DETERGENTS

Detergents The main surfactants used in detergents and personal care products

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Résumé : Les tensioactifs sont des molécules amphiphiles. Ils peuvent être anioniques, cationiques, non ioniques ou amphotères. Ce sont les principaux ingrédients rencontrés dans les détergents et les produits d'hygiène corporelle. Ils doivent répondre à des exigences de plus en plus strictes en matière de biodégradabilité et doivent être fabriqués de plus en plus à partir de matières premières renouvelables. Les tensioactifs anioniques, en particulier les sulfonates d'alkylbenzène, sont actuellement les tensioactifs les plus utilisés dans les détergents et les produits d'hygiène corporelle. Parmi les tensioactifs non ioniques, ceux possédant des motifs oxyéthylénés sont les plus courants et ceux issus entièrement des matières premières renouvelables, tels que les alkylpolyglucosides (APG), joueront probablement un rôle important dans le futur.

Mots-clés : détergent, produit d'hygiène corporelle, tensioactif, amphiphile, anionique, cationique, non ionique, amphotère.

Summary : Surfactants are amphiphile molecules. They can be anionic, cationic, nonionic or amphoteric. They are among the main ingredients encountered in detergents and personal care products. They have to meet increasingly more stringent requirements of biodegradability and come from renewable raw materials. Anionic surfactants, particularly alkylbenzene sulfonates, are, at the present time, the most widely used surfactants in detergents and personal care products. Among the nonionics, those with ethyle oxide groups are the most common and those coming from entirely renewable raw materials, such as alkyl polyglucosides (APG), are expected to play an important role in the future

Keywords : detergent, personal care product, surfactant, amphiphile, anionic, cationic, nonionic, amphoteric.

ARTICLE

Surfactants are among the most essential and important ingredients encountered in laundry detergents, dishwashing detergents, cleaning products, cosmetic hair-care and personal care products which represent the main applications of these compounds. The detergents and personal care products use nearly 60% of all surfactants. These compounds have a distinct toxic activity on aquatic organisms on account of their surface activity. Their function is to remove soil (oil, grease, dust, particles...) from solid surfaces and to keep it in suspension in the wash solution, preventing redeposition on clothes. The detergency is essentially governed by two factors: the solubility of the surfactants and their critical micelle concentration (CMC).

The choice of a surfactant for a laundering product depends on numerous factors such as wash temperature, type of textile, foam level desired, builder used (phosphate or non-phosphate), the product form (liquid, conventional, concentrated powder) and the process of manufacture. In addition, surfactants have to meet increasingly more stringent requirements in regard to environmental compatibility (biological degradability and ecotoxicity).

The present article deals with the surfactants mainly used in detergents and personal care products.

Classification of surfactants [1-3]

A surfactant molecule consists of two parts. One part is hydrophobic (insoluble in water) and the other one is hydrophilic (soluble in water). These molecules are highly active in the interfaces between air and water or oil and water. They have a number of names including surface active agents, detergents, surfactants or amphiphiles. There are four main classifications of surfactants: anionic, nonionic, cationic and amphoteric surfactants.

Anionic surfactants

When the polar group, which is linked in a covalent manner with the hydrophobic part of the surfactant, carries a negative charge ($-COO^-$, $-SO_3^-$, $-SO_4^-$) the surfactant is called anionic: soaps, alkylbenzenesulfonates, fatty alcohol sulfates... are all anionic active surface agents.

Cationic surfactants

When the polar group carries a positive charge ($-NR_1R_2R_3^+$), the surfactant is cationic: dimethyl distearyl ammonium chloride is an example of this category.

Nonionic surfactants

Nonionic surfactants have a polar group that cannot be ionized in an aqueous solution. The hydrophobic part consists of the fatty chain. The hydrophilic part contains non ionizable atoms of oxygen, nitrogen or sulfur; solubility is obtained as a result of the formation of hydrogen bonds between the water molecules and certain functions of the hydrophilic part, for example the ether function of the polyoxyethylene (hydration phenomenon).

In this category, we find mainly derivatives of polyoxyethylene (POE) or polyoxypropylene (POP), but sugar esters and alkanolamides can also be included.

Amphoteric surfactants

Amphoteric surfactants are components with a molecule forming a dipolar ion. Cetylamino-acetic acid, for example, produces the two following forms in an aqueous environment:

$C_{16}H_{33} - NH_2^+ - CH_2 - COOH$

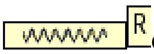
Cationic
in acidic medium

$C_{16}H_{33} - NH - CH_2 - COO^-$

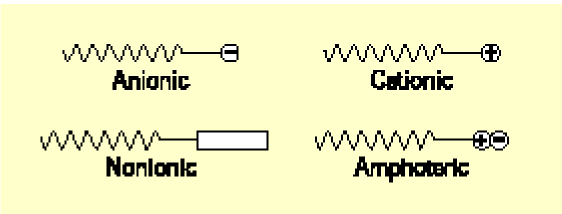
Anionic
in alkaline medium

In all of these molecules, the hydrophobic part is made up of an alkyl or fatty chain. This is represented by:

$CH_3 - CH_2 - CH_2 - CH_2 - - -$

or  or

The four types of surfactants are represented by the following symbols:



For readers who may be less familiar with these kinds of products, we say that these detergent molecules have a "head" (the hydrophilic part) and a "tail" (the hydrophobic part).

In each classification, we can find natural or renewable surfactants and synthetic surfactants as discussed below.

The main surfactants used in detergent and personal care products [4]

Anionic surfactants

Alkylbenzene sulfonates (ABS)

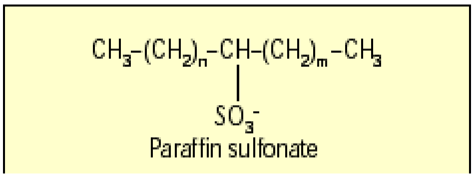
Alkylbenzene sulfonates (ABS) are the most widely used surfactants. They can be branched (e.g.

tetrapropylenebenzene sulfonate or TPS) or linear (linear alkylbenzene sulfonates or LAS) *(Figure 1)*. The former are used in only very few countries because of their slow rate of break-down by micro-organisms (biodegradability).

It should be noted that because the double bond can be either at the end or inside the carbon chain, isomers are obtained with the phenyl group in positions 1, 2 or 3. Among anionic surfactants, LAS are the most sensitive to the presence of Ca^{2+} and Mg^{2+} ions in water. Hence, if the amount of builders used is insufficient, calcium LAS precipitates are formed, reducing detergency. On the other hand, without precipitation, LAS detergency increases with concentration up to 0.6 g/l. In terms of volume, LAS are the most important surfactant for detergent powders.

Paraffin- or alkane sulfonates (SAS: secondary alkane sulfonates)

These products have not yet been used in detergents because of their relatively high cost. In view of their greater biodegradability in an aerobic environment, they represent a potential source of anionic surfactants.



Primary alcohol sulfates (PAS)

$R-O-SO_3H$

Fatty alcohol sulfuric acid

In the future, these anionic surfactants will probably be natural PAS (biodegradability and renewable materials).

****-olefin sulfonates (AOS)*** *[5]*

$H_3C-(CH_2)_m-CH=CH-(CH_2)_n-SO_3H$

α-olefin sulfonic acid (AOS)

with $m + n = 9 - 15$; $n = 0, 1, 2...$; $m = 1, 2, 3...$

*-olefin sulfonates (AOS) are a mixture of alkene sulfonates and hydroxy alkane sulfonates. Contrary to other surfactants, for which the C_{12} alkyl chains show the highest surface activity, olefin sulfonates present a maximum activity when C_{14} and C_{16} olefins are used. These anionic surfactants are less sensitive to water hardness than alkylbenzene sulfonates or fatty alcohol sulfates. In the USA, washing products do not include AOS because it can irritate the skin if used in the presence of chlorine bleach, a product much used there for whitening. On the other hand, AOS have been used successfully for many years in laundry powders and personal care products (shampoos and liquid hand soaps) throughout Asia, particularly in Japan and Korea. These surfactants have good cleaning and foaming properties.

Alkyl ether sulfates (fatty alcohol ether sulfates: FES)

$R–O–(CH_2–CH_2–O)_n–SO_3^-$
Alkyl ether sulfates
If R = lauryl, we have LES
or lauryl ether sulfate

This type of surfactant is mainly used in liquid formulations, for dishes, liquid detergents and shampoos.

Ether sulfates differ from alkyl sulfates by the ether glycol units between the carbon chain and the sulfate group as follows:

$R–O–SO_3Na$	Alkyl sulfates

$R–O–(CH_2–CH_2–O)_n–SO_3Na$	Alkyl ether sulfates

Ether sulfates are obtained in two stages:

1) Addition of ethylene oxide molecules to the fatty alcohol.

2) Sulfatation of the ethoxylated fatty alcohols by a mixture of air/SO_3 (as for alkyl sulfonates), and then neutralization using different alkaline components such as sodium hydroxide, ammonia, alkyl amines...

The properties of alkyl ether sulfates are largely determined by the number of ethylene glycol units in the starting ethoxylated fatty alcohols. The most widely used ether sulfates are Lauryl Ether Sulfates with n = 2 or 3 for which ideal behavior regarding foam and detergency is obtained.

Acyl (or cococyl) isethionates (Figure 2)

These surfactants are sold under the brand HeO S 3390 - 2 (Hoechst) or Fenipon AC (GAF). They have extraordinary properties of mildness to skin and stability (hydrolysis) in aqueous solution. As their solubility in water is relatively poor at room temperature, they are mainly used in creams or thickened liquids (shampoos and foam baths) and in toilet bars. In addition, on account of their excellent skin compatibility and emollient properties, sodium acyl isethionate can be used in baby products and in facial-wash formulations.

Methyl ester sulfonates (MES) *[6]*

These surfactants were looked at closely in the 1960s. At that time, costs were high because tallow was the raw material used. Nowadays, with the availability of palm oil, prices are becoming more competitive. The best performance is obtained from C_{16}-C_{18}. They are used both in powder and liquid detergents, particularly in South East Asian countries (notably Japan) *(Figure 3)*.

Soaps

$$R\text{-}COONa$$

Soap

In Europe, soaps are used in detergents only as antifoaming agents. They are also used in liquid detergents and soap based shower gels. In developing countries, they are used for all-purpose products.

Nonionic surfactants

Fatty alcohol poly(ethylene glycol) ether or fatty alcohol ethoxylate (FAE)

$$R\text{-}O\text{-}(CH_2\text{-}CH_2\text{-}O)_n\text{-}H$$

Fatty alcohol ethoxylated

Among commercial nonionic surfactants, those made from fatty alcohols with ethylene oxide are the most commonly used. These fatty alcohols can be:

* Natural: they are produced from vegetable oils and fats. Although there are many processes to obtain natural fatty alcohols, the most common way consists in the reduction of either fatty acids or fatty esters.

* Synthetic: the alcohols obtained by the Ziegler method have alkyl chain with an even number of carbon atoms (C_{12} to C_{20}). On the other hand, the alkyl chain of the alcohols obtained by the Oxo process can have an odd number or an even and odd number of carbon atoms. Commercial products belonging to this class and regularly used in Europe are:

- Dobanols (Shell) having even and odd number of carbon atoms;

- Synperonics (ICI) having odd number of carbon atoms.

* Secondary: examples of commercial products are Tergitol 15 -S -5 and 15 -S -7EO (Union Carbide).

Ethylene oxide (EO) and propylene oxide (PO) copolymers (EO/PO adducts)

$$H\text{-}(O\text{-}CH_2\text{-}CH_2)_m\text{-}O\text{-}(CH_2\text{-}\underset{CH_3}{CH}\text{-}O)_n\text{-}(O\text{-}CH_2\text{-}CH_2)_m\text{-}H$$

Ethylene and propylene oxides copolymers

These surfactants are obtained by adding propylene oxide to propylene glycol, followed by an addition of ethylene oxide. The abbreviated form is written as follows:

$$HO(EO)_m(PO)_n(EO)_mH$$

To obtain better alkaline stability, it is preferable to invert the addition of propylene and ethylene oxide providing the following formula:

$$HO(PO)_m(EO)_n(PO)_mH$$

The ratio PO/EO can vary between 4:1 and 9:1 with a minimum molecular weight of approximately 2000. These derivatives are mainly used in automatic dish washing products because of their low foaming profile. The main product used is the one for which m = 2 and n = 32. Although these molecules are not very biodegradable, they are nevertheless used because of their low toxicity (LC_{50} > 100 mg/l) and also their minimal effect on aquatic life.

Amine oxides (Figure 4)

These surfactants are very stable in the presence of oxidizing agents including very strong ones such as chlorine bleach. They can show either nonionic or cationic behavior depending on the pH; they are never anionic. They are excellent foamers and good thickeners when used in combination with anionic surfactants.

Alkyl amines

$R-CH_2-NH_2$
Alkyl amines

Alkyl amines are used in detergents as a source of softening agents.

Alkanolamides

Monoethanolamides are used to increase or to stabilize foam in fatty alcohol ether sulfate-based formulations (dishwashing liquids and shampoos). They also have thickening, pearlizing, and softening properties depending on the carbon R chain. These derivatives are very compatible with the skin and have very good foaming properties *(Figure 5)*.

Alkyl polyglucosides (APG) *[7-9]* (Figure 6)

Alkyl polyglucosides (APG) were described for the first time by Emil Fisher more than 100 years ago and have been produced on a large scale since 1922. These surfactants consist of fatty alcohol as the hydrophobic part and glucose as the hydrophilic part, the hydrophilicity being variable through the degree of oligomerization. Their synthesis (the Fisher synthesis) is done using entirely renewable products. APG are used in powder formulations, and in particular in liquid detergents, dishwashing liquids and shower gels. They possess high foaming power, show a high foam-stabilizing and stability and viscosity-increasing effect in combination with anionic surfactants, such as alkylbenzene sulfonates, and are mild on the skin and readily biodegradable. APG can be expected to play an important role in the future.

Alkyl polyglucosamides

Other glucose derivatives, such as alkyl glucosamides, which are obtained from monosaccharides (e.g. hextose), with the same advantages as APG are also used in detergent formulations. In these molecules the hydrophobic part is an acyl group whilst the hydrophylic part is made up of sugar, whose cycle is opened by hydrogenation *(Figure 7)*.

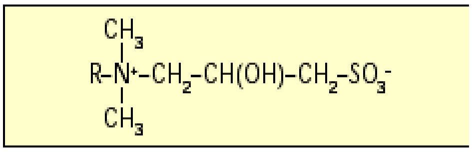
Amphoteric surfactants

Amphoteric surfactant behave like cationic surfactants at low pH, and like anionic surfactants at high pH. At medium pH, they carry both positive and negative charges and they have the structure of a bipolar ion. Unlike amphoterics, surfactants called "zwitterionics" maintain a bipolar structure in a large range of pH. In this group of products, alkyl betaines and alkylamido betaines are the most commonly used *(Figure 8).*

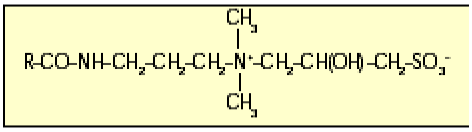
In most cases, R is the lauryl group. This product is used most frequently in shampoos, foam baths, and even dishwashing liquids because of its good detergency, its foaming properties and its compatibility with skin. This product is called Coco Amido Propyl Betaine (CAPB).

Amphoteric surfactants with a sulfonate group instead of carboxylate are called sulfobetaines or sultaines. Here are some examples:

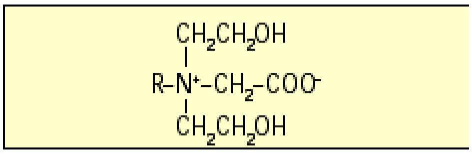
- Akyl sulfobetaines:



- Alkyl amidopropyl sulfobetaines:



- Ethoxylated betaine:



CONCLUSION

Some surfactants, such as N-alkyl taurides, N-acyl sarcosinates, polyoxyethlene carboxylates, although having excellent required properties for detergents and personal care products have not be mentioned in the present article because their volumes are not really important.

On account of environmental constraints, the new generations of surfactants have to meet criteria of biodegradability and come from renewable raw materials. Linear alkylbenzene sulfonates (LAS) have progressively replaced alkylbenzene sulfonates (ABS) for biodegradability reasons and vegetable oil-based fatty alcohol sulfates (PAS), which are biodegradable and renewable, are slowly gaining ground, gradually replacing probably LAS. The new molecules such as alkyl polyglucosides (APG), N-methyl glucosamide or methyl ester sulfonates (MES) are readily synthesized, biodegradable, renewable and perform well but are still expensive. Combinations of APG with the right nonionic surfactants provides a positive effect on removing oily stains. Their softening properties are better than those of nonionic surfactants. Quaternary esters are already being used and will be still more widely used in the near future. The most widely used nonionic surfactants are still ethoxylated fatty alcohols which, in time, will come from vegetables sources and will have a narrower ethylene oxide distribution. Finally, we can think that raw materials containing one or several nitrogen atoms will be used less and less on account of the potential problem posed by the formation of nitrosamines.

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Illustrations

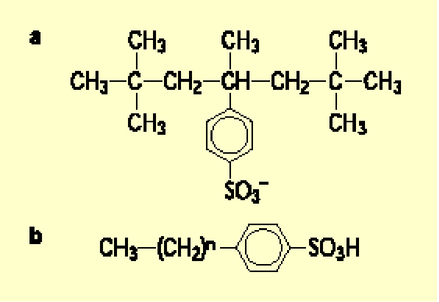

Figure 1. a*: Tetrapropylenebenzene sulfonate or TPS.*
b: *Linear alkylbenzene sulfonates or LAS.*

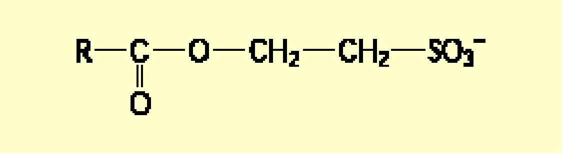

Figure 2. *Acyl isethionates.*

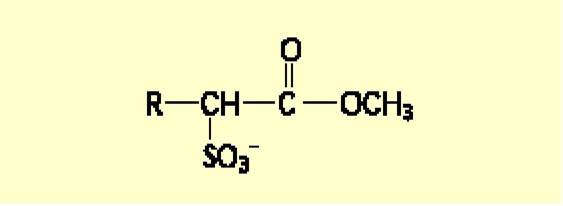

Figure 3. *Methyl ester sulfonate.*

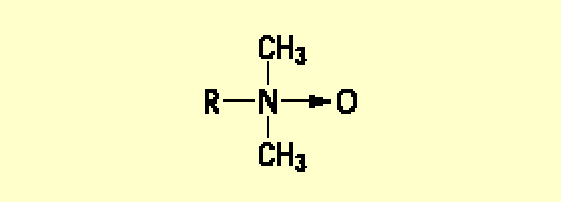

Figure 4. *Amine oxide.*

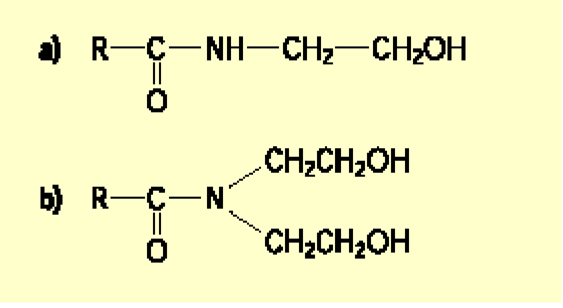

Figure 5. a: *Alkyl monoethanolamide.*
b: *Alkyl diethanolamide.*

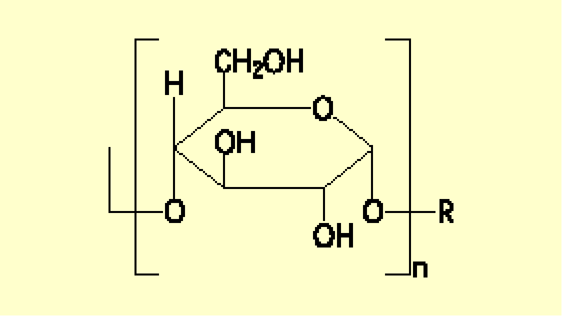

Figure 6. *Alkyl polyglucoside (where n = 1 to 3, and R = C9 - C13).*

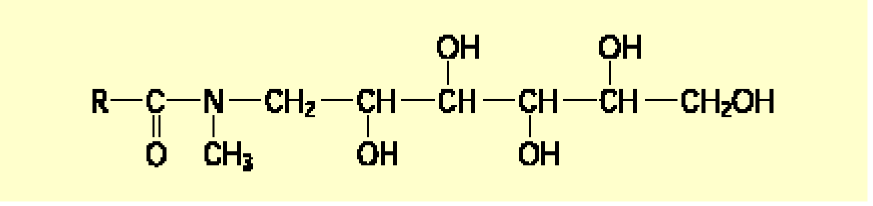

Figure 7. *N-methyl alkylglucosamide.*

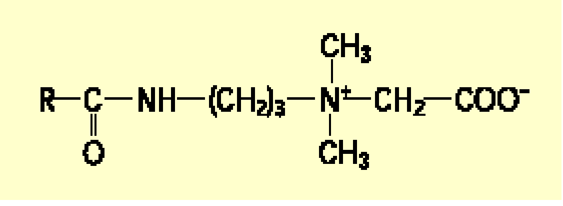

Figure 8. *Amidopropyl betaine.*