Surfactants - Surface Active Agents

Introduction

The best way to start an introduction to such a subject would be to back up just a little and explain some terms used in the industry and define the origin of surface-active agents.

The definition for a detergent is a cleaning agent. The main cleaning agent used in earlier days was soap. This term means a compound formed from the reaction of a fatty acid with a base such as caustic soda, forming the sodium soap of the acid. The more commonly used cleaning agent in this day and age is the synthetic detergent (SYNDET) which is a formulation such as TIDE or FAB. The essential difference between the soaps and the newer synthetic detergents lies in the fact that the soap molecule occurs ready-made in nature. As we have seen above, it consists of a long-chain fatty acid modified only to the extent that the acidic hydrogen is replaced by a sodium atom from caustic soda. The synthetic detergents are not derived directly from natural products but are tailor-made, or built up artificially, synthesized in the laboratory. These synthetic detergents are made from a wide variety of raw materials such as certain petroleum constituents, coal tar derivatives, compounds derived from cracking gases, chemically modified fatty acids, and a host of others. We now have described a detergent and the difference between a soap and a synthetic detergent, so let's continue by discussing some of the components of a synthetic detergent a little more in detail.

The components of a synthetic detergent can be classified in two categories: the surfactants (abbreviation for surface-active agent) and the builders.

The surface-active agent is the principal component of a synthetic detergent but is also assisted in its cleaning agent role by the builders used (sometimes called built detergents). Builders such as the phosphates, metasilicates, and carbonates aid in emulsifying soils and suspending dirt in aqueous solutions. The surface-active agents are compounds that have two groups present in the molecule: one being hydrophobic in nature and one being hydrophilic in nature. Here we should stop and explain that hydrophilic means water-liking and hydrophobic means water-hating or oil-liking. So when you have a surface-active agent with two groups present, you have a chemical compound that has surface-active properties or the ability to affect the interfacial relationship between two dissimilar substances such as oil and water.

Classification

Now that we have discussed and defined a surface-active agent and various terms used in conjunction with these compounds, we must classify them into the three groups commonly known in industry: the anionics, cationics and nonionics.
Anionics

An anionic surface-active agent is the reaction product of an organic compound such as a high molecular weight acid or alcohol with an inorganic compound such as sodium hydroxide or sulfuric acid, yielding a product wherein the organic part of the molecule, or the water-insoluble part of the molecule, has a negative charge and the water-soluble part of the molecule wherein the sodium ion has a positive charge. For example, soap is an anionic and has the following structure:

\[
\begin{align*}
H & \quad H \quad H \quad H \quad H \quad H \quad H \quad H \quad H \quad O \\
H & \quad C \quad C \quad C \quad C \quad C \quad C \quad C \quad C \quad C \quad C \quad C \quad C \quad C \quad C \quad C \quad O \quad Na
\end{align*}
\]

Also, the reaction product of a long-change alcohol and sulfuric acid, and thus neutralized with sodium hydroxide has the following structure:

\[
\begin{align*}
H & \quad H \quad H \quad H \quad H \quad H \quad H \quad H \quad H \\
H & \quad C \quad C \quad C \quad C \quad C \quad C \quad C \quad C \quad C \quad C \quad C \quad O \quad SO_4 \quad Na
\end{align*}
\]

The anionics have the advantage of being high and stable foaming agents; however, they do have the disadvantage of being sensitive to minerals and the presence of minerals in water (water hardness) or pH changes.

Cationics

Cationics are formed in reactions where alkyl halides react with primary, secondary, or tertiary fatty amines. Here the water-insoluble part of the molecule has a positive charge and the water-soluble part of the molecule is negatively charged, thus giving it the name of a cationic surface-active agent.

Cationic surface-active agents reduce surface tension and are used as wetting agents in acid media. However, a disadvantage of a cationic surface-active agent is that they have no detergent action when formulated into an alkaline solution.

Nonionics

This is the group of surface-active agents we are most concerned with since it is the classification all of Texaco Chemical Company's surface-active agents fall into. Nonionic surface-active agents have a hydrophobic/hydrophilic balance wherein there is neither a negative nor a positive charge in either part of the molecule, thus giving it the nonionic terminology. These surface-active agents have the advantage that they are not affected by
water hardness or pH changes as the anionic and cationic surfactants are, and in many cases it is an advantage that they are considered medium to low foaming agents. It is especially advantageous when a very low foaming surface-active agent is required. An example of the chemical structure of a nonionic surface-active agent is shown below in the reaction product of lauryl alcohol and ethylene oxide.

\[
H \ H \ H \ H \ H \ H \ H \ H \ H \ H \\
H \ C - C - C - C - C - C - C - C - C - C - C - C - (OCH_2CH_2)_nOH \\
H \ H \ H \ H \ H \ H \ H \ H \ H \ H
\]

**Types of Nonionics**

**Alkylphenol Ethoxylates**

Various alkylphenols are used as the hydrophobic portion of many surface-active agents. The alkylphenols most commonly used for the preparation of surface-active agents are the nonyloctyl-, dodecyl-, and dinonylphenol. In some cases, amylphenol is used as a hydrophobic group for surface-active agents as well as phenol itself. The main manufacturers of the nonylphenol ethoxylates at the present time are Texaco Chemical Company, Rohm & Haas, General Aniline & Film, Olin Mathieson, and Union Carbide. Rohm & Haas and General Aniline & Film both manufacture the ethoxylates of octylphenol. General Aniline & Film also manufactures the ethylene oxide adducts of dodecyl- and dinonylphenol. At the present time, Texaco Chemical Company does not manufacture ethylene oxide adducts of octyl-, dodecyl-, and dinonylphenol even though they do have the technology to do so. They do manufacture ethylene oxide adducts of phenol on a custom basis.

**Alcohol Ethoxylates**

The three types of alcohols most commonly used for ethoxylation are primary alcohols produced by Shell Chemical Company, the Ethyl Corporation, and Conoco, along with primary alcohols from natural sources. The secondary alcohols that are ethoxylates are produced by Union Carbide Chemical Company. Branched chain alcohols are also ethoxylates but are being phased out due to their biologically hard character. The main producer of these alcohols is Enjay Chemical.

The primary and secondary alcohol ethoxylates have become very popular during the last decade simply because they are more biodegradable than the alkylphenol ethoxylates. Branched chain alcohol ethoxylates such as tridecyl alcohol ethylene oxide adducts are biologically hard and are used only where biodegradability is of minor concern and the excellent wetting properties of these products are required.

**Nonionic Surface-Active Agents**

The nonionic surface-active agents made by Texaco Chemical Company can be divided into three categories: These are oil soluble, water dispersible, and water-soluble. Below is
a table of the nonionic surface-active agents in each of these three categories:

<table>
<thead>
<tr>
<th>Oil Soluble</th>
<th>Water Dispersible</th>
<th>Water Soluble</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surfonic N-10</td>
<td>Surfonic N-60</td>
<td>Surfonic N-95, N-120, N-150, N-200, N-300, N-400, LF-7, LF-17</td>
</tr>
<tr>
<td>Surfonic N-40</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As you can see from the above table, most of the nonionic surface-active agents manufactured by Texaco Chemical Company are water-soluble. We should take time at this point to define the term HLB value. The HLB value is the hydrophil/lipophilic (hydro-phobe) balance. This value then is an indication of the oil or water solubility of the product. The lower the HLB number the more oil soluble the product; and in turn the higher the HLB number the more water-soluble the product is. Below is a formula of how HLB values are calculated:

\[
\text{Mole wt. EO} \times \text{moles EO} \times .20 = \text{HLB}
\]

Quite frequently a customer will ask for the HLB number or value of a product which is their means of characterizing a particular product with respect to its oil or water solubility.

Cloud point is also a measure of the hydrophil/lipophil balance of a surface-active agent. When a surfactant can have its cloud point run in an aqueous solution, it is therefore a water soluble surface active agent; whereas, when a surfactant must have its cloud point run in an aqueous/solvent mixture, it is either water dispersible or oil soluble in character. Nonionic surface-active agents are less soluble at elevated temperatures in aqueous solutions and, therefore, exhibit a cloud point which varies with the hydrophil/lipophil balance of the nonionic surface-active agent.

As you can see, we have divided the nonionic surface-active agents into three categories based on their water solubility and have given two means by which a surfactant can be categorized, these being either by calculating the hydrophil/lipophil balance or by running a cloud point which is a measure of this balance.