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Reviews

Sulfonation Technology for Anionic Surfactant Manufacture

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Abstract:

This paper presents an overview of reactor technology and reaction chemistry for surfactant manufacture via sulfonation with sulfur trioxide. The manufacture of surfactants derived from linear alkylbenzenes, primary alcohols, ethoxylated alcohols, and alpha olefins is described.

Introduction

Sulfonation is the predominant route to manufacturing of anionic surfactants other than soap. The fundamentals of sulfonation technology have been developed largely in the detergents industry, but many of the more recent advances have been equally driven by quality requirements for surfactants to be used in personal products and cosmetics applications.

This paper is intended to provide an overview of modern sulfonation technology and the underlying science, with particular emphasis on the manufacture of those surfactants which are most relevant to personal products and cosmetics products.

Scope

Sulfonation in the broadest sense of the word can be used to refer to the introduction of a sulfonic acid group, or its corresponding anionic sulfonate group, into an organic compound. Conversion of a hydroxyl group to a sulfate group (sulfation) is also covered by this broad definition. Reagents can be electrophilic (e.g., sulfur trioxide and its complexes, sulfuric acid, chlorosulfonic acid, or oleum) or nucleophilic (e.g., sodium sulfite). Free radical sulfonation of paraffins by sulfur dioxide and oxygen is also practised. The scope of this paper is restricted to sulfonation and sulfation by sulfur trioxide, which has become the most widely used method.

General Features of Sulfonation by Sulfur Trioxide

Sulfur trioxide is a liquid in the temperature range 32−44.5 °C. Below 32 °C a solid form begins to crystallise out, although this can be inhibited, down to a temperature of 16.5 °C, by small amounts of stabilising additives.[1] Liquid sulfur trioxide is not much used as a direct sulfonating agent, but in some commercial sulfonation plants it is vapourised and diluted with air to provide a gaseous sulfonating agent. In many plants, however, sulfur trioxide is not stored as such but is produced on site by sulfur burning and catalytic oxidation, the resulting sulfur trioxide/air mixture being fed continuously to the sulfonation reactor.

Sulfur trioxide is a very reactive sulfonating and sulfating agent. Accurate rate constants are rarely available, being too large to be conveniently measurable, but sulfonation and sulfation reactions are often described as “instant” or diffusion controlled. These reactions are highly exothermic, heats of reaction being of the order of 150−170 kJ/mol[1] (this includes ca. 25 kJ/mol for the heat of absorption of gaseous sulfur trioxide in the organic substrate[2]). Sulfur trioxide can also act as an oxidising agent, presumably via hydride abstraction, leading to colour formation. For the common surfactant feedstocks, it appears that oxidation has a higher activation energy than sulfonation or sulfation.

Sulfonation Reactors

The simplest way to carry out a sulfonation reaction with sulfur trioxide is to bubble the required amount of a gaseous sulfur trioxide/air mixture into the stirred feedstock, the reaction exotherm being controlled by cooling and by adjustment of the rate of addition. This batch process (Figure 1) is a convenient method on the laboratory scale, particularly for alkylbenzene feedstocks, and is still practised to some extent on the commercial scale.

A refinement of this method is to carry out the reaction in a continuous stirred tank reactor system (Figure 1), the feedstock being fed at the base of the reactor, into which a gaseous sulfur trioxide/air mixture is also fed, the reaction product being allowed to overflow from the top of the reactor. A cascade of such reactors can be used, whereby part of the required total of sulfur trioxide is supplied to the first reactor, the partially converted mixture from this reactor is fed to the base of a second reactor to which further sulfur trioxide is supplied, and so on. Cascade reactor systems of this type, illustrated schematically in Figure 1, are still used quite extensively in the detergent industry, although tending to be superseded by film reactors (see below). The reason why a cascade reactor has advantages over a single continuous tank reactor is that the reaction mixture becomes more viscous as the conversion increases, making heat transfer and mass

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(1) Herman de Groot, W. *Sulfonation Technology in the Detergent Industry*; Kluwer: Dordrecht, 1991.

(2) Roberts, D. W.; Morley, J. O. *Comun. Jorn. Com. Esp. Deterg.* **1997**, *27*, 145.

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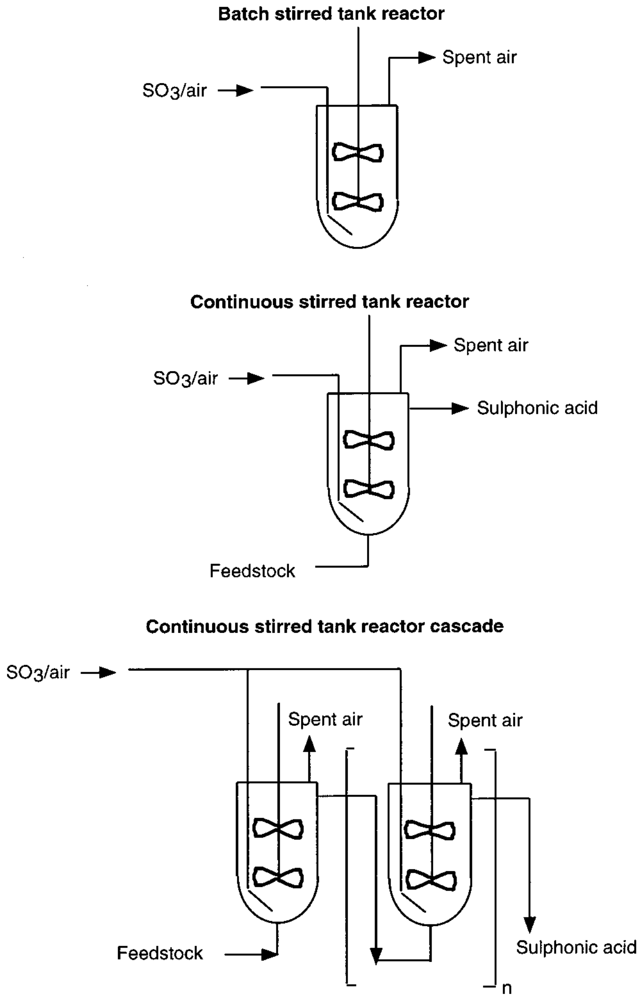

Figure 1. **Stirred-tank sulfonation reactors: External cooling jacket and internal cooling coils not shown.**

transfer less efficient. Consequently colour formation becomes more difficult to control as conversion increases. The cascade system addresses this difficulty by allowing sulfur trioxide addition in the later stages to be done more slowly.[1]

With the above types of reactors, it would be almost impossible to reduce the residence time of the reaction mixture below about 30 min. This is not a problem for sulfonation of alkylbenzene feedstocks, but it makes these reactors unsuitable for sulfonation of feedstocks such as primary alcohols, ethoxylated alcohols, and olefins. With these feedstocks the desired sulfonation and sulfation products are unstable in the acid form and need to be stabilised by neutralisation within a few minutes of their formation. To meet the need for capability to sulfonate or sulfate a range of different feedstocks, film reactors were introduced in the 1960s. Developments in the design of film reactors have continued up to the present. Nowadays the majority of new sulfonation reactors installed are of the film reactor type.

Principles of Film Reactor Design

The basic principle of a film reactor is that a stream of gaseous sulfur trioxide, diluted with air, is passed through a vertical tube, with the organic liquid feedstock flowing concurrently as a film along the tube wall (Figure 2). Usually the liquid and gas travel in a downward direction along the tube, and the reactor is referred to as a falling-film reactor (FFR). However, climbing-film reactors are also used in the industry. The main impetus for the flow of the organic liquid is the drag exerted by the gas on the film, the gravitational contribution being negligible. As the liquid and gas flow along the tube, sulfur trioxide is absorbed by the liquid and reacts to form the sulfonated product. The heat of reaction is removed by coolant applied to the other side of the tube wall. Because the surface-to-volume ratio of the film is high, the reaction exotherm can be efficiently removed within the short residence time (ca. 30 s) of the liquid.

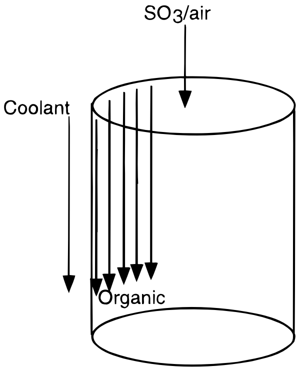

Figure 2. **Film reactor principle. The film is usually falling (FFR) but can be climbing. Typical dimensions (pilot plant): diameter, 25 mm; length, 6 or 2 m.**

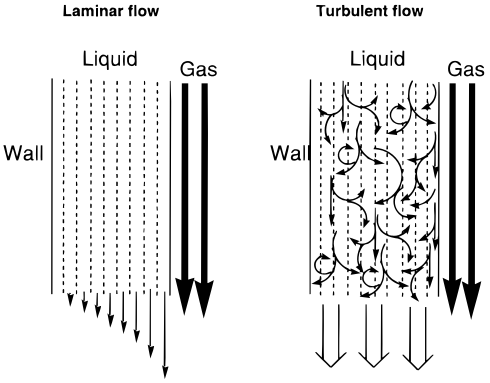

Figure 3. **Laminar and turbulent flow.**

The hydrodynamics and thermokinetics of FFR sulfonation are complex and interlinked. The flow pattern of the liquid down the reactor is predominantly laminar rather than turbulent (Figure 3), and consequently, as sulfur trioxide is absorbed at the gas/liquid interface, temperature and composition gradients develop in the radial direction as well as in the vertical direction. These gradients lead to differences in mass transfer and heat transfer characteristics at different points. The maximum temperature is reached at the gas/liquid interface near the top of the reactor and may exceed 100 °C. The viscosity of the film, being dependent on composition and temperature, varies substantially, leading to variation of film thickness along the length of the reactor (typically from less than 0.5 mm at the top of the reactor to ca. 2 mm at the bottom) and to radial and vertical variations in the degree of turbulence in the film. These characteristics make mathematical modelling of film sulfonation far from straightforward, but several models, differing in the nature of the simplifying assumptions made, have been published.[3-8] Film reactor modelling remains an active area of current research.

A typical pilot plant scale falling-film reactor consists of a vertical reactor tube of about 25-mm internal diameter and about 6 m in length. Such a reactor would have a throughput of ca. 40 kg/h of linear alkylbenzene sulfonic acid and, using a 5% solution of gaseous sulfur trioxide in air, would operate with a gas velocity of ca. 30 m/s.[1] In another type of design, a shorter film section is followed by a quench recycle loop. The film reactor is only about 2 m in length and the gas velocity is about double that for the 6-m film reactor. The gas/liquid mixture from the bottom of the film section is mixed with a cooled recycled stream of the liquid product, and this mixture is fed to a gas−liquid separator. The separated liquid is cooled and separated into two streams: one is recycled to the base of the film reactor, and one is taken off as product. The principle behind this design is that better mixing and heat transfer can be achieved in the quench recycle than in the lower section of a 6-m film reactor. On the other hand, the total residence time of the liquid reaction mixture is greater.

A film reactor cannot simply be scaled up by altering the tube dimensions, since the hydrodynamics would then become completely different. For example, suppose it is intended to increase the capacity by a factor of 10. If the diameter of the tube is increased by a factor of 10, so as to give the same film thickness at the top of the reactor, the cross-sectional area increases by a factor of 100. Thus to keep the molar proportion of sulfur trioxide to feedstock constant and the sulfur trioxide in air concentration the same, the gas velocity would be reduced by a factor of 10. The drag on the film would be correspondingly reduced, leading to a longer film residence time. To achieve complete absorption of the sulfur trioxide by the film, the reactor length would have to be increased by a factor of 10, which would clearly be impracticable.

There are two approaches used to overcome this scale-up problem. One is to scale up simply by increasing the number of tubes, each tube having the same dimensions as the single-tube pilot scale reactor. Multitube reactors of this type are used extensively. Another approach is to use an annular reactor, in which the gas is passed down the annular space between two concentric tubes, the liquid feedstock being supplied to the outer surface of the inner tube and to the inner surface of the outer tube. By changing the diameters of the concentric tubes, but keeping the annular gap the same, the capacity can be varied, without effect on the hydrodynamics. Reactors of this type are also commonly used in the industry.

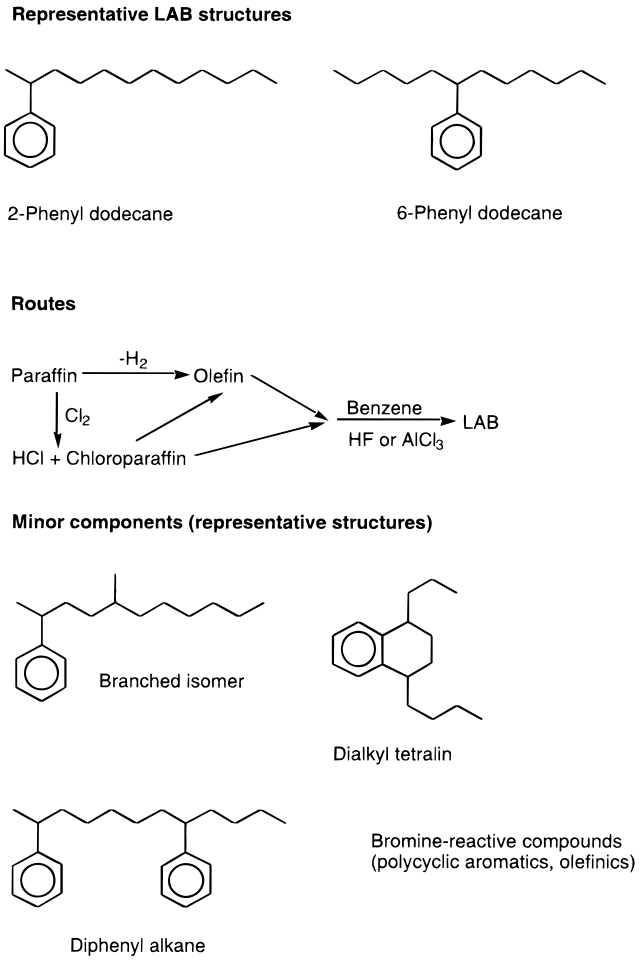

Figure 4. **Representative LAB structures, manufacturing routes, and minor components.**

Sulfonation conditions in a film reactor can be adjusted by modifying the throughput of the feedstock. This means a corresponding change in the sulfur trioxide throughput and, if the air throughput remains fixed, a change in the concentration of sulfur trioxide in the gas stream supplied to the reactor. For a given gas velocity, sulfur trioxide is absorbed by the film at a rate proportional to its concentration in the gas. Reducing the initial concentration of sulfur trioxide in air therefore reduces the temperature maximum in the film.

Other ways of adjusting sulfonation conditions are to change the coolant temperature (although in practice the scope is restricted by the need to maintain the reaction mixture sufficiently fluid) and to change the molar ratio of sulfur trioxide to feedstock. However, the scope to do this is limited by the need to achieve high conversion and the need to avoid oversulfonation leading to by-product and colour formation.

In carrying out a continuous sulfonation run, the throughputs and temperatures of feedstock, air, sulfur trioxide, and coolant are usually set at predetermined values and fine-tuning is done by making fine adjustments to the feedstock throughput in response to plant-side analysis of samples from the reactor outlet.

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(3) Johnson, G. R.; Crynes, B. L. *Ind. Eng. Chem. Process Des. Dev.* **1994**, *13*, 6.

(4) Mann, R.; Moyes, H. *AIChE J.* **1977**, *23*, 17.

(5) Davis, E. J.; Van Ouwerkerk, M.; Venkatesh, S. *Chem. Eng. Sci.* **1979**, *34*, 539.

(6) Tsuto, K.; Nakayama, M.; Imamura, S.; Majima, K. *Kagaku Kogaku Ronbunshu* **1985**, *11*, 369.

(7) Gutiérrez-González, J.; Mans-Teixidó, C.; Costa-López, J. *Ind. Eng. Chem. Res.* **1988**, *27*, 1701.

(8) Dabir, B.; Riazi, M. R.; Davoudirad, H. R. *Chem. Eng. Sci.* **1996**, *51*, 2553.

Sulfonation Chemistry

Sulfonation and sulfation reaction pathways vary according to the feedstock. In most cases the mechanism is more complex than a simple bimolecular reaction to form the required product. Usually the initial reaction can be followed by further, slower reactions. These points will now be illustrated by a discussion of the sulfonation or sulfation of linear alkylbenzenes, primary alcohols, ethoxylated primary alcohols, and olefins.

Linear Alkylbenzene Sulfonation. Linear alkylbenzene sulfonate (LAS) is the major anionic non-soap surfactant used in the detergent industry. It is made by sulfonation of linear alkylbenzenes (LAB). Although the manufacture of LAS has been practised for many decades, new insights into the sulfonation chemistry continue to emerge.

Commercial LAB is a mixture of isomers and homologues having the general structures shown in Figure 4, which also summarises the routes used in the petrochemical industry for LAB manufacture. The minor components shown amount to well under 10% in total. The dialkyltetralins are nowadays commonly specified at 1% or less, since their sulfonation products are less readily biodegradable than LAS. The presence of bromine-reactive compounds is associated with a tendency to form coloured by-products on sulfonation and a maximum bromine index (mg of bromine consumed by 100 g of sample) is usually quoted in LAB specifications.

Although the sulfonation of LAB is very rapid and for practical purposes may be treated as diffusion controlled, paradoxically it does not go to completion in FFR sulfonation but requires a further ageing step with a residence time of about 30−40 min at ca. 45−55 °C. Typically the conversion of LAB to LAS is about 90−92% when the reaction mixture emerges from the FFR, and it rises to about 97−98% after ageing. The explanation for this paradox[9] is that, accompanying the main reaction with overall stoichiometry

$$\mathrm{ArH} + \mathrm{SO_3} \rightarrow \underset{\text{LAS}}{\mathrm{ArSO_3H}} \qquad (1)$$

there is a side reaction with overall stoichiometry

$$2\mathrm{ArH} + 3\mathrm{SO_3} \rightarrow \underset{\text{LAS anhydride}}{\mathrm{ArSO_2OSO_2Ar}} + \mathrm{H_2SO_4} \qquad (2)$$

When the reactor is fed with sulfur trioxide and LAB in a 1:1 molar ratio, then to the extent that reaction 2 occurs there will be residual LAB when all of the sulfur trioxide has been consumed. This explains why the conversion at the base of the FFR is relatively low.

However, LAS anhydride and sulfuric acid together act as a slow sulfonating agent, and in the ageing step they sulfonate the residual LAB to produce more LAS, in a reaction with overall stoichiometry

$$\mathrm{ArH} + \mathrm{ArSO_2OSO_2Ar} + \mathrm{H_2SO_4} \rightarrow 3\mathrm{ArSO_3H} \qquad (3)$$

As a final step in LAS manufacture it is customary to add a small amount of water (typically less than 1%) after ageing, to hydrolyse any remaining LAS anhydride. The chemistry underlying the effect of water addition does not appear to have been fully investigated, but it is usually argued that residual LAS anhydride could continue to sulfonate under uncontrolled conditions during storage, leading to colour formation.

Another side reaction leads to formation of diaryl sulfones and sulfuric acid, the overall stoichiometry being

$$2\mathrm{ArH} + 2\mathrm{SO_3} \rightarrow \mathrm{ArSO_2Ar} + \mathrm{H_2SO_4} \qquad (4)$$

To the extent that it occurs, sulfone formation limits the maximum achievable conversion of LAB to LAS to a value below 100% and makes it impossible to completely avoid the presence of sulfuric acid (typically at levels in the range ca. 1−2%) in the final sulfonation product. Sulfone levels in the final product depend on the ratio of sulfur trioxide to LAB supplied to the reactor, but are usually below 1%.

Recently the mechanism of the main reaction, eq 1, has been explored by means of a molecular modelling approach.[2] Probably the simplest mechanism that can be envisaged is electrophilic attack of sulfur trioxide on LAB to produce a Wheland intermediate, which reacts further to form LAS. However, from ab initio calculations of the appropriate molecular orbital energies it appears that the activation energy for this reaction pathway would be too high to account for the reaction proceeding almost to completion within the 30-s residence time of commercial film reactors. An alternative mechanism has been proposed whereby in a first step LAS reacts with sulfur trioxide to form a short-lived pyrosulfonic acid. It may be noted that in FFR sulfonation the liquid at the gas/film interface will be composed mainly of LAS even when the overall conversion is low, since LAS is surface active. In the second step the pyrosulfonic acid reacts with LAB to produce 2 molar equiv of LAS: 1 molar equiv can be regarded as replacing the LAS consumed in the first step, and the other can be regarded as contributing to the increase in conversion. This proposed mechanism is shown in Scheme 1. For this mechanism the system need to be primed initially with a small amount of LAS or pyrosulfonic acid. The proposed priming sequence, via a 2:1 sulfur trioxide/LAB α-complex, is also shown in Scheme 1.

The side reactions 2 and 4 probably represent alternative reaction pathways starting from the pyrosulfonic acid. Possible mechanisms[9] are, for side reaction 2,

$$\mathrm{ArSO_3H} + \mathrm{ArSO_3SO_3H} \rightarrow \mathrm{ArSO_2OSO_2Ar} + \mathrm{H_2SO_4} \qquad (5)$$

and, for side reaction 4,

$$\mathrm{ArSO_2OSO_2Ar} + \mathrm{ArH} \rightarrow \mathrm{ArSO_2Ar} + \mathrm{ArSO_3H} \qquad (6)$$

These are not the only mechanisms which have been proposed,[10] but they are probably the simplest.

Primary Alcohol Sulfation. Primary alcohol sulfates (PAS) can be made by sulfation of primary alcohols. The major alcohol feedstocks are made either by reduction of fatty acids or esters from natural fats and oils (e.g., coconut oil, mainly C12/14, and tallow or palm oil, mainly C16/18)

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(9) Roberts, D. W. *Comun. Jorn. Com. Esp. Deterg.* **1995**, *26*, 369.

(10) Bosscher, J. K.; Cerfontain, H. Aromatic Sulfonation 20. *Recl. Trav. Chim. Pays-Bas* **1968**, *87*, 873.

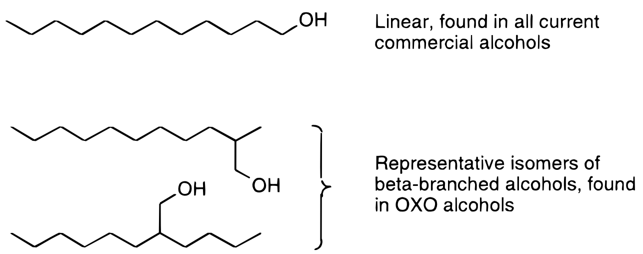
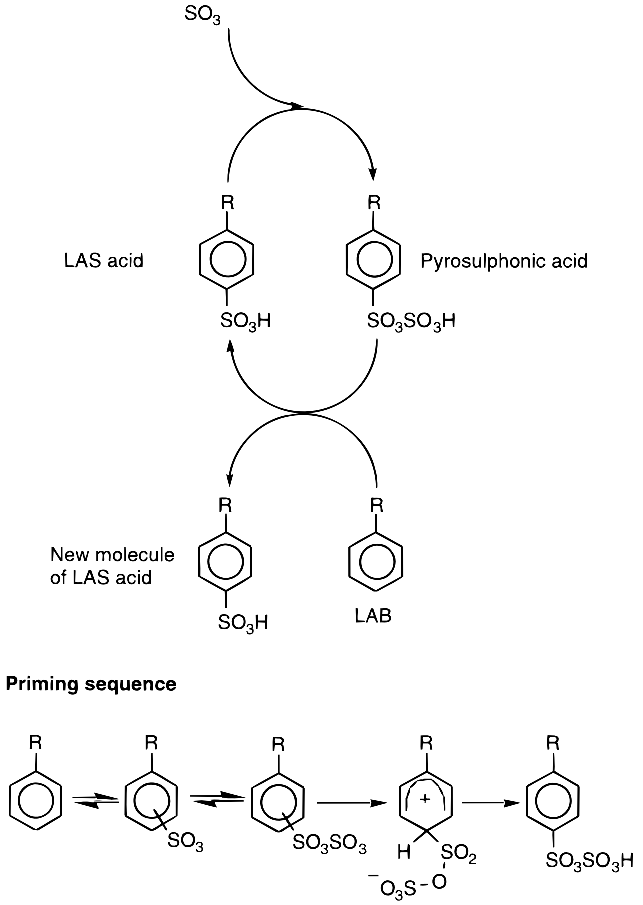


Figure 5. **Primary alcohols.**

Scheme 1. **Proposed mechanism for alkylbenzene sulfonation**



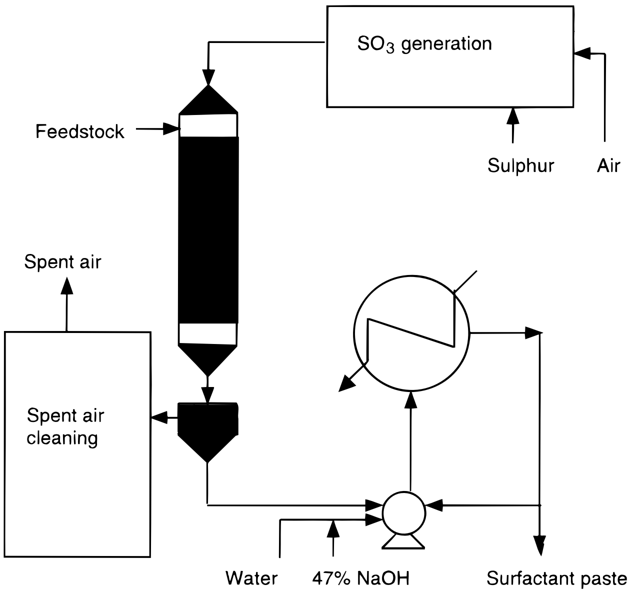
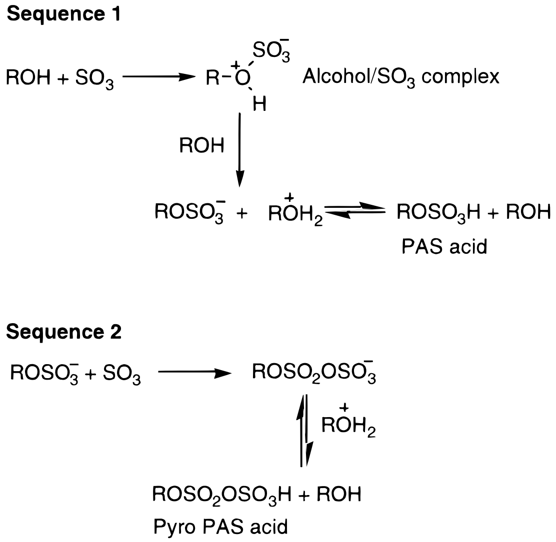


Figure 6. **PAS manufacturing process.**

Scheme 2. **Proposed mechanism for primary alcohol sulfation**



or from petrochemicals by the Ziegler or OXO processes. Structures of commercial primary alcohols are shown in Figure 5.

The sulfation chemistry of primary alcohols differs in several important respects from the sulfonation chemistry of linear alkylbenzenes. In particular, whereas the acidic reaction product mixture (LAS acid) from sulfonation of alkylbenzenes is stable, the acidic reaction product (PAS acid) from sulfation of primary alcohols decomposes rapidly. In consequence only short residence time reactors are really suitable for manufacture of PAS. Unlike the case with LAS, there is no need for an ageing step following FFR sulfonation; indeed post-FFR ageing would be detrimental to conversion in PAS manufacture. Furthermore, whereas LAS acid can be stored as such, PAS acid needs to be stabilised by conversion to a neutral salt.

The sulfation reaction mechanism is not known in detail, but appears to be more complex than a simple second-order bimolecular reaction. The pathway shown in Scheme 2 has been proposed.[11]

When PAS in its acidic form is allowed to decompose at temperatures in the range 40−50 °C (typical of the temperature at which the sulfation product leaves the film reactor), the identified products after neutralisation are the parent alcohol, sodium sulfate, and PAS as its sodium salt. On the basis of NMR studies, kinetic studies, and the overall stoichiometry, the decomposition reaction has been proposed[11] to be

$$3ROSO_3H \rightarrow \underset{\text{PAS anhydride}}{ROSO_2OSO_2OR} + ROH + H_2SO_4 \tag{7}$$

On neutralisation the PAS anhydride is converted to the sodium salt of PAS, so that the net effect of complete decomposition is the loss of one-third of the original PAS. The rates of decomposition are such that an increase of 1%

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(11) Roberts, D. W. *World Surfactants Congr., 4th* **1996**, *1*, 202.

in free oil (on a 100% PAS basis) requires 9 min at 40 °C or 3 min at 50 °C. These figures demonstrate why only a short residence time reactor is appropriate for alcohol sulfation, and why it is important to neutralise the sulfation product immediately after it is produced.

In a typical PAS manufacturing process (shown schematically in Figure 6), the alcohol is sulfated in an FFR and the acid is fed directly to a neutralisation loop in which it is neutralised with aqueous sodium hydroxide. The principle of the neutralisation loop is that the already neutralised and cooled material is used as a solvent for the neutralisation reaction, enabling the reaction exotherm to be efficiently dissipated. In a typical commercial neutralisation loop, the acidic sulfonation product, concentrated sodium hydroxide solution, and water are dosed continuously into a high-shear homogeniser together with a recycled stream of neutralised material. The mixture is then pumped through a heat exchanger, after which about 10% is discharged and the remainder is recycled to the homogeniser. For coconut type alcohols and their petrochemical equivalents, the sodium PAS can be made to a specification of ca. 1−1.5% free oil and 1−1.5% sodium sulfate, both figures on a 100% PAS basis. For tallow-type alcohols and their petrochemical equivalents, the free oil and sodium sulfate levels tend to be slightly higher.

Up to concentrations of about 27% (by weight), aqueous solutions or pastes of PAS are micellar and of low viscosity. At about 65−75%, the PAS is in the form of lamellar phase liquid crystals, and the paste is shear-thinning. Both types of paste can be made in commercial neutralisation loops. Between 27 and ca. 65%, PAS pastes are highly viscous due to the presence of cubic and hexagonal liquid crystal phases. In high concentration paste manufacture, this highly viscous concentration range is avoided where possible by starting up with the neutralisation loop already primed with previously made paste at ca. 70%. When it is not possible to prime the loop, the transition across this range is achieved by dosing excess sodium hydroxide as the PAS concentration increases above 27%: this has the effect of causing a direct transition from the micellar to the lamellar phase structure.

In aqueous solution, PAS as its sodium (or other) salt can undergo hydrolysis:

$$\mathrm{ROSO_3Na + H_2O \rightarrow ROH + NaHSO_4} \qquad (8)$$

At pH values above about 4, the reaction rate is independent of pH, but at around pH 4 the reaction becomes acid-catalyzed and, since the acidic sodium bisulfate is produced, autocatalytic. It has so far been established that the rate constants show a complex variation with initial PAS concentration, possibly indicating dependence on the nature of the micellar structures present.[11] At all pH values, the maximum decomposition rate constants are at about 70% PAS, corresponding to the lamellar phase structure. At 100 °C and 70% PAS the pseudo-first-order rate constants for the uncatalysed reaction and for reaction in the presence of 2% sulfuric acid are

uncatalysed:	$2 \times 10^{-2}\ \mathrm{h^{-1}}$
with 2% sulfuric acid:	$1.5\ \mathrm{h^{-1}}$

In commercial production of PAS, it is common to store the neutralised paste at a concentration of around 70%. Normally, because the uncatalysed reaction is very slow and there is usually a small amount of excess alkali remaining from the neutralisation reaction, no significant decomposition occurs over prolonged periods of storage. However, because 70% PAS acid is viscous and difficult to keep well mixed, local regions of high acidity in an overall alkaline batch of paste can initiate hydrolysis and lead to complete decomposition of the whole batch. To prevent this, it is important to ensure that the neutralisation reaction is well controlled so that acidic paste is not produced even over a short time period.

Ethoxylated Alcohol Sulfation. Sulfation of ethoxylated alcohols gives alcohol ether sulfates, AES. The parent alcohol is usually of C12/13 or C12/14 carbon number, and hence AES is also known as SLES (sodium lauryl ether sulfate). Ethoxylated alcohols are made by reaction of primary alcohols with ethylene oxide, usually with alkali catalysis but in some cases with acid catalysis,

$$\mathrm{ROH} + n\mathrm{CH_2H_4O} \rightarrow \mathrm{RO(CH_2CH_2O)}_n\mathrm{H} \qquad (9)$$

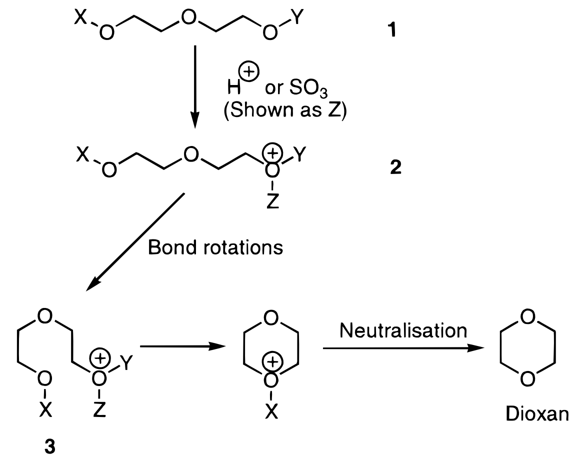
where C_2H_4O is ethylene oxide and the reaction product is ethoxylated E-*n* alcohol. The (CH_2CH_2O) grouping is often abbreviated as EO or sometimes just E, depending on the context. Note that in the above formula for the ethoxylated E-*n* alcohol the symbol *n* denotes an average value. An ethoxylated alcohol is a mixture of non-, mono-, di-, tri-, tetra-, and pentaethoxylated alcohols and so on, with *n* being the average number of EO groups. AES used in detergents and cosmetics usually has an average degree of ethoxylation in the range 1−3.

AES is, in terms of chemical structure, a subclass of PAS. The reaction sequence of ethoxylated alcohol sulfation to produce AES is probably similar to that for PAS.

In its acidic form AES is significantly more stable than PAS towards conversion loss. The acid decomposition reaction does not become significant unless the acid is kept for several hours before neutralisation.

Interestingly, although AES acid normally contains a significant amount of PAS acid (about 15% for a 3-EO AES, 30−40% for a 1-EO AES), the PAS acid in the mixture does not decompose any faster than the ethoxylated components. This applies even when PAS acid is the most abundant component of the mixture. For example, in a pilot plant FFR sulfation trial on an ethoxylated alcohol having an average degree of ethoxylation of 1.0 and a non-ethoxylated content of 38%, the acid, when neutralised immediately after its formation, was found to have a conversion of 99%. A sample neutralised after storage of the acid at 35 °C for 18 h had a conversion of 96%, and the composition of the free oil was similar to that of the feedstock. Similarly, in a pilot plant FFR trial on an ethoxylated alcohol having an average degree of ethoxylation of 0.8, the free oil level, on a 100% AES basis, rose only from 1.1% to 2.1% when the acid was stored at ca. 20 °C for 18 h before neutralisation.

Scheme 3. **Dioxan formation**



One of X and Y = alkyl group or alkyl-terminated EO chain
Other of X and Y = SO_3H group or OSO_3H-terminated EO chain

If the need to avoid conversion loss was the only issue, there would be no reason why ethoxylated alcohol sulfation could not be carried out in a variety of reactor types, for example, in a batch reactor or in a cascade reactor system. However, the acid produces small amounts of dioxan. For example, in the FFR trial on the E-0.8 AES referred to above, the dioxan level (on a 100% AES basis) rose from below 100 to over 1000 ppm on storage at 20 °C for 18 h. The need, for biological acceptability reasons, to avoid detectable dioxan levels in AES-based products makes it essential to use a short residence time reactor and to neutralise the acidic reaction product immediately. In fact it is probably true to say that the dioxan issue has been a major stimulus in the development of film reactor sulfonation technology over the past 10−15 years.

Any molecule in which two ethylene oxides are joined together is potentially capable, under the influence of acids (e.g., the OSO_3H group of AES acid) or Lewis acids (e.g., SO_3), of producing dioxan.

The general mechanism in the case of ethoxylated alcohol sulfation may be summarised, with reference to Scheme 3, as follows:

(1) An oxygen atom of an E-2 unit **1** is either protonated or complexed with SO_3, thereby becoming positively charged. (2) The charged molecule **2** adopts a steric configuration as shown by **3** whereby the oxygen shown attached to X can attack the CH_2 group attached to the positively charged oxygen, giving dioxan.

The extent to which dioxan is formed depends on various factors:

(a) The degree of ethoxylation of the feedstock. Not surprisingly, E-3 ethoxylates have a stronger tendency to produce dioxan than have E-2 ethoxylates.

(b) The ability of the species **2** to adopt the steric configuration **3** necessary for dioxan to be produced. This is easiest when neither X nor Y carries a long-chain alkyl group (most of the conformations which these can adopt would sterically hinder formation of conformation **3**). Therefore, polyethylene glycols (PEG), to the extent that they are present in the feedstock, will increase dioxan formation.

(c) The acidity of the reaction mixture. The more acidic, the more readily **1** can be protonated, leading to the dioxan-forming species **3** ($Z = H$). Since H_2SO_4 is a stronger acid than the OSO_3H group of AES acid, anything which leads to H_2SO_4 being present will increase dioxan formation. Any moisture in the feedstock will be converted to H_2SO_4 on contacting SO_3. Therefore, feedstock moisture content is an important factor in dioxan formation. Likewise any oleum droplets in the gas stream will contribute to dioxan formation. Although it is a weaker acid, the OSO_3H group of AES acid can also protonate **1**. This is most likely to occur when the AES concentration is high, that is, when the sulfation of the ethoxylated alcohol has gone to high conversion. This is one of the reasons why dioxan formation occurs mainly when high conversion has been reached, and why working to a higher free oil specification (i.e., lower conversion) tends to give less dioxan.

(d) The availability of alternative pathways for species **2**. In the early stages of sulfation the species **2** ($Z = SO_3$) will be formed readily. However, because there are still substantial quantities of unsulfated feedstock present, **2** can act as a sulfating agent, rather than undergoing the dioxan-forming reaction. When conversion is high, and particularly when SO_3 is supplied in excess, this alternative reactive pathway becomes unavailable. This is another reason why dioxan formation occurs mainly when conversion is high, and why over-sulfation gives rise to dioxan.

(e) Like most reactions, the rate of dioxan formation increases with increasing temperature, and the extent of reaction increases with time. For example, as mentioned earlier, the freshly neutralised AES from sulfation of an E-0.8 ethoxylate was below 50 ppm, but after 19-h storage of the acid, the dioxan level was above 1000 ppm.

Modern film reactors, operated according to the above principles, are able to produce AES with dioxan levels below 30 ppm

Alpha Olefin Sulfonation. Alpha olefin sulfonate (AOS) has been manufactured commercially, by sulfonation of alpha olefins, since the late 1960s.

The olefin feedstocks for AOS typically come from the petrochemical industry, being made from ethylene via methods such as the SHOP process or via the Ziegler process.

The first step in the reaction of alpha olefin with sulfur trioxide can for all practical purposes be considered as instantaneous, and it results in the formation of a four-membered-ring species, a β-sultone (Scheme 4). This apparently simple reaction has a special place in organic chemistry. It occurs concertedly, that is, the new C−O and C−S bonds are formed simultaneously,[12,13] in apparent violation of the Woodward−Hoffmann rules of orbital symmetry.[14]

Under commercial sulfonation conditions the β-sultone is unstable. It isomerises rapidly (the half-life at 27 °C is

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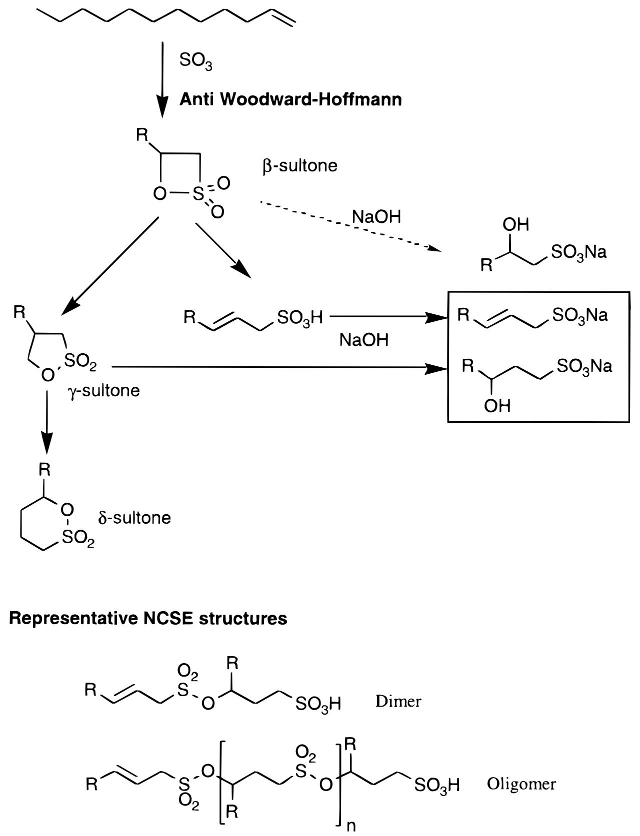
(12) Roberts, D. W.; Williams, D. L.; Bethell, D. *J. Chem. Soc., Perkin Trans. 2* **1985**, 389.

(13) Roberts, D. W.; Jackson, P. S.; Saul, C. D.; Clemett, C. J. NMR Evidence for β-Sultones as Initial Products in Reactions of Olefins with Sulfur Trioxide. *Tetrahedron Lett.* **1987**, *28*, 3383.

(14) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Academic Press: Weinheim, 1970.

Scheme 4. **Alpha olefin sulfonation**



less than 1.5 min) to a mixture of compounds (Scheme 4), among which the five-membered-ring γ-sultone and the alk-2-ene sulfonic acid are prominent. Oligomeric non-cyclic sulfonate esters (NCSEs) are also suspected to be major components. Under FFR sulfonation conditions most of the β-sultone has already decomposed by the time the reaction mixture reaches the base of the reactor.

If the reaction mixture is aged for a prolonged period or at high temperature (a few days at room temperature or about 1 h at 100 °C), further isomerisation occurs and the six-membered-ring δ-sultone becomes the major component of the mixture. However, under normal olefin sulfonation conditions δ-sultone is formed at only very low levels (typically less than 1%). On neutralisation, SO_3H groups of the alk-2-ene sulfonic acid and NCSEs are converted instantly to their sodium salts. If any β-sultone remains, it is converted rapidly to 2-hydroxysulfonate, $RCHOHCH_2SO_3Na$. It is important to minimise the formation of this by-product, which is undesirable because it has only very low water solubility.

The γ- and δ-sultones and the sulfonate ester grouping of NCSEs require more forcing conditions for their hydrolysis. Therefore in AOS manufacture a high-temperature hydrolysis step is provided after neutralisation. The resulting AOS is predominantly a mixture of alk-2-ene sulfonate (this has cis and trans isomers, both of which are present) and 3-hydroxy sulfonate (derived from γ-sultone and probably also from NCSEs). Smaller quantities of positional isomers of these major components are also present, as well as small amounts of disulfonated materials.

AOS	
$RCH{=}CHCH_2SO_3Na$	ca. 60% (including positional isomers)
$RCHOHCH_2CH_2SO_3Na$	ca. 30%
disulfonates	ca. 10%

Chemical Processing Aspects. Olefin sulfonation is appropriately described as a “sensitive” reaction. Mild sulfonation conditions are essential, if excessive formation of colour and polysulfonated material is to be avoided. However, it is important to sulfonate to a low free oil specification: unconverted olefin is only slightly solubilised in micellar solution and if present can cause odour and cloudiness of liquid products. Therefore a combination of mild conditions and relatively high mole ratio is necessary.

For the above reasons, reactors other than film reactors are not suitable for AOS. Typical recommended conditions for AOS are as follows.

film sulfonation:

water jacket temperatures	upper jacket 10−16 °C
(cf. 25−30 °C for LAS)	lower jackets 30−34 °C
olefin throughput	60% of nominal capacity for alkylbenzene sulfonation
SO_3 in air concn	2.5%
(cf. ca. 5% or more for LAS)	
SO_3:olefin mole ratio	1.06−1.07:1
(cf. 1.00 ± 0.01 for LAS)	

Conversion is not complete when the acid emerges from the base of the reactor. There is evidence (Roberts and Jackson, unpublished work from this laboratory) that at this stage some of the sulfur trioxide supplied is found in the form of “slow sulfonating agents” such as pyrosulfonic acids.

acid ageing:

residence time	<10 min, typically 5−7 min
temperature	45−55 °C

In this stage the conversion is maximised and isomerisation of β-sultone is completed.

neutralisation:

normal neutralisation loop process, at 50−60 °C

hydrolysis:

residence time	>30 min
temperature	>175 °C

This process is carried out in a continuous tubular reactor. The γ-sultone, NCSEs, and any δ-sultone and internal sultones which may be present are hydrolysed.

Skin Sensitisation Issues Concerning Sultones. Attention became focused on sultones in the mid-1970s, when the cause of a 1968 outbreak of contact dermatitis in Scandinavia was traced[15] to 2-chloro γ-sultones and α,β-unsaturated γ-sultones (Figure 7) which had been formed as contaminants in a batch of ether sulfate which had been used to formulate dishwashing liquids. The sulfation reaction had not been well controlled, resulting in some AOS being formed. The ether sulfate had then been bleached with hypochlorite under low-

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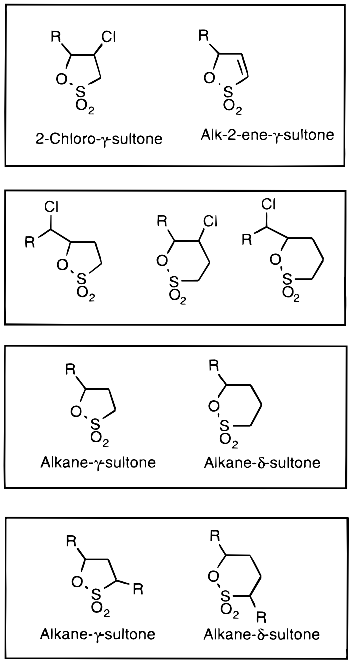
(15) Connor, D. S.; Ritz, H. L.; Ampulski, R. S.; Kowollik, H. G.; Lim, P.; Thomas, D. W.; Parkhurst, R. *Fette, Seifen, Anstrichtm.* **1975**, *77*, 25.



Type 1
Hypochlorite interaction products from alk-2-ene sulphonate. Highly potent skin sensitisers

Type 2
Hypochlorite interaction products from alk-3-and 4-ene sulphonates. No significant sensitisation potential. Resistant to dehydrochlorination

Type 3
Saturated terminal sultones, intermediates in AOS production. Moderate sensitisation potential. Not cross-reactive with type **1**.

Type 4
Saturated internal sultones, derived from internal olefins. Weak sensitisation potential.

Figure 7. **Sultones.**

pH conditions, and a reaction had occurred between the hypochlorite and the alk-2-ene sulfonate in the AOS impurity, resulting in the formation of 2-chloro γ-sultones and (via dehydrochlorination) α,β-unsaturated sultones.

These sultones are extremely potent allergens (exhibiting sensitisation potential down to levels of ca. 1 ppm) and can be formed if AOS is bleached with hypochlorite, particularly at pH's below neutral. They owe their sensitising ability to the Michael acceptor properties of the electron-deficient double bond in the unsaturated sultone,[16] which can readily be formed in vivo from the chloro sultone. However, it has been shown that chloro sultones and unsaturated sultones cannot be formed in AOS which is not treated with halogen bleach,[17] and by avoiding a bleaching step (or if necessary bleaching with hydrogen peroxide) it can be ensured that these sultones are not present in AOS. Alk-3-ene and alk-4-ene sulfonates present in AOS can also form chloro sultones (Figure 7), but these are not activated towards dehydrochlorination, do not give rise to unsaturated sultones, and exhibit no significant sensitising potential.[18]

Following the exposure of the chloro/unsaturated sultone issue, the saturated terminal γ- and δ-sultones which are intermediates in AOS production came under scrutiny. These sultones are also allergenic, but they are much less potent, exhibiting no significant sensitisation potential below about 100 ppm. Present day hydrolysers can get well below this specification.

Internal γ- and δ-sultones (Figure 7) can also be formed as minor impurities in AOS, arising from internal olefins either present as impurities in the feedstock or derived from alpha olefins by isomerisation during sulfonation. These sultones are much weaker sensitisers than the terminal saturated sultones,[19] and at the total sultone levels achievable with modern hydrolysers (well below 100 ppm) their sensitisation potential is insignificant.

A by-product of the extensive research effort on sultone sensitisation which took place within the detergent industry in the 1970s and 1980s was the development of a mathematical model based quantitative structure activity relationship (QSAR) approach to skin sensitisation,[20] which has subsequently been applied to the mechanistic interpretation of sensitisation datasets on a variety of completely different compounds.[21,22]

Overall the sensitisation issues relating to AOS are well understood, and provided they are taken into account in manufacturing, formulation, and marketing, the use of AOS in consumer products should not cause problems.

Concluding Observations

Current technology enables sulfonation reactions to be carried out in very high yields and conversions, without the use of solvents, producing surfactants to very tight specifications in terms of colour and levels of by-products. This represents a considerable achievement in the application of physical organic chemistry and chemical engineering principles to controlling the extreme reactivity of sulfur trioxide.

Although the overall stoichiometry of sulfonation reactions is usually simple, the reaction pathways are invariably more complex and not fully understood. Further developments in this area are likely in the future, both for sulfonation of current feedstocks and for new surfactants (e.g., methyl ester sulfonates and internal olefin sulfonates) derived from sulfonation of other raw materials.

GLOSSARY OF ABBREVIATIONS

AES	alcohol ether sulfate
AOS	alpha olefin sulfonate
EO (or E)	ethyleneoxy (CH_2CH_2O)
FFR	falling-film reactor
LAB	linear alkylbenzene
LAS	linear alkylbenzene sulfonate
NCSE	non-cyclic sulfonate ester
PAS	primary alcohol sulfate
SLES	sodium lauryl ether sulfate

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