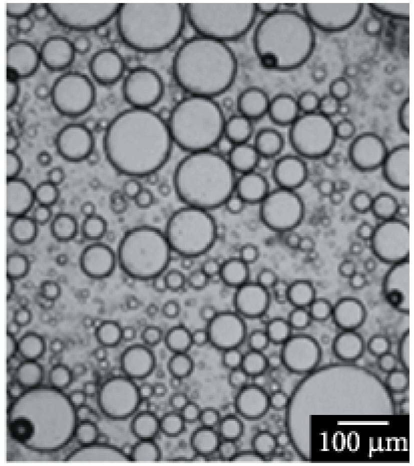
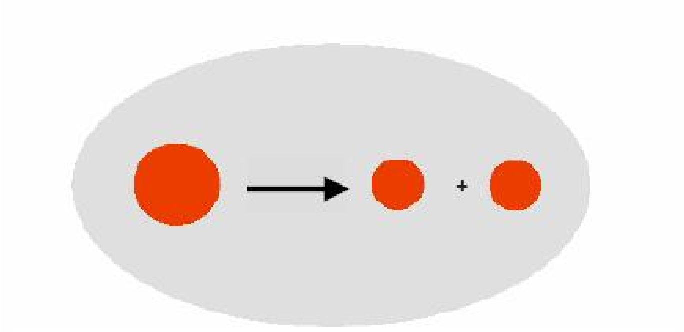
# Introduction

**Emulsion** – Suspension of liquid droplets (dispersed phase) of certain size within a second immiscible liquid (continuous phase).





$$\overrightarrow{\Delta G} = \gamma \times \Delta A >> 0$$

emulgeation requires large energy input

- 10 ml of an oil → 0.2 μm droplet $\quad If\ \gamma = 52\frac{mN}{m} \rightarrow work\ required = 2\ J$
- Work remains in the system as potential energy
  → The system is thermodynamically unstable and rapidly undergoes whatever transformations to reduce the energy
  → To make emulsion stable
    - Reduce $\gamma$ by 1 mN/m → work required reduced to 0.3 J
    - Also kinetics can play an important role

## Classification of emulsions

- Based on dispersed phase

  Oil in Water (O/W): Oil droplets dispersed in water (milk, etc)

  Water in Oil (W/O): Water droplets dispersed in oil (butter, etc)

- Based on size of liquid droplets

  0.2 – 50 **µm** Macroemulsions (Kinetically Stable)

  0.01 – 0.2 **µm** Microemulsions (Thermodynamically Stable)

As interfacial tension values fall, the ease of emulsion formation increases and the droplet size achievable decreases. Systems in which the interfacial tension falls to near zero ($<10^{-3}$ mN/m) may emulsify spontaneously under the influence of thermal energy and produce droplets so small (<100 nm diameter) that they scatter little light and give rise to clear dispersions. The microemulsions so formed occupy a place between macroemulsions and micelles and are thermodynamically stable.

Microemulsions usually require the presence of both a surfactant and a cosurfactant (e.g. short chain alcohol)

# Emulsifying agents

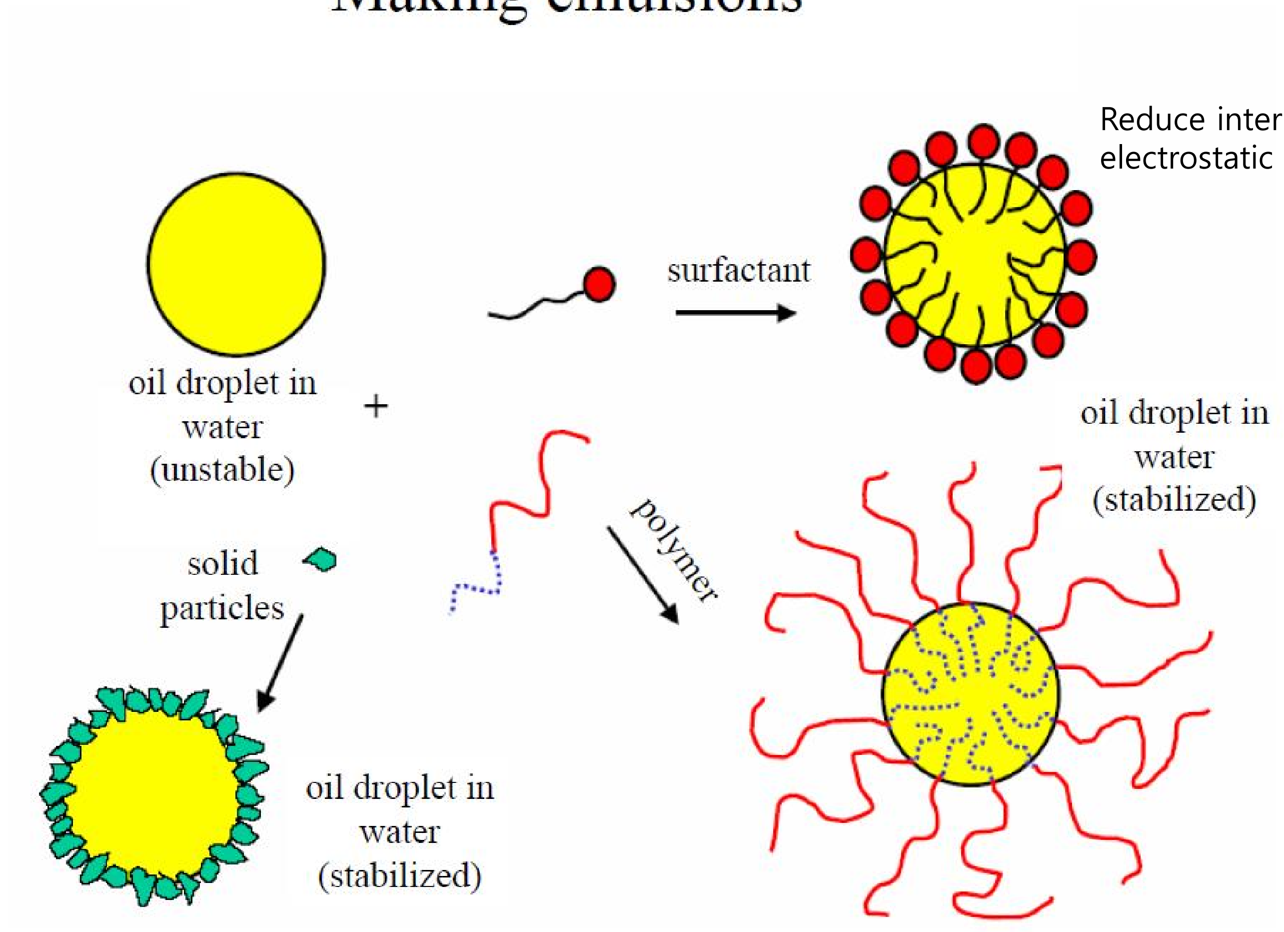
Stable suspensions of liquids constituting the dispersed phase, in an immiscible liquid constituting the continuous phase is brought about using emulsifying agents such as surfactants

Function: 1) lower the surface tension
2) retard the drop reversion into bulk separation

Emulsifiers must exhibit the following characteristics to be effective as emulsifiers

- good surface activity (must be adsorbed at the interface)
- Should be able to form some type of film or barrier at the interface that will prevent or retard drop flocculation and coalescence

# Making emulsions



Reduce interfacial tension
electrostatic barrier

Do not directly affect interfacial tension
but form a physical barrier
Particles should be partially wetted by
both liquids phases, but with a slight
preference for the external phase

Steric and electrostatic interactions
More important as stabilizers, preventing
drop flocculation and coalescence

# Common Emulsifying Agents

## Polymers

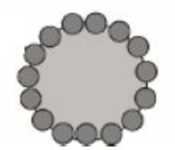
Proteins, Starches, Gums, cellulosics, PV alcohols, Polyarcrylic Acid, Polyvinylpyrrolidone

- Mechanism: 1) reduce interfacial tension
  2) form barrier (electrostatic and/or electrostatic)
  3) increase the viscosity of the system and impart added kinetic stability

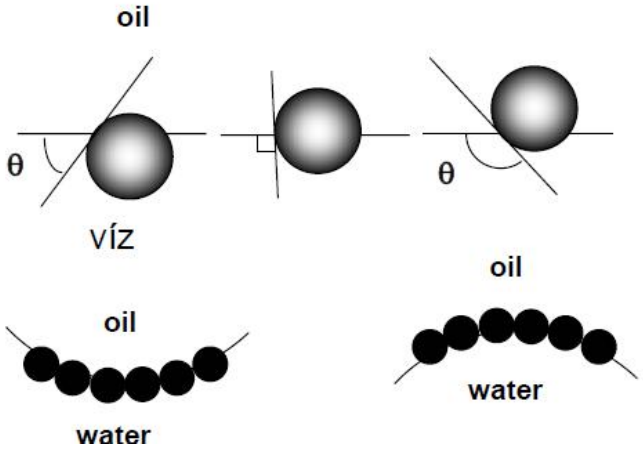
## Solids

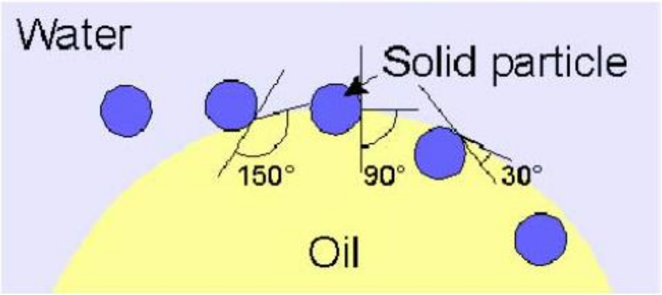
Finely divided solids with amphiphilic properties such as soot, silica and clay, may also act as emulsifying agents

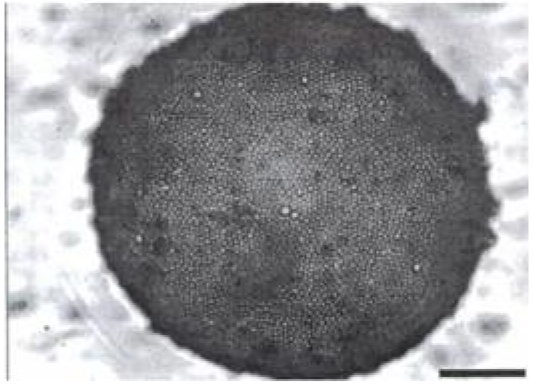
- Mechanism: Do not directly affect interfacial tension but form a physical barrier
- Particles should be partially wetted by both liquids phases, but with a slight preference for the external phase



# Pickering emulsions







Particles should have limited colloidal stability in both liquids, otherwise their tendency to locate at the oil-water interface will not be sufficiently strong:
Contact angle is close to $90^o$.

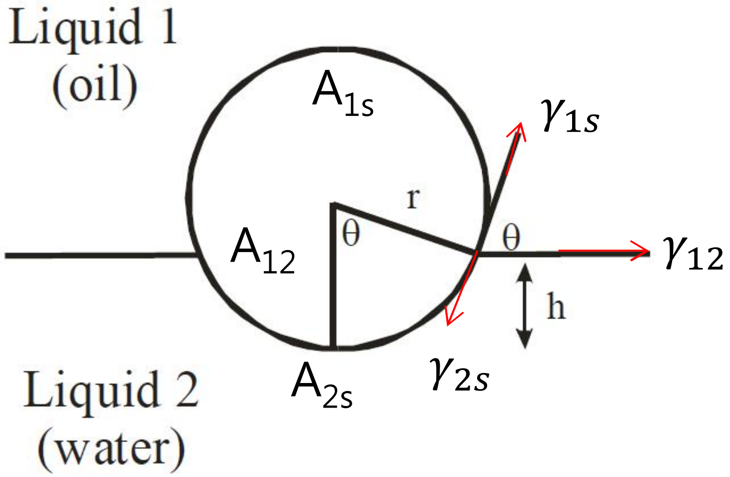
Hydrophobic solid particles stabilize W/O emulsions
: basic sulfates of Fe, Cu, Ni, Zn, Al ($\theta>90$)

Hydrophilic solid particles stabilize O/W emulsions. ($\theta<90$)
: carbon black, rosin, lanolin: W in kerosene, or benzene

When particles are “adsorbed” at the surface, they are hard to remove – the emulsion stability is high.

Crude oil is a W/O emulsion and is old!!

# Particles as emulsion stabilizers



$$\gamma_{1s} dA_{1s} + \gamma_{2s} dA_{2s} + \gamma_{12} d\gamma_{12} = 0$$

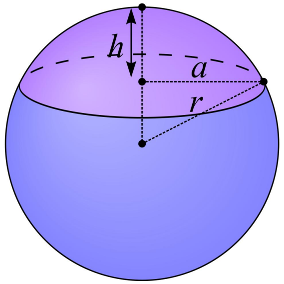
$$\gamma_{2s} - \gamma_{1s} = \gamma_{12} cos\theta \,, \qquad cos\theta = 1 - h/r$$

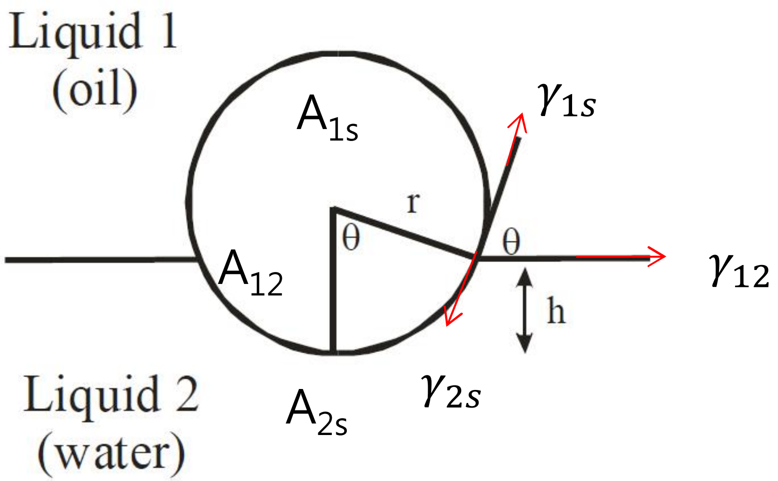
$$W_{a(1)} = \gamma_s + \gamma_1 - \gamma_{1s} = \gamma_1 (1 + cos\theta_1)$$

$$W_{a(2)} = \gamma_s + \gamma_2 - \gamma_{2s} = \gamma_2 (1 + cos\theta_2)$$

$$\gamma_{12} cos\theta = \gamma_1 cos\theta_1 - \gamma_2 cos\theta_2$$

$$surface\ area: 2\pi rh$$





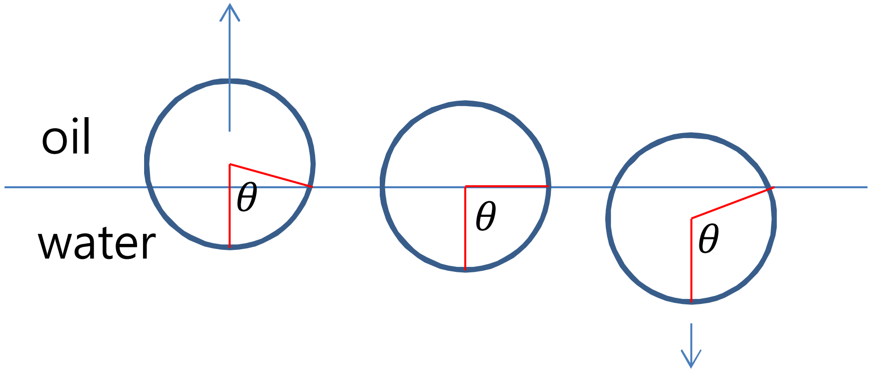
Free Energy Desorption required to remove the particle from the interface into the oil phase

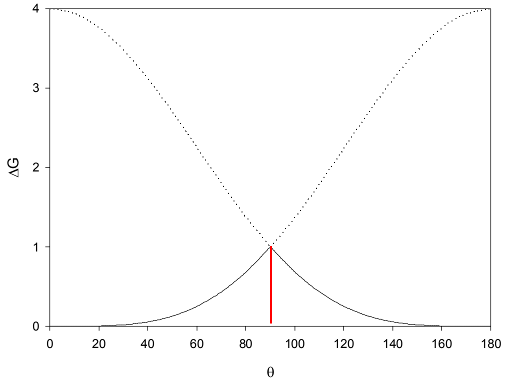
$$\nabla G_1 = 2\pi r^2 (1 - cos\theta)(\gamma_{1s} - \gamma_{2s}) + \pi r^2 (1 - cos^2\theta)\gamma_{12}$$

$$= \pi r^2 \gamma_{12}(1 - cos\theta)^2$$

Free Energy Desorption required to remove the particle from the interface into the water phase

$$\Delta G_2 = \pi r^2 \gamma_{12}(1 + cos\theta)^2$$





# Common Emulsifying Agents

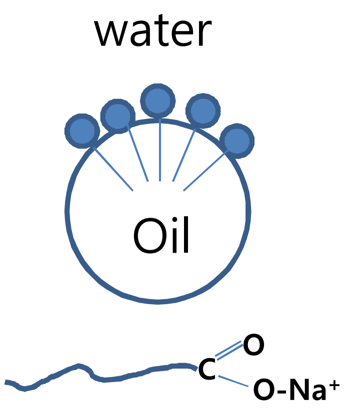
**Surfactants**

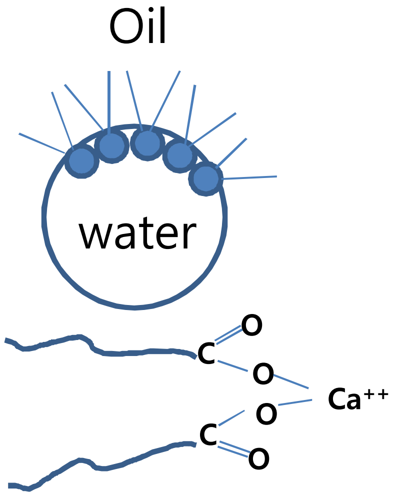
Anionic – Sodium stearate, Potassium laurate
Sodium dodecyl sulfate, Sodium sulfosuccinate
Nonionic – Polyglycol, Fatty acid esters, Lecithin
Cationic – Quaternary ammonium salts, Amine hydrochlorides

- Mechanism: 1) reduce interfacial tension
  2) form barrier (electrostatic and/or electrostatic)

# Emulsion Type

## 1. Chemical structure of surfactant





- Alkali metal salts of fatty acid soap produce o/w emulsions while di- and trivalent soaps results in w/o emulsions.
- Hydrophilic head > hydrophobic tail → o/w emulsion and vice versa
- The liquid in which the surfactant is most soluble will the continuous phase in the final emulsion: Bancroft's rule
  - Sodium Oleate (water soluble)→ O/W emulsion $CH_3(CH_2)_7CH=CH(CH_2)_7COONa$
  - Calcium Oleate (oil soluble) → W/O emulsion

$$\begin{array}{l} CH_3(CH_2)_7CH=CH(CH_2)_7COO- \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad Ca \\ CH_3(CH_2)_7CH=CH(CH_2)_7COO- \end{array}$$

# HLB (hydrophilic -lipophilic balance) values

The amphiphilic nature of many emulsifying agents (particularly non/ionic surfactant) can be expressed in terms of an empirical scale of so-called HLB

1 ―――― HLB Scale ―――― 20

Oleic acid

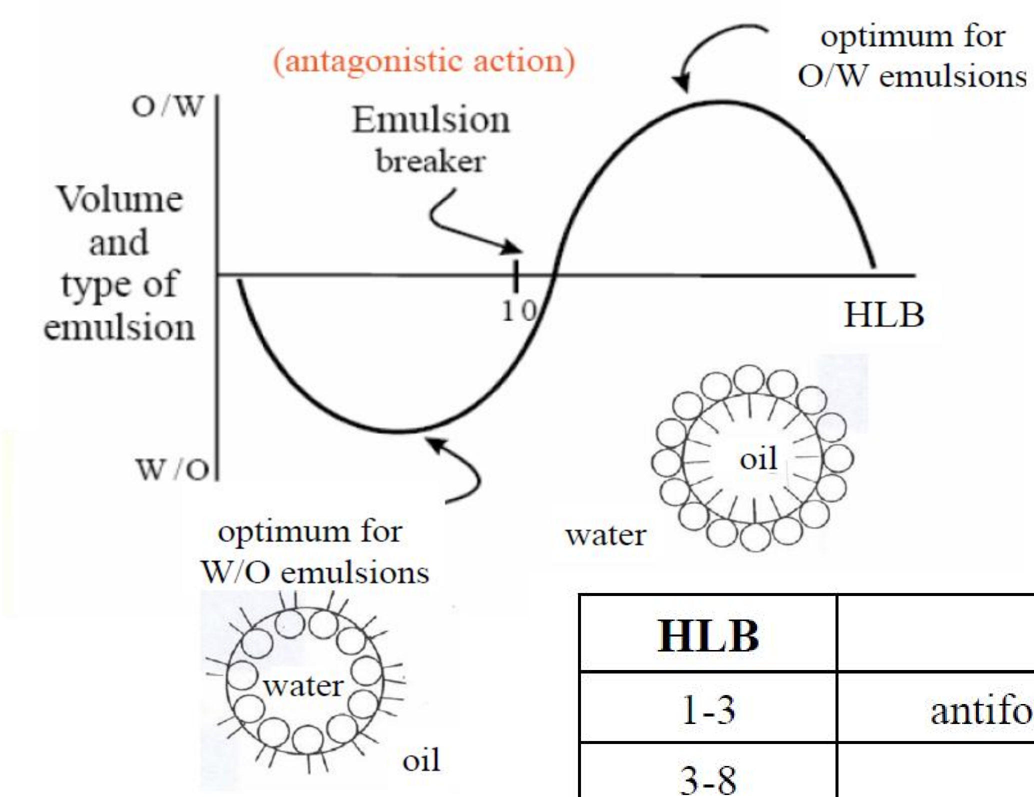
Sodium Oleate

Originally developed by Griffin

$$HLB = 1W_1 + 20W_2$$

$W_1: wt.\ fraction\ of\ oleic\ acid,\quad W_2: wt.\ fraction\ of\ sodium\ oleate$

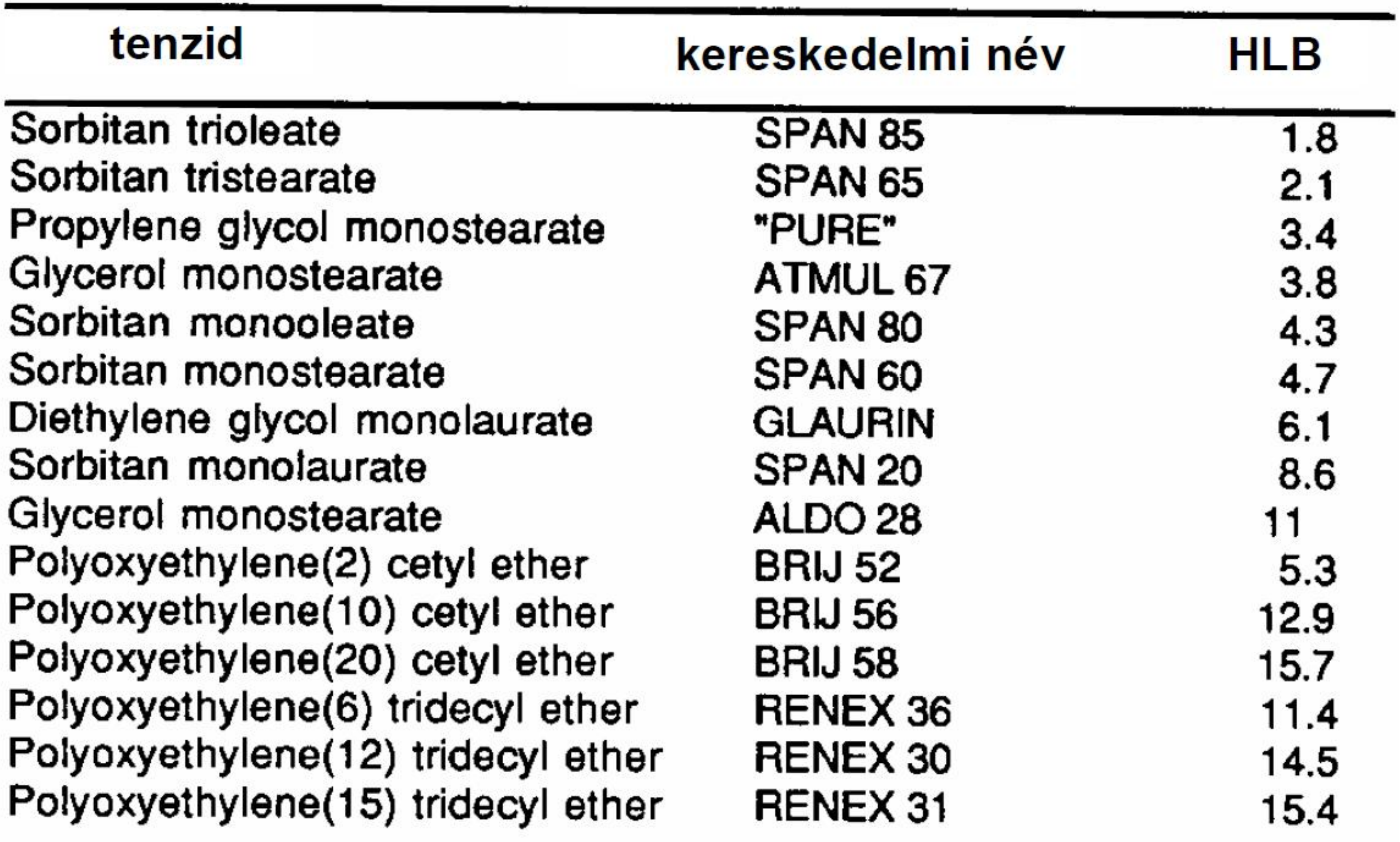
HLB numbers >10 have an affinity for water (hydrophilic) and number <10 have an affinity of oil (lipophilic). Ionic surfactants have recently been assigned relative HLB values, allowing the range of numbers to extend to 60.



| HLB | APPLICATIONS |
|---|---|
| 1-3 | antifoaming agents; inverse micelles |
| 3-8 | W/O emulsifiers |
| 7-9 | wetting agents |
| 10-16 | O/W emulsifiers |
| 13-16 | detergents |
| 15-18 | solubilizers |

**Application of surfactants on the basis of their HLB**

# HLB values for typical nonionic surfactants structures



| tenzid | kereskedelmi név | HLB |
|---|---|---|
| Sorbitan trioleate | SPAN 85 | 1.8 |
| Sorbitan tristearate | SPAN 65 | 2.1 |
| Propylene glycol monostearate | "PURE" | 3.4 |
| Glycerol monostearate | ATMUL 67 | 3.8 |
| Sorbitan monooleate | SPAN 80 | 4.3 |
| Sorbitan monostearate | SPAN 60 | 4.7 |
| Diethylene glycol monolaurate | GLAURIN | 6.1 |
| Sorbitan monolaurate | SPAN 20 | 8.6 |
| Glycerol monostearate | ALDO 28 | 11 |
| Polyoxyethylene(2) cetyl ether | BRIJ 52 | 5.3 |
| Polyoxyethylene(10) cetyl ether | BRIJ 56 | 12.9 |
| Polyoxyethylene(20) cetyl ether | BRIJ 58 | 15.7 |
| Polyoxyethylene(6) tridecyl ether | RENEX 36 | 11.4 |
| Polyoxyethylene(12) tridecyl ether | RENEX 30 | 14.5 |
| Polyoxyethylene(15) tridecyl ether | RENEX 31 | 15.4 |

# Calculation of HLB numbers (Davies and Rideal)

## HLB numbers of functional groups

| Hydrophilic groups | HLB | Lipophilic groups | HLB |
|---|---|---|---|
| $-SO_4Na$ | 38.7 | -CH- | -0.475 |
| -COOK | 21.1 | $-CH_2-$ | |
| -COONa | 19.1 | $-CH_3-$ | |
| -sulfonic group ($-SO_3H$) | 11.0 | -CH= | |
| quaternary ammonium ($\equiv N)^+$ | 9.4 | $-(CH_2-CH_2-CH_2-O-)$ | -0.15 |
| ester (sorbitan ring) | 6.8 | | |
| ester (free) | 2.4 | | |
| -COOH | 2.1 | | |
| -OH (free) | 1.9 | | |
| -O- | 1.3 | | |
| -OH (sorbitan ring) | 0.5 | | |

**Example:** calculation of HLB number for 1-hexadecanol (cety alcohol) $C_{16}H_{33}OH$

$$HLB = 7 + m \times H_h - n \times H_l = 7 + 1.9 + 16(-0.475) = 1.3$$

It should be kept in mind that HLB numbers are not additive in some systems or compounds.

Nevertheless HLB numbers helped to systemize and optimize the emulsion systems.

For mixed emulsifiers, HLP number can be approximated by algebraic addition

***50 % Span 60 (HLB = 4.7) és 50 % Tween 60 (HLB = 14.9)?***
**$4.7 \times 0.5 + 14.9 \times 0.5 = 9.8$**

***? which combination of emulsifiers is appropriate from Span 80 (HLB = 4.3) and Tween 80 (HLB = 15.0) for "required" HLB 12.0?***

**($4.3*(1-x) + 15*x = 12$; 28% & 72%)**

# Solubility Parameter

- Theoretical approach to explain HLB
- Solubility parameter, $\delta$ : cohesive energy density of a material
  - Originally developed by Hildebrand to explain the solubility of materials in various solvent
  - The higher the cohesive energy, the more sticky the interaction between molecules

| | $\delta$, $(J/cm^3)^{0.5}$ | Boiling Point | Viscosity |
|---|---|---|---|
| Water | 47.9 | 100°C | 1.0 cP |
| Diethyl ether | 15.1 | 35°C | 0.23 cP |

  - cohesive energy: intermolecular interactions (dispersion force, hydrogen bonding, dipole interactions ---)
    - Nonpolar materials: low values of $\delta$
    - Polar materials: intermediate values
    - Hydrogen bonding materials: high values

- Cohesive interaction energy between two unlike molecules

$$E_{c(AB)} = \delta_A \times \delta_B$$

1. Mixture of water($\delta$=47.9) and hexane ($\delta$=14.9)

$$E_{c(WH)} = 47.9 \times 14.9 = 714$$

$$E_{c(WW)} = 47.9 \times 47.9 = 2294$$

$$E_{c(WW)} \gg E_{c(WW)} \rightarrow do\ not\ mix$$

2. Mixture of water($\delta$=47.9) and glycerol ($\delta$=33.7)

$$E_{c(WG)} = 47.9 \times 33.7 = 1614$$

$much\ stronger\ interaction\ between\ water\ and\ glycerol$

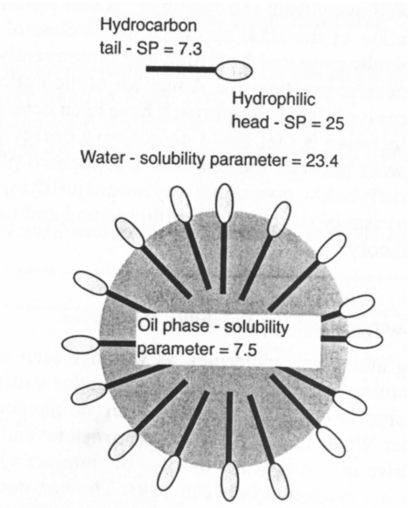
→ two materials mix well

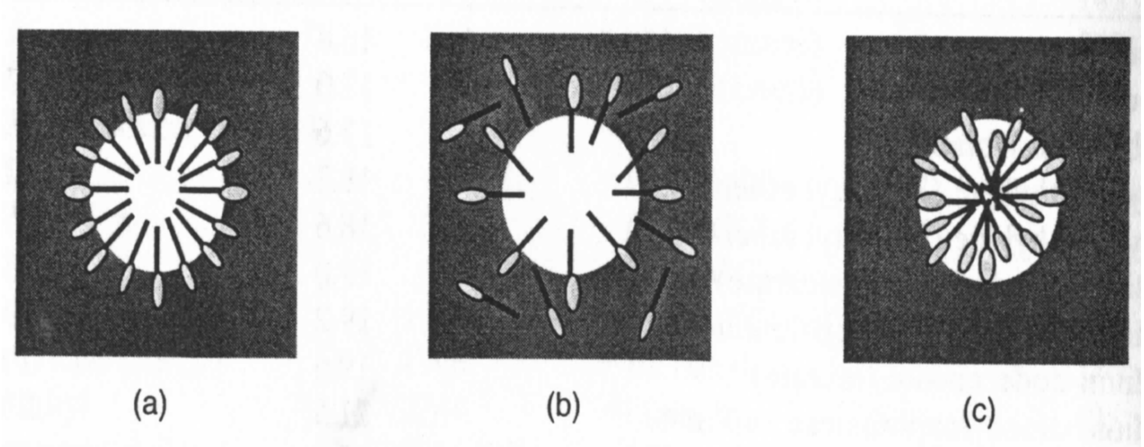
→ For miscibility of two materials, $\delta$ $must\ be\ similar$

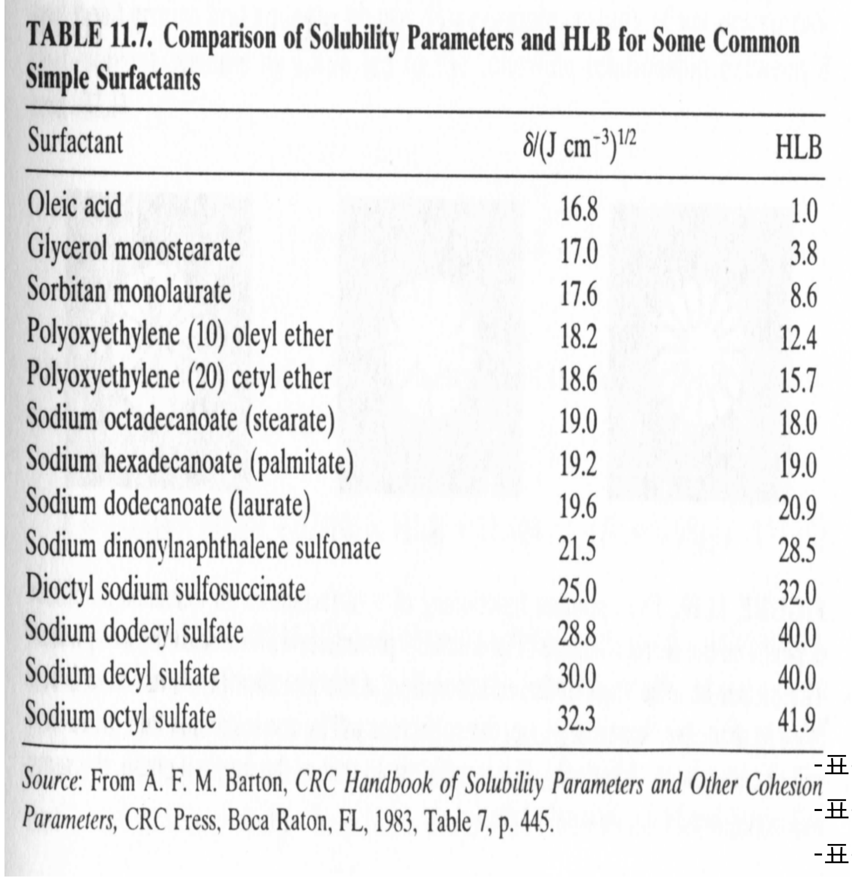
→ "like" dissolve "like"

# Solubility Parameter, Surfactant and Emulsions

- For emulsion stabilization, surfactants have a strong interactions with both the water and oil phase
  - If water interactions are too dominant, the molecule ill tend to be too soluble in the aqueous phase, and will loose effectiveness at the oil-water interface
  - The goal is to balance the cohesive interaction of the surfactant tail with that of oil phase and that of the head with the aqueous phase.



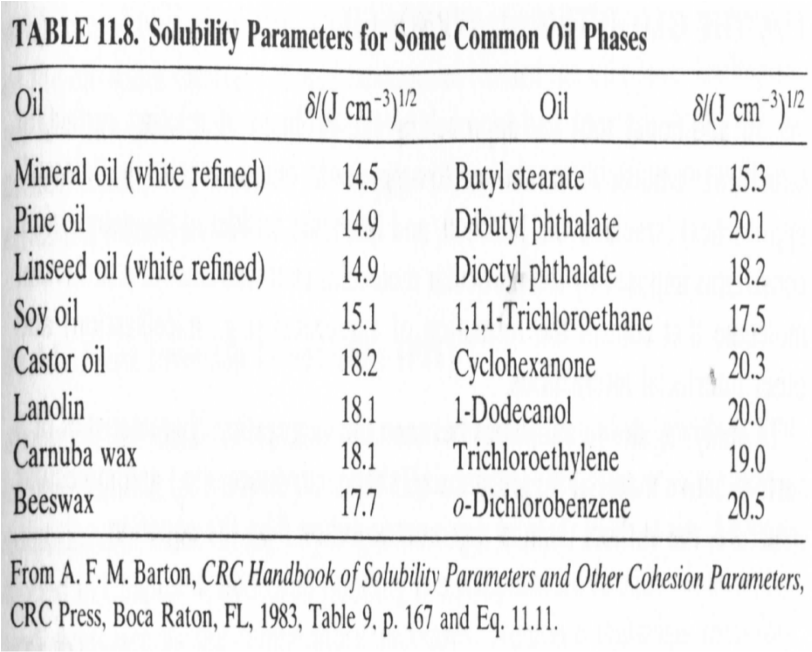




### TABLE 11.7. Comparison of Solubility Parameters and HLB for Some Common Simple Surfactants

| Surfactant | $\delta/(\mathrm{J\ cm^{-3}})^{1/2}$ | HLB |
|---|---|---|
| Oleic acid | 16.8 | 1.0 |
| Glycerol monostearate | 17.0 | 3.8 |
| Sorbitan monolaurate | 17.6 | 8.6 |
| Polyoxyethylene (10) oleyl ether | 18.2 | 12.4 |
| Polyoxyethylene (20) cetyl ether | 18.6 | 15.7 |
| Sodium octadecanoate (stearate) | 19.0 | 18.0 |
| Sodium hexadecanoate (palmitate) | 19.2 | 19.0 |
| Sodium dodecanoate (laurate) | 19.6 | 20.9 |
| Sodium dinonylnaphthalene sulfonate | 21.5 | 28.5 |
| Dioctyl sodium sulfosuccinate | 25.0 | 32.0 |
| Sodium dodecyl sulfate | 28.8 | 40.0 |
| Sodium decyl sulfate | 30.0 | 40.0 |
| Sodium octyl sulfate | 32.3 | 41.9 |

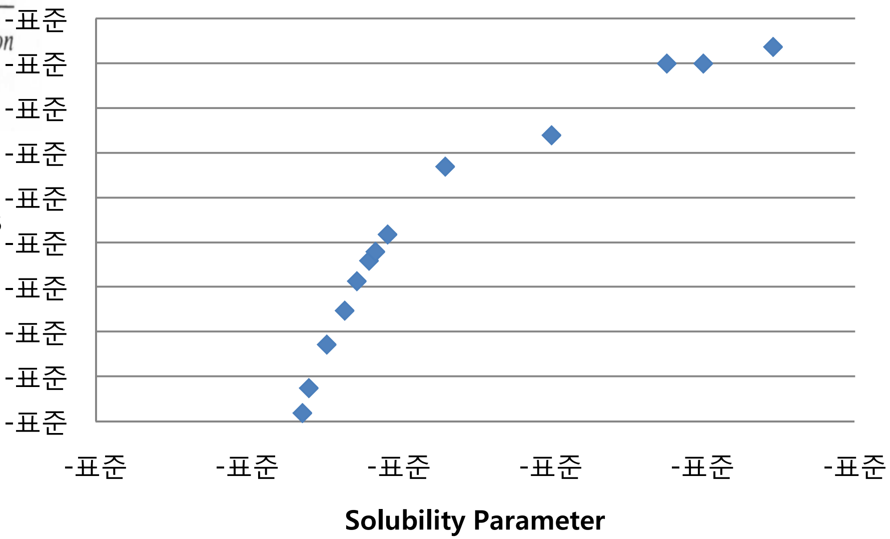
*Source*: From A. F. M. Barton, *CRC Handbook of Solubility Parameters and Other Cohesion Parameters*, CRC Press, Boca Raton, FL, 1983, Table 7, p. 445.



### TABLE 11.8. Solubility Parameters for Some Common Oil Phases

| Oil | $\delta/(\mathrm{J\ cm^{-3}})^{1/2}$ | Oil | $\delta/(\mathrm{J\ cm^{-3}})^{1/2}$ |
|---|---|---|---|
| Mineral oil (white refined) | 14.5 | Butyl stearate | 15.3 |
| Pine oil | 14.9 | Dibutyl phthalate | 20.1 |
| Linseed oil (white refined) | 14.9 | Dioctyl phthalate | 18.2 |
| Soy oil | 15.1 | 1,1,1-Trichloroethane | 17.5 |
| Castor oil | 18.2 | Cyclohexanone | 20.3 |
| Lanolin | 18.1 | 1-Dodecanol | 20.0 |
| Carnuba wax | 18.1 | Trichloroethylene | 19.0 |
| Beeswax | 17.7 | *o*-Dichlorobenzene | 20.5 |

From A. F. M. Barton, *CRC Handbook of Solubility Parameters and Other Cohesion Parameters*, CRC Press, Boca Raton, FL, 1983, Table 9, p. 167 and Eq. 11.11.



# Surfactant Packing Parameter

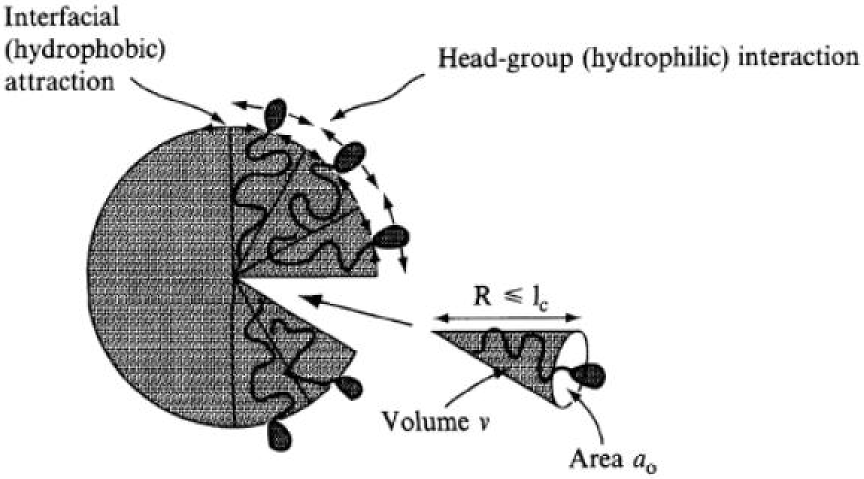
- Conceptual framework that relates molecular parameters (head group area, chain length and hydrophobic tail volume) and intensive variables (temperature, ionic strength etc.) to surfactant microstructures
- Critical Packing Parameter / Packing Parameter

$$CPP \text{ or } P = \frac{v}{l \cdot a_0}$$

v: volume of hydrocarbon core

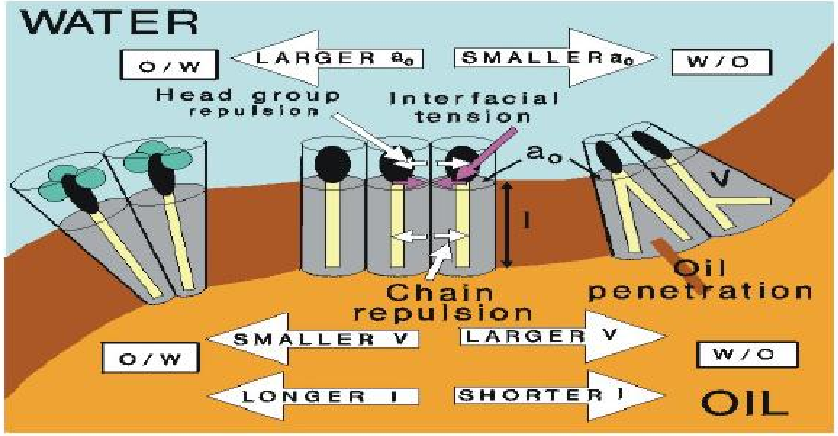
l: hydrocarbon chain length

$a_0$: <u>effective</u> head group area



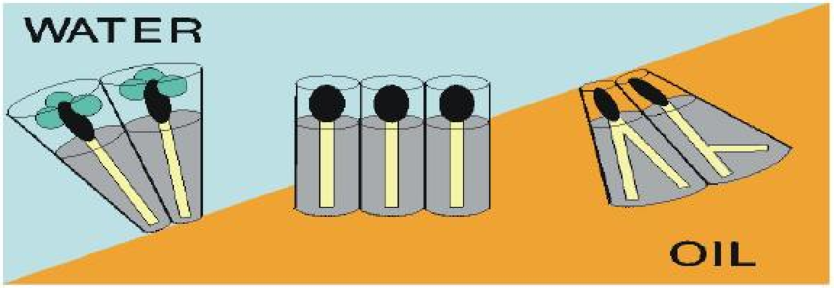
# Packing Parameter is inversely related to HLB

P = packing parameter = $\frac{V}{a_o\, l}$



| P | 1/3 | 1/2 | 1 | 2 | 3 |
|---|---|---|---|---|---|
| HLB | 40 | 20 | 10 | 2 | 1 |

HLB = hydrophile - lipophile balance



**mid point of packing parameter**

**P = 1**

**analogous to**

**HLB 10**

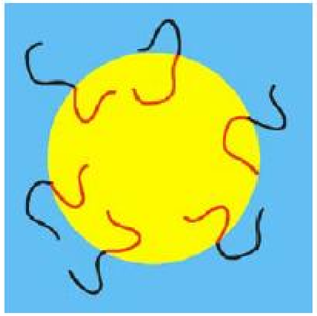
**at P = 1/ HLB = 10, surfactant has equal affinity for oil and water**

# The type of emulsion (O / W or W / O) is affected by:

- the ratio of the oil to water (non-polar to polar) phase;
- the chemical properties and the concentration of the emulsification agent;
- the temperature; the presence of additives;
- for solid particles as the stabilizing agents (Pickering emulsions)
  the wetting conditions (contact angles of the oil and water phases on the solid)

# Stabilization of emulsions

- emulsifiers: mostly surfactants
- hydration forces: O / W
- steric forces: W / O
- electrostratic forces: ionic surfactants
- polymers: steric forces (entropy stabilization)
- solid powders: hydrophobic forces (+ wetting)



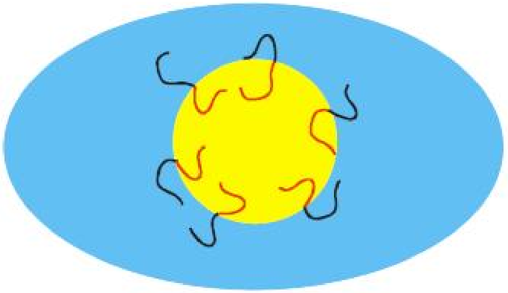
# Stability of emulsions - II

**Electrostatic stabilization** – at lower volume fractions

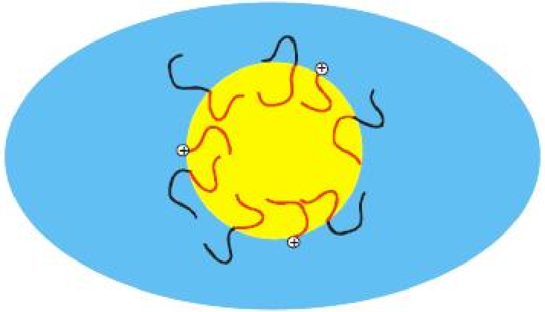
**Steric stabilization** – at all volume fractions

**Additional factors** –

1. Steric stabilization is enhanced by solubility in both phases:



2. Mixed emulsifiers (cosurfactants) are common. They can come from either phase.



3. Temperature is important – solubility changes quickly.

# Emulsions are kinetically stable!

Rate of coalescence – measure of emulsion stability.

It depends on:

**(a) Physical nature of the interfacial surfactant film**

For Mechanical stability, surfactant films are characterized by strong lateral intermolecular forces and high elasticity (Analogous to stable foam bubbles)

**Mixed surfactant system preferred over single surfactant.**

(Lauryl alcohol + Sodium lauryl sulfate: hydrophobic interactions)

NaCl added to increase stability (electrostatic screening)

# Emulsions are kinetically stable!

## (b) Electrical or steric barrier

Significant only in O/W emulsions.

In case of non-ionic emulsifying agents, charge may arise due to

(i) adsorption of ions from the aqueous phase or

(ii) contact charging (phase with higher dielectric constant is charged positively)

No correlation between droplet charge and emulsion stability in W/O emulsions

# Emulsions are kinetically stable!

**(c) Viscosity of the continuous phase**

Higher viscosity reduces the diffusion coefficient

Stoke-Einstein's Equation $D = \frac{KT}{6\pi\eta a}$

This results in reduced frequency of collision and therefore lower coalescence. Viscosity may be increased by adding natural or synthetic thickening agents.

Further, $\eta \uparrow$ as the no. of droplets$\uparrow$

(many emulsion are more stable in concentrated form than when diluted.)

# Emulsions are kinetically stable!

**(d) Size distribution of droplets**

Emulsion with a fairly uniform size distribution is more stable than with the same average droplet size but having a wider size distribution

**(e) Phase volume ratio**

As volume of dispersed phase ↑ stability of emulsion ↓

(eventually phase inversion can occur)

**(f) Temperature**

Temperature ↑, usually emulsion stability ↓

Temp affects – Interfacial tension, *D,* solubility of surfactant, Brownian motion, viscosity of liquid, phases of interfacial film.

# Phase inversion in emulsions

## Bancroft's rule

Emulsion type depends more on the nature of the emulsifying agent than on the relative proportions of oil or water present or the methodology of preparing emulsion.

Based on the Bancroft’s rule, it is possible to change an emulsion from O/W type to W/O type by inducing changes in surfactant HLB / CPP.

In other words...
Phase Inversion May be Induced.

# Inversion of emulsions (phase inversion)

O/W→ W/O

1. The order of addition of the phases

   W →O + emulsifier → W/O

   O →W + emulsifier → O/W
2. Nature of emulsifier

   Making the emulsifier more oil soluble tends to produce a W/O emulsion and vice versa.
3. Phase volume ratio

   Oil/Water ratio↑ →W/O emulsion and vice versa

# Inversion of emulsions (phase inversion)

4. Temperature of the system

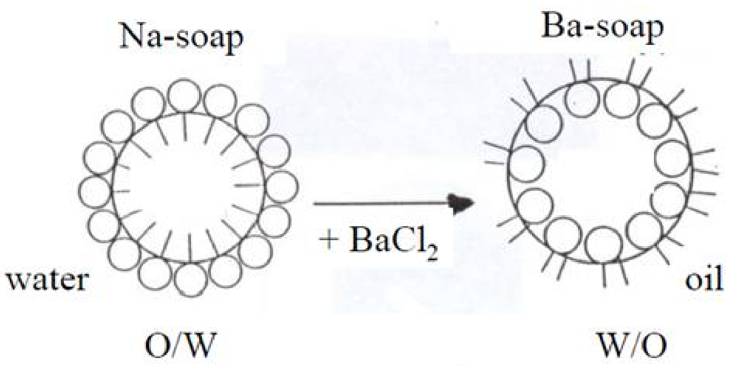
   ↑Temperature of O/W (polyoxyethylenated nonionic surfactant) makes the emulsifier more hydrophobic and the emulsion may invert to W/O.

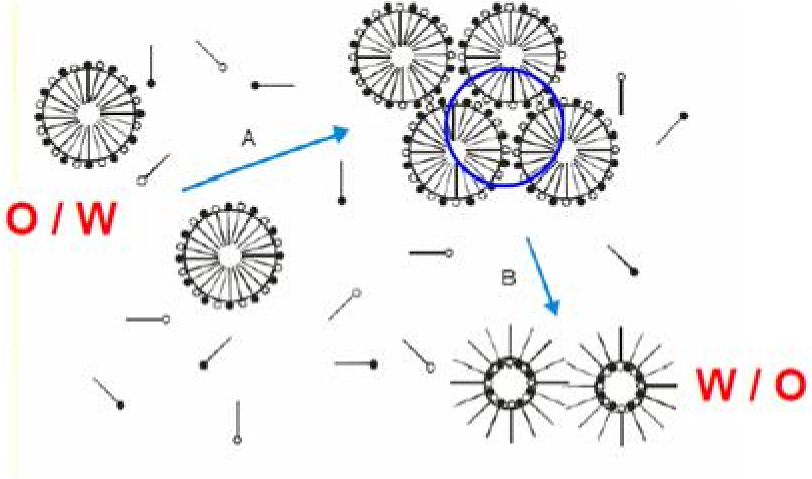
5. Addition of electrolytes and other additives.

   Strong electrolytes to O/W (stabilized by ionic surfactants) may invert to W/O

   Example. Inversion of O/W emulsion (stabilized by sodium cetyl sulfate and cholesterol) to a W/O type upon addition of polyvalent Ca.

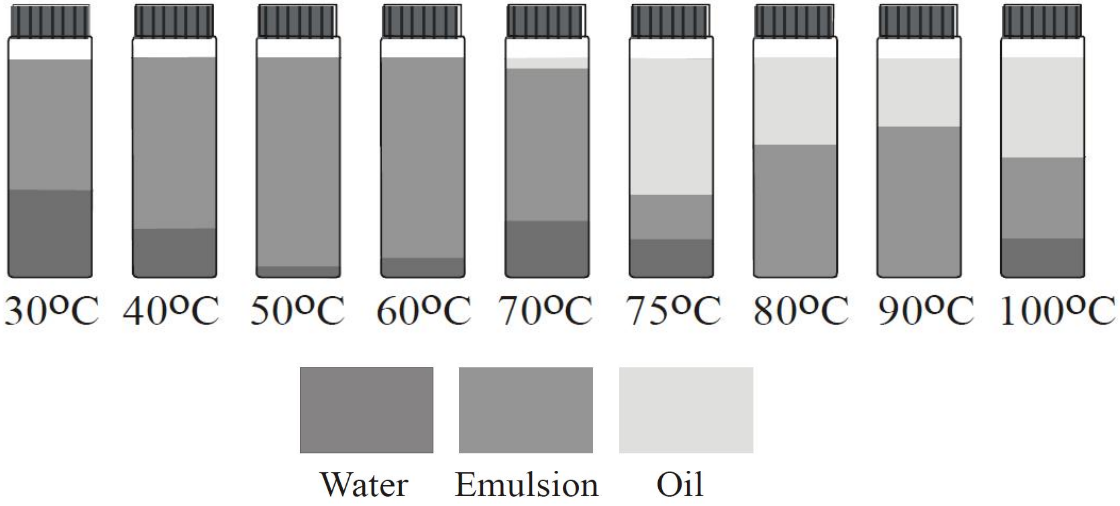
# Phase inversion induced by the change in the HLB / CPP





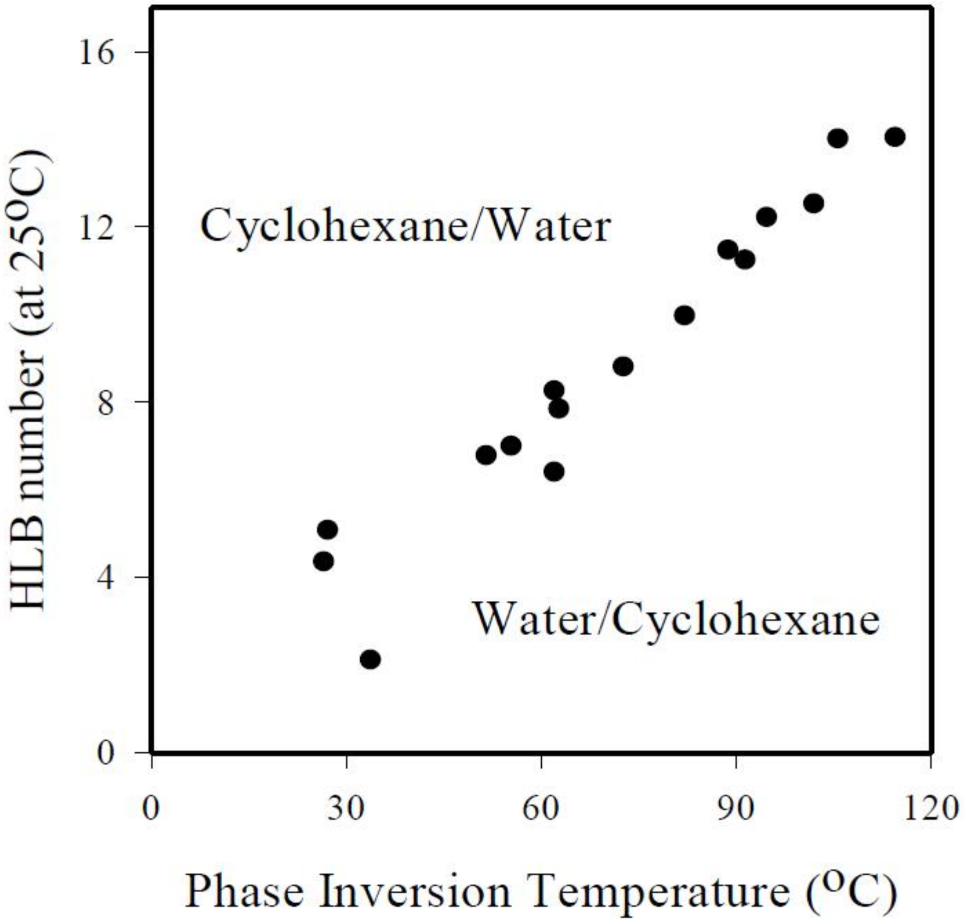
Increasing the concentration of droplets (A) make them get closer until they "pinch off" into smaller, opposite type of emulsion (B).

# Phase inversion temperature



- HLB number varies with temp. because the relative solubilities of the liphophile and the hydrophile vary with temp.
- The variation of solubility with temp. is most profound for nonionic emulsifiers containing a PEO hydrophile.
  - Water soluble at low temp. → O/W emulsion
  - Oil soluble at high temp. → W/O emulsion

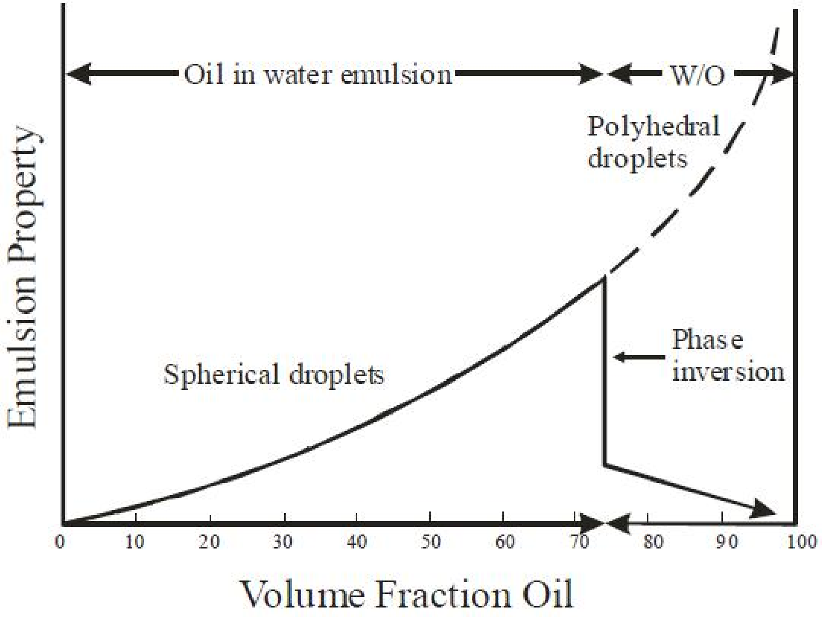
# HLB and the Phase Inversion Temperature



# Physical properties of emulsions

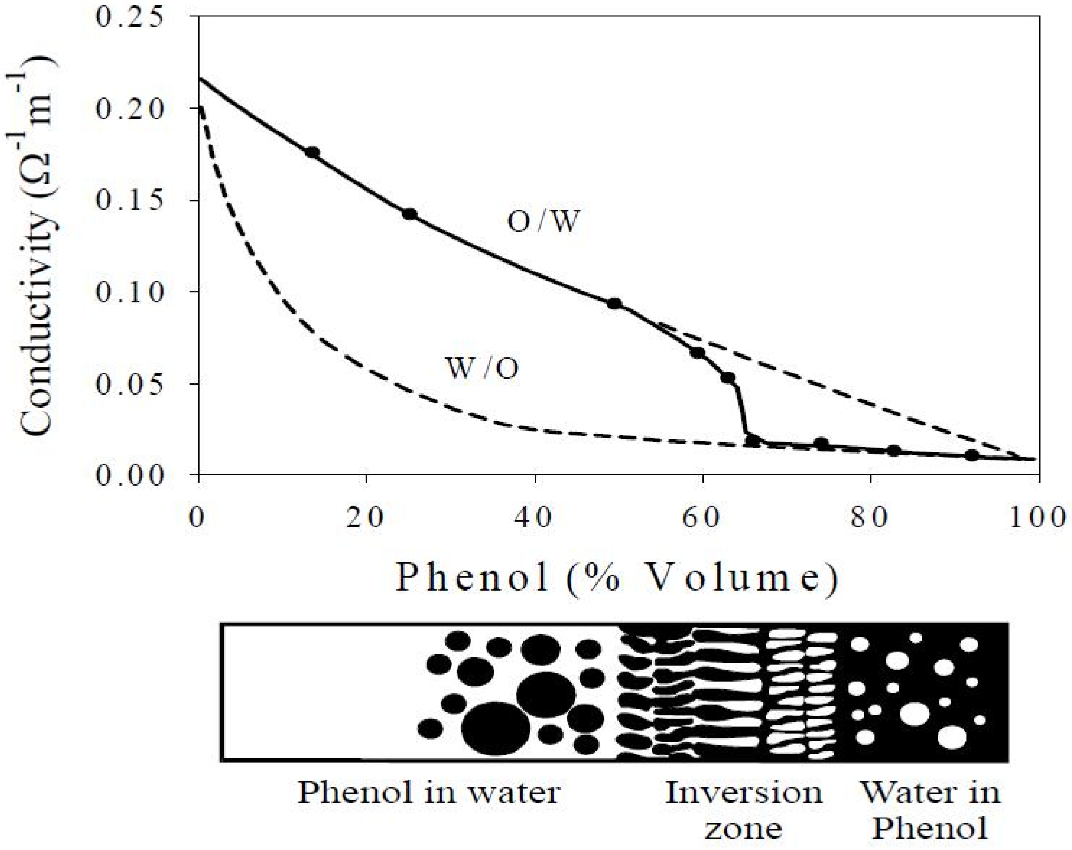
- **Identification** of “internal” and “external” phases; W/O or O/W
- **Droplet size and size distributions –** generally greater than a micron
- **Concentration of dispersed phase** – often quite high. The viscosity, conductivity, etc, of emulsions are much different than the continuous phase.
- **Rheology** – complex combinations of viscous (flowing) elastic (when moved a little) and viscoelastic (when moved a lot) properties.
- **Electrical properties –** useful to characterize structure.
- **Multiple phase emulsions –** drops in drops in drops, …

# The Variation in Emulsion Properties with Concentration



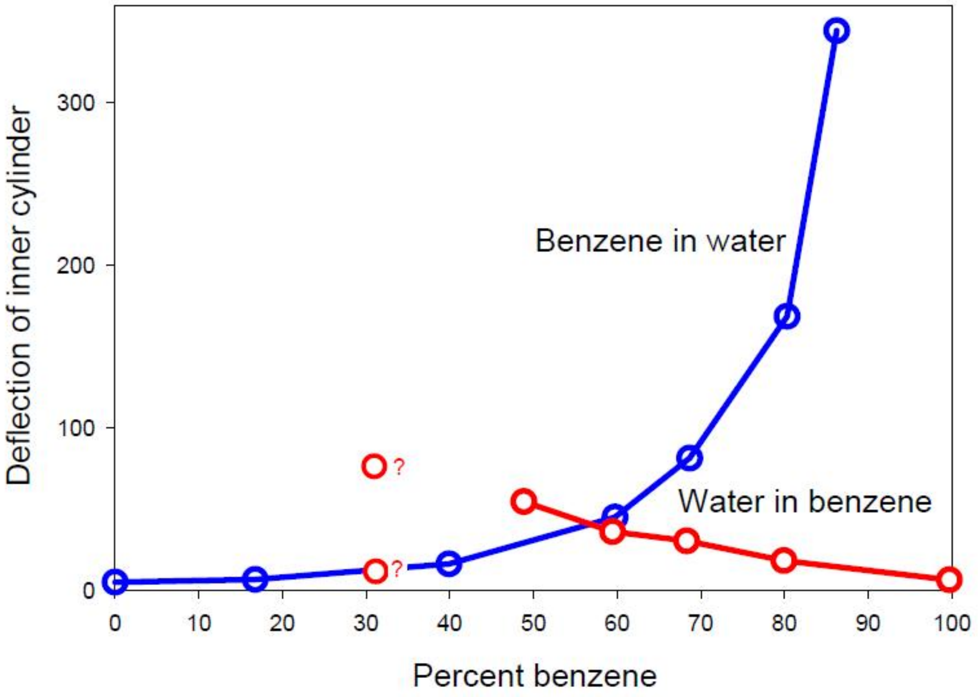
The variation of properties of emulsions with changes in composition. If inversion occurs, there is a discontinuity in properties, as they change from one curve to the other. Above 74% there is either a phase inversion or the droplets are deformed to polyhedra.

# Conductivity of Emulsions



The specific conductivity of aqueous potassium iodide and phenol emulsions as a function of composition (Manegold, p. 30).

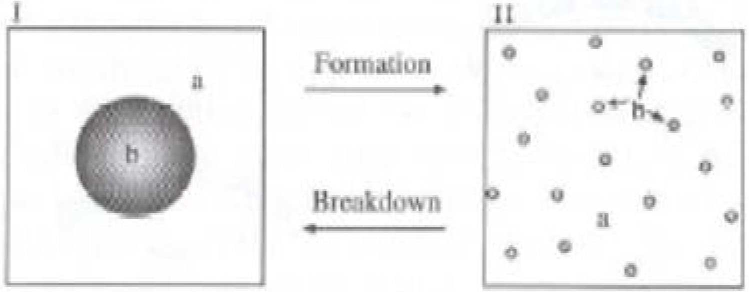
# Viscosities of two types of emulsion



In concentrated emulsions, the emulsion droplets become in contact, and the flow of the emulsion is impeded by interference of the droplets with one another.

# Making emulsions

- Mode of action of making emulsions
  - Fluid streams at high velocities are forced against each other resulting in cavitation, turbulence, and shear.
- Emulsification proceeds in two steps
  - mechanical mixing
  - stabilization
- Main methods
  - Method of phase inversion
  - High speed mixers
  - Condensation methods: solubilize an internal phase into micelles



# High Speed Mixers - Impart shearing forces

## Rotor-Stator Disperser

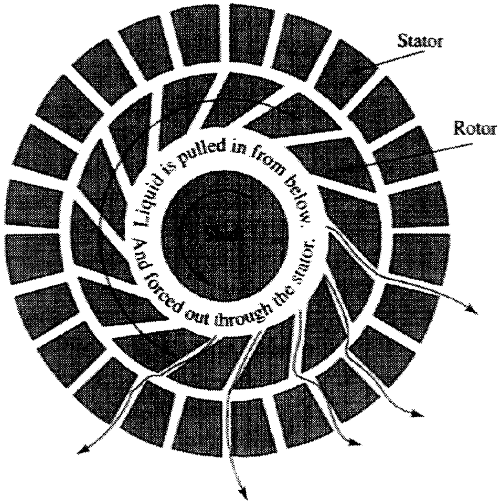


**Figure 5.1** A Kady mill rotor and stator.

High shear generated from the spinning rotor rotating at 5,000 – 20,000 rpm.

## Colloid Mill

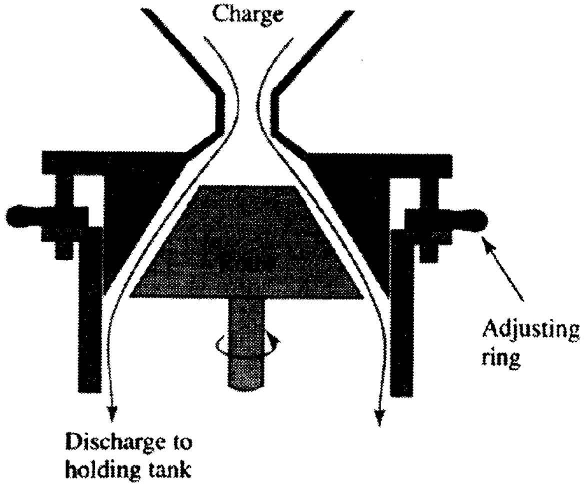


**Figure 5.2** Section of a vertical colloid mill.

The liquid/liquid mixture as it passes through the narrow gap, liquid films breakup into small drops. The rotor rotates at 1,000 – 20,000 rpm.

## Homogenizer

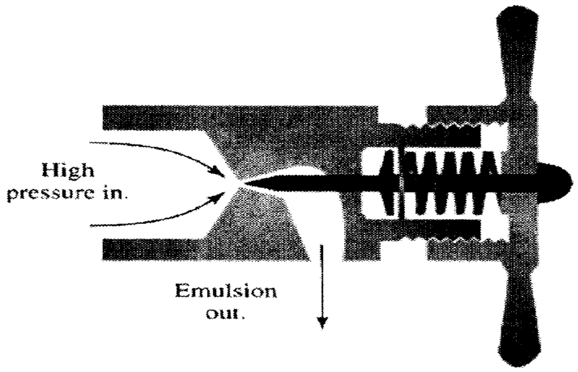


**Figure 5.3** Section of a single-stage homogenizer.

Pump liquid mixture at high pressure (up to 12,000 psi) through a small orifice against a spring loaded plunger

## Sonolator

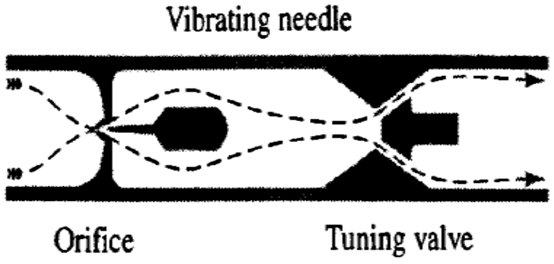
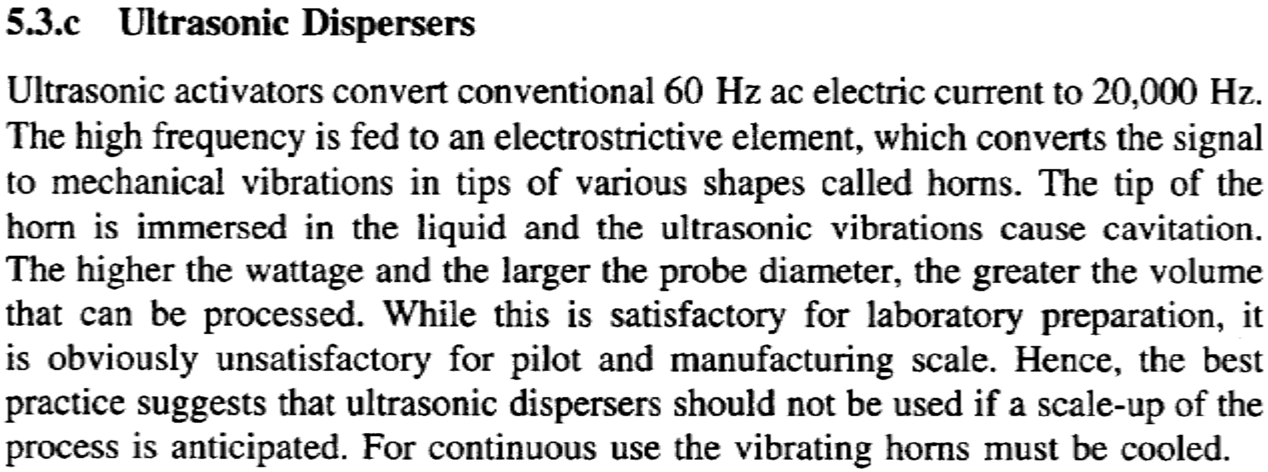


**Figure 5.4** Schematic diagram of the Sonolator.

Variation of homogenizer. Pump liquid mixture at lower pressure (up to 5,000 psi)



### 5.3.c Ultrasonic Dispersers

Ultrasonic activators convert conventional 60 Hz ac electric current to 20,000 Hz. The high frequency is fed to an electrostrictive element, which converts the signal to mechanical vibrations in tips of various shapes called horns. The tip of the horn is immersed in the liquid and the ultrasonic vibrations cause cavitation. The higher the wattage and the larger the probe diameter, the greater the volume that can be processed. While this is satisfactory for laboratory preparation, it is obviously unsatisfactory for pilot and manufacturing scale. Hence, the best practice suggests that ultrasonic dispersers should not be used if a scale-up of the process is anticipated. For continuous use the vibrating horns must be cooled.

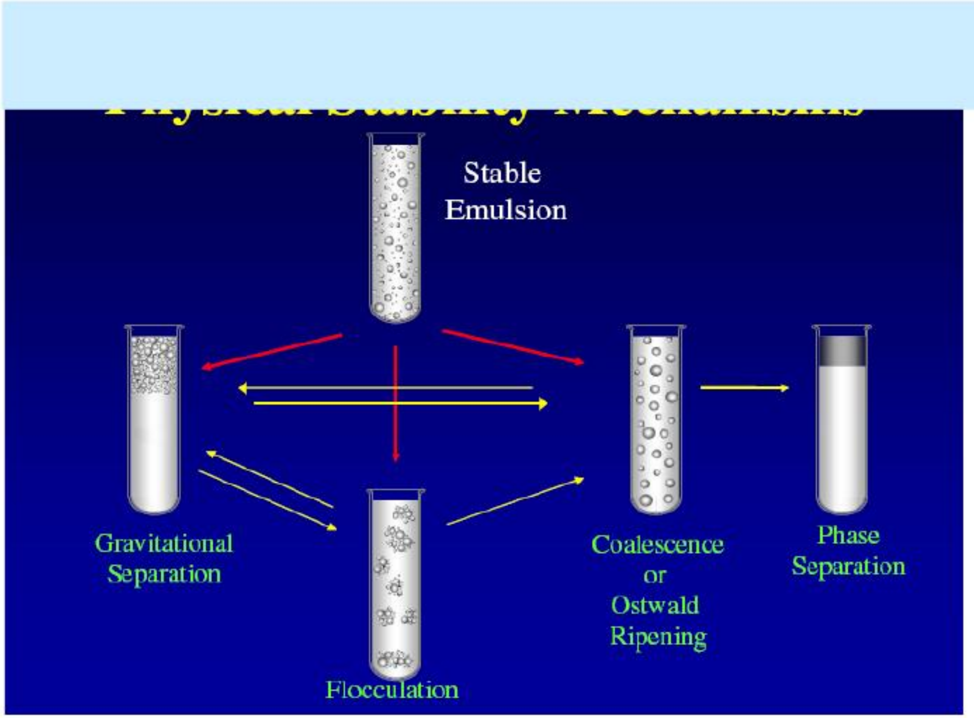
# Emulsion stability

- The term “emulsion stability” can be used with reference to three different phenomena
  - creaming (or sedimentation)
  - flocculation
  - breaking of the emulsion due to the droplet coalescence.
- Eventually the dispersed phase may become a continuous phase, separated from the dispersion medium by a single interface
- The time taken for phase separation may be anything from seconds to years, depending the emulsion formulation and manufacturing condition.

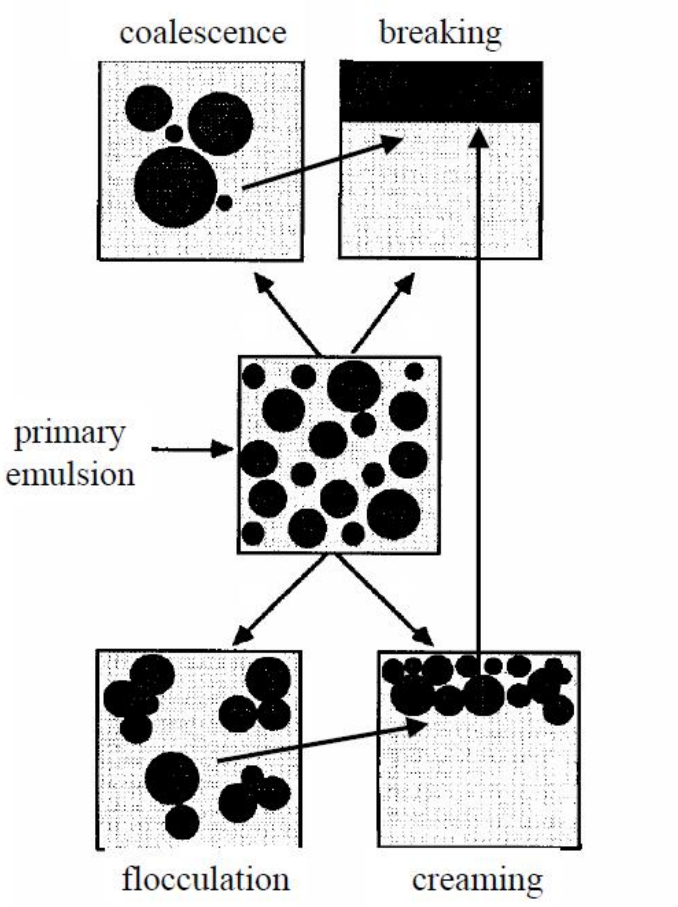
# Emulsion stability

Factors favoring **emulsion stability**

1. Low interfacial tension
2. Steric stabilization. Mechanically strong interfacial film (proteins, surfactants, mixed emulsifiers are common. **Temperature is important**)
3. Electrical double layer repulsions (at lower volume fractions)
4. Relative small volume of dispersed phase
5. Narrow size distribution
6. High viscosity (simply retards the rates of creaming, coalescence, etc.)
7. Reduced gravitational separation: reduced density difference, reduced droplet size, increased continuous phase viscosity



# Breaking emulsions



# Demulsification – breaking emulsions

First, determine type, O/W or W/O. Continuous phase will mix with water or oil.

- Chemical demulsification, i.e. change the HLB
  - Add an emulsifier of opposite type.
  - Add agent of opposite charge.
- Freeze-thaw cycles.
- Add electrolyte. Change the pH. Ion exchange
- Raise temperature.
- Apply electric field.
- Filter through fritted glass or fibers.
- Centrifugation. Induce contact between droplets with consequent coalescence

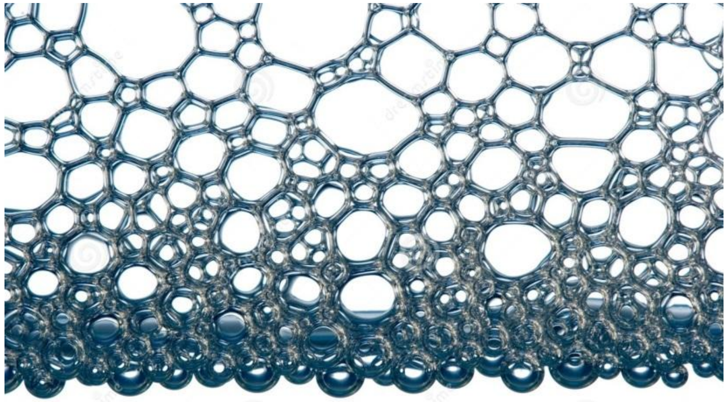
Add Ca to emulsions stabilized with alkali metal soap, converting soaps to water-insoluble.
Adding a cationic surfactant to anionic systems.
Adding a surfactant with a very different HLB.
Add electrolyte to reduce the electrostatic repulson.

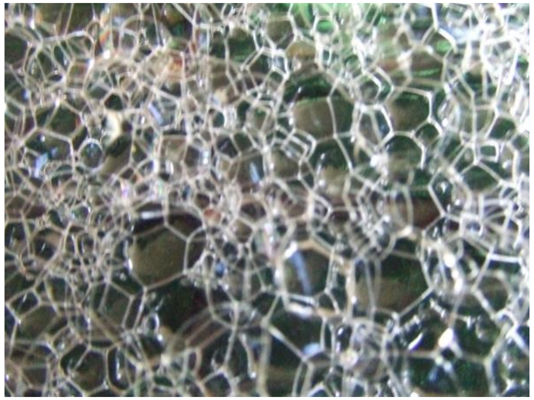
Adsorption of the stabilizer decreases with temp.
In some case, emulsifying agent is thermally decomposed
PEO or PPO become insoluble at higher temp.

Contact with hydrophilic filter bed surface leads to a separation of phase

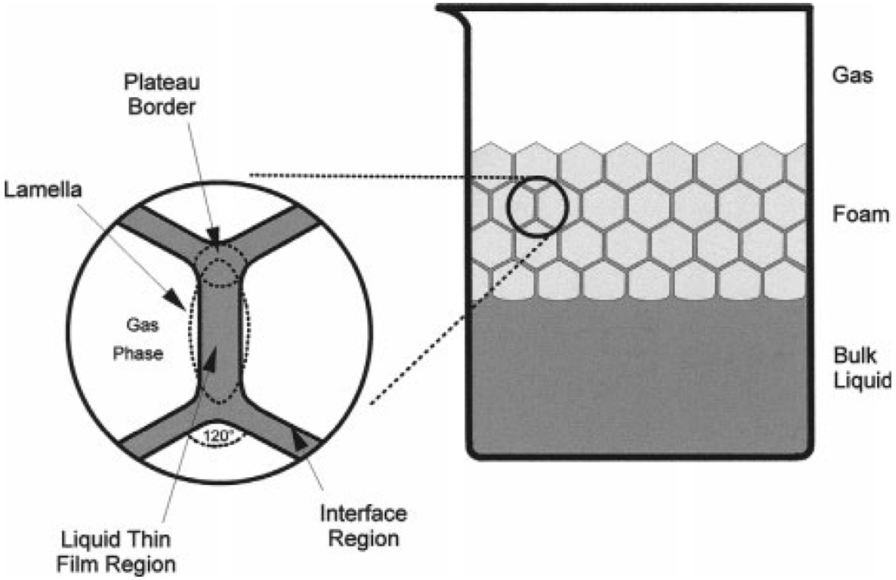
# Foams

- A foam is a colloidal dispersion in which a gas is dispersed in a continuous liquid phase.
- The three-dimensional foam bubbles are spherical in wet foams (i.e., those with gas volume fractions of up to $\Phi = 0.74$, the maximum volume fraction possible for an internal phase made up of uniform, incompressible spheres), but the foam bubbles start to distort in drier foams, in the range $0.74 < \Phi < 0.83$ approximately). In still drier foams the foam cells take on a variety of polyhedral shapes ($\Phi > 0.83$, approximately).





- The arrangement of films coming together at equal angles of 120 (called the Steiner angle) results from the equalization of the surface tension vectors, or contracting forces, along the liquid films. The bubbles in a foam arrange themselves into polyhedra such that, along the border of a lamella, three lamellae always come together at angles of 120; the border where they meet is termed a Plateau border. In three dimensions, four lamellae meet at a point at the tetrahedral angle, approximately 109.



- **Forces in the lamellae:**
  - Gravity Force: drainage of liquid
  - Capillary Force: flow from higher pressure region to the low pressure region in the plateau area, causing thinning of the films, eventually leading to film rupture and collapse of foam.
  - Opposing force
    - Marangoni effect:

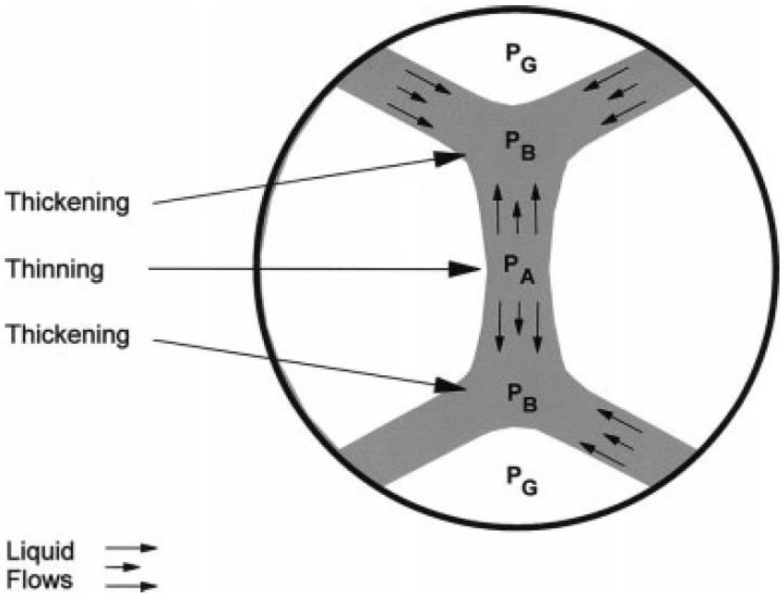
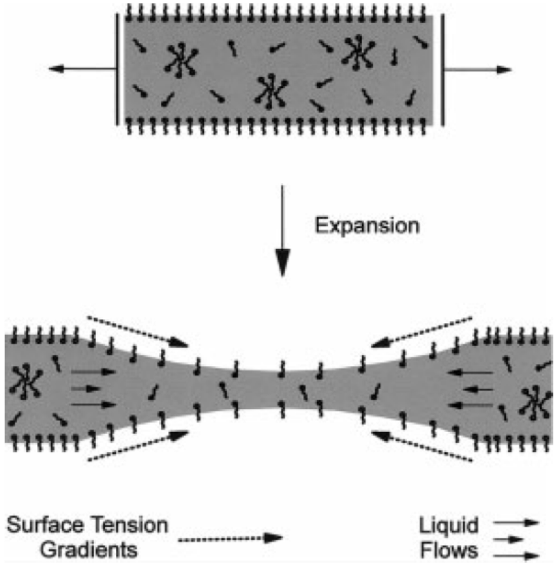


**Figure 3.26** Pressure differences across the curved surfaces in a foam lamella leading to $P_A > P_B$ and liquid flow towards Plateau borders at the expense of film thinning.

- Foams are partly characterized by their relative stability to film drainage and rupture. In most cases “stable” foams are caused by the presence of a foaming agent residing at the gas–liquid surface. Surfactant adsorption at the L/G interface lowers the interfacial energy and makes it easier to create and maintain the large interfacial area associated with having many gas bubbles in a liquid. It also increases the interfacial viscosity, which promotes stability as well.
- Foaming ability reaches its maximum at or above the cmc of the surtactant.
- Ionic surfactants are better foamers than non-ionics, presumably because their ionic head groups increase the stability of the foam through electrostatic repulsion between the two sides of the foam lamella.
- Generally, foaming ability increases with increasing alkyl chain length in the hydrophobic group and decreases with branching in the hydrophobic group.
- Foaming also tends to be decreased by any structural factor that increases the cross-sectional area of the surfactant at the surface, e.g., branching in the hydrophobic group, an increase in the number of oxyethylene units in the hydrophilic group of non-ionics, or “capping” of the terminal hydroxyl of the polyoxyethylene group with a less water-soluble group.

# Marangoni Effect

- In order to be able to withstand deformations without rupturing, a thin liquid film must be somewhat elastic.
- When a surfactant-stabilized film undergoes sudden expansion, then immediately the expanded portion of the film must have a lower degree of surfactant adsorption than unexpanded portions because the surface area has increased. This causes an increased local surface tension which provides increased resistance to further expansions.
- The local rise in surface tension produces an immediate contraction of the surface. Since the surface is coupled by viscous forces to the underlying liquid layers, the contraction of the surface induces liquid flow from the low-tension region to the high-tension region.
- The transport of bulk liquid due to surface tension gradients is termed the Marangoni effect; it re-thickens the thin films and provides a resisting force to film thinning.



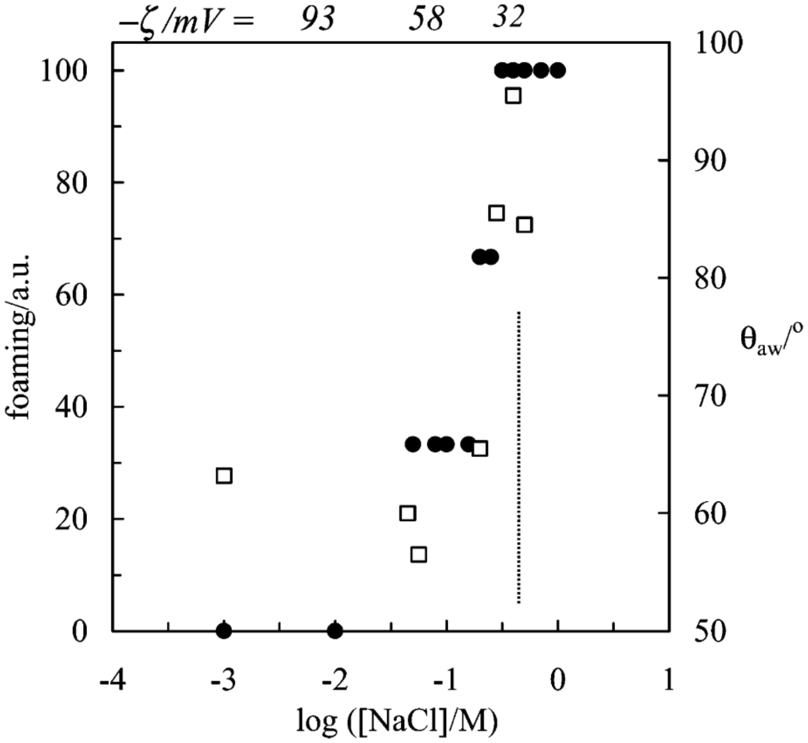
# Foam Stability

- Factors favoring foam stability

1) Low surface tension – makes it easier to form and maintain large interfacial area.
2) Low gravity drainage – decreases the rate of film thinning.
3) Low capillary suction – decreases the rate of film thinning.
4) High surface elasticity – counteracts the effect of surface perturbations.
5) High bulk viscosity – reduces the rate of film thinning.
6) High surface viscosity – reduces the rate of film rupture.
7) High electric double layer repulsion – increases disjoining pressure and reduces the rates of film thinning and rupture.
8) High steric repulsion – reduces the rates of film thinning and rupture.
9) Low dispersion force attraction – decreases the rates of film thinning and rupture.

# Foam Stabilization with Solid Particles

- In the presence of surfactant, the foam stability is affected by the surfactant type, particle size and concentration.
  - Hydrophilic particles can enhance aqueous foam stability by collecting in the plateau borders of the foam and retarding film drainage.,
  - Hydrophobic particles enter the airwater surfaces of the foam and cause destabilization via the so-called bridging-dewetting mechanism.



- Not many studies on foam stabilization in the absence of surfactants.

  - Stable foams were only obtained when particles coagulation is induced by reducing electrostatic repulsion with addition of either

    1) electrolyte (NaCl) :

    2) cationic surfactant (DTAB) : charge neutralization)

# Process for Foam Generation

- Bubbling gas into a liquid or solution
- Causing a stream of liquid to fall onto a pool of liquid or solution, thereby engulfing air bubbles,
- Suddenly reducing the pressure on a solution of dissolved gas, causing rapid nucleation and growth of gas bubbles within the solution,
- Turbulent mixing such that air is whipped into a liquid or solution, as with a beater, paddle- or propeller-stirrer, vortex mixer, blender, etc.,
- Co-injecting gas and liquid into a mechanical foam generator, which uses pressure drop, turbulence and/or tortuous flow pathways to cause bubble pinch-off and sub-division.