# Emulsions – Part 2

## a little (theory): emulsion stability

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

topics:

(some) thermodynamics

surfactant properties

degradation of emulsions

Ostwald ripening

aggregation

phase inversion

phase separation

# Some Thermodynamics (emulsion formation by comminution)

If two components are completely compatible they do not form an interface as it is the case for dilute gases or two mutually soluble liquids. In this case, the free energy of mixing is negative.

It is exactly the opposite if two incompatible components forming an interface upon mixing. If a stable interface is formed the free energy of formation must be positive.

This behavior finds its expression in a special form of the Gibbs-Helmholtz equation where $U^S$ is the total surface energy for a given interface (S), $\sigma$ is the interfacial tension, and T is the absolute temperature .

$$U^S = \sigma - T\left(\frac{\partial\sigma}{\partial T}\right)_S \qquad \left(\frac{\partial\sigma}{\partial T}\right) < 0 \quad \text{for most systems}$$

The preparation of emulsions requires energy to disperse the organic phase (solvent or solution) in water.

In order to get an idea about the thermodynamics the change in the Gibbs free energy of the system ($\Delta G$), provided by the particular dispersing procedure at constant composition and pressure, can be expressed by:

$$\Delta G = \Delta H - T \cdot \Delta S$$

The entropy ($\Delta S$) is a measure of the extent of disorder in the system and hence measures the extent of size reduction of the organic phase (or increase in droplet number). The increasing disorder during the formation of an emulsion means a positive $\Delta S$ contributing to stability.

$\Delta H$ is the enthalpy of the system and can be considered as the binding energy of the organic bulk material or the energy input needed to achieve a certain average droplet size.

If a volume change during the emulsification is neglected the enthalpy corresponds to the internal energy which is the sum of the work required to expand the interfacial area (ΔW) and an amount of heat which results from wasting a part of the energy input .

The increase in the energy of an emulsion compared to the non-emulsified components is equal to ΔW. This amount of energy can be considered as a measure of the thermodynamic instability of an emulsion.

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

ΔW 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 ΔA and subsequently in ΔW. The conclusion is straightforward that ultimate stability against coalescence processes is only achieved if σ approaches zero.

## unmixed (u) state of components 1 and 2
(continuous phase: 1 and dispersed phase: 2)

surface liquid/vapor
interface 1/S

$S$

$1$

$2$

container
interface 1/C

interface ½
(macrodrops)
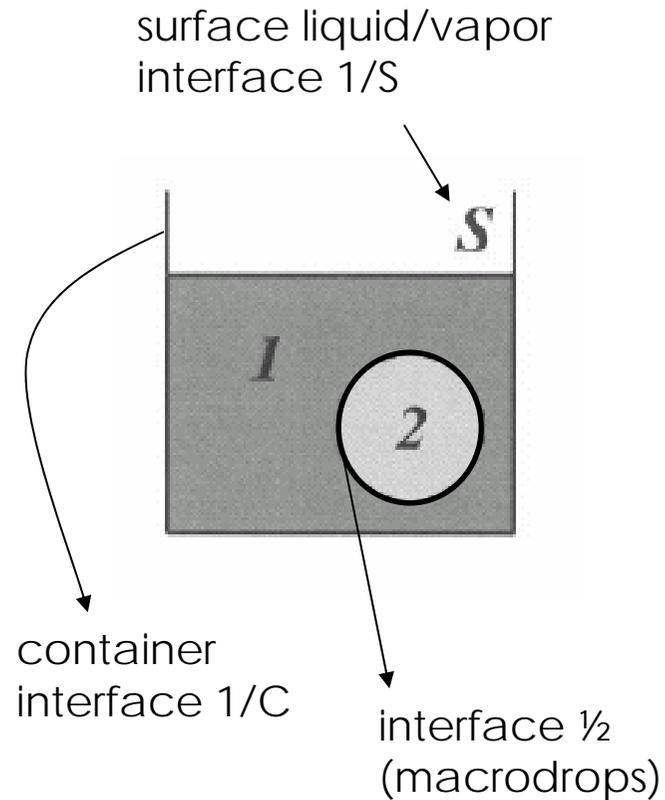
$$G^u = G_1 + G_2 + G_{12}^u + G_{1S}^u + G_{1C}$$

$$G_{12}^u = \sigma_{12} \cdot A_{12}^u \qquad G_1, G_2 \text{ bulk properties}$$

$$G_{1S}^u = \sigma_{1S} \cdot A_S$$

$$G_{1C} = \sigma_{1C} \cdot A_C$$

$$A_{1S} \ll A_{12}^u \longrightarrow G_{1S}^u \ll G_{12}^u \quad !$$

**in many cases but not always**

in almost all cases $G_{1C}$ is not considered **!**

**mixed** state of components 1 and 2
(continuous phase: 1 and dispersed phase: 2)
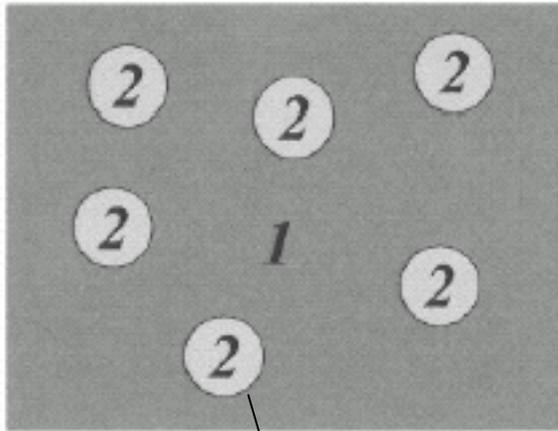


$$G^m = G_1 + G_2 + G_{12}^m + G_{1C} + (G_{2C}) - T \cdot \Delta S$$

$$G_{12}^m = \sigma_{12} \cdot A_{12}^m$$

configurational
entropy

interface 1/2
Interfacial tension: $\sigma_{12}$

**free energy of emulsion formation** between components 1 and 2
(continuous phase: 1 and dispersed phase: 2)

$$\Delta G_{form} = G^m - G^u = \sigma_{12} \cdot \Delta A - T \cdot \Delta S^m$$



in general:    $\sigma_{12} \cdot \Delta A \gg T \cdot \Delta S^m$

→    $\Delta G_{form} \gg 0$    requires external
energy
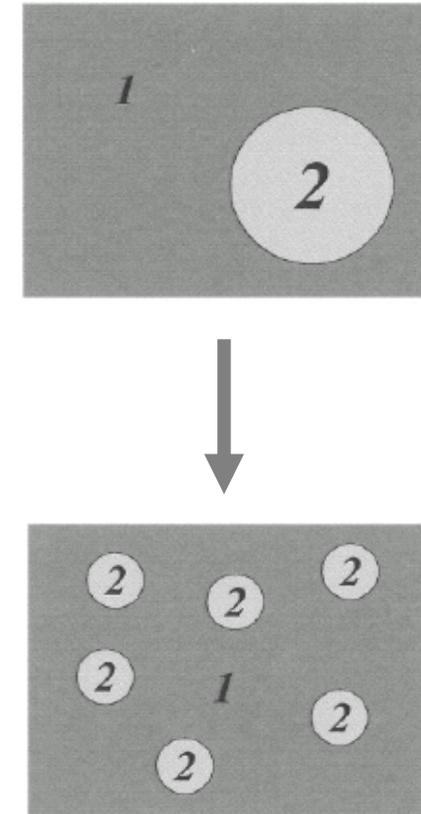


**!** **if $\sigma_{12}$ extremely low** $\rightarrow \Delta G_{form} \leq 0$ **spontaneous emulsification**

**free energy of emulsion breakdown** between components 1 and 2
(continuous phase: 1 and dispersed phase: 2)

$$\Delta G_{break} = -\Delta G_{form}$$

$\rightarrow \quad \Delta G_{break} \quad$ usually $\ll 0$

!

$\rightarrow \quad$ **breakdown is spontaneous**

if $\quad \Delta G_{form} \gg 0$

# Action of Emulsifiers

main actions:

reducing the
interfacial tension
between the phases
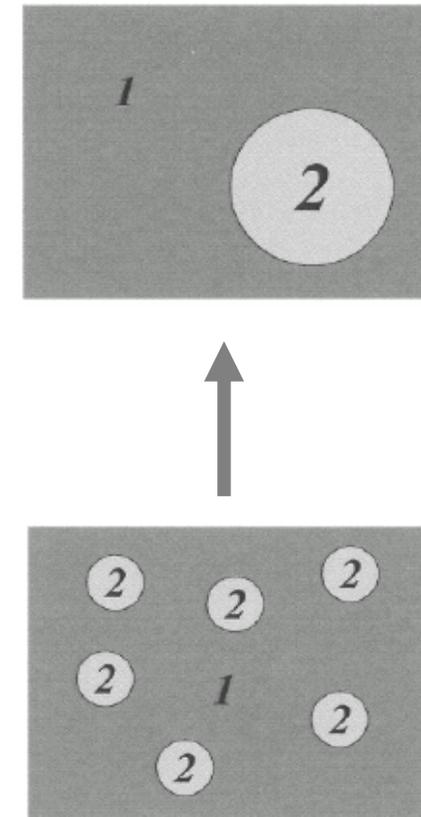
forming a barrier
between the phases
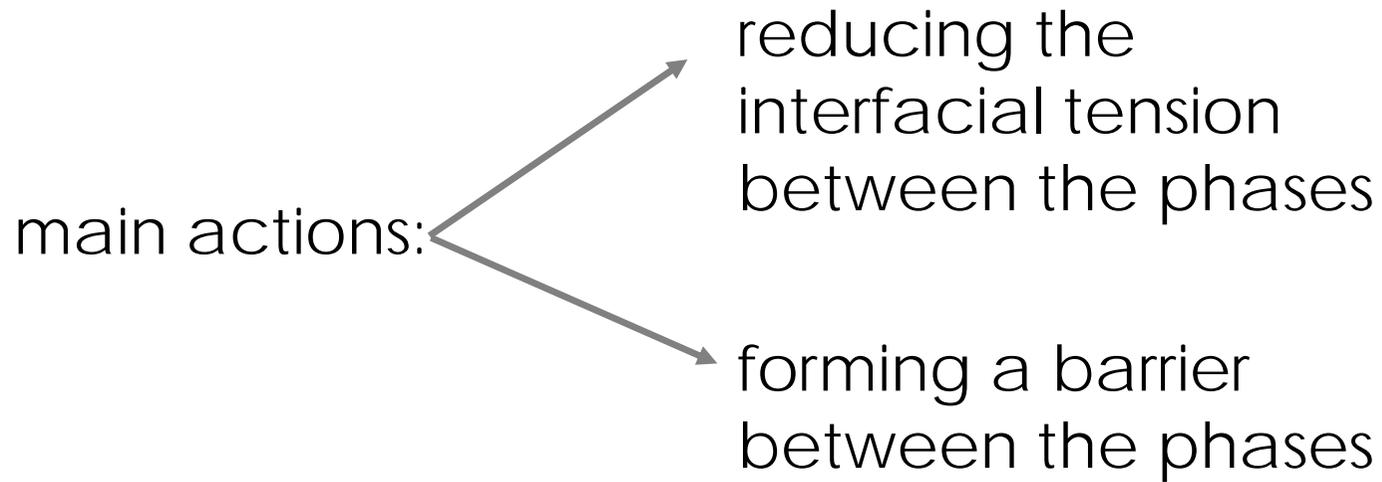
# Action of Emulsifiers
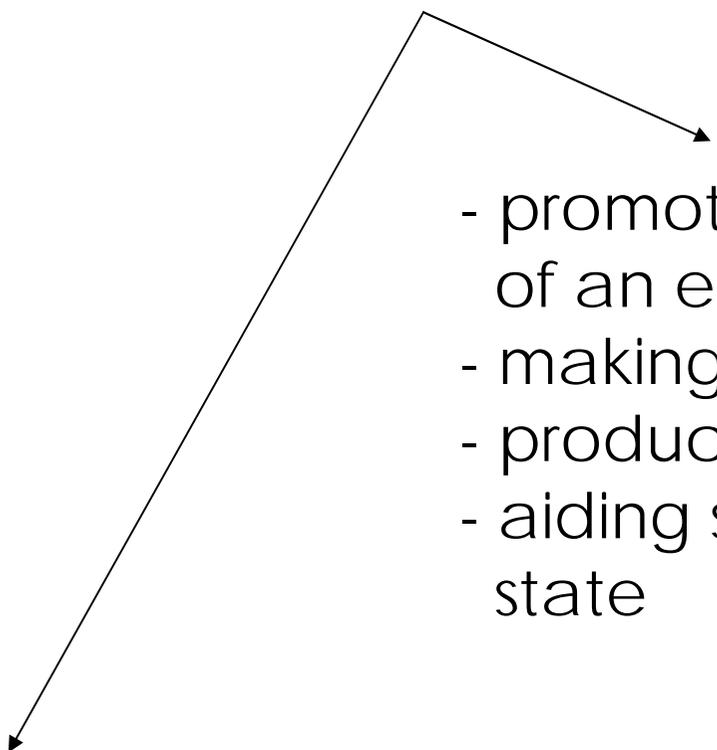
- promoting the formation
  of an emulsion,
- making it easier to prepare,
- producing finer droplet size,
- aiding stability to the dispersed
  state

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

# Gibbs - Marangoni Effect

convective motions due to differences in interfacial tension
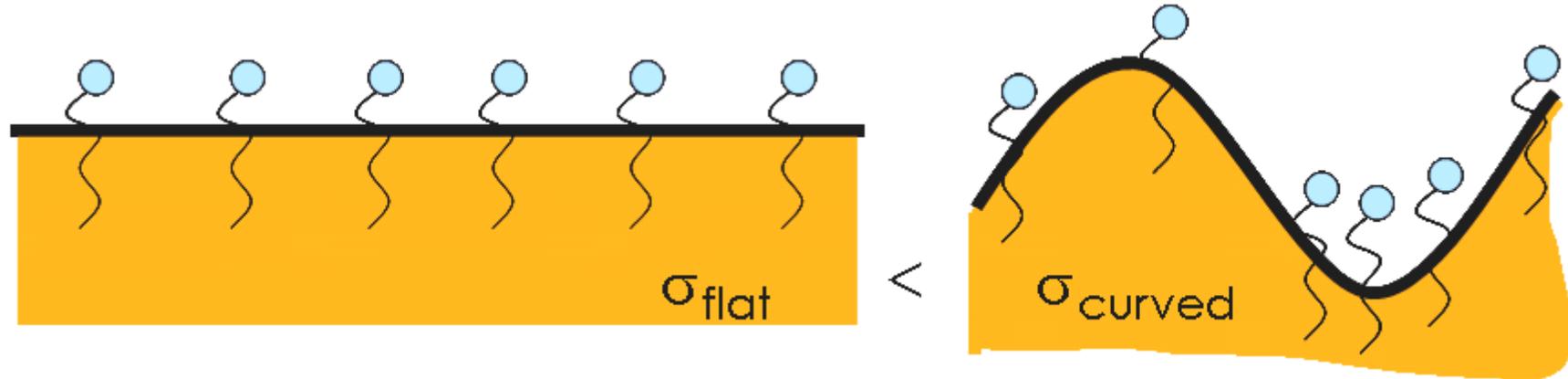
$$\sigma_{flat} < \sigma_{curved}$$

local differences in $\sigma$ at curved interfaces try to restore flat surface spontaneously

Additional action of surfactants: generation and maintaining of a gradient of the interfacial tension (gradient of the interfacial density of surfactant molecules) across the droplet surface during undulations caused by thermal or mechanical stresses. The latter effect also contributes to the stability of emulsions and is strongly connected with the Gibbs - Marangoni effect

# Gibbs - Marangoni Effect (2)

oil / gas

liquid

surfactant moves with the increasing surface tension

oil / gas          oil / gas

local increase in surface tension causes surfactants along with liquid to flow from thicker to the thinner section

liquid

gravity thins but „Marangoni" restores
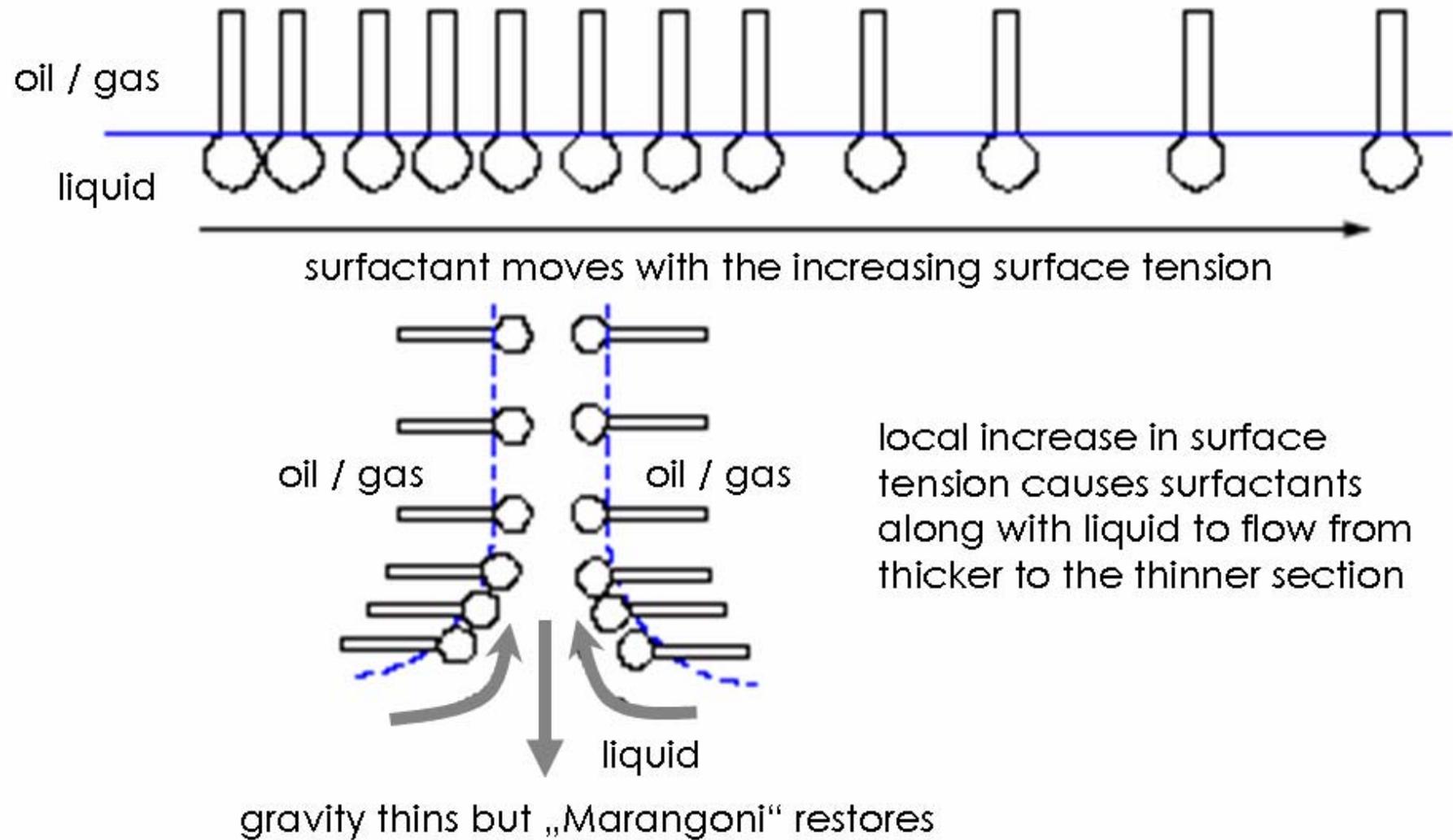
# A closer look at an emulsion droplet (O/W)
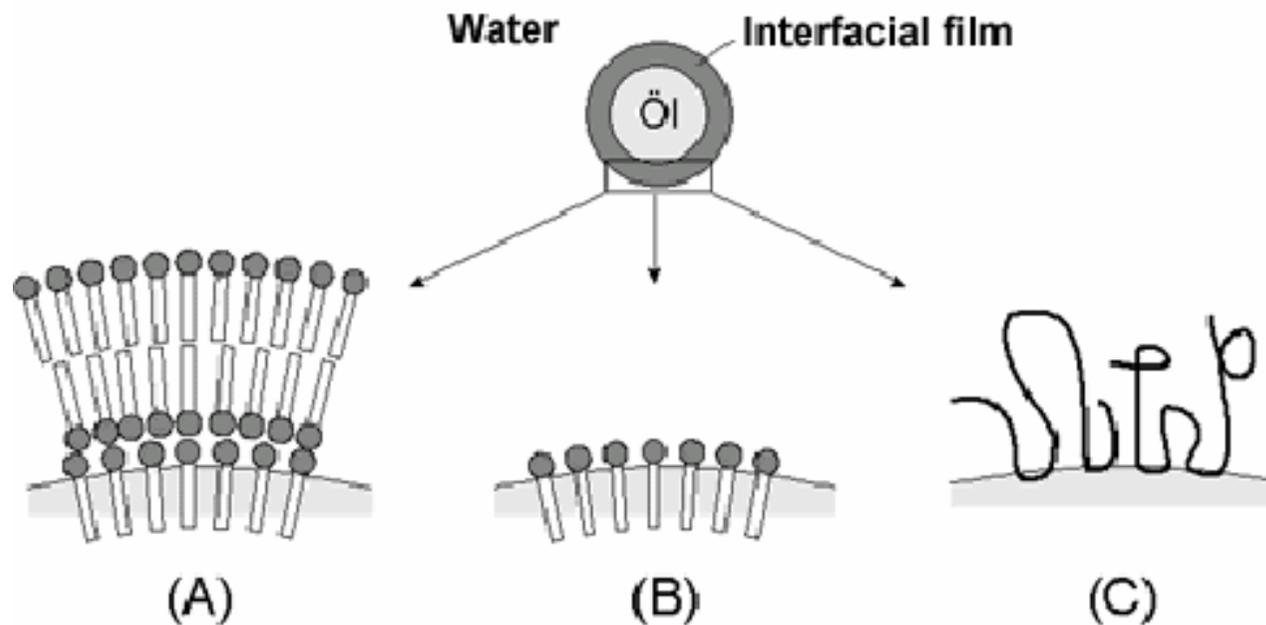


liquid crystalline surfactant film

monomolecular surfactant film

polymeric surfactant film (tail-loop-train model)

# Bancroft's rule

*The liquid in which the stabilizer has a higher solubility forms the continuous phase.*

„When water is the dispersing phase, the emulsifying agent should be a hydrophilic colloid (Höber). Höber does not draw the conclusion that the emulsifying agent should be an oleophile colloid in case the emulsion is to contain water in drops"*

*W. D. Bancroft J. Phys. Chem. 16 (1912) 177-233

# Classification of surface-active agents by HLB

## HLB - hydrophilicity lipophilicity balance*

| HLB VALUE | USE | EXAMPLE |
|---|---|---|
| 1 | Antifoaming Agent | Oleic Acid |
| 2 | Antifoaming Agent | Sorbitan Tristearate |
| 3 | Antifoaming Agent | Glyceryl Monostearate |
| 4 | Emulsifying Agent W/O | Sorbitan mono-oleate (Span 80) |
| 5 | Emulsifying Agent W/O | Glyceryl Monostearate |
| 6 | Emulsifying Agent W/O | Diethylene glycol monolaurate |
| 7 | Emulsifying Agent W/O; Wetting ans Spreading Agents | {none} |
| 8 | Emulsifying Agent W/O; Wetting and Spreading Agents | Sorbitan monolaurate (Span 20) |
| 9 | Emulsifying Agent O/W; Wetting and Spreading Agents | Polyethylene lauryl ether(Brij 30) |
| 10 | Emulsifying Agents O/W | Methyl Cellulose(Methocel15 cps) |
| 11 | Emulsifying Agents O/W | Polyoxyethylene monostearate (Myrj 45) |
| 12 | Emulsifying Agents O/W | Triethanolamine oleate |
| 13 | Emulsifying Agents O/W ; Detergents | Polyethylene glycol 400 monolaurate |
| 14 | Emulsifying Agents O/W ; Detergents | (none) |
| 15 | Emulsifying Agents O/W ; Detergents | Polyoxyethylene sorbitan mono-oleate (Tween 80) |
| 16 | Emulsifying Agent O/W ; Detergents: Solubilizing Agents | Polyoxyethylene sorbitan monolaurate (Tween 20) |
| 17 | Solubilizing Agents | Polyoxylene lauryl ether(Brij 35) |
| 18 | Solubilizing Agents | Sodium oleate |
| 19 | Solubilizing Agents | None |
| 20 | Solubilizing Agents | Potassium oleate |

# HLB-values of typical **food** emulsifiers

| Emulsifier | HLB value | ADI (mg/kg body weight) |
|---|---|---|
| Glycerol monostearate | 3.8 | Not limited |
| Diglycerol monostearate | 5.5 | 0 - 25 |
| Tetraglycerol monostearate | 9.1 | 0 - 25 |
| Succinic acid ester of monoglycerides | 5.3 | - |
| Diacetyl tartaric acid ester of monoglycerides | 9.2 | 0 - 50 |
| Sodium stearoyl-2-lactylate | 21.0 | 0 - 20 |
| Sorbitan tristerate | 2.1 | 0 - 25 |
| Sorbitan monostearate | 4.7 | 0 - 25 |
| Sorbitan monooleate | 4.3 | - |
| Poloxyethylene sorbitan monostearate | 14.9 | 0 - 25 |
| Propylene glycol monostearate | 3.4 | 0 - 25 |
| Polyoxyethylene sorbitan monooleate | 15.0 | 0 - 25 |

**HLB** - hydrophilic-lipophilic balance
**ADI** - acceptable daily intake

# HLB – pros and cons

Positives
- ✓ Excellent starting point
- ✓ Generally produces a fairly good emulsion

Negatives
Ignores the importance of:
- Electrical double layer
- Temperature effects of ethoxylates
- Fatty alcohols
- Placement of emulsifier
- % of emulsifier to be used
- Phase volume ratios
- Component interactions
- Liquid crystals

HLB value is important also for the stability of an emulsion
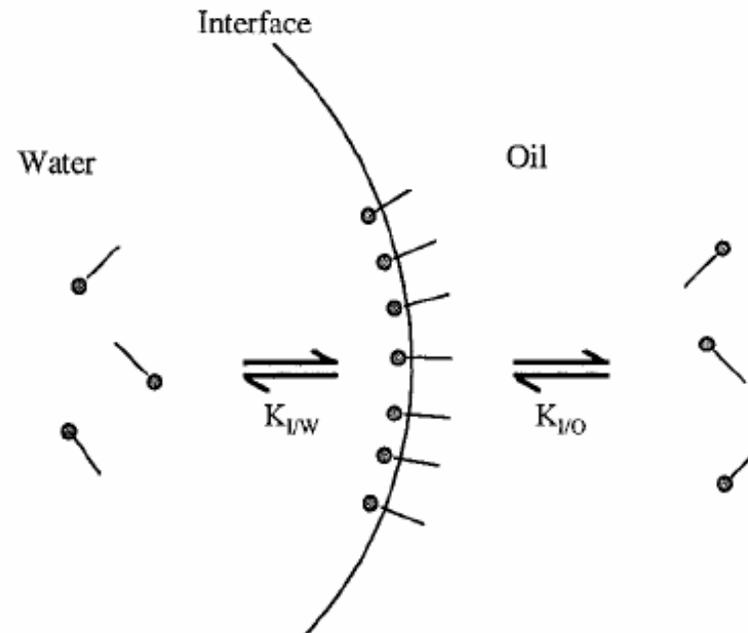


**Figure 1.** In microemulsions, all surfactant molecules are distributed between the oil, water, and interface.

the surfactant must be present at the interface - optimum HLB is necessary

**Table 1. Surfactants Used in This Study[a]**

| surfactant (Igepal) | abbrev | EO number | HLB | water soluble | oil soluble |
|---|---|---|---|---|---|
| CO-210 | $C_9PhE_{1.5}$ | 1.5 | 4.6 | no | yes |
| CO-430 | $C_9PhE_4$ | 4 | 8.8 | no | yes |
| CO-520 | $C_9PhE_5$ | 5 | 10.0 | no | yes |
| CO-530 | $C_9PhE_6$ | 6 | 10.8 | no | yes |
| CO-610 | $C_9PhE_{7.5}$ | 7.5 | 12.2 | yes | yes |
| CO-720 | $C_9PhE_{12}$ | 12 | 14.2 | yes | yes |

[a] The Igepal CO family of surfactants are nonylphenyl ethoxylates ($p\text{-}t\text{-}C_9H_{19}C_6H_4(OC_2H_4)_nOH$).

# surfactant properties (1) – Krafft temperature
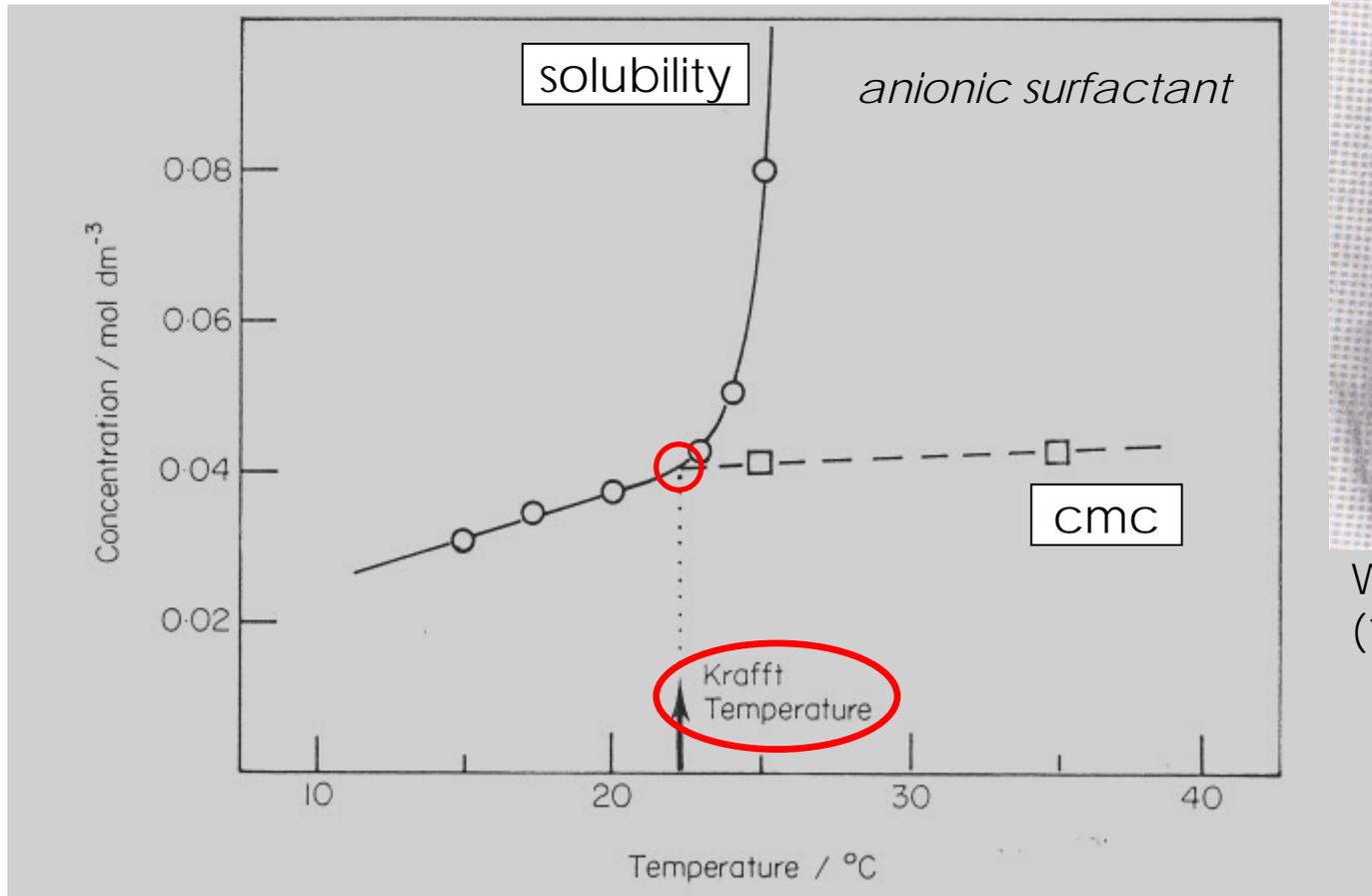


W. L. Friedrich E. Krafft
(1852-1923), Heidelberg

# Krafft Temperature - Examples



Phase Diagram SDS
$CH_3-(CH_2)_{10}-CH_2\text{-}OSO_3^-Na^+$
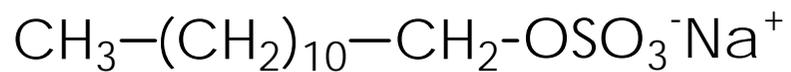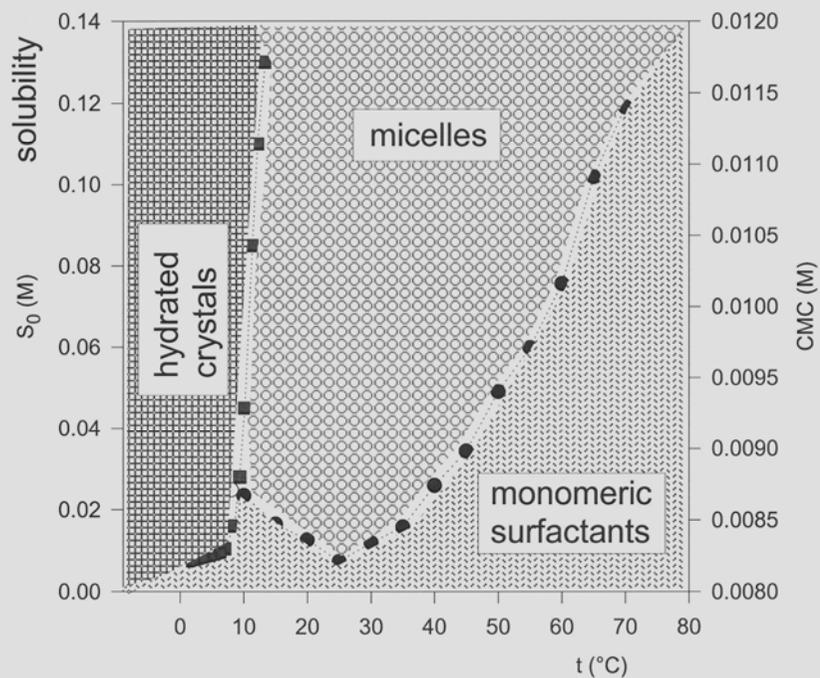
Phase Diagram SODS
$CH_3-(CH_2)_{16}-CH_2\text{-}OSO_3^-Na^+$
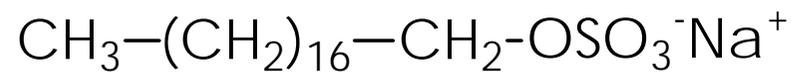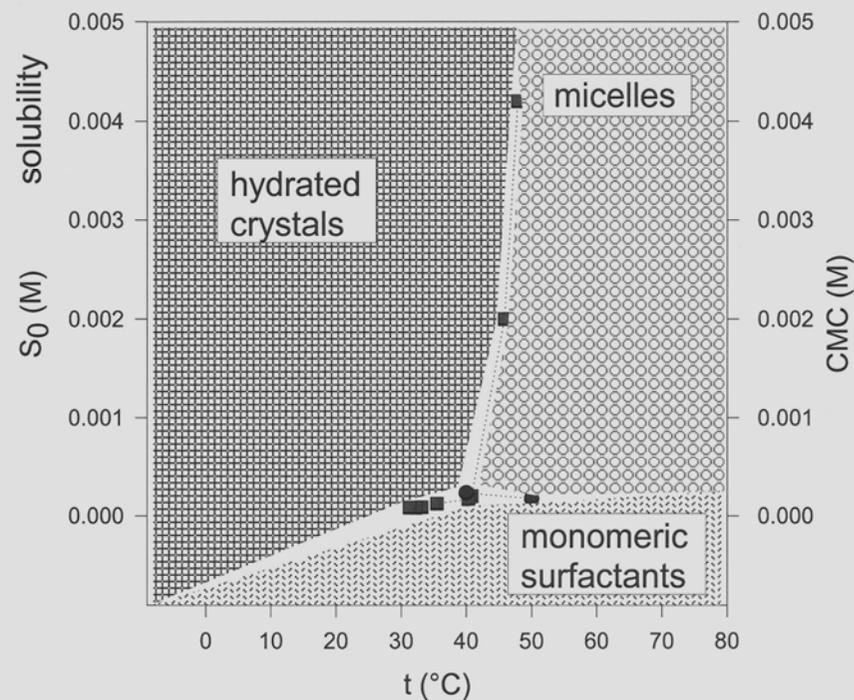
# Phase Inversion Temperature PIT

➢ As the temperature increases, the water solubility of ethoxylated nonionic emulsifiers becomes poorer (the HLB decreases).

➢ There is a temperature (PIT) at which the hydrophilic and lipophilic characteristics of the emulsifier are equal (relative to the required HLB of the oil phase).

➢ At this temperature the emulsion will exhibit a phase inversion.

➢ The PIT should be at least 20 °C higher than the storage temperature. Choose emulsifiers, and concentrations, to raise the PIT.

# Phase inversion temperature (PIT)
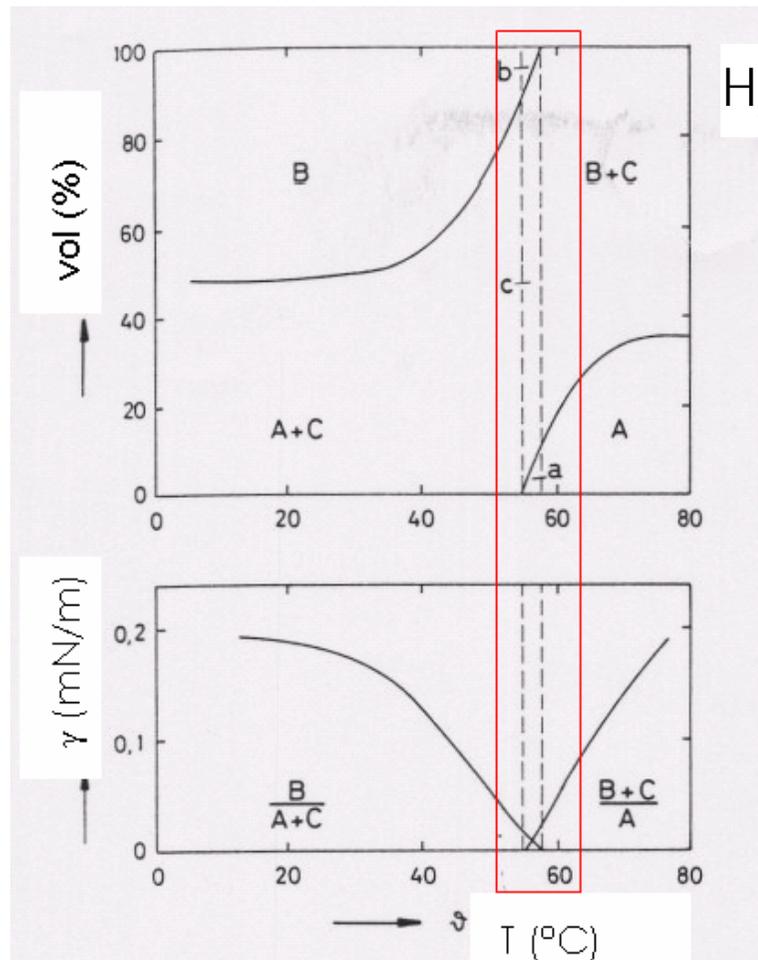


FIG. 1. (a) Volume fractions of the phases of the ternary system $H_2O-C_6H_{12}-NP_{8.6}$ versus temperature. (b) Interfacial tensions between the phases versus temperature (after (1)).

C.-U. Herrmann, G. Klar, M. Kahlweit
J. Coll. Interf. Sci. 82 (1981) 6-13

$H_2O$ (A) – cyclohexane (B) – $NP_{8.6}$ (C)

A: 47.5 – B: 47.5 – C: 5 wt-%

$NP_{8.6}$: $C_9H_{19}$—⬡—$O$$\left(CH_2-CH_2-O\right)_{8.6}$$H$
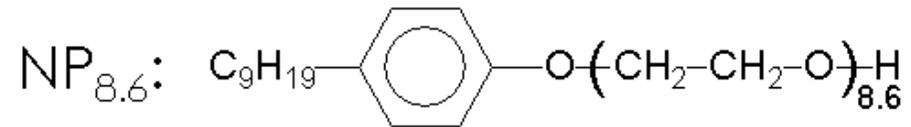
at RT: lower phase rich in A and C and an upper phase rich in B

as T raises volume fraction of the lower phase increases at the expence of the upper phase

at 55 °C a thrid phase (a), rich in A, appears at the bottom

in a small T-range three phases coexist (low interfacial tension)

further raise in T makes phase b to disappear leaving only an upper phase rich in B and C and a lower phase rich in A

# Emulsifiers may be selected by means of the HLB scale or by the phase-inversion temperature (PIT)
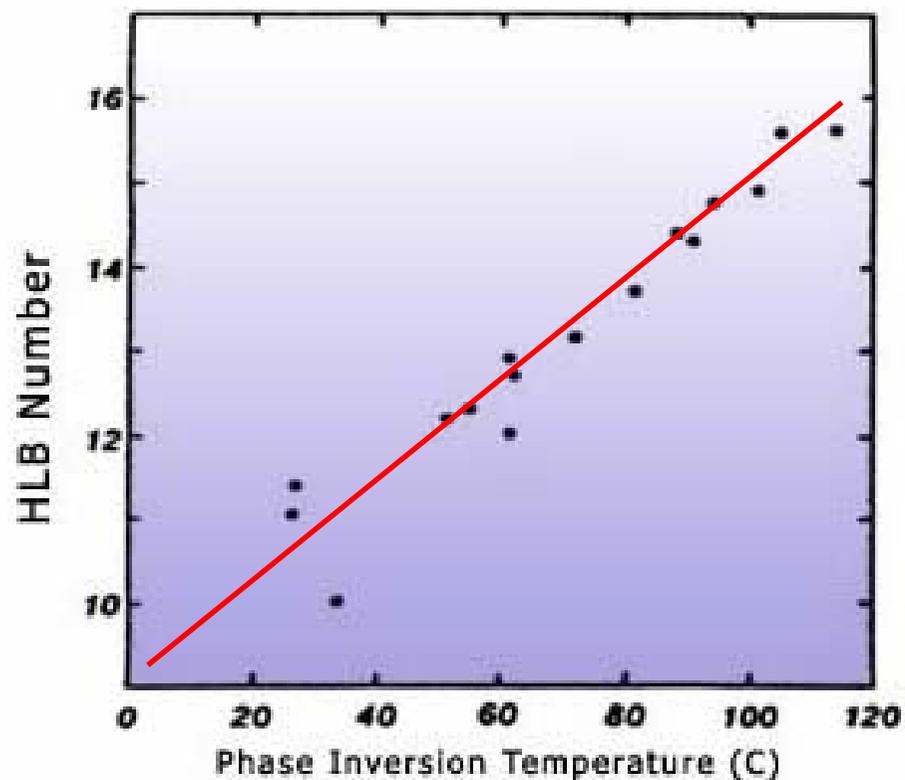


Fig 1. The correlation between the HLB number and the PIT temperature (in cyclohexane) of nonionic surfactants

# Requested Breakdown of Emulsions:

→ Demulsification

$$\Delta G_{break} = -\Delta G_{form}$$

→ $\Delta G_{break}$ usually « 0

→ breakdown is spontaneous
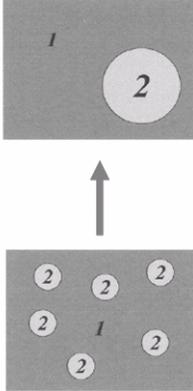
Yes, sometimes but not always when needed and not completely

## Important examples:

- oil recovery (oil in water emulsions)
- waste treatment (oil in water emulsions)

→ destroy the interfacial surfactant layer by demulsifiers

topic in its own right

## There are several strategies for counteracting emulsions:

- air flotation, ozonation or other oxidations

- modifying the surfactant's charge (addition of $CaCl_2$ or $MgSO_4$ changes surfactant solubility)

- Antagonist addition (charge neutralization)

- Increase the solubility of the surfactant in either bulk phase ( alcohol or other polar solvents, such as acetone to pull the surfactant out of the oil phase)

- If the aqueous phase is a brine, dilution with water might help

- Disrupt the oriented structure of the emulsifier's interfacial phase with demulsifiers which are materials not very soluble in either phase and hence concentrate at the interface (separation due to increasing the intermolecular distance and weakening the binding forces constructed by the emulsifier)

- Increase the ionic strength

# Degradation of Emulsions
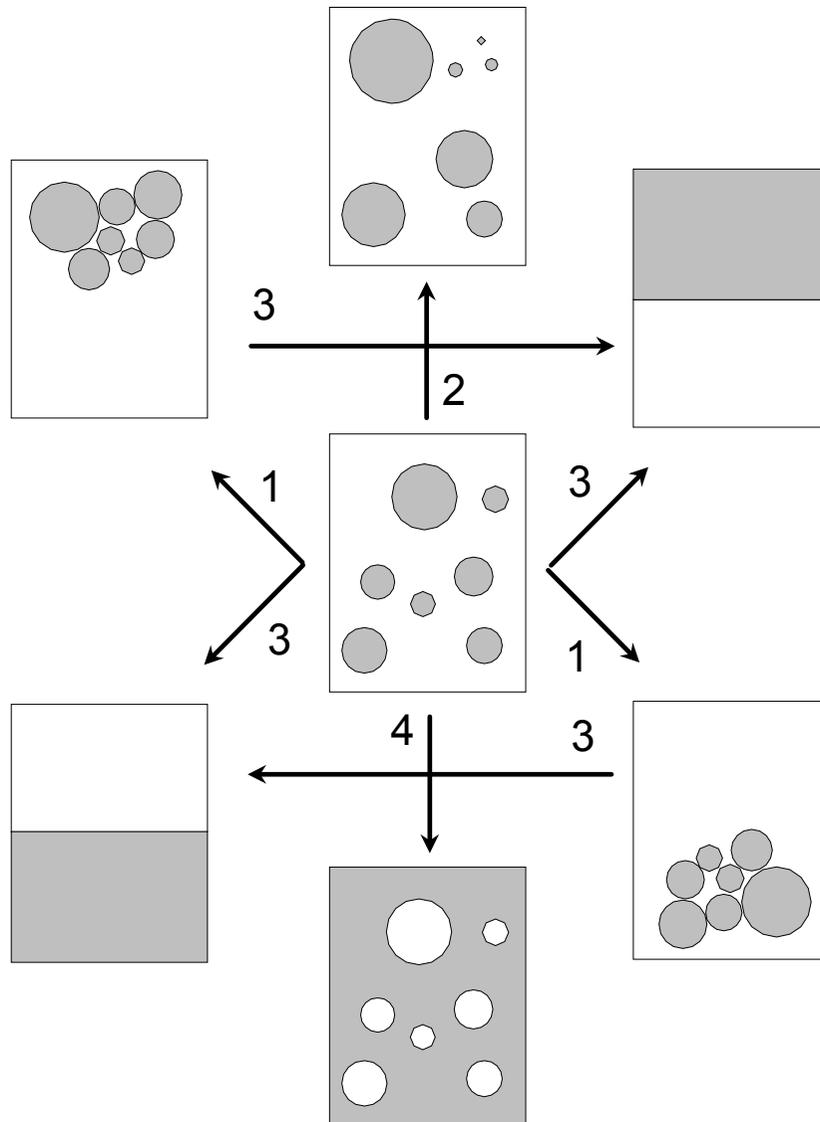


1 – phase separation

   (creaming, sedimentation)

2 – Ostwald ripening

3 – aggregation processes

   (flocculation, coagulation, coalescence)

4 – phase inversion

# Phase separation

stationary velocity for laminar conditions during phase separation:

$$V_{ps} = \left( \rho_d - \rho_c \right) \cdot \frac{D_d^2 \cdot g}{18 \eta_c}$$

<u>As a rule of thumb:</u>  $D_d > 1$ µm sedimentation and creaming
for $\rho_d > \rho_c$ and $\rho_d < \rho_c$

<u>$D_d <  1$ µm</u>: water and a common monomer / oil, Brownian motion keeps the droplets almost evenly distributed throughout the emulsion (if no other forces are acting)

The density of the disperse phase means exactly the density of the droplets during the motion. A moving droplet is composed of liquid-1, stabilizers, and in some cases also a certain amount of continuous phase which is entrapped in a layer surrounding the droplets.

# Phase Separation: Dispersed Phase

phase separation depends on density difference $\quad \Delta = \left( \rho_d - \rho_c \right)$

| chloroform / water | hexane / water |
|:---:|:---:|



oil



oil
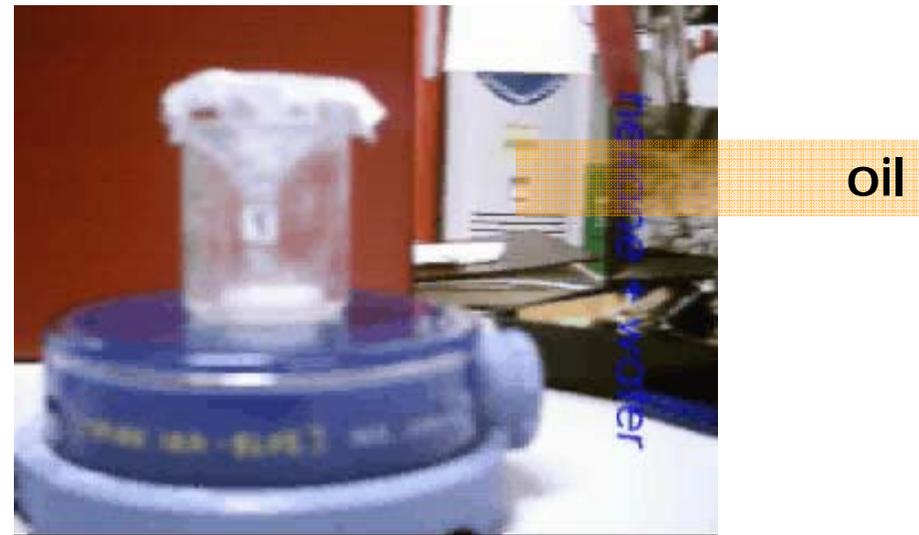
| sedimentation | creaming |
|:---:|:---:|
| $\Delta = 0.49845$ g cm$^{-3}$ | $\Delta = -0.3452$ g cm$^{-3}$ |

# Phase Separation: Dispersed Phase

phase separation is size dependent $\qquad D_d^2$

practical meaning: bimodal droplet size distributions

natural fresh milk, non homogenized:



cream 35% fat

8 % fat

butter & cheese
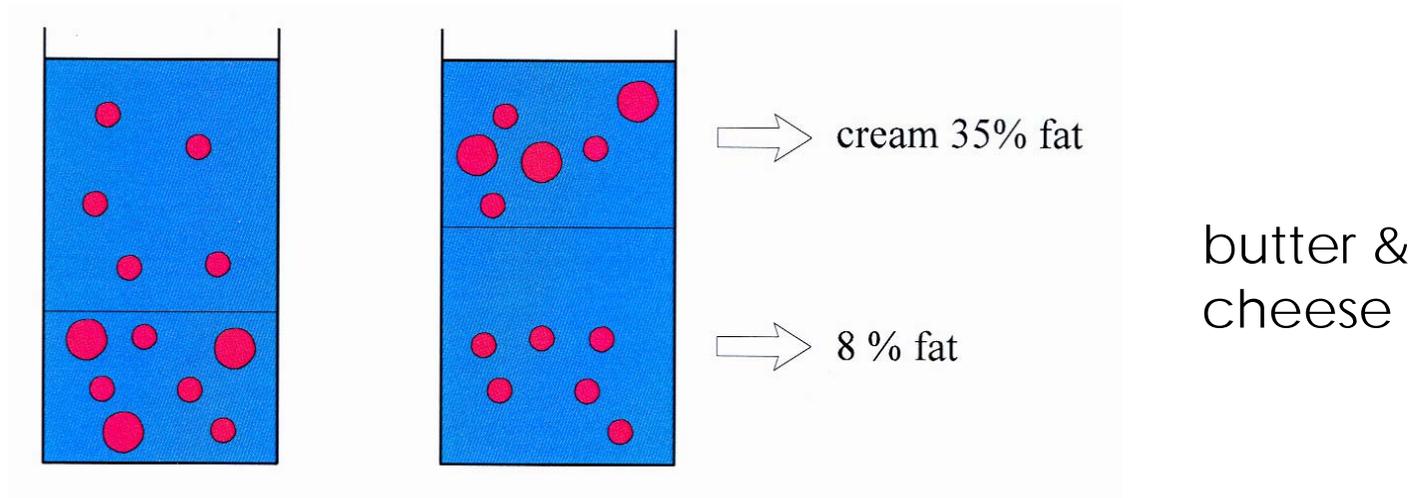
# Phase Separation: Continuous Phase

phase separation is viscosity dependent

$1/\eta_c$
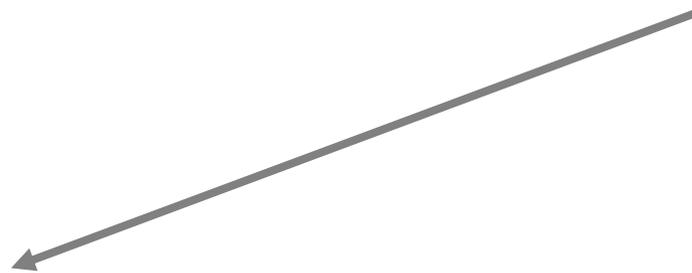
to reduce phase separation:

add gelling agents to increase
viscosity of the continuous
phase

# Aggregation Processes
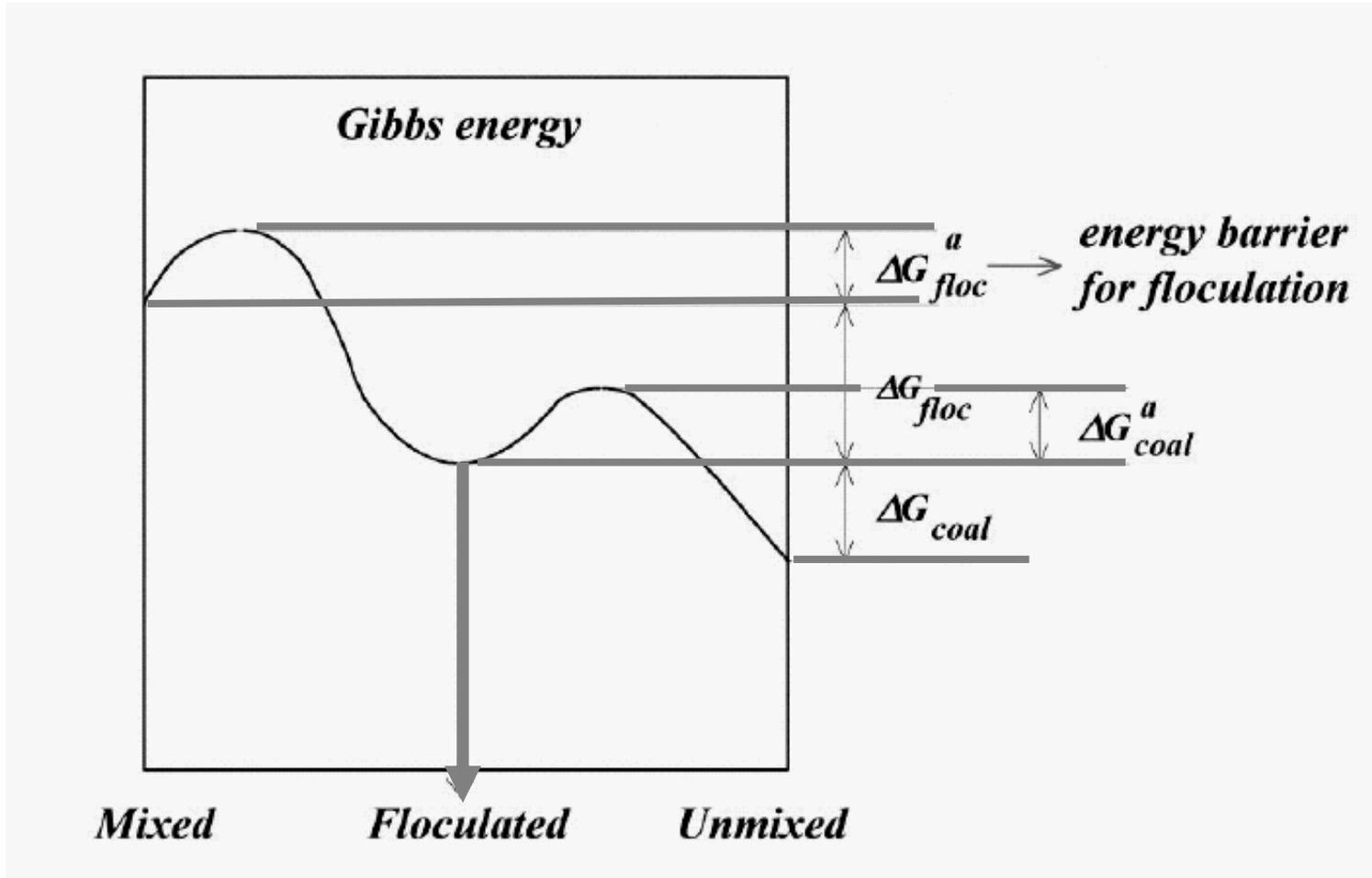


$$\Delta G^a_{coal} \rightarrow \text{rupture of interfacial film} \qquad \Delta G_{coal} = -\gamma_{12}\Delta A$$

# Stabilisierung von Kolloiden - Möglichkeiten
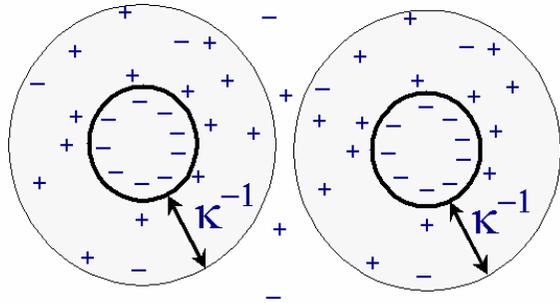


elektrostatisch
adsorbiert, kovalent
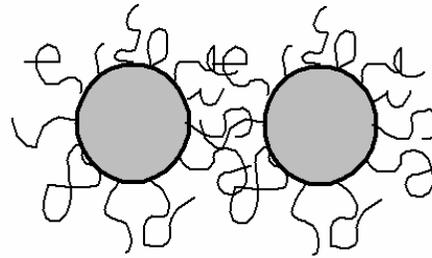
sterisch
adsorbiert, kovalent
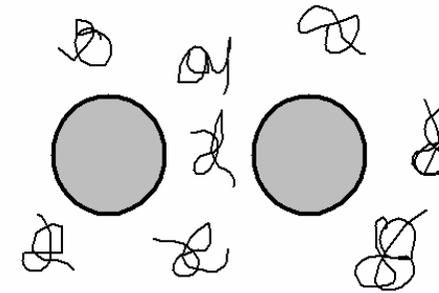
Depletion-Stabilisierung
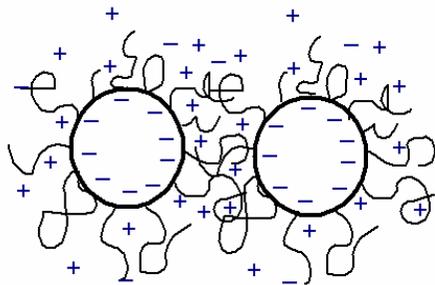
elektrosterisch

Ladungen auf der Teilchenoberfläche und
adsorbierte oder gebundene Polymere
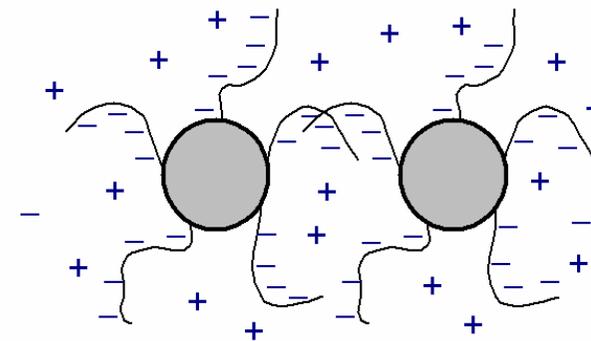
geladene Polymere
adsorbiert, kovalent

D. H. Napper, *Polymeric Stabilization of Colloidal Dispersions*,  AP **1983**

nicht maßstabsgerecht

# DLVO theory for charged spheres

**Born repulsion**

$V_{int} / \kappa_B T$

**primary maximum**
($V_{pm} > 15 \, k_B T$)

0

**secondary minimum**
($V_{sm} < 1,5 \, k_B T$ for reversible flocculation)

**primary minimum**
(ca. 2 times dispersions energy droplet - $H_2O$)

$d_{PP}$
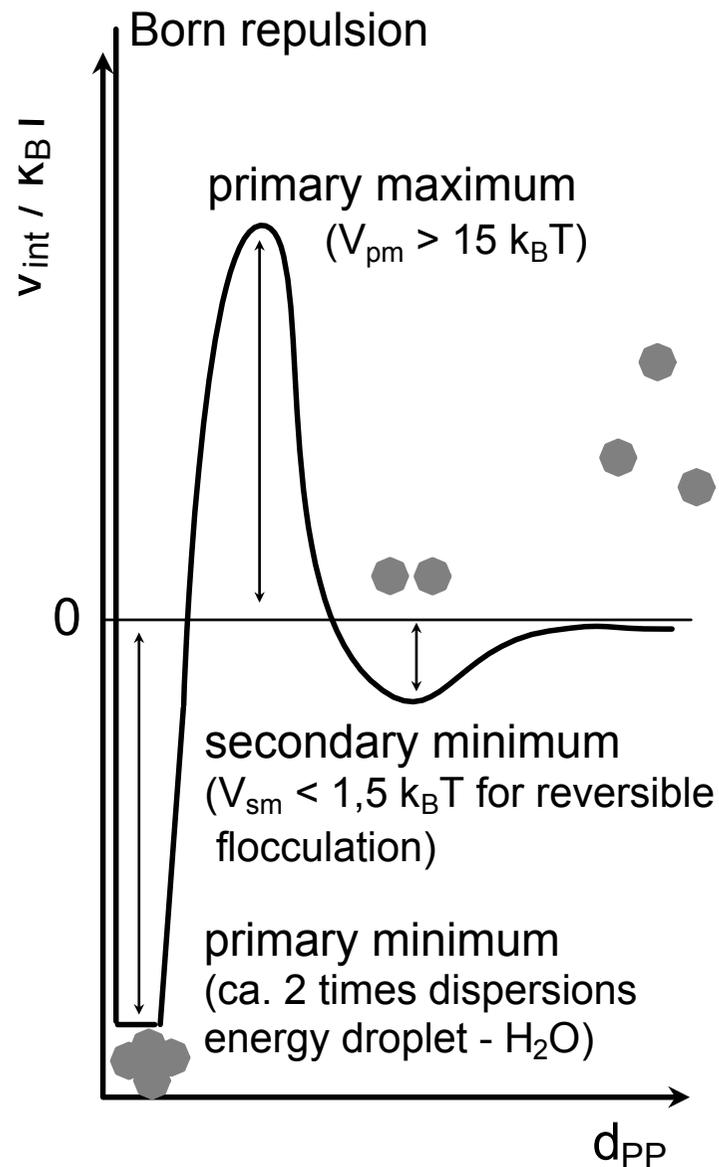
electrostatic double layer repulsion competes with van der Waals attraction

Derjaguin B.V., Landau L.D., *Theory of the stability of strongly charged lyophobic sols and the adhesion of strongly charged particles in solutions of electrolyte* Acta Physicochimica URSS 14 (**1941**) 633-662
Verwey E.J.W., Overbeek J.Th.G., **1948**, *Theory of the Stability of Lyophobic Colloids.* Elsevier, New York

E J W Verwey; J Th G Overbeek; K van Nes Publisher: New York, Elsevier Pub. Co., 1948.
Theory of the stability of lyophobic colloids; the interaction of sol particles having an electric double layer

# Ladungsstabilisierung von Kolloiden - Theorie

**Born Abstoßung der Elektronenwolken**

$V_{int} / k_B T$

**primäres Maximum**
($V_{pm} > 15\,k_B T$)

0

**sekundäres Minimum**
($V_{sm} < 1{,}5\,k_B T$ für reversible Flockung)

**primäres Minimum**
(2*Dispersionsenergie Polymer - $H_2O$)

$d_{PP}$
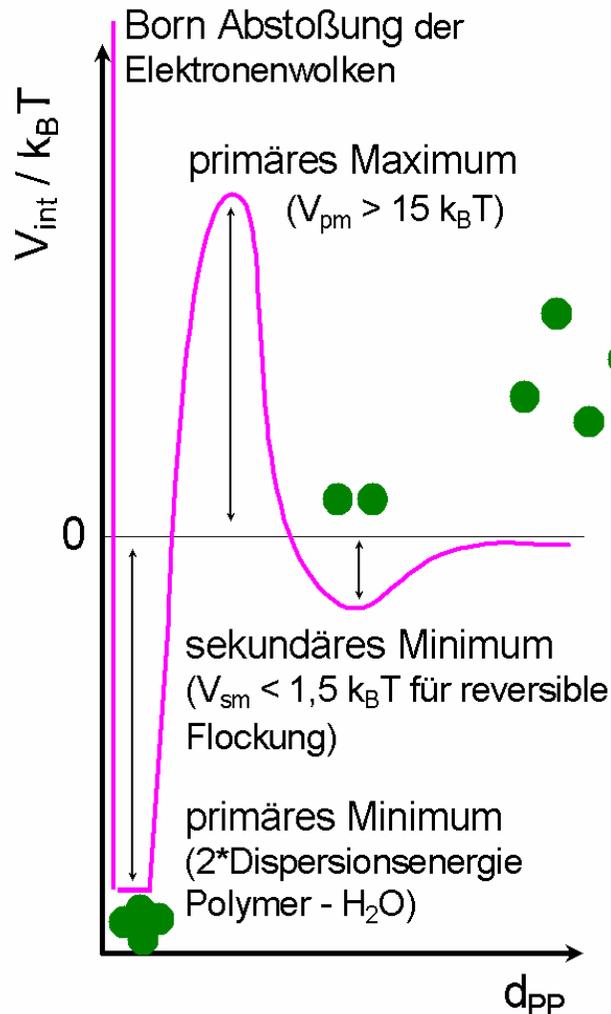
**Wechselwirkungsenergie**

$$V_{int} = V_A + V_{es} + V_{st} + V_{est} + V_{Born}$$

$V_A$ - van der Waals Anziehungsenergie:
Keesom, Debye, London, Hamaker
(Summierung über alle Atome zweier kolloidaler Teilchen), Hamaker Konstante $H_{xyx}$

$$V_A \propto H_{xyx} \cdot d_{PP}^{-1}$$

$V_{es}$ - elektrostatische Abstoßung

$$V_{es} \propto \exp(-\kappa \cdot d_{PP})$$

$V_{st}$ - sterische Abstoßung

$$V_{st} \propto d_{PP}^{2}$$

Wechselwirkungsparameter Stabilisator - Dispersionsmittel hat großen Einfluß

$V_{est}$ - elektrosterische Abstoßung

$V_{Born}$ - Abstoßung

$$V_{Born} \propto d_{PP}^{-14}$$

# Beeinflussung der Ladungsstabilisierung - Elektrolyte

## Kritische Koagulationskonzentration (KKK):

$$KKK \propto \frac{(\varepsilon\varepsilon_0)^3(k_BT)^5}{(ze)^6 H_{121}^2}\Gamma_0^4$$

hohe Ladungsdichte ($\Gamma_0 = 1$)

$$KKK \propto \frac{\sigma^{4/3}k_BT(\varepsilon\varepsilon_0)^{1/3}}{(ze)^2 H_{121}^{2/3}}$$

niedrige Ladungsdichte

**Schulze-Hardy Regel**: KKK ist 1 : 0,013 : 0,0016 für 1, 2, 3-wertige Gegenionen (empirisch gefunden für hochgeladene Teilchen)

$$\lambda_D = 1,762 \cdot 10^{-2}\left(\frac{T}{C_0}\right)^{1/2}$$

T = 333,15 K

$$\Gamma_0 = \tanh(\frac{z \cdot e \cdot \Phi}{4 \cdot k_B \cdot T})$$

| $C_0$ (M): | $10^{-3}$ | $10^{-2}$ | $10^{-1}$ | $10^0$ |
|---|---|---|---|---|
| $\lambda_D$ (nm): | 10,2 | 3,15 | 1,02 | 0,315 |

ab hier ist $\lambda_D$ zu gering, um rein elektrostatisch Stabilität zu verleihen

D.F. Evans, H. Wennerström "The Colloidal Domain", VCH 1994, p. 336/337

# Teilchen-Teilchen Wechselwirkung (1)
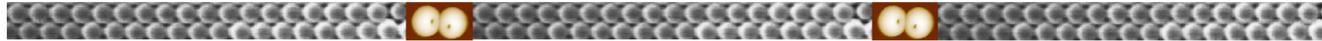
$$V_{int}(d_{PP}) = \pi \cdot a \left( -\frac{H_{121}}{12\pi} \cdot \frac{1}{d_{PP}} + \frac{64 \cdot k_B \cdot T \cdot C_0 \cdot \Gamma_0^2}{\kappa^2} \exp(-\kappa \cdot d_{PP}) \right)$$

$$\lambda_D = \kappa^{-1} = \left( \frac{\varepsilon \cdot \varepsilon_0 \cdot k_B \cdot T}{\sum_i (z_i \cdot e)^2 \cdot C_{i0}} \right)^{0.5}$$

$$\Gamma_0 = \tanh\left( \frac{z \cdot e \cdot \Phi}{4 \cdot k_B \cdot T} \right)$$

$V_{int}$ - Wechselwirkungsenergie
$k_B T$ - thermische Energie
$a$ - Teilchenradius
$H_{121}$ - Hamaker Konstante
$d_{pp}$ - Teilchenabstand
$C_0$ - Ionenstärke
$\Phi$ - Oberflächenpotential
$\kappa^{-1}$ - Debye'sche Abschirmlänge
$e$ - Elementarladung
$\varepsilon$ - Permittivität

D.F. Evans, H. Wennerström "The Colloidal Domain", VCH 1994, p. 336

# Teilchen-Teilchen Wechselwirkung (2)
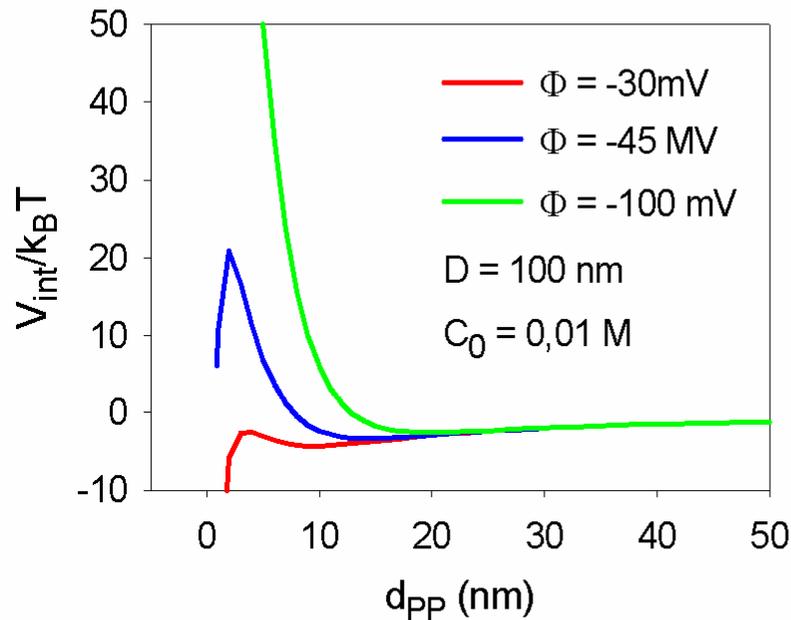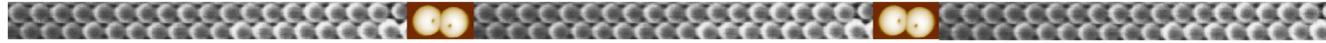


- → je höher das Oberflächen-potential um so größer die Stabilität
- → je größer die Teilchen um so höher die Stabilität
- → je niedriger die Ionenstärke um so größer die Stabilität

Graph legend:
- $\Phi = -30\,mV$ (red)
- $\Phi = -45\,MV$ (blue)
- $\Phi = -100\,mV$ (green)

$D = 100\,nm$

$C_0 = 0{,}01\,M$

Axes: $V_{int}/k_B T$ vs $d_{PP}\,(nm)$

$$V_{int}(h) = \pi \cdot a \left( -\frac{H_{121}}{12\pi} \cdot \frac{1}{d_{PP}} + \frac{64 \cdot k_B \cdot T \cdot C_0 \cdot \Gamma_0^2}{\kappa^2} \exp(-\kappa \cdot d_{PP}) \right) \quad \middle| \quad \Gamma_0 = \tanh\left( \frac{z \cdot e \cdot \Phi}{4 \cdot k_B \cdot T} \right)$$

D.F. Evans, H. Wennerström "The Colloidal Domain", VCH 1994, p. 336

**surface potential** is directly accessible by charge titration
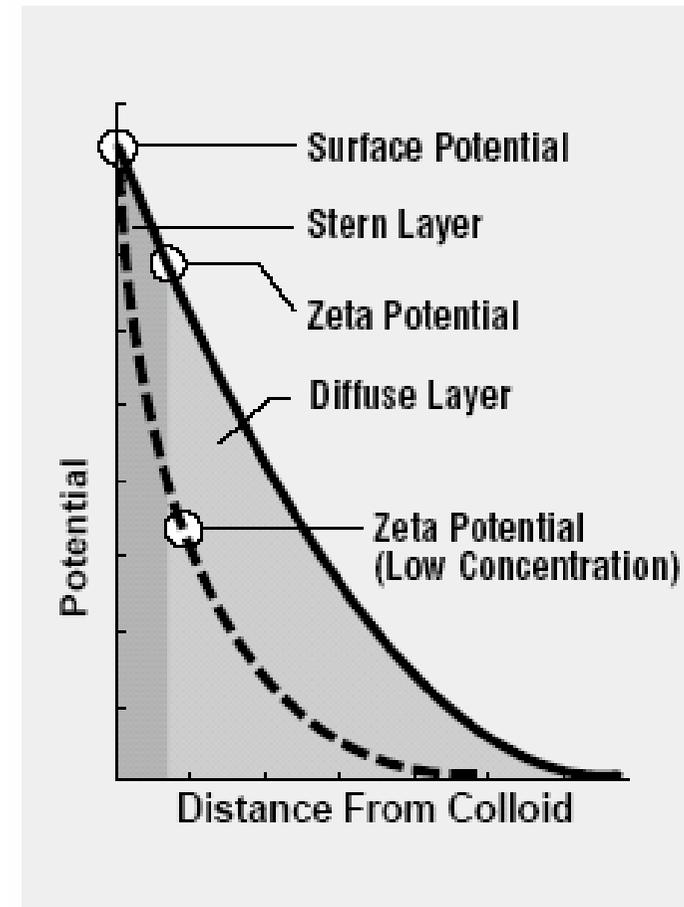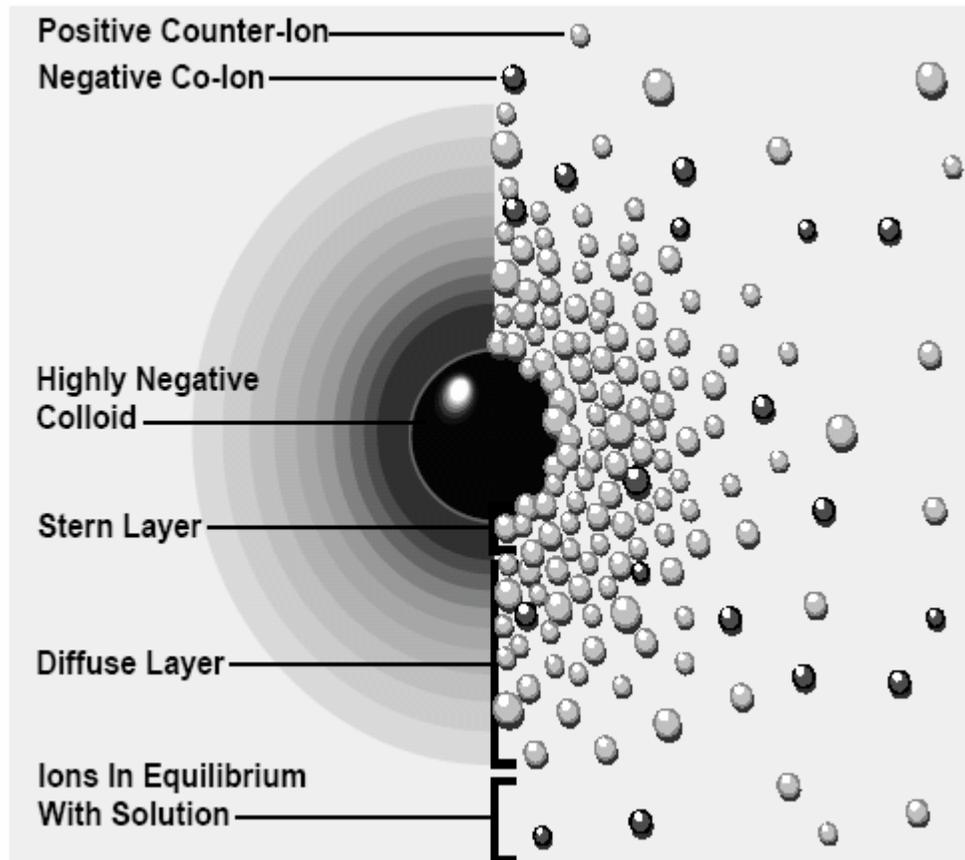


electrokinetic potential (**zeta potential**) is directly accessible by electrophoretic measurements

## Stability of Solution-Zeta Potential from "A Control of Colloidal Stability" by Thomas Riddick

| Stability | Average Zeta Potential (In millivolts) |
|---|---|
| Extreme to very good stability | −100 to −60 mv |
| Reasonable stability | −60 to −40 mv |
| Moderate stability | −40 to −30 mv |
| Threshold of light dispersion | −30 to −15 mv |
| Threshold of agglomeration | −15 to −10 mv |
| Strong agglomeration & precipitation | −5 to +5 mv |

# Aggregation Processes

**coalescence** is not a single stage process but comprises at least four <u>elementary steps:</u>

- contact at a distance that allows attractive interaction,
- the drainage of the continuous phase film between the drops,
- the rupture of the film,
- the collapse of the droplets.

→ nowadays aggregation processes can be prevented very effectively

# Soap Bubbles

face the force – visualize DLVO forces

microscope / CCD

air

air

air

air

water

film thinning

air
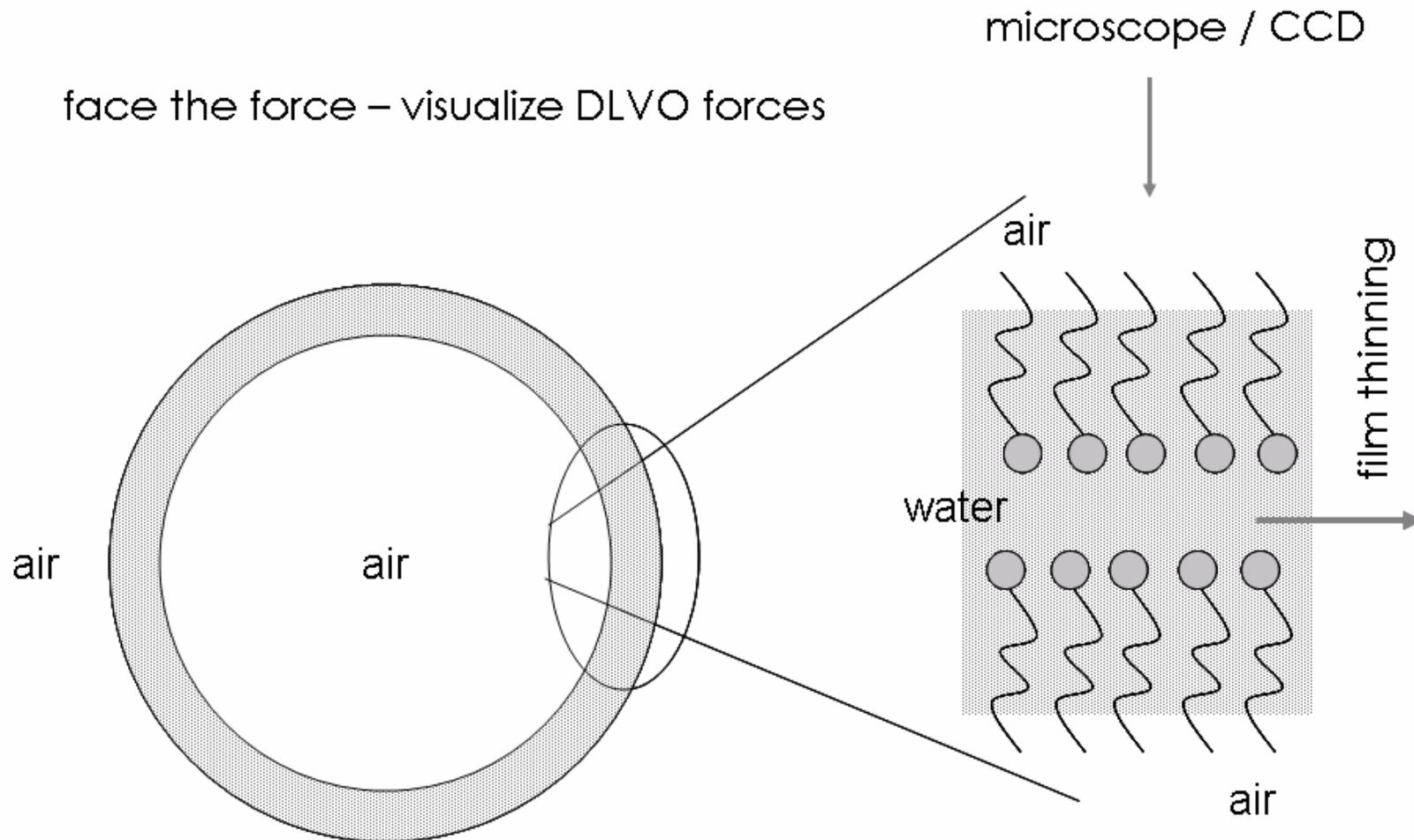
experiment & movies by **H.-J. Müller**
MPI Colloids & Interfaces, Interface Department

thin liquid films

# Common and Newton Black Films – Visualization of DLVO forces



movies H-J- Müller, KGF, IF
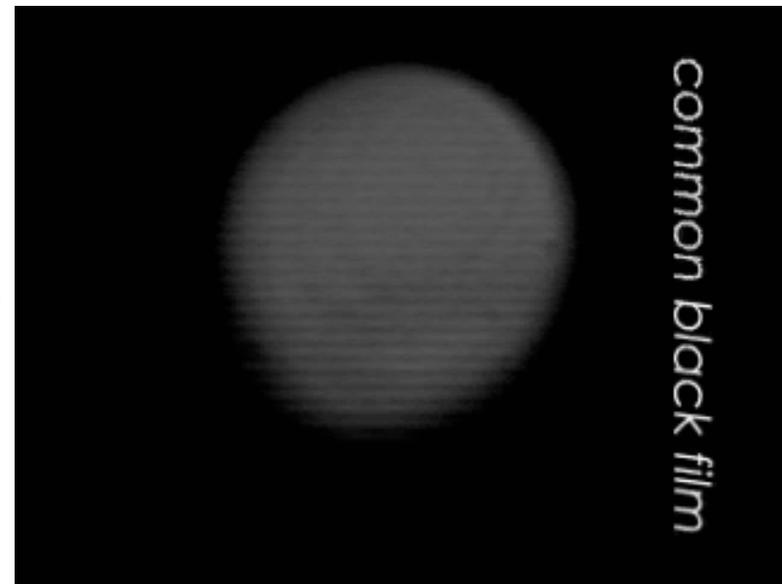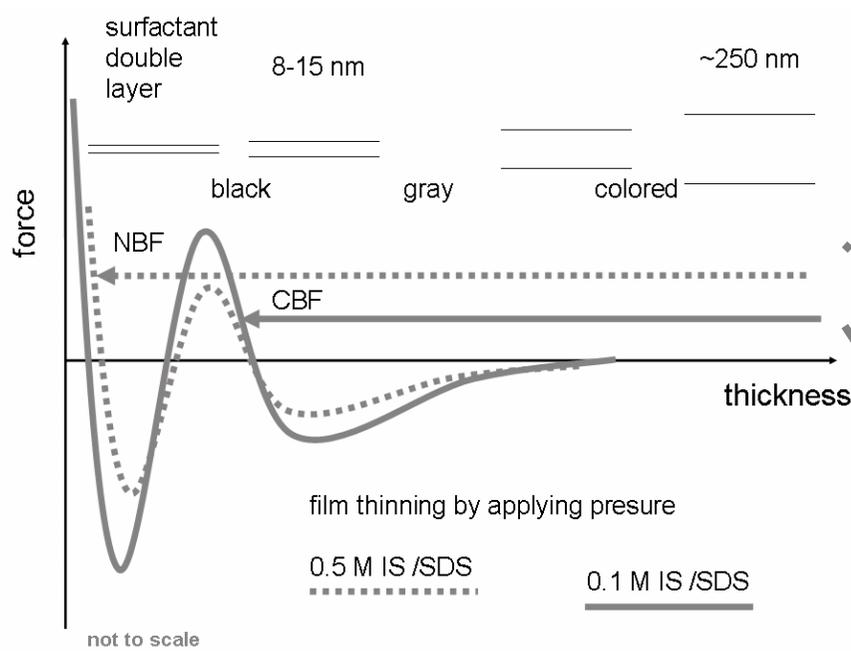
# Continuous Phase Film Stability:



film thinning →
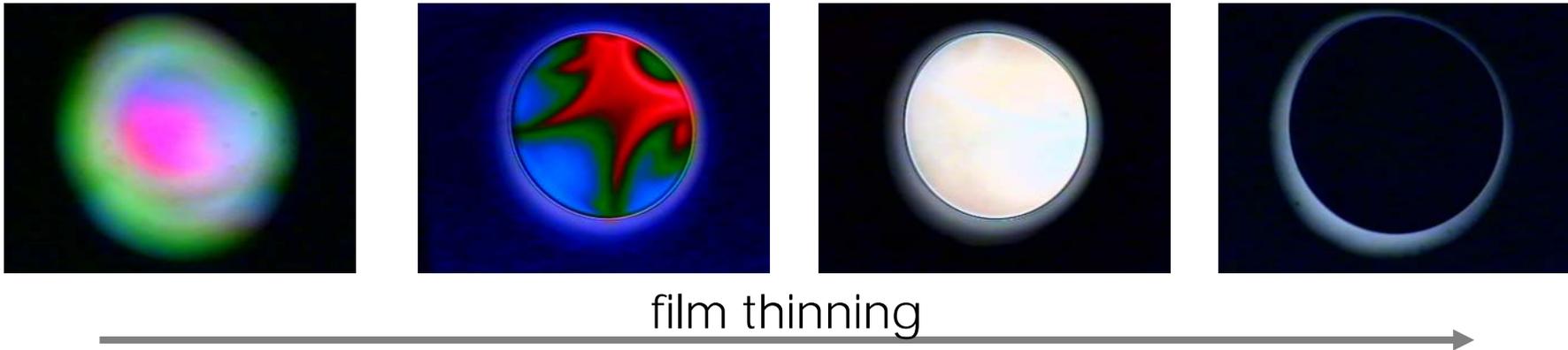
Light is reflected from each side of the film. These two contributions interfere in the familiar manner to give the colors of thin films by removing certain colors by destructive interference, just as seen in oil films and in the oxide films on tempered steel.

When the film thickness becomes less than about 1 µm the colors begin to appear, at first green and magenta, then the brighter colors of lower orders, including reds, blues and one good yellow or straw color.

At about 0.1 µm there is a white, but for thinner films the color approaches black (film invisible) as the light from front and back cancel.

**These colors serve to indicate the thickness of the films.**

# Kepler's Conjecture

(1571 – 1630)

Experiment shows that dropping the spheres in randomly will achieve a density of around 65%.

However, a higher density can be achieved by carefully arranging the spheres as follows. Start with a layer of spheres in a hexagonal lattice, then put the next layer of spheres in the lowest points you can find above the first layer, and so on - this is just the way you see oranges stacked in a shop.

This natural method of stacking the spheres creates one of two similar patterns called cubic close packing and hexagonal close packing. Each of these two arrangements has an average density of ~74 %.

The Kepler conjecture says that this is the best that can be done - no other arrangement of spheres has a higher average density than this.

The sphere packing problem has frustrated mathematicians for nearly four centuries.

## (hard) sphere packing problem
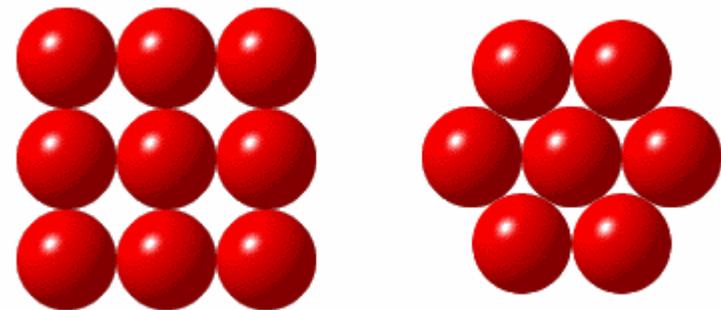


**highest possible volume occupied by solid spheres =**

$$\varphi_{max} \approx \frac{\pi}{\sqrt{18}} \approx 74\%$$
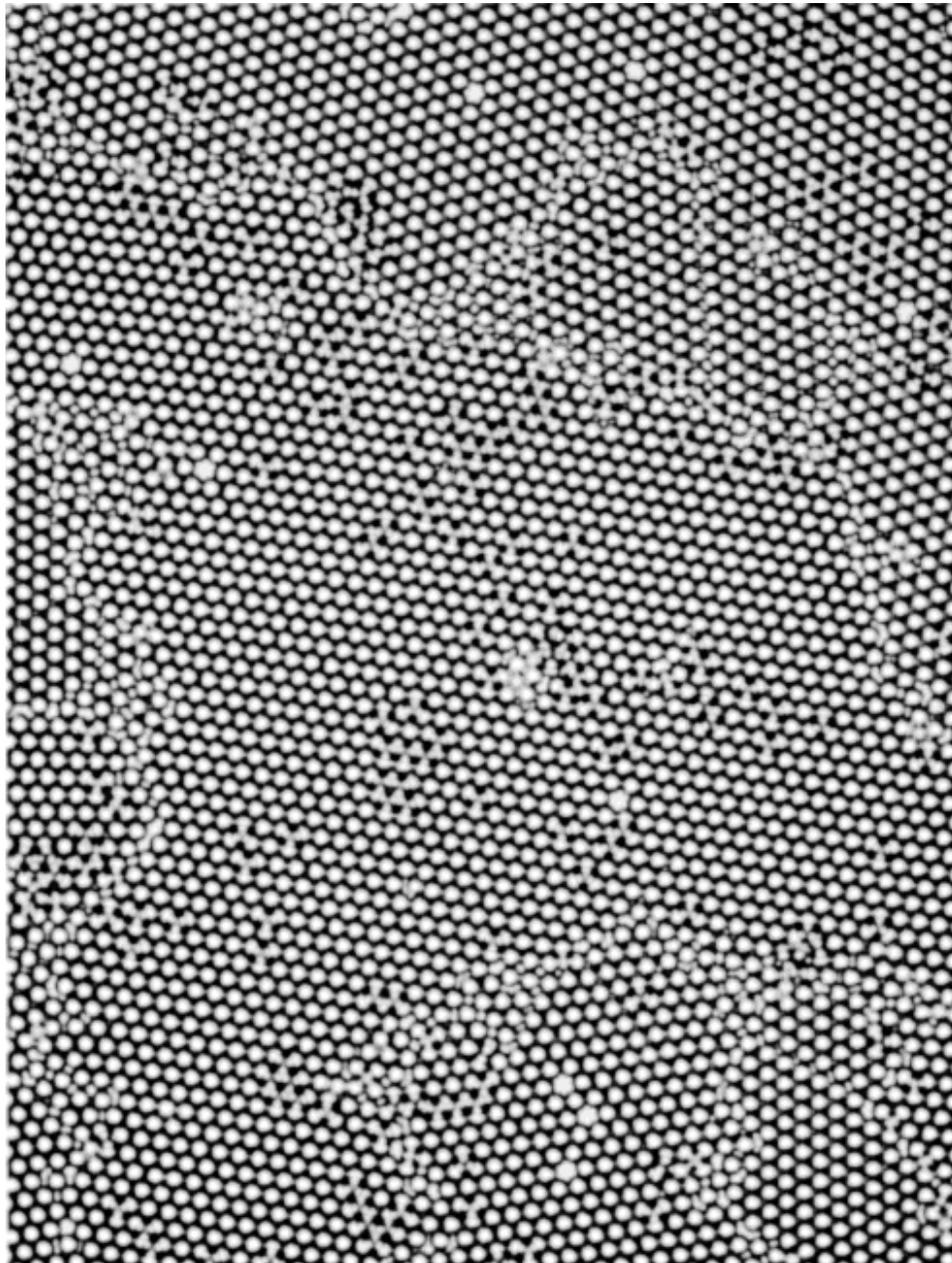
entropic swelling

highly **swollen PS particles**

(styrene, 1-chlorododecane)
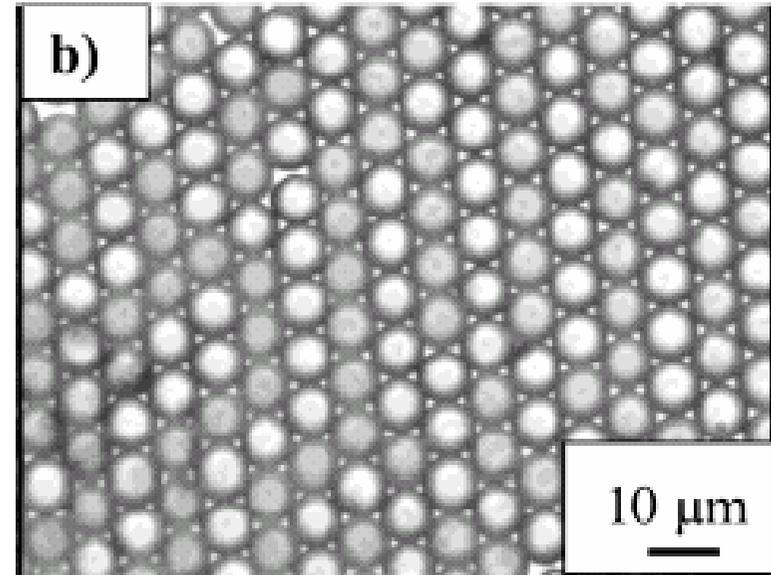


Macromolecules 2003, **36**, 648-653

monolayer formed from a 10 µm
diameter monodisperse
emulsion of **silicone oil** in water

Langmuir 2000, **16**, 347-351

# Highly Concentrated Emulsions: $\varphi_{max} > 74\%$



**1/1**

**3/1**

ratio water to oily
precursor polymer

transition from spheres
to polyhedron as
internal phase content
is increased

monodisperse
polyhedrons require less
total energy than
polydisperse spheres

**4/1**

**5/1**

10 µm
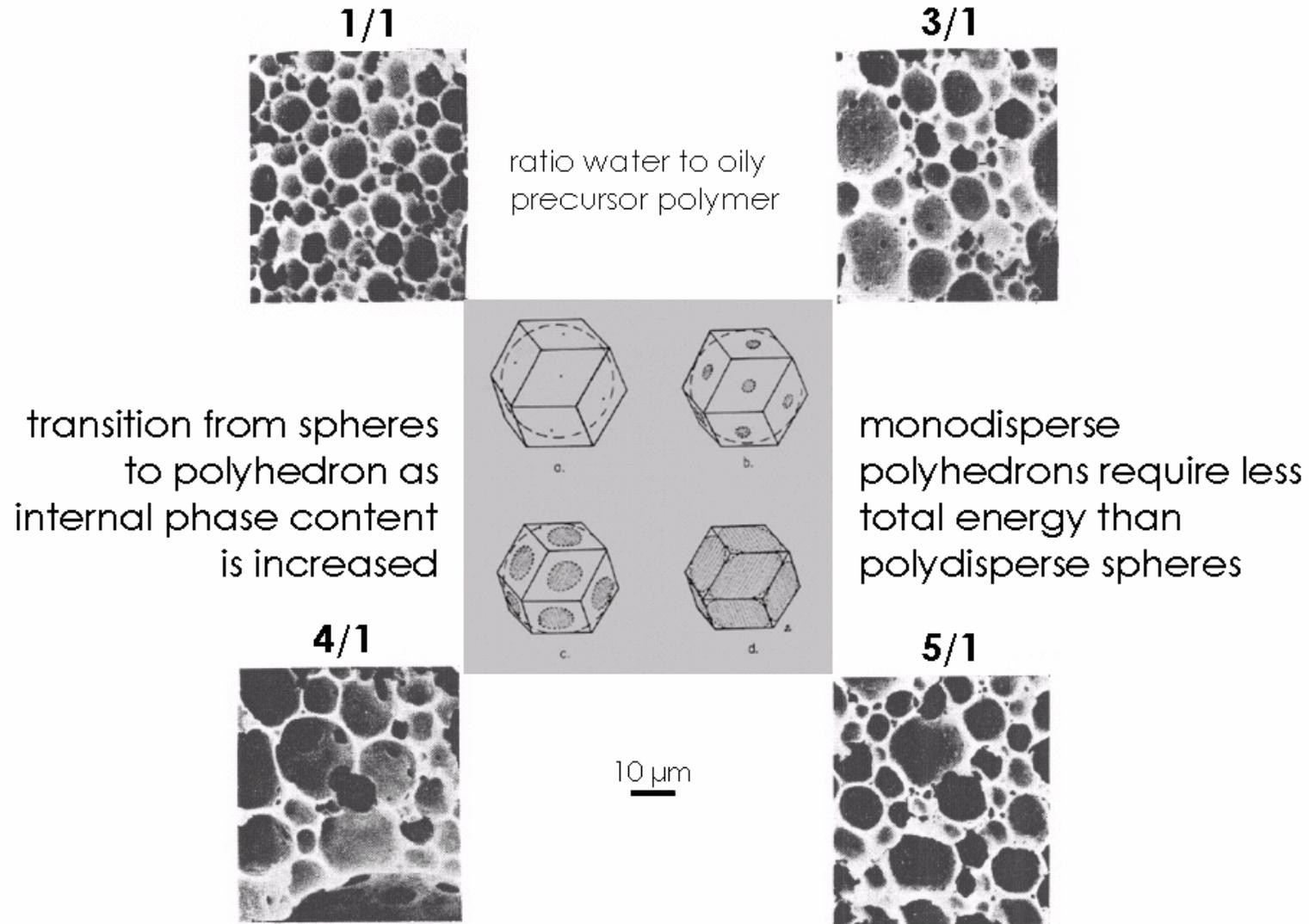
water in polymer emulsions (x-linked)

# Transition from Spheres to Polyhedrons:

rhomboidal dodecahedron

tetrakaidecahedron
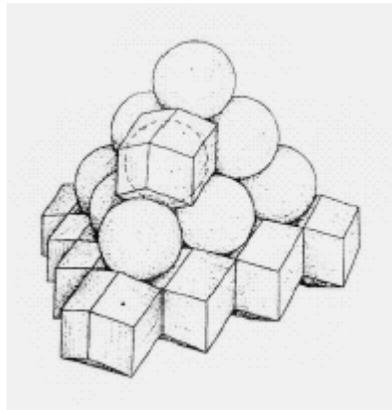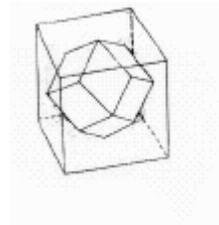


packing from 74% to 94%
internal phase volume
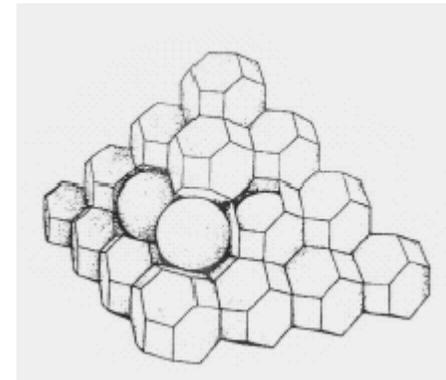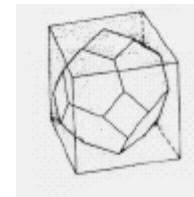
packing above 94%
internal phase volume

# Concentrated Emulsions a Practical Example:



diluted w/o emulsion

add H$_2$O

concentrated w/o emulsion

add H$_2$O

HIPE

heat

Highly porous polymer

Polystyrene polyhipe x2000 — 10µm
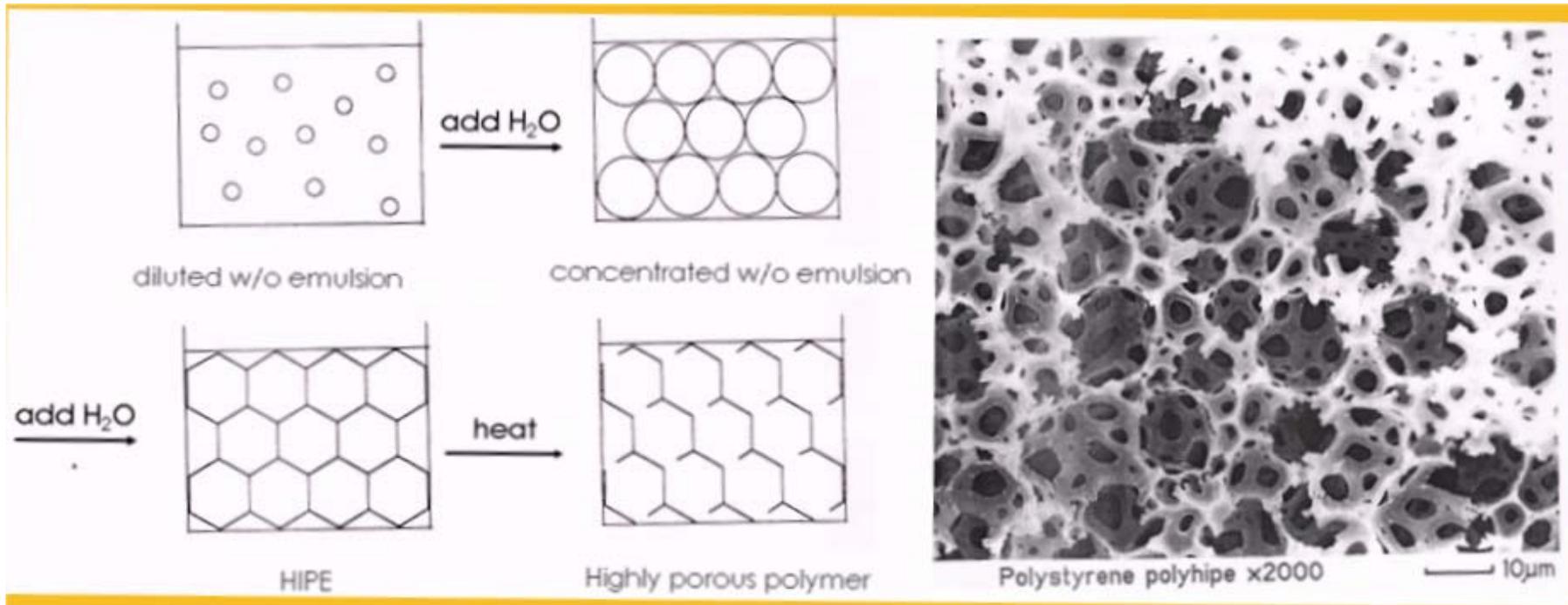
Adv. Polym. Sci. 126 (1996) 163-214

**HIPE: high internal phase emulsions**
The most studied system: w/o emulsion with styrene / divinylbenzene mixture as continuous phase and water as internal phase with a nonionic surfactant; polymerization with oil and water soluble initiators leads to polymer foam with open-cellular structure

➡ **Stabilization against flocculation is nowadays no issue anymore**

# Phase Inversion

important in the case of polymeric surfactants with a stabilizing moiety possessing a critical solution temperature

poly(ethylene glycol) based surfactants

<span style="color:red">temperature increases</span> → <span style="color:red">HLB decreases</span> of the surfactant and it may subsequently, in accordance with Bancroft's rule lead to stabilization of a water in oil instead of an oil in water emulsion.

phase inversion depends on:

• the polarity of the oil phase,
• the kind of electrolyte and its concentration,
• other additives (organic, water-soluble solvents increasing oil solubility in water),
• the oil volume fraction.

# Ostwald Ripening (OR)

a direct consequence of the polydispersity of the DSD whereby even thermal fluctuation in $D_d$ or in the curvature may cause it

chemical potential of a dispersed phase compared to that of the same bulk material

$$k_B T \cdot \ln C(D) = \frac{4 \cdot \sigma \cdot v_m}{D_d} + k_B T \cdot \ln C_{\infty,1}$$

concentration of the disperse phase just at the interface (C(D) where $\sigma$ holds)

$C_{\infty,1}$ being the solubility of the disperse (C1) phase in the continuous medium

## two important points:

✓ Ostwald ripening requires to occur a certain solubility of the dispersed phase (C1) in the continuous phase

✓ Direct contact between the droplets is not necessary as molecular diffusion through the continuous phase leads to an increase in $D_d$

**OR is a topic in its own right**

# LSW theory for single component drops:

rate of OR for a single component drop ($W_{OR1}$)

$$W_{OR1} = \frac{8 \cdot \tilde{D}_1 \cdot C_{\infty,1} \cdot \sigma \cdot v_{m,1}}{9 \cdot RT}$$

$$D(t) = \sqrt[3]{W_{OR} \cdot t + D_0^{\,3}}$$

emulsions stabilized with sodium dodecyl sulfate

$W_{OR1}$ (cm$^3$ s$^{-1}$)

MMA
BA
STY
TBS
$C_9$
$C_{10}$
LMA
$C_{11}$
$C_{12}$
$C_{13}$
$C_{14}$
$C_{15}$
$C_{16}$

Figure 2

$C_{\infty,1}$   water solubility (v/v)

$D(t)$ (nm)

$D_0 = 100$ nm

MMA
BA
STY
TBS
LMA

Figure 3

$t$ (min)
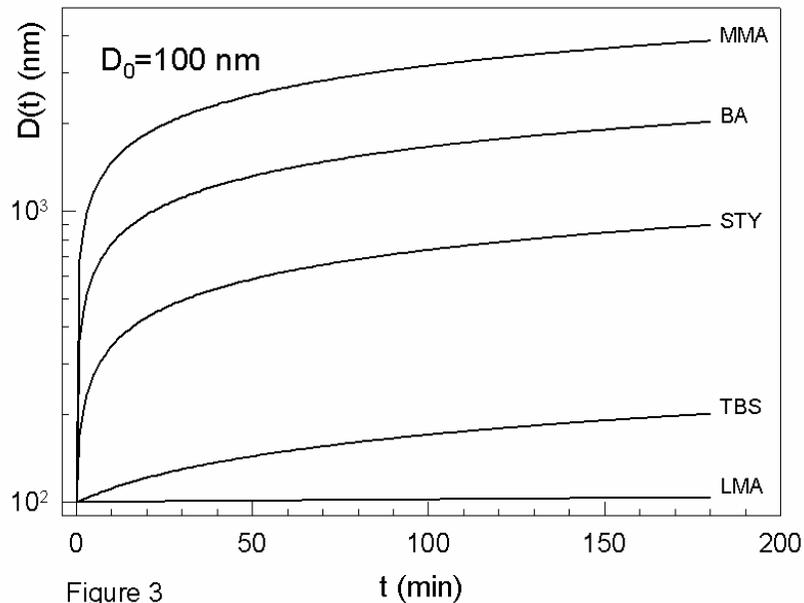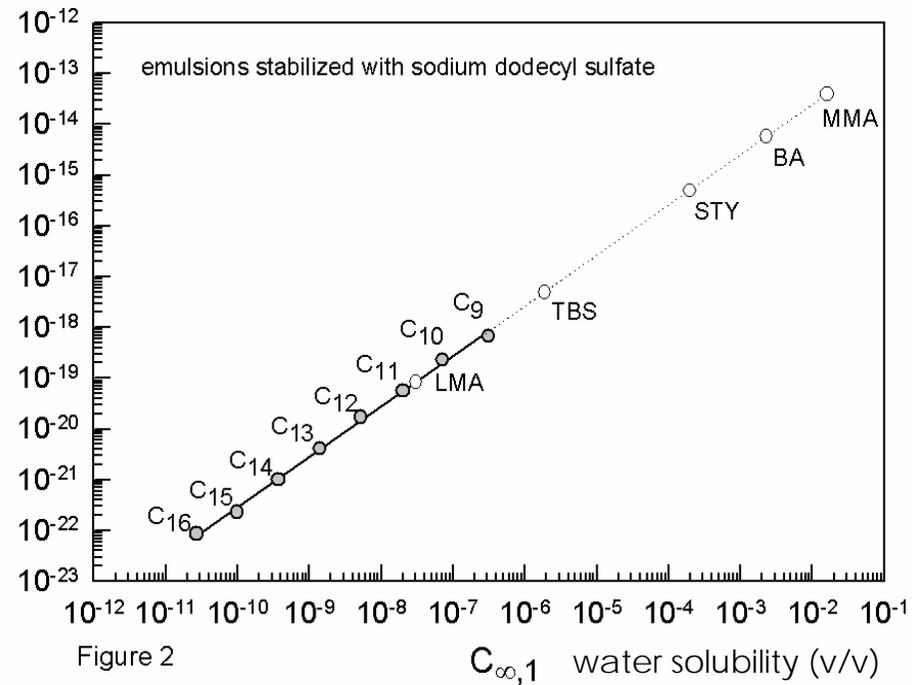
## LSW theory:
I. M. Lifshitz, V. V. Slezov Zh. Exp. Teor. Fiz. 35 (1958) 479-492
C. Wagner Z. Elektrochem. 65 (1961) 581-591

$\sigma$ — interfacial tension drop to water

$v_{m,1}$ — molar volume of C1

**the solubility of C1 in the continuous phase ($C_{\infty,1}$)**

**is crucial for the stabilty of emulsions thereof**

# OR – continued 1

→ it might be possible to stabilize emulsions against Ostwald ripening by addition of small amounts of a third component (**compound- 2**) which preferentially should dissolved in liquid-1 and not in the continuous phase

→ this was done by Higuchi and Misra and experimentally verified by stabilization of carbon tetrachloride emulsion in water with hexadecane

→ Ostwald ripening in the presence of **compound-2** was theoretically investigated by Kabalnov et al.

Higuchi, W. I. and J. Misra, Physical degradation of emulsions via the molecular diffusion route and the possible prevention thereof, *J. Pharmaceutical Sci*., **51**, 459 - 466 (1962)

Kabalnov, A. S., A. V. Pertzov and E. D. Shchukin, Ostwald ripening in two-component disperse phase systems: application to emulsion stability, *Coll. Surf*., **24**, 19 - 32 (1987)

properties of Compound- 2 are crucial

$$C_{\infty,2} \ll C_{\infty,1}$$

$$C_{\infty,2} = 0$$
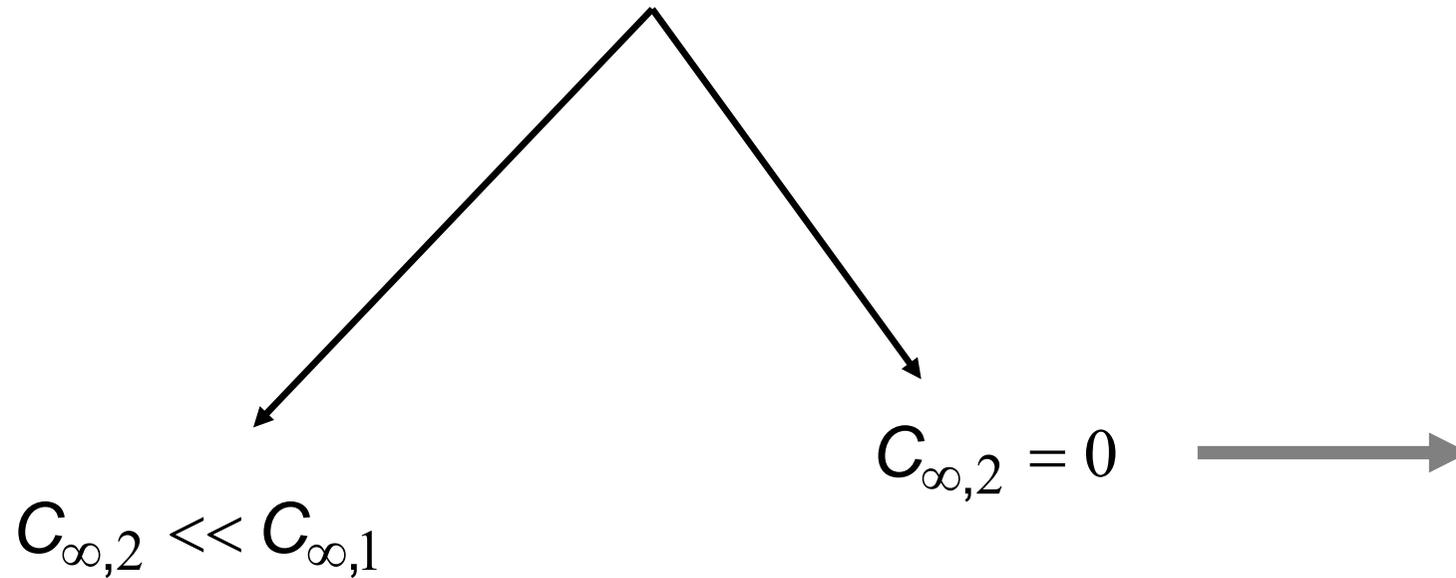
a zero solubility $\neq$ a very low solubility !!!

hexadecane emulsions degrade (slowly) via OR

# OR – continued 3

$$C_{\infty,2} = 0 \longrightarrow$$ which means that the total number of droplets remains constant.

$$\phi'_{2,e} - \frac{4\sigma \cdot v_{m,1}}{k_B T} \cdot \frac{1}{D'_{d,e}} = \phi''_{2,e} - \frac{4\sigma \cdot v_{m,1}}{k_B T} \cdot \frac{1}{D''_{d,e}}$$

situation at equilibrium (subscript e) regarding the second component (subscript 2) for two particles (superscripts ' and '') with different diameters.

However, the distribution of liquid-1 from small to large particles changes the composition of the droplets. It increases the volume fraction of compound-2 ($\phi_2$) in the smaller particles and decreases it in the larger ones.

Indeed, investigations on Ostwald ripening with sedimentation field-flow fractionation in fluorocarbon emulsions confirmed the theoretical prediction that compound-2 is enriched in smaller drops [Weers, J. G. and R. A. Arlauskas, *Langmuir*, **11**, 474 - 477 (1995) ].

# OR

To compensate for the Ostwald ripening requires $\phi_2$-values depending on the droplet size in the sense that smaller drops require a higher $\phi_2$ and *vice versa*. **However, this is practically impossible to control during the initial emulsification process.**

from the chemical potential at equilibrium follows a condition for $\phi_{2,i}$ that the system can reach the equilibrium and Ostwald ripening will stop. Here the subscript i stands for initial conditions and  stands for the initial average droplet size

$$\phi_{2,i} > \frac{4\sigma \cdot v_{m,1}}{3k_B T \cdot \bar{D}_{d,i}}$$

If this condition is not met the particles cannot reach equilibrium and Ostwald ripening will further increase the differences in the chemical potential for particles with different sizes.

# OR – continued 5

the addition of a completely water-insoluble hydrophobe during the emulsification does not *per se* prevent Ostwald ripening.

Ostwald ripening takes place in any case, except an exactly monodisperse droplet size distribution

it will either lead to an equilibrium after a certain maturation time or not (i.e., indefinitely ripening until phase separation is completed)

An additional effect arises if compound-2 is surface active. During the equilibration of liquid-1 $\sigma$ decreases in the small drops and increases in the large ones. This decreases the driving force for the re-distribution of liquid-1 and hence would additionally stabilize the emulsion against Ostwald ripening.

Emulsions either natural or man-made are essential parts of life on earth:

food
cosmetic
construction
health care
medicine
information techn.
biology
materials
paved surfaces

see you next week:

$\longrightarrow$ μ-emulsions & miniemulsions