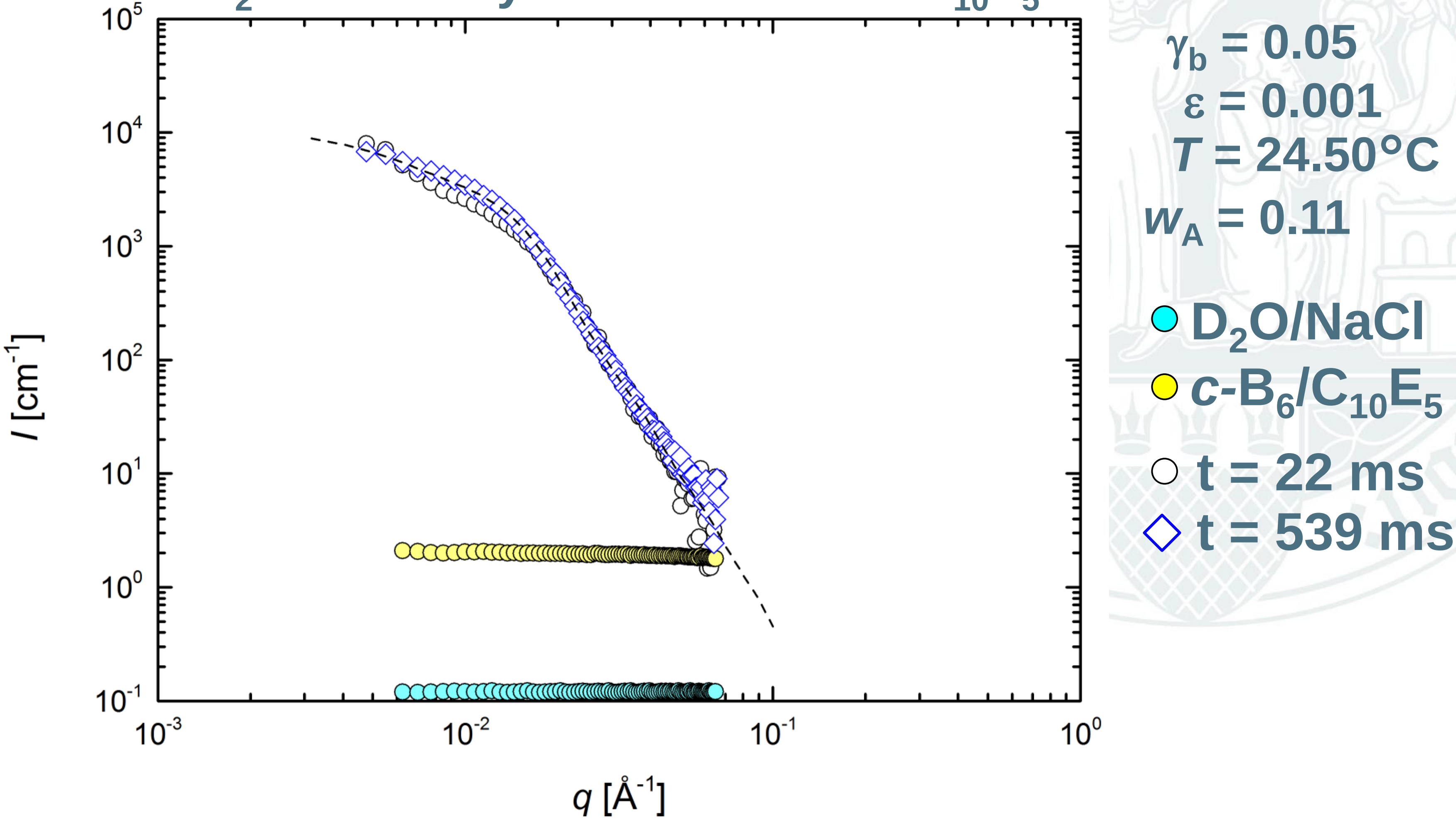
Microemulsion Formation Kinetics

D_2O/NaCl – cyclohexane-h12 – $C_{10}E_5$



$\gamma_b = 0.05$

$\varepsilon = 0.001$

$T = 24.50°C$

$w_A = 0.11$

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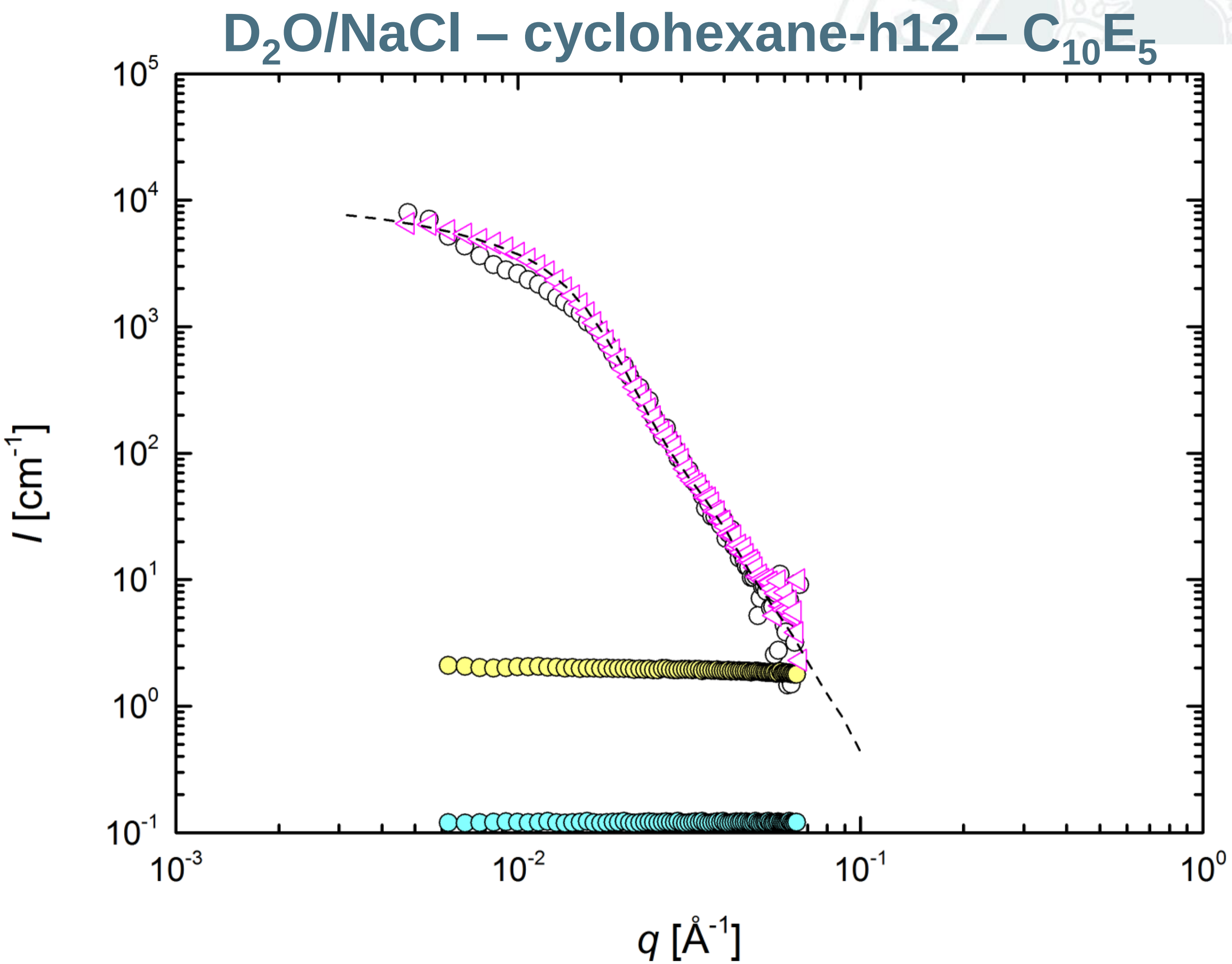
Microemulsion Formation Kinetics



$\gamma_b = 0.05$

$\varepsilon = 0.001$

$T = 24.50°C$

$w_A = 0.11$

- $D_2O/NaCl$
- *c*-$B_6/C_{10}E_5$
- t = 22 ms
- t = 891 ms

J. S. Pedersen, J Appl Crystallogr, 1994, 27, 595-608.
M. Kotlarchyk, S. H. Chen and J. S. Huang, Phys Rev A, 1983, 28, 508-511.
M. Gradzielski, D. Langevin, L. Magid and R. Strey, J Phys Chem-Us, 1995, 99, 13232-13238.
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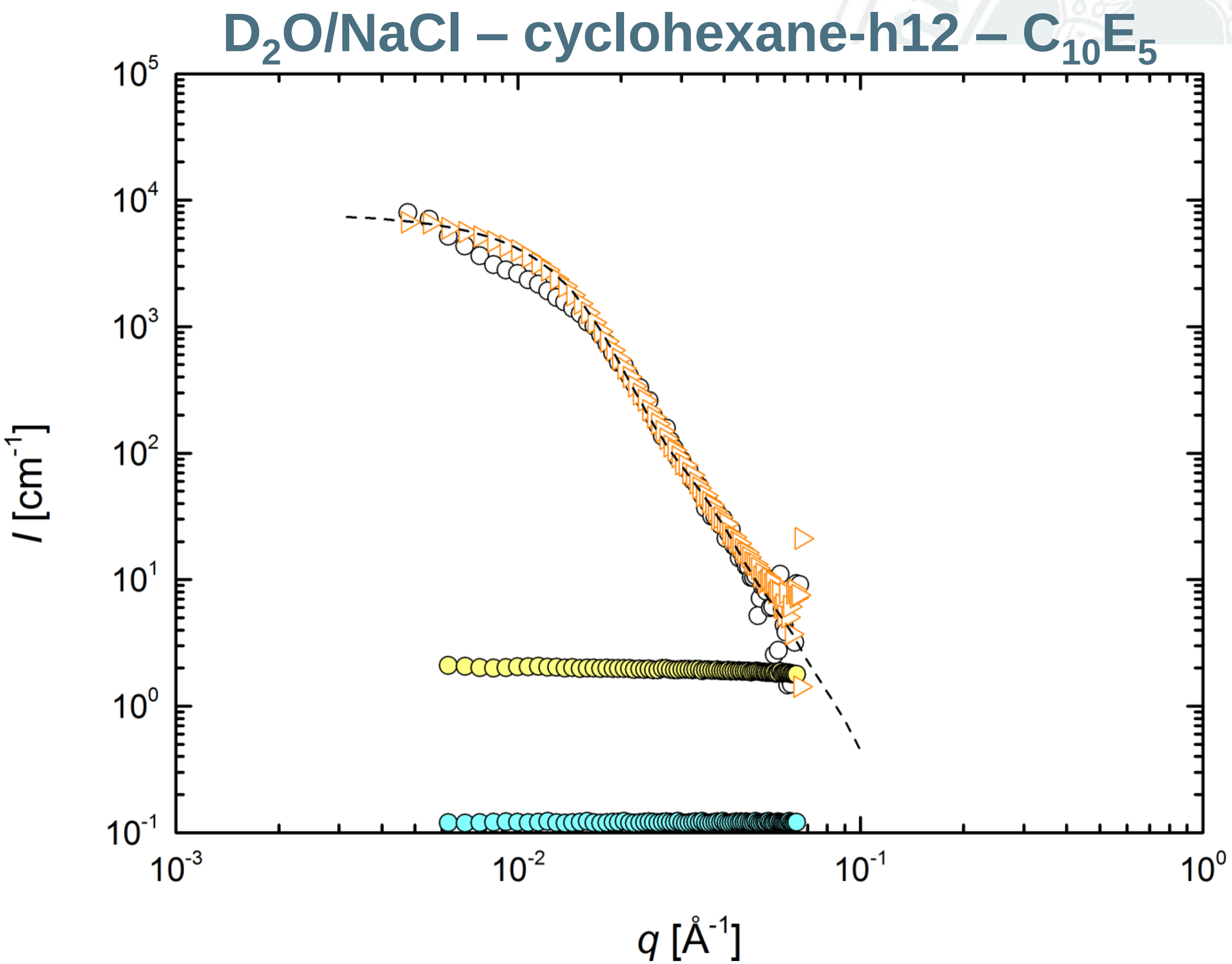
Microemulsion Formation Kinetics



$\gamma_b = 0.05$
$\varepsilon = 0.001$
$T = 24.50°C$
$w_A = 0.11$

- $D_2O/NaCl$
- $c\text{-}B_6/C_{10}E_5$
- t = 22 ms
- t = 1408 ms

J. S. Pedersen, J Appl Crystallogr, 1994, 27, 595-608.
M. Kotlarchyk, S. H. Chen and J. S. Huang, Phys Rev A, 1983, 28, 508-511.
M. Gradzielski, D. Langevin, L. Magid and R. Strey, J Phys Chem-Us, 1995, 99, 13232-13238.
T. Foster, T. Sottmann, R. Schweins and R. Strey, J Chem Phys, 2008, 128.

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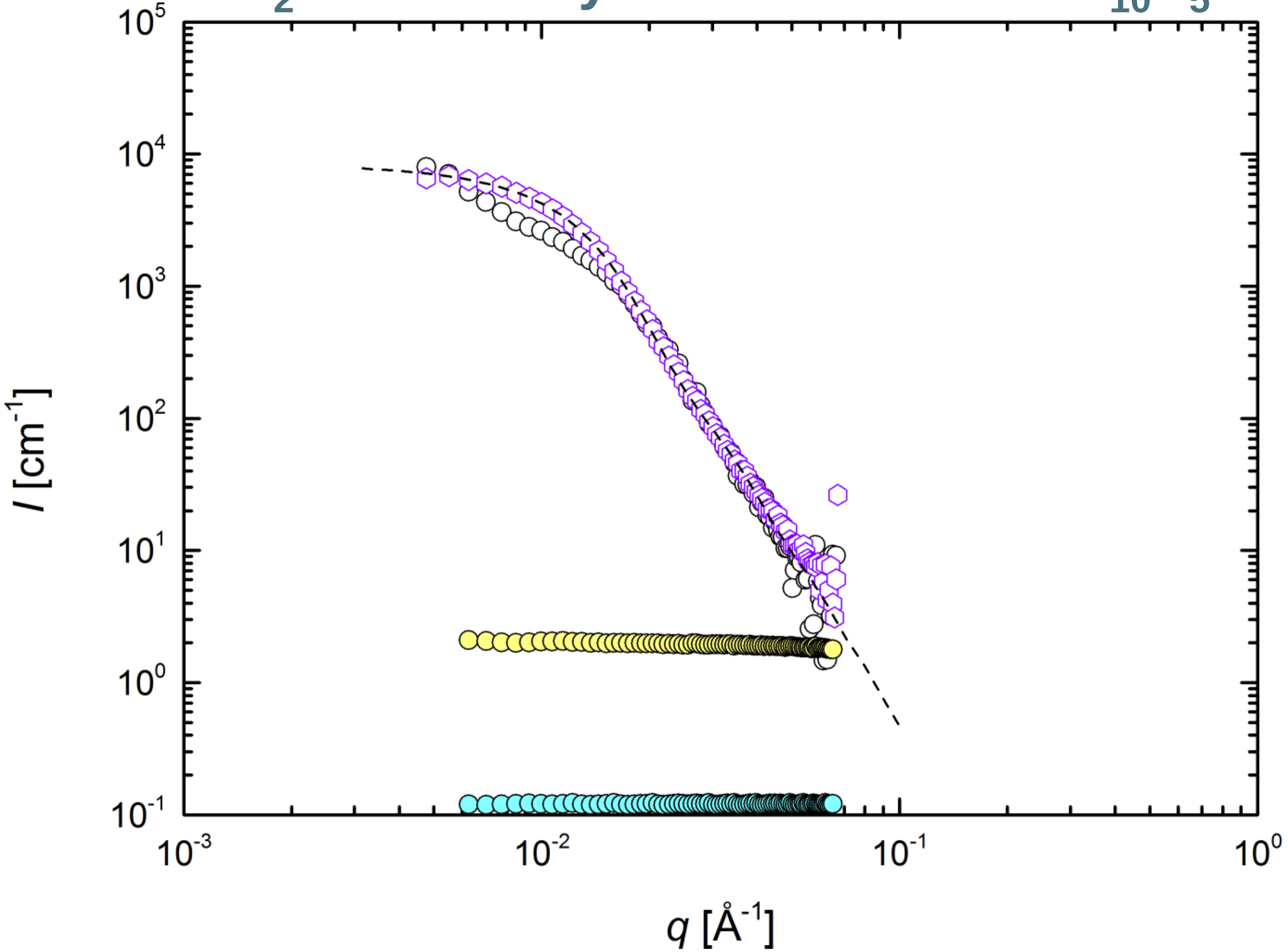
Microemulsion Formation Kinetics

$D_2O/NaCl$ – cyclohexane-h12 – $C_{10}E_5$



$\gamma_b = 0.05$
$\varepsilon = 0.001$
$T = 24.50°C$
$w_A = 0.11$

- $D_2O/NaCl$
- c-$B_6/C_{10}E_5$
- t = 22 ms
- t = 2163 ms

J. S. Pedersen, J Appl Crystallogr, 1994, 27, 595-608.
M. Kotlarchyk, S. H. Chen and J. S. Huang, Phys Rev A, 1983, 28, 508-511.
M. Gradzielski, D. Langevin, L. Magid and R. Strey, J Phys Chem-Us, 1995, 99, 13232-13238.
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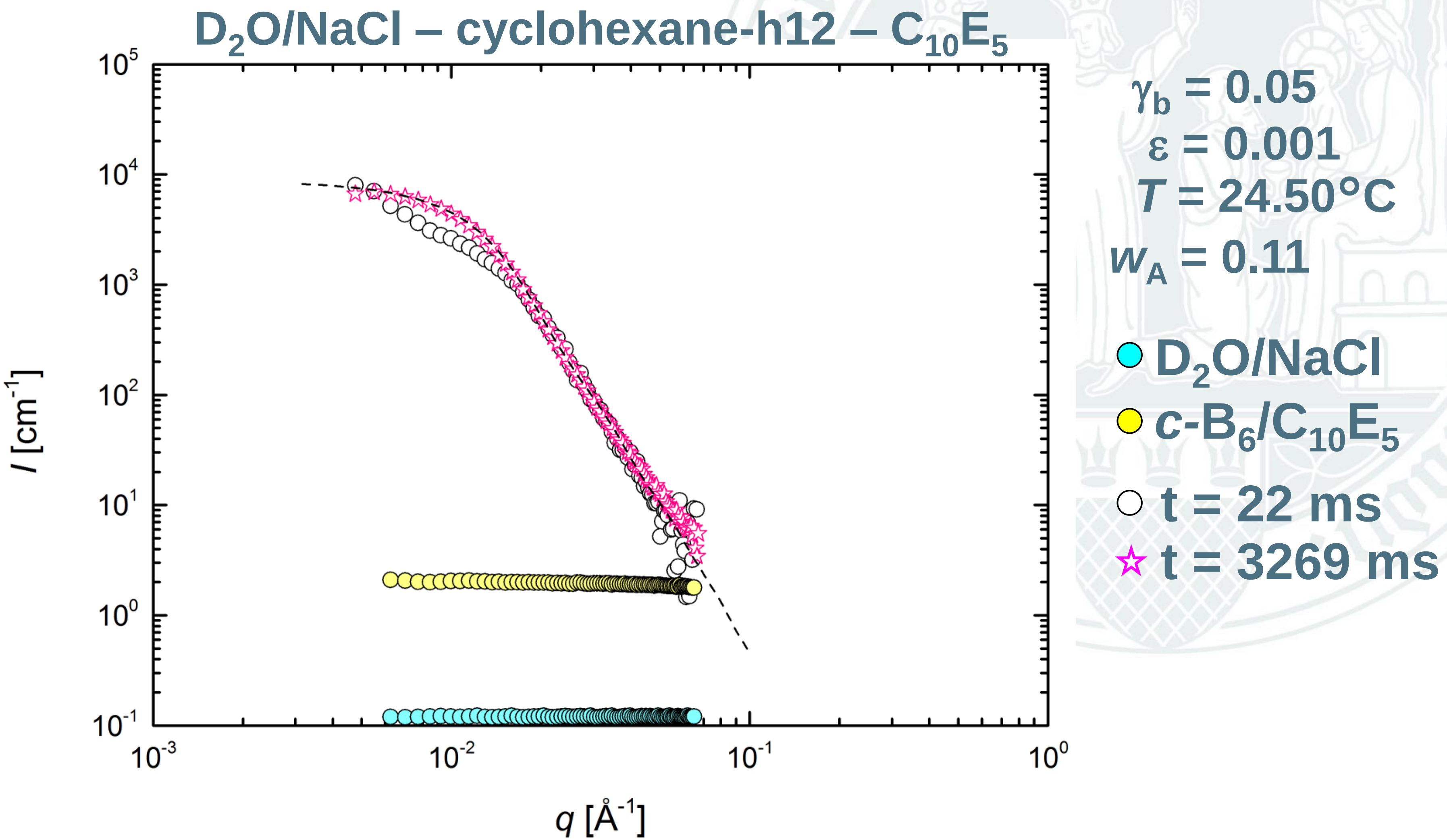
Microemulsion Formation Kinetics



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M. Kotlarchyk, S. H. Chen and J. S. Huang, Phys Rev A, 1983, 28, 508-511.
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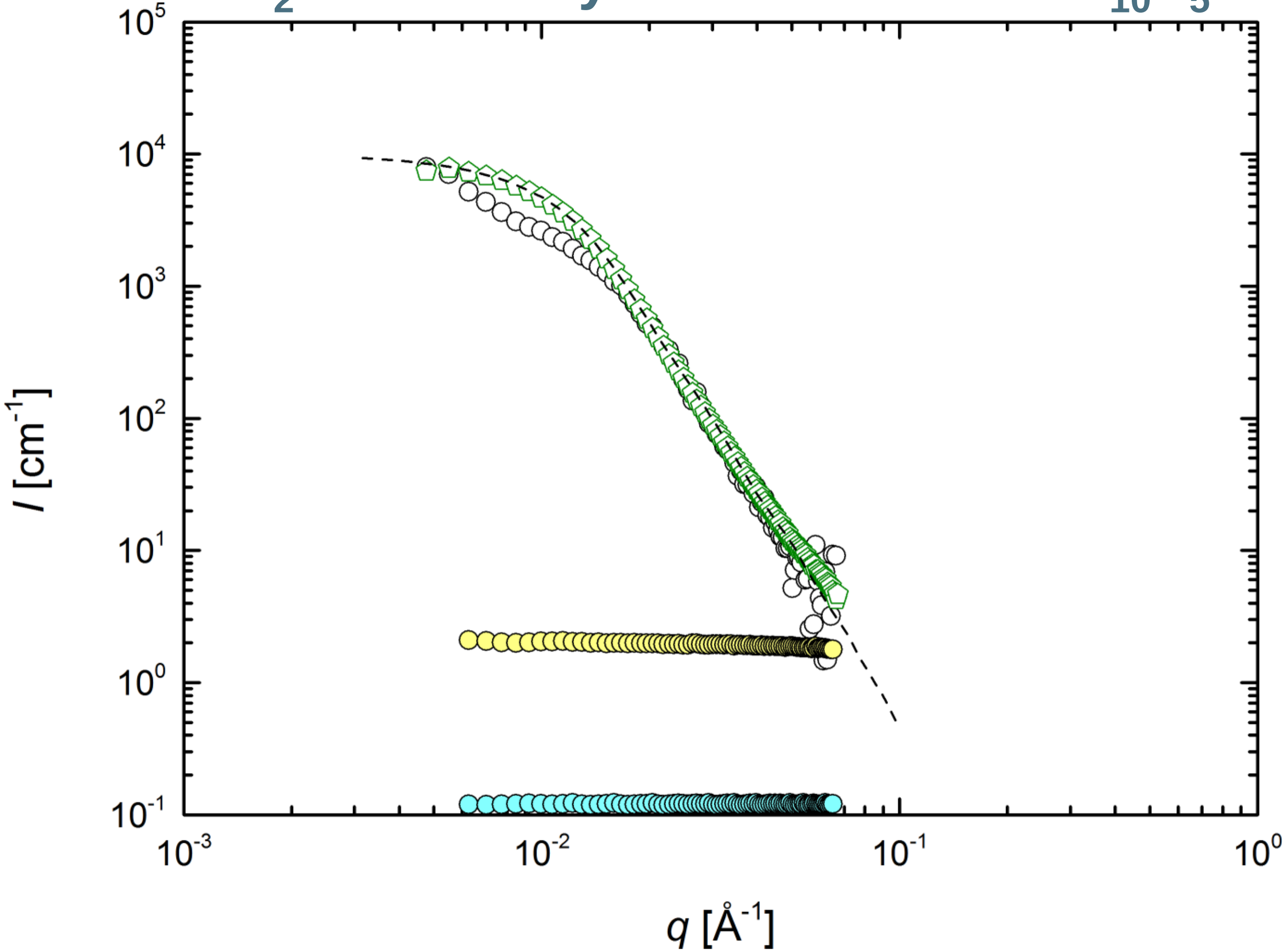
Microemulsion Formation Kinetics

D_2O/NaCl – cyclohexane-h12 – $C_{10}E_5$



$\gamma_b = 0.05$

$\varepsilon = 0.001$

$T = 24.50°C$

$w_A = 0.11$

- D_2O/NaCl
- *c*-$B_6/C_{10}E_5$
- t = 22 ms
- t = 180000 ms

J. S. Pedersen, J Appl Crystallogr, 1994, 27, 595-608.
M. Kotlarchyk, S. H. Chen and J. S. Huang, Phys Rev A, 1983, 28, 508-511.
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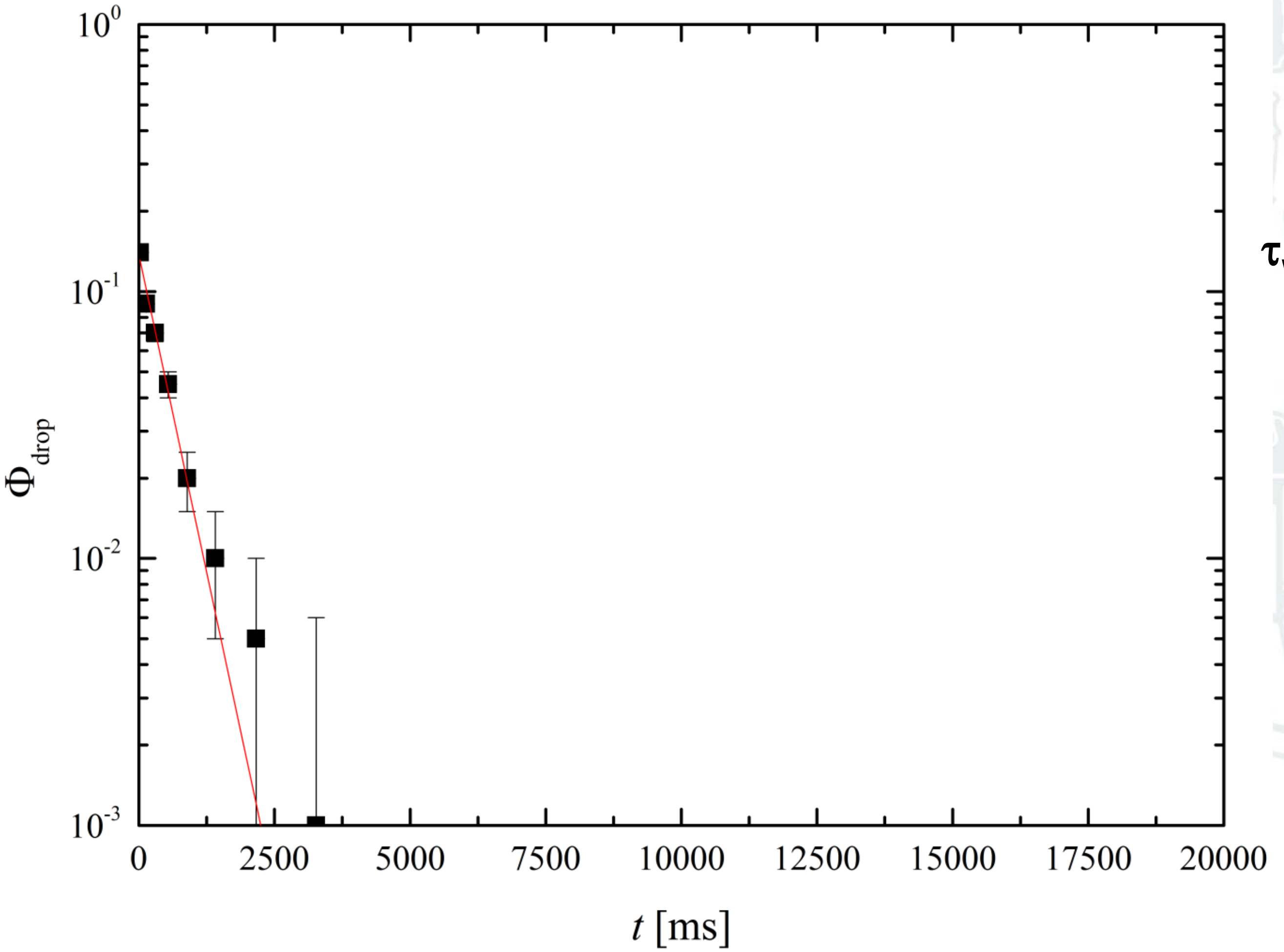
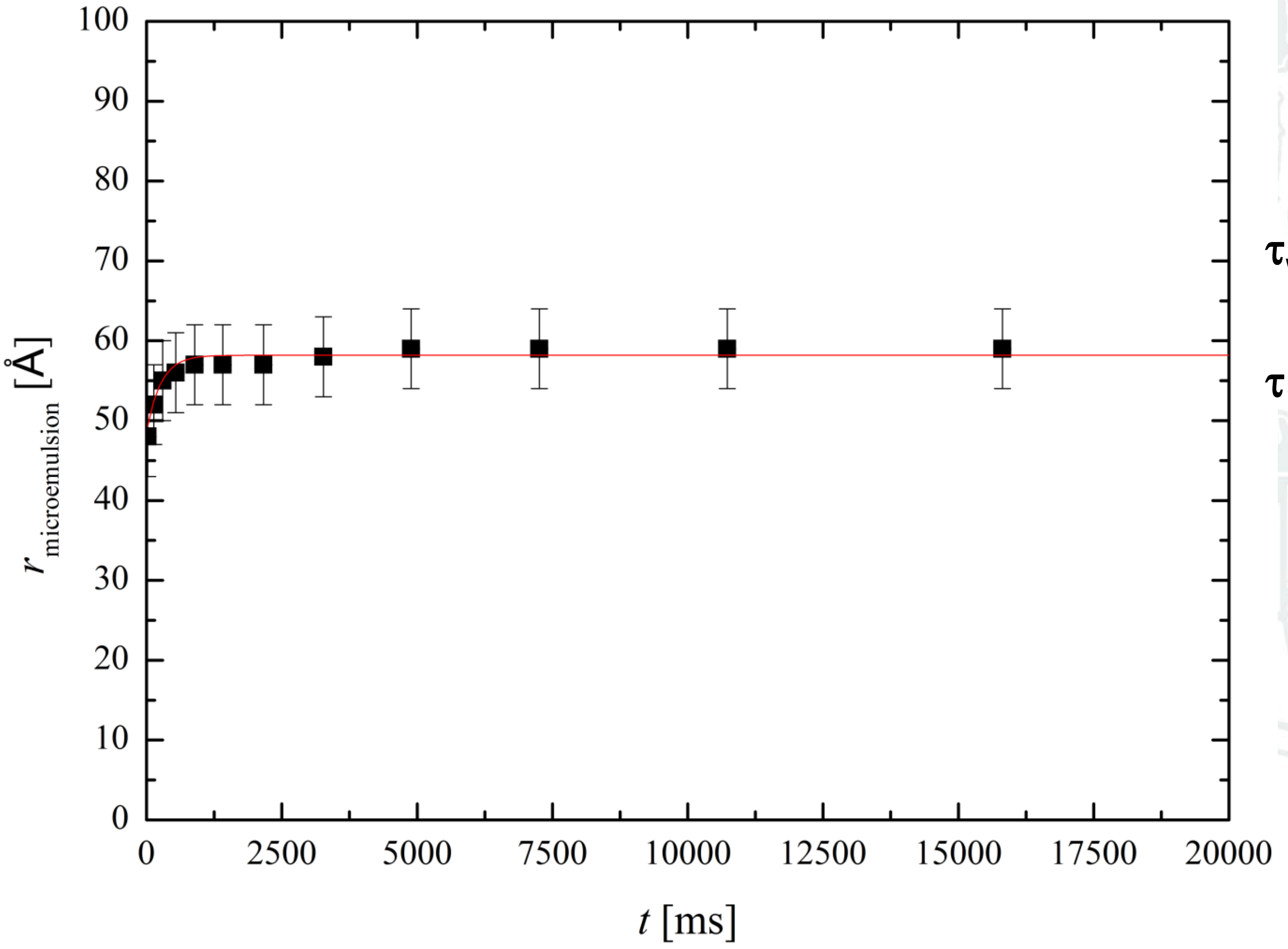
Time-resolved Water Uptake



$$\Phi_{drop}(t) = A \cdot e^{-\frac{t}{\tau}}$$

$\tau_{water\text{-}uptake}$ **= (430±35) ms**

Time-resolved Radial Growth



$$r_{\mu E}(t) = A \cdot e^{+\frac{t}{\tau}} + r_{\mu E,0}$$

$\tau_{\text{water-uptake}}$ **= (430±35) ms**

$\tau_{\text{radial growth}}$ **= (260±99) ms**

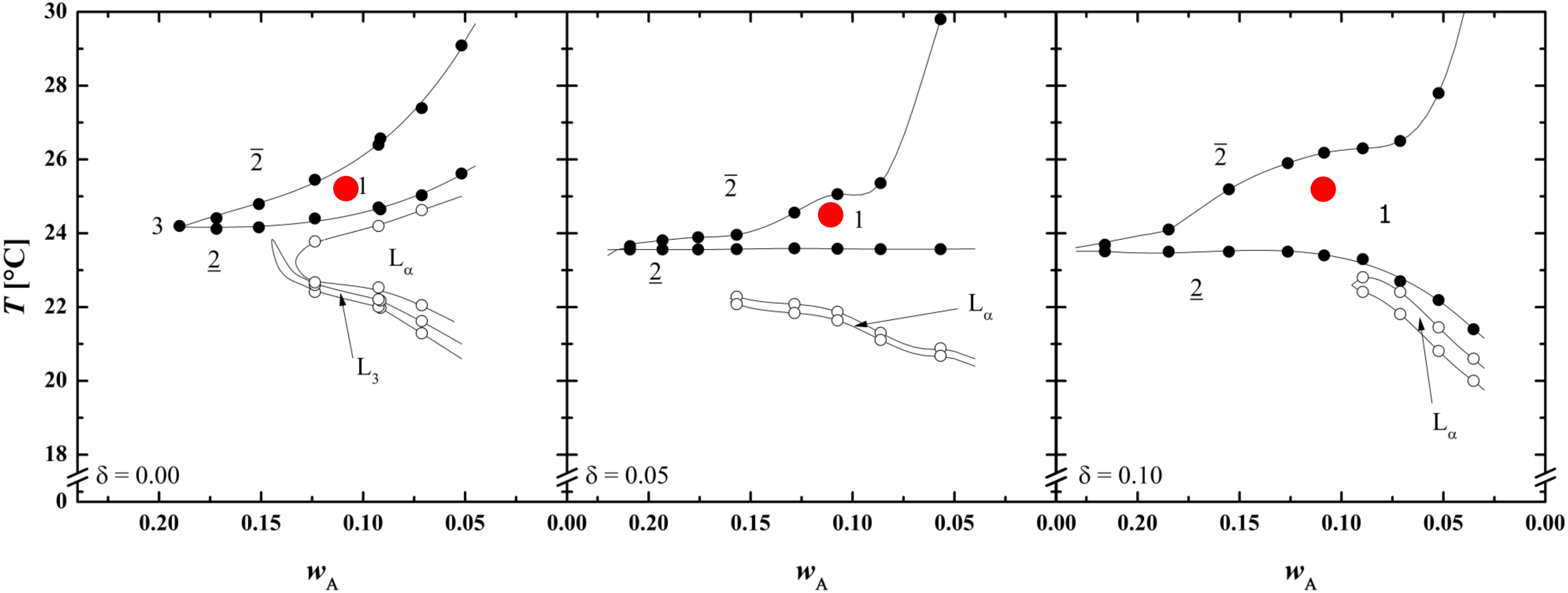
The Influence of Amphiphilic Polymers

D_2O/NaCl – cyclohexane-d12 – $C_{10}E_5$/PEB4.8-PEO4.8

$\varepsilon = 0.001$, $\gamma_b = 0.05$

Bulk contrast

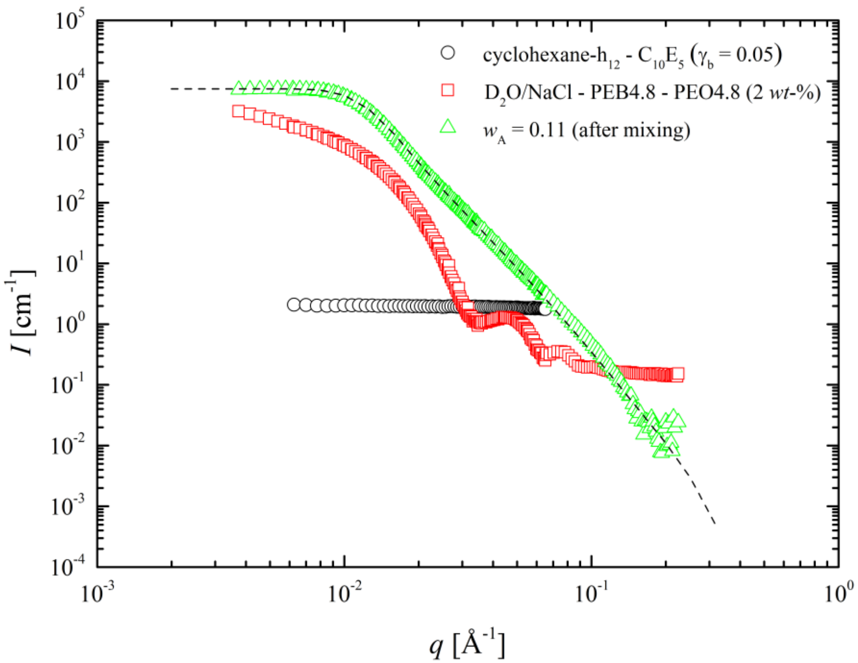
Film contrast

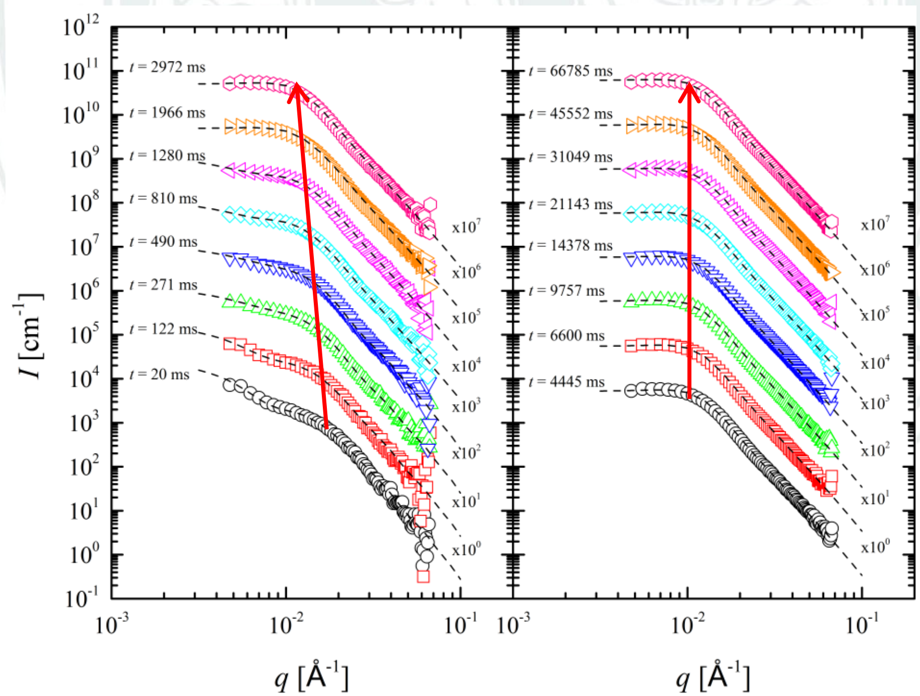


The Influence of Amphiphilic Polymers

D_2O/NaCl – cyclohexane-h12 – $C_{10}E_5$/PEB4.8-PEO4.8

$\varepsilon = 0.001$, $\gamma_b = 0.05$, $\delta = 0.05$ (bulk contrast)





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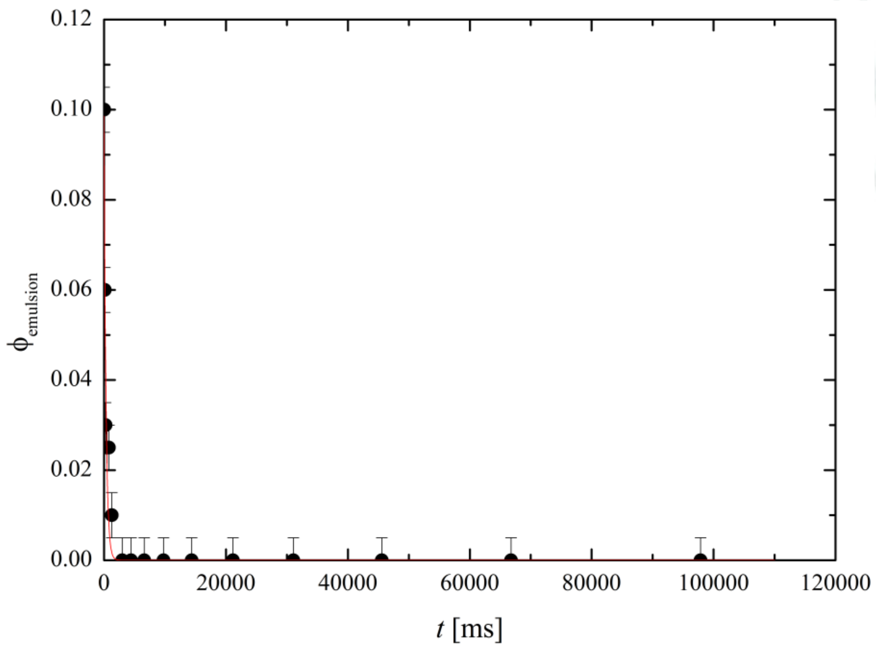
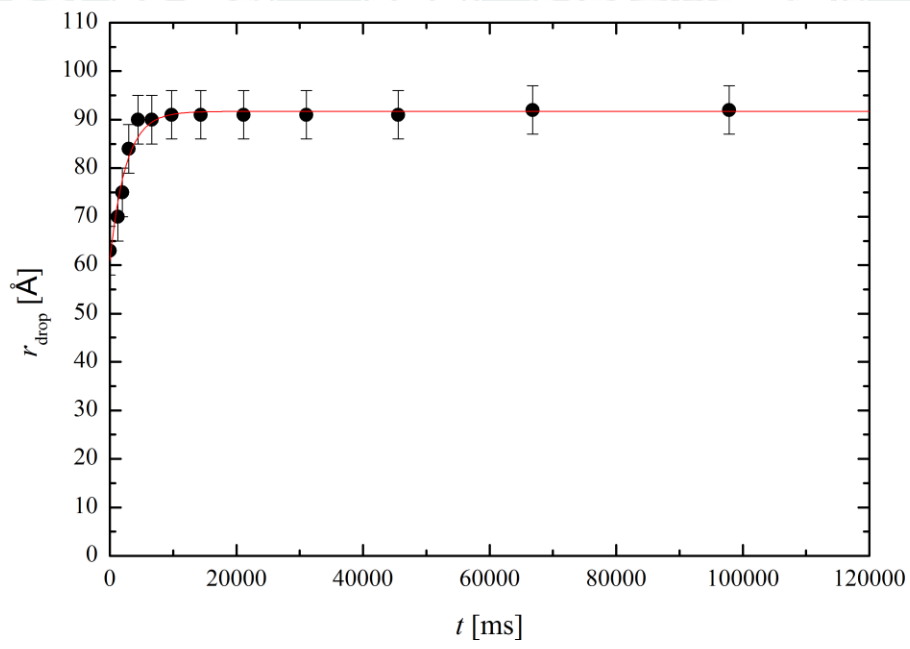
The Influence of Amphiphilic Polymers

D_2O/NaCl – cyclohexane-h12 – $C_{10}E_5$/PEB4.8-PEO4.8
$\varepsilon = 0.001$, $\gamma_b = 0.05$, $\delta = 0.05$ (bulk contrast)



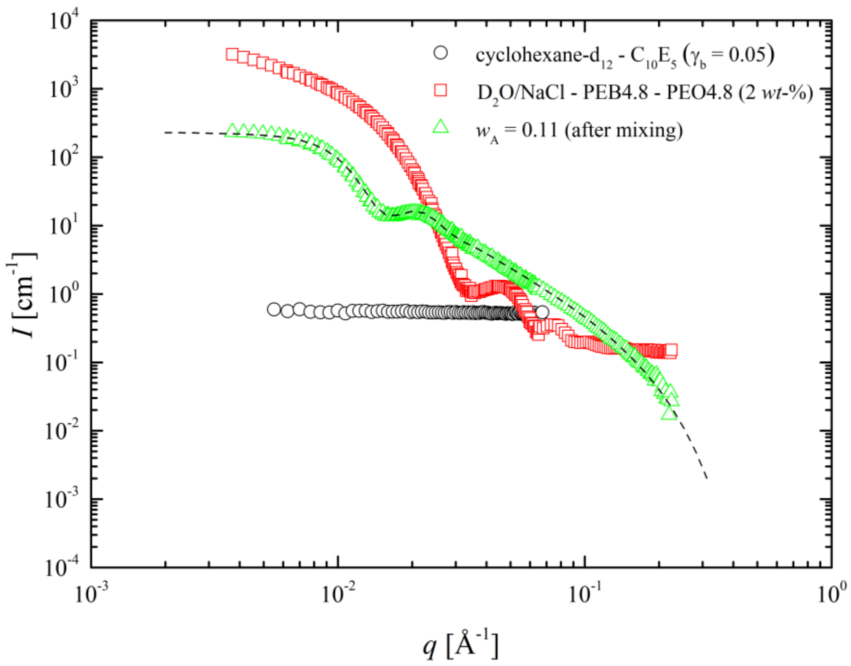


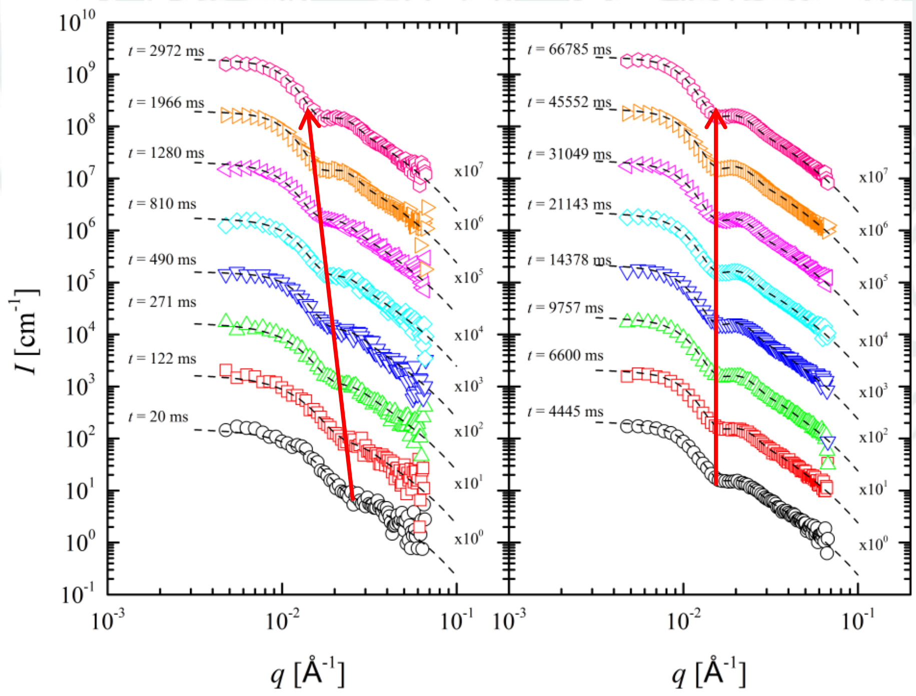
$\tau_{water\text{-}uptake}$ = (313±48) ms

$\tau_{radial\ growth}$ = (1600±167) ms

The Influence of Amphiphilic Polymers

D_2O/NaCl – cyclohexane-d/h12 – $C_{10}E_5$/PEB4.8-PEO4.8
ε = 0.001, γ_b=0.05, δ = 0.05 (film contrast)





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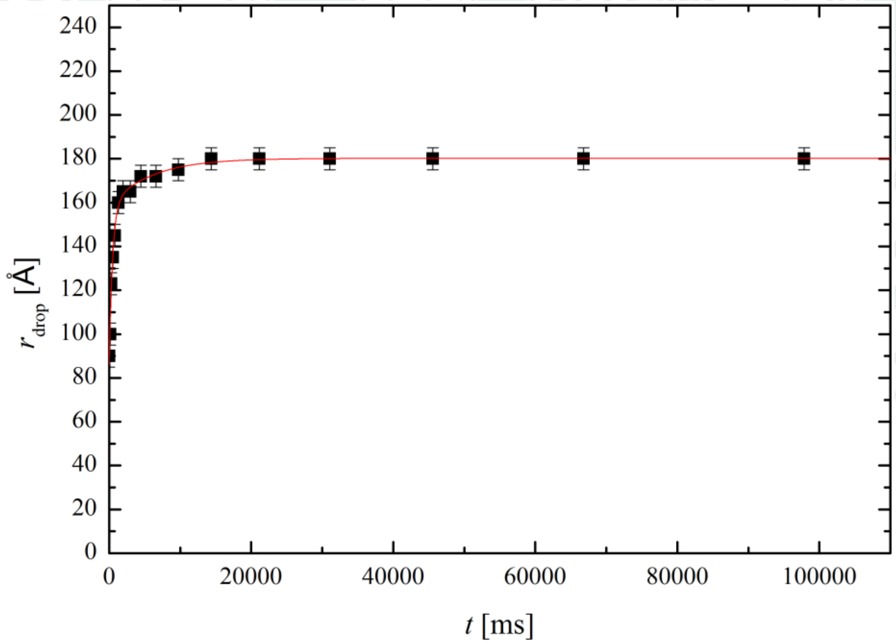
The Influence of Amphiphilic Polymers

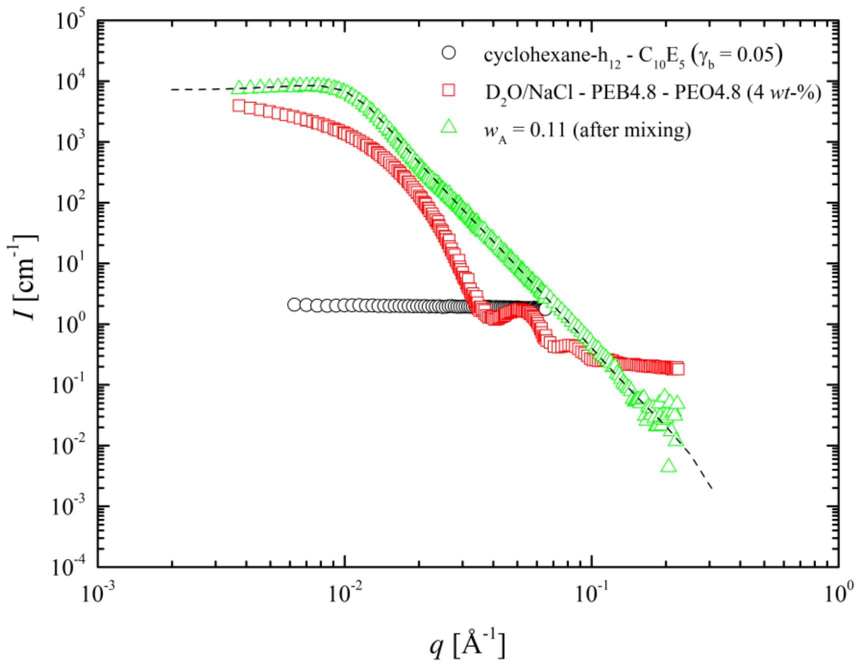
D_2O/NaCl – cyclohexane-h12 – $C_{10}E_5$/PEB4.8-PEO4.8
ε = 0.001, γ_b=0.05, δ = 0.05 (film contrast)

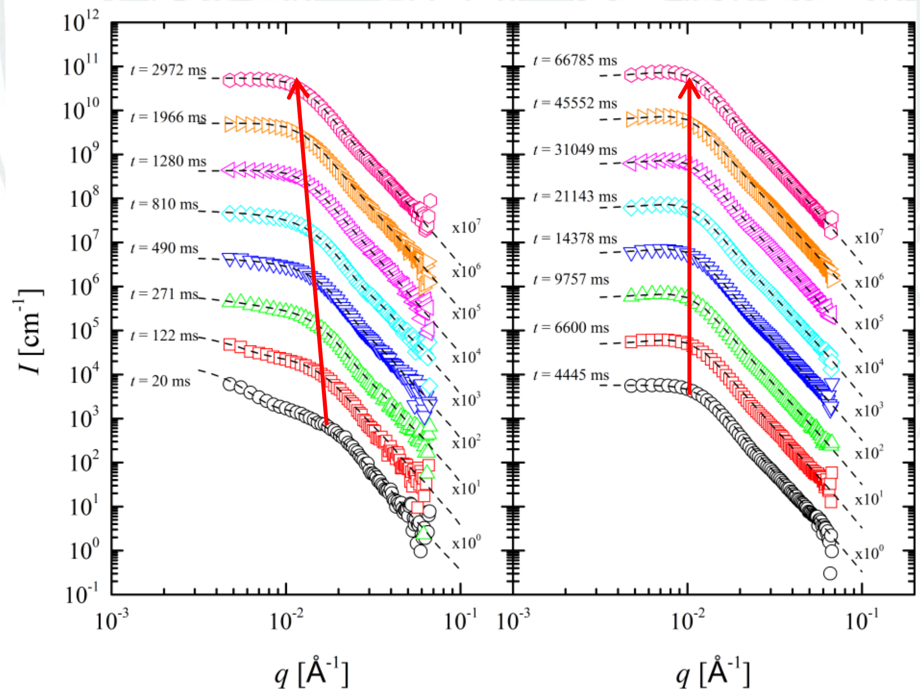


$\tau_{\text{radial growth}}$ = (1725±138) ms

The Influence of Amphiphilic Polymers

D_2O/NaCl – cyclohexane-h12 – $C_{10}E_5$/PEB4.8-PEO4.8
$\varepsilon = 0.001$, $\gamma_b = 0.05$, $\delta = 0.10$ (bulk contrast)





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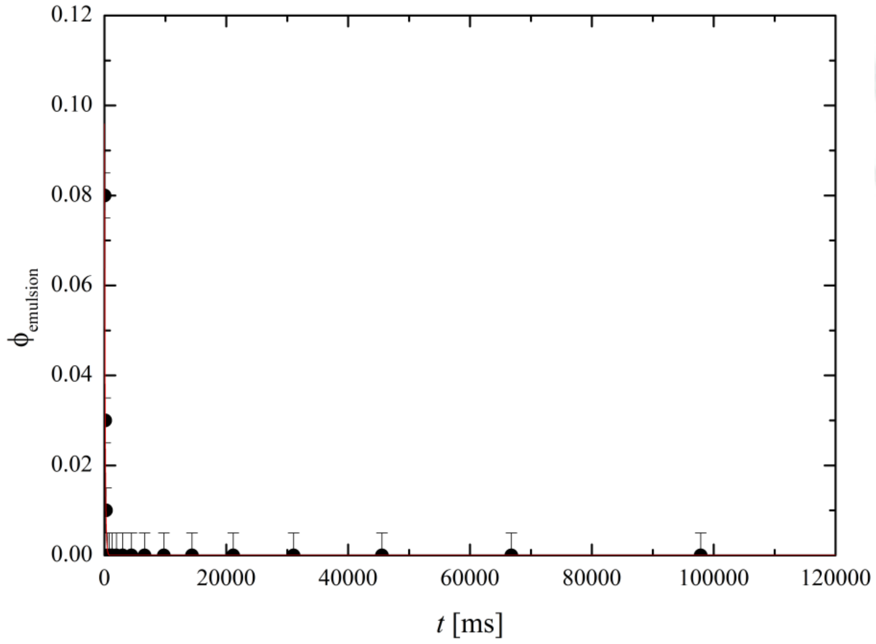
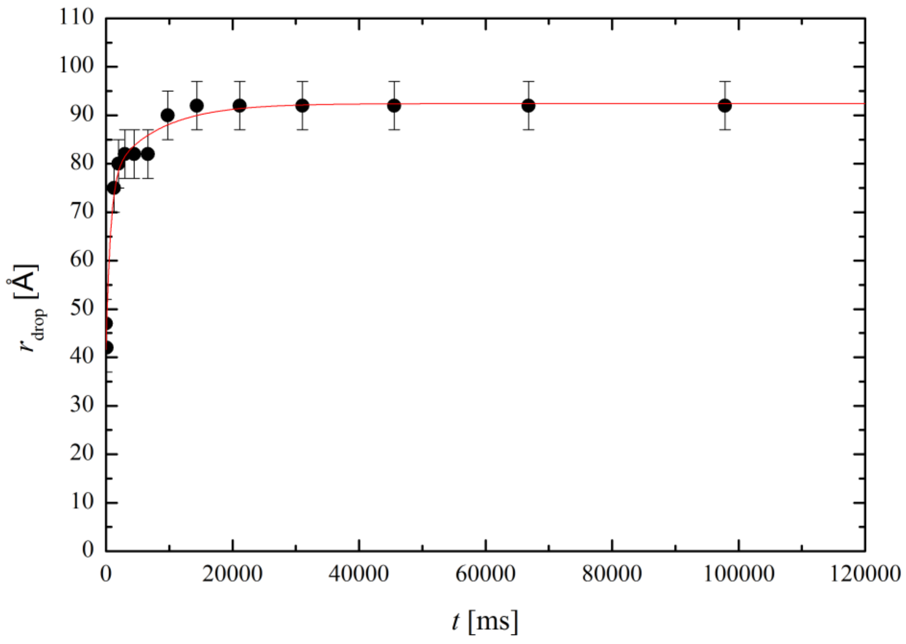
The Influence of Amphiphilic Polymers

D_2O/NaCl – cyclohexane-h12 – $C_{10}E_5$/PEB4.8-PEO4.8
$\varepsilon = 0.001$, $\gamma_b = 0.05$, $\delta = 0.10$ (bulk contrast)



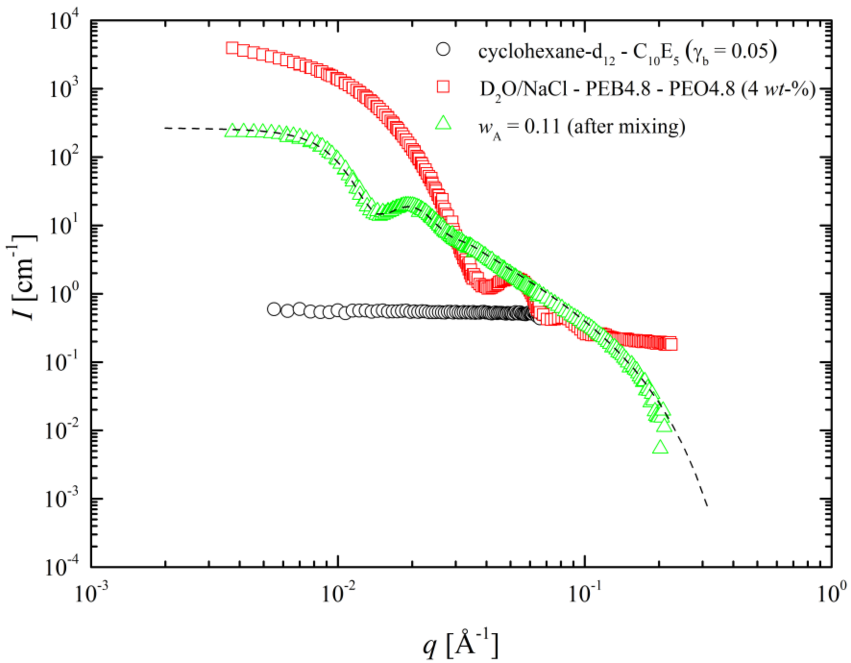


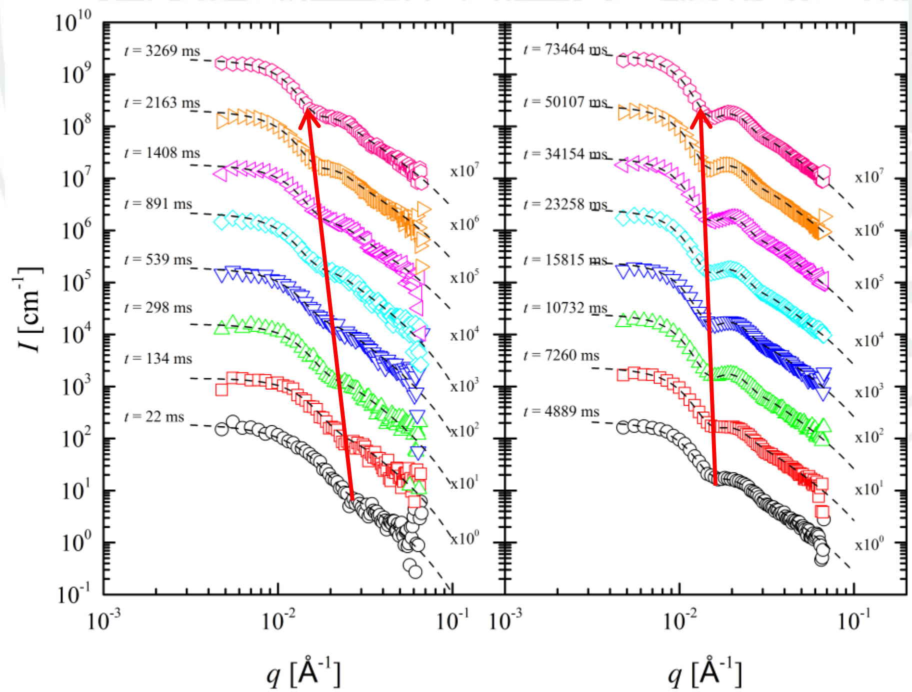
$\tau_{water\text{-}uptake}$ = (98±13) ms

$\tau_{radial\ growth}$ = (6215±1436) ms

The Influence of Amphiphilic Polymers

D_2O/NaCl – cyclohexane-d/h12 – $C_{10}E_5$/PEB4.8-PEO4.8
ε = 0.001, γ_b=0.05, δ = 0.10 (film contrast)





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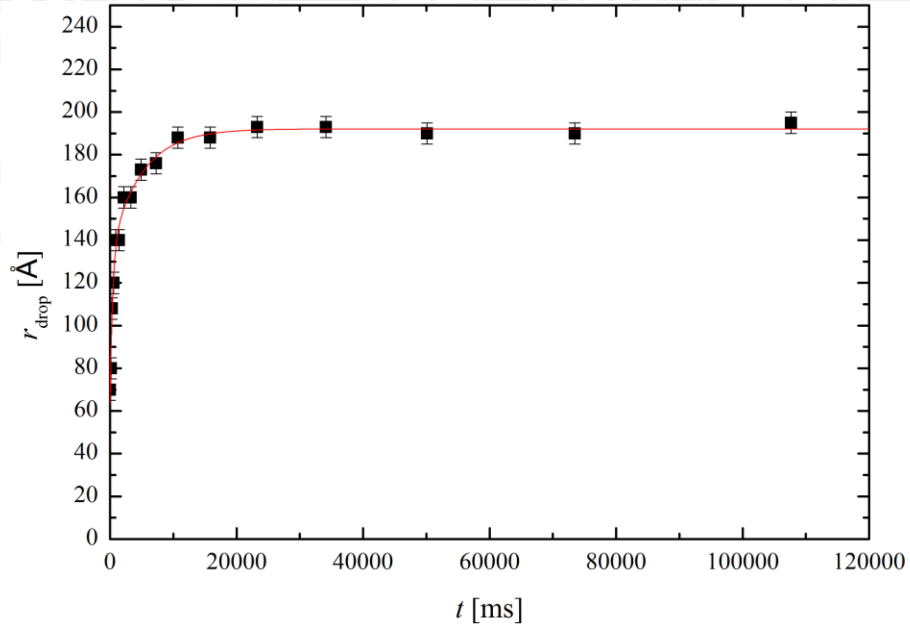
The Influence of Amphiphilic Polymers

D_2O/NaCl – cyclohexane-h12 – $C_{10}E_5$/PEB4.8-PEO4.8
$\varepsilon = 0.001$, $\gamma_b=0.05$, $\delta = 0.10$ (film contrast)



$\tau_{radial\ growth}$ = (5925±1876) ms

Theoretical background

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

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

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

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

Approximate structure size: $\xi \approx 2\pi / q_{\max/\min}$

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