

# Detergents and Surfactants

## Introduction:

Synthetic detergents have similar molecular structures and properties as soap. Although the cleansing action is similar, the detergents do not react as readily with hard water ions of calcium and magnesium. There are over a thousand synthetic detergents available in the United States. Detergent molecular structures consist of a long hydrocarbon chain and a water soluble ionic group. Most detergents have a negative ionic group and are called anionic detergents. The majority are alkyl sulfates. Others are "surfactants" (from surface active agents) which are generally known as alkyl benzene sulfonates.

<b>Quiz:</b> Which part of the molecule is soluble in water?	<input type="text" value="Answer"/>
Which part of the molecule is insoluble in water?	<input type="text" value="Answer"/>
Which part of the molecule is interacts with dirt or oil?	<input type="text" value="Answer"/>

## Anionic Detergents

Anionic means a negatively charged molecule, remember this by anionic (a negative). The detergency of the anionic detergent is vested in the anion. The anion is neutralised with an alkaline or basic material, to produce full detergency.

Dealing with the common anionic detergents, they can be placed into the following main groupings:

Alkyl Aryl Sulphonates

Linear alkyl benzene sulphonate would be the highest quantity used of any detergent in the world, and the alkyl aryl sulphonates as a group would represent more than 40% of all detergent used.

They are cheap to manufacture, very efficient, and the petroleum industry is a starting point for the base raw material. The most important alkyl aryl condensate is DDB (dodecyl benzene). DDB is sulphonated to DDBSA (dodecyl benzene sulphonic acid), and this in turn is used as a detergent base, where it is neutralised with a base, such as sodium hydroxide, monoethanolamine, triethanolamine, potassium hydroxide, etc.

### **Long Chain (Fatty) Alcohol Sulphates**

Made from fatty alcohols, and sulphated, these are used extensively in laundry detergents. They can be produced with varying carbon chain lengths, but a C12 - C18 alcohol sulphate is a good choice.

### **Other groups**

Olefine Sulphates and sulphonates, alpha Olefine Sulphates and sulphonates, sulphated monoglycerides, sulphated ethers, sulphosuccinates, alkane sulphonates, phosphate esters, alkyl isethionates, sucrose esters

The anionic detergents are used extensively in most detergent systems, such as dish-wash liquids, laundry liquid detergents, laundry powdered detergents, car wash detergents, shampoo's etc.

### **Cationic Detergents:**

Another class of detergents has a positive ionic charge and is called "cationic" detergents. The detergency is in the cation, which can be a substantially sized molecule. Strong acids are used, such as Hydrochloric Acid to produce the Cl anion as the "neutralising" agent, although in essence, no neutralisation takes place in the manufacturing process. In addition to being good cleansing agents,

they also possess germicidal properties which make them useful in hospitals. Most of these detergents are derivatives of ammonia.

These have poor detergency, and are used more for germicides, fabric softeners, and specialist emulsifiers.

You cannot generally mix cationic and anionic detergents together, as it causes precipitation. The cationic detergents invariably contain amino compounds. The most widely used would be the quaternary ammonium salts, such as cetyl trimethylammonium chloride, a well known germicide.

A cationic detergent is most likely to be found in a shampoo or clothes "rinse". The purpose is to neutralize the static electrical charges from residual anionic (negative ions) detergent molecules. Since the negative charges repel each other, the positive cationic detergent neutralizes this charge.

It may be surprising that it even works because the ammonium (+1) nitrogen is buried under the methyl groups as can be seen in the space filling model

### **Neutral or non-ionic detergents:**

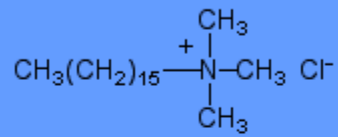
As the name implies, no ionic constituents are present. They are "ionically" inert.

Nonionic detergents are used in dish washing liquids. Since the detergent does not have any ionic groups, it does not react with hard water ions. In addition, nonionic detergents foam less than ionic detergents. The detergent molecules must have some polar parts to provide the necessary water solubility.

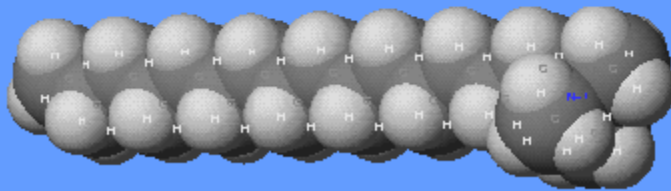
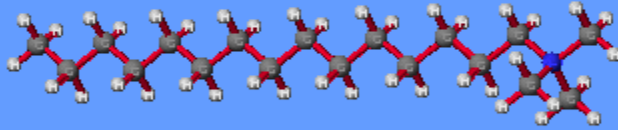
In the graphic, the polar part of the molecule consists of three alcohol groups and an ester group. The non-polar part is the usual long hydrocarbon chain. The vast majority of all nonionic detergents are condensation products or ethylene oxide with a hydrophobe. This



## Cationic Detergent

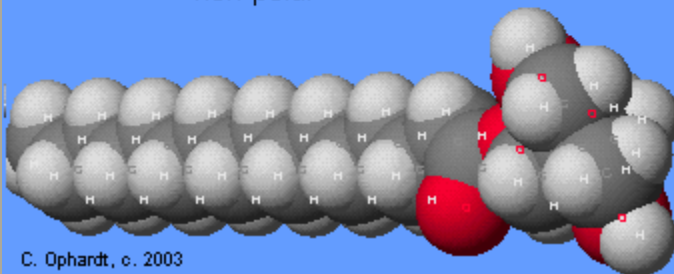
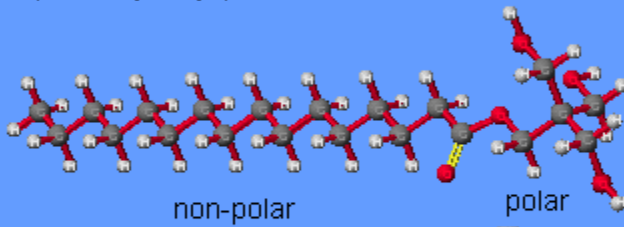
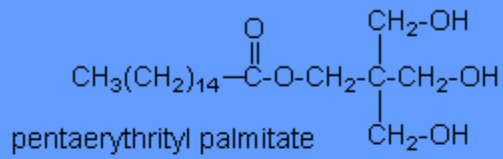


trimethylhexadecylammonium chloride



C. Ophardt, c. 2003

## Nonionic Detergents



C. Ophardt, c. 2003

## **Biological Detergent Theory and Application**

### **Biological Detergents**

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In general, biological detergents are most commonly used to disrupt the bipolar lipid membrane of cells in order to first free and then solubilize membrane-bound proteins. Some detergents can also be used to solubilize recombinant protein, while others find their usage in the stabilization, crystallization, or denaturation of proteins. Additional applications include the extraction of DNA and RNA, the solubilization of specimens for diagnostic applications, the lysis of cells, the preparation of liposomes, the prevention of reagent and analyte precipitation from solution, and the prevention of non-specific binding in immunoassays.

The value of detergents in these applications is derived from their amphiphilic nature. Each detergent molecule is characterized by a hydrophilic "head" region and a hydrophobic "tail" region. The result of this characteristic is the formation of thermodynamically stable micelles with hydrophobic cores in aqueous media. This hydrophobic core provides an environment that allows for the dissolution of hydrophobic molecules or domains of proteins.

The concentration at which micelles begin to form, which is the maximum monomer concentration, is the critical micelle concentration (CMC). The CMC constitutes a measure of the free energy of micelle formation. The lower the CMC, the more stable the micelle and the more slowly molecules are incorporated into or removed from the micelle. The average number of monomers in a micelle is the aggregation number (AN). The CMC and AN are highly dependent on factors such as temperature, pH, ionic strength, and detergent homogeneity and purity. At low temperatures detergents will form a cloudy crystalline suspension. As the temperature increases, the crystals dissolve to form monomers if the concentration is below the CMC or micelles if the concentration is above the CMC. The temperature at which micelles form from crystals is the critical micelle temperature

(CMT). The triple point, the temperature at which crystals, monomers, and micelles are in equilibrium, is the Krafft Point.

When selecting a detergent, the first consideration is usually the ionic form of the hydrophilic group, which is anionic, cationic, zwitterionic, or non-ionic. Anionic and cationic detergents typically modify protein structure to a greater extent than the other two classes. The degree of modification varies with the individual protein and the particular detergent. Ionic detergents are also more sensitive to pH, ionic strength, and the nature of the counter ion, and can interfere with charge-based analytical methods. Alternatively, most non-ionic detergents are non-denaturing, but are less effective at disrupting protein aggregation. Zwitterionic detergents uniquely offer some intermediate class properties that are superior to the other three detergent types in some applications. Offering the low-denaturing and net-zero charge characteristics of non-ionic detergents, zwitterionics also efficiently disrupt protein aggregation.

Ease of removal or exchange is often a factor in the selection of a detergent. Some of the more common removal methods include dialysis, gel filtration chromatography, hydrophobic adsorption chromatography, and protein precipitation. The CMC value associated with the detergent is a useful guide to hydrophobic binding strengths – the higher the CMC, the weaker the binding and the easier the removal. Another useful parameter is the micelle molecular weight, which indicates relative micelle size. In most cases, the smaller the micelle, the easier the removal. If protein-detergent complexes are to be separated based on the molecular size of the protein, a small micelle size is usually preferred. The micelle molecular weight is simply the aggregation number multiplied by the monomer molecular weight.