EMULSIONS

An emulsion is a mixture of two immiscible substances whereby one substance (the dispersed phase) is dispersed in the other (the continuous phase). Example – oil and water.

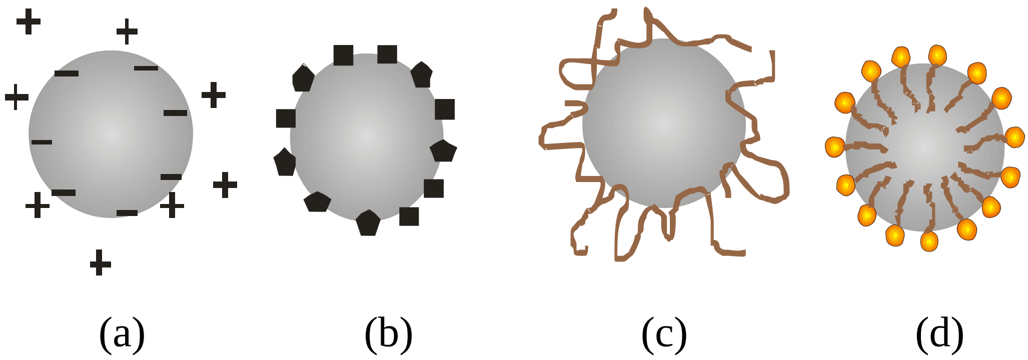
Emulsions normally have a cloudy appearance, because droplets are typically larger than a micron and the many phase interfaces scatter light that passes through the emulsion.

Characteristic of Emulsions:

- They are unstable
- Do not form spontaneously
- Requires energy input through shaking, stirring, homogenizers.
- Thermodynamically unstable.
- Revert to the stable state of phase separation into oil and water.

Addition of surface active substances improves its kinetic stability of so that, once formed, the emulsion does not change significantly over storage.

Classification of emulsifiers and stabilizers



(a) Presence of adsorbed ions or non surface active salts.
- ⇒ Has little effect on interfacial tension.
- ⇒ Provide electrostatic barrier between incoming drops.
- ⇒ Do little to facilitate emulsification.

(b) Colloidal sols.
- ⇒ Has little effect on interfacial tension.
- ⇒ Provide electrostatic barrier between incoming drops, thus prevention drop coalescence.
- ⇒ Do little to facilitate emulsification.

⇒ Depends on the size of particles and interfacial interactions between solid surface and the two liquids.

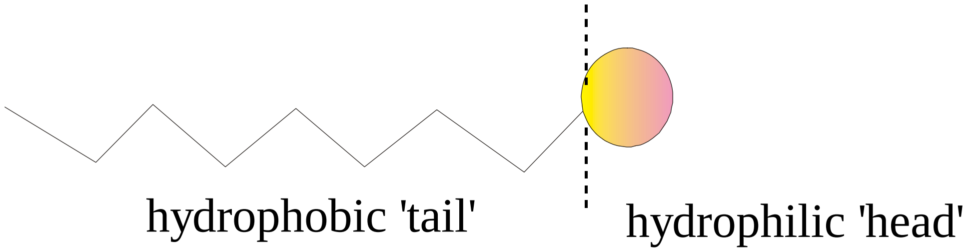
(c) Polymer molecules
- ⇒ Surface active properties.
- ⇒ Acts as stabilizers
- ⇒ Action by steric and/or electrostatic interactions.

(d) Surfactants
- ⇒ Decrease interfacial tension.
- ⇒ Impart stability.

Emulsifiers

Often refer to biologically surface-active components like proteins, mono- and diglycerides, fatty acids and phospholipids The purpose is to prevent the emulsion droplets from fusing together by creating repulsive droplet-droplet interactions at the droplet surface.

- stabilize *o /w* or *w/o* emulsions by absorbing at the interface by lowering the interfacial tension energy.
- to ensure extensive mixing of oil and water.



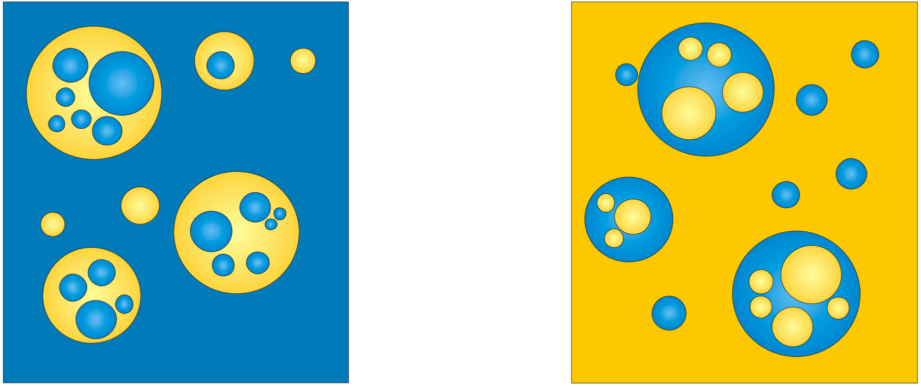
Example: monoglycerides, sorbitan monostearate, polysorbate 60.

Classical diagram of emulsion types

a) oil-in- water emulsion

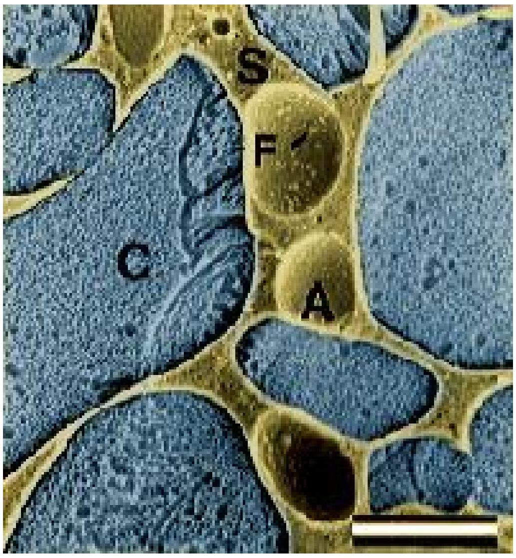
b) water-in-oil emulsion

(c) Multiple emulsions



(i) Water-in-oil-in-water emulsion (ii) Oil-in-water-in-oil emulsion

Example:



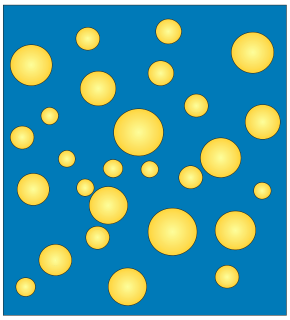
cryo-SEM, shows a cross section of frozen ice cream, illustrating the four microscopic phases of frozen ice cream: ice crystals (blue - 'C'), air bubbles ('A'), fat droplets ('F' - for details see the micrograph at right), and the unfrozen phase ('S' - yellow)

Typical ingredients:
Milkfat: >10% - 16%
Milk solids-not-fat (snf): 9% - 12%
Sucrose: 10% - 14%
Corn syrup solids: 4% - 5%
Stabilizers: 0% - 0.4%
Emulsifiers: 0% - 0.25%
Water: 55% - 64%

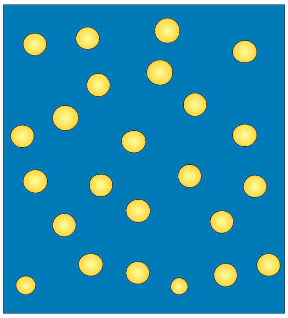
Milk proteins

Milk proteins can function as secondary emulsifiers. The protein molecules interface with either oil and water, or oil and air to reduce interfacial tension. One advantage of using milk proteins for their emulsifying properties is potential labeling claims. For example, milk proteins can replace eggs and the emulsification of lecithin in cholesterol-free spoonable and pourable salad dressings. They can also fully or partially replace eggs in cakes, bread and aerated desserts. Another advantage of milk proteins is their multifunctionality. In addition to emulsification, they can provide viscosity, water binding capability, adhesion or gelling.

Polydispersity of Emulsion



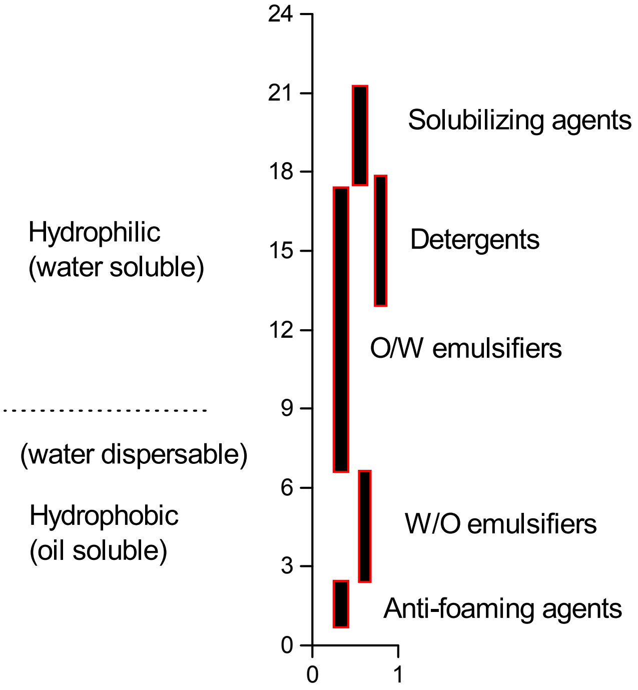
(a) Polydisperse emulsion



(b) Monodispersed emulsion

Hydrophile-Lipophile Balance (HLB)

A means of selecting the most effective non-ionic surfactant stabilizer for a given oil. Only as a reasonable approach to the choice of single or mixed emulsifiers. To calculate the HLB of surfactants and matches the HLB of the surfactant mixture, in the case of O/W systems, to that of the oil being emulsified. The HLB number of surfactant is calculated according to certain empirical formulae and for non-ionic surfactants the values range from 0 to 200 on an arbitrary scale.



The HLB number of non-ionic surfactant of the polyoxyethylene class:

$$HLB = \frac{(mol\%hydrophilicgroup)}{5}$$

e.g. polyethylene glycol HLB = 20.

The HLB of polyhydric alcohol fatty acid esters such as glycerol monostearate:

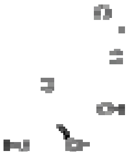
$$HLB = 20\left(1 - \frac{S}{A}\right)$$

Where, S = saponification number of the ester and
A = the acid number of the acid.

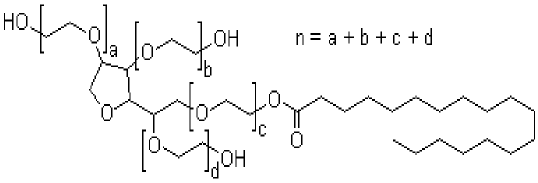
e.g., polysorbate (Tweens) HLB valuse ranges 9.6 to 16.7.

Sorbitan esters (Spans) HLB is 1.8 to 8.6.

The HLB of polysorbate 20 is 16.7, *S* being 45.5 and *A*, 276.

Sorbitan monostearate 	
IUPAC name	Octadecanoic acid [2-[(2*R*,3*S*,4*R*)-3,4-dihydroxy-2-tetrahydrofuranyl]-2-hydroxyethyl] ester
Other names	Span 60 food additive (emulsifier) (E number: E 491

Tween 60



Polyethylene glycol sorbitan monostearate; Polyoxyethylene sorbitan monostearate
$C_{24}H_{46}O_6\cdot(C_2H_4O)_n$

For those materials for which it is not possible to obtain saponification numbers, e.g. beeswax and lanolin derivatives, the HLB is calculated from:

$$HLB = (E + P)/5$$

E is the percentage by weight of oxyethylene chains,

P is the percentage by weight of polyhydric alcohol group (glycerol or sorbitol) in the molecule.

The HLB system has been put on a more qualitative basis by Davies and Rideal who calculated group contributions to the HLB number such that the HLB was calculated from,

$$\text{HLB} = \Sigma\ (\text{hydrophilic group number} - \Sigma(\text{lipophilic group number}) + 7.$$

Table: Hydrophilic and lipophilic group number.

Hydrophilic groups	Group number	Lipophilic groups	Group number	Derived groups	Group number
$—SO_4Na^+$	+38.7	—CH—	-0.475	$—(OCH_2CH_2)—$	+0.33
$—COOK^+$	+21.1	$—CH_2—$	-0.475	$—(OCH_2CH_2CH_2)—$	-0.15
$—COONa^+$	+19.1	$—CH_3$	-0.475		
$—SO_3Na^+$	+11.0	=CH—	-0.475		
N(tertiary amine)	+9.4	$—CF_2—$	-0.870		
Ester (sorbitan ring)	+6.8	$—CF_3$	-0.870		
Ester (free)	+2.4				
—COOH	+2.1				
—OH (free)	+1.9				
—O— (ether group)	+1.3				
—OH (sorbitan ring)	+0.5				

The HLB of a mixture of surfactants containing fraction *f* of *A* and (1-*f*) of B is an algebraic mean of the two HLB numbers.

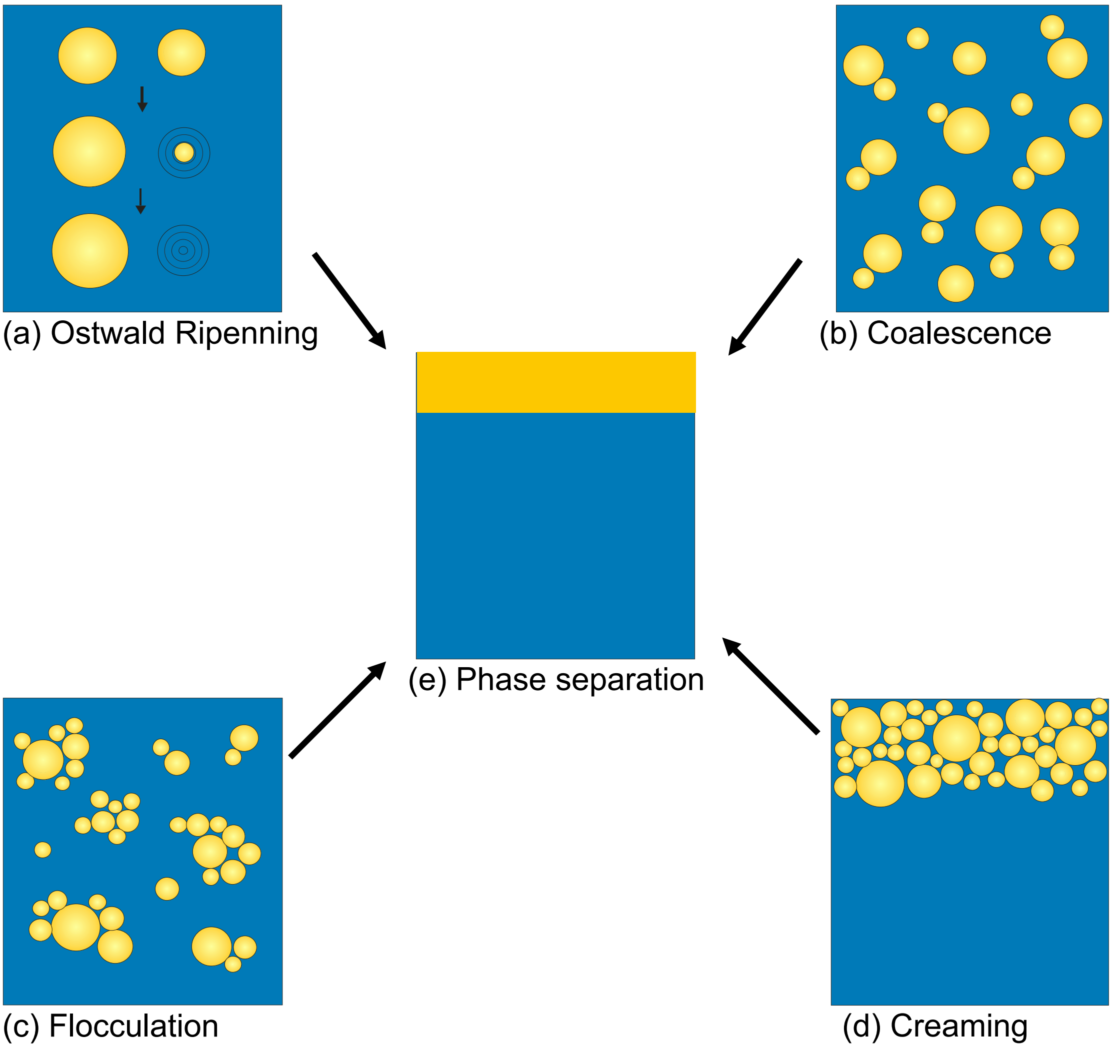
$$\text{HLB}_{\text{mixture}} = f\text{HLB}_A + (1-f)\text{HLB}_B.$$

Mixture of surfactants give more stable emulsion than single surfactant.

Can produce a stable O/W emulsion when we have an optimal HLB values. it is also possible to formulate stable systems with mixture of surfactants well below the optimum by means of forming a viscous network in the continuous phase. The viscosity of the medium surrounding the droplets prevents their collision and this overrides the influence of the interfacial layer and barrier forces due to the presence of absorbed layer.

E,g. A stable liquid paraffin-in-water emulsions with surfactant combinations having HLB as low as 3.9. The stable emulsions were thixotropic, indicating that the surfactant were contributing to the structural viscosity of the system and thereby contributing to stability by preventing creaming.
A stable liquid paraffin emulsions with cetyl alcohol-cetyl polyoxyethylene ether combinations having HLB as low as 1.9; this stability undoubtedly arises from the viscous nature of both interface and bulk phases. Confirmed by rheologycal measurement.

Emulsion destabilization



The four mechanisms which can be identified in the process of breaking down an emulsion are Ostwald ripening, creaming, aggregation, and coalescence.. The process of breakdown of an emulsion can be influenced in two ways:

- the use of mechanical devices to control the size of droplets
- the addition of stabilizing chemical additives (emulsifiers).

Ostwald ripening

It is a phenomenon describing the evolution of inhomogenous droplets over time. One droplets becomes larger at the expense of another droplet. One explanation is related to the diffusion of monomer from smaller to larger droplets due to the greater solubility of the single monomer molecules in the larger monomer droplets. The rate of this diffusion process is linked to the solubility of the monomer in the continuous (water) phase of the emulsion.

Coalescence

The action of droplets coming together that leads to **flocculation** of the emulsion droplets.

creaming

The migration of one of the substances to the top of the emulsion under the influence of buoyancy or centripetal force when a centrifuge is used. Creaming is a criterion of instability in commercial formulations.

It is imperative, to recognise the stability towards creaming is dependent on the rheological character of the emulsion far more than on the interfacial characteristics of the interfacial film.
The influence of surfactants on the viscosity of the continuous phase is therefore of primary importance on the emulsion stability.

Coalescence and Emulsion Stability

Emulsions are inherently unstable.

What is the driving force of coalescence?

Expect reduction in Gibbs free energy (ΔG) that can be achieved by reduction in the size of the O/W interface and decrease in entropy.

$$\Delta G = \gamma.\Delta A - T.\Delta S$$

Where, *A* is the area of the O/W interface and γ is the interfacial tension.

Droplet coalescence is irreversible and is a first-order process.

The rate-determining steps could be,

- the drainage of the continuous liquid film between two approaching droplets
- film collapse from mechanical distortion when equilibrium thickness has been reached

At surfactant concentrations > CMC the rate of film drainage, the Reynolds equation for liquid flow between rigid discs, thinning rate,

$$-\frac{dD}{dt} = \frac{2FD^3}{3\pi\eta R_c^4}$$

Where *F* is the net interdroplet attraction force,

η is the viscosity of the continuous phase,

R_c is the radius of the discs.

Processes that enhance stability against coalescence are:

1) The Gibbs-Marangoni effect

Replenishment of interfacial surfactant from high surfaces access to low concentration area, where a surfactant concentration gradient already exists. This leads to osmotic retention of liquid from the continuous phase.

2) Viscoelastic properties

Viscoelastic behaviour of the adsorbed emulsifier film resists mechanical ‘rupture’.

3) Born hydration repulsion.

This becomes effective when emulsifier head groups surrounded by a solvation layer approach each other to distances ≤ than the thickness of the layer (~3 nm). The solvation layer has to be dispersed to allow closer contact, which is counteracted by the hydration energy. Though of considerable magnitude, this repulsion is not capable of avoiding long-distance interactions like flocculatio*n*.

4) Steric repulsion.

When the size and geometric extension of molecules in the adsorbed film prevent droplets from approaching each other.

5) Electrostatic repulsion

According to the DLVO theory, which describes the balance between attractive (Van-der-Waals-) and repulsive (electrostatic) forces, droplet approach and *flocculation* can be diminished.

Coalescence is accompanied by *flocculation* and sometimes also *creaming*. The first describes the adhesion of dispersed droplets, which yet remain single bodies. The latter describes the movement of the less dense phase to the upper region of the container. In both cases the droplet number and their size distribution remain unchanged, and although distribution of the droplets becomes inhomogeneous, this can often readily be reversed by gentle agitation.

Interfacial multilayers of surfactant may enhance flocculation, but allow easy redispersion since multilayers are sensitive to shear force at the same time enhances mechanical stabilisation against coalescence during droplet collision.

On the other hand, may also facilitate the formation of larger aggregates which in turn promotes creaming hence, also facilitate coalescence. This is true for polydisperse systems where different creaming rates produce enhanced droplet encounter rates.

Zeta potential

Increase Zeta potential gives rise to enhanced stability against various stress factors as predicted by DLVO-theory

Sometimes coalescence was enhanced or flocculation increased after addition of electrolytes or charged lipids.

MICROEMULSIONS

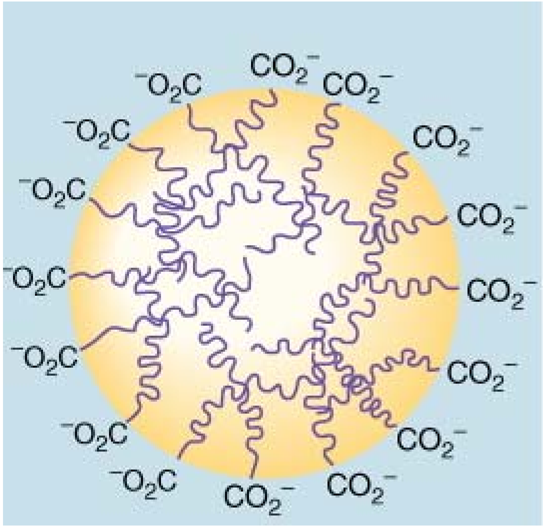
A self-assembly system when two immiscible liquid spontaneously form small droplets in the presence of surface active agent.
Microemulsions – self assembly system form spontaneously.

Surfactants ‘monolayer’ in water-oil interface stabilize the emulsions.
Simple way to make microemulsions :

1) Dissolve surfactant in oil
2) Add some desired volume of water
3) Shake to give microemulsion

Compare in emulsion system , the size distribution of the emulsions depends on how vigorously the solution is shaken.

Microemulsions



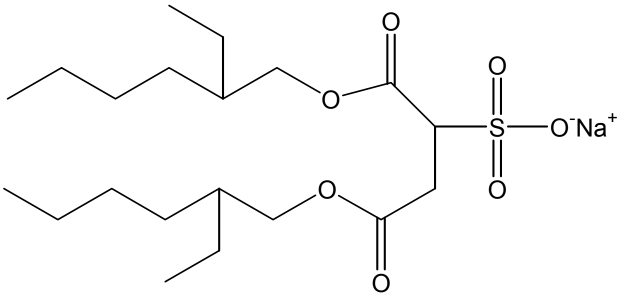
Example: oil-in-water microemulsion.

Characteristics of microemulsion:

1. size ~ 1 – 50 nm
2. Optically transparents, i.e optical size << λ of light, c.f. visible region is 0.1 – 1.0 μ.
3. Spherical and monodispersed e.g: emulsion produced by Na^+ AOT (bis-ethyl hexyl sulfosuccinate sodium salt)

4. thermodynamically stable.
5. form spontaneously, has low interfacial tension, ΔG is +ve and very small.
6. Typically stable over 50° C temperature range.
   Possible phenomena >50° C, the emulsion system
   maybe crossing the phase boundary.
7. kinetically unstable e.g. in micelles and vesicles
   $\text{monomer} + (\text{monomers})_n \leftrightarrow (\text{monomers})_{n+1}$.
8. Can obtain different morphologies, rods, worms and disks – which are also precursors to liquid crystals.
9. Both water-in-oil and oil-in-water systems.

Example:



Aerosol OT:

Bis-ethylhexyl sulphosuccinate sodium salt

Structurally a “WEDGE SHAPE”. Favours negative curvature. Chain branching helps packing into a curvature shape. An ideal packing shape for water in oil, reversed micelle.

Producing microemulsion

Microemulsion can be prepared based on the following equation,

$$w_o = C.\frac{[H_2O]}{[Surf]}$$

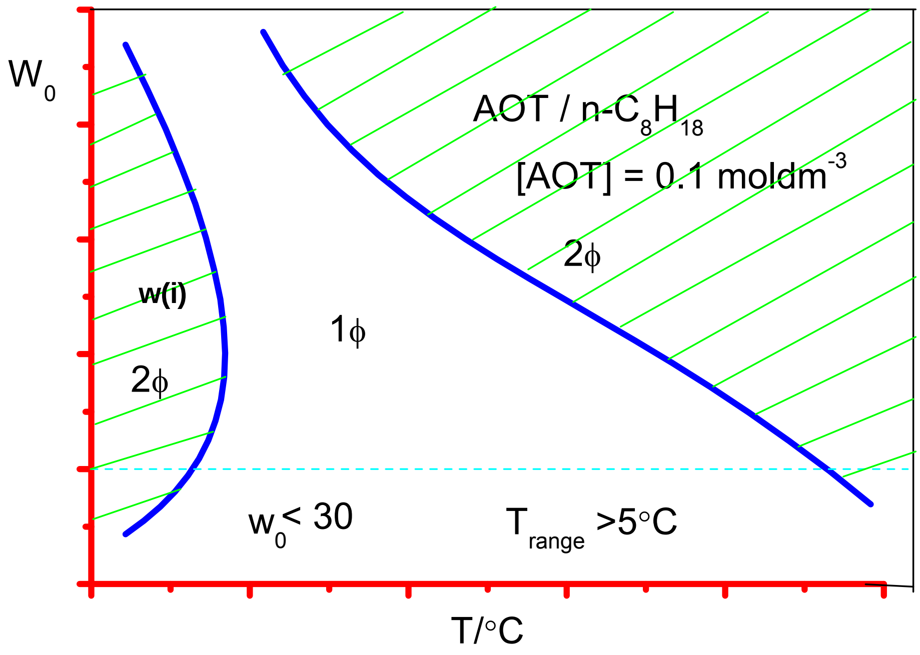
Where, w_o is the arbitrary unit value, sometimes is known as Ro-value

C is a constant related to the partial volume of the surfactant and water.

$[H_2O]$ is the water concentration.
[Surf] is the surfactant concentration.

The R_o-value id directly related to the size of microemulsion which is also dependent on temperature of the medium. By plotting different Ro with respect to temperature, a stability diagram is obtained.

Stability Diagram / Phase Diagram

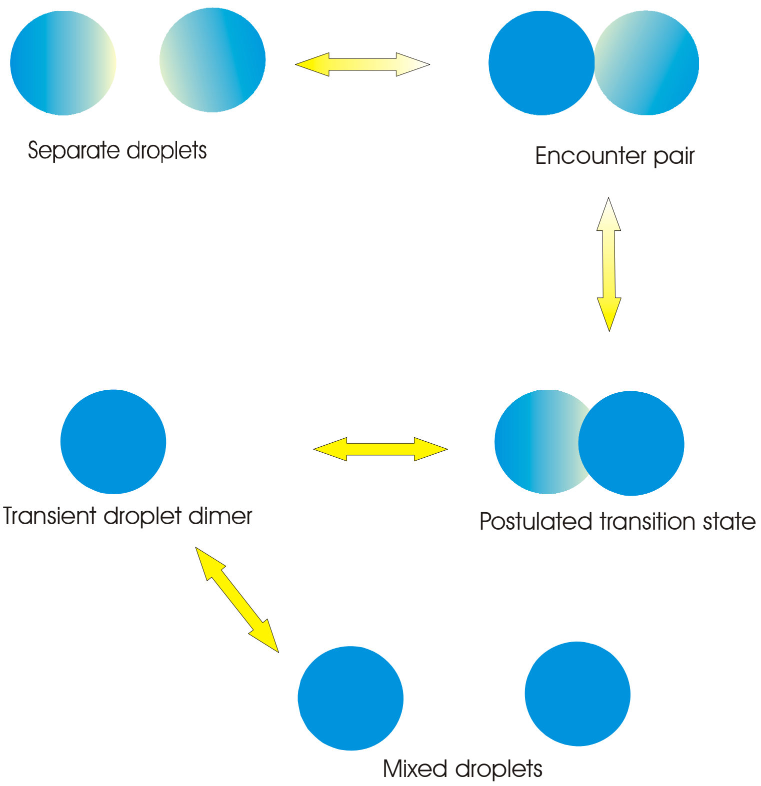


Group Partial molar Volume of water at 65°C

Group	Volume, Å^3
CH_3	54.3
CH_2	26.9
CH	20.6
C_6H_4	102.8
SO_3^-	61
H_2O	29.9
D_2O	30.2
Na^+	-11

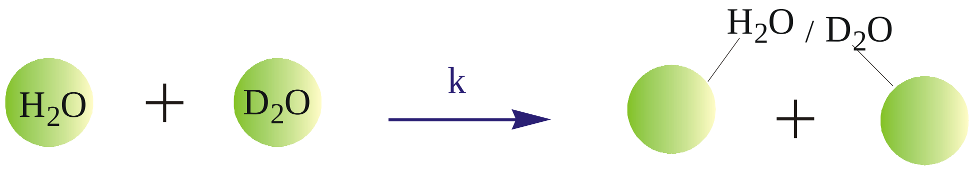
$$R_o = \frac{3\overline{V}_{H_2O}}{\overline{A}_{Surf}} \cdot \frac{[H_2O]}{[Surf]}$$

Reaction In Microemulsion



1.Process is reversible. Unlike in emulsion system i.e irreversible.

2.” Dumb bell shape” is very unlikely a collision process, however, *k*-rate of diffusion controlled process.



3.

$k = 10^6\, dm^3 mol^{-1} s^{-1}$ (one in 10^4 collision effective)

USES of MICROEMULSION

1. Effective dispersing mechanism for some food flavouring in the food industry and cosmetic /pharmaceutical.

2. Controlled synthesis of ;

a) Polymer – reaction and size determined by the size of microemulsion.

b) Nanoparticles e.g CdS, $CaCO_3$

$Ca(NO_3)_2 + Na_2SO_4 \rightarrow CaSO_{4\,(s)}$

$BaCl_2 + Na_2SO_4 \rightarrow BaSO_{4(s)}$

Surfactant : AOT or $C1_2E_4$ or NH_4DEHP

Oil : cyclohexane , n- alkanes.

Nanospheres (8-10 nm) – nanowires (10-100 μm) depending on ω_o-value.

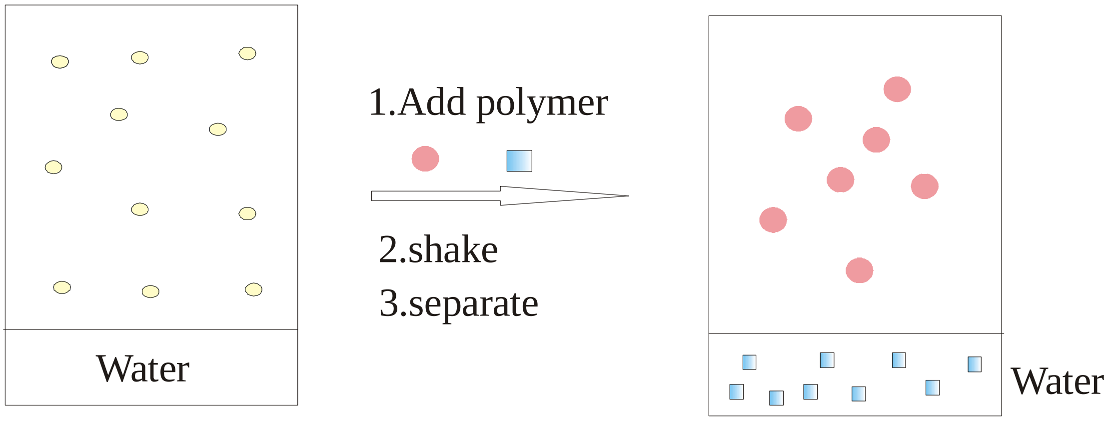
3. Enzyme mediated chemical synthesis.

Get enzyme reversal process i.e condensation favoured over hydrolysis.

$$R-CO-OH+R'OH \xrightarrow{peptidase\,/\,lipase} R-CO-OR'+H_2O$$

$$R-CO-OH + R'NH_2 \xrightarrow{peptidase} R-CO-NH-R' + H_2O$$

4. Liquid membranes for selective separations (L_2 phase)



Ability for droplet phase to take up polymer depends on charge on polymer and charge on surfactant. Opposite charge will get transfer.

5. Liquid-liquid selective separation of metals in one processing. Most metals are negatively charge –form cluster.
Extraction of metals from aqueous to oil will largely depend on changes on the metals and surfactants.