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Review Article

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Toxicity and environmental aspects of surfactants

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Abstract: As the single largest class of specialty chemicals, surfactants are consumed in huge quantities in our daily life and in many industrial areas. In the past, the attention was focused entirely on technical performance. However, starting from the 1970s and 80s, surfactant related environmental concerns have become the main driving force to upgrade surfactant production technology to make more benign or “greener” products. For this reason, environmental issues, dermatological effects, and oral toxicity are the main priorities when surfactants are considered for a specific purpose. In this paper, we present five cases to demonstrate how the surfactant industry tackles these challenges to mitigate the environmental and health effects associated with surfactant consumption. We also discuss the important role played by surfactants in a current carbon capture and storage (CCS) strategy to reduce the CO₂ level in the atmosphere. Surfactant-based stable CO₂ foam flooding is a well-established enhanced oil recovery technique. It has been considered to be an economically realistic procedure to sequester large amounts of CO₂ in geological formations.

Keywords: surfactants; biodegradation; toxicity; CO₂ foam; carbon capture and storage

1 Introduction

Surfactants are used in a variety of applications, ranging from food and pharmaceuticals to mineral ore flotation and oil recovery. The world-wide annual production is around 30 million metric tons, which makes surfactants the single

largest class of specialty chemicals. The total market value of surfactants is around 50 billion US dollars.

Since almost all surfactants end up either in nature or in sewage plants environmental aspects have a high priority for the surfactant industry. Rate of biodegradation and aquatic toxicity are parameters that largely govern the development of new surfactants today and the OECD (Organization for Economic Co-operation and Development) has issued test guidelines. The European Union has taken the lead in implementation of rules to protect the environment. The most important regulation is REACH, which stands for Regulation, Evaluation, Authorization and Restriction of Chemicals. It entered into force in June 2007, with a phased implementation over one decade. All surfactants produced or sold in the EU are regulated by REACH. The regulation does not only concern the surfactant as such; it also covers formulated products, such as laundry detergents. The European Green Deal is a more recent initiative. It aims to ensure zero emissions by 2050, making Europe a climate-neutral continent. More environmentally benign, “greener”, surfactants are today seen as more important than better surfactants from a performance point of view. However, that has not always been the case. The environmental concern related to surfactants started to be an issue in the 1970s and 80s. Before that, focus was entirely on technical performance, and the higher the chemical stability of a surfactant, the better.

It is not only about the environment, however. Surfactants are consumed by both humans and animals. Surfactants are needed in a broad variety of food and feed, where they serve as emulsifiers, dispersants, foaming agents, etc. Surfactants are also important ingredients in pharmaceutical formulations. It is obvious that surfactants used for applications in the food, feed, and pharma sectors need to have minimal oral toxicity.

Surfactants are also the key ingredient in many personal care products, such as shampoos, body cleansers, hair conditioners, various types of ointments, etc. This means that they will be deliberately applied on bare skin, all over the body, which, in turn, means that they must be safe from a dermatological point of view. Minimal skin toxicity is a prerequisite for surfactants used for such applications.

In this review we present cases related to surfactants where environmental issues, dermatological effects, and

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oral toxicity have been in focus. The cases we discuss are well-known and rather arbitrarily chosen. The purpose of the review is not to give an exhaustive coverage of all such cases related to surfactants; the aim of the article is to present relevant case studies to illustrate how the surfactant industry has tackled the challenges that arise from the biological activity of surface-active agents.

At this point it may be relevant to point out that biological activity is by no means a generally unwanted property of a surfactant. On the contrary, an antimicrobial effect can be taken advantage of. Many surfactants have a bactericidal effect. This applies to many synthetic surfactants, but it also applies to biosurfactants, both glycolipids and lipopeptides. In fact, antimicrobial peptides, which are cationic amphiphiles, are known to kill both Gram-positive and Gram-negative bacteria, as well as fungi and enveloped viruses.¹ Among the synthetic surfactants, the cationic amphiphiles stand out as having a particularly powerful biological effect. Benzalkonium chloride (alkyldimethylbenzylammonium chloride) has been used as a wound disinfectant since the 1940s and so-called ‘quats’, to which category benzalkonium chloride belongs, are also used as wood preservatives and in a variety of consumer products such as hand sanitizers and wet wipes.²

2 Historical perspective

Soap is the first man-made surfactant and soap-making is a craft with deep historical roots. The first report of ‘detergent properties’ of soap is engraved on a Sumerian clay tablet from around 2500 BC found in Mesopotamia. It gives instruction of how to wash wool with soap.³

Much later, soap production initiated what is today the detergent industry. In 1806 William Colgate started a soap-making business in New York called Colgate and Company and at about the same time William Procter and James Gamble started a soap and candle business in Cincinnati, USA. At Port Sunlight in the UK two brothers, William and James Lever, started to produce “Sunlight soap” in 1885. Lever Brothers later merged with the Dutch margarine producer Margarine Unie to become Unilever. Unilever is the world’s largest soap manufacturer today.

Soap, although man-made from triglycerides, is considered a natural surface active agent. Synthetic surface-active agents started to be produced more than 100 years later from a demand of the growing household detergent industry. The first commercial laundry detergent that combined bleach and detergency was Persil, introduced in 1907 by Henkel and other brands soon followed. The detergent industry had noted two main shortcomings with soap: strong pH dependence and low

tolerance to hard water. They knew that sulfonated and sulfated products were better in both respects. The first sulfonated surfactants were isopropyl-naphthalene sulfonates, but they were soon replaced by alkylbenzene sulfonates made by reacting benzene with an olefin using a Lewis acid catalyst, such as AlCl_3 , an example of a Friedel-Crafts alkylation.

The first alkylbenzene sulfonates appeared in the 1930s and were based on propylene tetramer as alkyl moiety. The result was an alkylbenzene sulfonate with a highly branched alkyl chain and it soon became a large-volume surfactant. However, due to environmental concern it was replaced in the 1960s by an isomer with a linear alkyl chain attached to the benzene ring. This product, linear alkylbenzene sulfonate, soon became the work-horse surfactant in detergents and many other products. The environment-driven change from branched to linear alkylbenzene sulfonates will be discussed in Section 3.1.

Nonionic surfactants originated from the discovery in the 1920s that long-chain alcohols could be reacted with ethylene oxide to form what is today called ethoxylated alcohols. During the 1930s surface active ethoxylated products were made not only from fatty alcohols but also from fatty acids, fatty amines, fatty acid esters, and alkylphenols. The ethoxylation reaction is very versatile. With the ethoxylation technology not only the length of the hydrophobic tail of the surfactant but also the length of the polar headgroup can be tailor-made. Alkylphenol ethoxylates soon became popular, partly because alkylphenols, in particular octyl- and nonylphenol, were cheap starting materials. Later, however, alkylphenol ethoxylates have been phased out and been replaced by fatty alcohol ethoxylates because of environmental concerns. This will be dealt with in Section 3.2.

The whole class of ethoxylated products have more recently come in focus from a toxicity point of view. Ethylene oxide, the starting material for all ethoxylation processes, is a reactive molecule, which is now classified as carcinogenic and mutagenic. For this reason, the surfactant producers have developed a technology to eliminate unreacted ethylene oxide from their products. However, the risk of having even traces of a toxic compound remaining in a surfactant that may be put on the skin in a personal care product is problematic. Another issue that the producers of ethoxylated products must deal with is that during the ethoxylation the toxic product 1,4-dioxane is formed in small amounts. This compound is also carefully removed after the ethoxylation step but, like the situation with ethylene oxide, the risk of having traces of 1,4-dioxane in a surfactant formulation that may be applied on the skin, is a serious concern for the cosmetics industry. And an even worse case is if an edible surfactant would contain detectable amounts of these toxic products. The problems with traces of ethylene

oxide and 1,4-dioxane in nonionic surfactants are dealt with in Section 3.4.

The two other surfactant classes, cationic and zwitterionic surfactants, which in terms of volume are much smaller than the anionics and the nonionics, came somewhat later. Cationic surfactants normally have a quaternary ammonium group as polar headgroup attached to one or two long alkyl chain(s) and are often referred to as ‘quats’. (A long-chain amine can also be a cationic surfactant if the pH is such that the amino group is protonated.) An important type of cationic surfactant is amphiphiles with two long alkyl chains attached to the headgroup, so-called ‘dialkyl quats’. The dialkyl quats soon became the active ingredient in textile softeners. However, with time it was realized that the dialkyl quats were harmful to the marine environment. This resulted in a rapid change in the industry from dialkyl quats to the so-called ‘diester quats’, similar in structure but with ester bonds separating the long hydrophobic chains from the quaternary ammonium group. This transition will be dealt with in Section 3.3 of this review.

Zwitterionic surfactants have one negatively charged and one positively charged group. If the negative charge is a sulfate or a sulfonate group, it is permanently charged but if it is a carboxylate group it will become neutral if the carboxylate group becomes protonated. This will lead to a change in character of the surfactant, from a zwitterionic with a net zero charge, to a cationic amphiphile. This is taken advantage of in the formulation of products that are supposed to be particularly mild to the skin and the eye, i.e. advantageous from a dermatological point of view, as will be discussed in Section 3.5.

Finally, in Section 3.6 we discuss the role of surfactants as foaming agents to generate stable CO₂ foams for enhanced oil recovery. This procedure is also a realistic way to store carbon in geological formations to reduce the CO₂ level in the atmosphere.

3 Transitions driven by environmental concern or by oral toxicity or dermatological issues

3.1 From branched alkylbenzene sulfonates to linear alkylbenzene sulfonates

The branched alkylbenzene sulfonates have a branched alkyl chain attached at the benzene ring through a Friedel-Crafts alkylation reaction. The branched alkyl moiety is usually a propylene oligomer and propylene tetramer soon

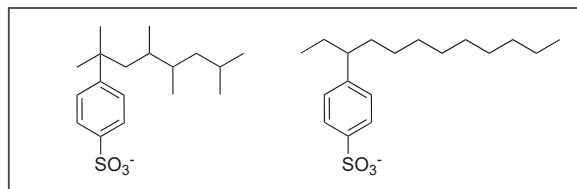


Figure 1: Branched (left) and linear (right) alkylbenzene sulfonate.

became the alkyl chain of choice. The subsequent sulfonation results in the SO₃ group being almost exclusively in *para* position to the alkyl chain. The commercial product is a mixture of isomers, and a representative structure is shown in Figure 1.

The surfactant usually comes with sodium as counterion but the calcium salt, as well as salts of quaternary ammonium ions, are also commercially available. The structures shown in the figure are just examples of the many isomers that the commercial surfactants are composed of.

The sodium salt of the branched alkylbenzene sulfonate was introduced on the market in the beginning of the 1930s and it soon became the most important synthetic surfactant in both household cleaning and industrial cleaning formulations. Its popularity was partly due to a relatively low price and partly to its excellent performance. The raw materials, propylene tetramer, benzene, and the sulfonating reagent, which was initially oleum, were readily available at the time and both the alkylation and the sulfonation reactions could be performed in high yields. The surfactant was a good wetting and foaming agent and was effective in solubilizing oily soil. It was insensitive to pH and relatively resistant to hard water.

The branched alkylbenzene sulfonate (BAS) was the work-horse surfactant for the detergent industry until the 1960s when problems related to poor biodegradation started to become obvious. Persistent foams that were attributed to BAS were found in rivers and lakes, as well as in sewage plants. Biodegradation tests, which were introduced at that time, showed that BAS was very resistant to degradation by microorganisms. Figure 2 shows an example of an unwanted foam. The high stability of the surfactant, which had been regarded as an asset when it was developed and introduced on the market, was now seen as a severe problem.

The industry's response to the biodegradation problem with BAS was to replace it with its linear counterpart, linear alkylbenzene sulfonate (LAS), which is also shown in Figure 1. BAS is still used in certain industrial applications where biodegradability is not important, but the volumes are small.

The linear alkylbenzene sulfonates were originally made by alkylating benzene with an alkyl chloride using



Figure 2: Extensive foaming at the wrong place. Picture from Fremont, California taken from Wikipedia.

AlCl_3 as catalyst followed by sulfonation. In the process used today an olefin is used instead of the alkyl chloride and the catalyst is usually HF. The product obtained, the LAS, has a straight alkyl chain attached to the benzene ring by any position on the chain except the two terminal ones. Thus, LAS, like BAS, is a mixture of isomers. The number of carbon atoms in the alkyl chain can be varied but 12 is the most common. (In fact, since the alkyl chain is a distillation fraction, the number of carbon atoms is not an integer; the value is 11.7–11.8 for most commercial products today). This product, often called dodecylbenzene sulfonate, is now the largest synthetic surfactant in terms of volume, with an annual sale of 4 million tons. It is often the main constituent of household detergents and many other cleaning products, where it is usually combined with a nonionic surfactant. It is readily biodegradable.^{4,5}

Thus, environmental concerns triggered a switch from one alkylbenzene sulfonate to another, both produced world-wide in very large scale. The transition could have been dramatic, but it was smooth. The technology to produce LAS was similar to that used since decades to produce BAS and the same surfactant companies could produce the new surfactant in the same plant as the old one. For some applications the highly branched structure of BAS, with as many as six methyl groups, gave a character to the surfactant that was different from what LAS could offer. Methyl groups provide hydrophobicity to the surfactant tail and the more such groups, the more hydrophobic is the tail. However, for most applications the difference in performance between BAS and LAS was small. In hard water LAS even proved to be superior to BAS in detergency.⁶

There are many reports about the toxicity of BAS to bacteria and protozoa in sewage treatment processes.^{7,8} Acute

toxicity of BAS to various freshwater fish has also been documented.^{9,10}

The biodegradation of alkylbenzene sulfonates is now believed to be well understood. The degradation starts with a breakdown of the alkyl chain followed by elimination of the sulfonate group and finally degradation of the benzene ring.^{11,12} For a linear alkyl chain biodegradation is initiated by ω -oxidation of a terminal methyl group generating first a terminal alcohol, then an aldehyde and ultimately an acid. The chain is subsequently degraded by β -oxidation. For a branched alkyl chain, this mechanism does not apply; instead, an α - and β -oxidation mechanism has been demonstrated.¹³ Combined α - and β -oxidation is rare in microorganisms, which explains why the branched alkylbenzene sulfonates degrade so slowly in the environment. However, with prolonged acclimatization, they will ultimately be degraded.¹²

3.2 From alkylphenol ethoxylates to fatty alcohol ethoxylates

Nonyl- and octylphenol ethoxylates were introduced on the market at about the same time as the branched alkylbenzene sulfonates, i.e. during the 1930s. The alkylphenols were made by Friedel-Crafts alkylation of phenol with branched olefins using an acid catalyst and they were subsequently ethoxylated. Ethylene oxide had been known since 1859, when it was synthesized by treating 2-chloroethanol with potassium hydroxide. However, it took until the 1930s for industrial production to start based on the development of the direct oxidation of ethylene with oxygen or air over a silver catalyst. The ethoxylation is normally initiated with potassium

hydroxide which transforms the alkylphenol to alkylphenolate. The phenolate anion attacks the oxirane ring, initiating the polymerization. The length of the oxyethylene chain will simply depend on the ratio of ethylene oxide to alkylphenol. The product is always a broad mixture of homologues, and the homologue distribution can to some extent be varied by the choice of catalyst.

Figure 3 shows the structure of nonylphenol ethoxylate. Since the nonyl group is a mixture of isomers, the resulting surfactant will be a mixture of species with different structures in the alkyl chain (besides the broad distribution of homologues in the polyoxyethylene chain). Figure 3 also shows a typical homologue distribution of an alkylphenol ethoxylate.

There are many similarities between alkylphenol ethoxylates and the branched alkylbenzene sulfonates although the ethoxylates are nonionic and the sulfonates are anionic surfactants. Both became popular rapidly due to a combination of low price and good performance and both shared the undesirable property of being harmful to the environment.

During the 1970s and 80s it became increasingly clear that alkylphenol ethoxylates not only exhibited slow biodegradation, but they were also toxic to marine organisms. Thus, the surfactant failed in OECD's two main criteria related to classification of surfactants: (1) *rate of biodegradation*, which states that >60% of the surfactant should have degraded into CO₂, water and minerals by biological processes within 28 days, and (2) *aquatic toxicity*, where the LD₅₀ value for fish should be above 1 mg/L. Since the alkylphenol ethoxylates did not meet these criteria, they were gradually phased out of markets, starting with consumer products such as laundry detergents and continuing with formulations for industrial use. In addition to relatively slow biodegradability and high aquatic toxicity, alkylphenol ethoxylates were found to exhibit hormone-like effects. In mammals and in fishes they can cause endocrine

disruptive effects as they appear to feminize juvenile males by acting like oestrogens. The endocrine effect is today regarded as the most serious and was the main driving force behind the ban on this type of products in Europe in 2001.¹⁴

The alkylphenol ethoxylates have largely been replaced by fatty alcohol ethoxylates with similar hydrophilic-lipophilic balance (HLB). However, this transition was not as smooth as the transition from branched to linear alkylbenzene sulfonates, discussed above. The alkylphenol moiety contains many methyl groups, as can be seen in Figure 3, while a natural fatty alcohol has only one methyl. Synthetic alcohols may be branched but they rarely contain more than two methyl groups. As discussed in the previous section, the more methyl groups in a surfactant tail, the more hydrophobic is the tail. Another difference between alkylphenol ethoxylates and fatty alcohol ethoxylates is the geometry of the surfactant. The alkylphenol moiety is voluminous compared to a fatty alcohol chain, particularly if the chain is linear. Surfactants with voluminous tails have higher values of the critical packing parameter (CPP) than surfactants with a long, straight chain, which, in turn, make them align better at surfaces and interfaces.¹⁵

A third difference between alkylphenol ethoxylates and fatty alcohol ethoxylates is that the former, but not the latter, contains π -electrons. Surfactants containing π -electrons may form charge-transfer complexes with surfaces that contain electron-deficient olefinic bonds. This type of attractive interaction may be of importance when a surfactant acts as a dispersing agent for organic particles, e.g. certain organic pigments. Figure 4 illustrates formation of a charge transfer complex between an alkylphenol ethoxylate and a surface containing an olefinic bond.

A fourth and important difference between an alkylphenol ethoxylate and a fatty alcohol ethoxylate is that the

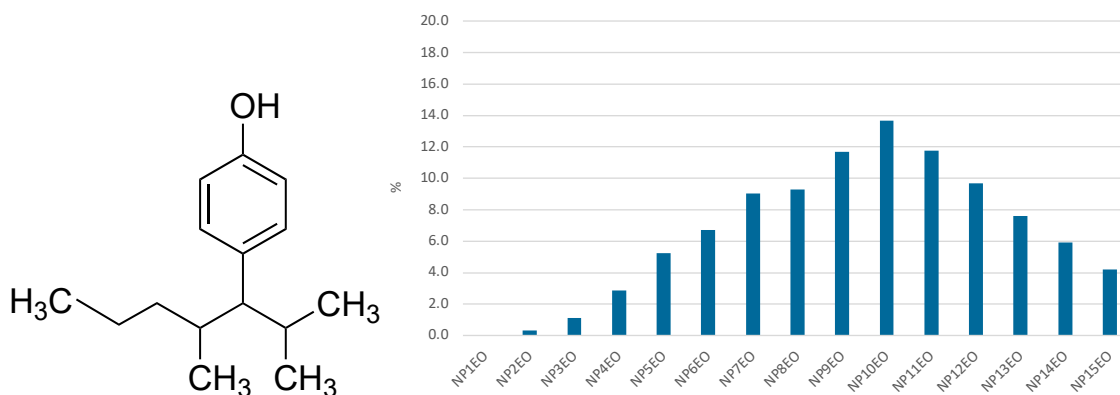


Figure 3: Nonylphenol (left) and the homologue distribution, which is a Poisson distribution, for nonylphenol with 10 mol of ethylene oxide added (deca(ethylene glycol)monononylphenyl ether) (right). The structure shown in the left figure is just one example of the many isomers that the commercial nonylphenol is composed of.

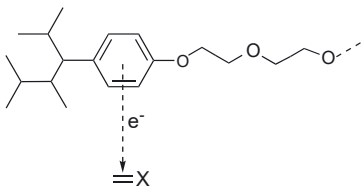


Figure 4: Nonylphenol ethoxylate can interact with a double bond in a surface by formation of a charge-transfer complex.

homologue distribution obtained from the ethoxylation process is different. The phenolic hydroxyl group is more acidic than an alcoholic hydroxyl group. This means that the phenolic hydroxyl group will preferentially be deprotonated, which, in turn, means that there will be no, or little, unreacted alkylphenol left after the ethoxylation, even for surfactants with only few moles of ethylene oxide added.¹⁶ While a typical fatty alcohol with four mol of ethylene oxide will contain (15–20) % unreacted fatty alcohol, nonylphenol with four mol of ethylene oxide contains less than 1% unreacted nonylphenol. Unreacted fatty alcohol can constitute an odor problem.

From the above it is obvious that replacing alkylphenol ethoxylates by fatty alcohol ethoxylates has not been a straightforward process. They are still used in applications such as emulsion polymerization, pigment dispersion, and textile processing; however, the quantities are small compared to what they used to be. As a result, the concentrations of alkylphenol ethoxylates and its degradation products found in rivers and estuaries are nowadays at least one order of magnitude lower than what they were in the 1980s.

In sewage plants and in the environment alkylphenol ethoxylates break down from the hydroxyl end giving metabolites with progressively shorter oxyethylene chains. The terminal hydroxyl groups of the homologues may oxidize to carboxyl groups. The rate of degradation diminishes as the oxyethylene chain becomes shorter because of increasing hydrophobicity of the molecule. Nonylphenol with one or two oxyethylene units are typical long-lived metabolites.^{14,17} It is these degradation products that are responsible for the endocrine effects discussed above.

3.3 From dialkyl quats to diester quats

Quaternary ammonium compounds with two short and two long alkyl substituents, often called ‘dialkyl quats’, were introduced in the 1960s as the active ingredient in textile softeners, also named conditioners. The long alkyl chains are typically straight-chain hexadecyl or octadecyl (often named ‘hydrogenated tallow’) and the short substituents may be

methyl, ethyl, or hydroxyethyl. The surfactants come with a counterion, which may be chloride, acetate, or methyl sulfate. These amphiphiles are very hydrophobic. In water they form gels and liquid crystals instead of micellar solutions.²

Very hydrophobic surfactants often exhibit slow biodegradation and the diquats are no exception. Regardless of the choice of counterion the products did not meet OECD’s criterion for ‘readily biodegradable’. The values for aquatic toxicity for the dialkyl quats were not a problem but that is not enough. Without approved values for both biodegradation and aquatic toxicity a product will not be approved within the OECD countries. Consequently, the industry was forced to look for alternative structures with similar properties. This search resulted in amphiphiles with similar structure but with ester bonds connecting the long alkyl chains and the central quaternary ammonium group, so-called ‘diester quats’. The structures of a dialkyl quat and a diester quat are shown in Figure 5. The transition from the dialkyl quats to the ester quats happened during a period of around 10 years, from 1985 to 1995. This was much faster than the transition from BAS to LAS and from alkylphenol ethoxylates to alcohol ethoxylates and the reason for the quick move was a strong market pull. The market for these surfactants is almost entirely the personal care segment and environmental concern is a much stronger driving force for consumer products than for industrial products. The main customers for these surfactants were the ‘big soapers’, i.e. Procter & Gamble, Unilever, Henkel, etc., and a ‘green’ profile is of high priority for these companies.

As can be seen from the figure, the dialkyl quat and the diester quat have very similar structures. Their physical chemical behavior is also similar, and their softening performance is about the same.¹⁸ However, the routes by which they are prepared differ widely. The dialkyl quats are made by reacting a long-chain nitrile with a long-chain amine to give a secondary amine, which is then methylated to a tertiary amine and subsequently quaternized with methyl chloride or some other alkylating agent. The diester quats, on the other

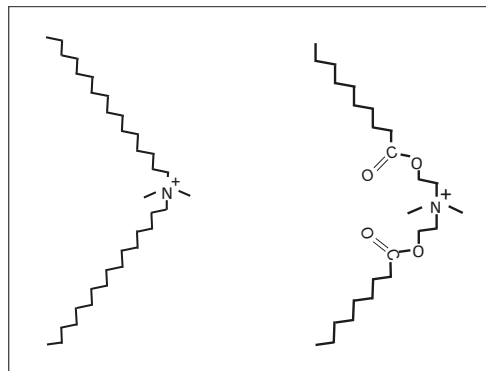


Figure 5: A dialkyl quat (left) and a diester quat (right).

hand, are produced by reacting a fatty acid (or a reactive derivative of the acid) with a diol containing a quaternary ammonium group.

Different equipments are used for the two syntheses, which means that from an industrial point of view the transition from dialkyl quats to diester quats was not as straight-forward as the change from branched to linear alkylbenzene sulfonates. However, as mentioned above, the strong demands from the market around 1990 made it a fast transition.

The diester quats break down readily in the environment. Lipases are efficient catalyst for the ester bonds and the generated fatty acids biodegrade quickly.¹⁹

3.4 Toxicity problems with traces of ethylene oxide and 1,4-dioxane in ethoxylates

Ethoxylated surfactants are made by reacting a long-chain alcohol, acid, amine, etc., with ethylene oxide. As mentioned above, ethylene oxide has been used as an industrial chemical since the 1930s and ethoxylation is one of the major chemical processes today. Ethylene oxide, a three-membered ring, is highly reactive and it was soon realized that it is a chemical that should be treated with caution. One indication of its biological activity is that one of its early uses was as a sterilant in the healthcare industry. Today, we know that ethylene oxide can cause damage to the brain and nervous system. It is classified as both carcinogenic and mutagenic.^{20,21}

The surfactant industry has a long tradition of handling ethylene oxide in a safe manner, so the problem is not there. The problem lies in the minute residues of unreacted ethylene oxide in the surfactants. Ethylene oxide is a volatile compound with a boiling point of 11 °C; thus, it is easily removed by evaporation. The surfactant industry takes advantage of the high volatility and has developed methods to reduce the level of unreacted ethylene oxide to extremely low values.

Low values of residual ethylene oxide are particularly important for ethoxylated surfactants intended for the food, feed, pharma and personal care sectors. The threshold value of ethylene oxide in such products is very low and has been reduced as the analytical methods to quantify ethylene oxide has become more sophisticated. Advanced GC-MS methods today typically report detection limits for ethylene oxide in surfactants in the range of (0.01–1) ppm, depending on the type of surfactant and the preparation techniques.

The detection limit for ethylene oxide in cosmetic products is also very low, often around 1 ppm. In the EU the limit today is as low as the detection limit. The maximum allowed level of ethylene oxide in surfactants intended to come into contact with food is 0.1 mg/kg (0.1 ppm). These

levels are indeed low, and, in addition, ethylene oxide is produced *in vivo* when we metabolize ethylene, which is present naturally in our bodies. We inhale ethylene from various sources, such as burning of biomass, incomplete combustion of fossil fuels, forest fires, exhaust from vehicles, etc.²² Both ethylene oxide and ethylene are also components of tobacco smoke, and smokers and nonsmokers therefore have different exposure profiles to ethylene oxide. The concentration of ethylene oxide in different organs have been determined in animal trials.²³

Against this background one would, from a scientific perspective, regard the minute amounts of ethylene oxide from surfactants as a negligible problem; however, that is not the case. The consumers today are very observant of what is in the products they buy. The mere fact that there can be traces of a carcinogenic and mutagenic compound in a surfactant that goes into cosmetic products or into food is today a problem for ethoxylated products and opens the door for alternative surfactants, not based on ethoxylation.

Another toxicity issue for ethoxylated surfactants is that of 1,4-dioxane, a substance that is classified as potentially carcinogenic. 1,4-Dioxane (often referred to as just ‘dioxane’ since the 1,2- and 1,3-isomers are not important) has a long tradition as a solvent for textiles, paper, flame retardants, and adhesives. Its acute toxicity is low with an LD₅₀ of 5170 mg/kg in rats but there are indications that it may be a carcinogen. It was listed as “reasonably anticipated to be a human carcinogen” by the U.S. Department of Health and Human Services in 2016.^{24,25} Consequently, its use as a solvent has dramatically decreased during the last decades.

Dioxane is produced commercially by acid-catalyzed dehydration of diethylene glycol. However, it is also generated as a biproduct in ethoxylated products. Dioxane is formed in the normal process of making fatty alcohol ethoxylates by treating a fatty alcohol with ethylene oxide but the amount of dioxane formed with the traditional alkaline catalyst is very low.^{26–28} Ethoxylation of a fatty alcohol can also be made with a Lewis acid catalyst such as SnCl₄ or BF₃ and the level of dioxane formed is then much higher.¹⁶ Partly for that reason the acid route is not much used today.

The big concern with 1,4-dioxane in surfactants relates to sulfated fatty alcohol ethoxylates, the so-called alcohol ether sulfates. The typical alcohol in these products is dodecanol (lauryl alcohol) and the number of oxyethylene units is only two or three. Laureth sulfate is a commonly used name for these products and its formula is given below, see Figure 6. Laureth sulfate is frequently used in personal care products, hand dishwashing liquids, and many other consumer products.

Laureth sulfate is made by adding two or three mol of ethylene oxide to dodecanol followed by sulfation. Under

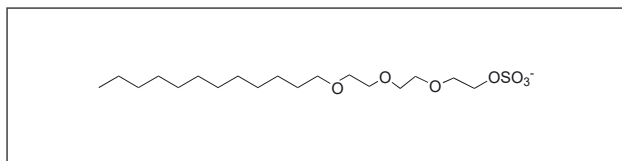


Figure 6: Laureth sulfate, an important surfactant in many consumer products.

the strongly acidic sulfation step, dioxane will be generated. A fraction of the laureth sulfate will decompose into 1,4-dioxane, SO_3 and an alcohol ether sulfate that has lost two oxyethylene units. This means that if the intended laureth sulfate contains three oxyethylene units there will be a small fraction of dodecanol with only one oxyethylene unit and if the intended laureth sulfate contains two oxyethylene units the biproduct will be dodecanol. The reaction scheme is shown in Figure 7.

1,4-Dioxane is a liquid with a boiling point of 101°C . This means that evaporation under vacuum is an obvious way to reduce the content in the surfactant. However, such a treatment does not eliminate all dioxane and other methods, such as adsorption on specific high-surface materials, are used in order to reduce the levels further. However, in the end there will always be traces of dioxane left in the surfactant, which means that the formulated product will not be completely free from the potentially carcinogenic biproduct. A recent report stated that in the US 53 % of laundry detergents, 59 % of shampoos, 62 % of body cleansers, and 69 % of dish soaps contained 1,4-dioxane levels above 1 ppm.²⁷

Measuring very low levels of 1,4-dioxane in water is nowadays relatively straight-forward using advanced gas chromatography techniques. Measuring the dioxane content in consumer products is much more complex, however. Consumer products are complex formulations containing a diversity of ingredient classes, including surfactants, solvents,

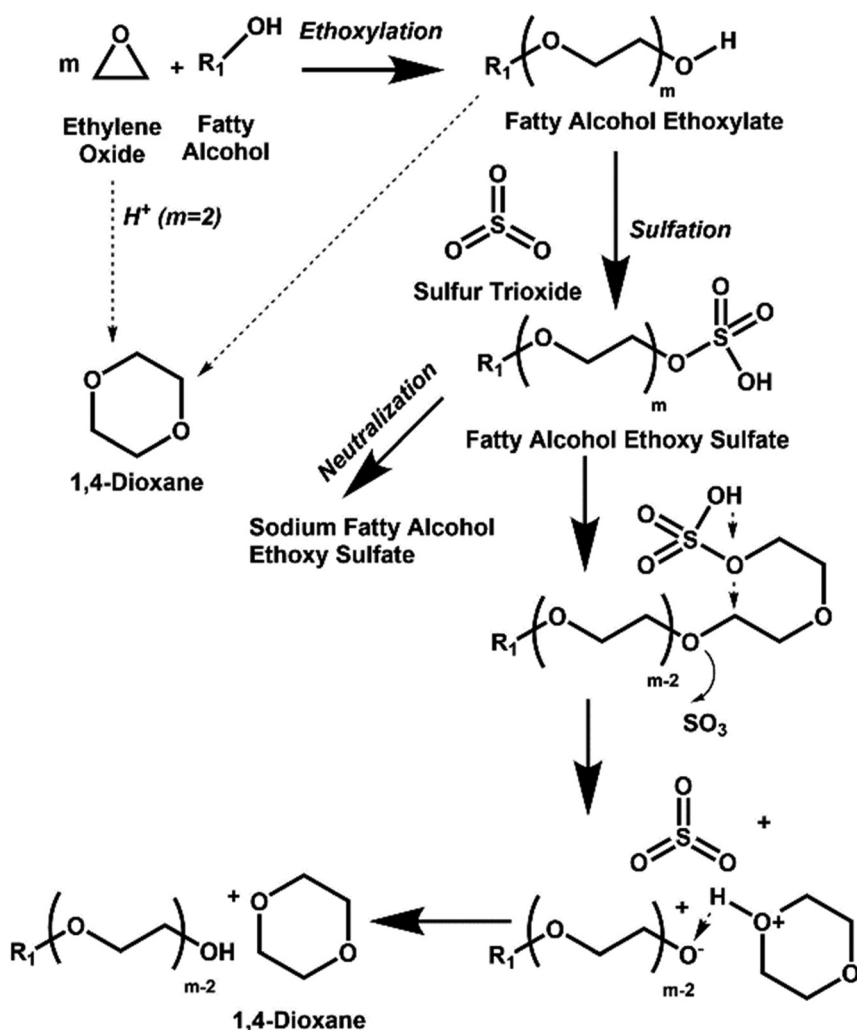


Figure 7: Formation of 1,4-dioxane during the synthesis of laureth sulfate. (Redrawn from ref. 27).

dyes, pigment, perfumes, polymers, preservatives, and so forth. It is therefore a challenge to quantify the dioxane content in these products down to ppm levels. The best approach appears to be capillary GC with MS or possibly MS-MS detection.²⁹

Thus, ethoxylated surfactants, and in particular fatty alcohol ether sulfates, suffer from a problem with residual traces of dioxane in the products. The levels are very low, probably so low that the hazard can be neglected on scientific grounds. However, the consumer does not always follow what science tells. Like with remaining traces of ethylene oxide in ethoxylated surfactants, the mere risk of having 1,4-dioxane, a potentially carcinogenic substance, in a surfactant for personal care products is something that a growing number of consumers will not accept. It is, therefore, a major concern for the surfactant industry today.

Taken together, the small amounts of unreacted ethylene oxide and generated 1,4-dioxane in surfactants made by ethoxylation are regarded as a problem and have become one of the main driving forces behind the ambition to replace ethoxylated surfactants with something else. The alternative can be synthetic amphiphiles with a polyhydroxyl moiety instead of a polyoxyethylene chain as polar headgroup. The polyol may be either sugar or polyglycerol. There is currently a rapidly growing activity both in academia and in the surfactants industry to develop nonionic surfactants with glycerol instead of ethylene oxide as building block for the polar headgroup.

Another alternative is to switch to biosurfactants, which may be produced by macroorganisms or microorganisms. Examples of the first category are saponins and lecithin. Saponins are obtained from a variety of plants, the most well-known being the soap bark tree, *Quillaja saponaria*. Lecithin can be of either plant or animal origin, examples being soybean lecithin and egg lecithin, respectively. Lecithin has been a commercial surfactant since long back and has an established position on the market while saponins can be regarded as emerging amphiphiles with limited commercial use today.

Natural surfactants produced by microorganisms are also growing in importance, the most prominent types being sophorolipids and rhamnolipids. These biosurfactants are produced by fermentation of either yeast or bacteria. Sophorolipids are produced by many non-pathogenic yeasts, principally from *Starmerella* genus, and rhamnolipids are produced by the pathogenic bacterium *Pseudomonas aeruginosa*. These natural surfactants are commercial and have found use in a wide variety of areas, the personal care sector probably being the most important today. The volumes are still small compared to the synthetic surfactants but are steadily growing. The fact that they are completely free of ethylene oxide and dioxane is used for the promotion. The high production cost is

the main obstacle for a more rapid expansion. Biotechnological production of surfactants is still expensive compared to chemical synthesis even when cheap carbon sources, such as sugar and vegetable oil, are used. The reaction time is long, the yield is relatively low and the work-up is cumbersome. It is likely that the price difference between biotechnological and chemical production will decrease in the future.

3.5 Use of specific zwitterionic surfactants to achieve formulations with low skin toxicity

All surfactants show some kind of biological activity. They are designed to adsorb at surfaces, and they are usually able to penetrate porous material. Skin is a porous material, and it is then not surprising that many surfactants, when applied to skin, elicit irritant reactions. Surfactants are capable of interacting both with proteins and lipids in the stratum corneum. By penetrating through this layer, surfactants are also able to affect living cells in deeper regions of the skin.³⁰

It has been known for a long time that some classes of surfactants are more skin irritating than others. Anionic and cationic surfactants are generally seen as more problematic than nonionic and zwitterionic surfactants. Cationics, in particular, have a reputation of causing skin and eye irritation, which is not surprising since this surfactant class has a long history as bactericides. Hence, they are more biologically active than the other surfactant classes.

One of the reasons why nonionic and zwitterionic surfactants are less irritating than ionic surfactants is believed to be that they have much lower values of the critical micelle concentration (CMC). For the same length of the hydrophobic tail the nonionic and zwitterionic surfactants have two orders of magnitude lower CMC than the ionic surfactants. The reason for this is that they do not carry any counterions. There is a considerable entropy penalty involved in the micellization of ionic surfactants because it leads to an accumulation of counterions around the micelle.¹⁵

When formulating a personal care product, e.g. a shampoo, one cannot only go for mildness. Performance, such as cleaning and degreasing for a shampoo, is essential so a compromise may have to be made between good performance and mildness to skin and eye.

The first shampoos on the market were relatively eye-irritating but this changed with the discovery that when a fatty alcohol ether sulphate, a so-called laureth sulfate, see Section 3.4, was combined with certain zwitterionic surfactants a very mild formulation was obtained, which also exhibited good technical performance. The choice of zwitterionic surfactant was critical. Only those that could switch

between a zwitterionic and a cationic state would work. Betaine surfactants and amine oxide surfactants are the zwitterionic surfactant types most commonly used for the purpose.

The pronounced mildness of such formulations can be explained as follows (and illustrated in Figure 8 for a betaine surfactant): The betaine surfactant is zwitterionic at neutral pH but if the carboxylate group becomes protonated it will turn into a cationic surfactant. This happens if the pH is reduced but a shampoo or a cleanser should have a pH of 5–6, which is the normal pH of the hair and scalp. Deviations from this pH can be harmful, particularly for persons with dry skin.³¹ A pH of 5–6 is above the pK_a of the carboxyl group, so one would then expect the betaine surfactant to stay zwitterionic. However, when put into an aqueous solution together with the laurath sulfate the possibility appears to form mixed micelles involving the anionic surfactant and the betaine surfactant in protonated form, i.e. in the form of a cationic surfactant. Formation of mixed micelles of one anionic and one cationic surfactant is thermodynamically favored for the same reason as why micelles of nonionic surfactants are favored: there are no counterions around the micelle and, hence, no entropy penalty related to counterions. Formation of such a mixed micelle is so favorable that it triggers protonation of the carboxylate group.

This means that the micelles are composed of one anionic and one cationic surfactant, the laurath sulfate and the protonated betaine surfactant, respectively. Such mixed micelles have very low CMC values, which means that the concentration of the unimers is very low. The unimers are an anionic surfactant and a zwitterionic surfactant, which is a good cleaning and degreasing combination. The low unimer concentration is advantageous from a dermatological standpoint because it is the unimers, not the micelles, that are skin irritating. Micelles have no surface activity and will not interact with the skin surface. This is a formulation that possesses surfactant synergy,

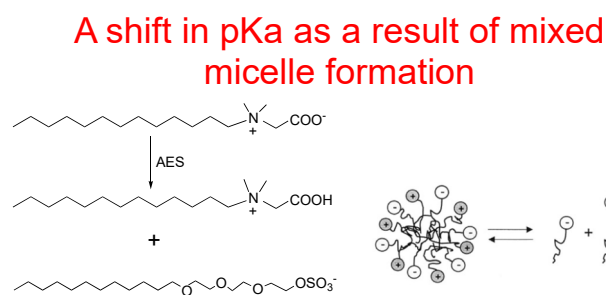


Figure 8: A betaine surfactant may take up a proton and become a cationic surfactant when put into an aqueous solution together with an anionic surfactant, such as laurath sulfate, even at a pH higher than the pK_a of the carboxyl group. The driving force is the possibility to form mixed micelles of anionic and cationic surfactant.

meaning that the combination is better than the individual constituents. Such a combination is milder to the skin and eye than either of the two surfactants alone. Anionic surfactants alone can be relatively skin irritating. In this type of formulation, the zwitterionic surfactant is said to impart mildness to the laurath sulfate.

3.6 Surfactant-based CO₂ foam flooding for both enhanced oil recovery and carbon storage

Among the many versatile applications of surfactants, such as detergents, emulsifiers, wetting agents, etc., foam generation ability is one of the most important and has been exploited extensively. It was well understood that when a liquid (usually water) is agitated with gas, foam will be generated by the formation of gas cells whose walls consist of thin liquid films called lamellae. If surfactants are present in the aqueous phase, the surfactant molecules tend to adsorb onto the gas-liquid interface with their hydrophobic chain oriented toward the gas and the hydrophilic group toward the liquid, resulting in a decrease of the gas-liquid interfacial tension and an increase of the film elasticity (Figure 9). This helps to prevent lamella rupture and bubble coalescence, which contributes significantly to stabilization of the foam.³²

In the petroleum industry, gas injection and water alternate gas (WAG) injection are two stimulation techniques used by operators to increase oil recovery.³⁴ However, due to the low gas density and the low viscosity and high mobility of the injected fluids, severe fingering and channeling are encountered during gas or WAG implementation. This leads to quick gas breakthrough and poor sweep efficiency. To address these issues, foam flooding, which holds much higher viscosity compared to gas and WAG, was developed. Laboratory and field tests have demonstrated that foam flooding is able to improve both areal and vertical sweep.^{33,35} As oil displacement is strongly dependent upon sweep efficiency, the use of a viscous foam is a way to achieve efficient oil recovery. Among the gases used to generate foams, CO₂ is advantageous because of its relatively high solubility in oil, which gives reduction of the oil viscosity, facilitates reaching a miscible state (low minimum miscibility pressure), and decreases the interfacial tension.^{36,37} In addition, the carbon capture and storage (CCS) strategy to handle the ever-increasing global temperature is gaining considerable attention across the world. CO₂ Enhanced oil recovery (EOR), as a CCS technique, has been considered a realistic way to reduce the amount of greenhouse gases in the atmosphere from an economical point of view.^{37,38} In this process, CO₂ is used as

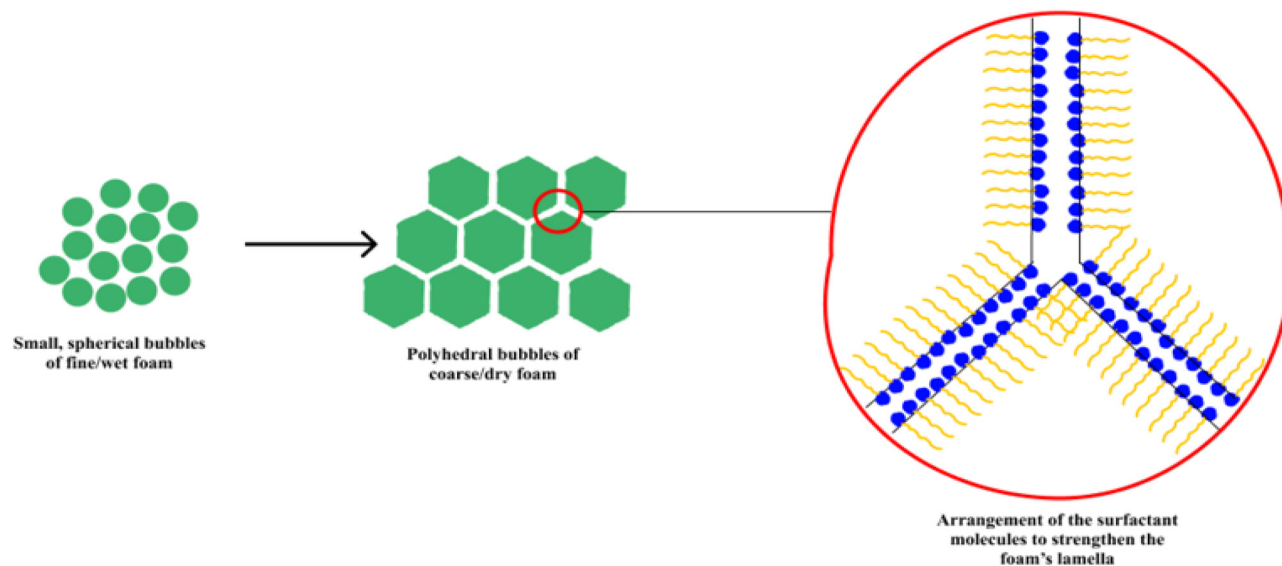


Figure 9: Arrangement of surfactant molecules at the foam lamella.³³

a valuable resource to boost oil production, while at the same time storing large amounts of anthropogenic CO₂ permanently in the geological subsurface formations. Therefore, foam flooding with CO₂ is believed to be a viable way to address the growing climate change concerns.

As mentioned previously, surfactants are commonly used to generate foams. Depending on the target reservoir properties such as temperature, formation brine salinity, and formation mineralogy, different kinds of surfactants have been found to be optimal to generate sufficiently stable CO₂ foams for EOR purposes. For instance, Qichao et al. reported the use of sodium lauryl polyoxyethylene ether sulfate, an important anionic surfactant, to generate CO₂ foam for carbonate reservoirs.³⁹ Roozbahani et al. tested another important anionic surfactant, sodium dodecylbenzene sulphonate, for CO₂ foam flooding for both EOR and CCS purposes.³⁷ Sodium dodecylbenzene sulphonate is widely used in EOR because of its excellent foaming ability, low tendency for adsorption on the reservoir rock, high detergency, and cost-effectiveness. Gauteplass et al. used an alpha olefin sulfonate, an anionic surfactant with high foaming ability, to generate viscous foams to maintain favorable mobility control in fractured reservoirs.⁴⁰ Besides anionic surfactants, both zwitterionic and nonionic surfactants have been explored for the creation of CO₂ foams for EOR. Ming et al. studied a zwitterionic surfactant, the pentasodium salt of *N,N,N'*-dodecyl diethylene triamine pentaacetic acid, to generate stable foams in a saline environment for post-polymer flooding EOR. The oligomeric surfactant possessed superior foaming performance compared to the corresponding monomeric surfactant. A pilot test was conducted

based on the laboratory results and promising results were obtained.⁴¹ Nonionic surfactants, which possess high tolerance to salinity, were also investigated by various researchers in the field of CO₂ foam EOR. Pandey et al. used Triton X-100 as a foaming agent to investigate the rheology, stability, and viscoelasticity of CO₂ foams, as well as the influence of different electrolytes on foam properties.⁴²

During the past two decades, with the rapid development of nanotechnology and the deepened insight into foam formation mechanisms, use of nanoparticles has attracted considerable interest as a way to create more stable and robust CO₂ foams. Numerous studies have verified that the incorporation of specifically modified nanoparticles into conventional surfactant formulations can significantly improve foam stability under harsh reservoir conditions. The nanoparticles can irreversibly adsorb at the gas-liquid interface, thus retarding foam coalescence, disproportionation, and film drainage.^{38,43–50} It is anticipated that the synergism between surfactants and nanoparticles will push CO₂ foam flooding to a new stage, which beneficially affects the environment by sequestering large amounts of carbon in geological formations.

4 Conclusions

We have here presented five cases where one type of surfactant has been, or is about to be, replaced by another. For three of the cases, environmental concern has been the driving force. For two of these, the branched alkylbenzene sulfonate that was replaced by its close relative linear

alkylbenzene sulfonate and the dialkyl quat that was replaced by the diester quat, a product with very low rate of biodegradation was replaced by a product that was rapidly degraded by microorganisms. For the third case, a class of surfactants that was toxic to the marine environment, the alkylphenol ethoxylates, was substituted by fatty alcohol ethoxylates, which exhibits much less aquatic toxicity. The first two transitions proceeded smoothly, while replacing nonylphenol ethoxylates with an environmentally more benign surfactant turned out to be more difficult and the transition has to some extent been made at the price of loss in performance.

This review also discusses the problem related to ethoxylated surfactants for use in applications such as food, feed, pharma, and personal care. Ethoxylated products contain minute amounts of two small molecules that are classified as carcinogenic or potentially carcinogenic, ethylene oxide and 1,4-dioxane, respectively. It is not possible to completely remove them from the surfactant, which is a concern for many consumers. Consequently, there is now a growing interest to replace ethoxylated surfactants with other classes of amphiphiles, e.g. polyol-based synthetic surfactants or natural surfactants, such as saponins, sophorolipids and rhamnolipids.

The review also presents a case where a clever formulation has made it possible to produce consumer products with an excellent dermatological profile. A mixture of two different surfactants, a cationic and a zwitterionic surfactant, gives much less skin and eye irritation than the individual surfactants alone. This is of particular value for products such as baby shampoos and facial cleaners.

Finally, the review discusses surfactant-based CO₂ foam flooding. This is an established EOR procedure. However, it is also a procedure to sequester CO₂ by storing it deep down in subsurface geological formations. Thus, the use of surfactants to generate CO₂ foam for EOR purposes has a dual benefit: increasing oil production and reducing the level of CO₂ in the atmosphere. CO₂ foam flooding can probably be seen as an economically more realistic CCS technique than many other such techniques proposed in the literature.

From the examples given in this article it should be clear that environmental and toxicity concerns has been, and continues to be, a very important driving force for the development of surfactants and surfactant formulations.

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