Shape Fluctuations of Microemulsion Droplets Studied by Neutron Spin Echo (NSE)

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Content

- Surfactant aggregates in solution
- Why NSE?
- Experimental system
- Data analysis

Surfactants

Oils and water do not mix! Why?
Water is a polar liquid, $\varepsilon = 81$
Oils are non polar, $\varepsilon \sim 2$
(ε - dielectric const.)

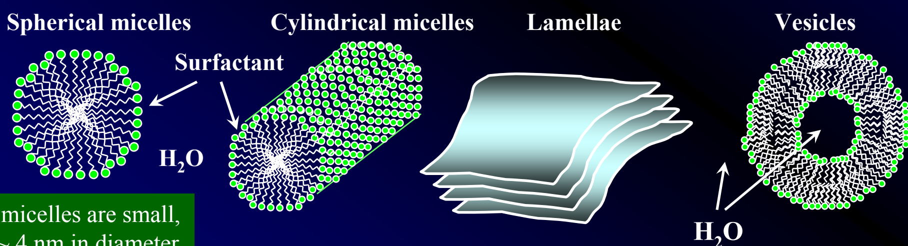
Surfactant = “Surface Active Agent”

Surfactant molecule: two portions

Hydrophobic tail
CH_3-CH_2-CH_2- …
CF_3-CF_2-CF_2- …

Hydrophilic head
$SO_3^-Na^+$
$NH_3^+Cl^-$
-$(OCH_2CH_2)_n$-

When surfactants are dissolved in water:
- reduce the surface tension because they are adsorbed on the surfaces
- form variety of aggregates – micelles, lamellae, bicelles, vesicles, etc



micelles are small,
~ 4 nm in diameter

Applications

Surfactants are very useful to:

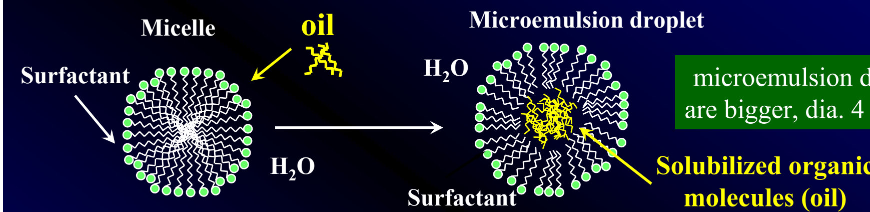
• Reduce the interfacial tension
• Solubilize oils in water
• Stabilize liquid films & foams
• Modify the interparticle interactions
• Stabilize dispersions
• Modify the contact angle & wetting
• …

Surfactants in our daily life:

• Food – mayonnaise, margarine, ice cream, milk, …
• Industry – lubricants, stabilizers, emulsifiers, foamers, detergents, …
• Medicine – drugs, bio applications, (lungs), …
• Cosmetics – moisturizers, lotions, healthcare products …
• Agriculture – aerosols, fertilizers …
• …

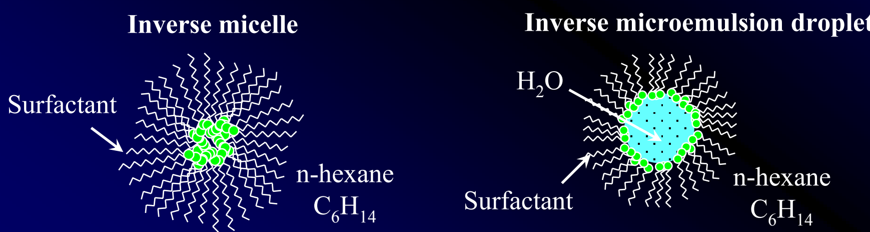
Micellar properties

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



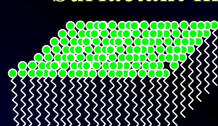
microemulsion droplets are bigger, dia. 4 - 50 nm

Surfactants form "inverse" micelles in oils:



Properties of the surfactant film

Surfactant film

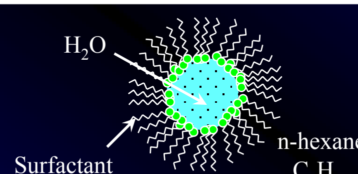


Parameters:
- Molecular structure
- Additives
- Ionic strength
- Co-surfactant
- Temperature, pressure etc.

Properties of the surfactant film:
- Interfacial tension
- Lateral elasticity
- Spontaneous curvature
- Bending elasticity
- Saddle splay elasticity

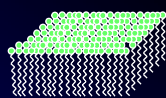
$$E = \int \left[\gamma + \frac{k}{2}\left(\frac{1}{R_1} + \frac{1}{R_2} - \frac{2}{R_s} \right) + \frac{\bar{k}}{R_1 R_2} \right] dS$$

Microemulsions:
- Thermodynamically stable, isotropic, and optically transparent solutions
- $R \sim 2 - 50$ nm (good scatterers)
- The curvature of the surfactant film can be controlled

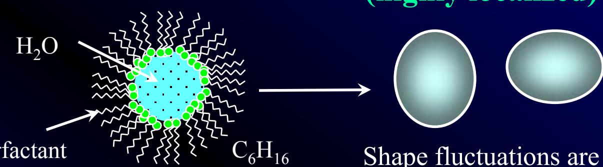


How to measure bending elasticity

Surfactant film:
bending elasticity



The surfactant film is a very soft material
Bending elasticity ⇒ Thermal undulations
(highly localized)



Shape fluctuations are in a very short time and length scales!

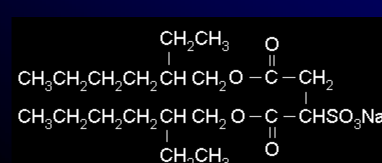
- SANS: static method
- NMR relaxation times: relaxation model?
- Dynamic light scattering: large T & L scales
- **NSE:** T scale ~ 0.01 - 100 ns, L scale ~ 1 - 10 nm

Experimental

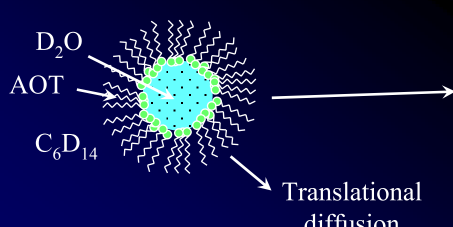
Shape fluctuations in **AOT/D_2O/C_6D_{14}** microemulsion

Surfactant molecule:

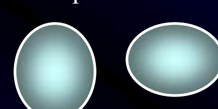
AOT



Inverse microemulsion droplet



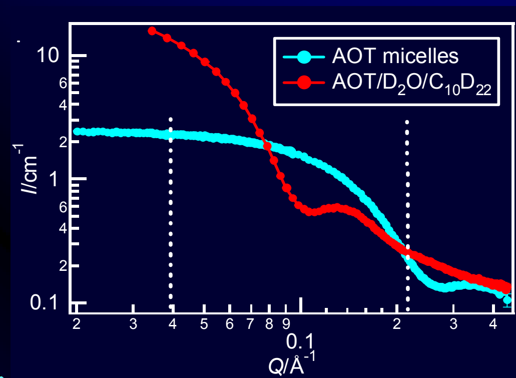
Shape fluctuations

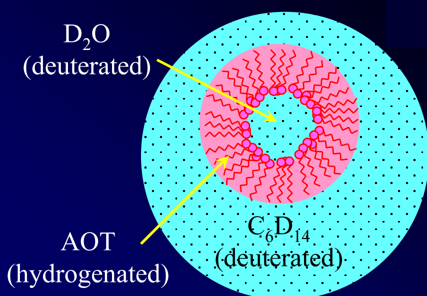


Shell contrast

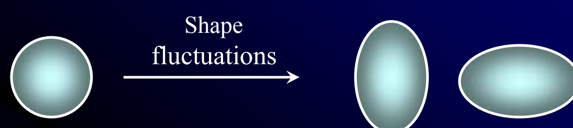
cross section (barn)
H: 82.0 D: 7.6

SLD ($\times 10^{-6}$ Å^{-2})	
n-hexane	-0.49
H_2O	-0.56
d-hexane	6.5
D_2O	6.4

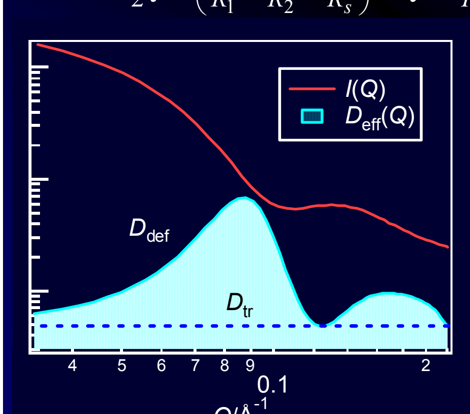




Data analysis



$$E_{bend} = \frac{k}{2}\int dS\left(\frac{1}{R_1}+\frac{1}{R_2}-\frac{2}{R_s}\right)+\bar{k}\int dS\,\frac{1}{R_1 R_2}$$



Expansion of *r* in spherical harmonics with amplitude *a*:

$$r(\Omega) = r_0\left(1+\sum_{l,m} a_{lm}\mathrm{Y}_{lm}(\Omega)\right)$$

Frequency of oscillations of a droplet:

$$\lambda_2 = \frac{k}{\eta R_0^3}\left[4\frac{R_0}{R_s} - 3\frac{\bar{k}}{k} - \frac{3k_B T}{4\pi k} f(\phi)\right]\frac{24\eta}{23\eta' + 32\eta}$$

Summary of data analysis

Micelles:

translational diffusion

$$\longrightarrow \frac{I(Q,t)}{I(Q,0)} = \exp\left[-D_{eff}\, Q^2 t\right]$$

Microemulsions:

translational diffusion + shape deformations

$$\longrightarrow \frac{I(Q,t)}{I(Q,0)} = \exp\left[-D_{eff}(Q) Q^2 t\right]$$

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

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

$$f_2(QR_0) = 5\left[4 j_2(QR_0) - QR_0 j_3(QR_0)\right]^2$$

Goal: Bending modulus of elasticity

$$k = \frac{1}{48}\left[\frac{k_B T}{\pi p^2} + \lambda_2 \eta R_0^3 \frac{23\eta' + 32\eta}{3\eta}\right]$$

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

$<|a|^2>$ – mean square displacement of the 2-nd harmonic – **amplitude of deformation**

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

Summary

- **NSE is a dynamic scattering method that yields the intermediate scattering function *I*(*q*,*t*). NSE has the highest energy resolution among the neutron scattering methods, which is achieved by using the neutron precession in magnetic fields as an “internal” clock**

- **NSE is suitable for studies on soft condensed matter:**

- Brownian diffusion in micellar systems
- Shape fluctuations of lipid membranes and thin films
- Intra-molecular diffusion of proteins
- Local segmental diffusion of polymers in solution
- Intra- and inter- molecular dynamics of polymer melts and glasses
- Other thermal fluctuations of soft matter etc (time scale: 0.01 – 200 ns)

- **Some limitations:**

- The samples must produce strong scattering
- Hydrogenated samples in deuterated matrix are the best choice
- Samples must not be magnetic
- The scattering should be in appropriate *Q*-range ($0.04 < Q < 1.7$ Å^{-1})