

Surfactants - A Primer

An in-depth discussion of the behavior of common types of surfactants.

The term surfactant is derived from the words surface active agent. Surfactants provide remarkable benefits in many textile wet processes. A surface active chemical is one which tends to accumulate at a surface or interface. An interface is the area of contact between two substances. Where the interface is between two substances not in the same phase, the interface is usually called a surface. Clearly, the chemical processes that take place at the solid/liquid surface between textile fibers and water often determine the success or failure of the process.

Examples of important events in textile chemical processes that involve interaction of surfaces include wetting, dispersing, emulsification, chemical or dye adsorption on fibers, adhesion, vaporization, sublimation, melting, heat transfer, catalysis, foaming and defoaming. Specific functions of surface active agents include removing soil (scouring), wetting, rewetting, softening, retarding dyeing rate, fixing dyes, making emulsions, stabilizing dispersions, coagulating suspended solids, making foams, preventing foam formation and defoaming liquids.

The surface tension of a liquid is an internal pressure caused by the attraction of molecules below the surface for those at the surface of a liquid. This molecular attraction creates an inward pull, or internal pressure, which tends to restrict the tendency of the liquid to flow and form a large interface with another substance.

The surface tension (or inter-facial tension if the interface is not a surface) determines the tendency for surfaces to establish contact with one another. Therefore, surface tension is responsible for the shape of a droplet of liquid. If the surface tension is high, the molecules in the liquid are greatly attracted to one another and not so much to the surrounding air.

If the droplet of water is in contact with a solid such as a

fabric, its shape will also be affected by the surface tension at the solid/liquid interface. If the surface tension in the liquid is lower, the droplet forms a more ellipsoidal shape.

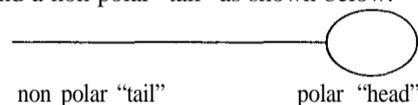
The following are the surface tensions for some liquid substances:

<u>SUBSTANCE</u>	<u>SURFACE TENSION</u>
water	73 dynes/cm
mercury	480 dynes/cm
benzene	28 dynes/cm
ethanol	22 dynes/cm

Because of its lower surface tension, ethanol will flow and form a larger area of contact (surface) with a solid than with water. Mercury, with its very high surface tension, does not flow but breaks into droplets if given the opportunity.

Surface active agents interfere with the ability of the molecules of a substance to interact with one another and, thereby, lower the surface tension of the substance. Surfactants used in industrial applications usually cause a dramatic decrease in surface tension when used at low concentration.

Chemically, surfactants are amphipathic molecules. That is, they have two distinctly different characteristics, polar and non polar, in different parts of the same molecule. Therefore, a surfactant molecule has both hydrophilic (water-loving) and hydrophobic (water-hating) characteristics. Symbolically, a surfactant molecule can be represented as having a polar "head" and a non polar "tail" as shown below.



The hydrophobic group in a surfactant for use in aqueous medium is usually a hydrocarbon chain but may be a fluorocarbon or siloxane chain of appropriate length. The hydrophilic group is polar and may be either ionic or nonionic.

Since surfactant molecules have both hydrophilic and hydrophobic parts, the most attractive place for them in water is at the surface where the forces of both attraction and repulsion to water can be satisfied. One other way that surfactants interact to satisfy natural forces of attraction and repulsion between molecules is by formation of micelles. Surfactant molecules aggregate in water forming micelles (see Figure I). Micelles consist of hydrophobic interior regions, where hydrophobic tails interact with one another. These hydropho-

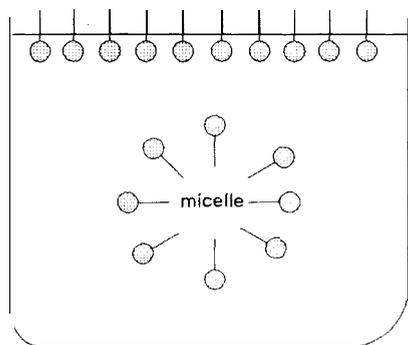


Figure 1. Schematic representation of surfactant molecules at surface and surfactant micelle in bulk liquid. (From "Textile Coloration and Finishing," Carolina Academic Press, Durham, N.C.)

bic regions are surrounded by the hydrophilic regions where the heads of the surfactant molecules interact with water.

At very low concentration in water, surfactant molecules are unassociated. At higher concentration of surfactant in water, micelles form. The concentration at which micelles form is called the critical micelle concentration (CMC). The surface tension of water undergoes a precipitous decrease, and the detergency of the mixture increases dramatically at the CMC.

Types (Classes) Of Surfactants

Surfactants fall in the following classifications according to the nature of the hydrophilic group:

- anionic: hydrophilic head is negatively charged;
- cationic: hydrophilic head is positively charged;
- nonionic: hydrophilic head is polar but not fully charged; and
- amphoteric: molecule has both potential positive and negative groups; charge depends on pH of the medium.

Carboxylates

Anionic surfactants are the most widely used of the four classes. Important types of anionic surfactants are carboxylates, sulfonates, sulfates and phosphates.

Most carboxylate surfactants are soaps. Soaps are alkali metal salts of fatty acids. Fatty acids are carboxylic acids derived from or contained in animal or vegetable fats or oils. They contain linear hydrocarbon groups and may be either saturated or unsaturated. The

most important fatty acids used for manufacturing of surfactants are as follows:

- steric acid: $C_{17}H_{35}COOH$ (saturated); solid at room temperature;
- palmitic acid: $C_{16}H_{33}COOH$ (saturated); solid at room temperature;
- lauric acid: $C_{11}H_{21}COOH$ (saturated); solid at room temperature; and
- oleic acid: $C_{17}H_{33}COOH$ (unsaturated at C_9-C_{10}); liquid at room temperature.

Those with less than 10 carbons are too soluble in water to have good surface activity. Those with more than 20 carbons in a linear configuration are too insoluble in water to use in aqueous medium.

Sodium is the most common cation in soap. But potassium and ammonium are also common. Soaps are effective as cleaning agents in aqueous medium. Since soaps are relatively weak acids, the free acid is liberated in acidic medium. The free acids are insoluble in water. Therefore, soaps are only effective in alkaline medium.

Soaps can be made by neutralization of free fatty acids by alkali metals hydroxides by alkaline hydrolysis (saponification) of fats and oils (see Figure 2). Fats and oils belong to the lipid family. The chemistry of oils as used in making soaps is identical to that

alkyl, aryl, or alkylaryl hydrophobe. Since the sulfonate group is a strong acid, the sulfonate surfactants are soluble and effective in acidic as well as in alkaline medium.

The calcium and magnesium salts are soluble in water, so sulfonate surfactants are not greatly affected by hard water. The sodium salt sulfonate surfactants are soluble and effective even in the presence of electrolytes such as sodium chloride and sodium sulfate.

Since the sulfonate surfactants are resistant to hydrolysis by both hot acid and alkali, they are very useful for textile scouring formulations. Since sulfonation is relatively inexpensive, sulfonate surfactants are found in high-volume products. Sulfonate surfactants include alkylsulfonates, alkylbenzenesulfonates, lignin sulfonates, naphthalenesulfonates and petroleum sulfonates.

Lignin is a byproduct of paper manufacture. Sulfonated lignin is a very good dispersing agent for solids in water and finds textile applications mainly as a dispersing agent in specialty chemicals and dyes. Lignin sulfonates are unsuitable for many applications because of their dark color and because they do not produce much lowering of the surface tension of water.

Esters of sulfosuccinic acid, such as

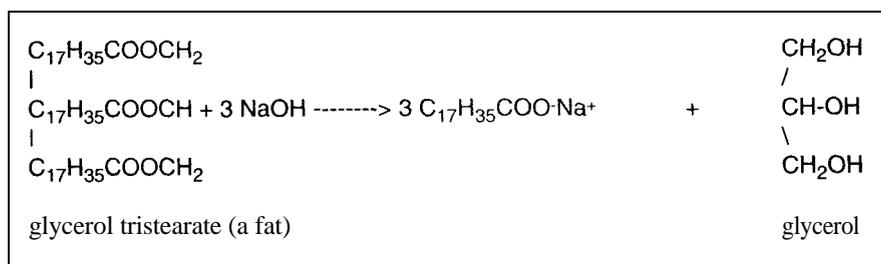


Figure 2.

of fats. Fats are solid. Oils are liquid. Generally, lipids with more saturated hydrocarbon content are more firm and have higher melting temperatures than those with unsaturated hydrocarbon groups. Fats are esters of the trihydric alcohol, glycerol. Fatty acids are produced by alkaline hydrolysis (saponification) of fats. The soap (fatty acid solid) thus formed is separate from the glycerol byproduct by neutralization of the alkali or addition of salt to precipitate the soap.

Sulfonates

The sulfonate group is an effective solubilizing group when attached to an

dioctyl (2-ethylhexyl) sulfosuccinate (DOSS), are excellent fast-wetting surfactants. Sulfosuccinate ester surfactants are very soluble in water. They do not emulsify oils so they are not good scouring agents. They are soluble in organic solvents making them useful in dry cleaning. They are not acceptable for some aqueous applications since they are hydrolyzed by hot acid or alkali.

Sulfates

Various fatty alcohols can be reacted with chlorosulfonic acid or sulfur trioxide to produce their sulfuric acid esters. The properties of these surfactants depend on the alcohol chain length as

well as the polar group and are often mixtures or blends comprised of several alcohols of different lengths (see Figure 3).

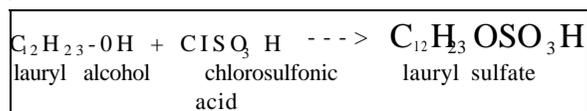


Figure 3.

These surfactants are sulfates rather than sulfonates like those described above. Because of the presence of an additional oxygen atom, the sulfates are more hydrophilic than the sulfonates. However, the sulfate group is less stable to hydrolysis than is the sulfonate group.

The sodium salt is most common although salts with diethanolamine, triethanolamine or ammonia are used in cosmetics and shampoos. Sodium lauryl sulfate is an excellent foaming agent. Foaming properties are enhanced when some unsulfated fatty alcohol is retained in the product.

Phosphate esters of fatty alcohols are useful surfactants. Resistance of phosphate surfactants to acid and hardness ions is poor. Because of these limitations and their relatively high cost, phosphate surfactants are mainly specialty products. Since phosphate surfactants are excellent emulsifiers under strongly alkaline conditions, they are effective for scouring of oil and wax from textile materials.

Nonionic Surfactants

Nonionic surfactants have diverse uses in textiles, and the volume used is large. Of the several types of nonionic surfactants, the polyoxyethylenated alkylphenols and the polyoxyethylenated linear are the most common (see Figure 4).

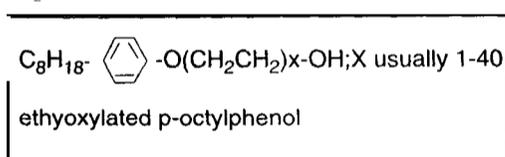


Figure 4.

The hydrocarbon group is the hydrophobic part of the surfactant while the chain of ethylene oxide groups is the hydrophilic part of the molecule. The length of the ethylene oxide chain is controlled by the relative amounts of reactants used and determines how hydrophilic the surfactant is.

Nonionic surfactants are compatible with other types of surfactants. Their low foaming tendency can be an advantage or disadvantage depending on requirements. They are good dispersing agents in many cases. They are more effective than sulfonate surfactants in removing soil from hydrophobic fibers but are

inferior to anionic surfactants for soil removal from cotton.

Nonionic surfactants, like most ethylene oxide derivatives, exhibit inverse solubility characteristics and may precipitate with increase in temperature of their solutions. This sometimes precludes their use in high temperature applications but can be an advantage in that elevation of the temperature can be used to destroy activity of the surfactant if desired. The temperature at which precipitation occurs is called the "cloud point" of the surfactant.

The properties of a nonionic surfactant can be tailored somewhat for a particular use by controlling the relative amounts of hydrophilic and hydrophobic character. The relative amounts of hydrophilic and hydrophobic character may be expressed as the hydrophile-lipophile balance (HLB) of the surfactant. HLB values are sometimes assigned by observation of and experience concerning the emulsification behavior of surfactants. Likewise, HLB values can be assigned to substances that must be emulsified. Matching the HLB values of substance to be emulsified and the surfactant is a good starting point for selection of an appropriate surfactant.

HLB values may be used as an indicator of the emulsification behavior of surfactants. As a general rule, surfactants with good oil solubility produce water-in-oil (w/o) emulsions while more water soluble surfactants produce oil-in-water (o/w) emulsions. HLB values are a good indicator of behavior of surfactants in water as is shown below:

B e h a v i o r i n W a t e r	
1-4	Not dispersible
3-10	Form milky dispersions
10-13	Form translucent dispersions
> 13	Form clear solutions

Therefore, emulsification behavior should be predictable from HLB values. In practice, HLB values can only be used as a rough guide to surfactant selection because variables such as temperature and nature of the substances to be emulsified are important. In many cases, a mixed surfactant system will produce better emulsification than a single surfactant.

Cationic Surfactants

Most of the uses of cationic surfactants result from their ability to adhere to and modify solid surfaces. Cationic surfactants are important as corrosion inhibitors, fuel and lubricating oil additives, germicides and hair conditioners. Important applications of cationic surfactants in textiles include their use as fabric softeners, fixatives for anionic dyes and dyeing rate retarders for cationic dyes. Cationic and anionic surfactants are usually incompatible. Cationic surfactants are compatible with nonionics and zwitterionics. Usage of cationic surfactants is small compared to anionics and nonionics.

Two common types of cationic surfactants are long chain amines and quarternary amine salts. The long chain amine types are made from natural fats and oils or from synthetic amines. They are soluble in strongly acidic medium but become uncharged and insoluble in water at pH greater than 7.

Quaternary amine type cationic surfactants are very important as fabric softeners. They absorb on the surface of fibers with their hydrophobic groups oriented away from the fibers. This reduces the friction between fibers and imparts a soft, fluffy feel to the fabric. This same mechanism accounts for the behavior and use of cationic surfactants as hair conditioners. Quaternary ammonium salts are effective in neutral and alkaline as well as acidic medium.

Zwitterionic Surfactants

Zwitterionic surfactants also impart a feel of softness to textile materials. Zwitterionic surfactants are compatible with all other classes of surfactants and are soluble and effective in the presence of high concentrations of electrolytes, acids and alkalies. They exhibit cationic behavior near or below their isoelectric points and anionic behavior at higher pH. The isoelectric point depends on the structure of the surfactant. m