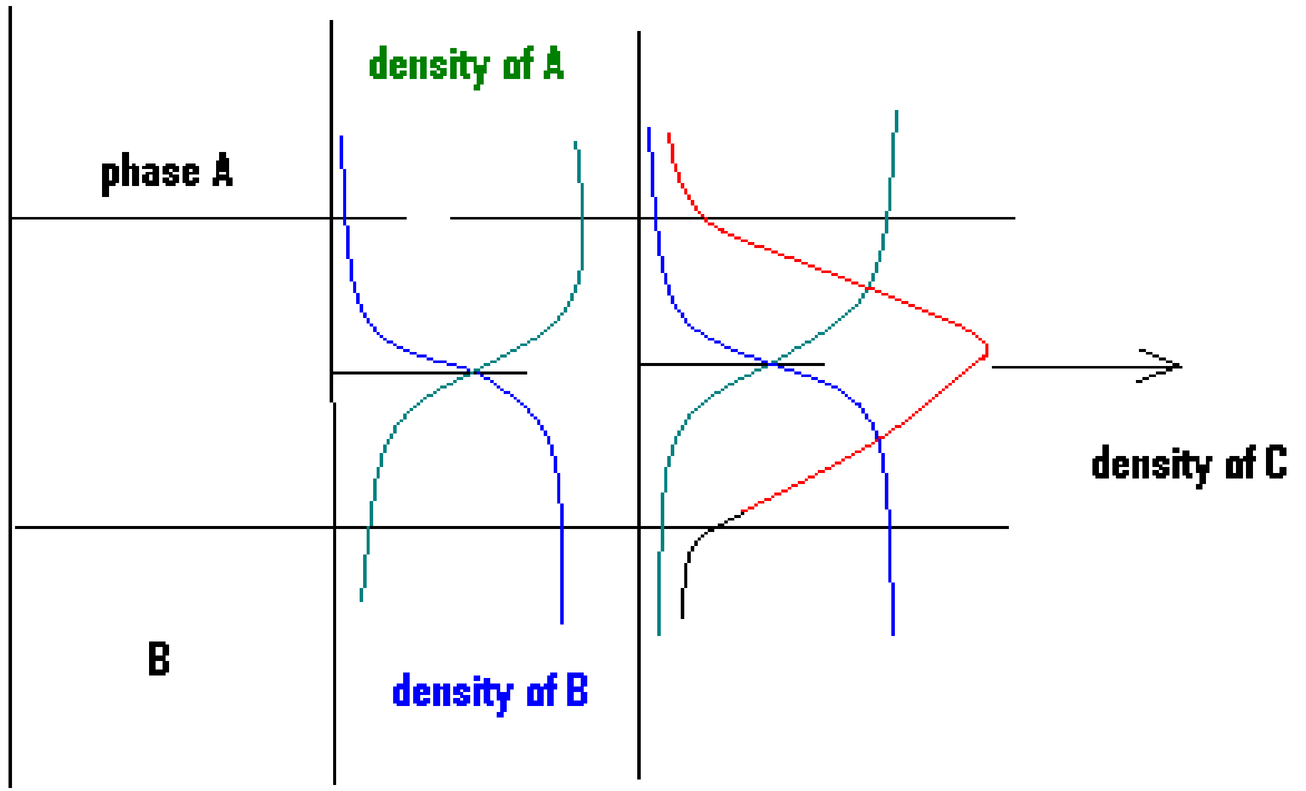
Surfactants

Basic concept of Surfactants

- ❑ Surfactants are organic molecules with amphiphilic nature.

- ❑ Have a **hydrophobic portion** (generally a long fatty chain) and a **hydrophilic head** (an anion or a cation and sometimes an ethylene oxide chain).

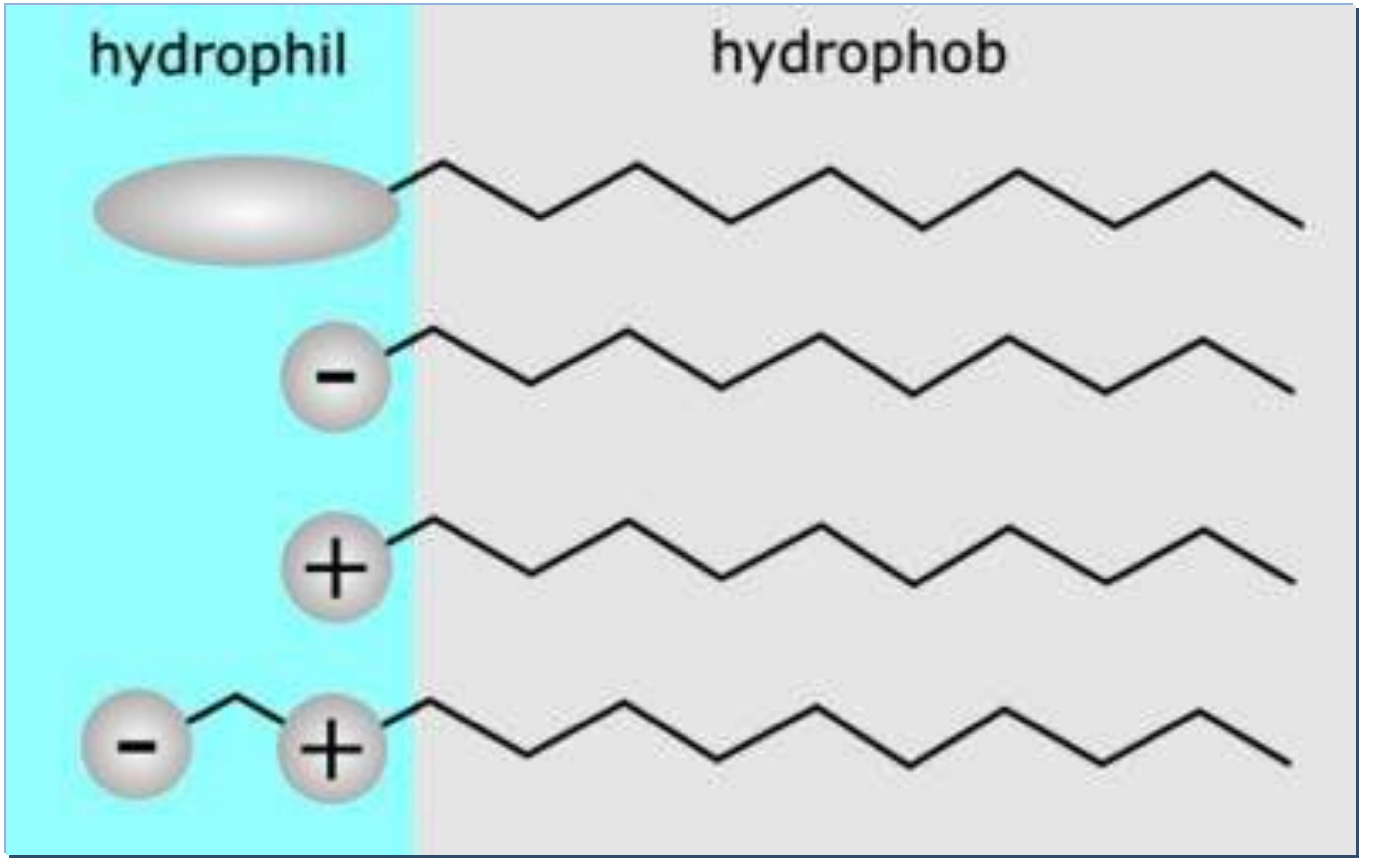
- ❑ Due to its dual nature a surfactant tries to occupy space in the boundary of a hydrophilic & a hydrophobic medium.



Relative densities of materials at the interface between two bulk liquids is shown by green and blue curves. ‘C’ is interfacially active component.

A surfactant (surface active agent) lowers the equilibrium interfacial tension between the medium in which it is dissolved and any other contacting fluid.

Structure of Surfactant



Hydrophobic tail is compatible with a hydrophobic medium while the head is compatible with a hydrophilic medium

One of the most important tasks a surfactant performs is <u>reducing the surface tension of the medium in which it is dissolved.</u>

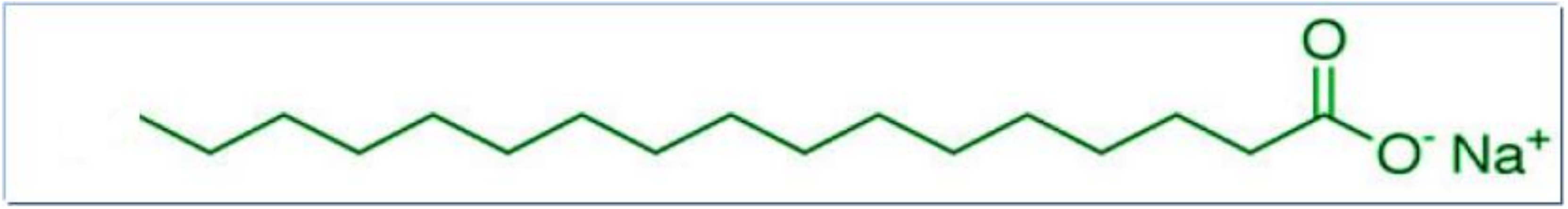
✓ This helps the treatment liquor to wet the surface to be treated in a more effective way.

- Desized cotton fabric is hydrophobic and repels water. If one tries to scour it with a caustic solution, the wetting is not good

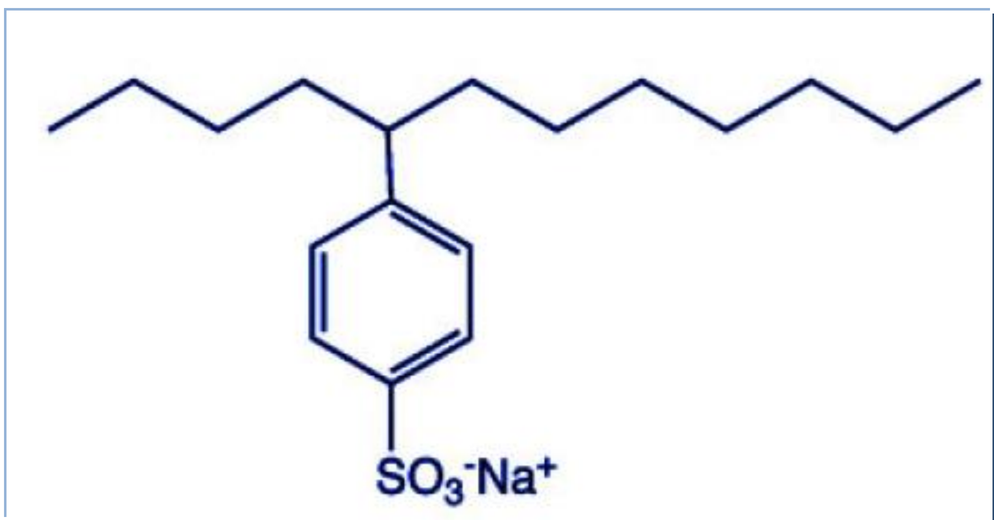
- Unless the scouring liquor wets the fabric properly, scouring will not be efficient

- However, if a wetting agent is added to the scouring liquor, it is able to wet the fabric suitably

Surfactants: Example

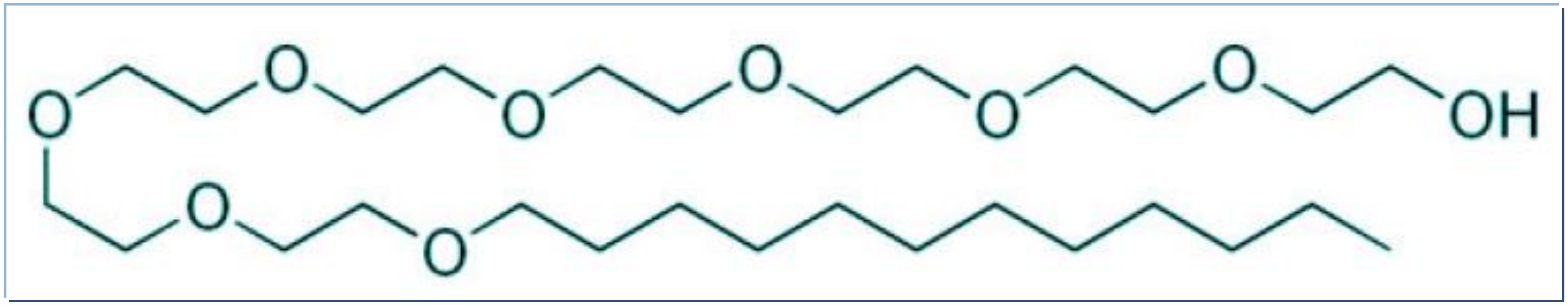


Cetyl (C16), the most common component of most soap, anionic surfactant



4-(5-Dodecyl) benzenesulfonate, a common anionic surfactant

Non-ionic Surfactant

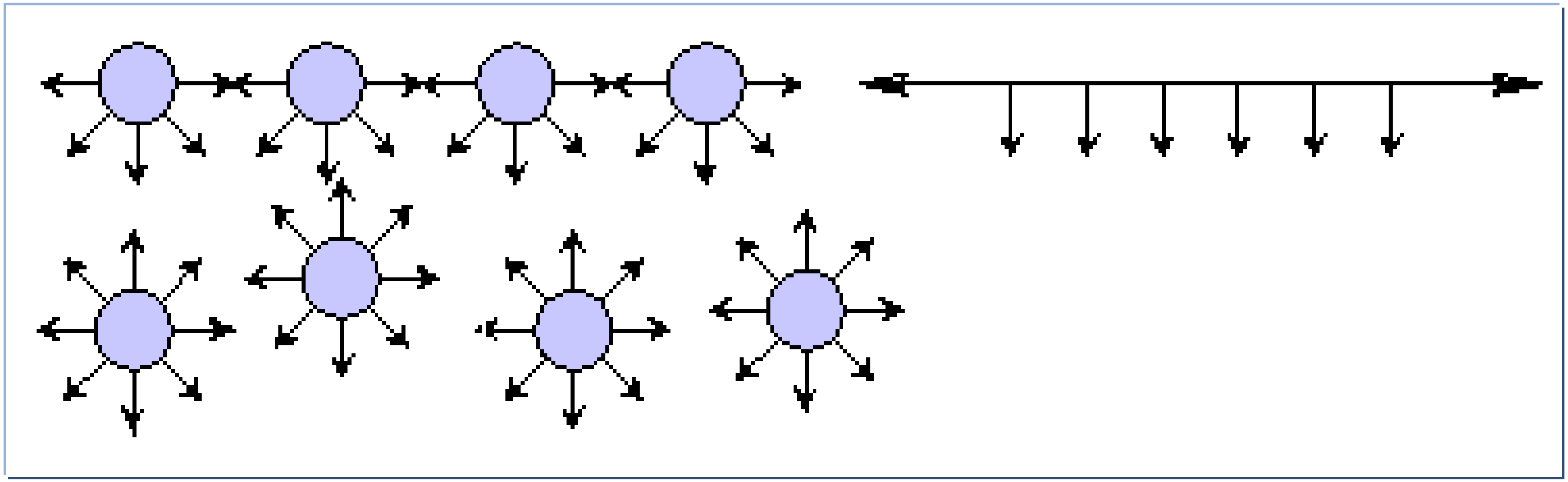


Octaethylene glycol monododecyl ether ($C_{12}E_8$)

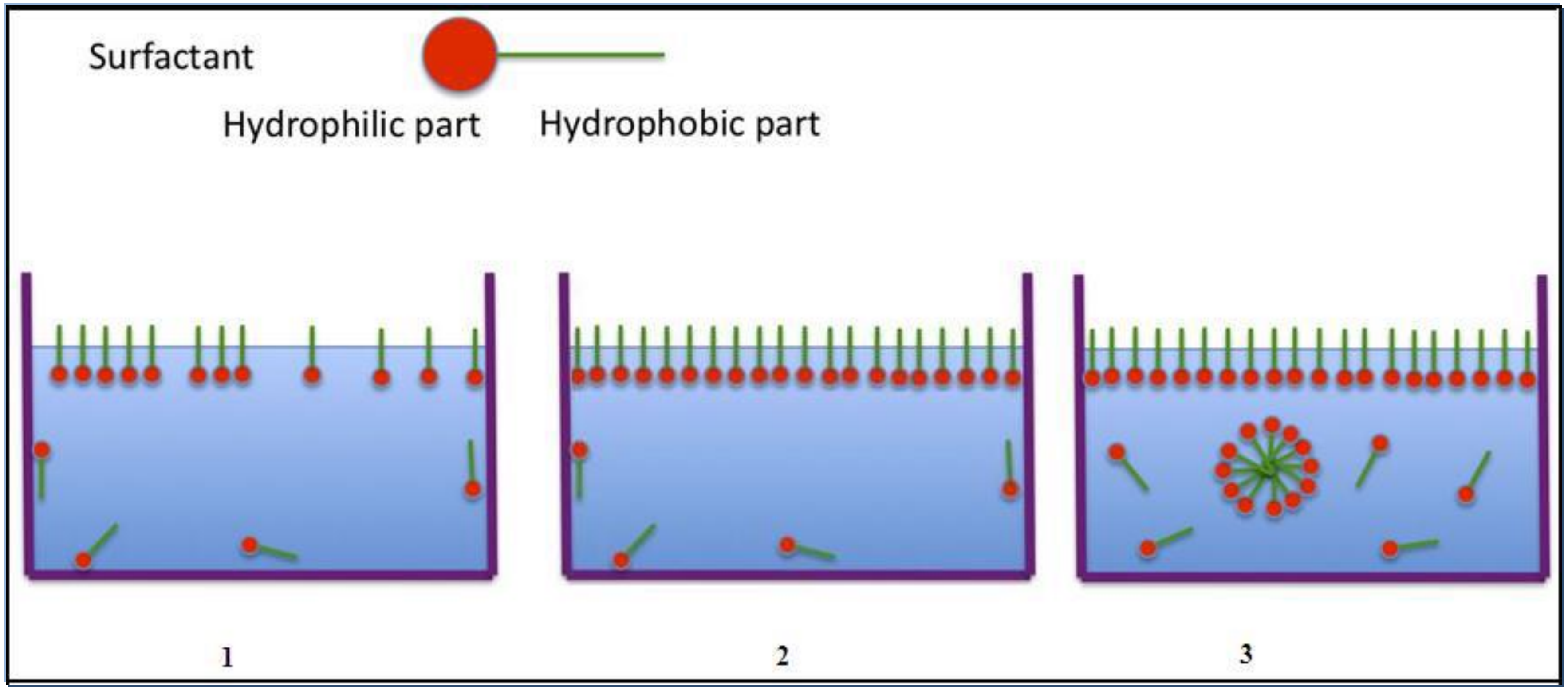
Surface tension reduction in presence of Surfactant

When a surfactant is added to the water, the surfactant molecule invariably goes to the air-water interface to replace the water molecules.

✓ This reduces the net pull on top layer of the water molecules & hence surface tension of water goes down.



Surfactant Aggregation in Solution



How are the impurities removed ?

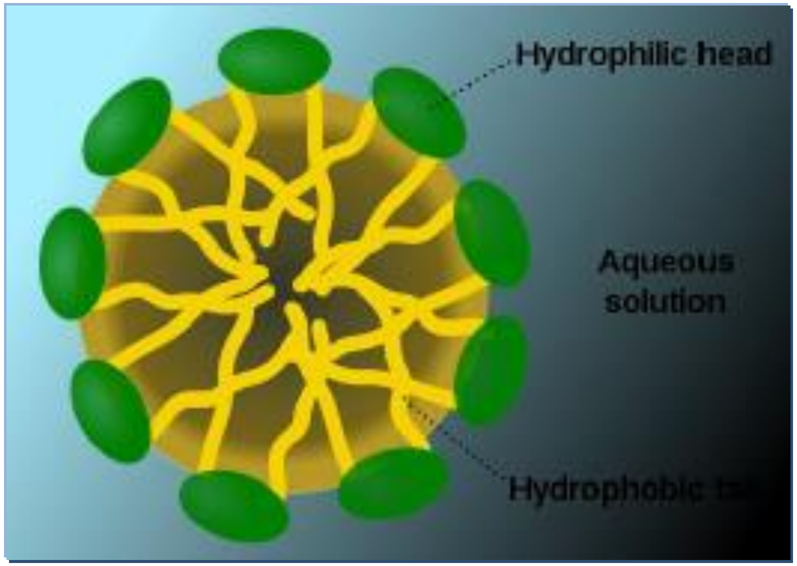
If surfactant is dissolved in water, its molecule tend to come to **air-water interface in such a way that hydrophobic fatty chain is oriented outwards in the air(1), while the hydrophilic head remains submerged in water.**

- As more surfactant is added in water, it keeps moving to the surface (2) up to saturation.

- The extra surfactant molecules move in the bulk and form **microstructures to shield the hydrophobic fatty chain from water (3).**

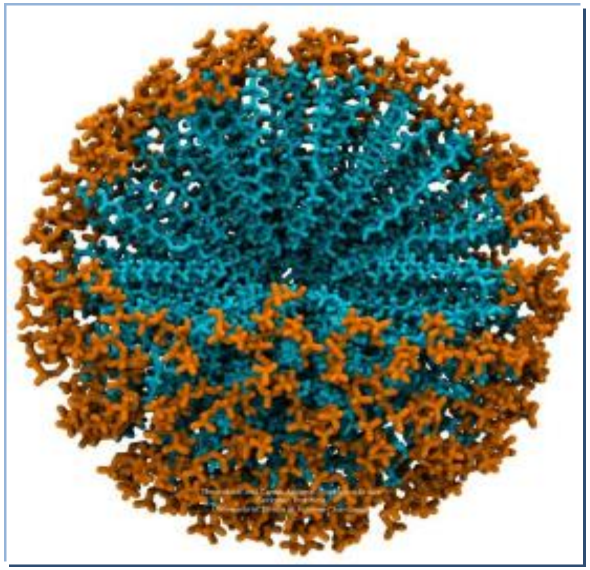
CMC:

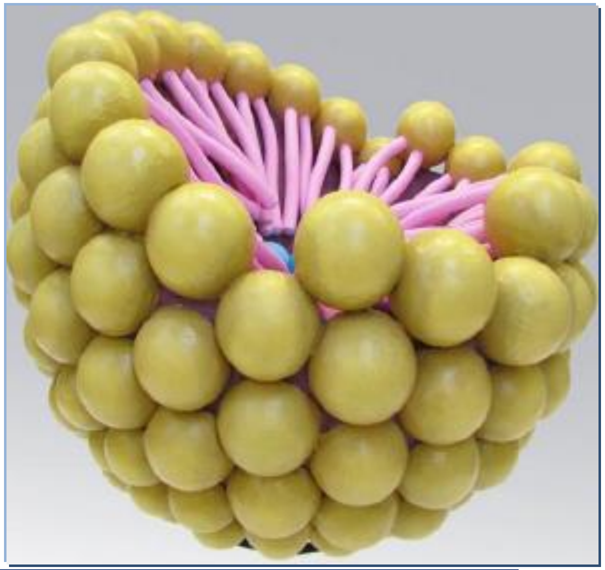
The concentration at which the micelles or aggregates start forming is known as critical micelle concentration (CMC).



- Large no. of monomers (50-100) assemble to form a closed aggregate.

- Non-polar parts shielded from water.



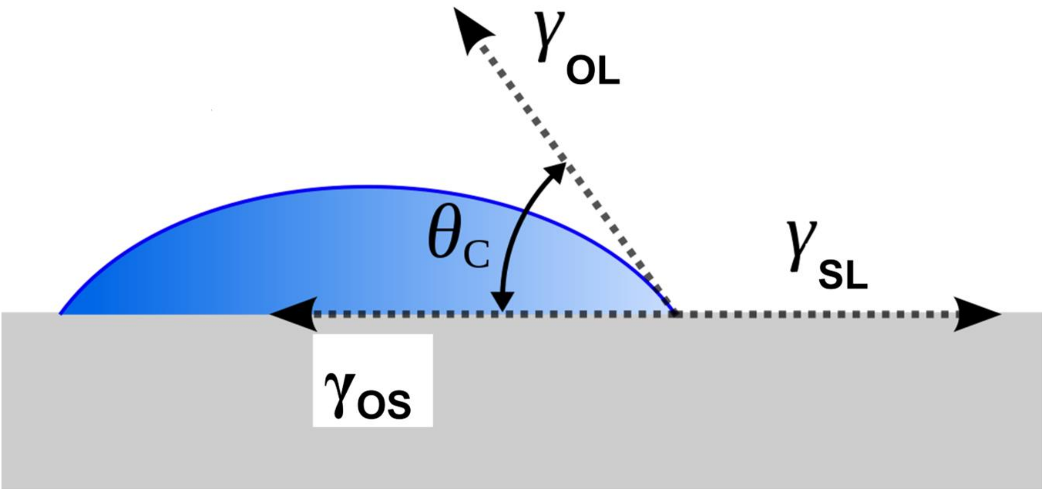


Mechanism of Impurities Removal

- ❖ **Roll-up**
- ❖ **Emulsification**
- ❖ **Solubilization**

MECHANISM OF IMPURITIES REMOVAL

(1). Roll-up:



A drop of oil on a substrate is put in an liquid medium.

❖ The forces acting on the droplets are:

Υ_{OS} : (surface tension at oil solid interface)
Υ_{SL} : (surface tension at solid liquid interface)
Υ_{OL} : (surface tension at oil liquid interface)

At equilibrium these forces are balanced as: $\boxed{\Upsilon_{SL} = \Upsilon_{OS} + \Upsilon_{OL} \mathrm{Cos}\theta}$

Roll-up: Mechanism of impurities removal………

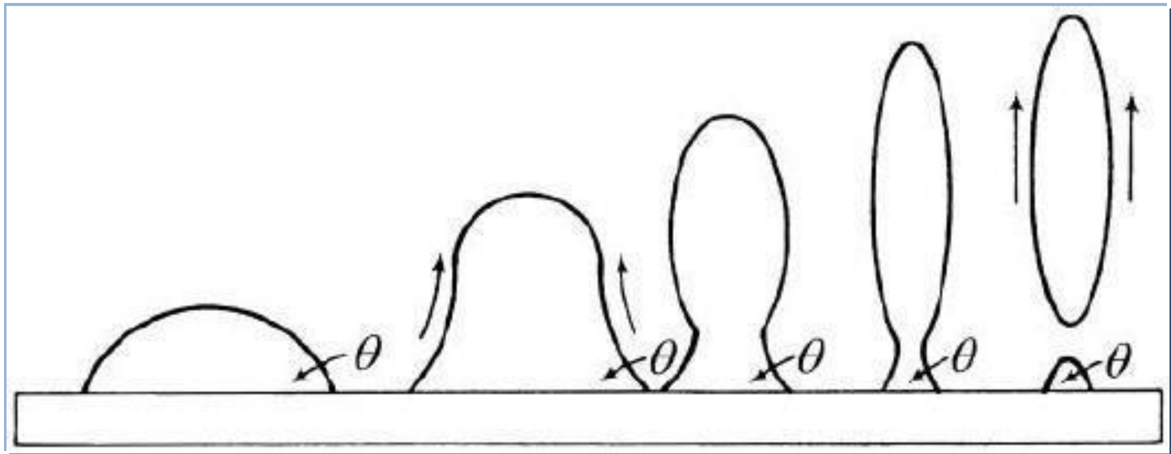
- When a surfactant is added, γ_{SL} goes down which causes θ to increase.

- The net result is the tendency of the drop to become rounder by roll-up.

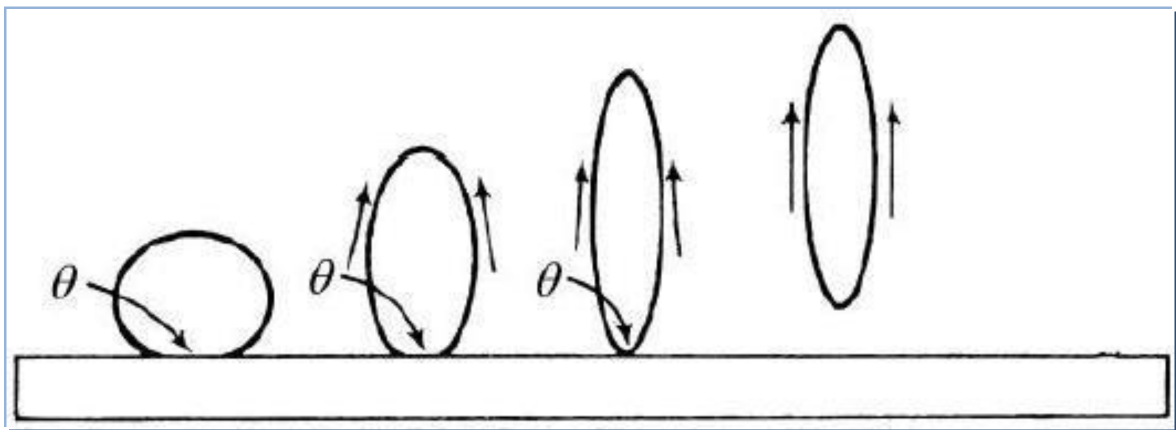
- With sufficient mechanical agitation, the droplet may become spherical and get detached from the original drop, leaving behind some residual oil.

- It is important to keep the drop in suspension to prevent it from re-deposition.

Roll-up: Mechanism of impurities removal……



With mechanical agitation only (θ –constant)



Due to surfactant-(θ keeps increasing)

(2). Emulsification: Mechanism of impurities removal

- An emulsion is a dispersion of a liquid in another liquid in which it is not soluble.

- When two immiscible liquids are mixed & shaken vigorously, one of them breaks into small droplets and gets dispersed in another.

- However, such a dispersion is thermodynamically unstable hence the liquids again form two distinct continuous phases.

The way of dispersion of one liquid phase in another becomes stable, which is known as emulsion

Emulsification: Mechanism of impurities removal……

- An emulsifier is a surfactant whose molecules cover the surface of two droplets.

- One portion of the surfactant molecule becomes compatible with one phase and the other part with second phase.

- This way of dispersion of one liquid phase in another becomes stable, which is known as emulsion.

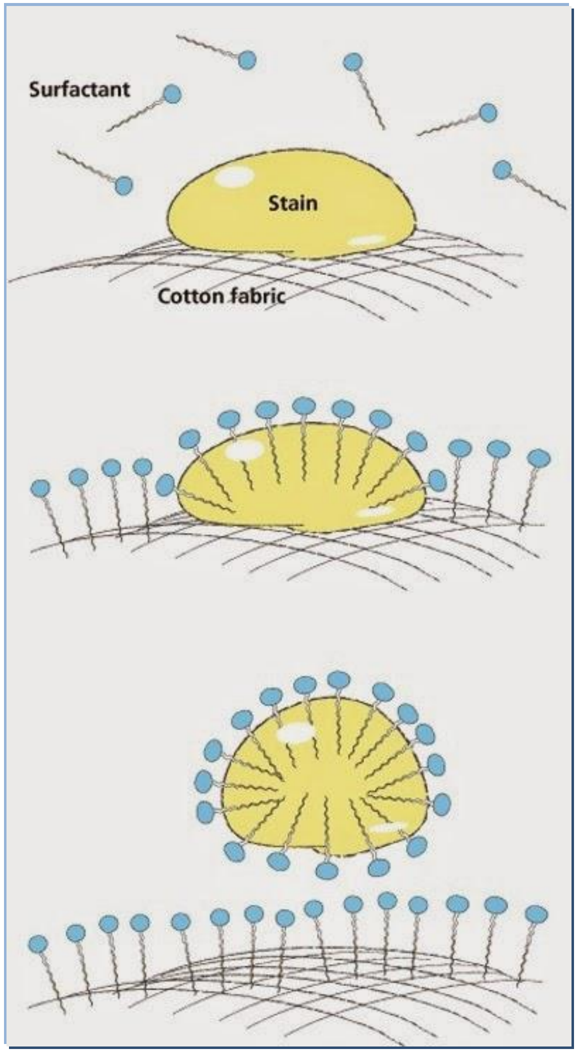
(**Milk is a common example of emulsion of fat in water**)

Emulsification: Mechanism of impurities removal……

- In an emulsion, the size of dispersed droplets is not defined and may vary to a large extent.

- Removal of hydrophobic impurities from textiles using surfactant in an aqueous medium by emulsification is a common mode.

- Agitation helps and is provided either by movement of goods, liquor or both.



(3). Solubilization: Mechanism of impurities removal

The hydrophobic impurity may be removed by solubilization also.

Two Ways:

(a) Using a surfactant (above CMC)

(b) Solubilization using a solvent

(3a). Using a surfactant above CMC

- When the micelle traps the hydrophobic soil in its central cavity, it is removed by solubilization.

- It is similar to emulsification; however, the disposed droplet size is almost constant and is almost equal to the cavity inside micelle. Such system can be treated as one phase system.

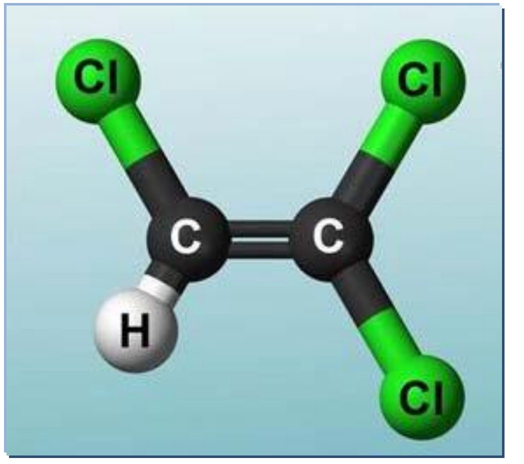
(3b). Solubilization using a solvent

Two approach:

Using a solvent to dissolve away the hydrophobic soil. For example, common dry cleaning uses organic solvents to remove hydrophobic greasy or oily soils from textile materials. At industrial scales, this has safety & logistical problems related to handling of large amount of organic solvents.

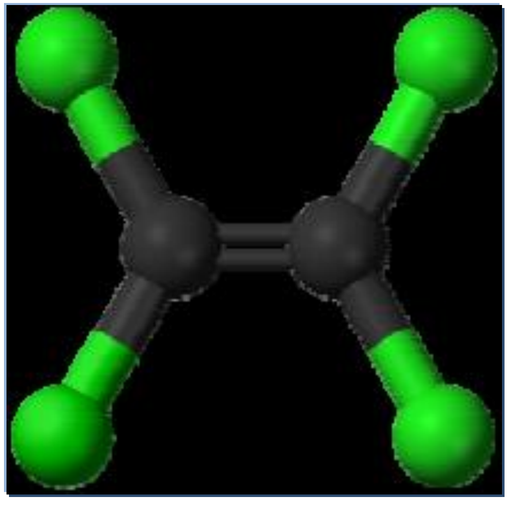
A solvent may be emulsified in an aqueous medium and the resultant emulsion, which may contain only a small amount of solvent may be used to remove the oily soil.

Trichloro ethylene
(B.P. : 87 ^{o}C, Non-flammable)



Trichloroethylene (TCE)

Perchloro ethylene
(B.P. : 121^{o}C, Non-flammable)



Perchloroethylene (PCE)

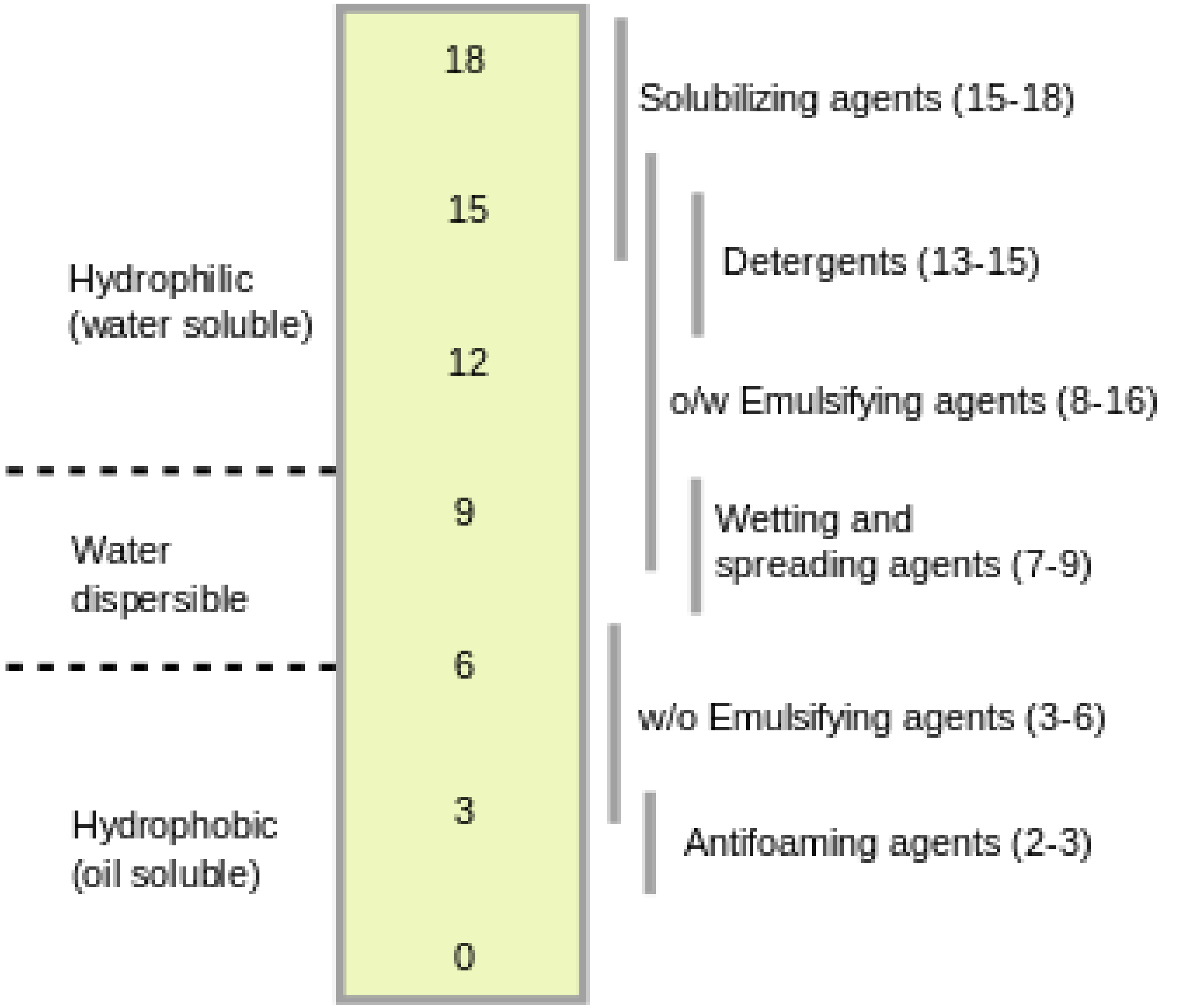
Concept of HLB value

For surfactants & oils/fats/waxes, etc.

HLB stands for **hydrophile lipophile balance**. It indicates relative fraction of hydrophilic and hydrophobic components in a surfactant, oil, solvent, etc.

HLB Value	Characteristic
1-4	Not miscible in water
4-8	Dispersible in water
8-12	Milky emulsion in water
>12	Soluble in water

Concept of HLB value



HLB value………..

- Silicon oil, HLB –9
- Kerosene oil, HLB –12

❖ For emulsification of a particular impurity, a surfactant of similar HLB value is selected.

- Either single component.
- Combination of two different HLB surfactants.

For scouring 13 - 13.5% HLB value surfactants are used.

Determination of the Required HLB values
and
Blending of Surfactants

Oils used in the formulation of emulsions require a certain HLB value to be formulated as:

Either, **w/o emulsion** or **o/w emulsion**.

For the same oil, the required HLB value for O/W emulsion is ***higher*** *than the required HLB value for W/O emulsion.*

Oil	O/W emulsion	W/O emulsion
Stearic acid	15	6
Cetyl alcohol	15	-------------
Stearyl alcohol	14	-------------
Lanolin, anhydrous	12	8
Mineral oil, light	12	4
Liquid paraffin	10.5	4
Castor oil	14	-------------
Beeswax	9	5
Petrolatum	7-8	4
Wool fat	10	8

Calculation of the required HLB for a mixture of oils, fats or waxes.

- **Multiply the required HLB of each ingredient by its fraction from the total oily phase.**

- **Add the obtained values to get the total required HLB for the whole oily phase.**

Example:

Problem

Liquid paraffin:	**35%**
Wool fat:	**1 %**
Cetyl alcohol:	**1%**
Emulsifier system :	**7%**
Water to	**100%**

HLB (liquid paraffin): 10.5

HLB (wool fat): 10.0

HLB (cetyl alcohol): 15.0

What is the total required HLB no.?

The total percentage of the oily phase is 37.

The proportion of each is:

- Liquid paraffin: 35/37 x 100 = 94.6%
- Wool fat: 1/37 x 100 = 2.7%
- Cetyl alcohol: 1/37 x 100 = 2.7%

The total required HLB number is obtained as follows:

Liquid paraffin (HLB 10.5) 94.6/100 X 10.5 = 9.93
Wool fat (HLB 10) 2.7/100 x 10 = 0.3
Cetyl alcohol (HLB 15) 2.7/100 X 15 = 0.4

Total required HLB = **10.63**

Calculation of ratio of emulsifier to produce a particular required HLB value

One of the most important aspects of the HLB system is that HLB values are additive if the amount of each in a blend is taken into account.

Thus, blends of high and low HLB surfactants can be used to obtain the required HLB of an oil.

The HLB of the mixture of surfactants, consisting of fraction x of A and (1-x) of B is assumed to be the algebraic mean of the two HLB numbers,

i.e.:

$$\textbf{HLB mixture} = x\,HLB_A + (1-x)\,HLB_B$$

Rearrangement of the above equation in percent (%) form will be:

$$A = 100\,(X - HLB_B)\,/\,(HLB_A - HLB_B)$$

$$B = 100 - A$$

Where, X is the required HLB of the surfactant (oil) mixture

PROBLEM

A formulator is required to formulate an o/w emulsion of the basic formula:

Liquid paraffin:	50 g
Emulsifying agents (**required HLB 10.5**):	5 g
Water to:	100 g

Calculate the fraction of Tween 80 (HLB of 15) and Span 80 (HLB of 4.3) used to produce a ***physically stable liquid paraffin emulsion.***

Solution

Assume that Tween 80 is A and Span 80 is B.

$$\mathbf{A = 100\ (X - HLB_B) / (HLB_A - HLB_B)}$$

$= 100\ (10.5 - 4.3) / (15 - 4.3)$
$= 57.9\%$

$$\mathbf{B = 100 – A}$$

$= 100 - 57.9 = 42.1\ \%$

$A = (57.9 \times 5) \times 100 = 2.89$ g
$B = 5 – 2.89 = 2.11$ g