



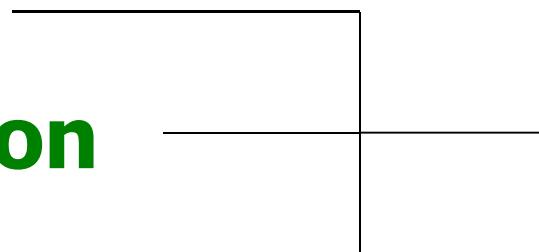
# Food Rheology

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# Mechanism reverting phenomena

- **Creaming**
- **Sedimentation**
- **Flocculation**
- **Phase inversion**
- **Coalescence**
- **Ostwald ripening**



**Reversible mechanism**

**Irreversible mechanism**

# Terminal velocity of droplet or particle

- **Stokes' law**

$$v_t = \frac{d^2 \cdot (\rho_2 - \rho_1) \cdot g}{18 \cdot \eta}$$

$v_t$  = terminal velocity

$\rho_1$  = density of fluid

$\rho_2$  = density of particle

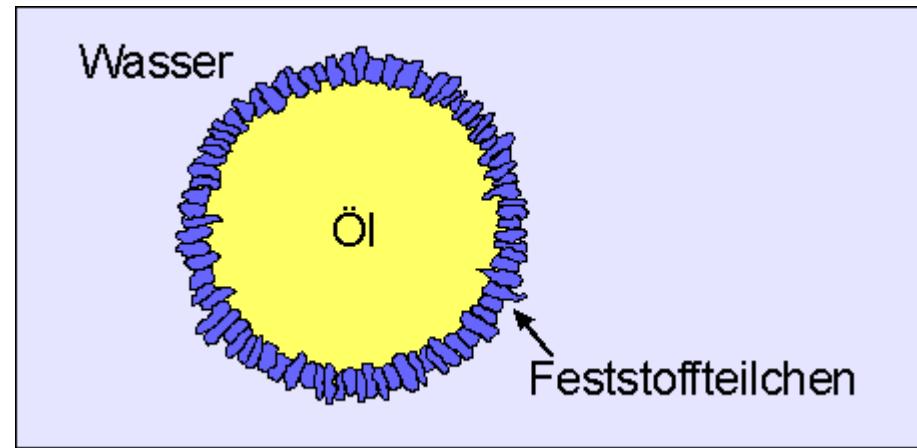
$\eta$  = viscosity of fluid

# Interaction between colloid particles

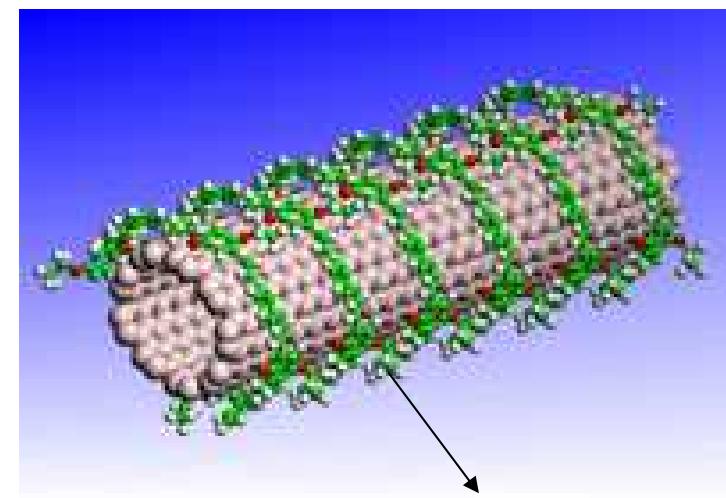
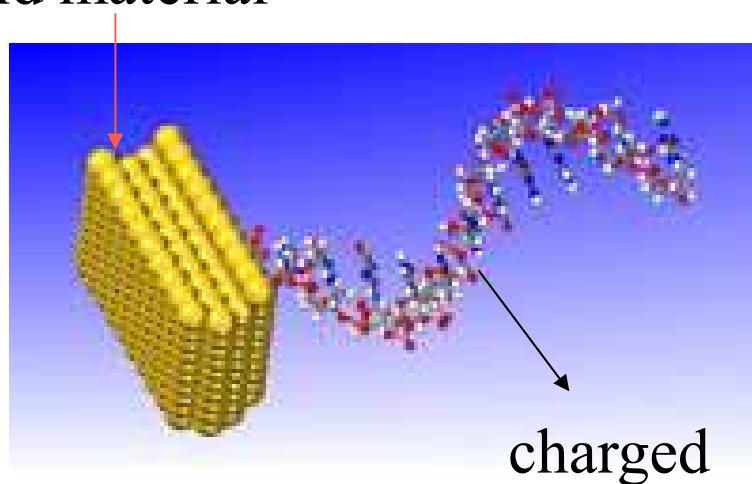
## Electrostatic interaction

Colloidal particles often carry an electrical charge and therefore attract or repel each other. The charge of both the continuous and the dispersed phase, as well as the mobility of the phases are factors affecting this interaction.

- difference of permittivity between dispersed phase and continuous phase
- ion adsorption on the surface of particle
- ionization of particle

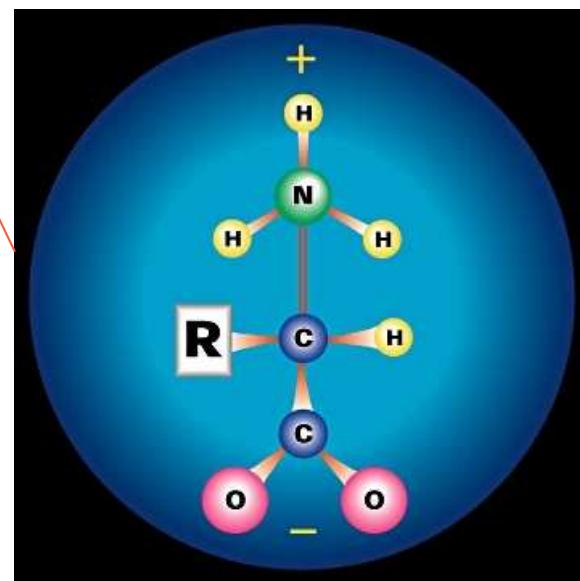
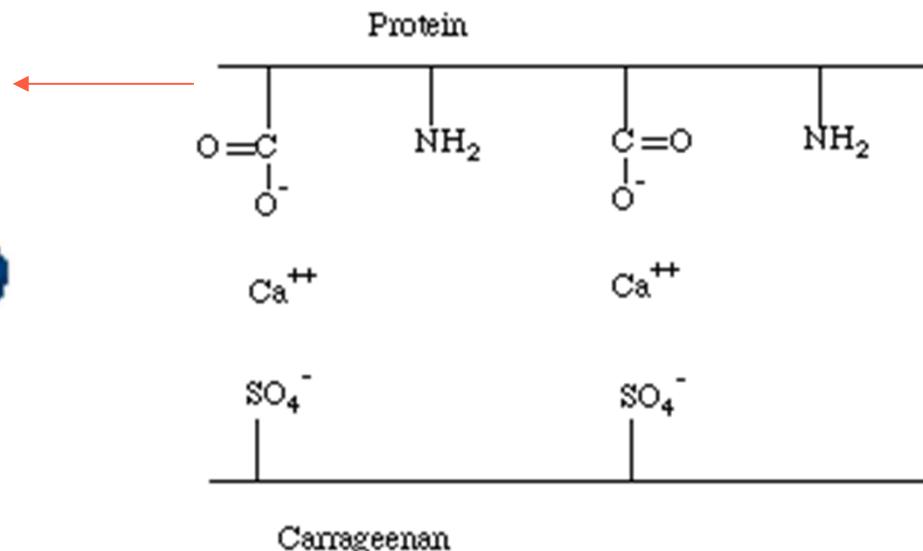
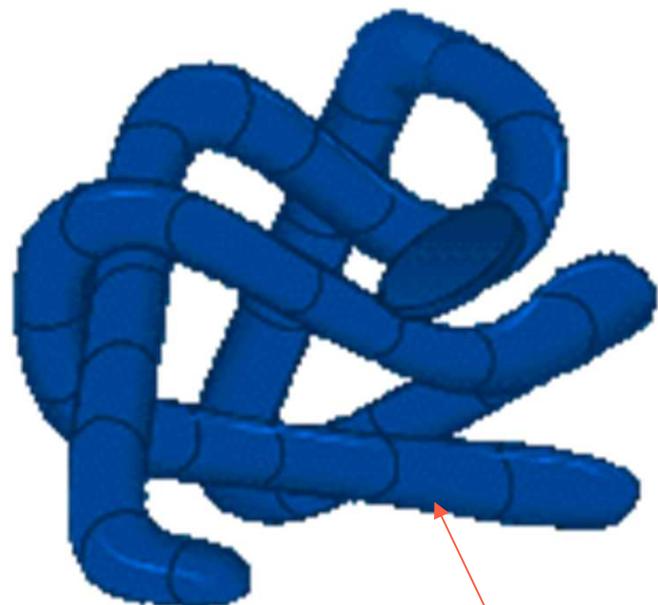


Solid material



charged

# Protein



# Amino acid

# Emulsion breaking theory

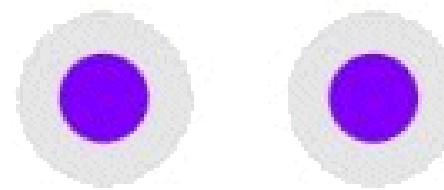
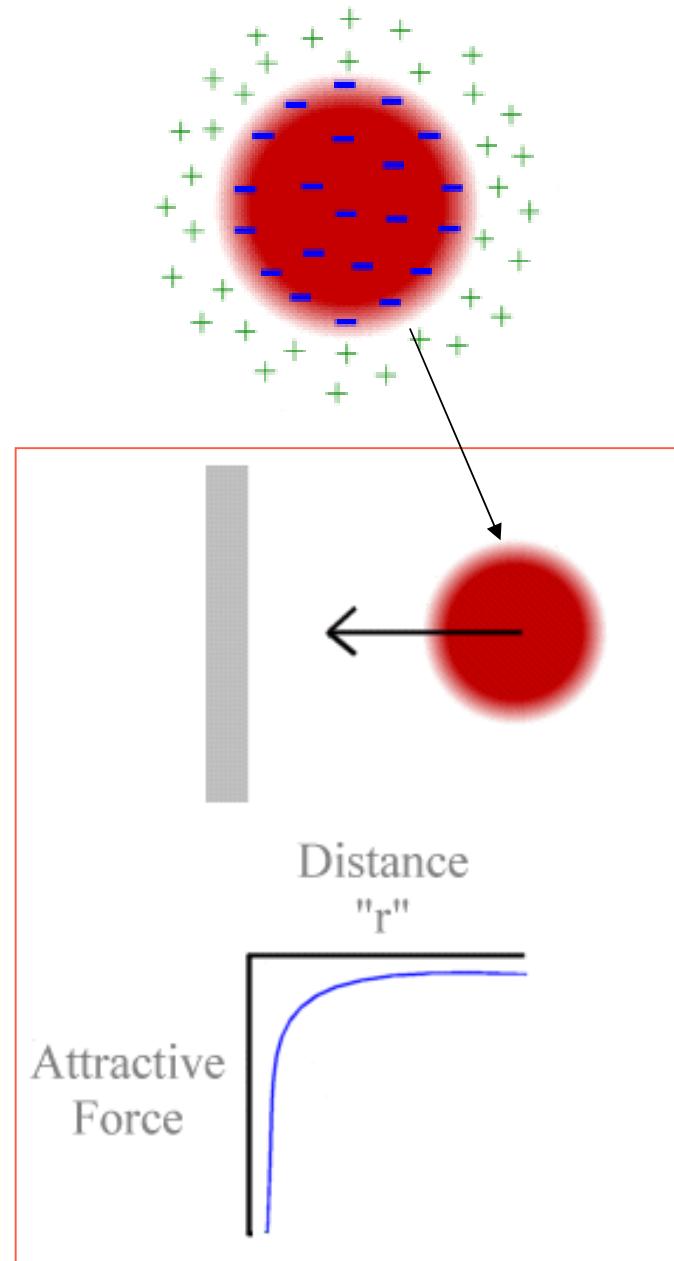
DLVO Theory (Derjaquin, Landau, Verwey and Overbeek)

The DLVO theory in its simplest form looks at ***the two main forces acting on charged colloidal particles*** in a solution. The two forces are:

1. electrostatic repulsion
2. van der Waals attractive force

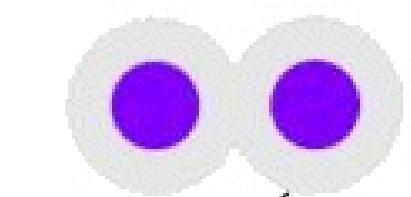
By adding these two opposite forces together it is possible to describe the overall force acting on a colloidal particle as it approaches another particle or a charged surface.

It is very important to realize that the overall shape of this resultant force depends on the ionic strength of the fluid because this affects the depth of the electric double layer and, therefore, the electrostatic repulsion.



### Physiological Ionic Strength

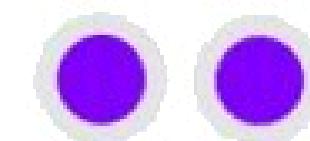
As particles approach each other the electric double layers overlap and cause repulsion



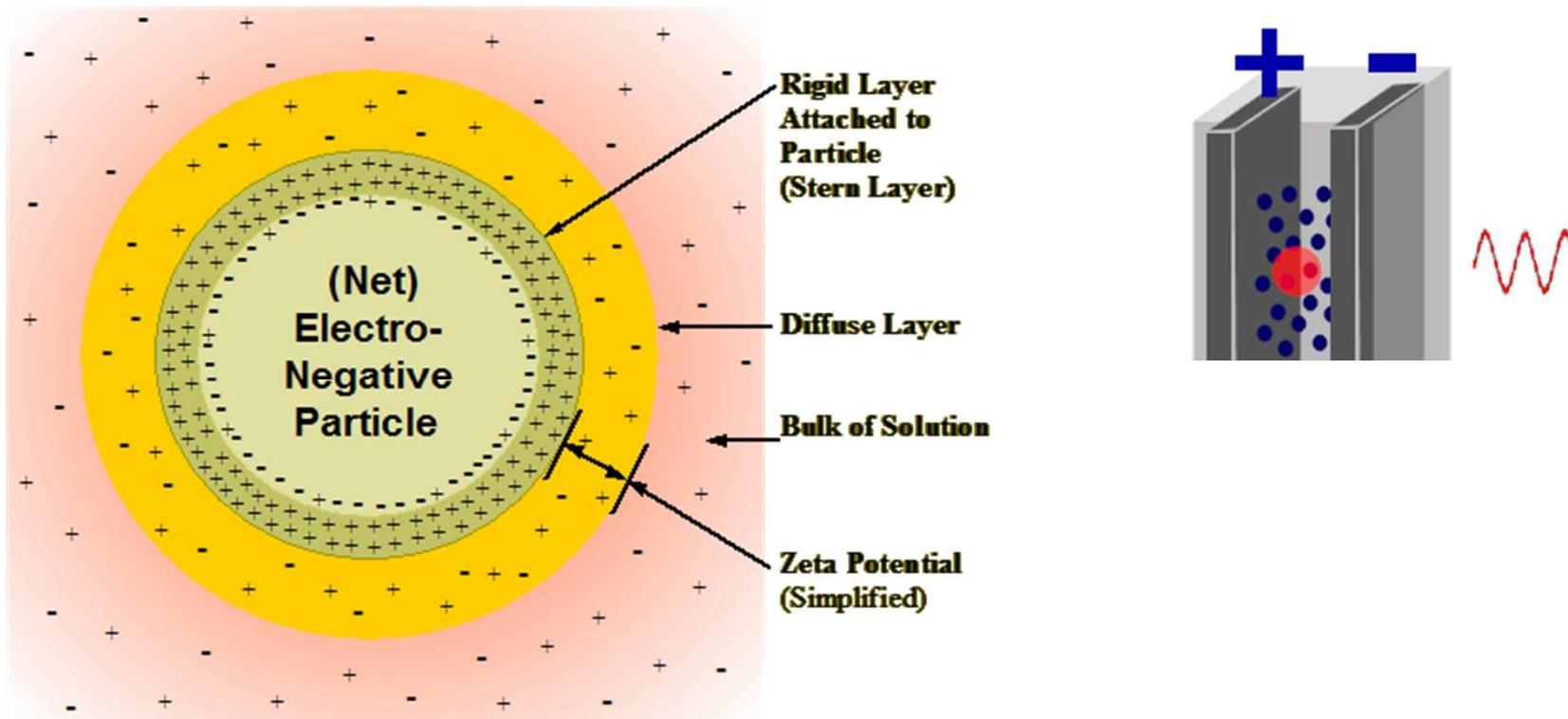
### Electric Double Layer

### Increased Ionic Strength

In increased ionic strength the electric double layers shrink which allows the cells to get closer without being repelled



When tiny minerals or organic particles (colloids) are suspended in a fluid, the negative ionic charge around the colloid is what maintains the dispersion or discreteness of the particles of the suspension.



When two particles come so close that their double layers overlap, they repel each other. **The strength of this electrostatic force depends on the zeta potential.**

If the zeta potential is too small (typically less than about 25 mV in magnitude), the repulsive force won't be strong enough to overcome the Van der Waals attraction between the particles, and they will begin to agglomerate. The suspension is said to be unstable when this happens.

A high zeta potential will prevent particle-particle agglomeration and keep the dispersion uniform and free flowing. Therefore, the goal in most formulations is to maximize the zeta potential.

# Smoluchowski (coagulation) equation

- Smoluchowski describes the evolution of the number density of particles of size  $x$  at a time  $t$ . Depending on time, the stability of dispersed phase in emulsion or suspension is reduced by flocculation or coalescence, thus their particle number is also reduced depending on time.

$$\frac{-dn}{dt} = \frac{4 \cdot k \cdot T}{3 \cdot \eta_o} \cdot n^2$$

$(k =$  Boltzmann coefficient

$: 1.381 \cdot 10^{-23} J/K$ .

Absolute

temperature

$\eta_o$ : Viscosity of continuous phase

$\mathcal{N}$  Particle number

$$\frac{-dn}{dt} = \frac{4 \cdot k \cdot T}{3 \cdot \eta_o} \cdot n^2 \longrightarrow \text{Eq. 1}$$

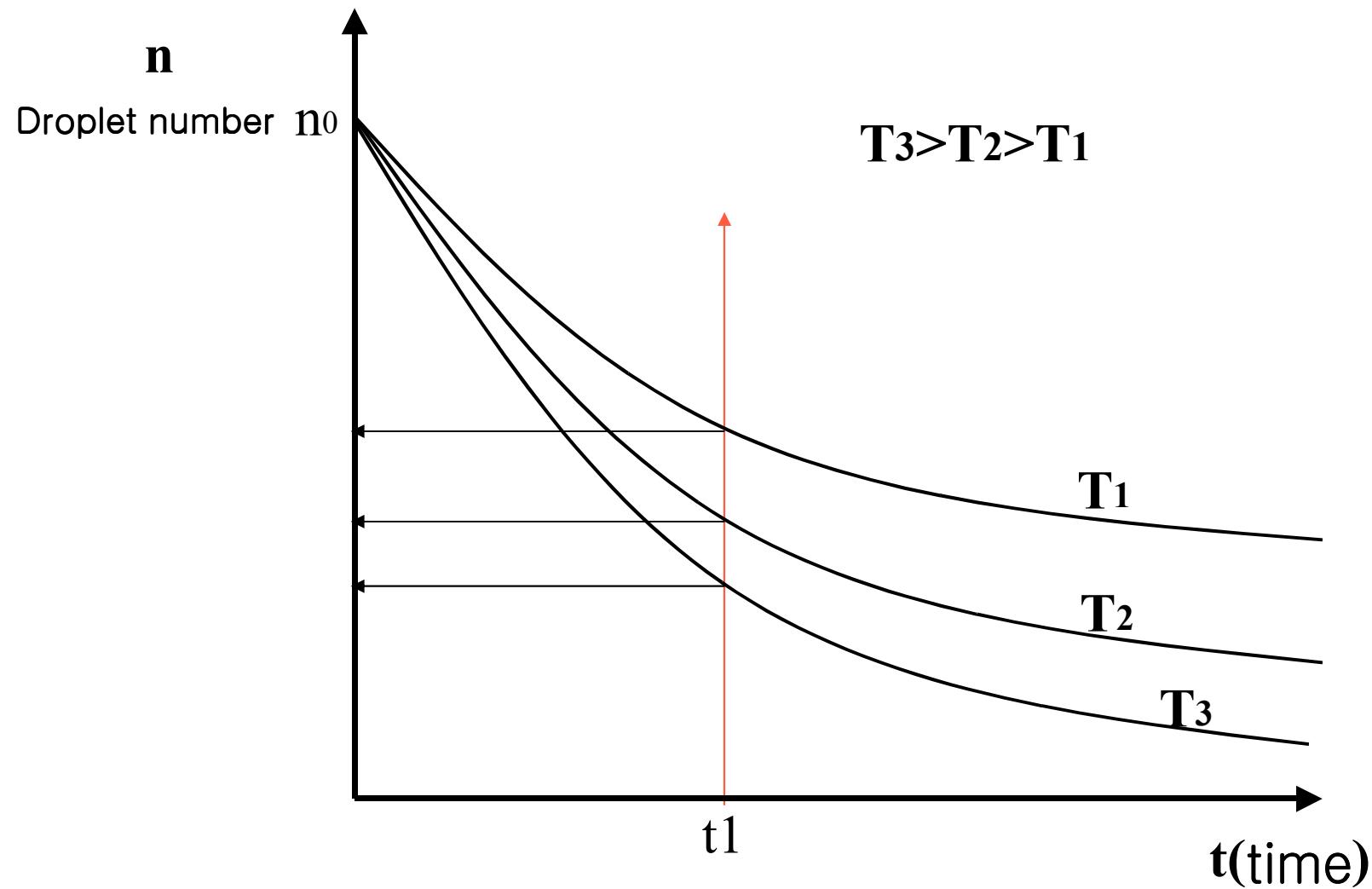
$$n^{-2} \cdot dn = \frac{-4 \cdot k \cdot T}{3 \cdot \eta_o} \cdot dt \longrightarrow \text{Eq. 2}$$

$$\int_{n_0}^{n_1} n^{-2} \cdot dn = \frac{-4 \cdot k \cdot T}{3 \cdot \eta_o} \cdot \int_{t_0}^{t_1} dt \longrightarrow \text{Eq. 3}$$

$$-\frac{1}{n_1} + \frac{1}{n_0} = \frac{-4 \cdot k \cdot T}{3 \cdot \eta_o} \cdot t_1 \longrightarrow \text{Eq. 4}$$

$$\frac{1}{n_1} - \frac{1}{n_0} = \frac{4 \cdot k \cdot T}{3 \cdot \eta_o} \cdot t_1 \longrightarrow \text{Eq. 5}$$

Therefore, above equation, the number of particles (dispersed phase) was dominated by temperature, viscosity, and initial dispersed phase



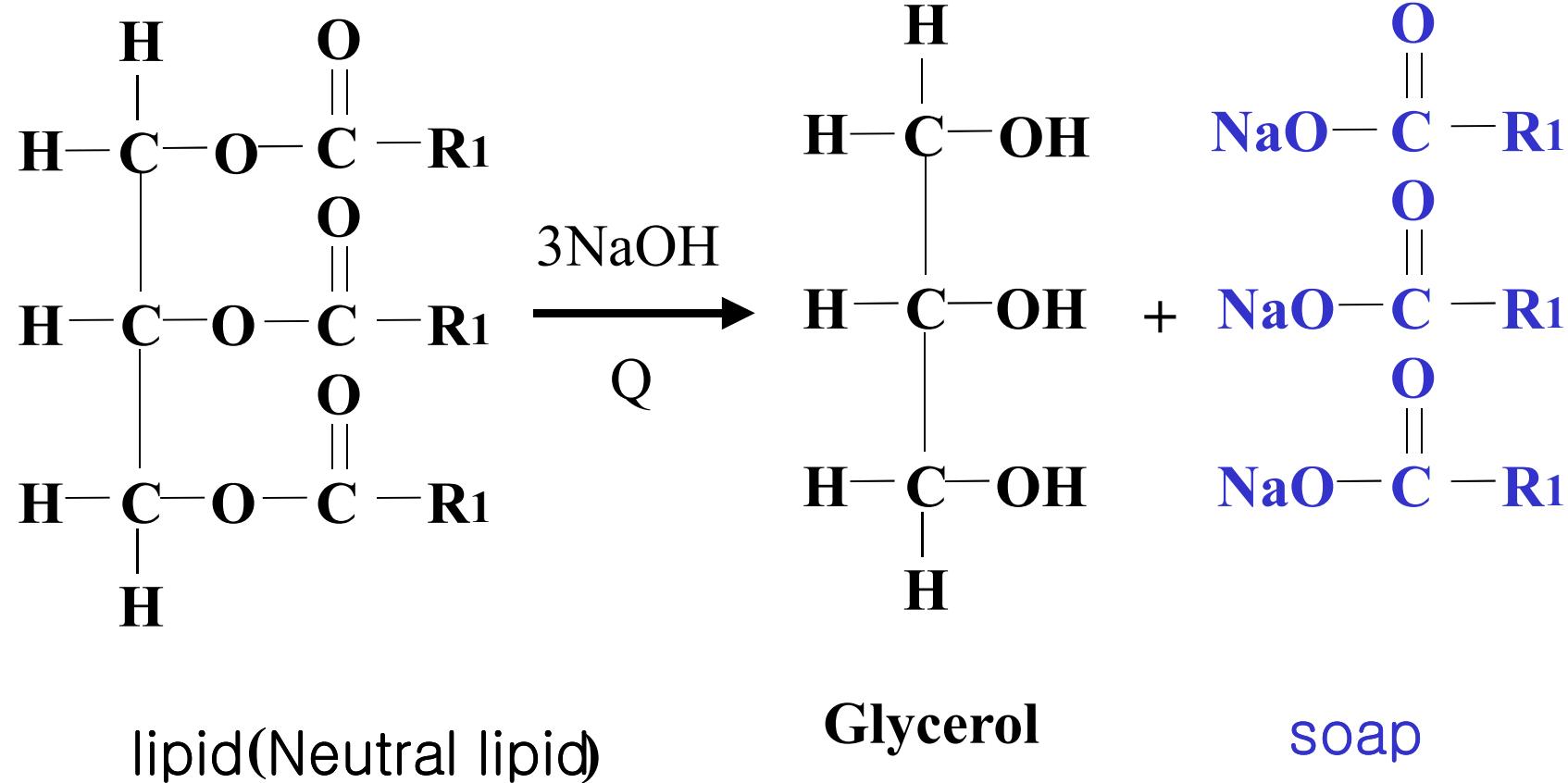
# How do you make the emulsion stable?

- To increase viscosity of continuous phase
- To make smaller size of dispersed phase
- To increase Z-potential
- To decrease surface tension between continuous phase and dispersed phase

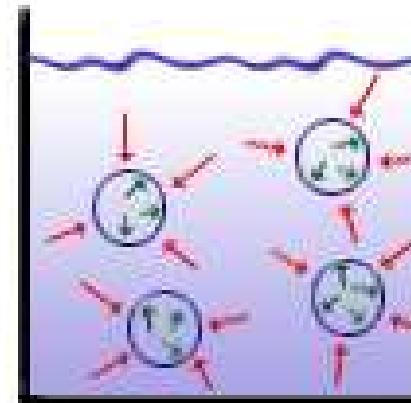
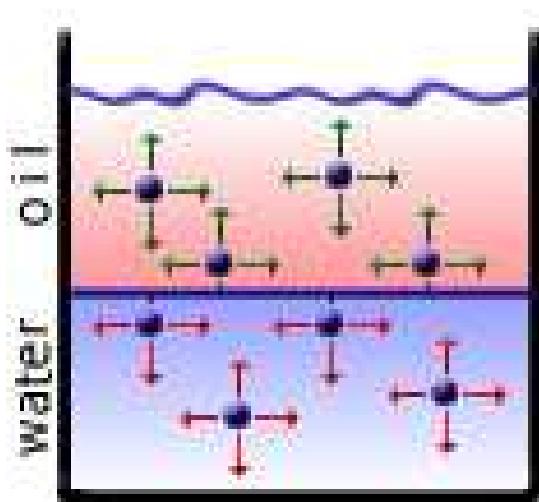
# Surfactant (emulsifier)

The term 'surfactant' is a blend of "surface **act**ing agent". Surfactants are usually organic compounds that are amphiphilic, meaning they contain both hydrophobic groups (their "tails") and **hydrophilic** groups (their "heads").

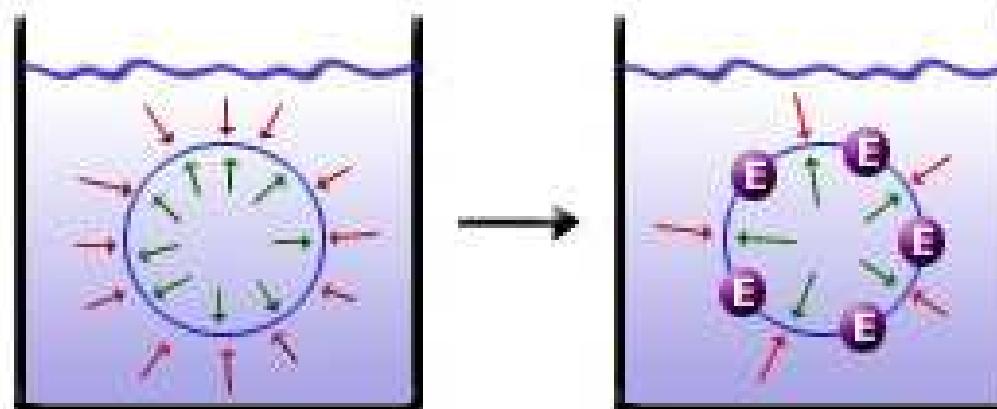
Surfactants **reduce the surface tension** of water by adsorbing at the liquid-gas interface or reduce the interfacial tension by adsorbing at the liquid-liquid.



## At liquid/liquid interface



## When an emulsion is formed



- reduces interfacial tension
- stabilizes emulsion

Addition of emulsifier(E) to the liquid/liquid interface

The surface tension (or interfacial tension),  $\gamma$ , is defined as the work required to create unit area of surface or interface; units  $\text{N m}^{-1}$ .

Typical interfacial tensions in food system range from 15 to 25 dynes / cm.

When an amphiphilic emulsifying agent is added to an emulsion system, the emulsifiers concentrate at the oil-water interface and lead to a reduction in interfacial tension to less than 10 dynes / cm.

# Interfacial Tension between Water and Various Oils

Purified Oil	Interfacial tension (dynes/cm)	
	25C	75C
Triolein	14.6	13.5
1,3-Dioleo-2-palmitin	14.5	12.5
Peanut (screw press)	18.1	-
Peanut (solvent extracted)	18.5	-
Cottonseed (screw press)	14.9	-
Olive	17.6	-
Coconut	12.8	-

# Application of surfactant

- **Detergents**
- **Fabric softener**
- **Emulsifiers**
- **Paints**
- **Adhesives**
- **Inks**
- **Anti-fogging**
- **Soil remediation**
- **Wetting**
- **Foaming agents**

# Application of surfactant

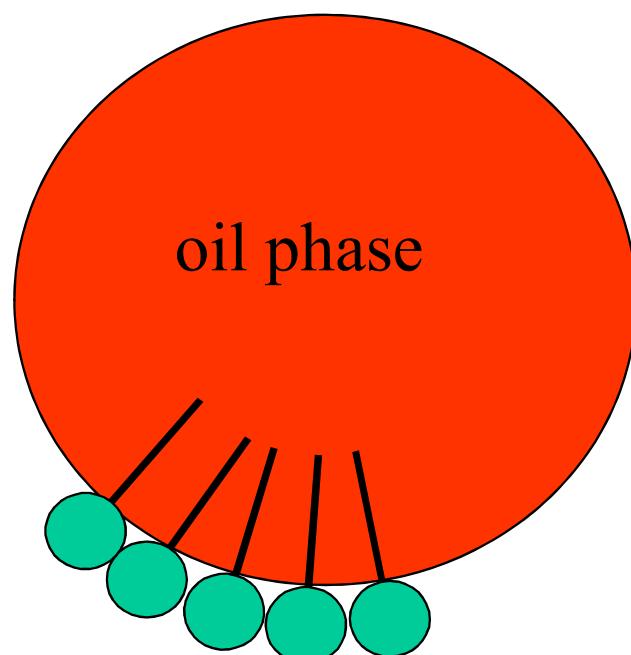
- An emulsifier is a substance which stabilizes an emulsion, frequently a surfactant. Examples of food emulsifiers are egg yolk (where the main emulsifying chemical is lecithin).

# Emulsifier

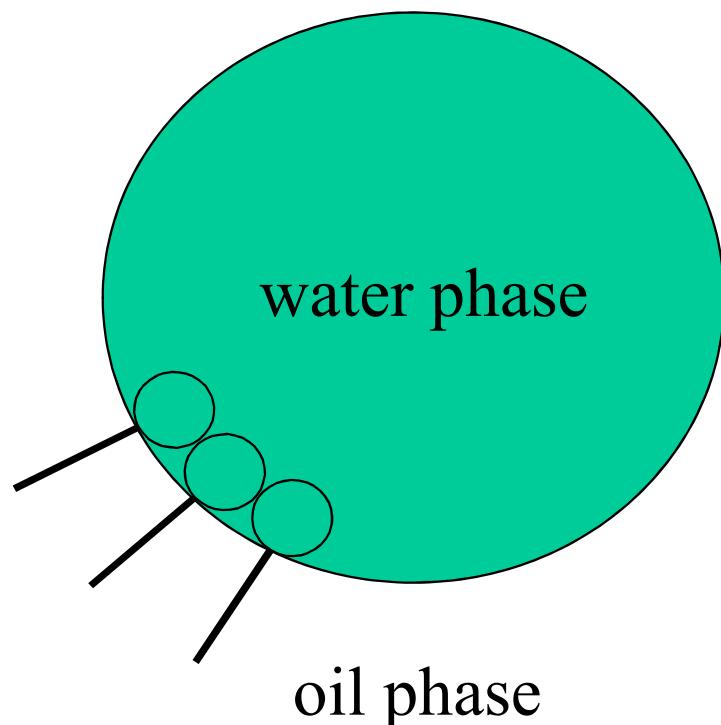
hydrophilic  hydrophobic

(OH, COOH, NH<sub>3</sub><sup>+</sup>...)

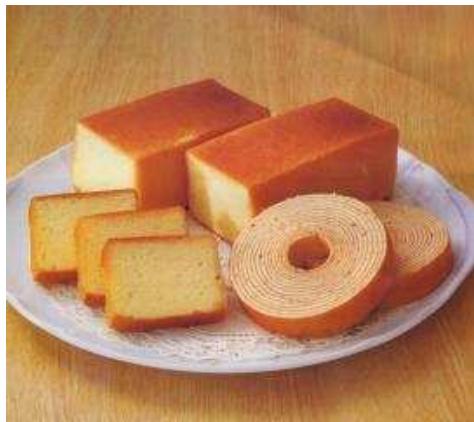
CH3-, H-, ...



water phase



oil phase



cake



sausage



chocolate

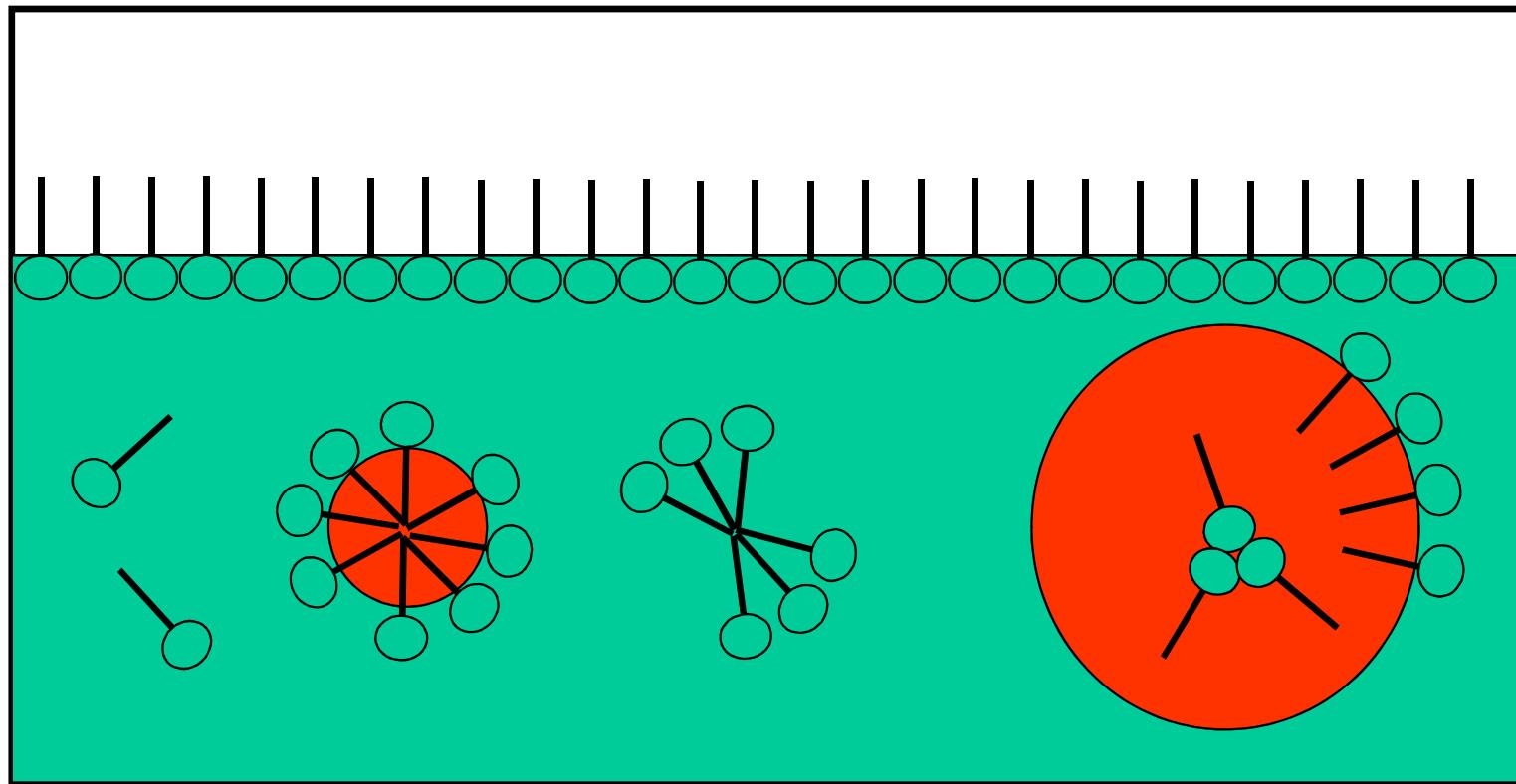


Ice cream

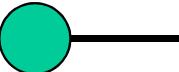
## Various adsorptive emulsifier type

emulsifier

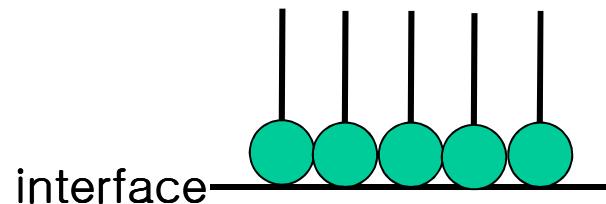
hydrophilic  hydrophobic



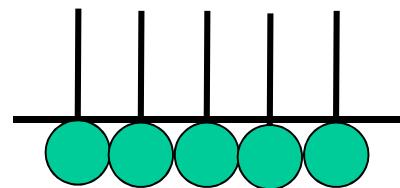
# emulsifier

hydrophilic  hydrophobic

oil phase

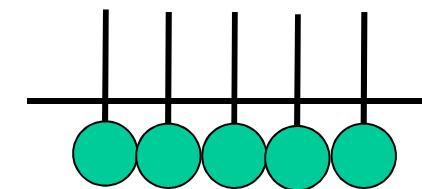


hydrophilic < hydrophobic



hydrophilic=hydrophobic

water phase



hydrophilic > hydrophobic

# Classification of surfactant

A surfactant can be classified by the presence of formally **charged groups in its head**.

**Ionic** : the **head** of an ionic surfactant carries a net **charge**

**Anionic**: negative charge

**Cationic**: positive charge

**Zwitterionic (amphoteric)**: head with two oppositely charged groups

Some commonly encountered surfactants of each type include:

## Ionic

### Anionic (based on sulfate, sulfonate or carboxylate anions)

Sodium dodecyl sulfate (SDS), ammonium lauryl sulfate, and other alkyl sulfate salts

Sodium laureth sulfate, also known as sodium lauryl ether sulfate (SLES)

Alkyl benzene sulfonate

Soaps, or fatty acid salts

### Cationic (based on quaternary ammonium cations)

Cetyl trimethylammonium bromide (CTAB) a.k.a. hexadecyl trimethyl ammonium bromide, and other alkyltrimethylammonium salts, Cetylpyridinium chloride (CPC), Polyethoxylated tallow amine (POEA)

Benzalkonium chloride (BAC)

Benzethonium chloride (BZT)

### Zwitterionic (amphoteric)

dodecyl betaine, Coco ampho glycinate,

Cocamidopropyl betaine

## Anionic surfactant

- Head of an ionic surfactant carries a net charge
- Effective at alkali solution (pH 10-14) resulting from increasing surface activity
- However, not effective at acidic solution (pH 2-5)

## Cationic surfactant

- Charge electrical cationic net the head of surfacant
- Effective at acidic solution about pH 2-5

## Zwitterionic surfactant

- Be suitable at wide range of pH from acidic to cationic solution
- However, not effective at isoelectric point (pI)

## Non-ionic surfactant

- non-ionization at solution
- can apply any solution independent on pH

## HLB System

According to the HLB, hydrophilic-lipophilic balance, system, surface-active agent can be assigned a numerical value to represent its relative hydrophilic and lipophilic property. Numerous mathematical equations are used.

$$HLB\text{-}value = \frac{M_{hydro}}{M_{total}} \times 20$$

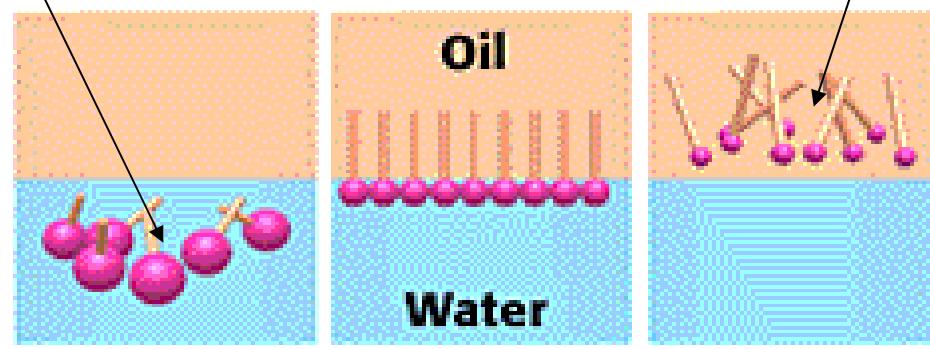
The hydrophilicity and lipophilicity are different among emulsifiers, and the balance between the two is called HLB value. The value ranges from 0 to 20.

An emulsifier with **higher lipophilicity** shows **a lower HLB** whereas **higher hydrophilicity** has **high HLB**, and the behaviors and functions to water depend on this HLB.

Characteristic behaviors related to water	HLB	ratio		functions	
		hydrophilic part	lipophilic part		
not dispersing	0	0	100	anti-foaming agent	
slightly dispersing	2	10	90	W/O emulsification	
	4				
milky dispersion	6	30	70	wetting agent	
	8				
stable milky dispersion	10	50	50	O/W emulsification	
transparent dispersion	12	60	40	cleaning agent	
colloidal solution	14	70	30	solubilizing agent	
	16				
	18	80	20		
	20				
		100	0		

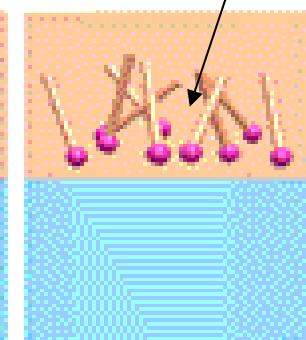
All compounds that have hydrophilic parts and lipophilic parts are not always useable as an emulsifier. when hydrophilicity is too great, such compounds **disperse into water and the ones with great lipophilicity would disperse into oil.**

### HLB and emulsifiers in water/oil



strongly hydrophilic  
High HLB

Oil  
Water  
good balance  
appropriate HLB



strongly lipophilic  
Low HLB

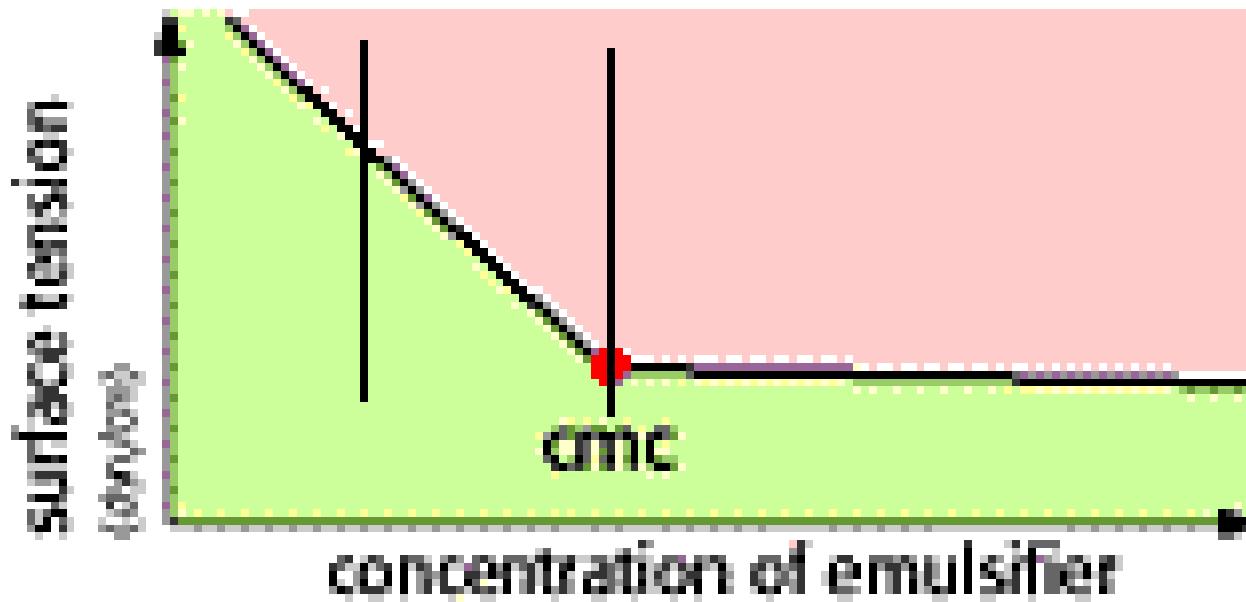
## **Micelle**

Because an emulsifier has opposite properties; hydrophilic and lipophilic, its solution does not become a simple aqueous solution but a colloidal solution, of which properties greatly vary depending on its concentration.

**In an extremely-diluted solution**, there is no special change, but the emulsifier gathers on the interface and the surface tension is reduced as an increase of its concentration.

As further increase of the concentration, a uniform mono molecular layer is made on the surface and the surface tension drops to the minimum.

A further increase of the concentration causes micelle formation, micelles formation occurs when the excess molecules, in which the lipophilic groups are positioned face to face gather and there is no change in the surface tension.



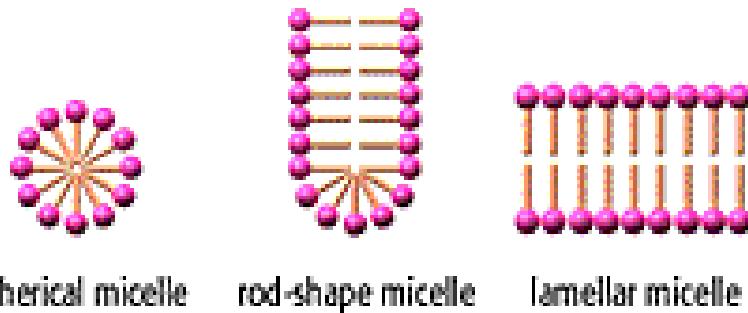
The concentration to start micelle formation is called **critical micelle concentration (cmc)**.

When the concentration exceeds cmc, ***spherical micelles*** appear at first and disperse into water.

A further increase in the concentration causes ***rod-shape micelles***.

Finally, ***lamellar micelles*** with higher structures called liquid crystal are produced.

### Types of micelle



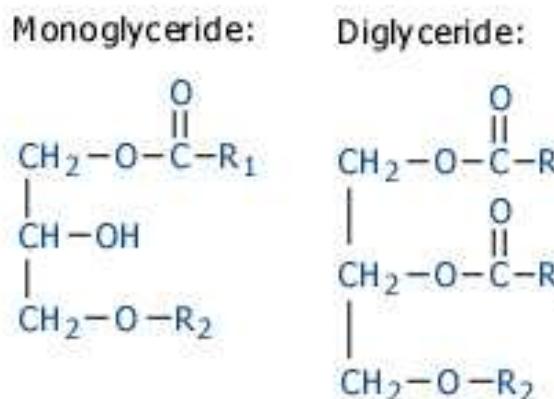
## Kind of Food Emulsifiers

Name	Common Name
Glycerin Fatty Acid Esters	Monoglyceride (MG)
Acetic Acid Esters of Monoglycerides	Acetylated Monoglyceride (AMG)
Lactic Acid Esters of Monoglycerides	Lactylated Monoglyceride (LMG)
Citric Acid Esters of Monoglycerides	CMG
Succinic Acid Esters of Monoglycerides	SMG
Diacetyl Tartaric Acid Esters of Monoglycerides	DATEM
Polyglycerol Esters of Fatty Acids	PolyGlycerol Ester (PGE)
Polyglycerol Polyricinoleate	PGPR
Sorbitan Esters of Fatty Acids	Sorbitan Ester (SOE)
Propylene Glycol Esters of Fatty Acids	PG Ester (PGME)
Sucrose Esters of Fatty Acids	Sugar Ester (SE)
Calcium Stearoyl di Lactate	CSL
Lecithin	Lecithin (LC)
Enzyme Digested Lecithin / Enzyme Treated Lecithin	

Generic or Chemical name	HLB
Sorbitan trioleate	1.8
Propylene glycol monostearate	3.4
Glycerol monostearate (non self-emulsifying)	3.8
Propylene glycol monolaurate	4.5
Sorbitan monostearate	4.7
Glyceryl monostearate (self-emulsifying)	5.5
Sorbitan monolaurate	8.6
Polyoxyethylene-4-lauryl ether	9.5
Polyethylene glycol 400 monostearate	11.6
Polyoxyethylene-4-sorbitan monolaurate	13.3
Polyoxyethylene-20-sorbitan monopalmitate	15.6
Polyoxyethylene-40-stearate	16.9
Sodium oleate	18.0
Sodium lauryl sulfate	40.0

## Mono- and Di-acylglycerides

- most commonly used emulsifiers
- highly lipophilic with HLB values range from 1 to 10
- produced by transesterification of glycerol and triacylglycerides
- used in bakery products, frozen desserts, icings, toppings, and peanut butter



Monoglycerides have various characteristics depending on the kind and the content of the fatty acid used as the raw material.

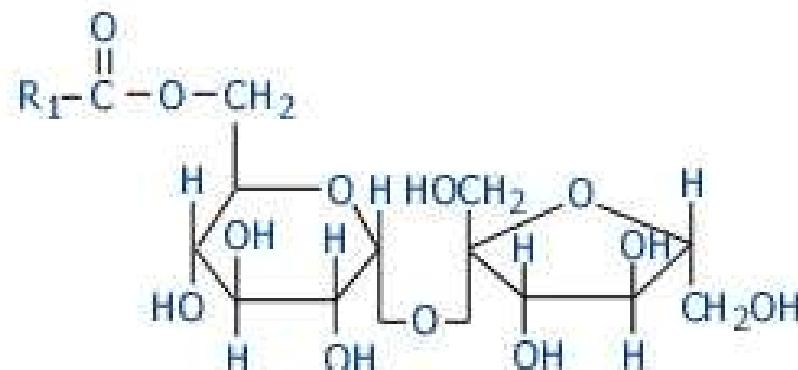
They are applied to much different fields;

- an emulsifier,
- foaming agent,
- anti-foaming agent,
- anti-tack agent,
- starch-modifying agent
- and anti-bacterial agent.

## Sucrose Esters

- approved in 1983
- are the mono-, di-, and tri- esters of sucrose with fatty acids
- usually with HLB values from 7 to 13
- mono-esters have HLB > 16 for o/w emulsions
- di-esters are good for w/o emulsion
- tri-esters have HLB ~1

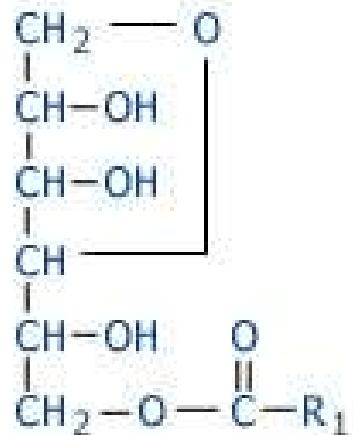
Sucrose esters:



## Sorbitan Esters

- sorbitan monostearate is the only sorbitan ester approved for food use
- produced by the reaction of sorbitol and stearic acid
- commercially known as SPAN 60
- HLB = 4.7
- used in conjunction with polysorbates in oil toppings, cake mixes, etc.

Sorbitan esters:

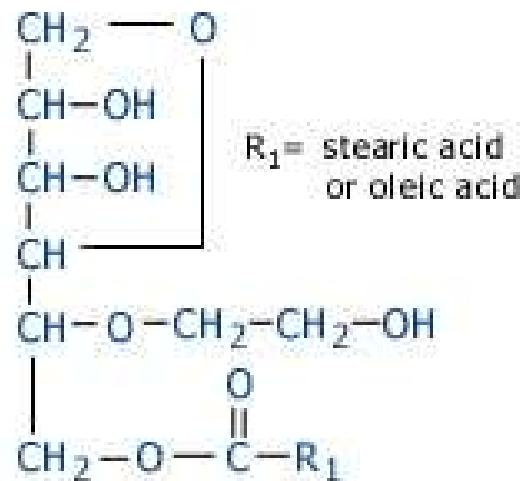


$\text{R}_1 =$  stearic acid

## Polysorbates

- polyoxyethylene sorbitan esters
- formed from the reaction of sorbitan esters with ethylene oxide
- 3 polysorbates are permitted for food use at limited amounts:

### Polysorbates:



### *Polysorbate 60*

- polyoxyethylene sorbitan monostearate or TWEEN 60
- HLB = 14.9
- sample applications include oil toppings, cake mixes, and cake icing

### *Polysorbate 65*

- polyoxyethylene sorbitan tristearate or TWEEN 65
- permitted for use in ice cream, frozen custard, ice milk, etc.

### *Polysorbate 80*

- polyoxyethylene sorbitan monooleate or TWEEN 80
- HLB = 15.0
- some special applications are for oils in special dietary foods, vitamin-mineral preparation, and fat-soluble vitamins.