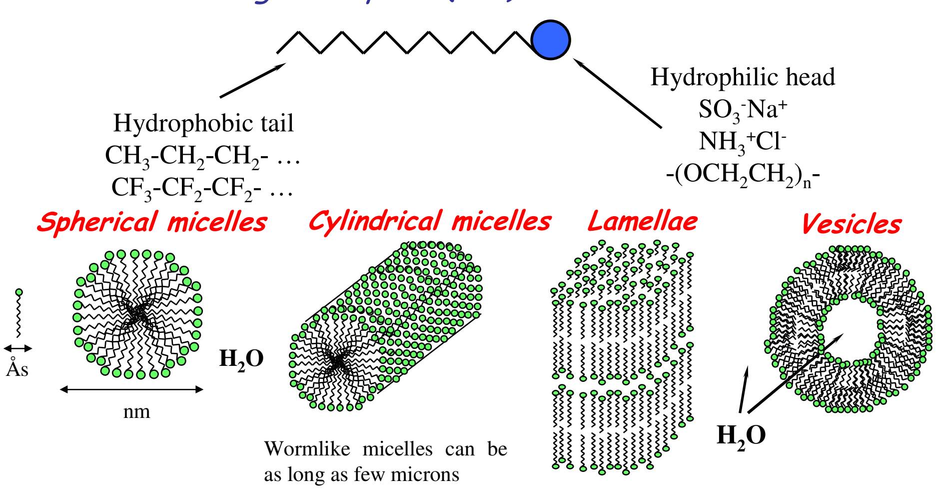
Data Analysis Exercise 1: Investigation of the Shape Fluctuations of a Spherical Surfactant Shell in a Microemulsion by NSE

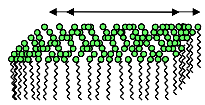
Surfactant aggregation in water

A surfactant ("Surface Active Agent") is soluble both in water and in organic liquids (oils)

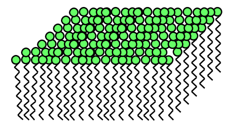


Properties of the surfactant film

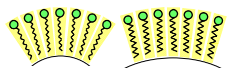
- Interfacial tension
- Lateral elasticity



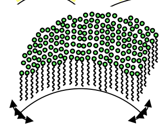
Surfactant film



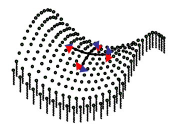
- Spontaneous curvature



- Bending elasticity



- Saddle splay elasticity



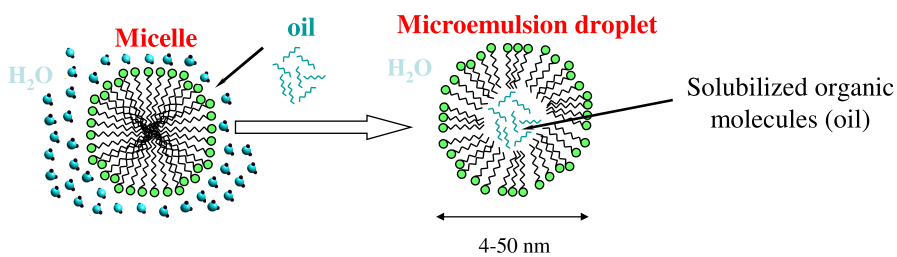
Properties of the surfactant film change with:
- Molecular structure
- Additives
- Ionic strength
- Co-surfactant
- Temperature, pressure etc.

$$E = \int \left[\gamma + \frac{k}{2}\left(\frac{1}{R_1} + \frac{1}{R_2} - \frac{2}{R_s}\right) + \frac{\bar{k}}{R_1 R_2} \right] dS$$ Helfrich Free Energy

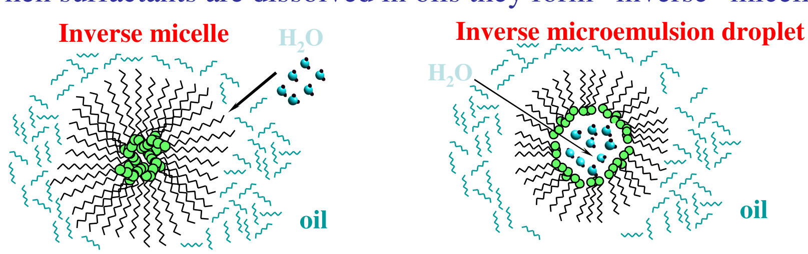
W. Helfrich, Z. Naturforsch. **28C**, 693 (1973).

Micelles and Microemulsions

Oils and water do not mix?!? The surfactants help them mix.



When surfactants are dissolved in oils they form "inverse" micelles, …



Microemulsion: How to study them

Structure

- Light Scattering
- Small Angle Scattering (Neutrons: SANS; x-rays: SAXS)
  - Large length scales (10 Å-1000 Å)
  - 'Low resolution diffraction technique'

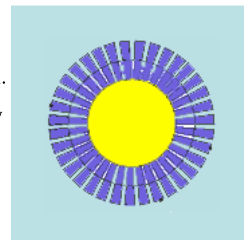
SANS:

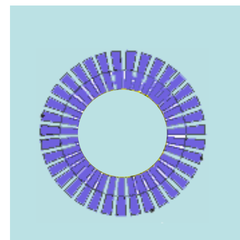
The intensity is the FT of the contrast distribution.

Contrast: Difference in Scattering Length Density

$$\rho = \frac{d}{M_w} N_A \sum_i b_i^{coh}$$

Contrast Matching Technique





Microemulsion: How to study them

Dynamics

Microemulsions move in solution because of thermal energy.

- Diffusion
- Shape fluctuations

Experimental techniques:

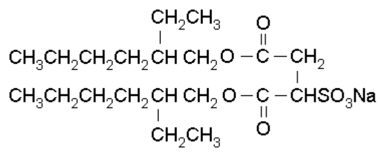
- Dynamic Light Scattering
- Nuclear magnetic resonance
- Neutron Spin-Echo (NSE)

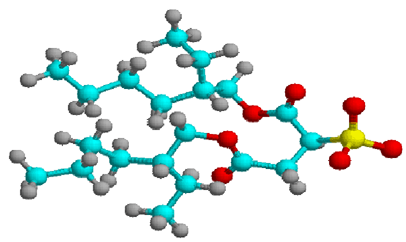
NSE: T scale ~ 0.01 – 100 ns, L scale 1 – 100 Å

The Sample

Shape fluctuations in AOT/water/hexane microemulsion

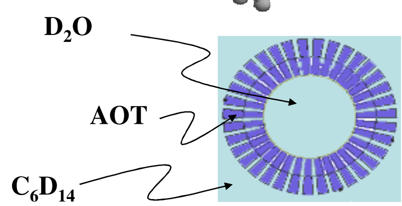
AOT



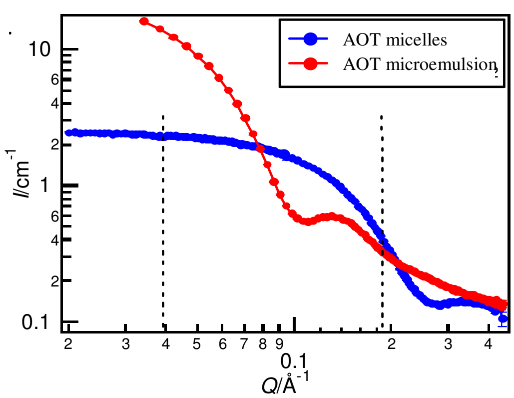


Inverse Microemulsion droplet

- Translational Diffusion
- Shape Fluctuations



SANS data



	σ_S (barn)	b^{coh} (fm)	b^{incoh} (fm)
H	82.03	-3.741	25.274
D	2.05	6.671	4.04

SLD ($\times 10^{-6}$ Å^{-2})

n-hexane	-0.67
H_2O	-0.56
d-hexane	6.14
D_2O	6.35
AOT	0.10

Data Analysis

Translational Diffusion ⇒ $$\frac{I(Q,t)}{I(Q,0)} = \exp\left[-DQ^2t\right]$$

$AOT/D_2O/C_6D_{14}$ Microemulsion
Translational Diffusion + shape fluctuations ⇒ $$\frac{I(Q,t)}{I(Q,0)} = \exp\left[-D_{eff}(Q)Q^2t\right]$$

The two dynamical processes are statistically independent.

$$D_{eff}(Q) = D_{tr} + D_{def}(Q)$$

$$D_{eff}(Q) = D_{tr} + \frac{5\lambda_2 f_2(QR_0)\langle|a_2|^2\rangle}{Q^2\left[4\pi[j_0(QR_0)]^2 + 5f_2(QR_0)\langle|a_2|^2\rangle\right]}$$

$$f_2(QR_0) = [4j_2(QR_0) - QR_0 j_3(QR_0)]^2$$

The goal is the bending modulus, k

$$D_{eff}(Q) = D_{tr} + \frac{5\lambda_2 f_2(QR_0)\langle|a_2|^2\rangle}{Q^2\left[4\pi[j_0(QR_0)]^2 + 5f_2(QR_0)\langle|a_2|^2\rangle\right]}$$

$$\boxed{k = \frac{1}{48}\left[\frac{k_BT}{\pi p^2} + \lambda_2 \eta R_0^3 \frac{23\eta' + 32\eta}{3\eta}\right]}$$

λ_2 – the damping frequency – **frequency of deformation**

$\langle|a|^2\rangle$ – mean square displacement of the 2-nd harmonic – **amplitude of deformation**

p^2 – size polydispersity, measurable by SANS or DLS

η and η' are the solvent and core viscosities

B. Farago, et al., *Phys. Rev. Lett.*, 65, 3348 (1990).
Y. Kawabata, et al., *Phys. Rev. Lett,*, 92, 056103 (2004).