Emulsions

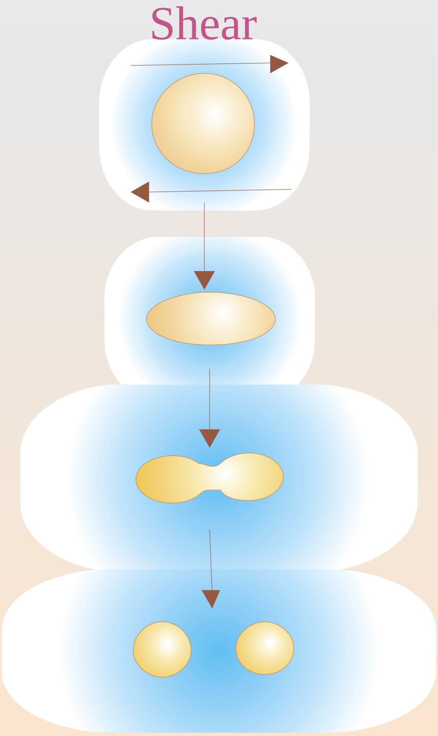
Lecture 8

Introduction

- Emulsion is a suspension of one liquid as drops or globules in a second liquid with which the first is not mixed.
- The emulsions are of utmost significance because of their large-scale commercial applications in many fields:
  - **Food,**
  - **Cosmetics,**
  - **Pharmacy,**
  - **Cutting fluids fo metal working,**
  - **Paints,**
  - **Oils,**
  - **Agricultural sprays, etc.**
- The emulsions play significant roles in living organisms.

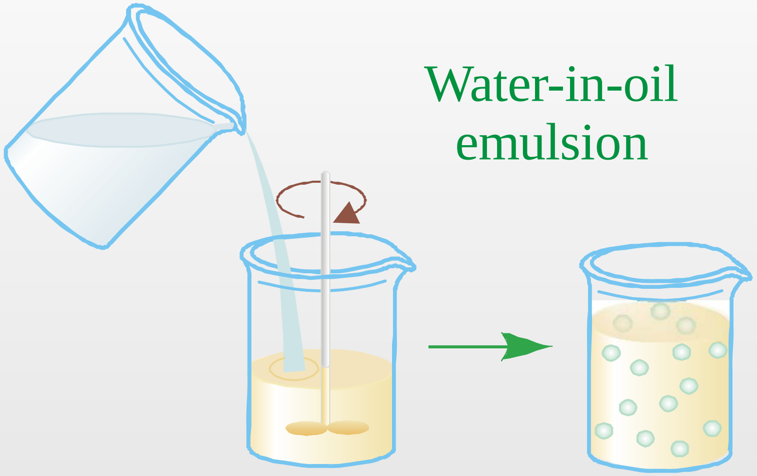
Emulsion preparation

- Emulsions are thermodynamically unstable systems.
  $\Delta G = \gamma\,\Delta A - T\Delta S$,
- The entropy favors, but it is too small.
- The A increase makes the formation unfavorable.



- Emulsion formation is possible under the action of shear force.
- A drop elongates and breaks in the middle into two smaller droplets.
- It happens if the pressure gradient exceeds the Laplace pressure.
- The energy required for the dispersion is even higher because of its dissipation as the heat caused by hydrodynamical resistance.

The processes of dispersion of one liquid in another are very inefficient, accompanied by significant heating.



- High-speed dispensers or blenders, which can provide high shear and elongational forces, are normally applied.
- An ultrasonic dispenser can also be used for the emulsion preparation. The breaking-up of droplets is due to local cavitations generated.

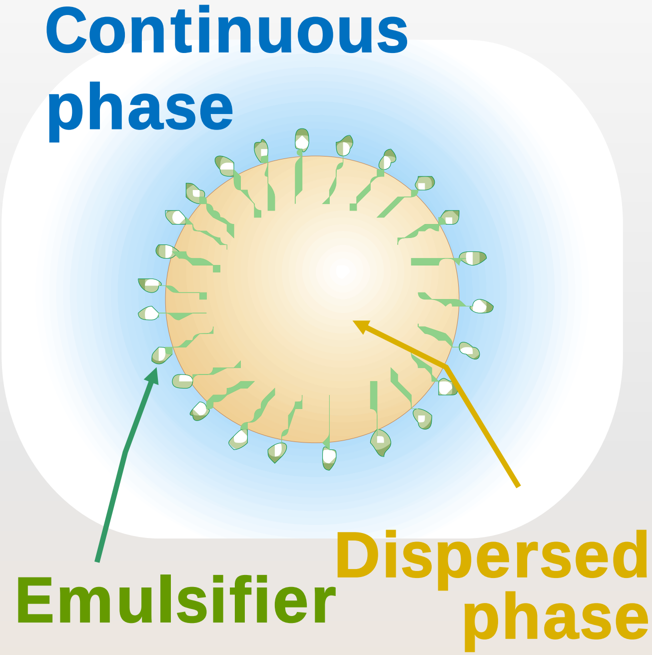
Spontaneous emulsification

Example: water – mixture of toluene with ethanol.

- When brining the liquids in contact, one can see the vibration of boundary, accompanied by the formation of water-in-toluene and toluene-in-water emulsions.
- The energy source is in an exothermic process of the mixing of water with ethanol. After the issue of ethanol into the water phase, the thus formed emulsion breaks fast into two immiscible liquids.
- The appearance of instability at interfacial boundary is known as the ***Marangoni effect***.

Terminology

- **Dispersing** or **continuous phase** or medium is a liquid in which there are droplets of another liquid.
- Oil is used to call the nonaqueous phase.
- **Disperse** or **dispersed phase** is droplets of liquids.
- **Emulsifying agent** or **emulsifier** is a substance, frequently surfactant, that is used to provide the dispersion of one liquid into another.



- **Stabilizer** is a substance, frequently polymer, or additive that prevents a phase separation of the emulsion into oil and water..

Emulsion types

- **Direct** or **oil-in-water emulsion**: continuous phase is more polar than the dispersed phase.
- **Revised** or **water-in-oil emulsion**: continuous phase is less polar than the dispersed phase.
- Determination of emulsion type:
- Measurement of conductivity is simple and effective.
- Change of emulsion type is **phase-inversion**. It is observed where conditions were changed or a solvent and substances were added.
- **Diluted emulsion**: amount of dispersed phase is few volume percents.
- **Concentrated emulsion**: the dispersed phase occupies more than 70 vol.%.

Emulsifiers

- Surfactants and low-molecular block co-polymers are usually used.
- High-molecular weight substances are less effective because of slow diffusion.
- Emulsifiers provide the lowering of interfacial tension γ. This enables:

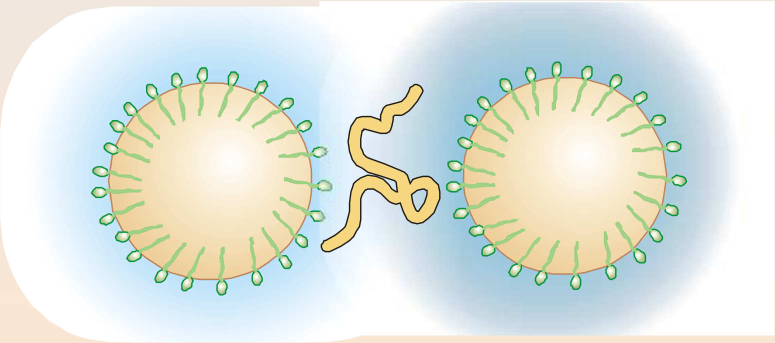
- Decrease the energy consumption;
- Prepare smaller droplets or higher surface-area emulsions;
- Stabilize the formed dispersion.

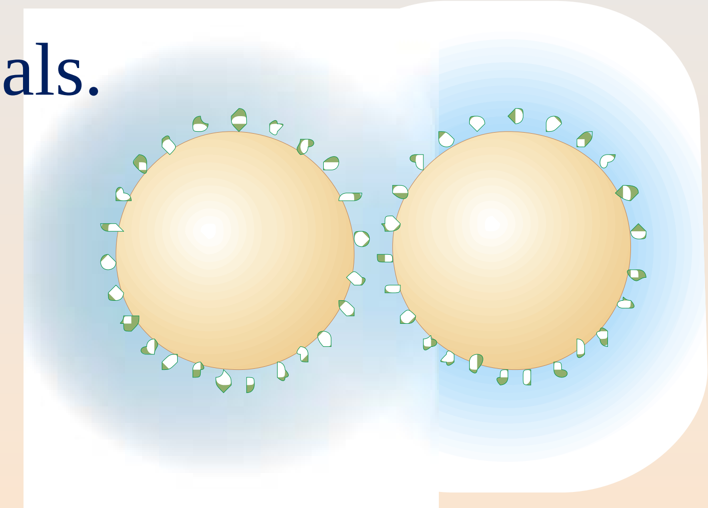
Stabilizers

- They provide the stabilization of emulsion prepared with the help of emulsifiers.
- This is reached via developing a sufficient repulsion between colliding droplets to maintain a film of the continuous phase between their surfaces.

Main types of stabilizers:

- Polymers; synthetic and natural (polysaccharides and proteins);
- Finely powdered solid materials.





Bancroft's rule

The phase, in which the surfactant is the most soluble, will be the continuous phase, that is:

- Water-soluble surfactants result in the generation of an oil-in-water emulsion;
- Oil-soluble ones, a water-in-oil emulsion.

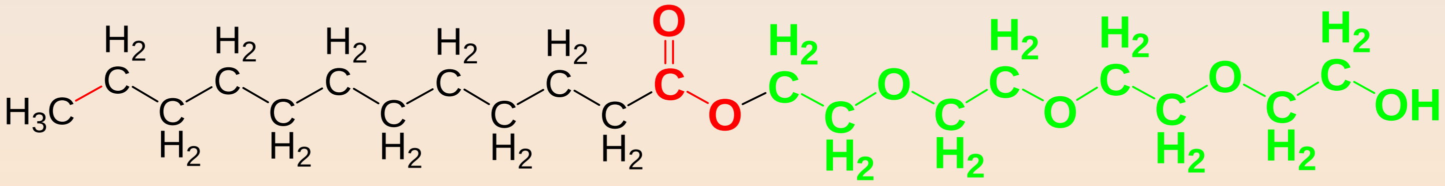
W. D. Bancroft
(1867 - 1953)

The rule is valid only for well-soluble surfactants!

Hydrophilic-lipophilic balance (HLB)

- To express quantitavely the emulsifying ability, Griffin (1949) suggested an arbitrary dimensionless scale for the classification of nonionic surfactants that accounts for the degree of their hydrophobicity and hydrophilicity
- This was made with the help of HLB numbers. To calculate them, Griffin developed certain empirical formulas.
- As an example, there is an equation for surfactants on the basis of fatty acids:

HLB number=20(1 - saponification number/acid number of the acid)



HLB number	Application
0-3	Antifoaming agent
4-6	Emulsifier (water-in-oil emulsion)
7-9	Wetting agent
8-18	Emulsifier (oil-in-water emulsion)
13-15	Detergent
15-18	Solubiliser

Advantages:

- The Griffin’s HLB numbers were the first rational system that established the relationship between the chemical structure of surfactant molecules and their surface activity.
- This facilitates the surfactant matching for a given formulation.

Disadvantage:

- This is an empirical system;
- It does not have a theoretical basis.

Davies’ approach

- He extended and simplified the Griffin’s scale.
- It was done through introducing HLB numbers assigned to groups constituting the surfactant molecules.
- This is based on the additivity law.

HLB number = $7 + \sum$ (hydrophilic group numbers) - $\sum$ (hydrophobic group numbers)

Hydrophilic group	HLB number
- SO_4Na	38.7
-COOK	21.1
-COONa	19.1
-N (tertiary amine)	9.4
-COOH	2.1
-OH (free)	1.9
-O-	1.3
-OH (sorbitan)	0.5

Hydrophobic group	HLB number
- CF_3	- 0.87
- CF_2-	- 0.87
- CH_3	- 0.475
- CH_2-	- 0.475

Matching of emulsifier

- Surfactant has to have the high surface activity; it reduces better the interfacial tension in emulsions.
- Oil-soluble surfactant emulsifies water in oil, while water-soluble one, oil in water.
- The emulsification is frequently more efficient by a mixture of oil-soluble and water-soluble surfactant. A possible effect can be caused by their access from both the sides of interfacial boundary that makes its dispersing easer.
- The HLB number of mixed surfactants is equal an algebraic mean of their HLB numbers normalized to the weight fraction of each of them in the mixture.

HLB numbers for solvents

- To improve further the HLB systems, it was extended to the solvents.
- Their numbers were found empirically.
- Method:
- Homologous series of surfactants were used to emulsify a solvent;
- The HLB number of member, of which the emulsions was formed easier and was more stable, was assigned to the solvent.

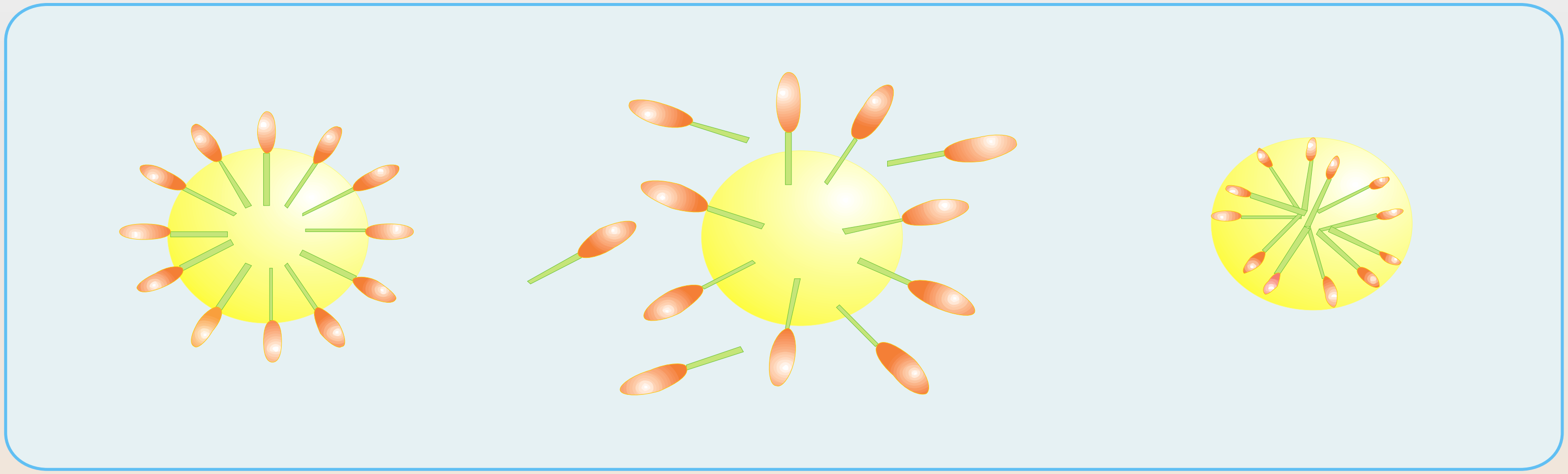
Solvent	HLB number
Benzene	15
Paraffin oil	14
Mineral oil	10
Pine oil	16
Xylol	14

- Rule: The HLB number for surfactants should be as closer as possible to the HLB of solvent.
- If there is a polar oil, it is necessary to take a more polar surfactant.
- Example:
  - A mixture of 20 % mineral oil (HLB = 10) and aromatic mineral oil (HLB = 13);
  - HLB of mixture = 10x0.2 + 13x0.8 = 12.4;
  - Surfactants $C_{12}EO_{24}$ (HLB = 17.0) and $C_{16}EO_{2}$ (HLB = 5.3);
  - HLB of mixture (60:40) = 12.32.
  - This surfactant mixture is optimal for emulsifying the mixed solvents.

Advantages and disadvantages of HLB System

- The HLB systems is empirical and qualitative.
- It can be applied only for the initial matching of surfactant(s) to develop a formulation.
- The HLB system does not take into account the change of properties of solvents when surfactants introduced.
- It is valid at room temperature.
- Regardless of its faults, the HLB system is still in extensive use since it was proposed by Griffin.

- Because of extensive and rather successful practical use, there was a number of attempts to provide a theoretical background of the HLB system.
- Perhaps one of the most reasonable is that based on cohesive energy densities and solubility parameters.



Solubility in both phases is comparable.

Solubility is better in continuous phase.

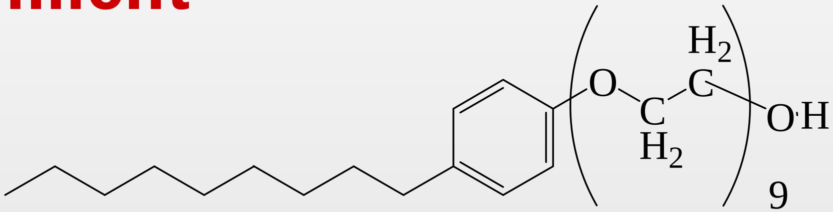
Solubility is better in dispersed phase.

Phase inversion temperature (PIT)

Shinoda's experiment

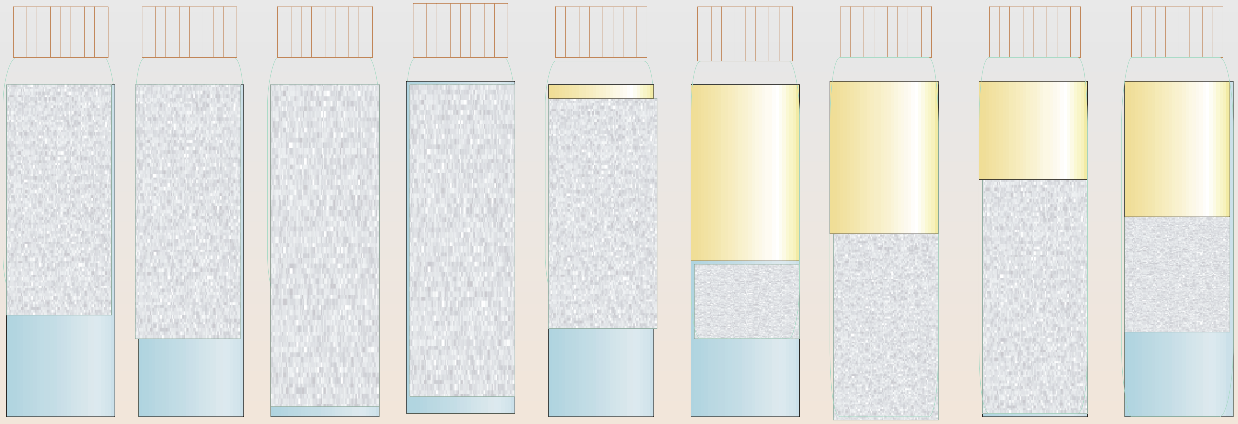
3 % Surrfactant

48.5 % Water and cyclohexane.



Emulsion

Aqueous solution



Nonaqueous solution

Emulsion

Aqueous solution

25 40 50 60 70 75 80 90 100ºC

← PIT →

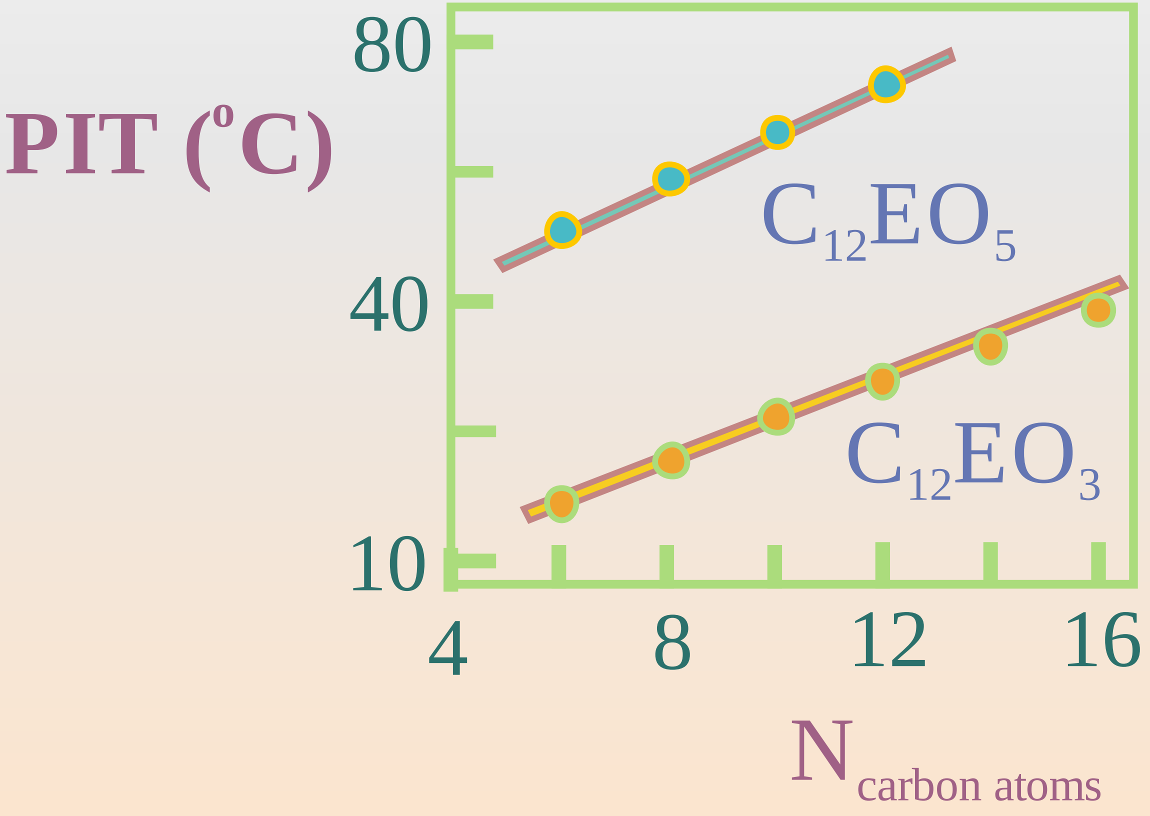
Oil-in-water emulsion

Water-in-oil emulsion

Main features of PIT

The PIT concept is valid for nonionic surfactant with PEO chains. A hydrophilic-lipophilic balance is attained in the emulsion.

The PIT depends on many factors:



- **Poly(ethylene oxide) chain length**: The longer chain; the higher PIT.
- **Oil nature**: the more nonpolar oil, the higher PIT. *Example*: nonylbenzene ethoxylate 9.6 PEO; PIT is ~ 20°C for benzene-water (1:1); 70°C for cyclohexane:water (1:1) and > 100°C for hexadecane:water (1:1).
- **Ionic strength**: Inorganic salts decrease usually the PIT. *Example*: 5 % NaCl results in a decrease of the PIT by 10°C.
- **Additives**: Substances increasing the polarity of oil (fatty acids, alcohols) lead to a decrease of the PIT, whereas water-soluble ones (ethanol, isopropanol), an increase of the PIT.
- **Water-to-oil ratio**: The PIT is rather independent of their volume ratio in the range from 0.2 to 0.8.

Practical importance of PIT

PIT knowledge allows preparing highly stable emulsions:

- ⌘ There is a minimal interfacial tension at the PIT that is favorable for dispersing liquids and lessening their dimension.
- ⌘ It is desirable to have a system with the PIT of which value is 40^{o}C higher of the temperature of emulsion use.

Methods

Method 1:

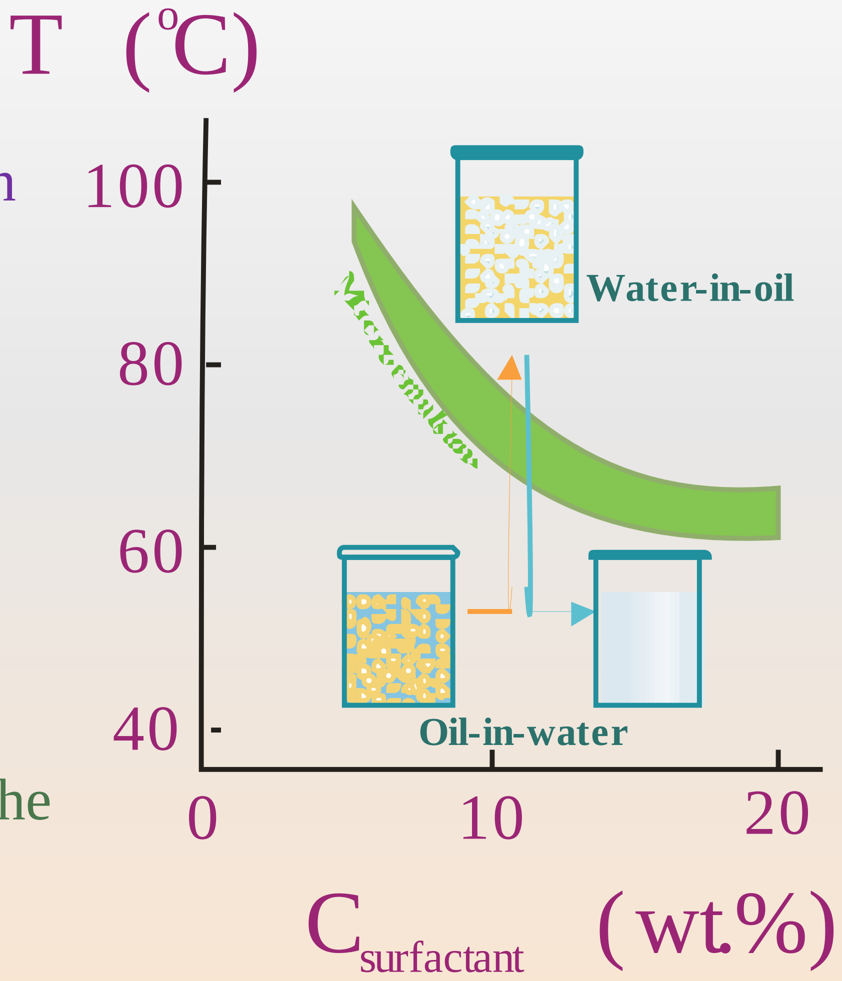
☸ (**a**) An emulsion is formed at temperature that 2-4 degrees lower than the PIT;

☸ (**b**) the solution is cooled fast up to the needed temperature.

***Method 2*:**

☸ (**a**) An emulsion is formed at temperature that a little higher than the PIT;

☸ (**b**) an addition of cooled water lowers sharply the temperature below the PIT. This results in the phase-inversion accompanied by a change of the emulsion type.



Application

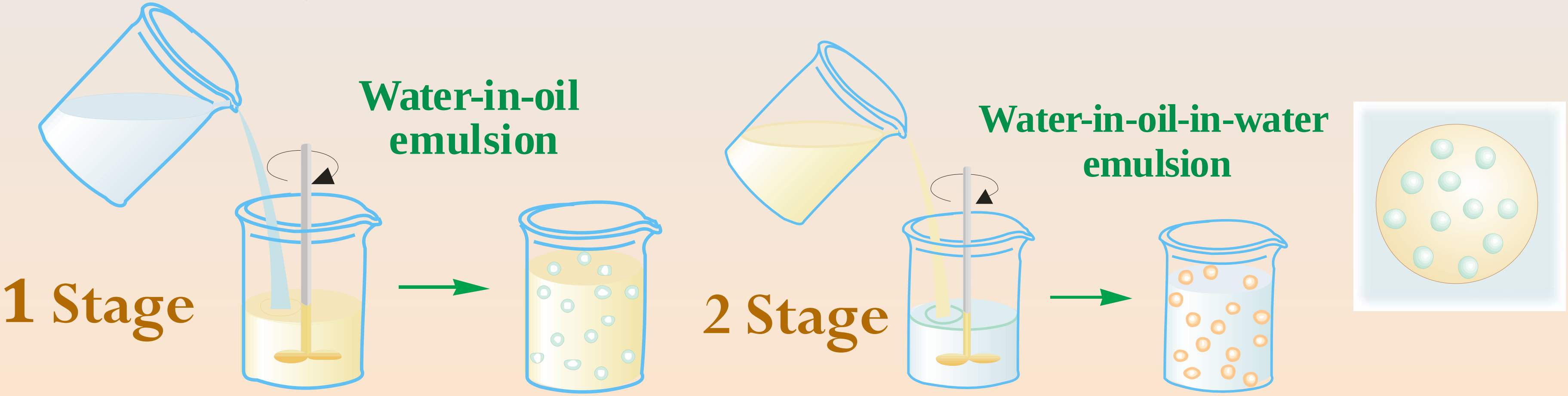
The methods are used mainly in cosmetic industry.

Advantages:

- They simplify the dispersing of highly viscous oils.
- The heating-cooling cycle enables preparing very fine oil-in-water emulsions with droplets of ca. 100 nm.
- These emulsions feature high stability.
- The saving of energy and shortening of production cycle are reached.

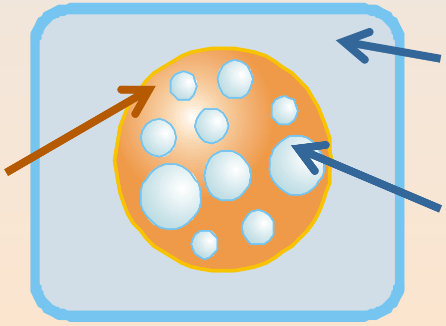
Multiple or double emulsions

- Three-phase systems: An initially prepared (primary) emulsion is dispersed then in a new continuous media to form a secondary emulsion.
- Types: water-in-oil-in-water or oil-in-water-in-oil. The former means that there are two water phases and one oil phase.
- Preparation in two stages: e. g. 1. A water-in-oil emulsion is prepared by using an oil-soluble surfactant; 2. This emulsion is dispersed in water with a water-soluble surfactant.



Features of multiple emulsions

- There two types of oil–water interfaces. An individual surfactant is optimized for each of them.
- One surfactant is taken with HLB value of 2-8, another, 6-16.
- The surfactants should not interfere with each other.
- The increased number of phases and surfactants makes the multiple emulsions less stable than the common emulsions.



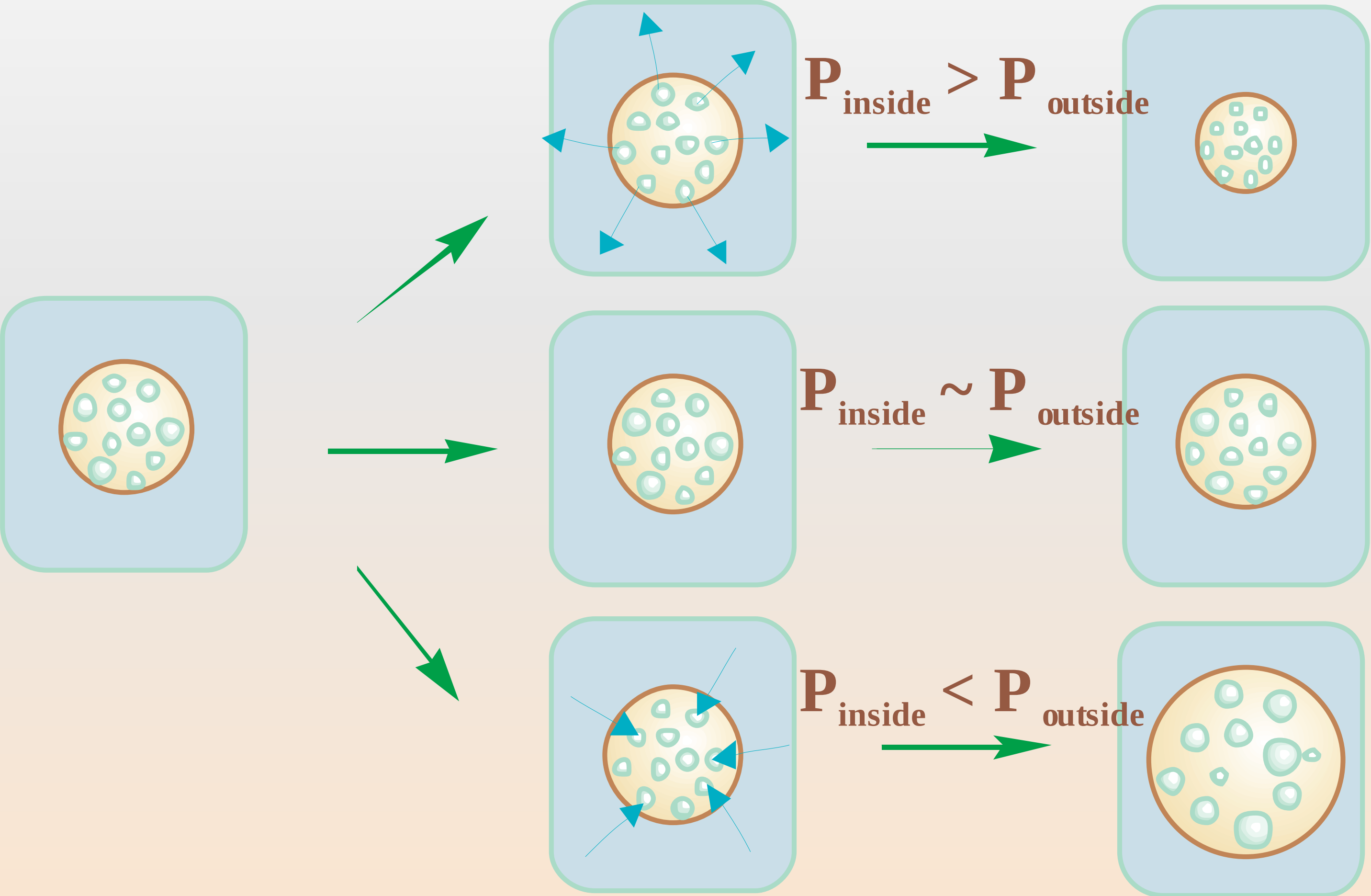
Continuous phase: Water

Dispersing and Dispersed phase: Oil

Dispersed phase: Water

- Multiple emulsions can be prepared by any of the common methods:
  - Agitation,
  - Sonication,
  - Phase inversion.
- Great care should be paid to the preparation of the final system. A vigorous treatment can cause the breaking of the primary emulsion and merging of the similar phases: water with water or oil with oil.

A formulation composition should be selected in such a manner that a significant osmotic pressure is excluded.



$P_{inside} > P_{outside}$

$P_{inside} \sim P_{outside}$

$P_{inside} < P_{outside}$

Applications

- Cosmetics,
- Pharmaceuticals,
- Controlled drug delivery,
- Wastewater treatment,
- Separations technologies.

They are based on:

- Solubilization of water soluble and insoluble substances at the same time;
- Separation of poor compatible substances;
- Preservation of unstable substances;
- Slowing-down release of substances.

Emulsions in time

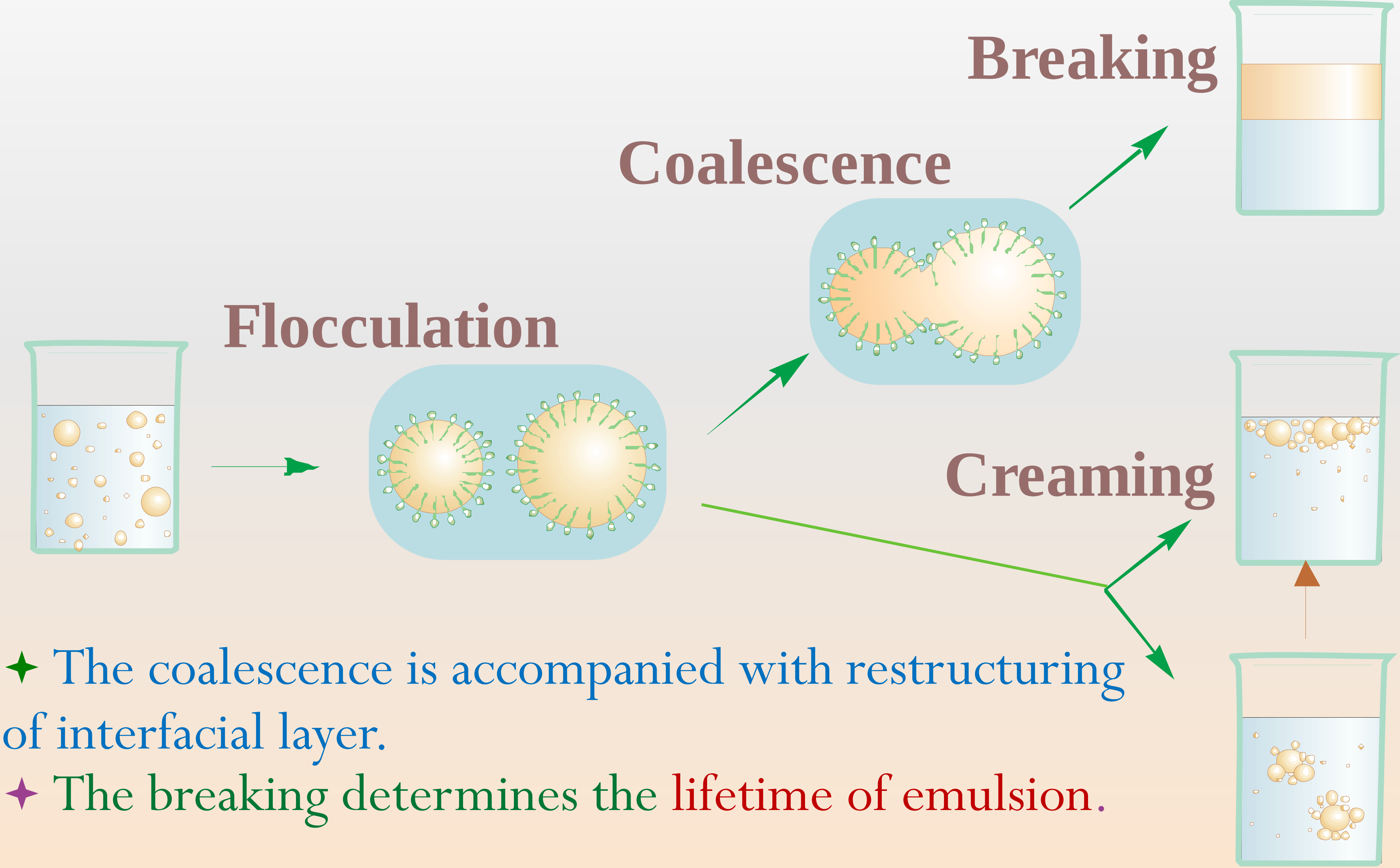
- The emulsions are thermodynamically unstable systems.
- After the preparation, various processes start immediately at nano- and microscopic levels that cause re-forming the two initial macroscopic phases.
- It is impossible to arrest these processes. They can be **only slowed down** via the forces of repulsion between droplets.
- This type of stability is called the **kinetic stability**.

Types of processes

- **Flocculation:** Droplets come in contact with each other, forming flocs or loose assemblies in which the identity of each is maintained. The process is reversible.
- **Coagulation:** This is like flocculation, but the mutual attachment of droplets is closer without the merging.
- **Creaming:** Macroscopic process of formation of apparently separated two continuous phases, one of which is enriched with flocculated droplets and another is depleted in them.
- **Coalescence:** Merging of two or more droplets, resulting in formation of a single drop of greater volume.
- **Breaking** of an emulsion: Macroscopic separation into two immiscible phases. This is a final stage of true loss in identity of individual drops as well as the physical and chemical properties of the emulsion.

The breaking of emulsion includes:

Flocculation → Coagulation → Coalescence.



✦ The coalescence is accompanied with restructuring of interfacial layer.

✦ The breaking determines the lifetime of emulsion.

Ostwald ripening

- It is typical of emulsion that large drops are grown at the expense of smaller ones with time.
- The phenomenon is caused by a difference in the Laplace pressure inside drops of radii r_1 and r_2. It determines also the differences in solubility (S) of dispersed phase in accordance with the Kelvin equation:

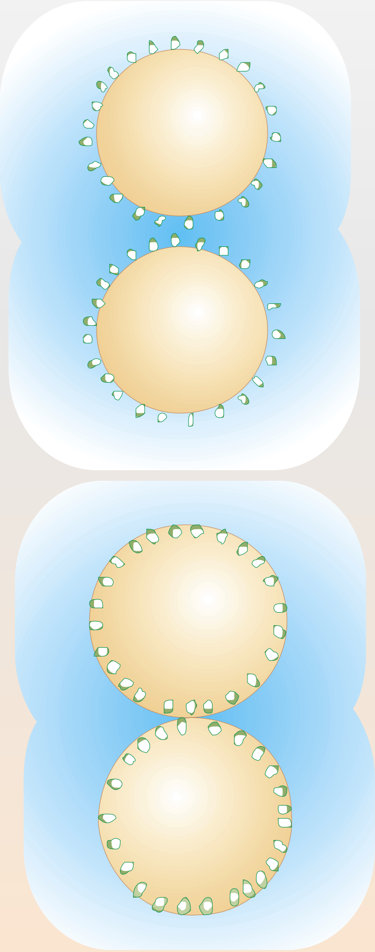
$$\ln(S_1 / S_2) = \frac{\gamma V}{RT}\left(\frac{1}{r_2} - \frac{1}{r_1}\right)$$

where V is the molar volume of dispersed phase.

- Because the solvent exchange proceeds through continuous phase, the solubility in this phase is primary important.
- It can be also mediated by micelles that can accelerate the ripening processes.

Stabilization of emulsions

Three main methods are used.



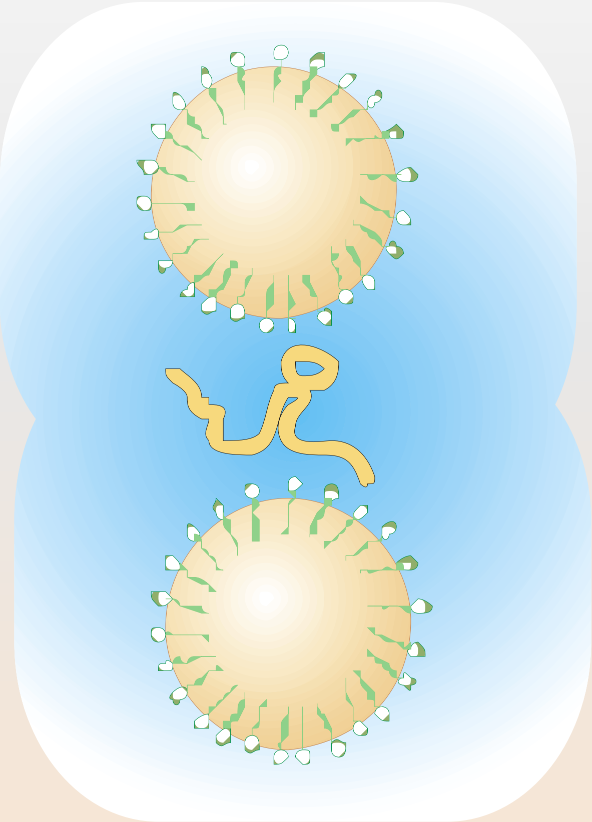
Method 1. **Finely dispersed powders.**

- Stabilization occurs only in a case of a powder that poorly wetted by the dispersed phase.
- Example: Hydrophobic powder occurs a stabilizing effect on a water-in-oil emulsion, but it does not, on a oil-in-water emulsion.
- Butter and margarine are an example of water-in-oil emulsion. Its stabilization is achieved by small crystals of fat adsorbed at their surface.

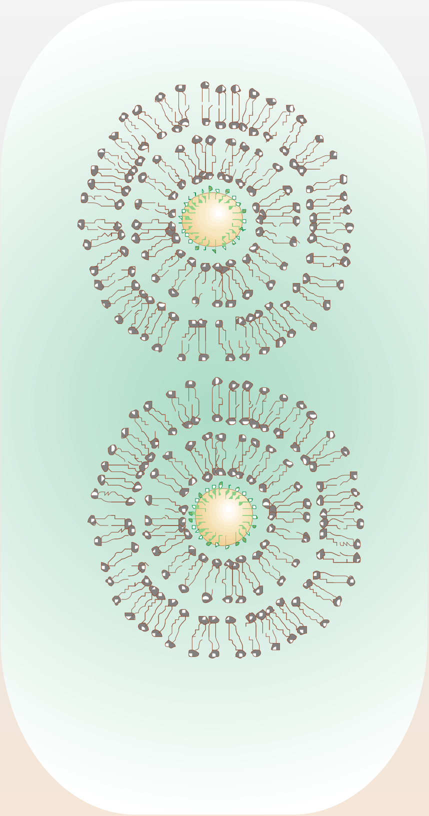
Method 2. **Polymers.**

The stabilization is achieved through a combination of:

- Steric hindrance;
- Electrostatic repulsion;
- Viscosity increase.



Method 3. **Multilamellar shell.**



Droplets are covered by a liquid crystalline shell of surfactant(s) that forms L_α mesophase.

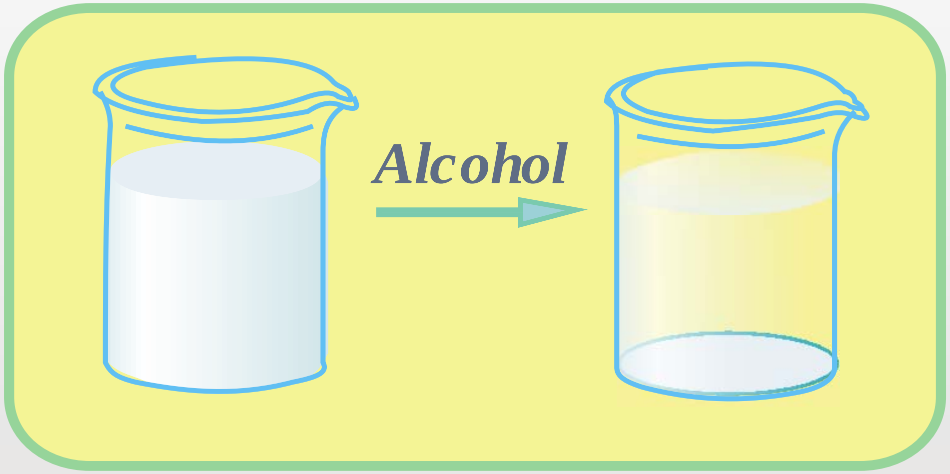
Advantages:

- ✦ Low interfacial tension that favors the dispersing;
- ✦ Highly stable shell providing steric hindrance to the flocculation.

Microemulsions

Introduction

J. H. Schulman's
experiments in the 1950s.



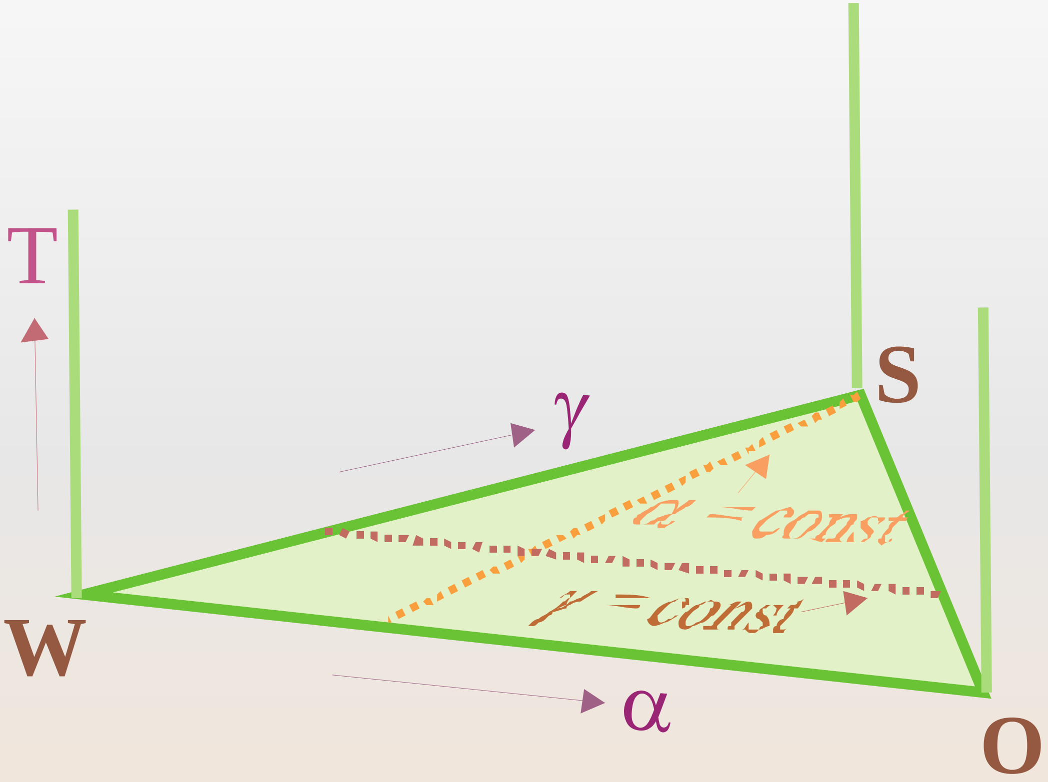
- He observed a conversion of turbid milky emulsions into optically transparent and highly stable mixtures after the addition of alcohols.
- Schulman called them as microemulsions.

Main features of microemulsions

- They are formed spontaneously, requiring little or no input of mechanical energy.
- The drop dimension is between 5 and 100 nm. Because they are much smaller than the wavelength of visible light, they do not significantly scatter light. Therefore, the microemulsions are normally transparent or slightly bluish or reddish.
- Microemulsions are thermodynamically stable, having essentially infinite lifetimes if there is no change in composition, temperature, and pressure.

Phase behavior

- The phase behavior in a water-oil-surfactant ternary system is quite complex. It depends on the contents and chemical nature of oil, water, electrolyte, surfactant and sometimes co-surfactant. The temperature and pressure are also influence on the phase state.
- These parameters determine the hydrophile-lypophile balance in the system that is of importance for the phase behavior.
- Bancroft's rule is valid to describe the phase behavior.



W - water;

O – oil;

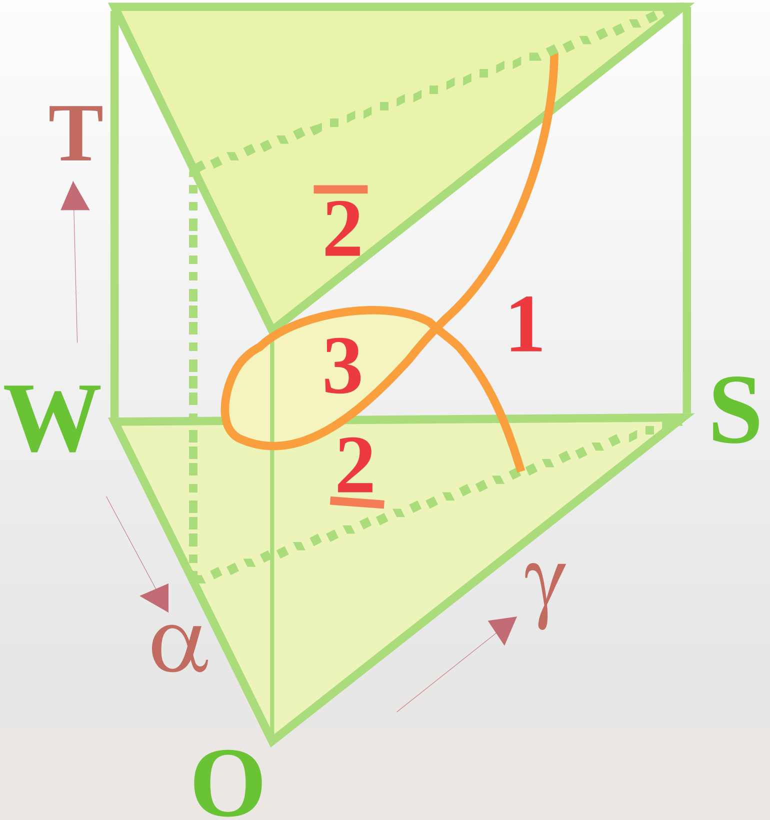
S – surfactant;

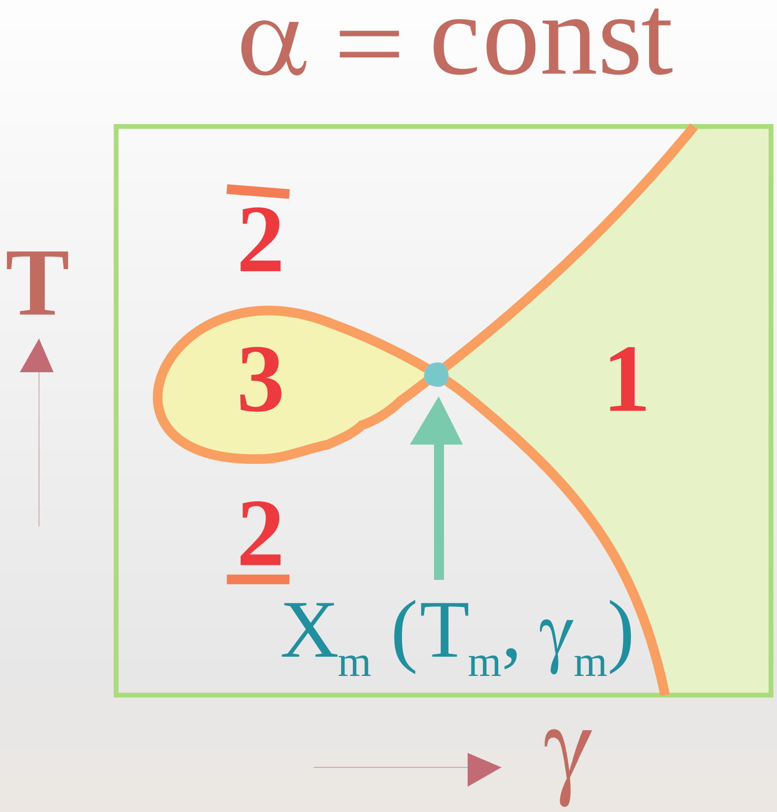
T – temperature;

$\alpha = O/(O+W)$, mass fraction of oil;

$\gamma = S/(S + O + W)$, mass fraction of surfactant.

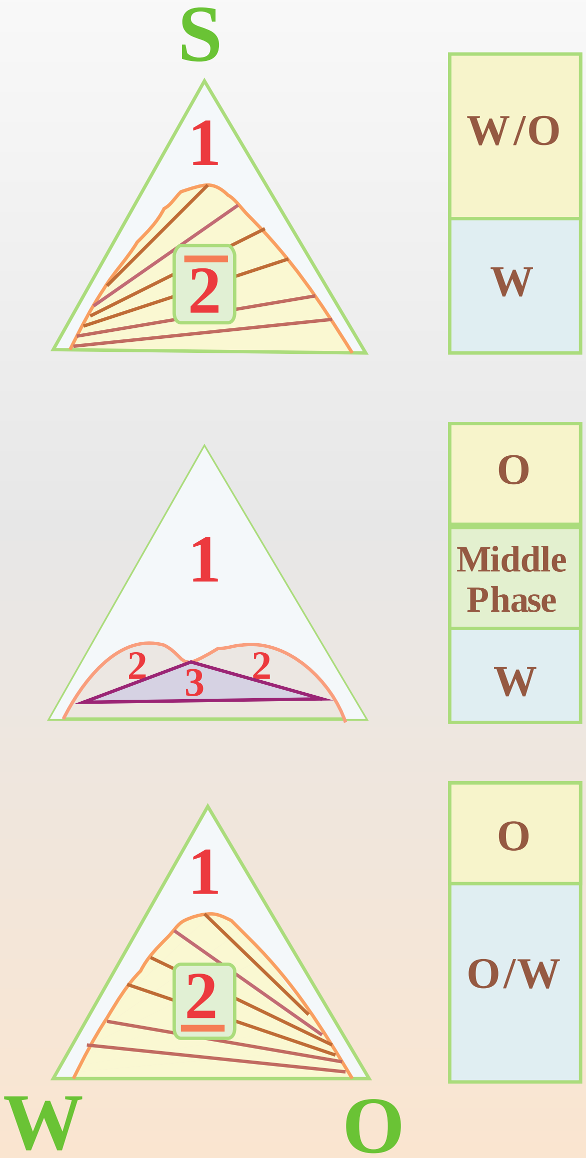
Each point in the phase prism is defined unambiguously by a certain set of ***α*, *γ and T*.**





The essential information about the phase behavior and microemulsion formation can be found from a vertical section of the prism at constant α variable surfactant concentration γ and **temperature**.

X_m is an important point that determines the mean temperature **T_m** of microemulsion formation and minimal surfactant concentration **γ_m** at which it takes place.



$T > T_m$

Winsor II

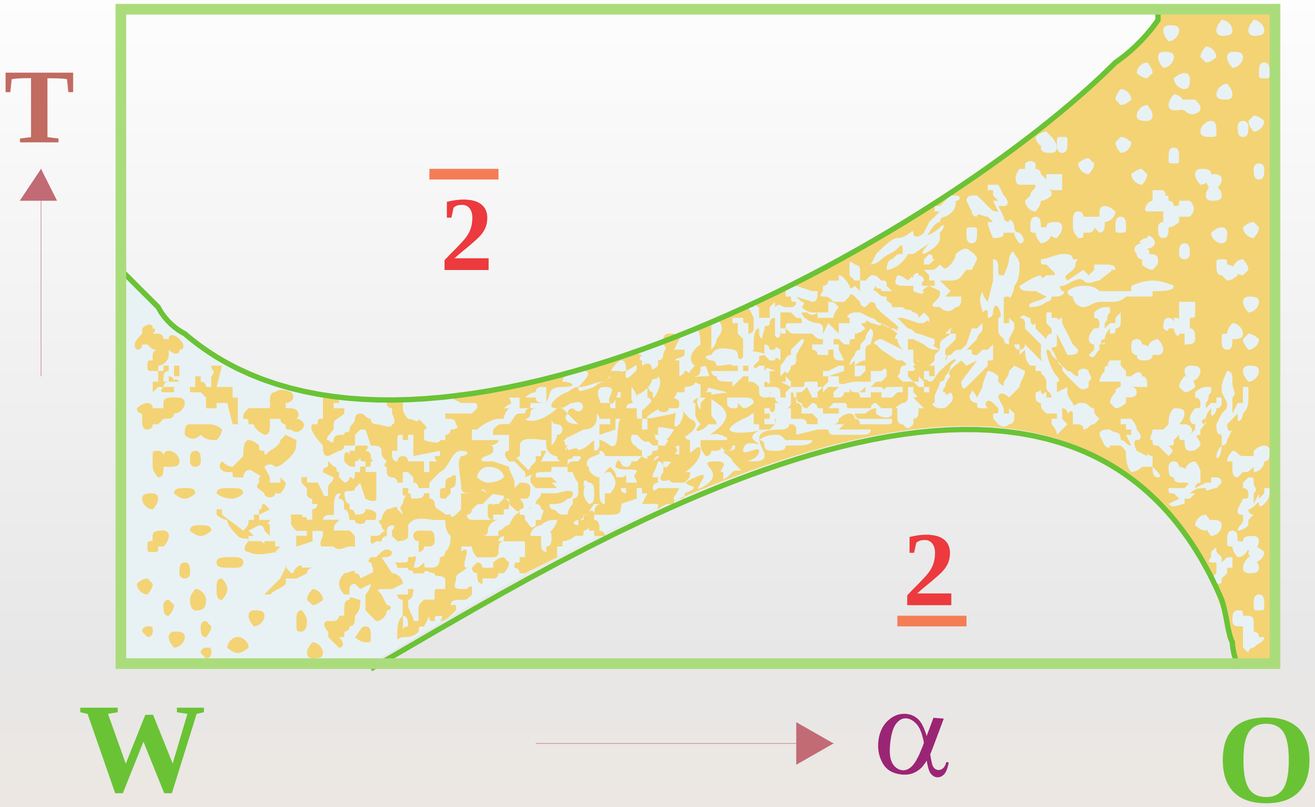
$T \sim T_m$

Winsor III

$T < T_m$

Winsor I

Isothermal cross-sections made at various temperatures in relation to the mean temperature.

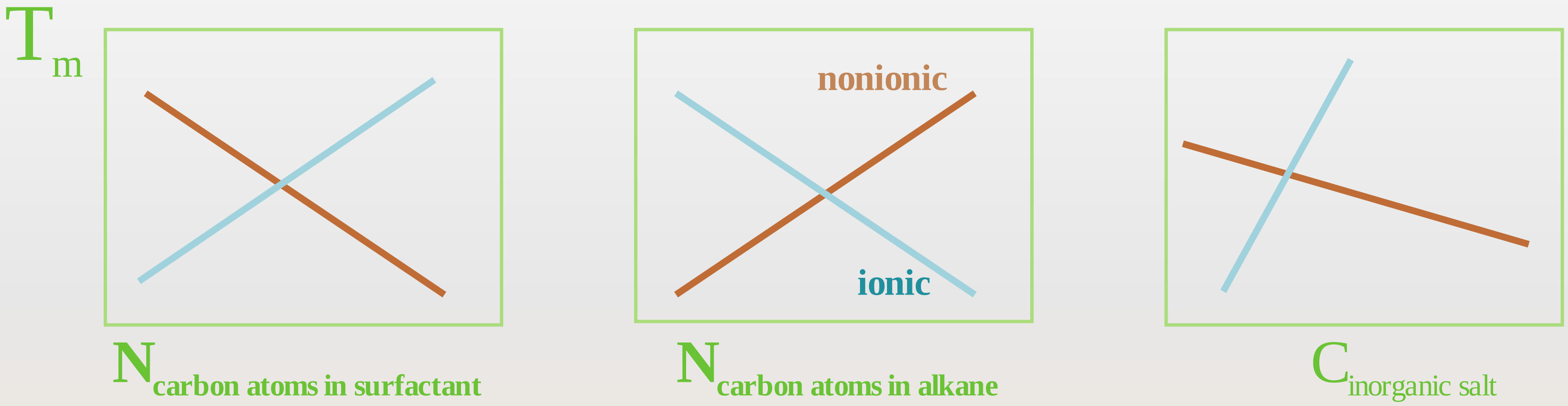


A cross-section of phase prism at constant amphiphile concentration. A single-phase region extends from the water-rich to the oil-rich side. Its structure is constantly changed. The upper two-phase region is Winsor II, the bottom, Winsor I.

Determination of conditions for microemulsion formation

- To determine the position and extension of the three-phase region within the phase prism, equal masses of water and oil can be taken. By adding various amounts of surfactant, it is necessary to examine the phase behavior with increasing the temperature.
- The following cases are possible:
  - A homogeneous mixture between the melting and boiling points at high surfactant concentration;
  - The phase sequence $\underline{2} \rightarrow 1 \rightarrow \overline{2}$ at somewhat smaller concentrations;
  - The phase sequence $\underline{2} \rightarrow 3 \rightarrow \overline{2}$ with further decreasing the concentration;
  - Two phases at all temperatures.

Main factors determining the microemulsion formation



Dependencies of mean temperature on the hydrophobicity of surfactant and oil phase as well as ionic strength of aqueous phase.

Surfactants

- Any surfactant can provide a microemulsion formation, but conditions sometimes are inconvenient.
- Nonionic surfactants with PEO residues forms microemulsions without a co-surfactant.
- Ionic surfactants require a co-surfactant (usually alcohols).
- Double-chained surfactants (e. g. didocecylammonium bromide) do not need co-surfactants.
- Useful surfactant is sodium di-(2-ethylhexyl)sulfosuccinate (AOT, Aerosol OT): It gives nanodrops of which dimension are determined by molar water-to-surfactant ratio w_o;

$$R = 1.75\, w_o + 15.$$

Interfacial tension

- A thermodynamically stable system can be formed if the free energy of the microemulsion phase is lower than that of the original mixture of oil and water.
- $\Delta G = \gamma_{o/w} A$ where A is the area of interface.
- A sharp increase of A is compensated by very low interfacial tension.
- The lowest value measured for ionic surfactants was around 10^{-5} mN/m, for nonionic, 10^{-4} mN/m.
- As usual, the γ is between 10^{-4} and 10^{-2} m/Nm.

Microemulsion and (macro)emulsion

- There are strong differences between them.
- Microemulsions are thermodynamically stable; they can be prepared by any order of mixing of ingredients.
- Macroemulsion droplets have minimum diameters of 100–200 nm, while microemulsions, 5-100 nm.
- This determines differences in their optical transparency.

Microemulsion and micelles

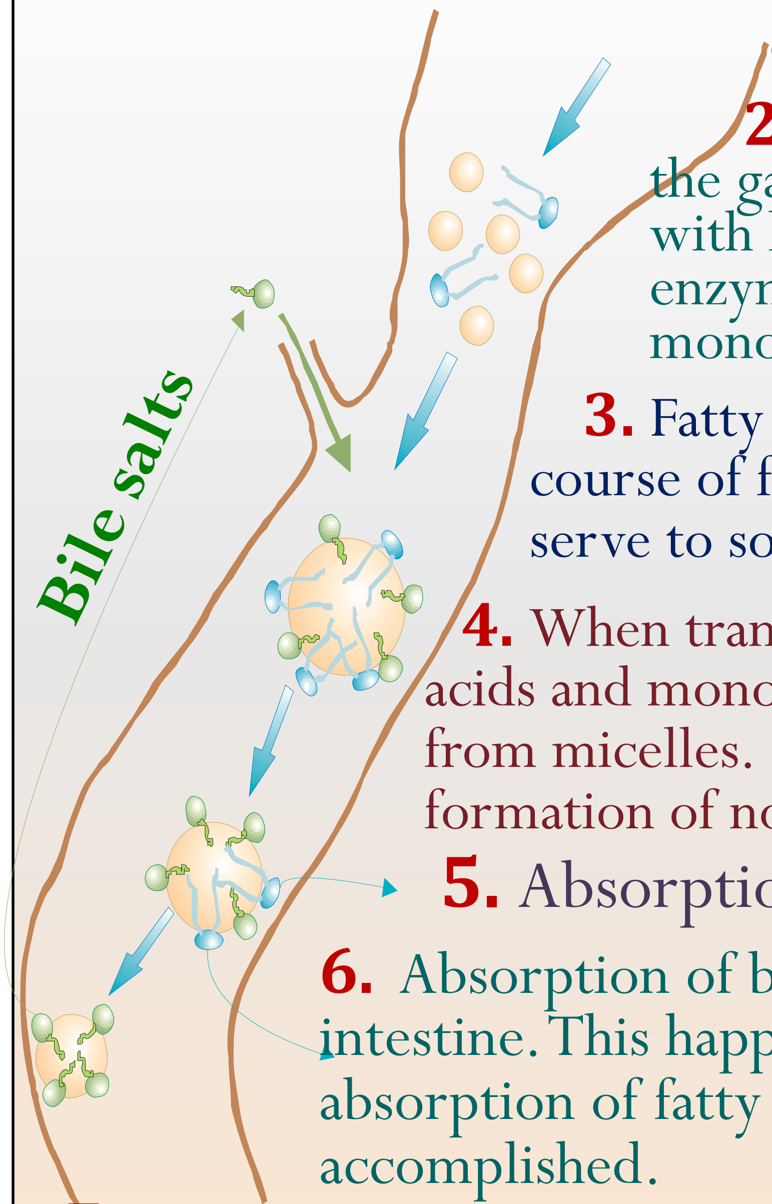
- Microemulsions are considered sometimes as systems of swollen micelles.
- This is based on their structural similarities.
- However, it is necessary to distinguish them from each other.
- Micelles are formed under many circumstances, whereas the microemulsion preparation is very sensitive to the composition of the system and the chemical structures of the various components.
- There is high distinction in the solubilizing capacity. The ratio of solubilized molecules to surfactant molecules in micelles does not usually exceeds 2, while it can reach 100 in microemulsions.
- The solubilized substances form a core in microemulsion, while it is absent in the micelles.

Applications

The will be considered in the next lecture.

Digestive track and fatty nutrient

- The digesting of food is the nice example of highly effective processes in living organisms that are based on colloidal transformations including emulsion, microemulsion and micelles.
- Lets consider the digestion of fats that consist mainly of triglycerides.
- The fats are an important source of energy providing ca. 9 cal/g, whereas the proteins and carbohydrates, about 6 cal/g.
- The fat digestion includes 7 stages.



1. **Stomach:** Cutting of food pieces; they enter into the upper small intestine.

2. Fats stimulate the secretion of bile salts from the gallbladder and pancreatic enzymes. The bile salts with lectihin and cholesterol emulsify fats. While the enzymes hydrolyze them to produce fatty acids and 2-monoglycerides.

3. Fatty acids and monoglycerides generated in the course of fat hydrolysis form micelles with bile salts that serve to solubilize them.

4. When transported through the small intestine, the fatty acids and monoglycerides are absorbed by the intestinal wall from micelles. The released bile salts are involved in the formation of novel micelles with newly generated fatty acids.

5. Absorption of lecithin and cholestrol.

6. Absorption of bile acids at the last section of the small intestine. This happens when the hydrolysis of fats and absorption of fatty acids with monoglycerides have been accomplished.

7. The bile salts are carried by the bloodstream into the liver where they are separated and returned into the gallbladder.

The digestion of fats in the living organisms is the example of highly efficient ”chemical technology” including the colloidal transformations that was developed by Nature.

- The pool of bile acids in the living body is about 30 g.
- Ca. 3 g participate in a process.
- They are used in up to 10 times per day.
- Their loss can reach 0.5 g (ca. 15 %).