# Emulsions – Part 1

Definition

Preparation methods

(some) Properties

Klaus Tauer
MPI Colloids and Interfaces
Am Mühlenberg, D-14476 Golm, Germany

# Dispersed Systems with Liquid Continuous Phases*

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| Dispersed phase | Technical term | Example |
|---|---|---|
| gas | foam | meringue, whipped cream |
| liquid | emulsion | milk, mayonnaise, butter |
| solid | sol, suspension | latex, paint, blood |

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Dispergere (Latin): to remove, to redistribute
Emulgere (Latin): to milk out
Suspendere (Latin): to keep in, to keep in floating

* water as continuous phase and an organic dispersed phase or vice versa (inverse emulsions)

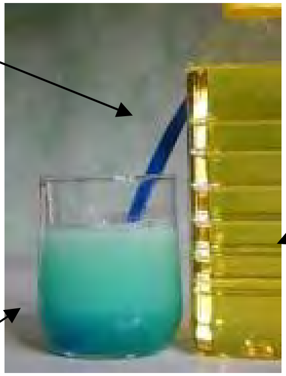
# What is an Emulsion?

- an emulsion is a liquid in liquid dispersion
- a (polymer) solution is also a liquid
  - (polymer) solutions can form emulsions
- an emulsion droplet interface has at any point the same interfacial tension (in contrast to many suspension particles)
- sometimes emulsions are subdivided arbitrarily regarding the droplet size (macro-, mini-, microemulsions) and hence general aspects might be lost

# Emulsification

| **comminution** | **condensation** |
|---|---|
| **(destruction)** | **(construction)** |
| mechanical energy or pressure is doing the job | thermodynamics takes care |
| the most widely used procedure (making a salad dressing in the kitchen) | swelling of colloidal systems such as micelles or solid (polymer) particles with liquids |

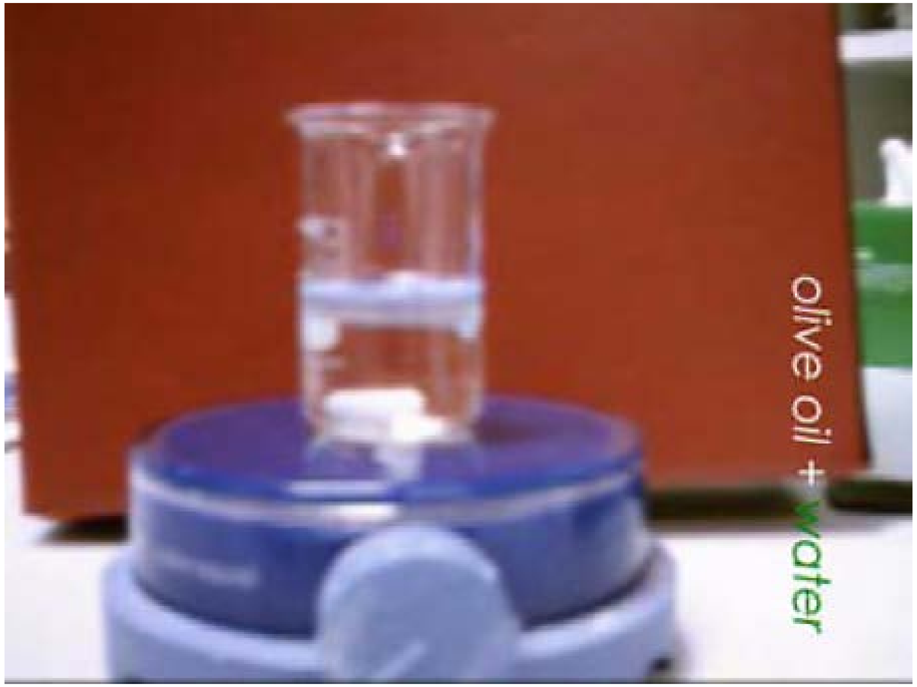
# Emulsification - Basics



this relation is (possibly) the oldest topic in colloid chemistry and much more also the oldest example of its practical application (pouring oil over water)

| <u>hydrophobe</u> | | <u>mediator</u> | | <u>hydrophile</u> |
|---|---|---|---|---|
| oily phase | ↔ | surfactants<br>emulsifiers<br>stabilizers | ↔ | water |

# Emulsion formation by comminution



olive oil & water

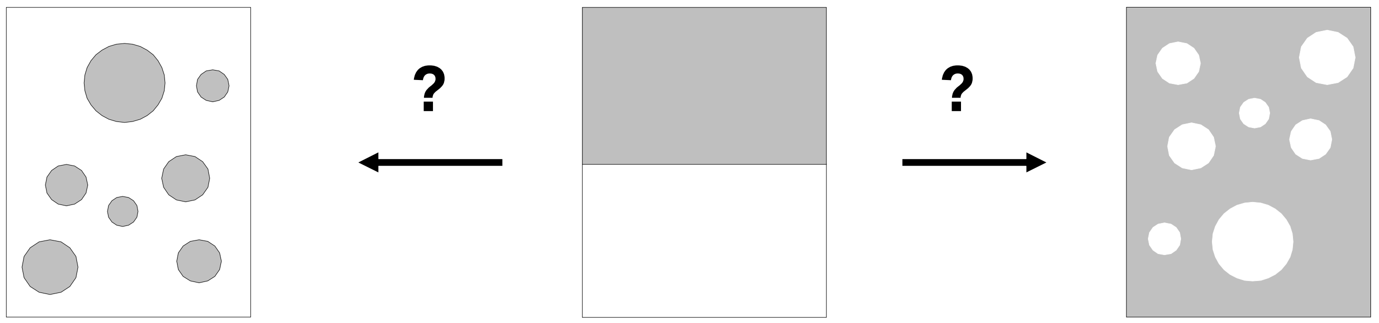
<u>Influenced by:</u>

- ✓comminution power
- ✓duration of the comminution
- ✓viscosity of both phases
- ✓interfacial tension
- ✓degradation after comminution is stopped

Σ a process with high complexity

# Comminution - Structure of the Emulsion

Which liquid forms the dispersed phase and which will be the continuous one?



influenced by the volume ratio of the liquids, the kind of the emulsifying agent, and its concentration in strong connection with the temperature.

most important property of the emulsifying agent is its solubility (in both phases) or in the case of the solid stabilizers the wetting behavior of both liquids

Bancroft's Rule (1912)

# Tests for Identification of Emulsion Types:

- Dilution test: emulsion can be diluted only with external phase
- Dye test: water or oil soluble dyes
- $CoCl_2$/filter paper test: filter paper impregnated with $CoCl_2$ and dried (blue) changes to pink when o/w emulsion is added
- Fluorescence: some oils fluoresce under UV light
- Conductivity: for ionic o/w emulsions
  (o/w emulsions conduct electric current)

# Action of Emulsifiers

main actions:

- reducing the interfacial tension between the phases
- forming a barrier between the phases

# Action of Emulsifiers

- promoting the formation of an emulsion,
- making it easier to prepare,
- producing finer droplet size,
- aiding stability to the dispersed state

controlling the type of emulsion that is to be formed: oil in water (O/W) or water in oil (W/O)

# Work of Emulsion Formation:

The increase in the energy of an emulsion compared to the non-emulsified components is equal to $\Delta W$.

This amount of energy can be considered as a measure of the thermodynamic instability of an emulsion.

$$\Delta W = \sigma \cdot \Delta A$$

$\Delta W$ is the free energy of the interface and corresponds to the reversible work brought permanently into the system during the emulsification process .

This makes an emulsion very prone to coalescence processes which lead to a decrease in $\Delta A$ and subsequently in $\Delta W$.

The conclusion is straightforward that ultimate stability against coalescence processes is only achieved if $\sigma$ approaches zero.

# Preparation of Emulsions by Comminution

input of mechanical energy by stirrers is the most important case

stirrers generate macro-eddies or macro-turbulences with a characteristic length in the order of the stirrer diameter.

macro-eddies decompose into micro-eddies with a characteristic length $\lambda$ which is also called **Kolmogorov length**

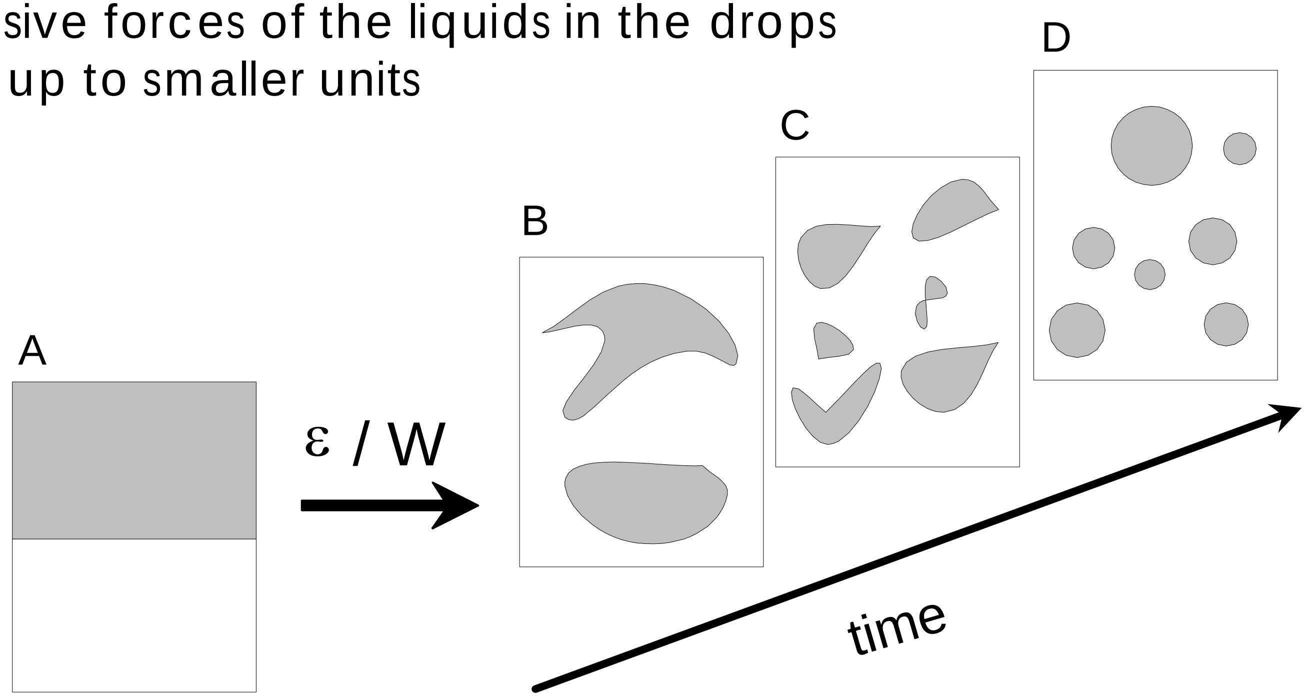
micro-eddies are finally responsible for the energy transfer and hence the breakage of the macroscopic phase

$$\lambda = \left(\frac{\nu^3}{\varepsilon}\right)^{1/4}$$

$\lambda$ relates to the kinematic viscosity of the solution ($\nu$) and the dissipation rate ($\varepsilon$) which is the power input by the stirrer (P) per mass (m)

# The Comminution Progress

as soon as the shear exerted by the turbulent micro-eddies on the droplet interface exceeds the cohesive forces of the liquids in the drops they split up to smaller units



$$\Delta P = \frac{\sigma}{(r_a + r_b)}$$

cleavage occurs as long as a balance between the external stress and the internal stress is reached

# The Comminution Process (1)

steady state DSD for different rotor / stator systems: $\phi = 0.1$, 50 mM SDS

| Machine | Conditions for $W_V = 5{\cdot}10^6$ J m$^{-3}$ | Maximum $D_d$ in DSD |
|---|---|---|
| STR [a)] | n = 500 rpm, $t_d$ = 60 min | 60 – 70 µm |
| Screw loop [b)] | n = 4000 rpm, v = 350 l h$^{-1}$ | 10 – 11 µm and 2 µm |
| Ultra turrax [c)] | n = 10.000 rpm, $t_d$ = 2 min | 10 – 11 µm and 2 µm |

experimental values

$$\Delta W = 5\cdot 10^{6}(J\cdot m^{-3}) = 10^{-2}(N\cdot m^{-1})\cdot \Delta A(m^{2}\cdot m^{-3})$$

theory

$$\Delta A = 5\cdot 10^{8}\, m^{2}\cdot m^{-3} \longrightarrow D = 1.3nm$$

a - STR – stirred tank reactor consisting of a cylindrical vessel (diameter 30 cm, volume 21.2 l) with a flat bottom and four symmetrical baffles and a six blade disc impeller with a diameter of 10 cm

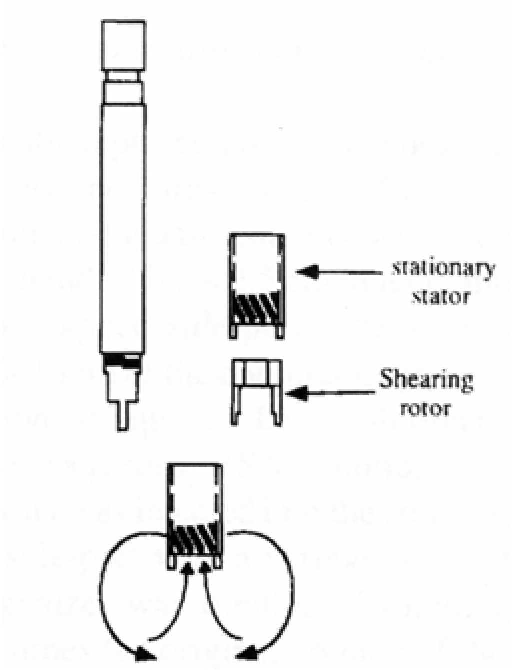
b - Screw loop reactor, volume of the dispersing zone about 64 ml and reactor volume 1.67 l

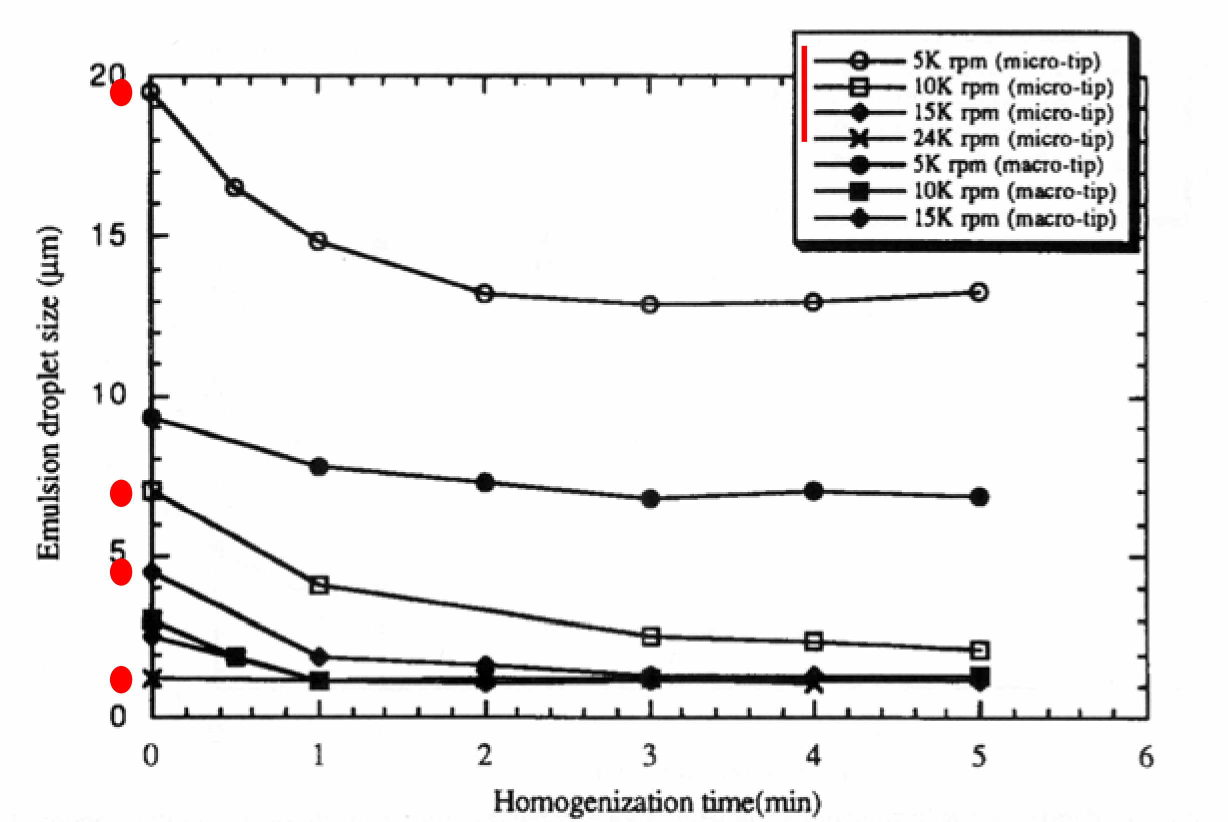
c - Ultra turrax T50 from IKA with a dispersing tool type S50-G45F used in a cylindrical vessel with a volume of 8 l

Ludwig, A., U. Flechtner, J. Prüss, H.-J. Warnecke, Formation of emulsions in a screw loop reactor, *Chem. Eng. Technol.*, **20**, 149 - 161 (1997)

# The Comminution Process (2)

0,4 g/ml PMMA in $MeCl_2$ in a 0,2 g/ml BSA solution (v:v = 10:2)
batch homogenizer



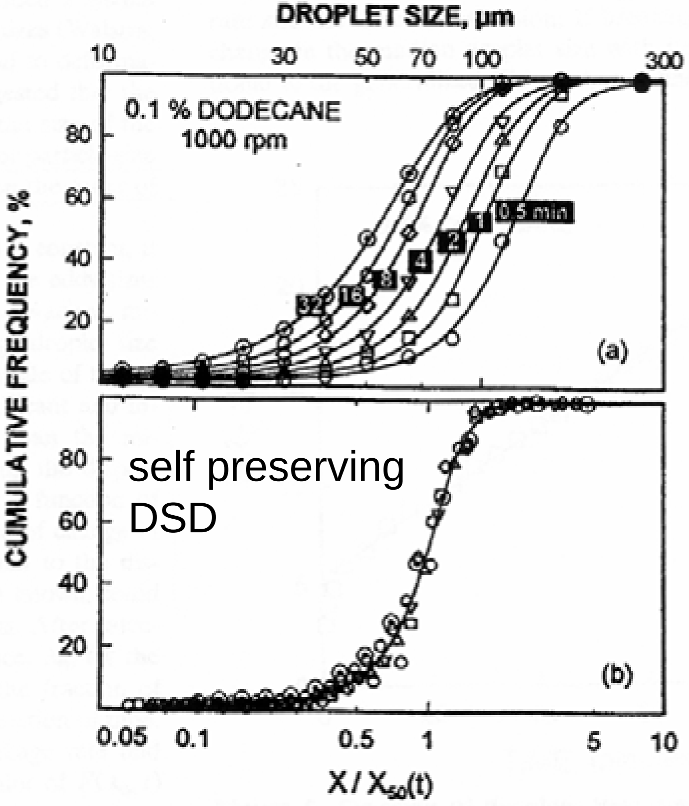


Y.-F. Maa, C. Hsu J. Controlled Release 38, 219-228 (1996)

**a steady state DSD is reached**

# The Comminution Process (3)

stirred tank, turbine-type stirrer

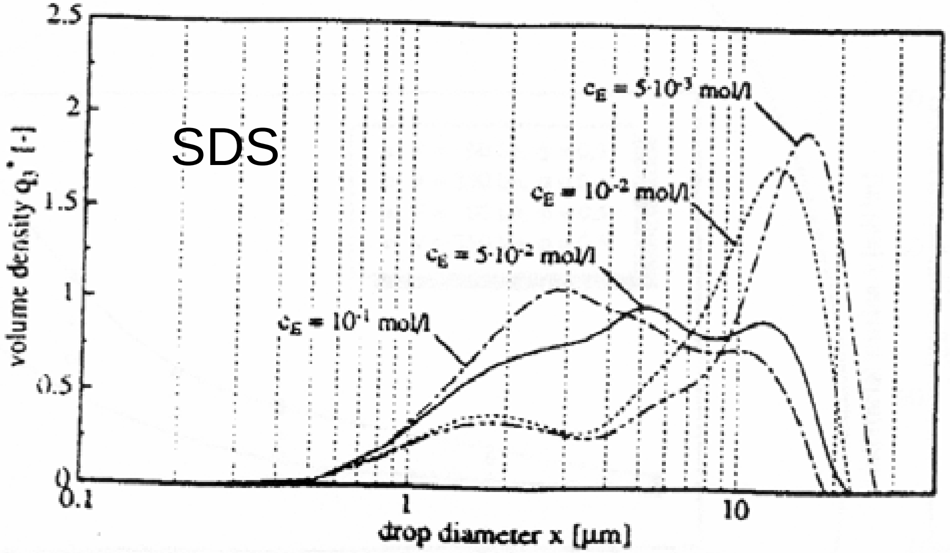


self preserving
DSD

**Figure 4.** (a) Size distribution of dodecane droplets in water at various times; (b) normalized size distribution of dodecane droplets in water.

H.+ M. Polat, S. Chander
AIChE Journal 45, 1866-1874 (1999)

soya oil, screw loop reactor



SDS

**Figure 5.** Drop size distributions at various emusifier concentrations. $N = 3000$ min, $\dot{V} = 50$ l/h, and $\varphi = 0.1$.

A. Ludwig, U. Flechtner, J. Prüss, H.-J. Warnecke
Chem. Eng. Technol. 20, 149-161 (1997)

# The Comminution Process (4)

viscoelastic force of the dispersed phase

solution viscosity is a direct measure of the viscoelastic force

emulsification of an aqueous bovine serum albumin solution in dichloromethane containing poly(methyl methacrylate) (PMMA) as stabilizer with different agitation machines

| Agitation machine | Relation |
|---|---|
| Rotor stator homogenizer | $D_d \propto \eta_d^{0.11} \eta_c^{-0.43}$ |
| Baffled mixed tank | $D_d \propto \eta_d^{0.22} \eta_c^{-0.42}$ |
| Static Mixture | $D_d \propto \eta_d^{0.004} \eta_c^{-0.56}$ |

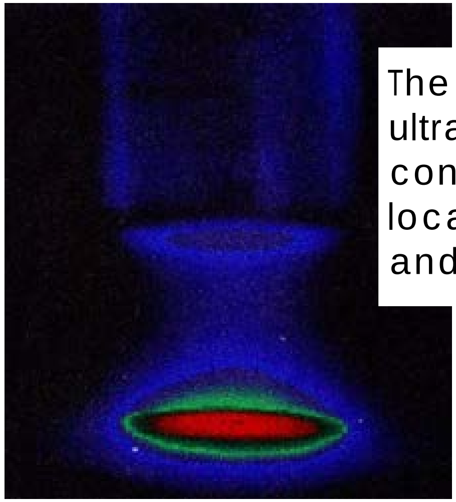
viscosity of the dispersed phase ($\eta_d$) and of the continuous phase ($\eta_c$)

increasing $\eta_c$ means increasing shear stress at a given comminution energy

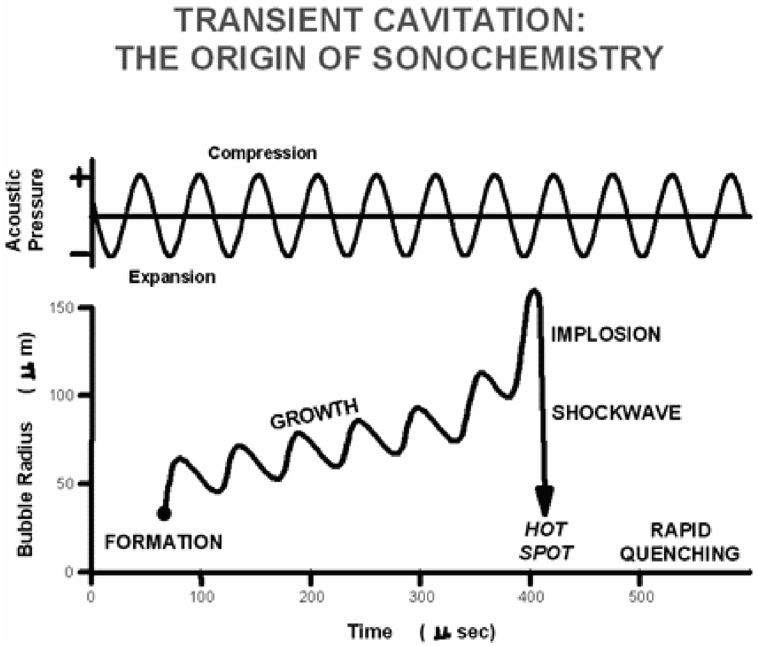
# Comminution by Ultrasound

(special kind of mechanical energy input )

Ultrasound means the application of high frequency vibrations. In a first step larger drops ($D_d$ » 100 µm) are produced in a way that instabilities of interfacial waves will be enhanced leading finally to the crushing. These drops are subsequently fragmented into smaller ones by acoustic cavitation. The use of ultrasound in emulsification processes is much more efficient than the application of rotor / stator systems.



The energy of the ultrasonic wave is concentrated into highly localized temperature and pressure “hot spots”



**Physical and chemical effects of cavitation**

[K. S. Suslick, University of Illinois, USA]

# action of ultrasound

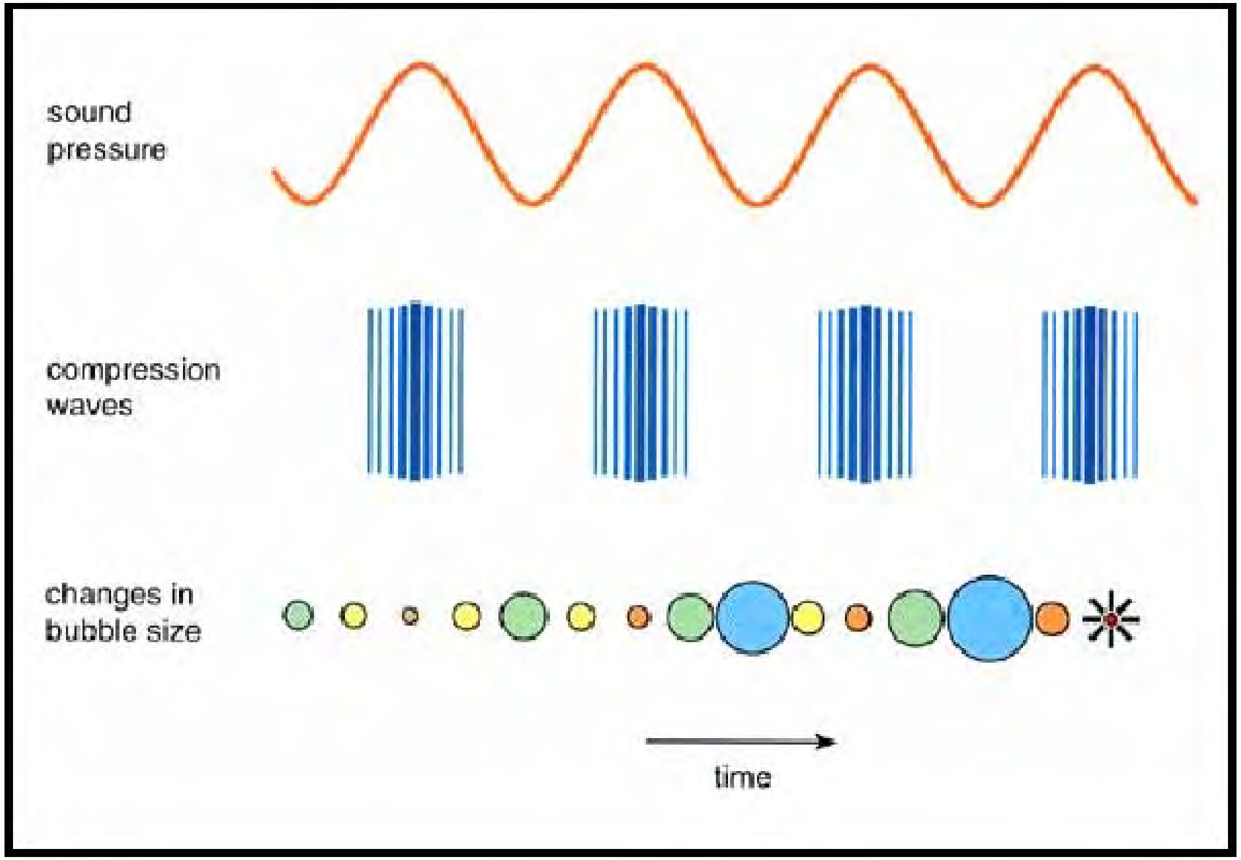


**Figure 3.** Liquids irradiated with ultrasound can produce bubbles. These bubbles oscillate, growing a little more during the expansion phase of the sound wave than they shrink during the compression phase. Under the proper conditions these bubbles can undergo a violent collapse, which generates very high pressures and temperatures. This process is called cavitation.

Once the cavity has overgrown, either at high or low sonic intensities, it can no longer absorb energy as efficiently. Without the energy input the cavity can no longer sustain itself. The surrounding liquid rushes in, and the cavity implodes. It is the implosion of the cavity that creates an unusual environment for chemical reactions.

[K. S. Suslick, University of Illinois, USA]

# Cavitation

Acoustical energy is **mechanical energy** i.e. it is not absorbed by molecules. Ultrasound is transmitted through a medium via **pressure waves** by inducing vibrational motion of the molecules which alternately compress and stretch the molecular structure of the medium due to a time-varying pressure. Therefore, the distance **among the molecules varies** as the molecules oscillate around their mean position.

If the intensity of ultrasound in a liquid is increased, a point is reached at which the intramolecular forces are not able to hold the molecular structure intact. Consequently, it breaks down and a **cavity** is formed. This cavity is called cavitation bubble as this process is called cavitation and the point where it starts cavitation threshold.

A bubble responds to the sound field in the liquid by expanding and contracting, i.e. it is excited by a time-varying pressure.

Two forms of cavitation are known: stable and transient. **Stable cavitation** means that the bubbles oscillate around their equilibrium position over several refraction/compression cycles. While **transient cavitation**, the bubbles grow over one (sometimes two or three) acoustic cycles to double their initial size and finally collapse violently.

## comminution and reaction

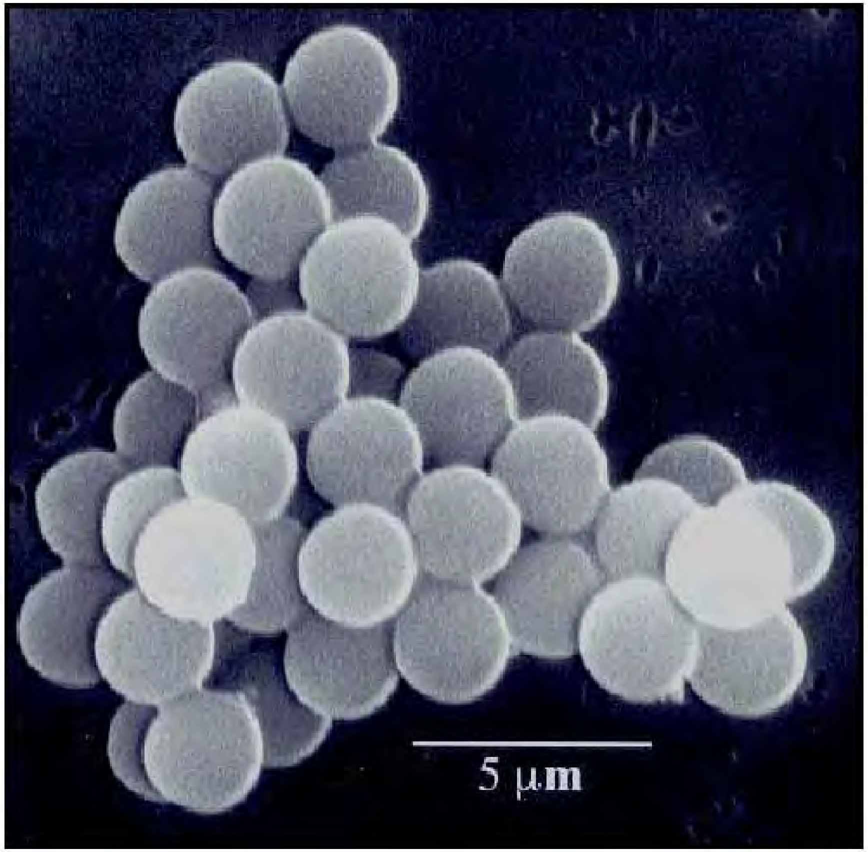


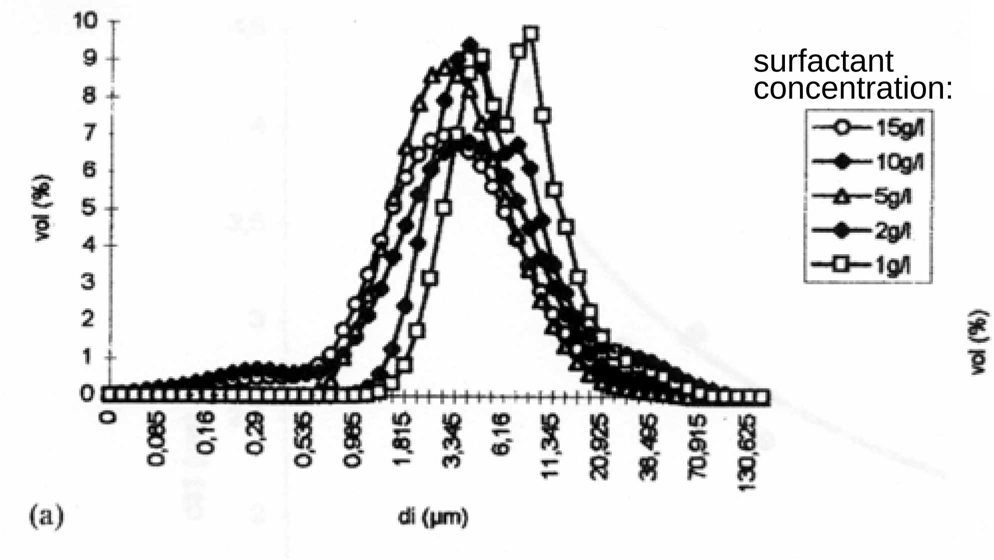
**Figure 9.** Protein microspheres filled with the oily hydrocarbon dodecane were formed by the ultrasonic irradiation of albumin solutions. Such microspheres may prove useful for drug delivery and medical diagnostic imaging.

One recent example is the use of high intensity ultrasound to make aqueous suspensions of long-lived proteinaceous microspheres filled with air or with water-insoluble liquids for medical applications (Figure 9). By itself, emulsification is insufficient to produce these long-lived microspheres; chemical reactions requiring oxygen are critical in forming them. Specifically, the sonolysis of water produces hydrogen atoms that react with oxygen to produce superoxide. Suslick and M. W. Grinstaff demonstrated that the proteinaceous microspheres are held together by disulfide bonds between protein cysteine residues and that superoxide is the cross-linking agent.

[K. S. Suslick, University of Illinois, USA]

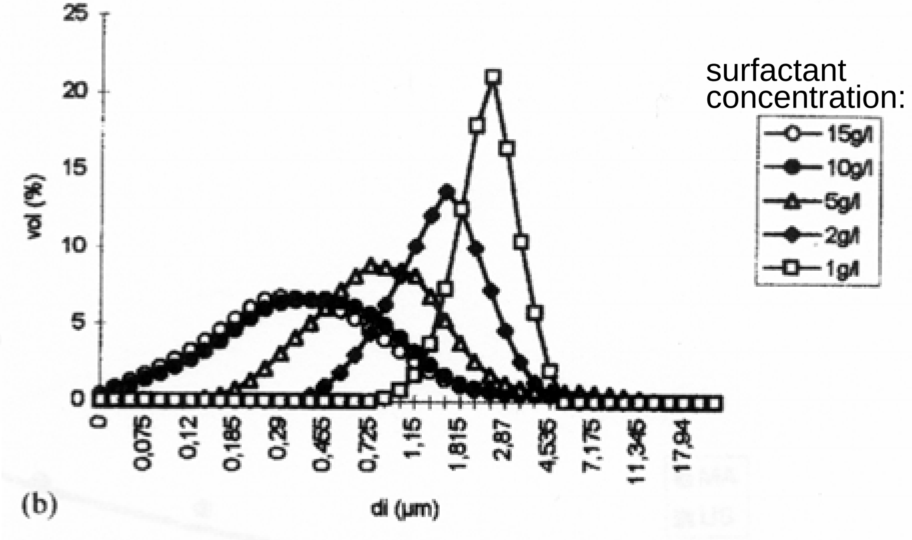
# Comminution by Ultrasound - A Practical Example 1

ultra turrax (n = 10.000 rpm, 170 W)



surfactant concentration:

ultrasound horn (20 kHz, 130 W)



surfactant concentration:

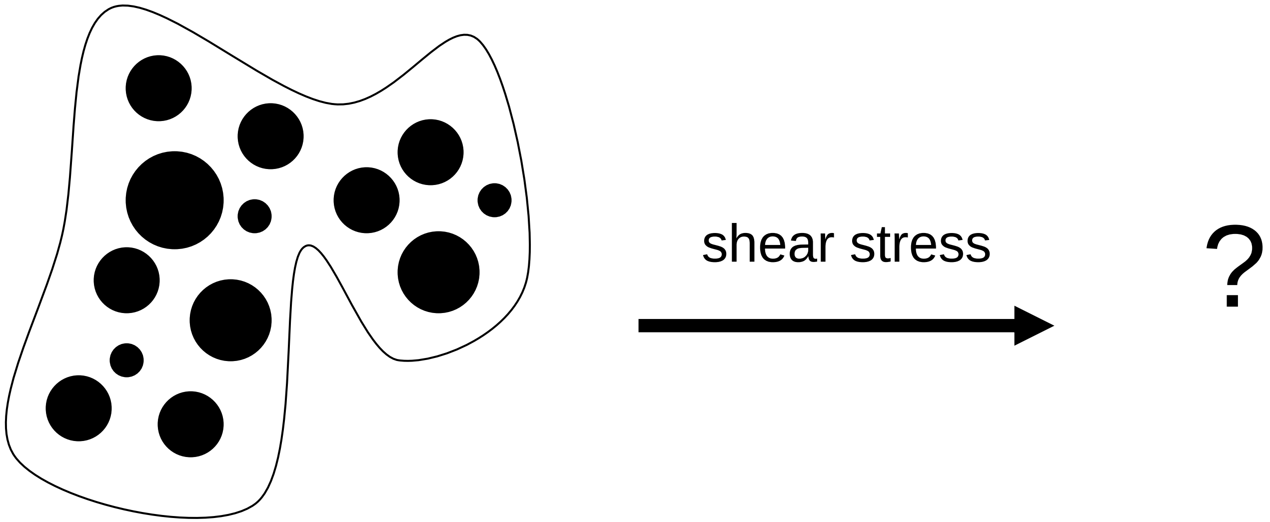
(25 % kerosene volume fraction; total volume of 80 ml) with a polyethoxylated (20EO) sorbitan monostearate surfactant (interfacial tension kerosene to water 9.5 mN $m^{-1}$

Abismail, B., J. P. Canselier, A. M. Wilhelm, H. Delmas, C. Gourdon, Emulsification by ultrasound. drop size distribution and stability, *Ultrasonics Sonochemistry*, **6**, 75 - 83 (1999)

# Comminution by Ultrasound - A Practical Example 2

# Consecutive emulsification

What will happen if an emulsion which was prepared by a certain comminution technique is exposed to a different shear stress ???



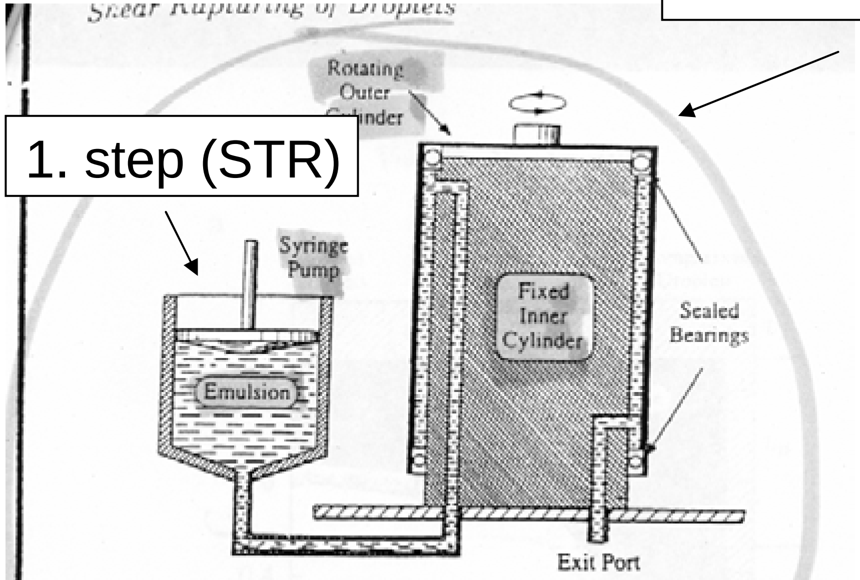
shear stress

?

Note, the shear stress is the product of shear rate and viscosity and hence it combines emulsion properties with properties of the comminution technique.

Mason, T. G. and J. Bibette, Shear rupturing of droplets in complex fluids *Langmuir*, **13**, 4600 - 4613 (1997)

# Shear Rupturing of Emulsion Droplets



2. step (Couette)

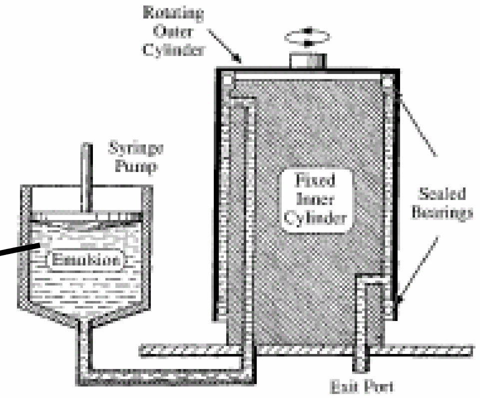
1. step (STR)

**Figure 4.** Schematic diagram of an injection couette shear mixer. The premixed emulsion, contained initially in the syringe, is pumped into the thin gap between the outer rotating and inner fixed cylinders. Sealed bearings prevent the sheared emulsion from escaping out the ends and force it to leave through the exit port.

The pre-emulsions consisted of poly(dimethylsiloxane) oil (volume fraction $\phi$) in water stabilized with a nonionic surfactant (nonylphenol with 7 ethylene oxide units (mass fraction with respect to water C).

At shear rates larger than 10 $s^{-1}$ in the Couette flow the polydisperse pre-emulsion starts to convert into monodisperse ones.

Mason, T. G. and J. Bibette, *Langmuir*, **13**, 4600 - 4613 (1997)



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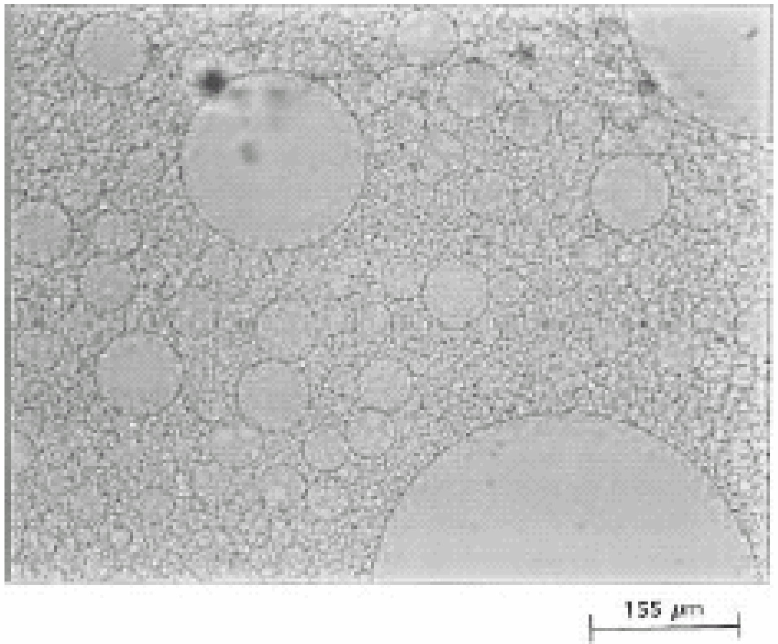
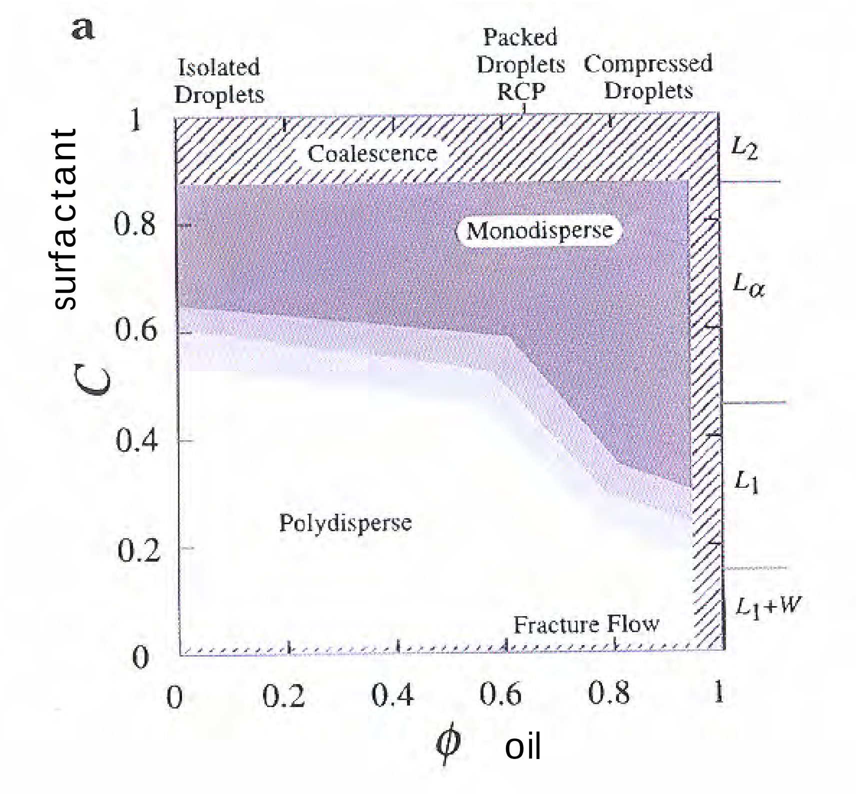


**Figure 3.** Microscope image of a typical premixed emulsion at $C = 0.4$ and $\phi = 0.7$. The premixed emulsion is polydisperse.

# Shear Rupturing of Emulsion Droplets, practical examples

$\dot{\gamma} \approx 10^{2}\,\mathrm{s}^{-1}$



$\dot{\gamma} > 10\ \mathrm{s}^{-1}$ in the Couette flow the polydisperse pre-emulsion starts to convert into monodisperse ones.

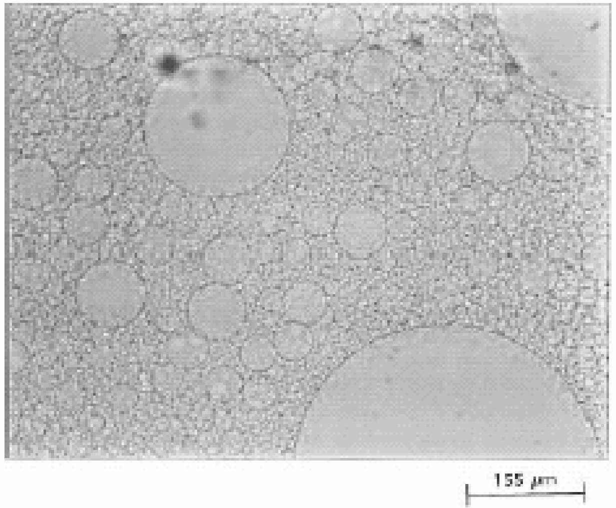
The dependence of the final droplet size on the emulsifier concentration is as expected: $D_d$ decreases with increasing C

**but**

$D_d$ decreases with increasing volume fraction of the organic phase

Mason, T. G. and J. Bibette, *Langmuir*, **13**, 4600 - 4613 (1997)

$D_d$ decreases with increasing volume fraction of the organic phase. This is a remarkable result as it indicates fundamental differences in the comminution mechanisms.



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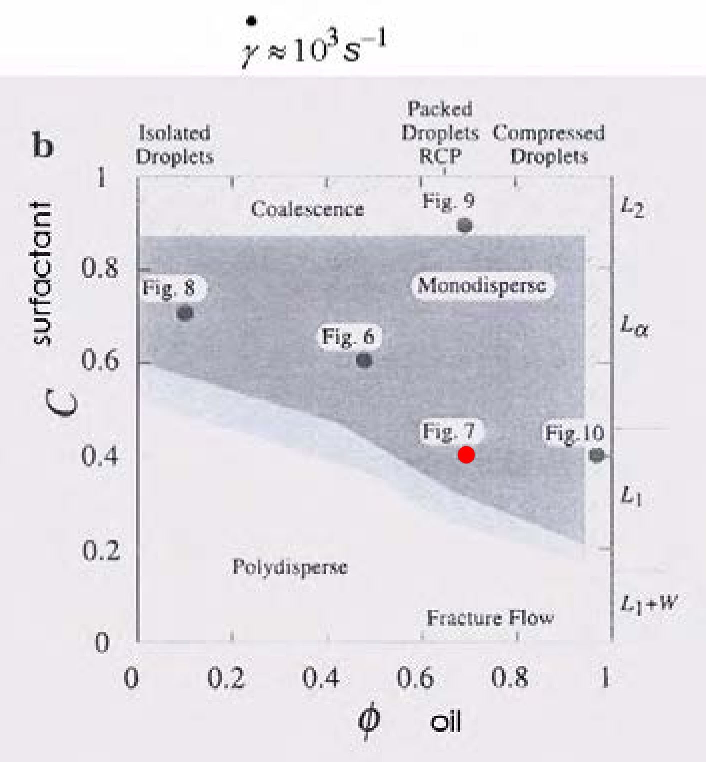

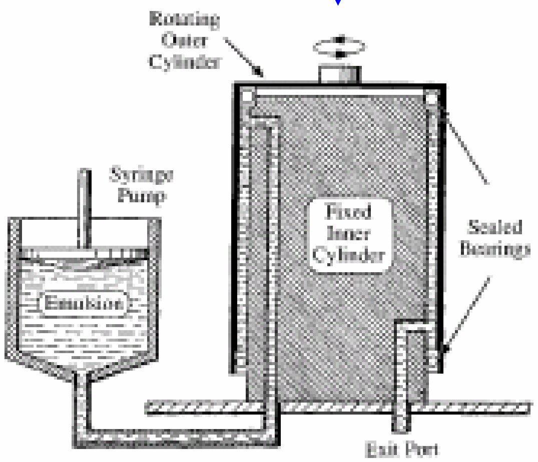

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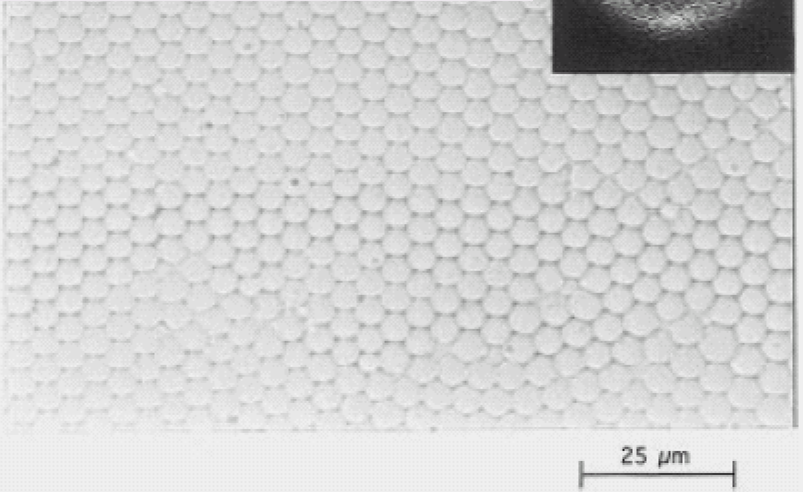
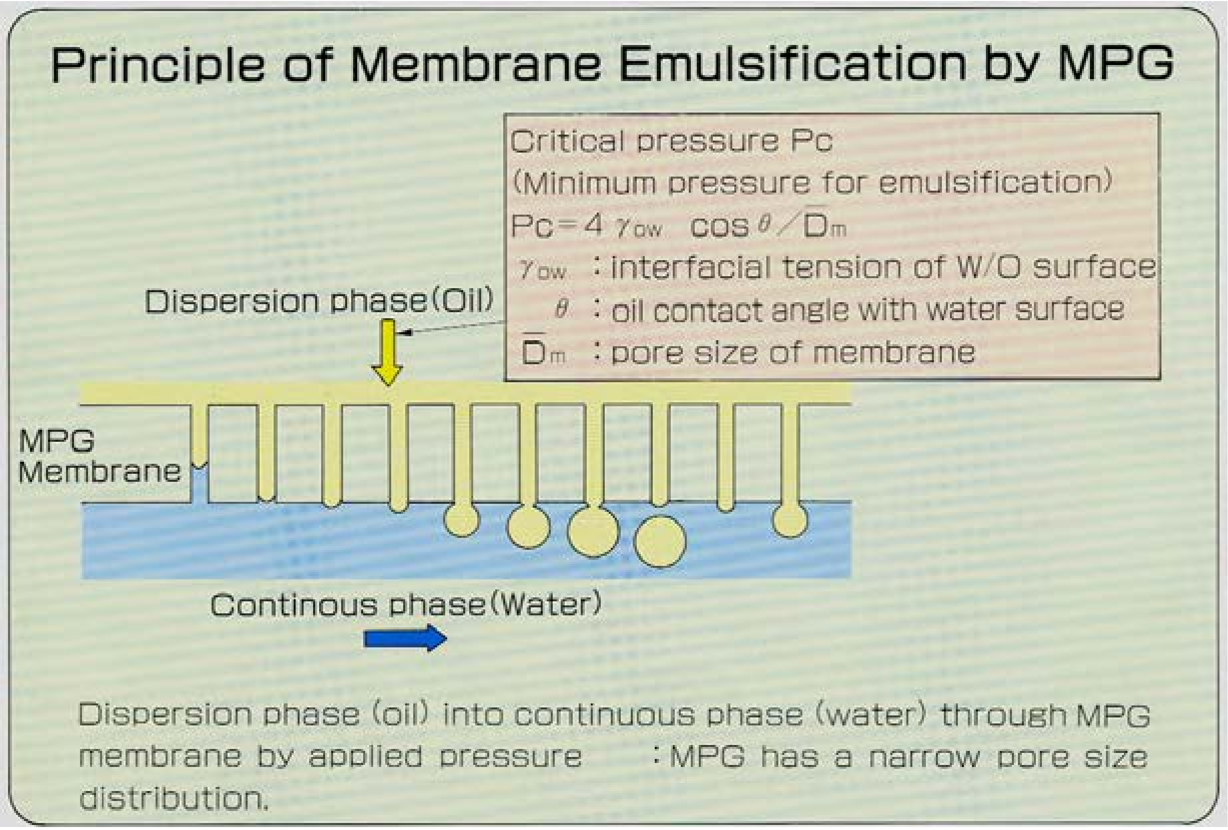


**Figure 7.** Microscope image of an ordered uniform emulsion after shear rupturing at $C \approx 0.4$, $\phi \approx 0.7$, and $\dot{\gamma} \approx 10^3\ \mathrm{s}^{-1}$. Inset: the light scattering pattern is a diffuse ring with six bright spots reflecting hexagonal spatial ordering of the droplets.

# Membrane Emulsification - Principle



## Principle of Membrane Emulsification by MPG

Critical pressure Pc
(Minimum pressure for emulsification)

$P_c = 4\gamma_{ow}\ \cos\theta / \overline{D}_m$

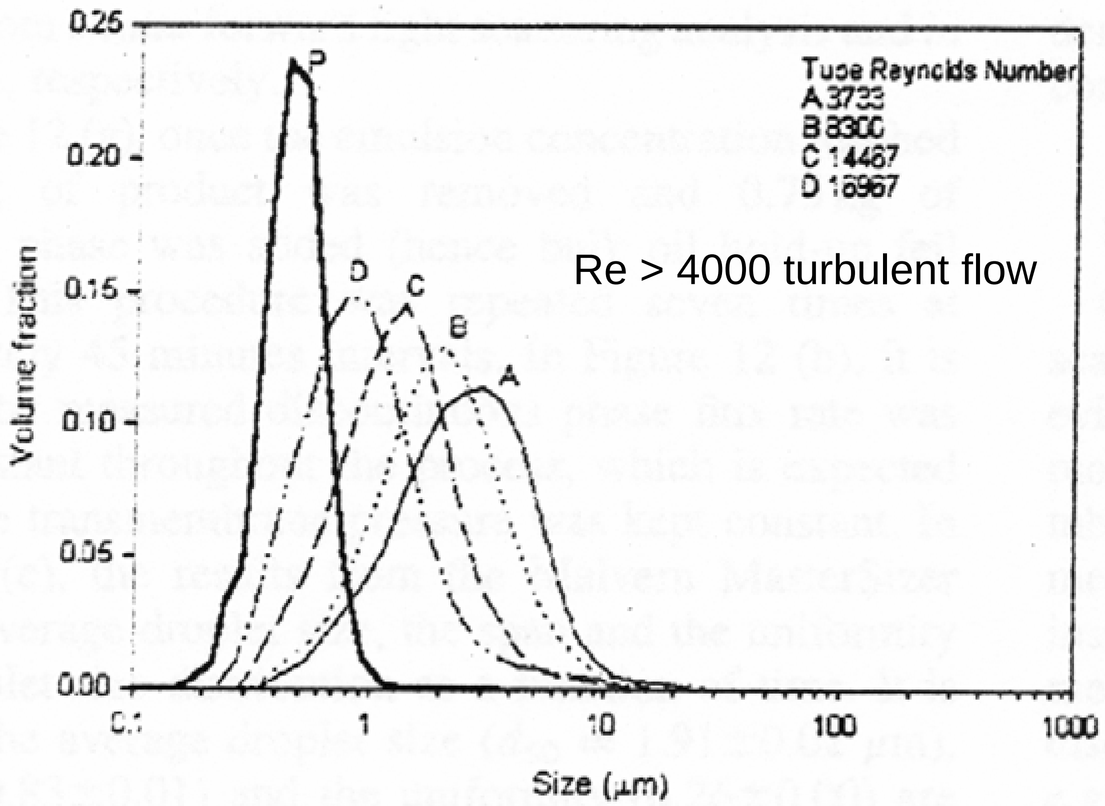
$\gamma_{ow}$ : interfacial tension of W/O surface
$\theta$ : oil contact angle with water surface
$\overline{D}_m$ : pore size of membrane

Dispersion phase (oil) into continuous phase (water) through MPG membrane by applied pressure : MPG has a narrow pore size distribution.

This technique was first reported at the 1988 autumn conference of the Japanese Chemical Engineering Society utilizing a micro-porous glass (MPG) membrane made of $CaO\text{-}Al_2O_3\text{-}B_2O_3\text{-}SiO_2$.

SPG info-material, Japan

# Membrane Emulsification - Results



Re > 4000 turbulent flow

*Figure 9.* Effect of increasing crossflow velocity on the droplet size distribution (A, B, C, D) produced from a membrane having the pore size distribution (P).

$$D_d = f \cdot D_M$$

f : 2 - 8

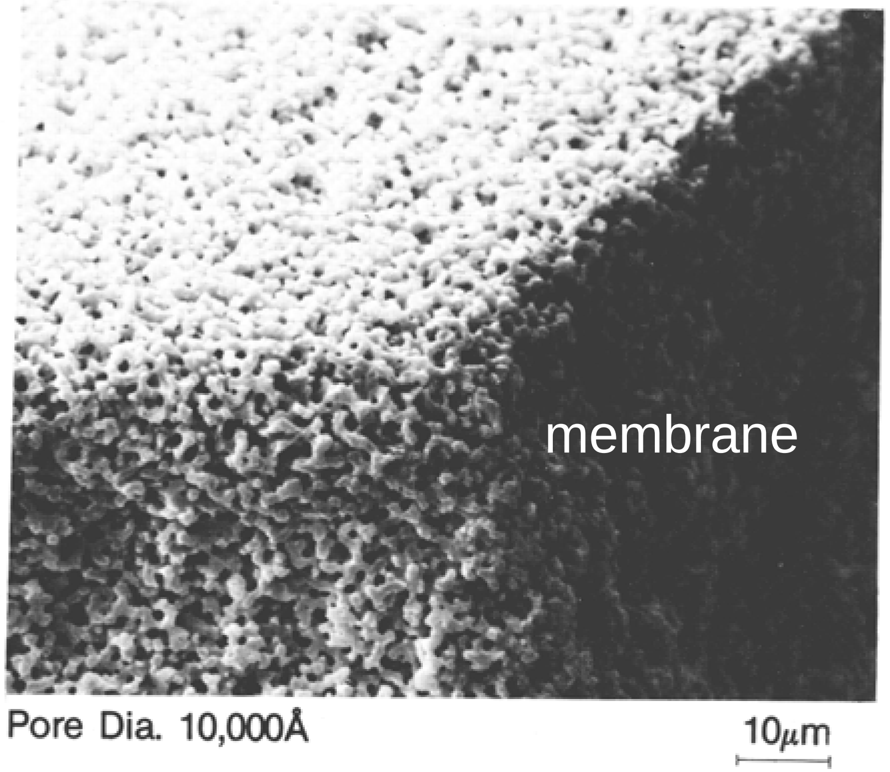
$D_M$ - pore diameter

$D_d$ – droplet diameter

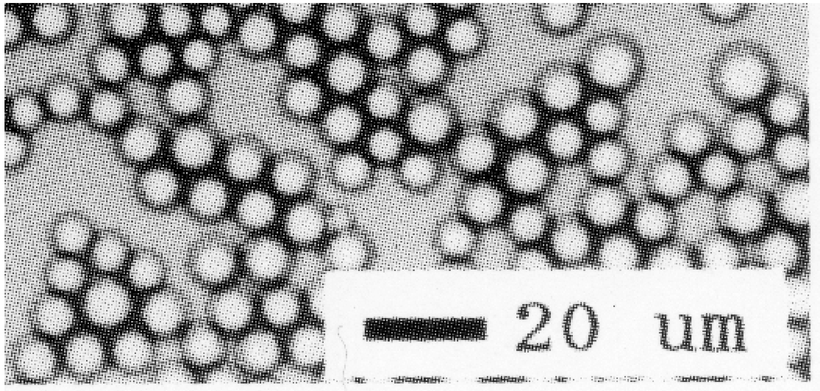
Continuous phase:
66.7 w% water
3 w% triethanolamine
0.3 w% sodium nipastat
Dispersed phase:
27 w% mineral oil
3 w% isosteric acid

Williams, R. A.; S. J. Peng, D. A. Wheeler, N. C. Morley, D. Taylor, M. Whalley and D. W. Houldsworth, Controlled production of emulsions using a crossflow membrane Part II: industrial scale manufacture, *TransIChemE* **76**, 902 - 910 (1998)

# Membrane Emulsification - more Results



monodispers drops



Oil phase: soy bean oil with 0.5 wt-% Span 80
Water phase: 1 wt-% NaCl solution
Membrane: hydrophobic SPG $D_m = 2{,}56\ \mu m$;
$\Delta P = 25$ kPa

SPG info-material, Japan

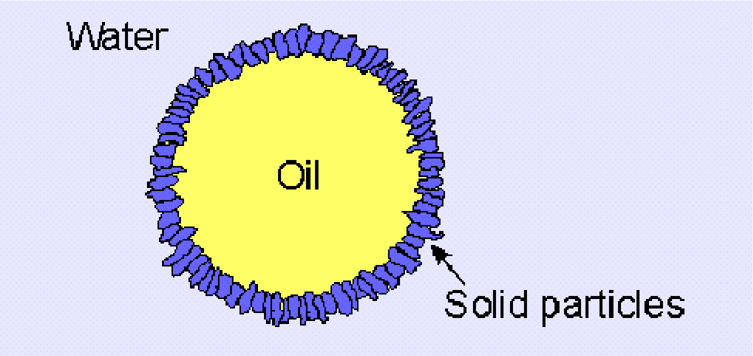
# Comminution - Summary

this emulsification process is influenced by various parameters:

- the volume phase ratio
- the viscosity of both phases
- the mutual solubility of both phases
- the kind and concentration of additives
- the diminution energy and the power input
- the stirrer as well as the vessel geometry
- thermodynamic changes during the emulsification process (reactions, temperature).

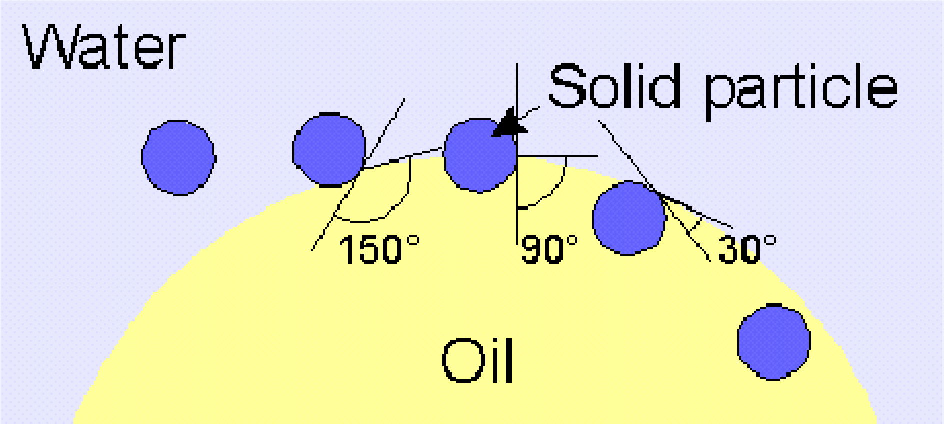
# Particles as Stabilizers -Pickering Emulsions (1)

W. Ramsden Proc. R. Soc. Lond. 72 (1904) 156-164
S. U. Pickering J. Chem. Soc. 91 (1907) 2001



any kind of particles: minerals
polymers

crucial is the wetting behavior:



contact angle
particle size
solids concentration
interparticular interaction

(R. Daniels)

# Particles as Stabilizers -Pickering Emulsions (2)

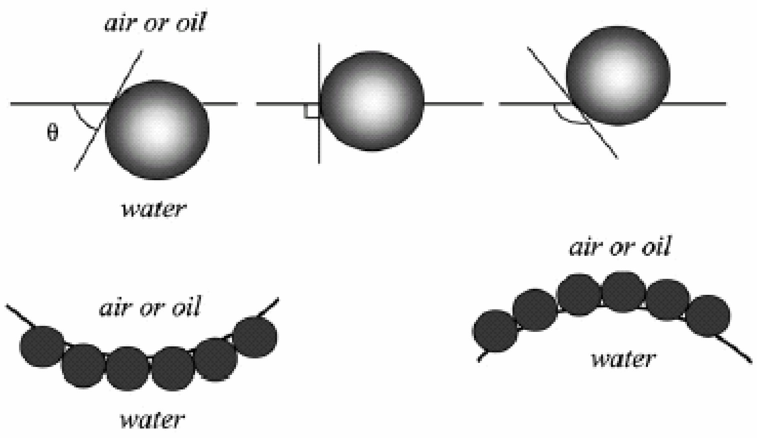


Fig. 1. (Upper) Position of a small spherical particle at a planar fluid–water interface for a contact angle (measured through the aqueous phase) less than 90° (left), equal to 90° (centre) and greater than 90° (right). (Lower) Corresponding probable positioning of particles at a curved fluid–water interface. For $\theta < 90°$, solid-stabilised aqueous foams or o/w emulsions may form (left). For $\theta > 90°$, solid-stabilised aerosols or w/o emulsions may form (right).

$$\boxed{E = \pi r^2 \gamma_{\alpha\beta}(1 \pm \cos\theta)^2}$$

Energy of attachment or removal of a particle to or from a fluid-fluid interface (E) is not only related to the contact angle ($\Theta$) but also to the interfacial tension ($\gamma_{\alpha\beta}$). Small enough particles - no effect of gravity. The sign inside the bracket is negative for removal into the water phase, and positive for removal into the oil phase.

If D~20 nm and $\gamma_{\alpha\beta}$~36 mN/m the particle is most strongly held in the interface for $\Theta$ = 90° with E = 2750 kT. Either side of 90°, E falls rapidly for 0 - 20° and 160 - 180° to less than 10 kT.

For $\Theta$ < 90° the particle is more hydrophilic and for $\Theta$ > 90 ° the particle is more hydrophobic.

Note, E depends on the square of the particle size!

B. P. Binks Curr. Op. Coll. Interf. Sci. 7 (2002) 21-41

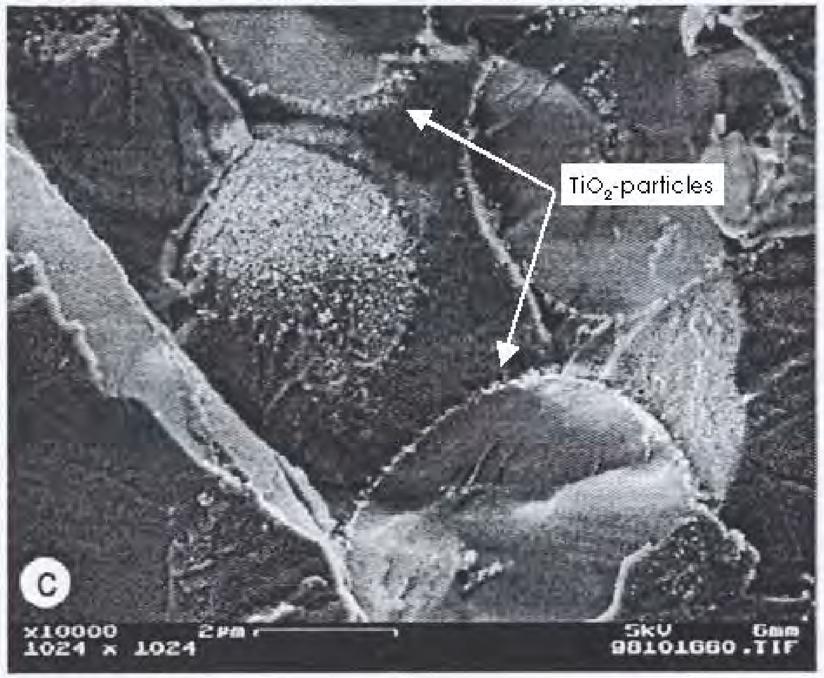
# Particles as Stabilizers -Pickering Emulsions (3a)

## Inorganic particles as stabilizers

O/W emulsion stabilized with $TiO_2$-particles

backscattered electron (BSE) imaging of cryo-fracture SEM
(high pressure frozen sample: -196 °C and 2200 bar)

S. Wiesner, S. S. Biel, K. P. Wittern, U. Hintze, R. Wepf Microscop. Microanal. 9 (2003) 510



→ technical of importance for: pharmaceutical and cosmetic products,
crude oil and oil recovery,
waste products in soils (O/W),
suspension polymerization of styrene
(with CaCO3, BaSO4, $Ca_5[(OH)|(PO_4)_3]$)
hydroxylapatite

# Particles as Stabilizers -Pickering Emulsions (3b)

## Latex particles as stabilizer

B. P. Binks, S. O. Lumsdon Langmuir 17 (2001)4540-4547

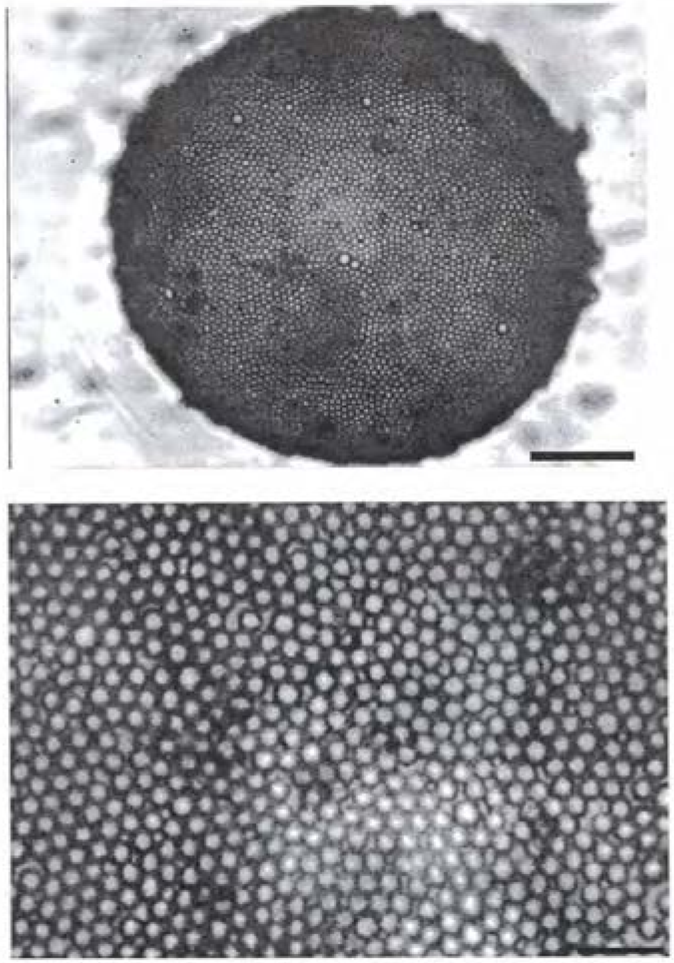
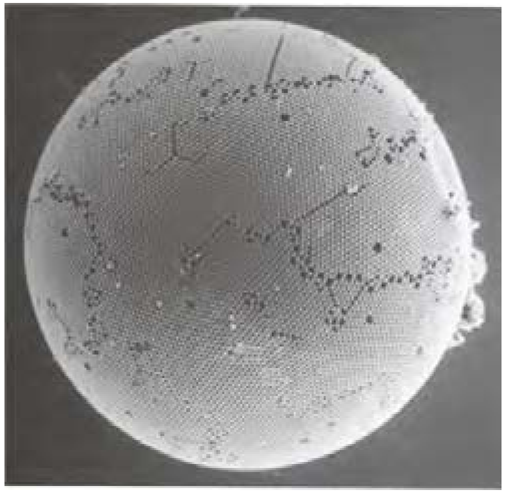


**Figure 3.** (upper) Optical microscope image of a single water-in-cyclohexane emulsion drop coated with 3.2 μm diameter hydrophilic latex particles ($\phi_w = 0.6$, 1 wt % in water). Scale bar = 50 μm. (lower) Enlarged portion of the water drop surface showing packing of individual latex particles. Scale bar = 15 μm.



a 760 μm diameter hollow sphere consisting of a monolayer of 7.9 μm monodisperse polystyrene particles flocculated onto a nitrogen bubble formed during seeded emulsion polymerization experiment aboard the space shuttle orbiter Challenger (STS 7, June 1983)

[J. W. Vanderhoff, O. Shaffer EPI Lehigh University, Bethlehem,USA]

## „Colloidosomes“

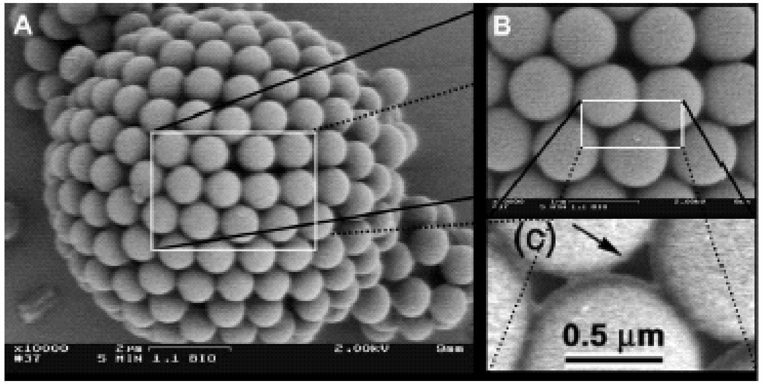
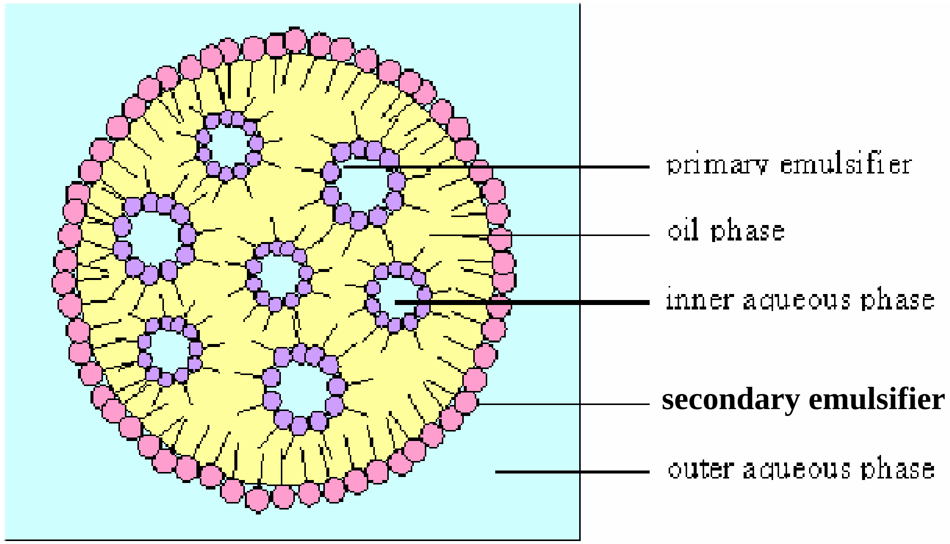


**Fig. 3. (A)** Scanning electron microscope image of a dried, 10-μm-diameter colloidosome composed of 0.9-μm-diameter polystyrene spheres, sintered at 105°C for 5 min. The colloidosome was formed with an oil droplet, containing 50 vol% vegetable oil and 50 vol% toluene. The water phase contained 50 vol% glycerol to increase its boiling temperature to allow the sintering. (**B** and **C**) Close-ups of (A) and (B), respectively. The arrow points to one of the 0.15-μm holes that define the permeability. To view these colloidosomes with the electron microscope, we washed them with ethanol and dried them in vacuum.

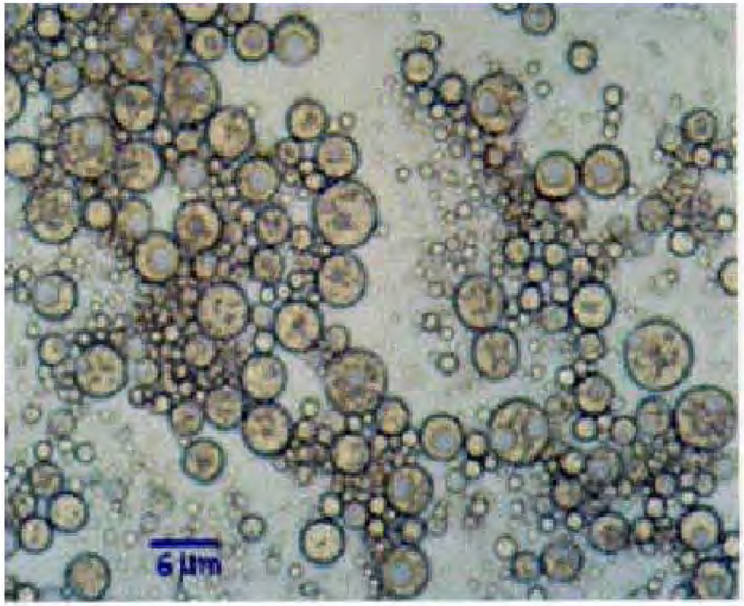
D. A. Weitz Science 298 (2002) 1006-1009

# Multiple Emulsions (1)

Emulsifying an emulsion in another continuous phase to get either W/O/W or O/W/O emulsions requires stabilizers with different HLB



**a W/O/W emulsion**

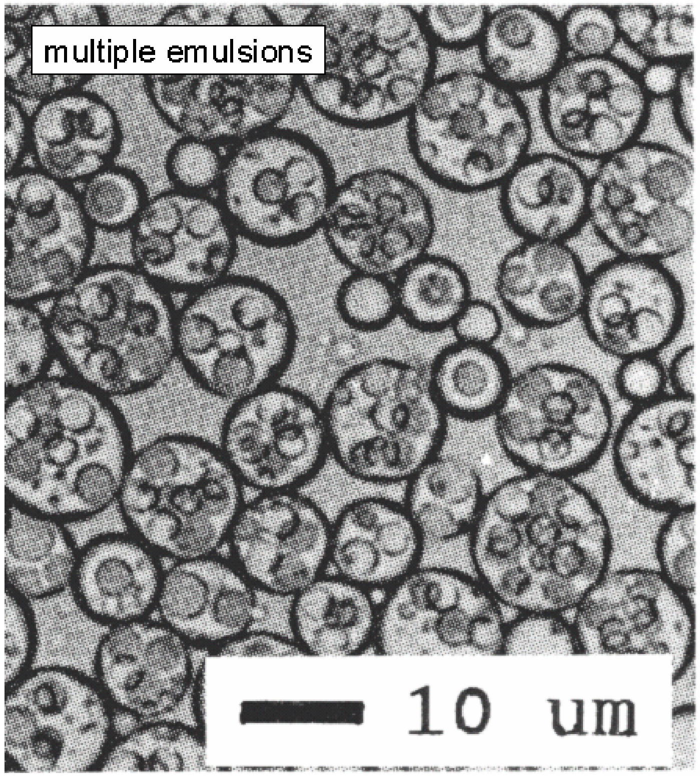


**A microscopic picture**

(M. Akhtar)

# Multiple Emulsions (2)

membrane emulsification



O/W:
Oil phase: soy bean oil with 1 wt-% PGCR
Water phase: 5 wt-% $Na_2PO_4/KH_2PO_4$ 4/1
Membrane: hydrophobic SPG $D_m = 0.36$ µm;
$\Delta P = 300$ kPa
W/O/W:
O/W in 1wt-% aqueous Tween 20 + 0.5 wt-% NaCl
Membrane: hydrophilic SPG $D_m = 2.8$ µm;
$\Delta P = 40$ kPa

SPG info-material, Japan

## hydrophilic and hydrophobic silica particles as stabilizer

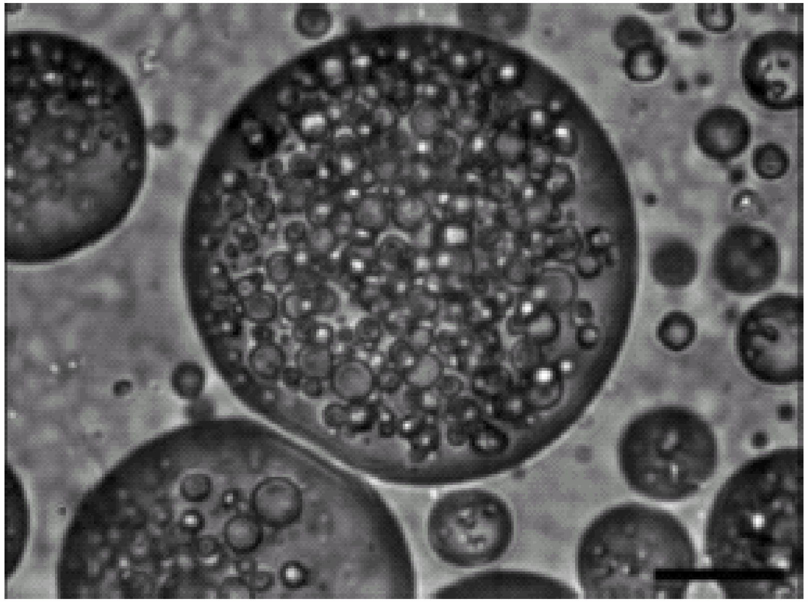


Fig. 9. Optical microscopy image of an o/w/o multiple emulsion stabilised by two types of silica particles. The system contains toluene and both hydrophilic (80% SiOH) and hydrophobic silica (51% SiOH). Inner oil drops are approximately 4 µm in diameter. The scale bar represents 20 µm (obtained during work described earlier [72**]).

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# Preparation of Emulsions by Condensation Techniques
# or
# The Gentle Way to Make Emulsions

- condensation does not require mechanical energy except sometimes gentle stirring to avoid creaming or settling due to density differences between both phases

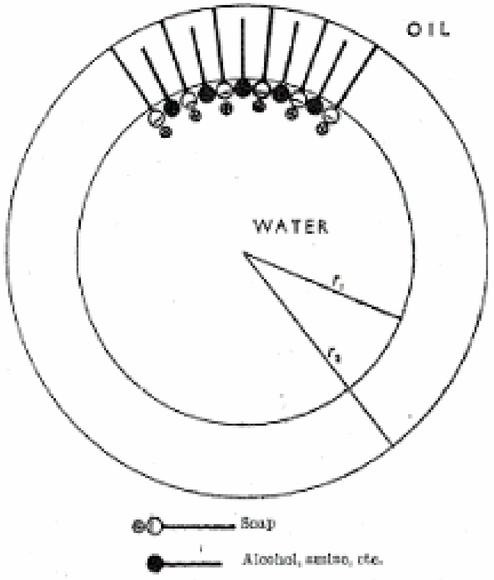
- mainly determined by thermodynamic principles

- swelling of preformed colloidal objects

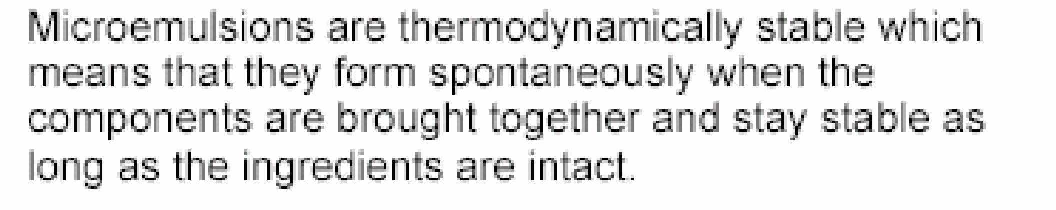
- sometimes in the presence of emulsifying or swelling adjuvant

# Microemulsions (1)

Transparent Water-in-Oil Dispersions :
the Oleopathic Hydro-Micelle

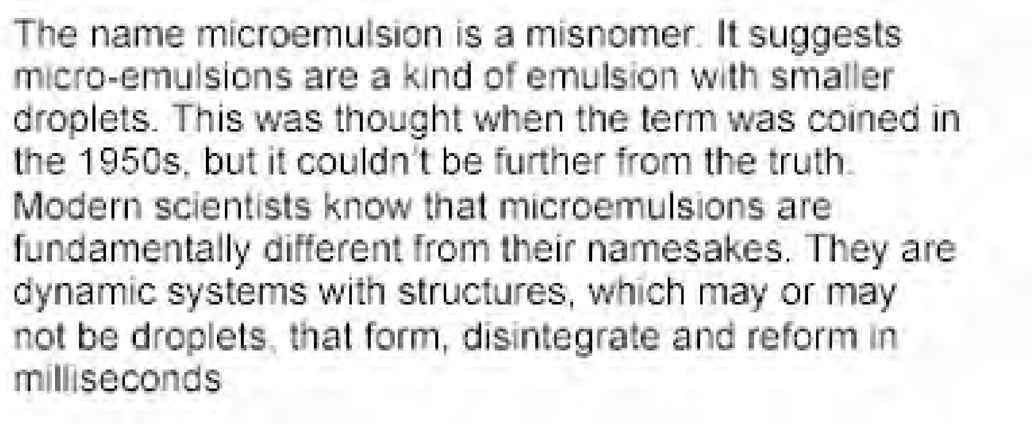


T. P. Hoar, J. H. Schulman
Nature 3847 (1943)102-103



Microemulsions are thermodynamically stable which means that they form spontaneously when the components are brought together and stay stable as long as the ingredients are intact.

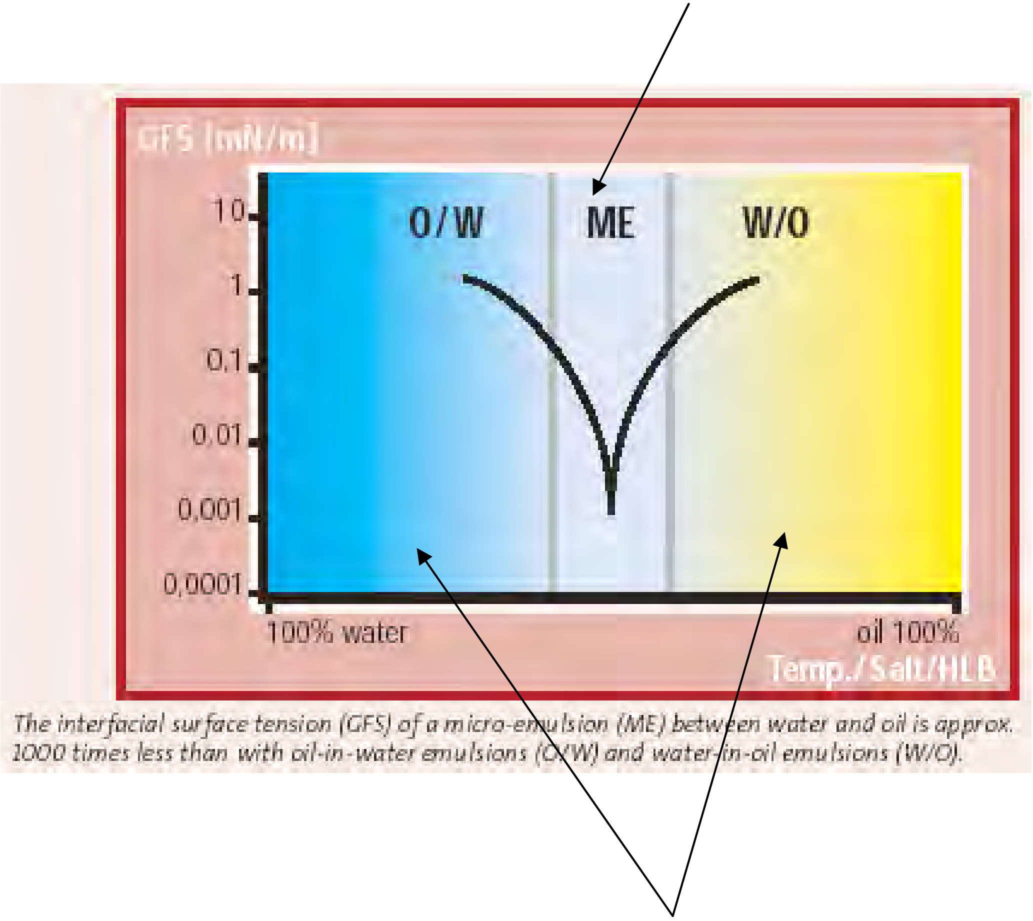
<u>but today‘s knowledge:</u>



The name microemulsion is a misnomer. It suggests micro-emulsions are a kind of emulsion with smaller droplets. This was thought when the term was coined in the 1950s, but it couldn't be further from the truth. Modern scientists know that microemulsions are fundamentally different from their namesakes. They are dynamic systems with structures, which may or may not be droplets, that form, disintegrate and reform in milliseconds

# Microemulsions (2)

apparently a single phase



*The interfacial surface tension (GFS) of a micro-emulsion (ME) between water and oil is approx. 1000 times less than with oil-in-water emulsions (O/W) and water-in-oil emulsions (W/O).*

two phases

more surfactant than dispersed phase

frequently surfactant plus co-surfactant (alcohol)

complicated phase diagrams

no direct contact between both phases

# Microemulsions (3)

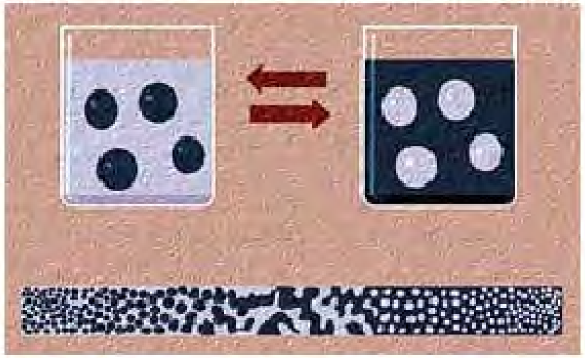


Figure two: Emulsions and microemulsions are very different in structure. Emulsions (top) consist of either oil droplets in water or water droplets in oil and there is a sharp transition between the two structures. The transition may be induced by a change in temperature or salt concentration. In a microemulsion (bottom) the structure may change continuously between a curvature towards water and a curvature towards oil—depending on conditions.

## comparing emulsions and microemulsions:

lower amount of surfactant
thermodynamically unstable
direct phase contact
interfacial tension 20-50 mN/m
turbid

higher amount of surfactant
thermodynamically stable
no direct phase contact
interfacial tension $10^{-4}$ mN/m
transparent

rule of thumb: high HLB is needed to prepare O/W emulsions, low HLB is needed to produce W/O emulsion and intermediate HLB gives µ-emulsion

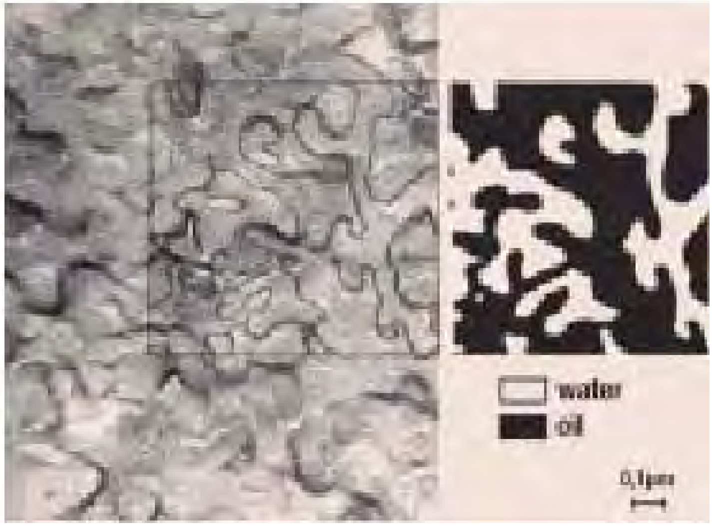
## stability of µ-emulsions:

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

Helfrich free energy (HFE) introduced 1973 by W. Helfrich explains interface and topological fluctuations involving the interface curvatures $c_1$, $c_2$ and the spontaneous interface curvature $c_0$.
K and $\overline{K}$ are moduli and associated with these fluctuations.

# Microemulsions (4)

O/W microemulsion



bicontinuous phase

emulsion

as microemulsions appear transparent
some people call them solutions

# Spontaneous Emulsification

since 50 years: fatty alcohols (for instance lauryl alcohol) act as emulsifying adjuvant for ammonium fatty acids soaps during emulsion polymerizations [40]

soap : alcohol in a 2 : 1 stoichiometry → polymerizable miniemulsion droplets are formed

This process obviously involves also the diffusion of the monomer through the aqueous phase into the structures formed by the mixed surfactant system. The synergistic action of the alcohol surfactant mixture results in a less power demand for the emulsification (gentle stirring is enough) and an enhanced droplet stability. This effect is called spontaneous emulsification and its mechanism is still a matter of controversial discussion.

Dewald, R. C., L. H. Hart and W. F. Carroll, Jr., *J. Polym. Sci.: Polym Chem. Ed.*, **22**, 2923 – 2930 (1984)

Ugelstad, J., P. C. Mork and A. Berge, Vinyl chloride polymerization in *Emulsion Polymerization and Emulsion Polymers*, (Eds. P. A. Lovell and M. S. El-Aasser), Wiley, Chichester, 1997

# Surfactant – Alcohol Mixtures

- surfactant alcohol mixtures possess a variety of exceptional properties : highest packing density, lowest interfacial tension, highest surface viscosity, minimum in droplet / bubble size, and formation of the most stable microemulsions.

  Jönsson, B., B. Lindman, K. Holmberg, and B. Kronberg, Surfactants and Polymers in Aqueous Solution, Wiley, Chichester, 1998

  Patist, A.; T. Axelberd and D. O. Shah, *J. Coll. Interf. Sci.*, **208**, 259 - 265 (1998)

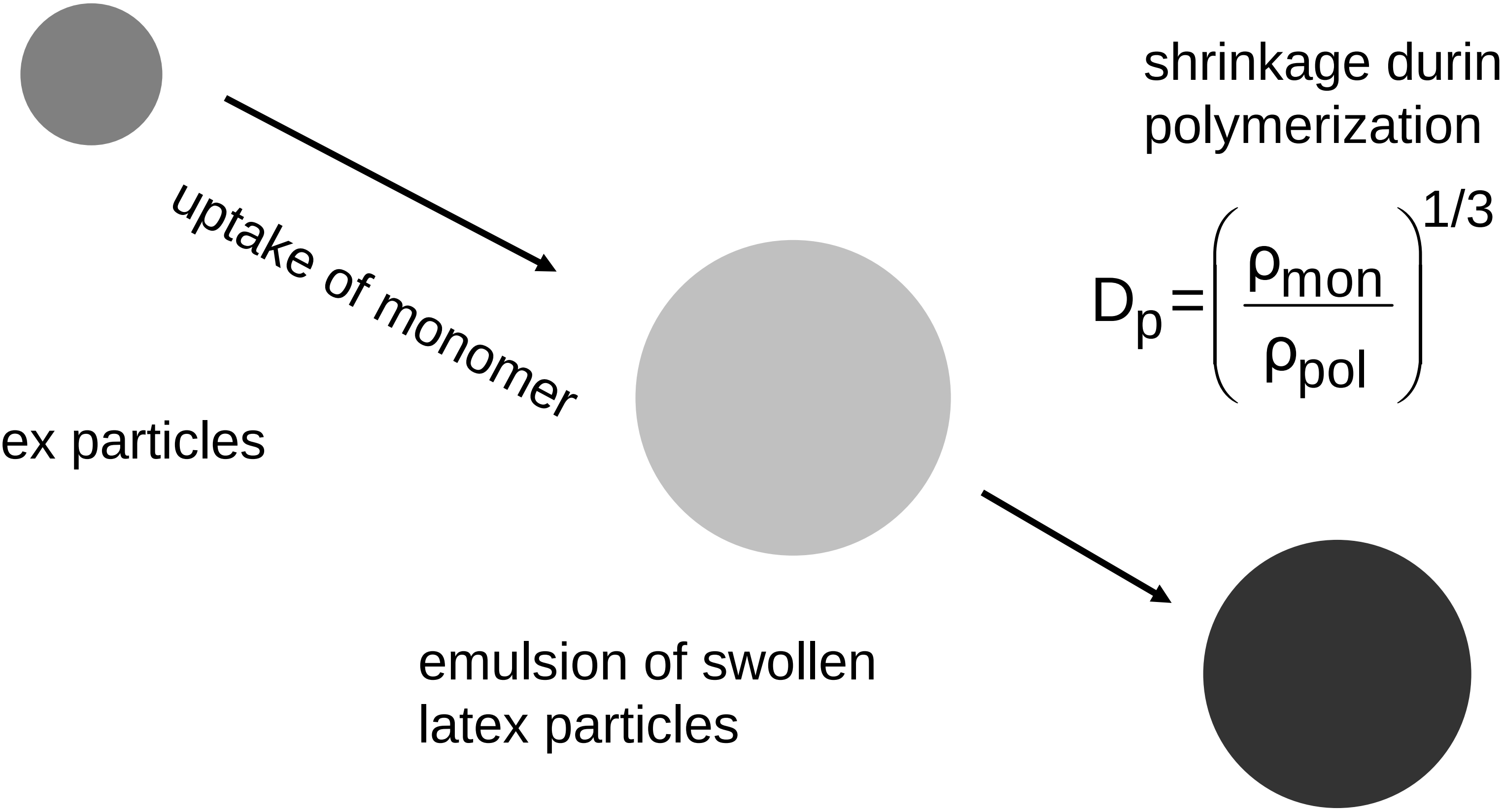
  Oh, S. G. , M. Jobalia and D. O. Shah, *J. Coll. Interf. Sci.*, **155**, 511 - 514 (1993)

- small amounts of a highly water-insoluble compound in the monomer phase prevents the formation of a miniemulsion

- importance of diffusion processes through the aqueous phase for the spontaneous emulsification.

**compound- 2**

# Swelling and Polymerization



uptake of monomer

latex particles

emulsion of swollen
latex particles

shrinkage during
polymerization

$$D_p = \left( \frac{\rho_{mon}}{\rho_{pol}} \right)^{1/3} \bullet D_d$$

final latex
particle after
polymerization

**promotion of swelling ???**

# Swelling – Some Theory

$$\ln\phi_1 + (1 - \frac{1}{j_2})\phi_2 + (1 - \frac{1}{j_3})\phi_3 + \phi_2^2 \cdot \chi_{1,2} + \phi_3^2 \cdot \chi_{1,3} +$$

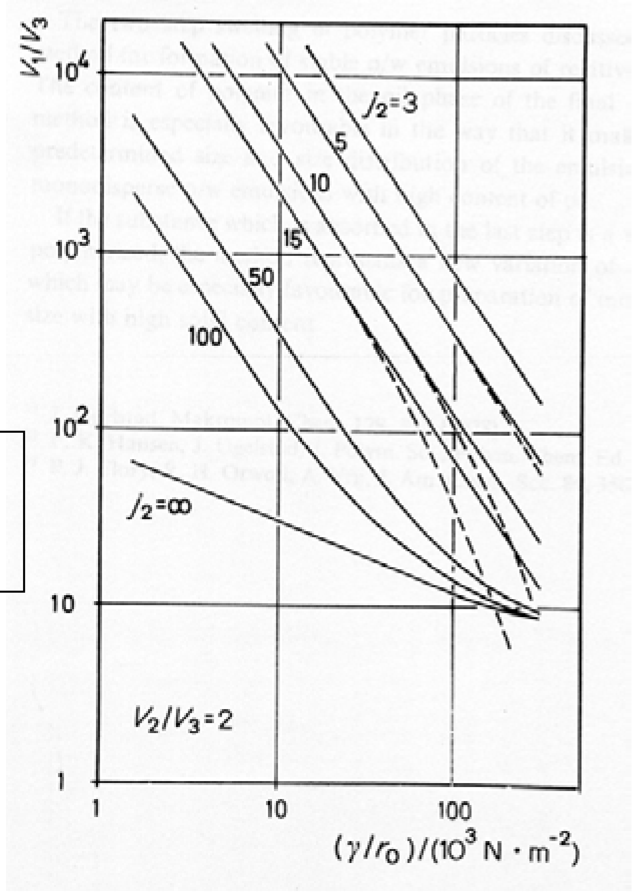
$$+\phi_2 \cdot \phi_3 (\chi_{1,2} + \chi_{1,3} - \frac{\chi_{2,3}}{j_2}) + \frac{4v_1 \cdot \sigma}{D \cdot RT} + \frac{P_{sw} \cdot v_1}{RT} = 0$$

j - degree of polymerization, c - interaction parameter, f - volume fraction, v - partial molar volume, D - equilibrium swollen particle size, RT - thermal energy

1 - monomer
2 - oligomer / **compound- 2**
3 - polymer

entropy promotes swelling

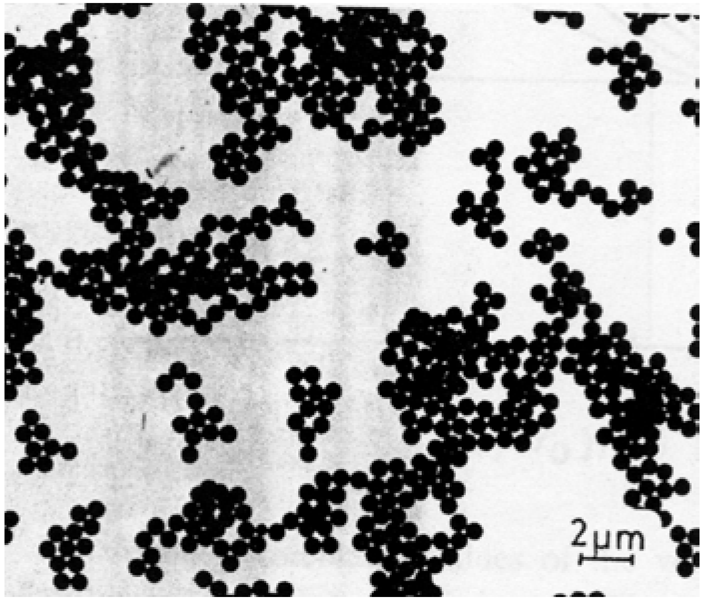
**swelling promoter**



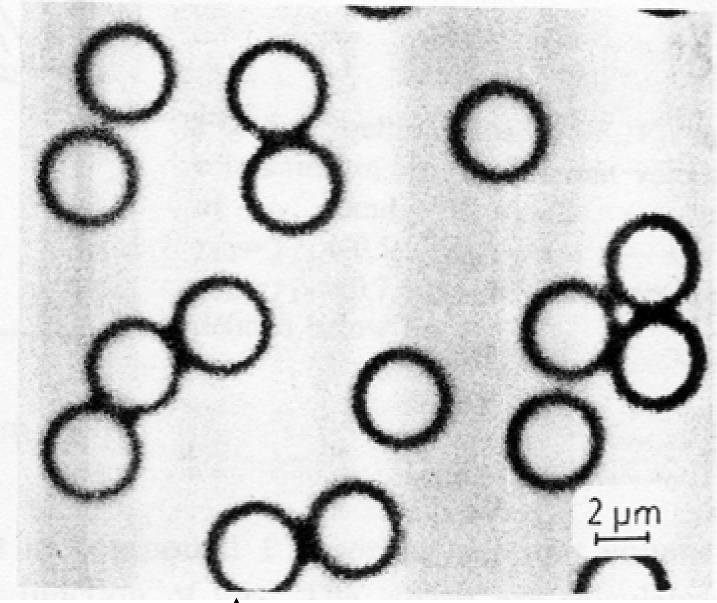
J. Ugelstad, K.H. Kaggerud, F.K. Hansen, A. Berge Makromol. Chem. 180, 737-744 (1979
K. Tauer, H. Kaspar, M. Antonietti Coll. Polym. Sci. 278, 814-820 (2000)

# Swelling – Some Examples

seed particles



emulsion droplets
(swollen particles)



1. chloro-decane
(promoter)

2. chloro-benzene
(oil)

J. Ugelstad, K.H. Kaggerud, F.K. Hansen, A. Berge Makromol. Chem. 180, 737-744 (1979

# Swelling of Latex Particles:

$$\left(\frac{2\cdot\gamma}{r}+P\right)\cdot\frac{v_1}{R\cdot T}=-\left[\ln(1-\phi_2)+(1-1/j_2)\cdot\phi_2+\chi\cdot\phi_2^2+\frac{v_1\cdot\rho_2}{\overline{M}_C}(\phi_2^{1/3}-\phi_2/2)\right]$$

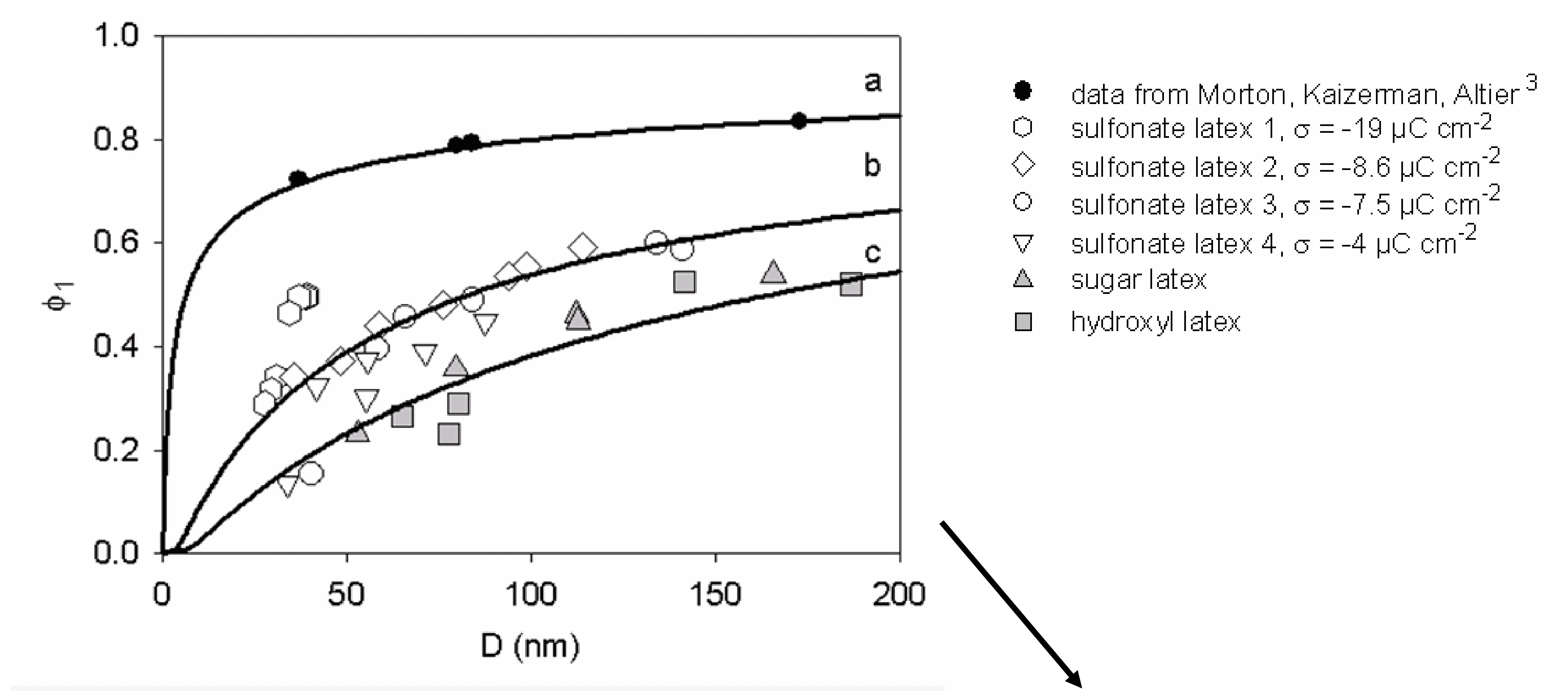
$$\gamma(r)=\gamma_\infty\cdot\left(1+\frac{2\cdot\lambda_1}{r}\right) \qquad \chi(r,\phi_2)=\chi_\infty\cdot\left(1+\frac{3\cdot\lambda_2}{r}\right)$$

$$P=P_0+\frac{P^*}{r} \qquad \chi_\infty(\phi_2)=0.431-0.311\cdot\phi_2-0.036\cdot\phi_2^2$$

The factor (Z) is introduced taking into account the transition from the quasi homogeneous microgel system in toluene over to the heterogeneous aqueous systems of charged polystyrene in the presence of toluene. The factor Z acts directly on $P_0$. $P_0$ represents the swelling pressure of chemically identical bulk materials and P* can be considered as a modulus describing the pressure increase with decreasing size of the sample.

Coll. Polym. Sci. 278, 814-820 (2000)

# Swelling of Latex Particles: Experimental Results



Experimental $\phi_1$ versus D relations symbols experimental data and curves calculated according to the equation (curve a) with size dependent corrections for $\gamma$, $\chi$, and P (curves b, c)

curve a: $\gamma = 3$ mN m$^{-1}$ and $P = 10^4$ N m$^{-2}$ (no size dependence)

curves b, c: $\lambda_1 = 2$ nm; $\gamma_\infty = 4$ mN m$^{-1}$; $P_0 = -8.018716 \cdot 10^5$ N m$^{-2}$; $Z = 1 \cdot 10^{-4}$;

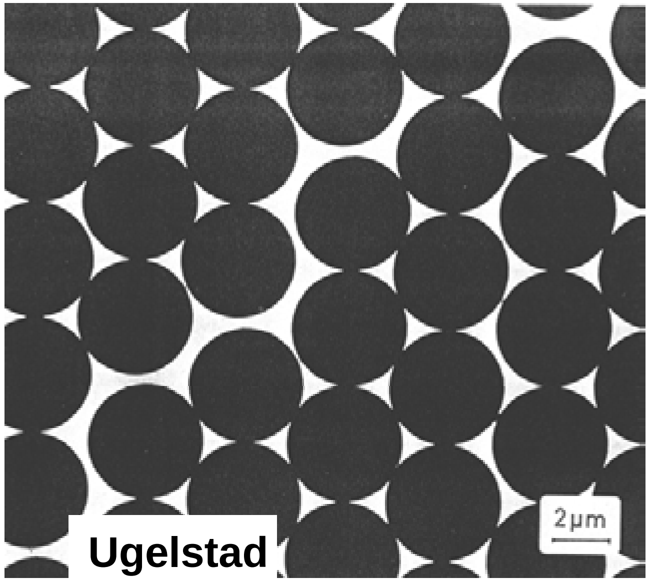
$P^* = 34.45$ mN m$^{-1}$; $T = 298.15$ K

curve b: $\lambda_2 = 17$ nm; curve c: $\lambda_2 = 43$ nm

influence of particle
surface chemistry

Coll. Polym. Sci. 278, 814-820 (2000)

# Swelling – Practical Meaning

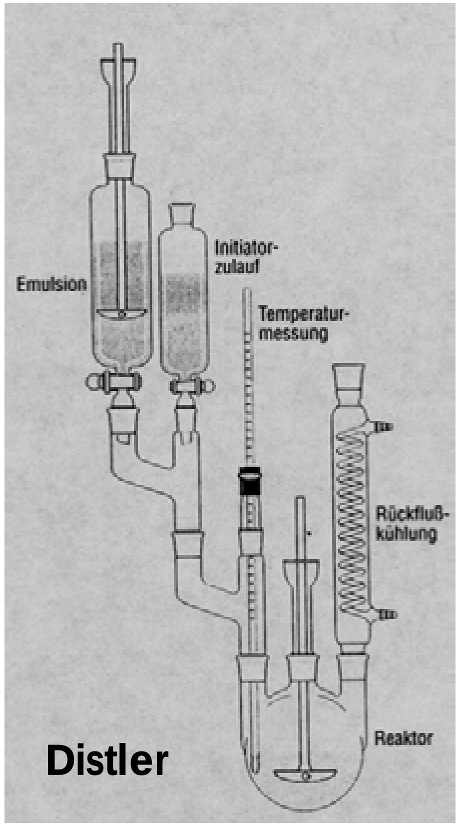


**Ugelstad**

monodispers latexes for medical applications ; e.g. „Dynabeads“

in technical scale production semibatch procedure with feeding a monomer emulsion; normal swelling of seed particles

~25·10$^6$ tons / y
(polymers worldwide)



**Distler**

see you next week:

→ a little (theory) on emulsion stability