Textile chemistry

8. Surfactants and detergents

Jakub Wiener

DETERGENT

Detergent - a preparation whose composition is adapted for practical purposes to achieve the greatest possible application effect.

Detergent - a mixture of surfactants and other substances.

Detergent contains:

the active ingredient (surfactant)

additional ingredients (additives)

Detergent is a product that has a great washing, cleaning and degreasing effect. It is usually composed of a mixture of substances. The basic component of a detergent is a surfactant (a tenside).

DETERGENTS - COMPOSITION

1. Surfactant (they wash) - 50%

2. Activating additives (help wash)

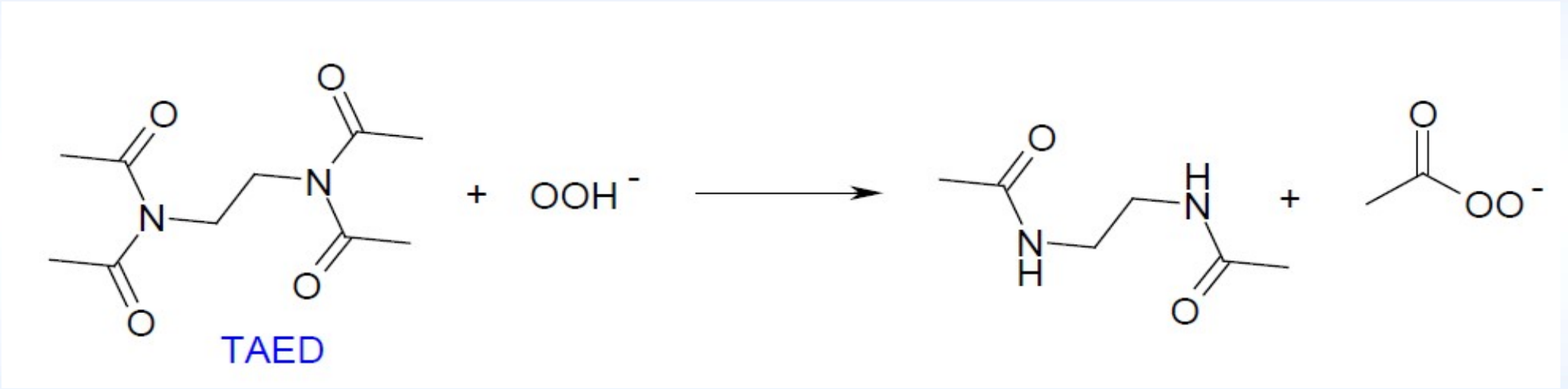
Sequestrants (Polyphosphates...)
Alkalis (Carbonates)
Anti-redeposition agents
Enzymes
Foam regulators

3. Auxiliary additives (do not wash, but improve the final impression)

Bleaches (Peroxoborates)
OZP
Antimicrobials
Perfume compositions
Fillers

Additives

Peroxide activator



Enzymes

Surfactants

Surfactant - substances that are able to accumulate at the phase interface and reduce the surface energy of the system

Phase interface between liquid and gas - interfacial tension is reduced.

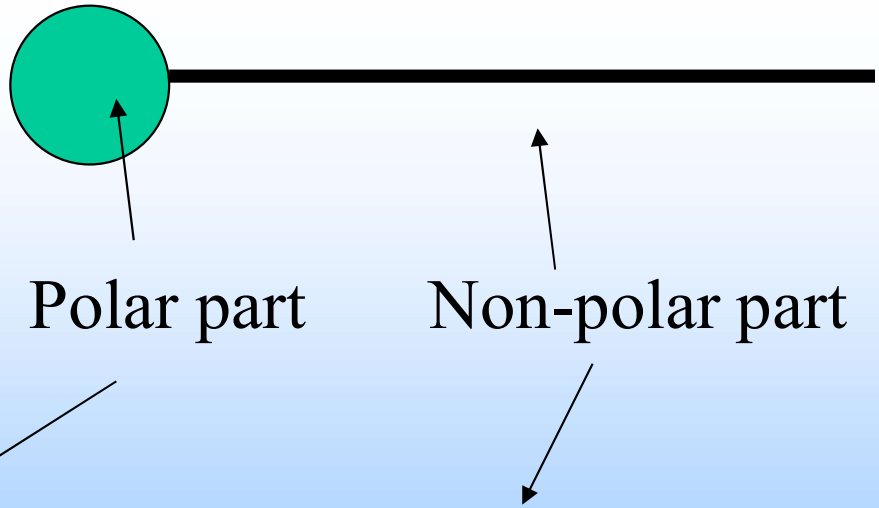
Phase interface between liquid and solid - interfacial tension is reduced.

Surfactants and their properties

Surfactants have an asymmetric, dipolar character. Their molecule consists of two parts:

- a hydrophobic, i.e. non-polar part, which consists of a long carbon chain .

- a hydrophilic, i.e. polar part, which is an ionogenic or non-ionogenic group

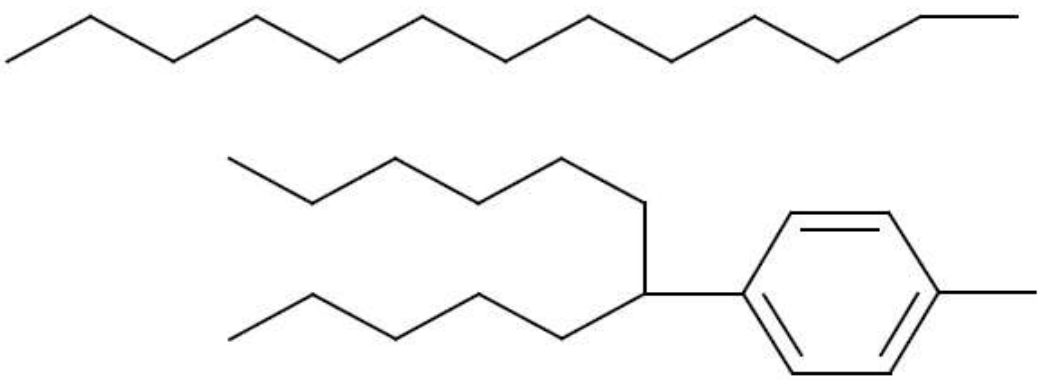


$NaSO_3$- CH_2 -CH_2 -CH_2 -CH_2 -CH_2 -CH_2 -CH_2 -CH_2 – CH_3

Surfactants

basic types of hydrophilic and hydrophobic groups

Hydrofob



$CF_3CF_2CF_2CF_2CF_2CF_2CF_2CF_2CF_2CF_2CF_2$—

Hydrofil

—COONa

—SO_3Na

—$N^+(CH_3)_4$ Cl^-

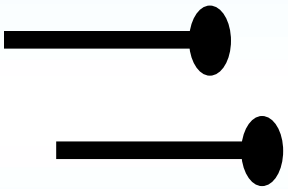
Surfactants

Higher concentration results in adsorption

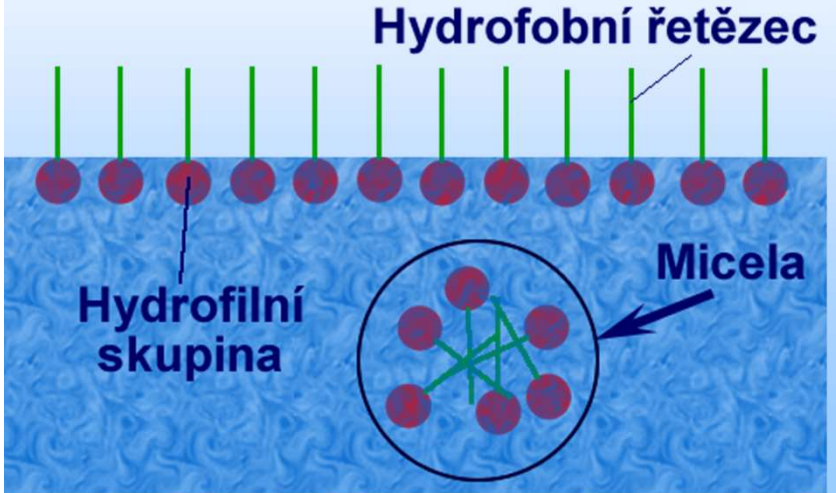
limited solubility

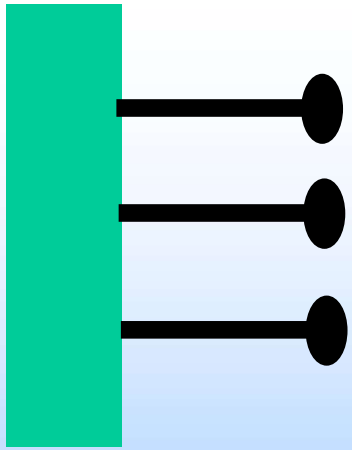
On other surfactant molecules

On phase interface



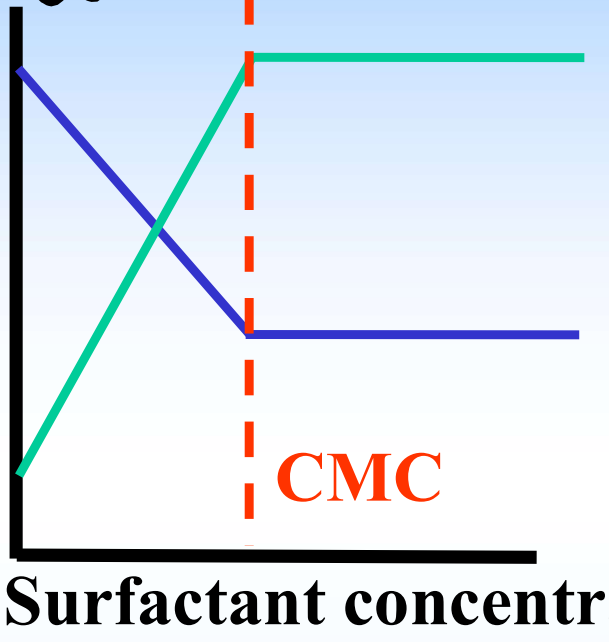
Micelle





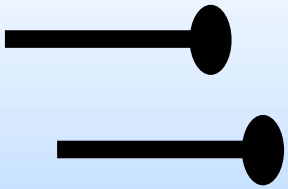
Interphase tension reduction

Surfactants



CMC = critical micellar concentration

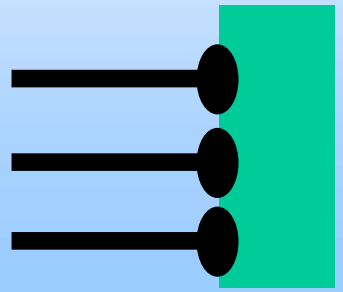
Higher concentration results in adsorption



Low solubility

On other molecules of surfactants

On interface



Surfactant

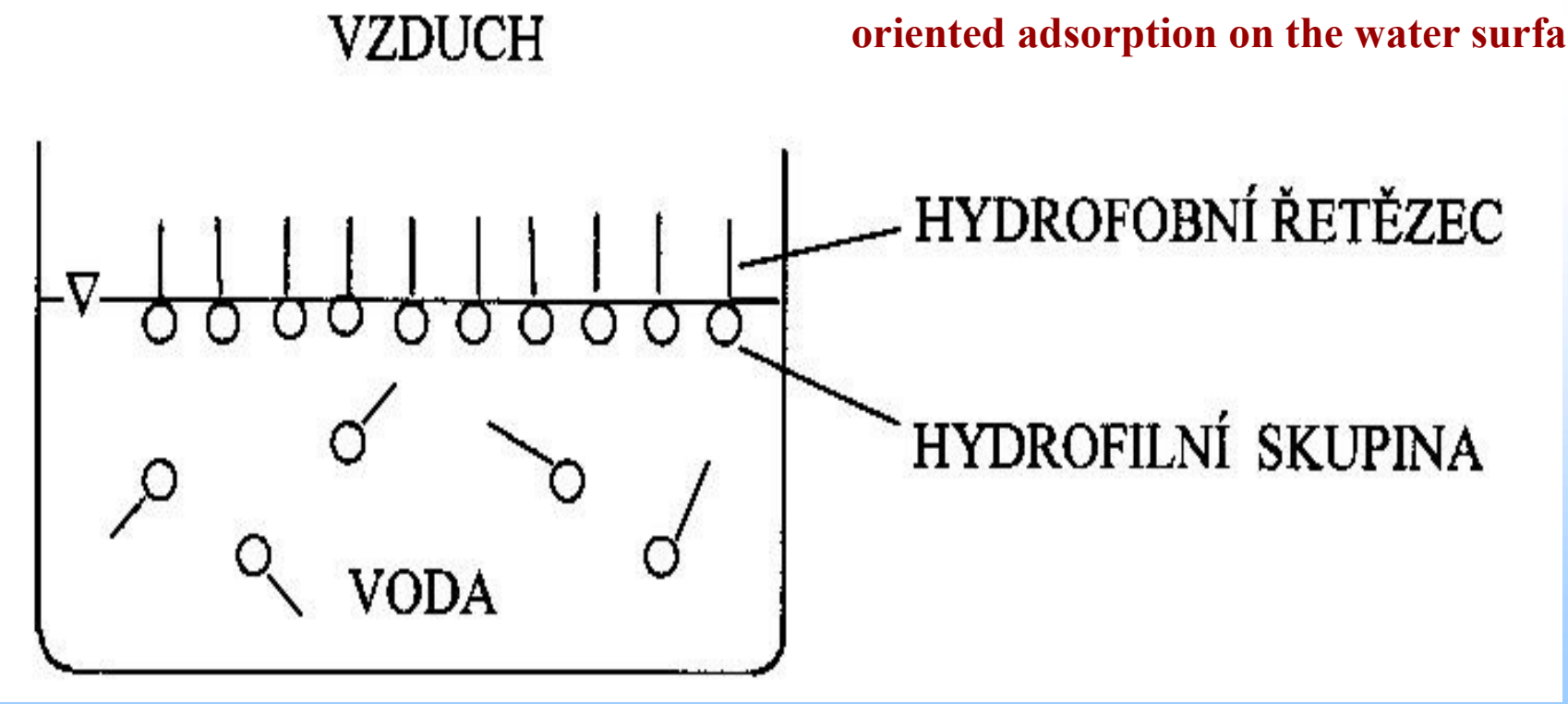
Dosage of detergent:
Little - unwashed fabric
Too much - washing does not remove all

But also:
too much detergent = more foam = water/foam penetrating the electronics of the washing machine = destroying the washing machine

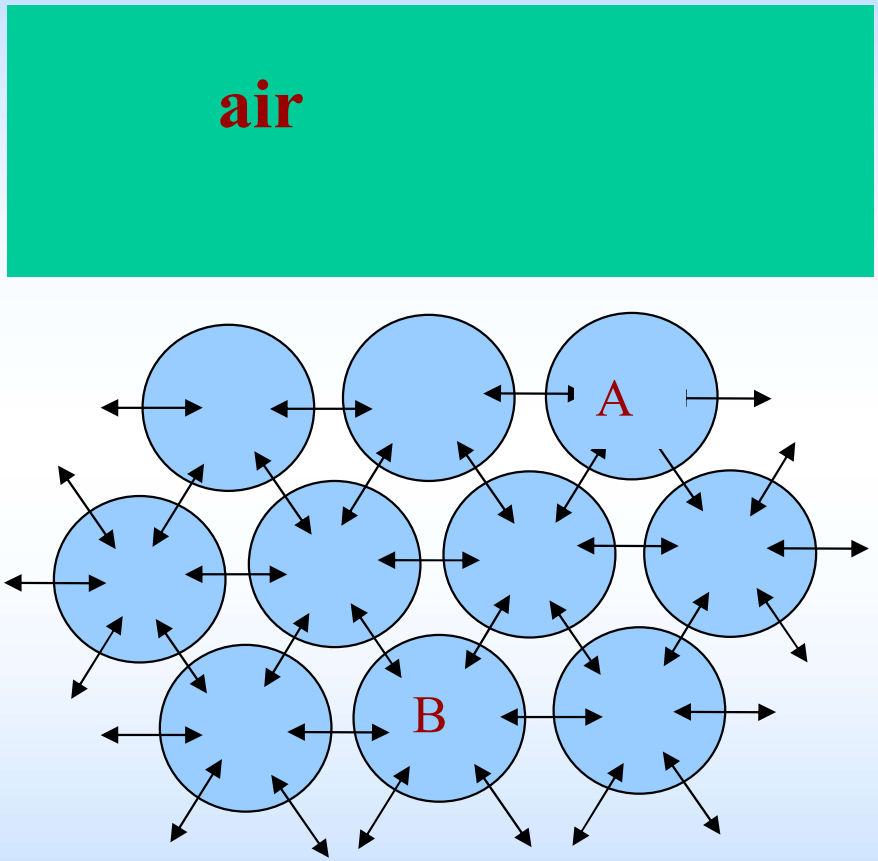
Surfactants

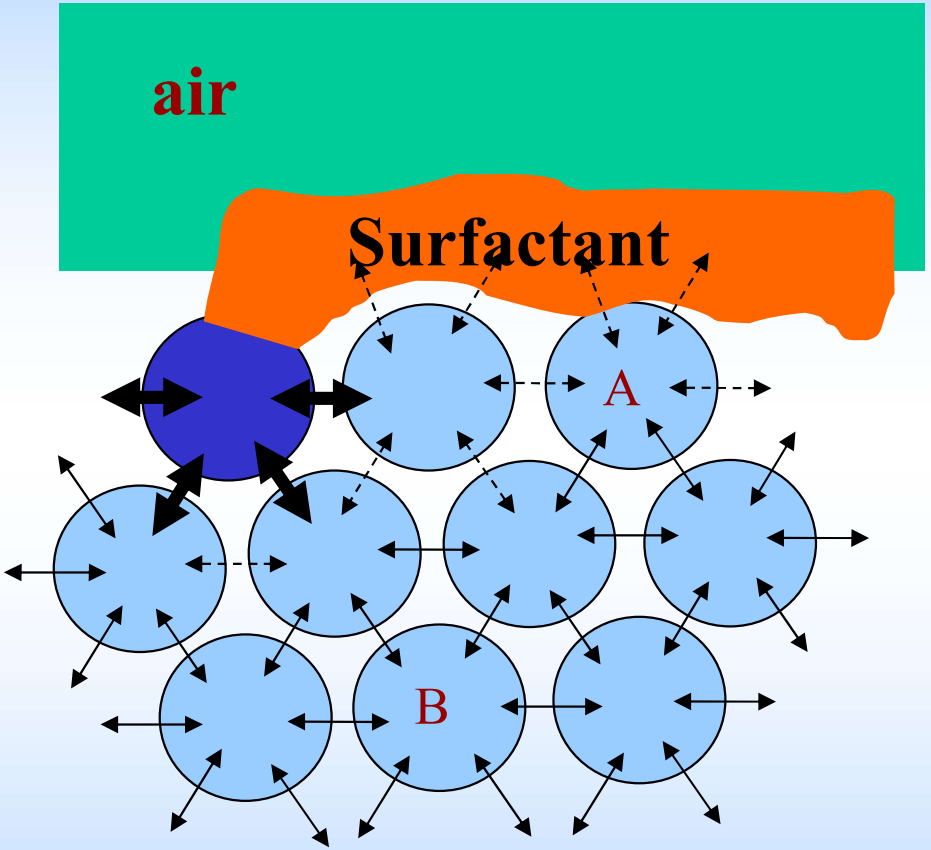
oriented adsorption

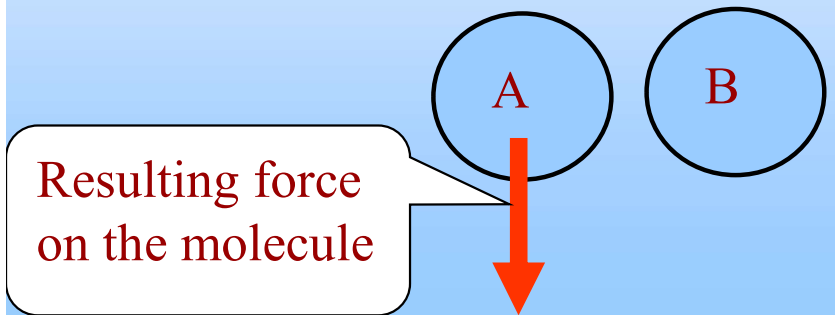
Surfactant molecules adsorb at the phase interface and form a monomolecular oriented surface film

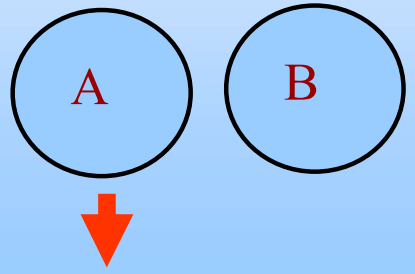


Surface tension and Surfactants









Low surface tension !!!

Properties of surfactants

Solubilization - dissolution of slightly water-soluble substances in aqueous solutions of Surfactants

Wettability - the ability of a liquid to disperse on the surface of a solid

Foaming ability - the formation of foam

Detergency - the ability to remove impurities from a solid substrate and convert them into a solution or dispersion

Emulsifying ability - formation of an emulsion - a dispersion system of two immiscible liquids

SOLUBILISATION

Solubilization - dissolution of slightly water-soluble substances in aqueous solutions of Surfactants

Solubilization - the ability to draw insoluble or sparingly soluble substances in water between hydrophobic chains and thus convert them into solution.

Factors affecting solubilization:

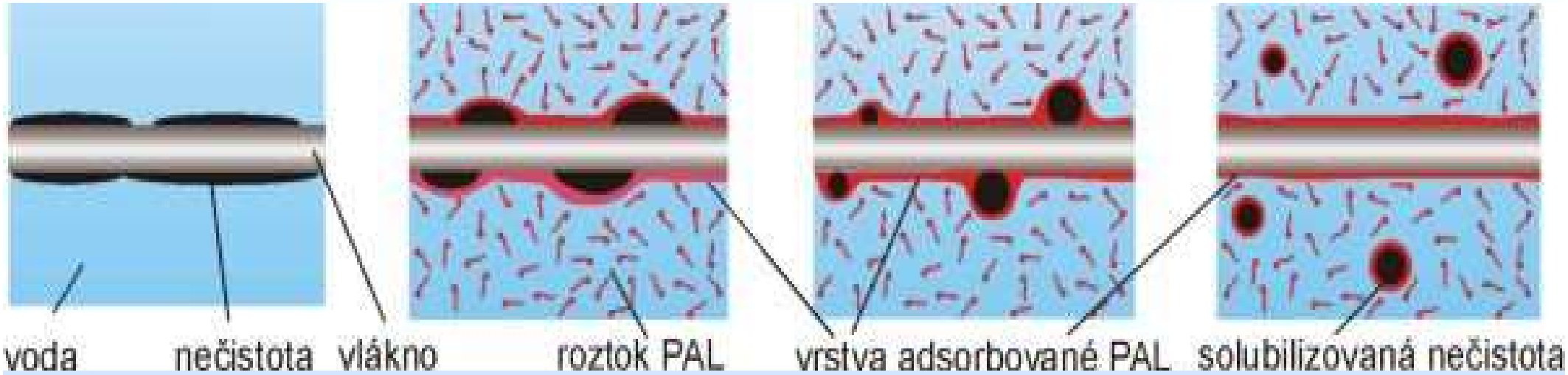
*** Surfactant concentration - solubilization occurs only after the CMC value is reached**

*** temperature - solubilization increases with increasing temperature**

*** composition of the solubilized substance**

DETERGENCE

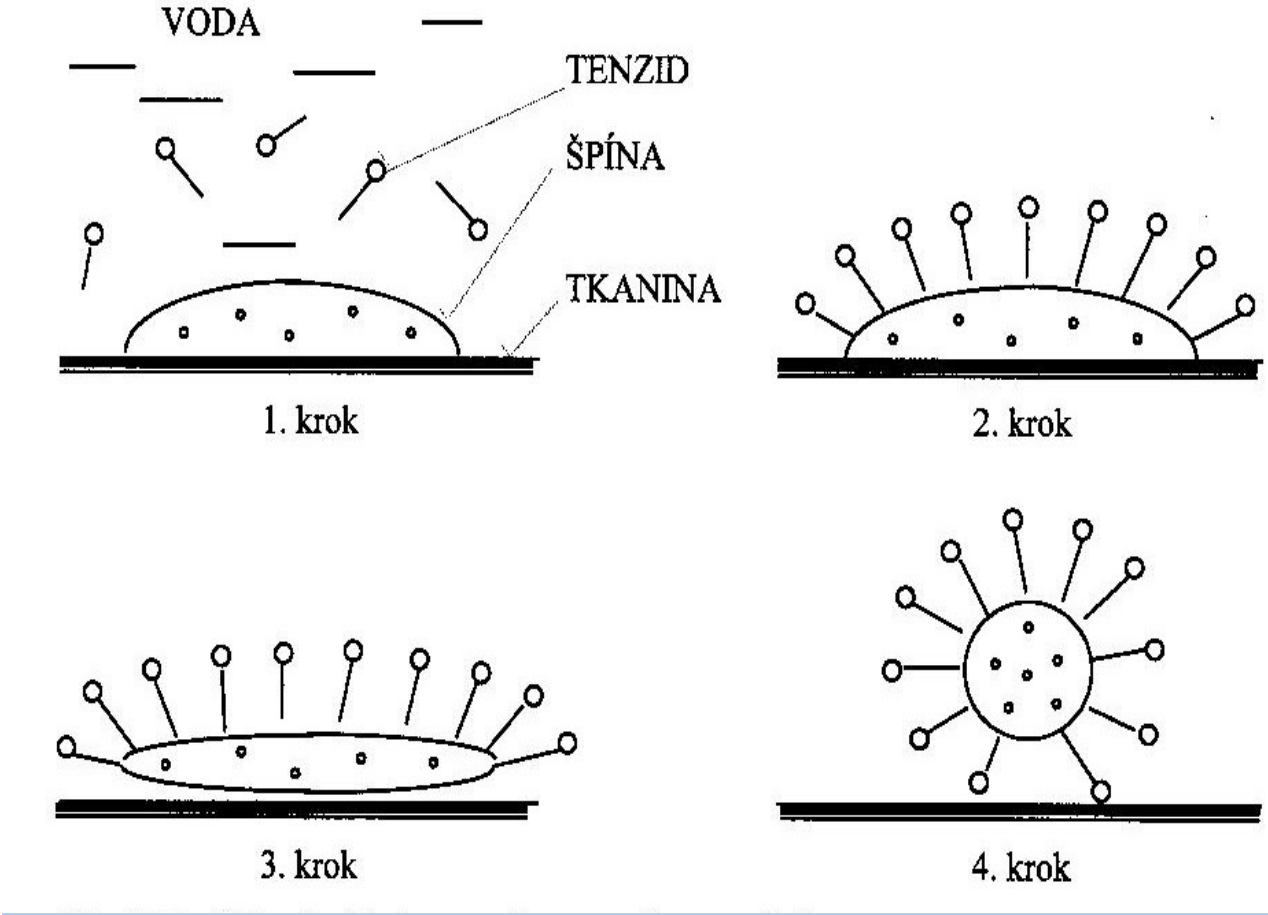
The impurities are gradually packed and released from the surface. As they move into solution, the released impurity particles are stabilised by solubilising them into micelles, which have a hydrophilic surface and cannot attach back to the clean solid surface.



The process of removing dirt from a textile fibre by the action of a detergent

DETERGENCE

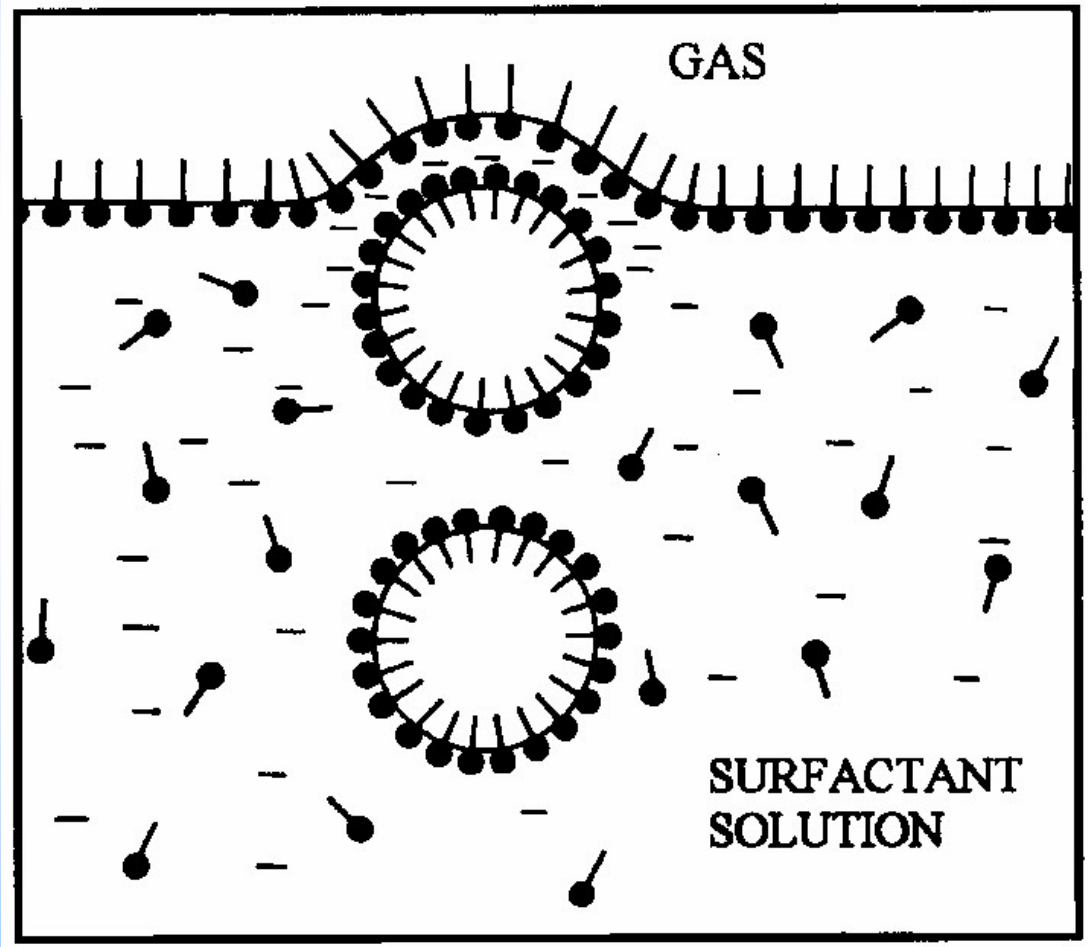
oriented adsorption - dirt removal



Primary phase
impurity release

Secondary phase
Prevention of redeposition (redeposition)

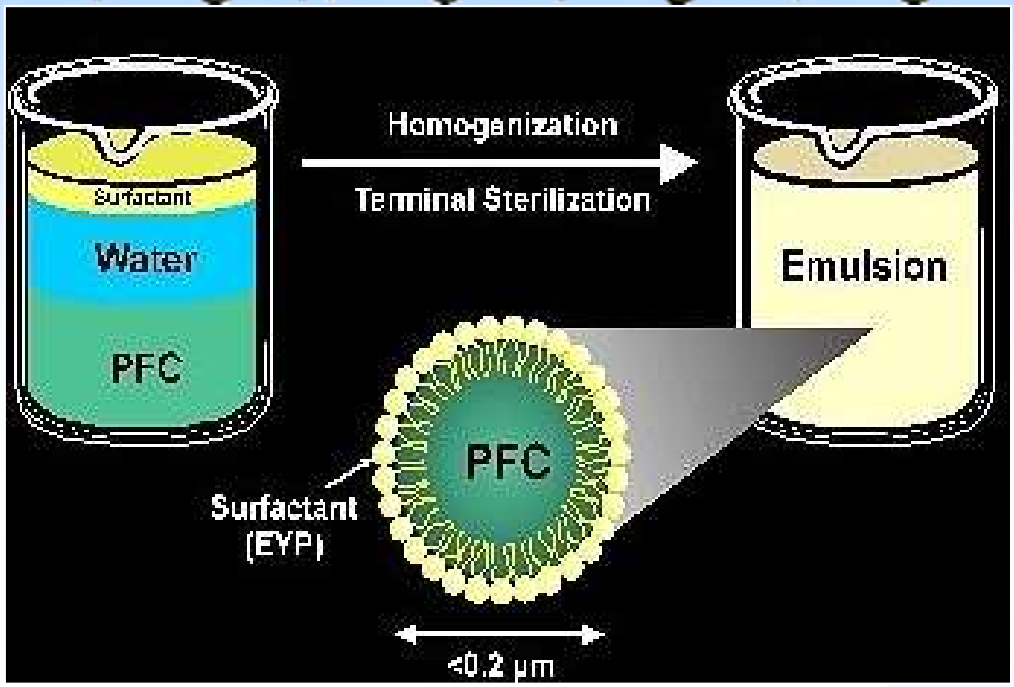
FOAMING ABILITY OF surfactantS

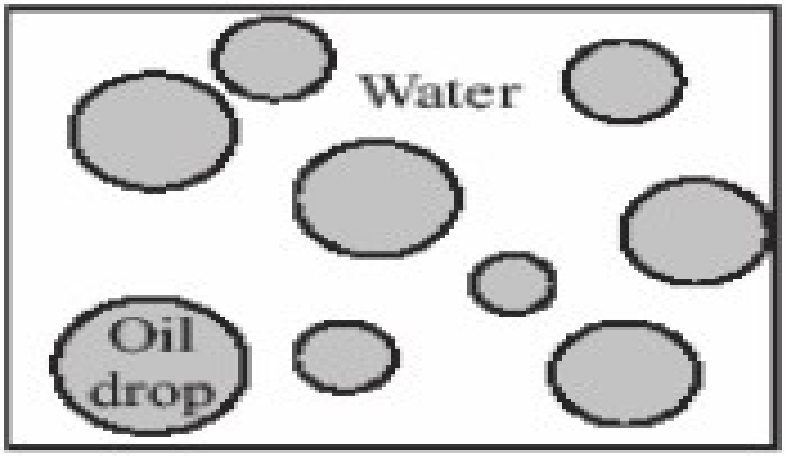


Foam:
- dispersion of a gas in a liquid
- pure liquids do not form a stable foam
- **Surfactant** is needed

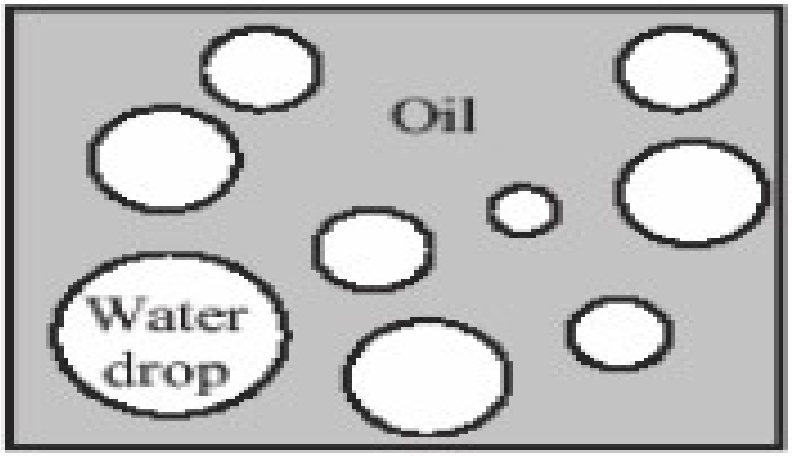
EMULSIFYING ABILITY OF Surfactant

Preparation of perfluorocarbon emulsion - for oleophobic treatment





Oil-in-water emulsion



Water-in-oil emulsion

Surfactants **and their properties**

According to the ionic character, we divide **Surfactants** into ionogenic (ionic) and non-ionogenic (non-ionic). Ionogenicity is distinguished by the electric charge that remains on the organic (functional) part of the surfactant molecule after its dissociation in water.

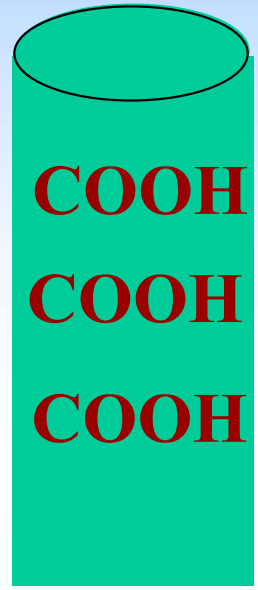
If the hydrophobic ion has a negative charge, it is an anionic (anionic) preparation; if it has a positive charge, it is a cationic (cationic) preparation.

Ionogenicity determines:

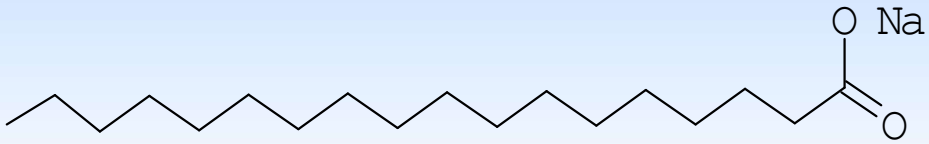
* the combinability of the preparations
*interaction with fibres (they are anionic)

Surfactants

Electrical charge of the fibre

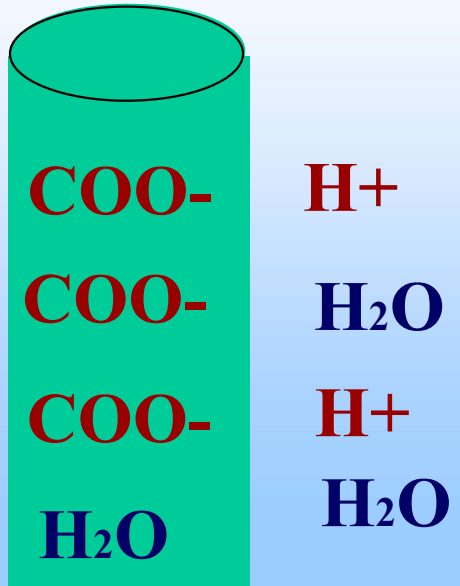


air air



Soap = anionic Surfactant

What will a surfactant molecule do in the region of the fiber ??



H_2O H_2O H_2O

H+ H+ H_2O H_2O

Anionactive (anionic)

Cationactive (cationic)

Non-ionogenic (non-ionic)

CLASSIFICATION OF surfactantS

Classification of Surfactant - based on the ionogenicity of the polar group, i.e. according to their dissociation in water

Anion-active (anionic) Surfactants
Cationactive (cationic) Surfactant s
Ampholytic (amphoteric) Surfactants
Non-ionogenic (non-ionic) Surfactants

CLASSIFICATION OF surfactant

1. **Anion-active (anionic) Surfactants (65% of production)**

The surface activity carrier is the anionic part of the surfactant molecule, which has a negative charge.

R - COONa salts of carboxylic acids

Např. $C_{17}H_{35}COONa$ $C_{17}H_{35}COO^- + Na^+$

anion

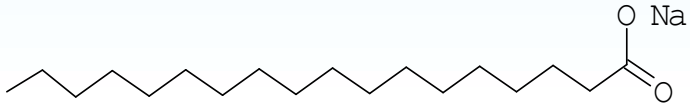
Soap

Soap

$C_{17}H_{35}$ — COONa sodium stearate

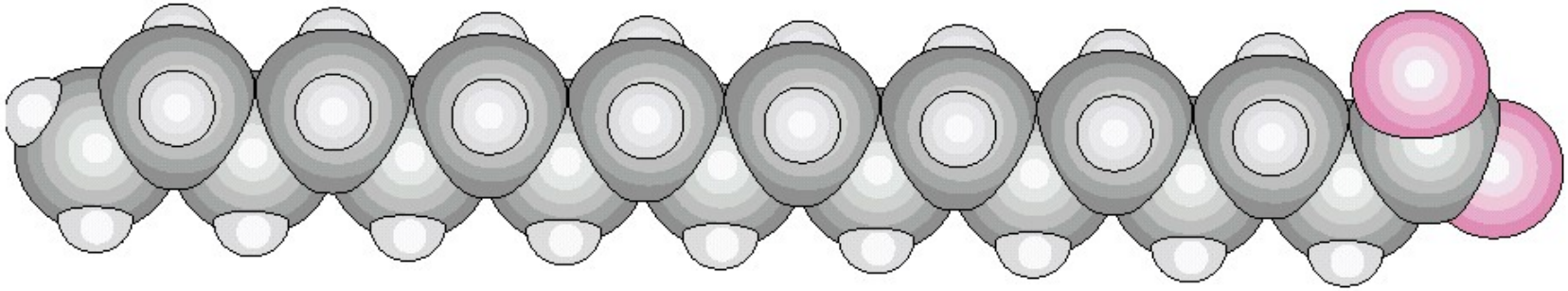
/\/\/\/\/\/—COO^- Na^+

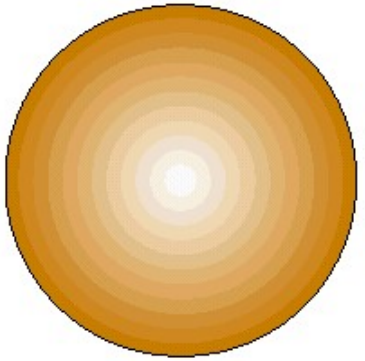
hydrophobic chain hydrophilic group



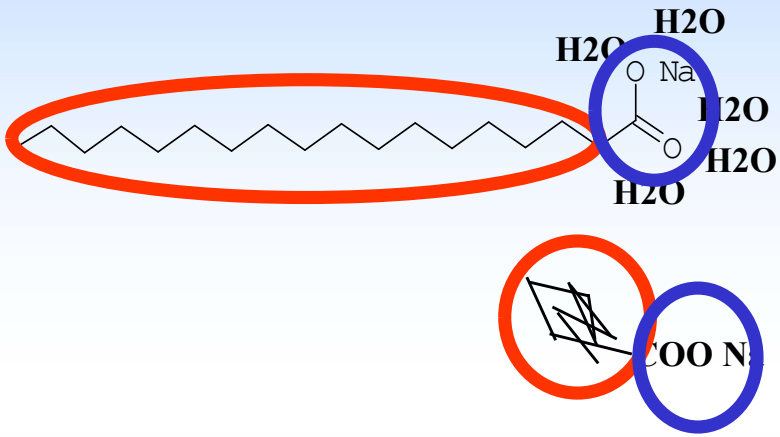
$CH_3(CH_2)_{16}-$ COO^- Na^+

hydrocarbon tail ionic head





Soap



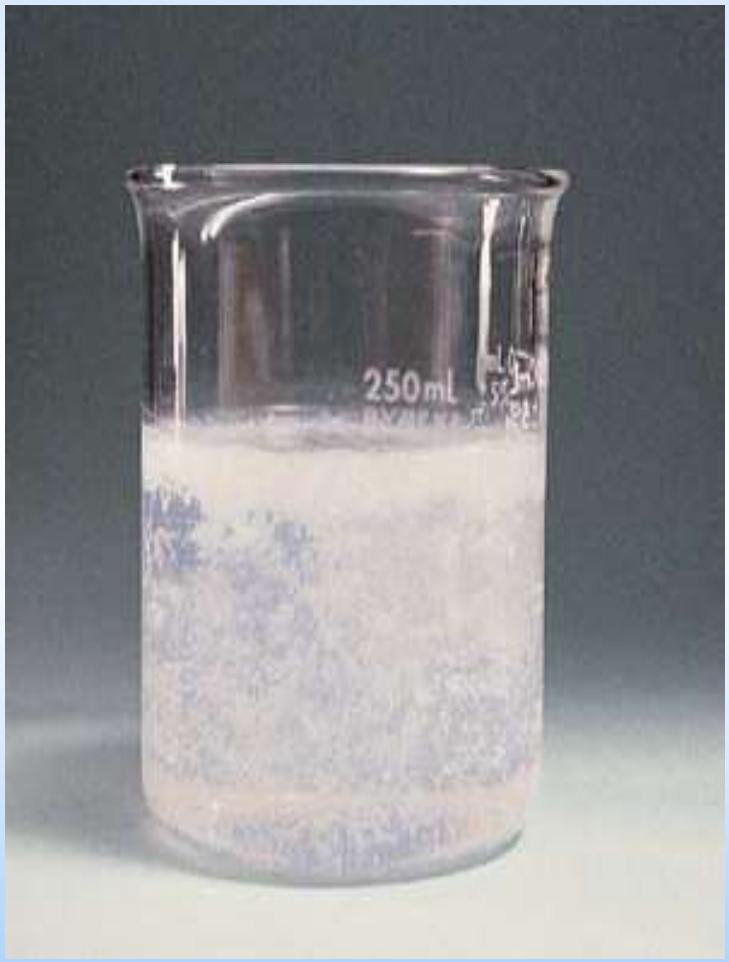
Low solubility, adsorption and aggregation tendency

Macroscopic 2D model: oil in soup

Soap

Soaps are unstable in acidic conditions and in hard water.

soap



Soap in hard water

Soap in acid water

Soap

Composition and properties of detergents

soaps - sodium salts of higher fatty acids

- high washing power

- dissociate and hydrolyse in aqueous media

- completely biodegradable

- precipitate in hard water containing Ca^{2+} and Mg^{2+} → water must be softened:

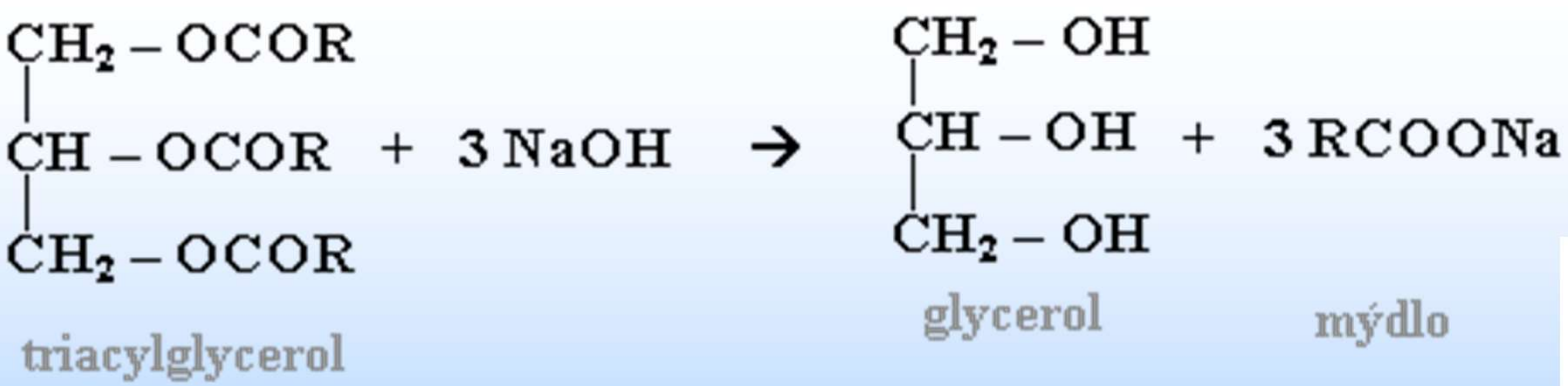
: precipitation with Na_2CO_3 or Na_3PO_4 phosphate

: elimination by sequestering agents

other surfactants - soluble in hard water

SAPONIFICATION OF FATS AND WAXES

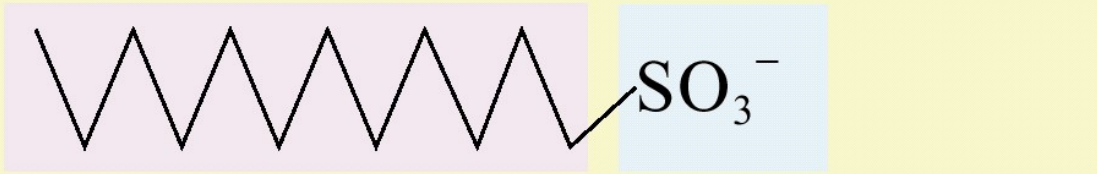
Fats - esters of glycerol with higher fatty acids
Waxes - esters of higher alcohols with higher fatty acids, more stable than fats



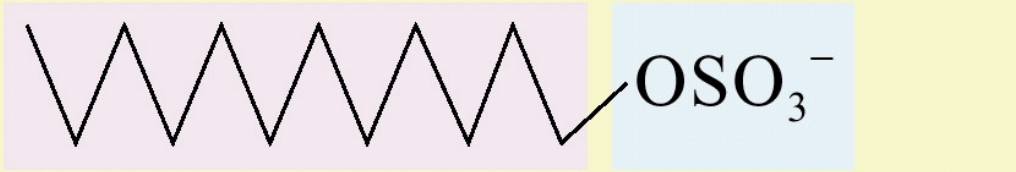
fat / oil

Other anionic surfactants

$R - SO_3Na$
sulfonate



$R - O - SO_3Na$
Sulfates



e.g. $CH_3(CH_2)_{11}$—⬡—SO_3^- Na^+

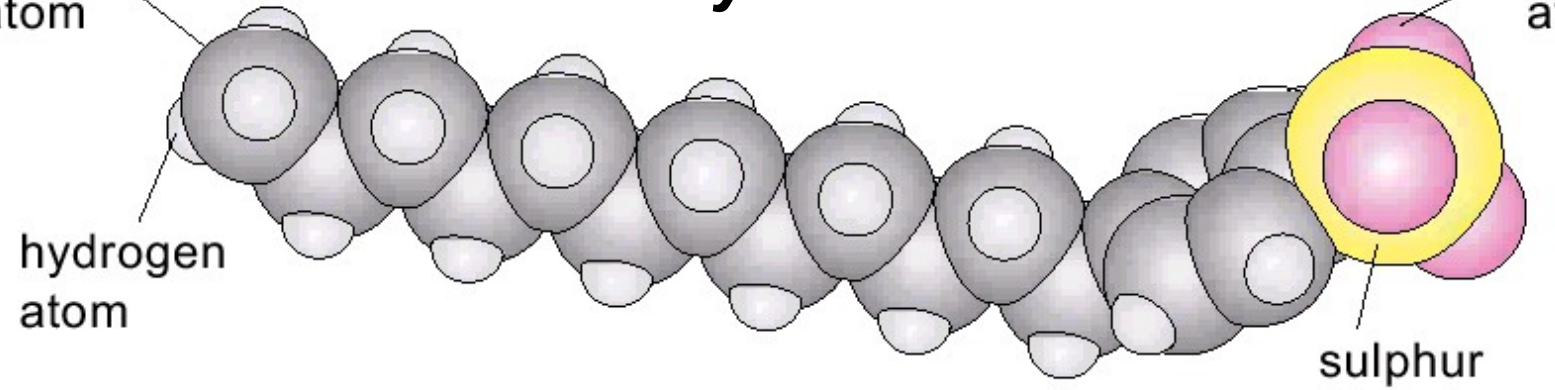
hydrocarbon tail — ionic head

sodium ion

carbon atom

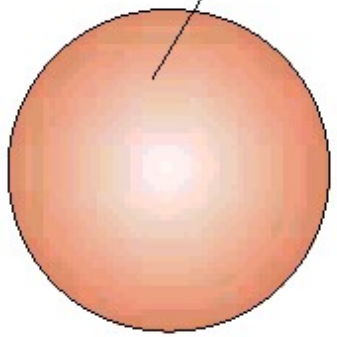
sodium alkylbenzene sulfonate

oxygen atom



hydrogen atom

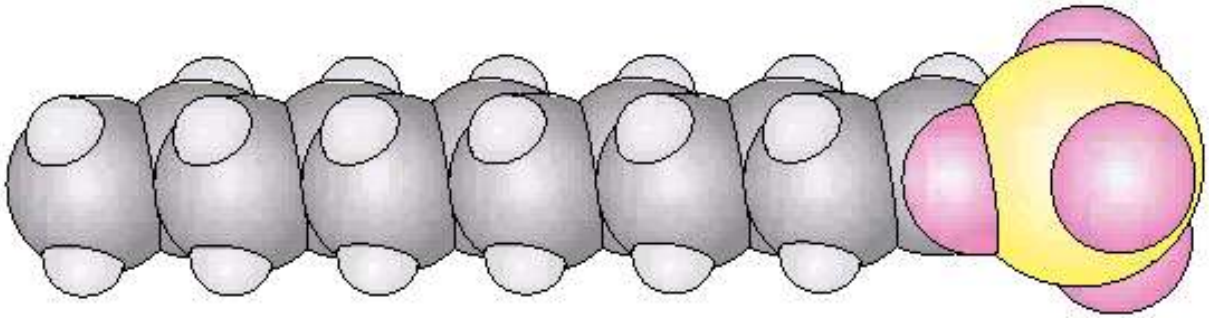
sulphur atom

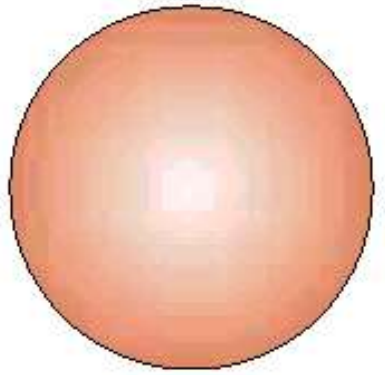


e.g. $CH_3(CH_2)_{11}$ — O – SO_3^- Na^+

hydrocarbon tail — ionic head

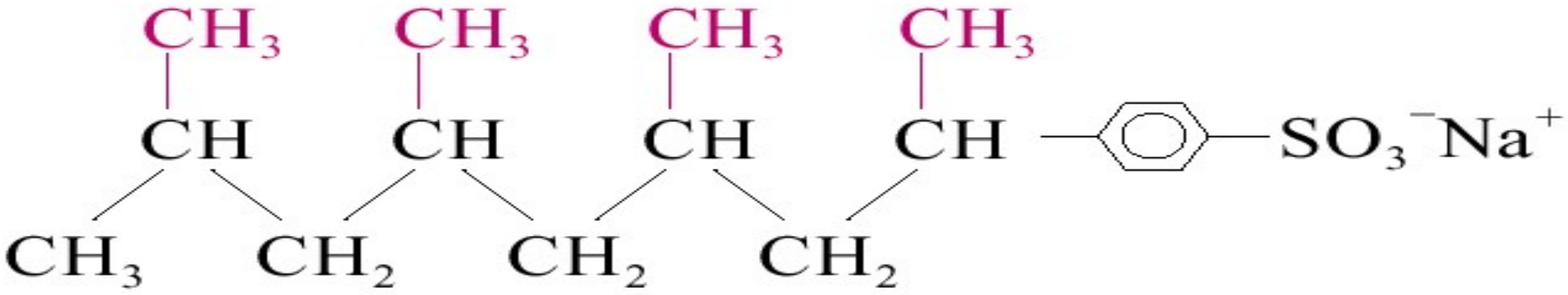
Sodium alkyl sulphate





Degradability of surfactants

(biodegradable)

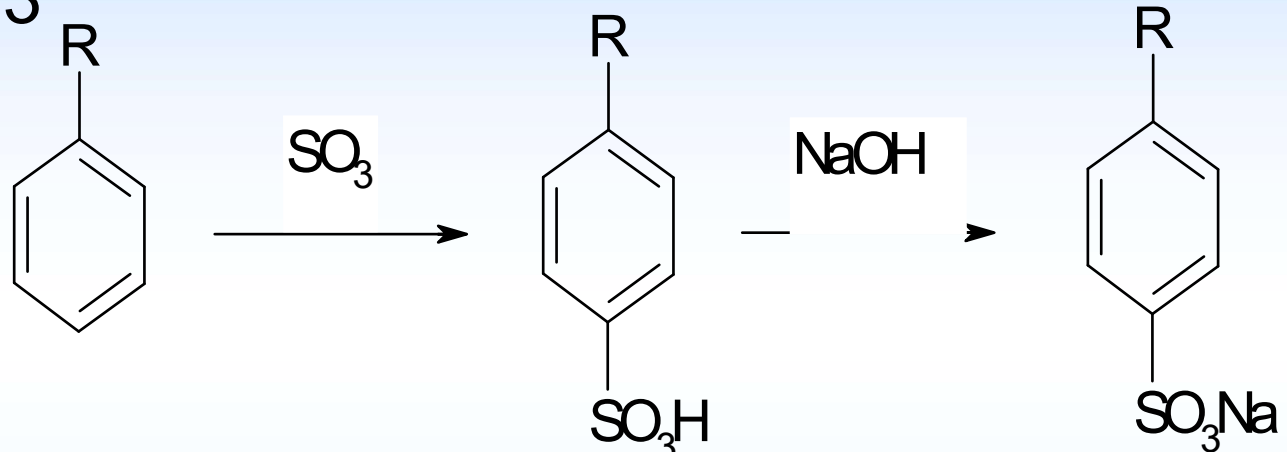


(non-biodegradable)

MANUFACTURE OF surfactantS

alkylbenzen
R = 10 - 13

sodium alkylbenzene sulfonate



$CH_3(CH_2)_{11}$–C$_6$H$_4$– $\xrightarrow{\text{conc. } H_2SO_4}$ $CH_3(CH_2)_{11}$–C$_6$H$_4$–SO_3H

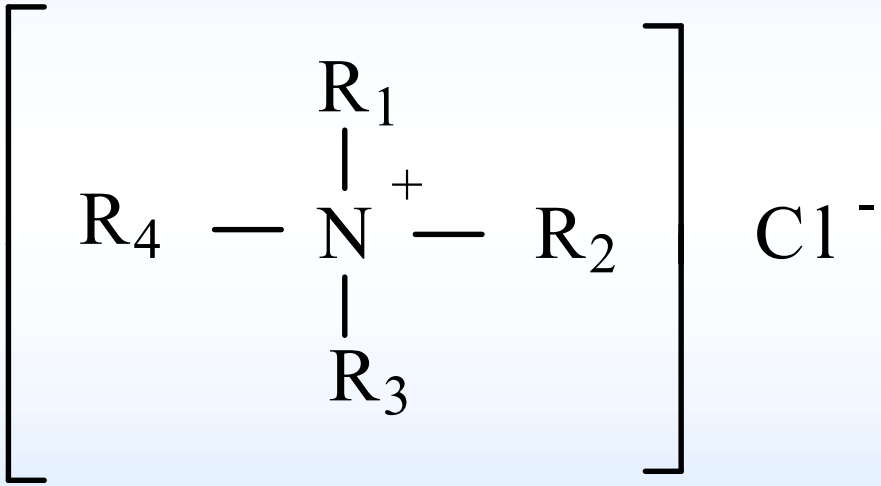
(from petroleum industry)

$\xrightarrow{NaOH}$ $CH_3(CH_2)_{11}$–C$_6$H$_4$–SO_3^- Na^+

sodium alkylbenzene sulphonate
(a synthetic detergent)

CLASSIFICATION OF surfactants

2. Cationic surfactants (10% of production)
The carrier of the surface activity is an organic cation.



quaternary ammonium salt

Use: microbial, softening and antistatic agents.
Cationic surfactants do not have detergency.

CLASSIFICATION OF surfactantS

3. Ampholytic (amphoteric) surfactants (5% of production)
They have a basic (amino) and an acidic (carboxy) group in the molecule.

$B^+ - R - K^-$

In an acidic environment

$$B^+ - R - K^- + H^+ \longrightarrow B^+ - R - K$$

cationic

In an alkaline environment

$$B^+ - R - K^- + OH^- \longrightarrow B - R - K^-$$

anionic

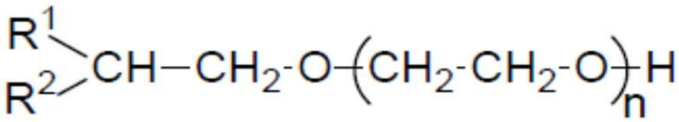
CLASSIFICATION OF surfactantS

4. Non-ionogenic (neonic) surfactants (30% of production)

do not dissociate in water

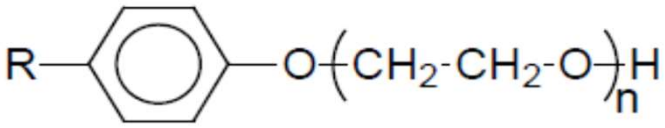
R — O (CH2 — CH2 — O)n H alkylpolyglycol ether

have very good dispersing and emulsifying effects



$R^1+R^2=C_{8-16}$ n=2-4

Alkyletoxyláty



$R=C_{8-12}$ n=5-7

Alkylfenoletoxyláty

AE = alkyl ethoxylate

Ethoxylation: alcohol + ethylene oxide (oxirane)

ROH + n C2H4O → RO(OC2H4)nH

surfactant consumption

Tenzid	Spotřeba (Mt)
Mýdlo	**9,0**
Lineární alkylbenzensulfonáty (LAS)	2,9
Alkylétersulfáty (AES)	0,8
Alkylsulfáty (AS)	0,6
Celkem výše uvedené syntetické anionické	**4,3**
Alkyletoxyláty (AE)	1,1
Nonylfenoletoxyláty (NPE)	0,6
Celkem výše uvedené neionické	**1,7**
Kationické kvarterní amoniové sloučeniny	**0,5**
Amfoterní	**0,1**
Jiné*	2,4
Celkem	**18,2**

APPLICATION OF surfactantS IN TEXTILE PROCESSES

Anionic and neonic surfactants - most used in textile wet processes.

Nonionic surfactants have some advantages: stability in pH, stability in hard water, compatibility with anionic and cationic agents.

Cationic surfactants - relatively little use due to limited compatibility and cost, not suitable for washing

Amphoteric surfactants - little use

surfactantS IN DETERGENTS

Anionic surfactants: LAS (linear alkyl benzene sulfonates)
AS (alkyl sulphates)

$R\text{-}C_6H_4\text{-}\ SO_3Na$	$R = C_{10\ -\ 13}$	LAS
$R\text{-}CH_2\text{-}O\text{-}SO_3Na$	$R = C_{11\ -\ 17}$	AS

Neonic surfactants: EA (ethoxylated alcohols)

$R\text{-}\ (CH_2\text{-}CH_2\text{-}O)n\ -\ H$	$R = C_{8\ -\ 18}$ $n = 3\ -\ 15$	EA

HLB

surfactants can be classified according to the HLB (hydrophilic-lipophilic balance) value. This auxiliary value characterises the ratio of the influence of the hydrophilic and lipophilic parts of the surfactant molecule on its properties. It is proportional to the ratio of the solubility of the surfactant in the aqueous and oil phase. The HLB value is expressed as a dimensionless number in the range 0-40, according to which surfactants can be divided into application groups.

HLB 1-3 defoamers
HLB 3-6 emulsifiers V/O (water in oil)
HLB 7-9 wetting agents
HLB 8-18 O/V emulsifiers
HLB 13-15 detergents (applies mostly to dispersion of dirt)
HLB 15-40 solubilisers (mostly refers to general dispersion)

1 (oleic acid) and 40 (sodium lauryl sulfate).

HLB

HLB values can be calculated according to various empirical formulas and are expressed as numbers. The most commonly used relationship is based on the contributions of individual groups in the molecule:

HLB = 7 + Σ (individual group contributions)

group	HLB		group	HLB
$–SO_4Na$	38,7		–CH–	-0,475
–COOK	21,1		$–CH_2–$	-0,475
–COONa	19,1		$–CH_3$	-0,475
≡N	9,4		=CH–	-0,475
–COOH	2,1		$–CF_2–$	-0,87
–OH	1,9		$–CF_3$	-0,87
–O–	1,3		$–(CH_2CH_2O)–$	0,33
			$–(CH_2CH_2CH_2O)–$	-0,15

Davies J.T., Rideal E.K.: *Interfacial Phenomena. 2nd Ed.* Academic Press, London 1963

Cloud point

=„Cloud point“

The cloud point, the temperature at which turbidity forms in a solution of a non-ionogenic surfactant, is one of the important characteristics of a surfactant

Above the cloud point, surfactants precipitate out of solution - turbidity (micelles) is formed

thermal dehydration of the oxyethylene groups of the surfactant

As the amount of polyoxyethylene groups increases, it becomes more hydrophilic, more soluble in water and its cloud point increases.

Evolution of detergent formulation

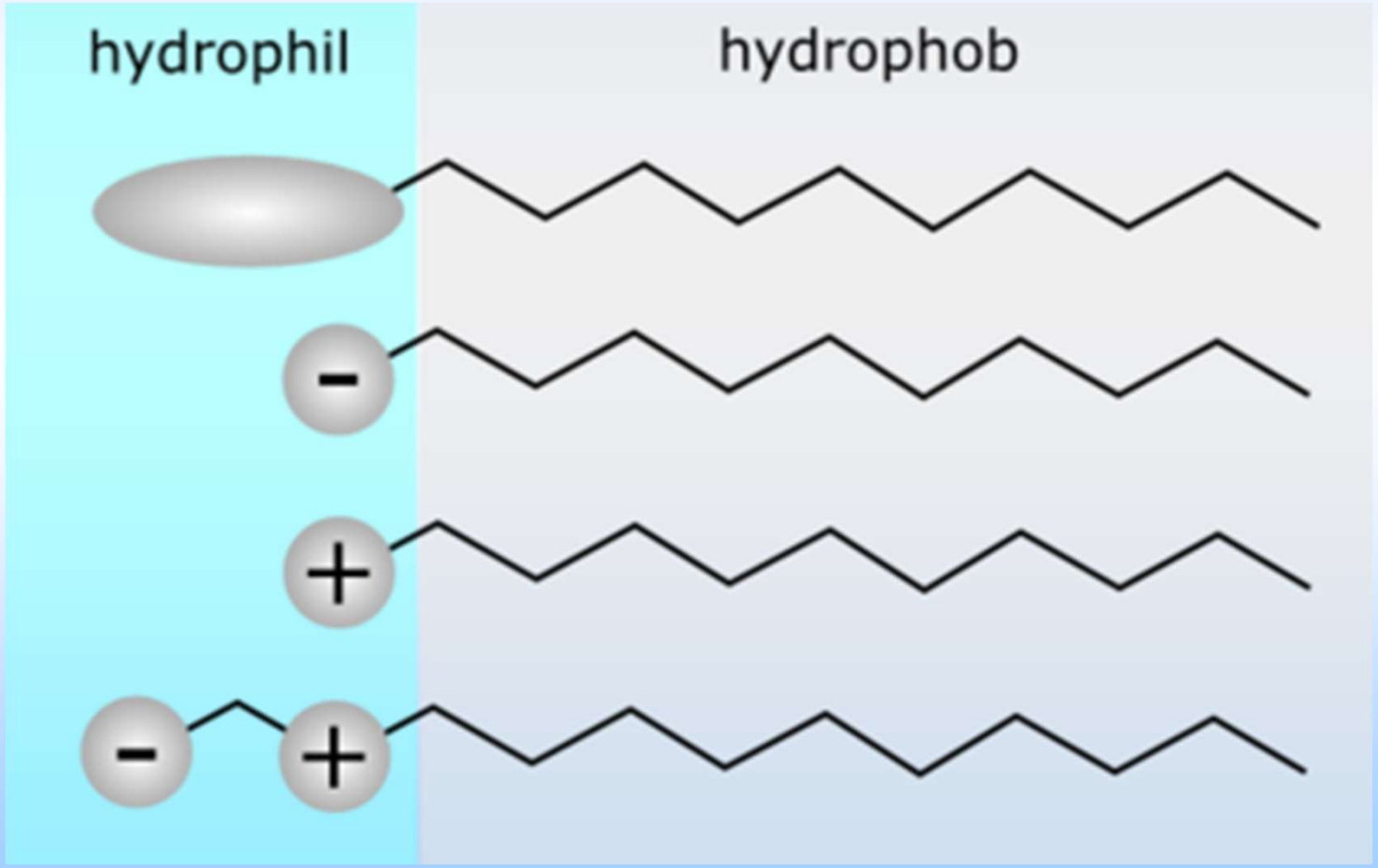
Složení práškových pracích prostředků

	1907	1953	1970	1983	1987	2000	2007
Mýdlo - Na	32	44	4	3	2	2	2
LAS - Na			7	8	8	6	6
AE			2	3	5	7	7
Polymer - Na				1	4	4	4
STP		10	40	24	20	20	0
Zeolit A				18	24	20	20
Dikřemičitan Na							10
Uhličitan Na	24	12	0	5	10	15	15
Perboritan Na	9	6	27	22	20	20	
Peruhličitan Na							16
TAED				1	2	3	3
Enzymy			1	1	1	2	2
			Automatické pračky →				

AE – Ethoxylated alcohols **TAED – peroxide activator, 40°C !**

LAS – linear alkyl benzene sulfonate **STP - $Na_5P_3O_{10}$**

A little test...



Ionogenicity ?

A little test...

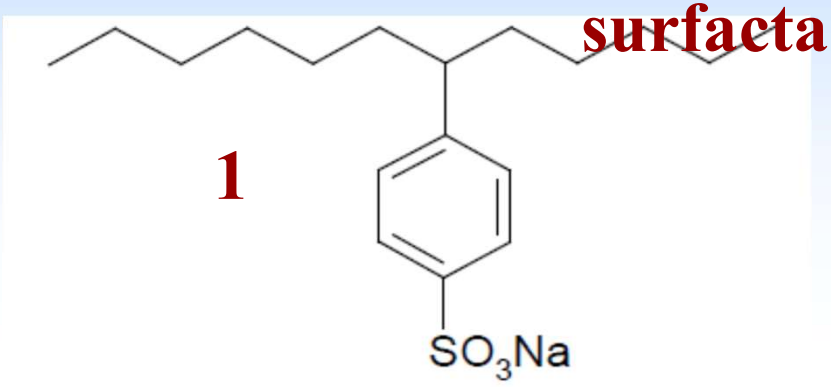
You will recognise these surfactants?

Which is:

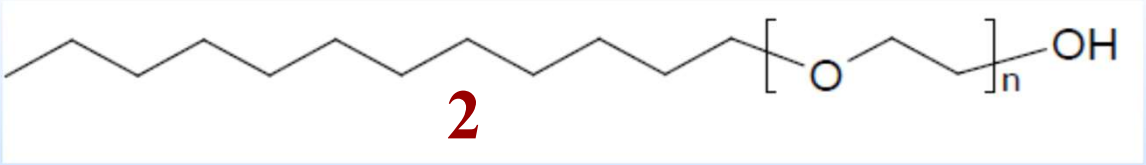
Soap?

AE - alkyl ethoxylate ?

LAS - linear alkyl benzene sulfonate ?



1



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Ionogenity ?

3

Thank you for your attention!