OLEOCHEMICAL SURFACTANTS TODAY

BAUMANN, H AND BIERMANN, M*

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The production of surfactants represents a vast area of application for technical oils and fats. The oleochemical industry is making great efforts to increase the proportion of oleochemical surfactants in the total world production of surfactants. Oleochemical surfactants have both economic and ecological advantages over products based on mineral oil. This survey discusses recent developments concerning anionic and non-ionic oleochemical surfactants, including the following: tallow alcohol sulphate; α-ester sulphonates; internal ester sulphonates from sulphoxidation of saturated fatty acid methyl esters and from SO_3 sulphonation of unsaturated fatty acid esters; oleic acid sulphonates; fatty alcohol ethoxylates with narrow homologue distribution; and carbohydrate-based surfactants. The survey reveals the great potential which lies in natural fats and oils as starting materials for the development of new surfactants.

INTRODUCTION

In 1990 worldwide fat production amounted to 81 million tonnes, of which 11.4 million tonnes were technically utilized or chemically processed (*Figure 1*). A major application of technical fats is the production of surfactants. In 1982, oleochemical surfactants accounted for 45 % of all the surfactants produced by the western industrialized nations (USA, Japan, Western Europe), which corresponds to about 1.8 million tonnes (Werdelmann, 1984). Soaps, which have an exceptional position are not considered further in the present paper. *Figure 2* shows the consumption of the most important surfactants in the industrialized countries in 1987 (Richtler *et al.*). The vigorous efforts of the oleochemical industry are destined to increase the proportion of

*Henkel KGaA, Duesseldorf, Germany

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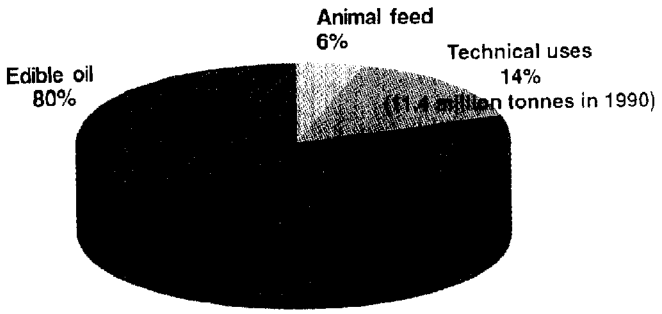


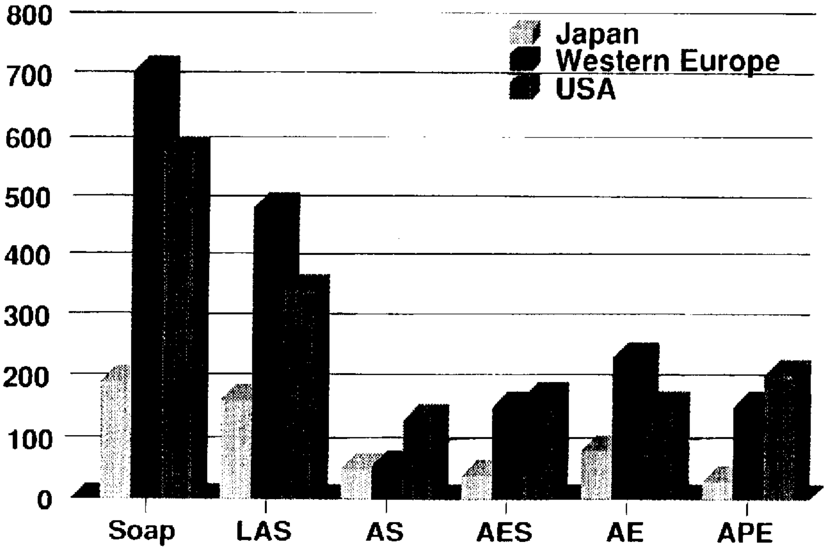
Figure 1. World usage of fats and oils.

oleochemical surfactants in the world-wide production of surfactants. Conditions are favourable for the attainment of this goal, especially nowadays when awareness that our raw material resources are finite, and understanding of environmental hazards have become more marked. In contrast to mineral oil, fats and oils are biological raw materials which are constantly renewed. This will be reflected – at least in the long term – in an economic advantage for chemical products from fats and oils, as compared with those from mineral oil. Favourable ecological characteristics can be expected from linear fatty acid molecules which have no branches or ring structures, and from the surfactants based on them.

A survey follows on some of the latest developments in the field of anionic and non-ionic oleochemical surfactants. The technical implementation of some of the possibilities discussed could give oleochemical surfactants the impetus needed for an increase in their production and usage.

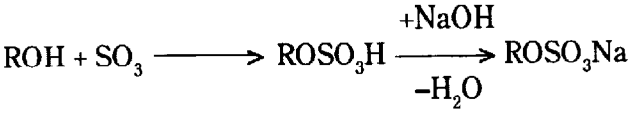
Anionic surfactants based on oleochemicals

To date no oleochemical anionic surfactant has been devised which could be widely utilized as a basic surfactant in washing, rinsing and cleaning agents. This means that there is a great development potential for such surfactants. What hints do we have on how to realize this potential? On account of their good detergency and ecological characteristics, fatty alcohol sulphates of $C_{16/18}$ chain length are suitable for use in detergents in powder form. They are best obtained by the conversion of fatty alcohols with SO_3/air mixtures in modern short-term sulphonation reactors (*Figure 3*). Problems encountered during the production of $C_{16/18}$ fatty alcohol sulphate must be attributed to the fact that a rapid decomposition of the $C_{16/18}$ alkyl sulphuric acid which is formed occurs at the increased reac-



LAS – Linear alkylbenzene sulphonate
AS – Alcohol sulphate
AES – Alcohol ether sulphate
AE – Linear alcohol ethoxylate
APE – Alkylphenol ethoxylate

Figure 2. Surfactant consumption in the USA, Japan and Western Europe (1987) ('000 tonnes).



$$ROH + SO_3 \xrightarrow{} ROSO_3H \xrightarrow[-H_2O]{+NaOH} ROSO_3Na$$

Figure 3. SO_3-sulphation of fatty alcohols.

tion temperatures needed. This is represented in *Figure 4,* where a comparison is drawn with $C_{12/14}$-alkyl sulphuric acid. The increased reaction temperatures are necessary because of the higher melting point of $C_{16/18}$ alcohol and the increased viscosity of $C_{16/18}$ alkyl sulphuric acid. Otherwise the sulphonation reactor cannot be operated optimally.

Technically, it is advisable that for the sulphation of $C_{16/18}$ fatty alcohol both the reaction time itself and the time between the end of sulphonation and the beginning of neutralization of the $C_{16/18}$ alkyl sulphuric acid with aqueous alkali should be as short as possible, in order to obtain a good yield of $C_{16/18}$ alkyl sulphate.

The oleochemical feedstock should be as cheap as possible thus making the production of the oleochemical surfactant profitable. The fatty alcohols which are at present produced on a large scale by catalytic high-pressure hydrogenation of fatty acid methyl esters only meet this requirement to a limited extent. For economic reasons, fatty acid methyl esters, obtained in one process by transesterifying fats with methanol on a large scale represent the more favourable starting material for production of oleochemical anionic surfactants (*Figure 5*). The simplest method of converting fatty acid methyl esters into anionic surfactants is the introduction of a sulphonate group in the alpha-position to the carboxymethyl group; this is achieved by reaction with SO_3/air mixtures with the formation of α-sulpho-fatty acid methyl esters (referred to, for short, as α-ester sulphonates) (*Figure 6*).

The α-ester sulphonates of $C_{16/18}$ chain length have been known for quite some time, and their physical, chemical, ecological and application characteristics seem to make them suitable substitutes for linear alkyl benzene sulphonates (LAS) (Stirton *et al.*, 1962; Stein *et al.*, 1970; Stein *et al.*, 1975 and Nagayama *et al.*, 1975). A technically advanced, profitable manufacturing process is still being sought; it should supply light-coloured α-ester sulphonates with good conversion levels in the form of processed aqueous pastes containing more than 50% water.

The process and the reaction conditions for the α-sulphonation of fatty acid methyl esters (high reaction temperatures, long reaction times) differ markedly from those used in other sulphonation reactions; for this reason an explanation of the mechanism of ester sulphonation and the reaction parameters derived from such an understanding appeared to be the necessary preconditions for the development of a technical manufacturing process. Various committees in the USA, Japan and Germany have dealt with this topic; at the first World Surfactant Congress in Munich, in 1984, it was concluded, on the basis of the reaction parameters derived from the optimal conditions for the manufacturing process, that ester sulphonation occurs in two reaction steps (Schmid *et al.*, 1984). In the first (rapid) reaction step *one molecule of ester reacts with 2 molecules of SO_3 to form a mixed anhydride.* In the second (slow) reaction step this anhydride by eliminating SO_3, serves as a sulphonation agent for the methyl ester that has not yet been converted (*Figure 7*). By the use of reaction kinetic tests the different intermediate levels leading to the mixed anhydride were demonstrated by Schmid (1984). Optimal reaction conditions for attaining degrees of sulphonation of more than 95% are achieved with an ester : SO_3 molar ratio of 1:1.2 and a reaction time of 30 minutes at 90° C. In order to obtain the light-coloured $C_{16/18}$ α-ester sulphonates which are preferred for application in detergents, besides observing optimal sulphonation conditions, emphasis should be given to the quality of fatty acid methyl ester to be used (derived from tallow, palm oil or palm stearin); an Iodine Value of less than 0.5 is only one of the prerequisites.

Even then, the sulphonation products still have to be bleached by oxidation (with H_2O_2 or sodium hypochlorite). At a concentration around 50%, $C_{16/18}$ α-ester sulphonates form high-viscosity aqueous pastes which cannot be further processed except by adding a viscosity regulator, *e.g.* ethoxylates alone or in combination with electrolytes (Henkel, 1983), or – as suggested by Lion Corp. (Lion, 1982) – by treating the crude sulphonic acid with methanol before neutralization.

When summarizing the results of these investigations it may be noted that today α-ester sulphonates can be produced on a large scale in the form of light-coloured, concentrated aqueous pastes.

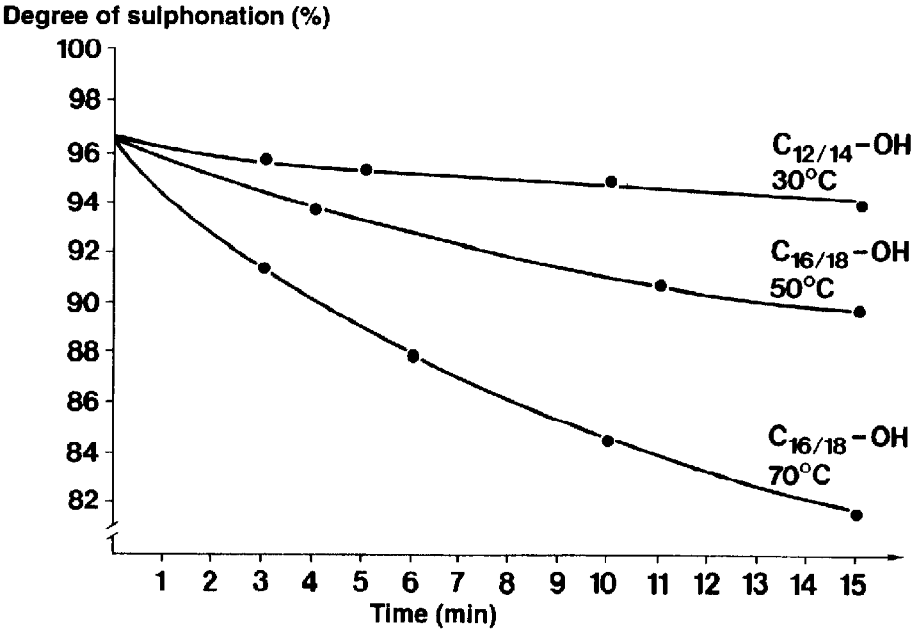


Figure 4. Thermal stability of alkyl sulphuric acid esters (Degree of conversion during the SO_3-sulphation of $C_{12/14}$ and $C_{16/18}$ fatty alcohols in relation to reaction temperature and time).

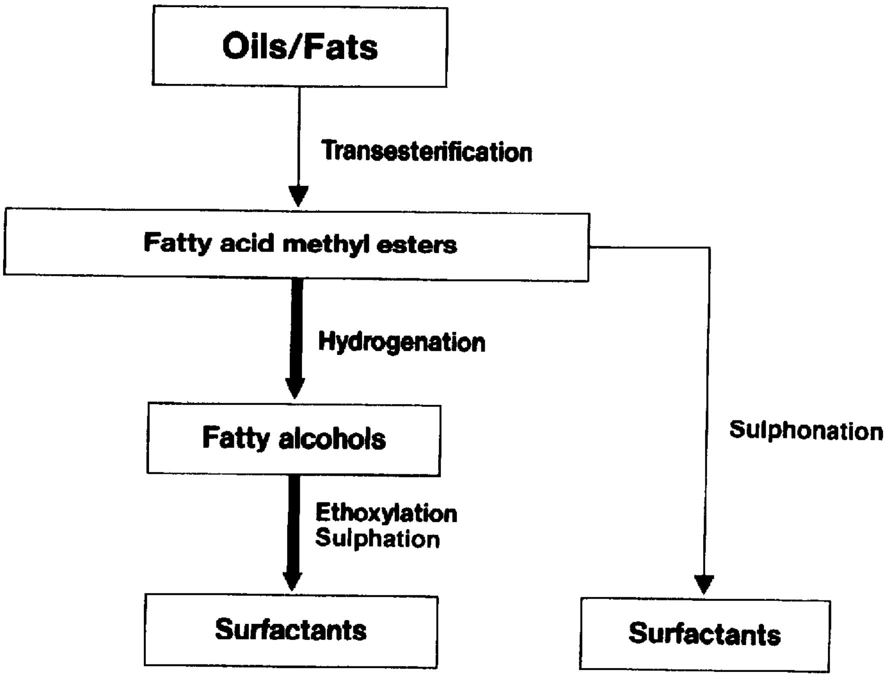


Figure 5. Reactions used in the manufacture of surfactants from oils and fats.

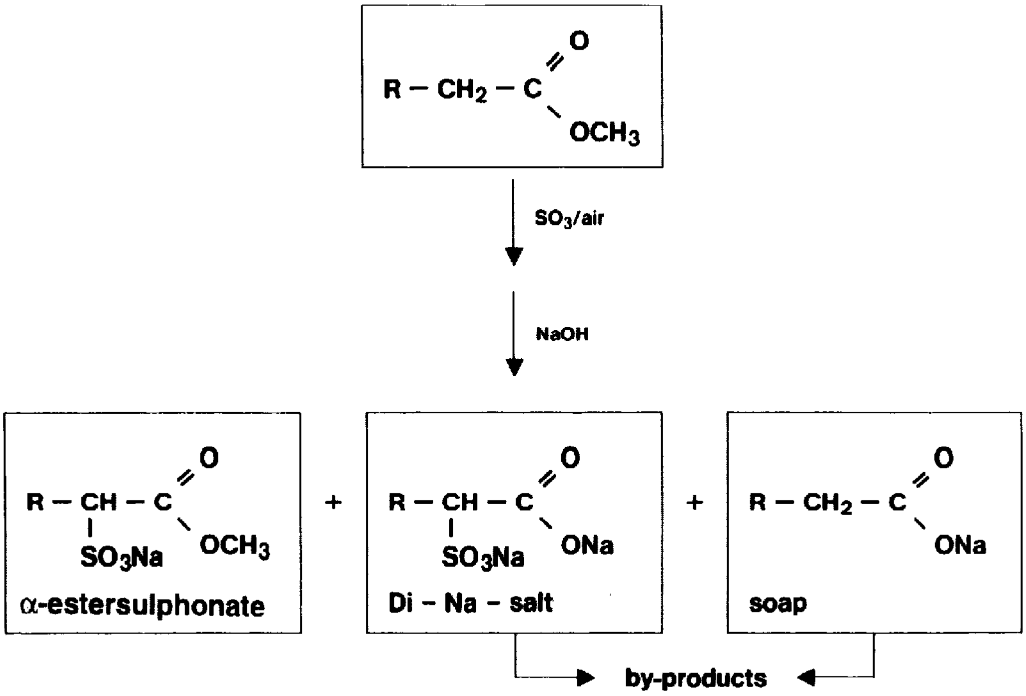


Figure 6. Sulphonation of saturated fatty acid methyl esters with SO_3.

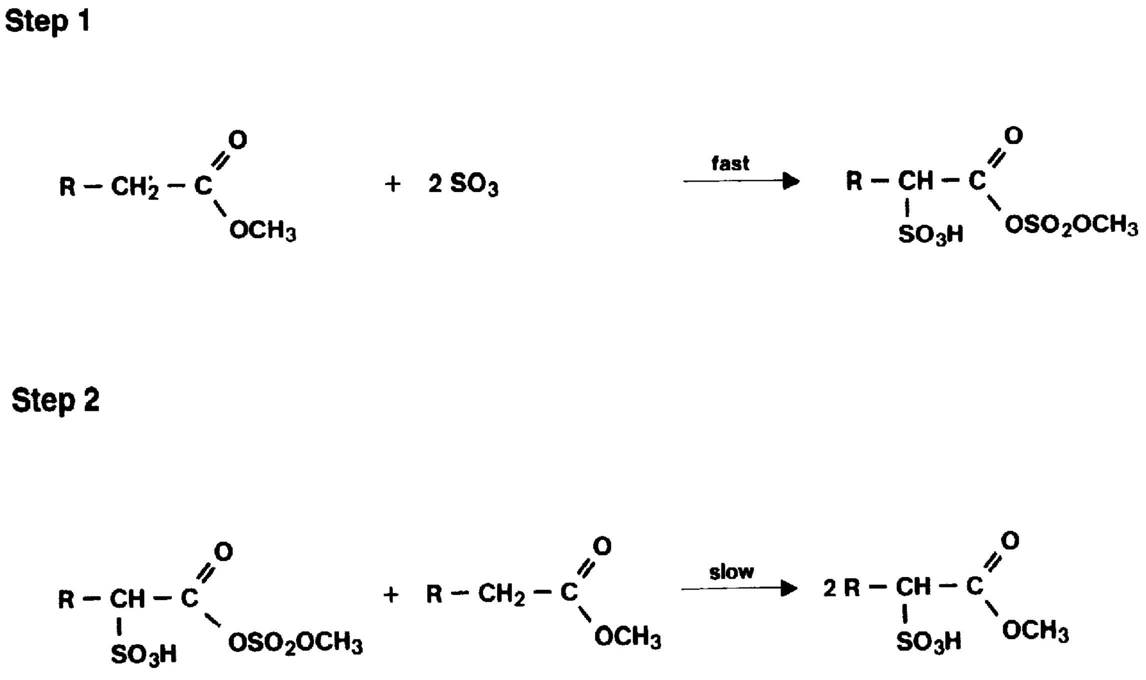


Figure 7. Reaction mechanism of the sulphonation of saturated fatty acid methyl esters.

Because of their limited water solubility $C_{16/18}$ fatty alcohol sulphates and α-ester sulphonates, which are effective for cleaning, are mainly suitable for application in washing, rinsing and cleaning agents in powder form; they are less suitable for the formulation of liquid products. A mean of filling this application gap was sought by developing ester sulphonates with an internal sulphonate group as a supplement to α-ester sulphonates. Improved water solubility was expected from such compounds (by analogy with the alkanesulphonates with sulphonate groups randomly distributed). Two methods of synthesis were examined; the sulphoxidation of saturated fatty acid methyl esters and the SO_3 sulphonation of unsaturated fatty acid methyl esters.

The sulphoxidation of saturated fatty acid methyl esters, *i.e.* their reaction with SO_2 and O_2 triggered by UV-light has been reported (Biermann, 1985). By analogy with the sulphoxidation of alkanes, the ester sulphonates produced show a more or less random distribution of the sulphonate group; these are the so-called ψ-ester sulphonates (*Figure 8*). However, owing to the inductive effect of the ester function, the random incorporation of the sulphonate group begins only from the γ-C-atom. As with the sulphoxidation of alkanes, the sulphoxidation of fatty acid methyl esters leads, after a few conversions, to disulphonates which exhibit no surfactant properties; therefore the reaction must be stopped at conversion levels below 5 per cent. For an industrial mode of operation this means that in a continuous process a separate extraction cycle has to be included for the separation of the sulphoxidation products from the starting material.

However, there are considerable restrictions when choosing a suitable extractant because of the reactivity of the ester bond. By contrast with the sulphoxidation of alkanes, water cannot be used as an extractant. The sensitivity to hydrolysis of the ester function in ψ-ester sulphonates accounts for the fact that the composition of the products obtained is far more complex than that of the alkanesulphonates (*Figure 9*). In neutralized sulphoxidation products there are always both soaps and mono- and disulphonated soaps as hydrolysis products of the corresponding methyl esters.

Compared with the corresponding α-ester sulphonates, ψ-ester sulphonates of C_{18} chain length show similar surface active characteristics, an improved foaming power, a higher water solubility and a better resistance to hard water; a washing and rinsing power that is crucial in practice – mainly in technically available product mixtures – does not suffice. Because of the displacement of the sulphonate group into the interior of the chain the favourable characteristics of the α-estersulphonates, good detergency and increased hydrolytic stability, were destroyed. On account of this and the costly production technology the ψ-estersulphonates are, from a technical point of view, a rather uninteresting surfactant group.

The sulphonation of unsaturated fatty acid methyl esters with SO_3/air mixtures was examined systematically using oleic acid methyl ester in a continuous laboratory falling film reactor (Behler, *et al.*,1988). It is known from the α-sulphonation of saturated fatty acid methyl esters that very small amounts of unsaturated compounds can seriously impair the colour quality of the alpha-estersulphonate; therefore it was very important to de-

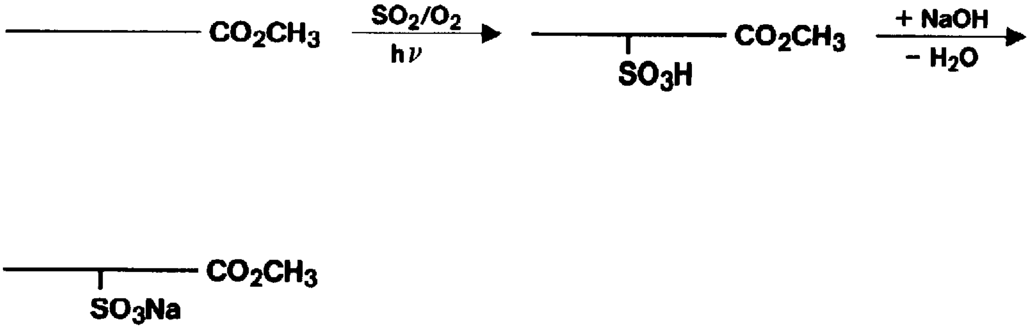


Figure 8. Sulphoxidation of fatty acid methyl esters.

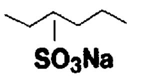
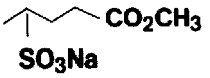
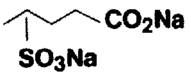
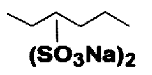
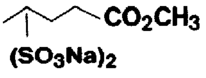
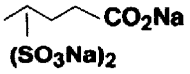
US	 **paraffin**	 **FAMe**  **soap**
mono-sulphonate	 **paraffin-ψ-MS**	 **Na-FAMe-ψ-MS**  **Na_2-FA-ψ-MS**
di-sulphonate	 **paraffin-ψ-DS**	 **Na_2-FA Me-ψ-DS**  **Na_3-FA-ψ-DS**
sulphate	**Na_2SO_4**	**Na_2SO_4** **$NaCH_3SO_4$**

Figure 9. Products from the sulphoxidation of paraffins and saturated fatty acid methyl esters.

termine optimal reaction parameters for the sulphonation of unsaturated fatty acid methyl esters in order to be able to obtain light-coloured internal fatty acid methyl ester sulphonates ('i-ester-sulphonates' hereafter) with high conversion levels. Temperatures of 15°C–30°C, a molar ratio of methyl ester to SO_3 of 1:1.1 to 1:1.2, and brief reaction times are favourable conditions for the SO_3-sulphonation of unsaturated fatty acid methyl esters. The acid-sulphonation products contain fractions which can be hydrolyzed, presumably sulphonic acid esters.

It is therefore not sufficient only to neutralize the sulphonation products from unsaturated fatty acid esters; a hydrolysis with aqueous alkali is necessary. Here, the sulphonation degree clearly increases. A mild saponification (*i.e.* avoiding an excess of alkali) of the sulphonation products of unsaturated fatty acid methyl esters has to be done in order to prevent ester hydrolysis. When the reaction conditions mentioned are met, i-ester-sulphonates are obtained with conversion levels of 87%–90%. After the oxidative bleaching (*e.g.* with H_2O_2) products of satisfactory colour quality result. An increasing excess of SO_3 and an increase in the reaction temperature result in an enormous deterioration of the oxidative bleachability and thus the colour quality of the i-ester sulphonates, without any definite increase in the degree of sulphonation.

During the sulphonation of unsaturated fatty acid methyl esters, the attack of SO_3 occurs mainly at the reactive double bond (*Figure 10*). Internal hydroxyalkane and alkene sulphonates with a terminal carboxy methyl group are the main

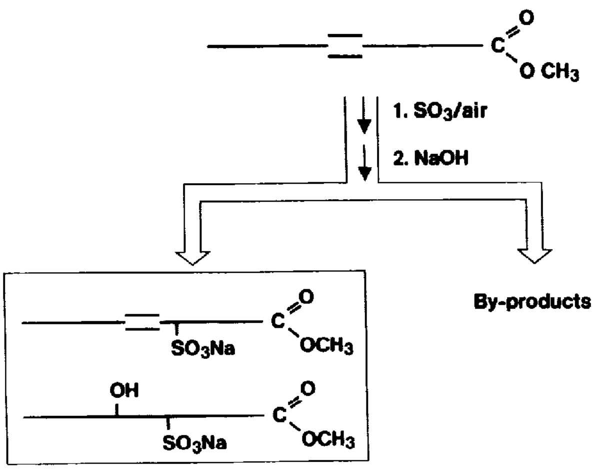


Figure 10. Sulphonation of oleic acid methyl esters: main reaction.

products. The ratio of hydroxyalkane to alkene sulphonate is about 3:2. By means of NMR-spectroscopic tests it was shown for the alkene sulphonate portion that different isomeric alkene carboxylic acid methyl ester sulphonates are formed in which the sulphonate group occupies different positions in relation to the double bond (mainly in the α-, β- and γ-positions relative to the double bond). There is a similar situation with regard to the hydroxy alkanesulphonate portion of the product. However, the precise product distribution and exact substitution conditions in the i-ester sulphonates have not yet been determined.

In the sulphonation of unsaturated fatty acid methyl esters side reactions may occur, such as an α-sulphonation (as in the case of saturated fatty acid methyl esters) and the insertion of SO_3 into the alkoxy bond of the ester function. The possible side effects are shown in *Figure 11.* NMR-spectroscopic tests on the acid sulphonation product showed the formation of less 4 mole per cent of sodium alpha sulpho oleic acid methyl ester. The insertion of SO_3 into the ester bond with formation of a compound anhydride of sulphonated oleic acid and methyl sulphuric acid occurs to only a small extent (about 4 mole per cent with 20 mole per cent excess of SO_3).

The product composition of oleic acid methyl ester sulphonates is represented in *Figure 12.*

Under the same reaction conditions methyl esters of other unsaturated fatty acids (*e.g.* erucic acid) and higher alkyl esters of oleic acid, such as n-propyl-, i-butyl- and 2-ethyl hexylester can also be sulphonated.

The i-ester sulphonates are low to weak foaming surfactants with good wetting capacities. Their detergency reaches a moderate level and does not achieve that of the alpha-ester sulphonates or of LAS. The i-ester sulphonates are easily bio-degradable and, in contrast to the alpha-ester sulphonates, they are also clearly water-soluble in high concentrations (50%–70%): they could therefore be suitable for the formulation of liquid products.

Oleic acid can also be sulphonated with SO_3 by applying similar reaction conditions to those for oleic acid methyl ester. The reaction obviously follows an analogous course so that (after alkaline hydrolysis of saponifiable structures) internal hydroxyalkane and alkene sulphonates with a terminal carboxylic group are the main products (oleic acid sulphonates). The characteristics of oleic acid sulphonates are basically similar to those of the i-ester sulphonates. The surface active characteristics are slightly less marked, but on the other hand there is the advantage of absolute hydrolytic stability.

Together with the simplicity of their industrial production in conventional sulphonation reactors, (by comparison, for example, with ψ-estersulphonates) the i-ester sulphonates and the oleic acid sulphonates are interesting surfactant components which because of their specific characteristics, could also be considered for industrial surfactant applications.

New non-ionic surfactants based on oleochemicals

Fatty alcohol ethoxylates, the most important class of non-ionic surfactants, are produced by the acid or alkali catalysed reaction of fatty alcohols with ethylene oxide. In industry alkaline catalysts such as sodium methylate or potassium hydroxide are mainly used; these give rise to a random mixture of fatty alcohol polyethylene glycol ethers with a very broad distribution of homologues. In recent years a great number of catalyst systems has been described in the patent literature which produce a narrow range of homologue distribution in the ethoxylation of fatty alcohols (Dillan *et al.*, 1986; Dillan, 1985). Alkaline-earth salts of alkoxy hydroxy fatty acids and/or of ether carboxylic acids have been reported as new catalyst systems of this kind (Behler, 1989). The effect of a narrow homologue distribution is represented in *Figure 13* for the ethoxylation of dodecanol with 3 moles of ethylene oxide. Fatty alcohol ethoxylates that have a narrow range of homologue distribution have several clear advantages over the conventionally produced products.

These advantages include the reduction of highly-volatile, pluming and odour-forming fractions, mainly by reducing the content of free fatty alcohol; better handling and processing because of low setting point; and a good thickening effect when added to aqueous anionic surfactant solutions (thus arousing interest in special fatty alcohol ethoxylates with a narrow range of homologue distribution as nitrogen-free thickeners).

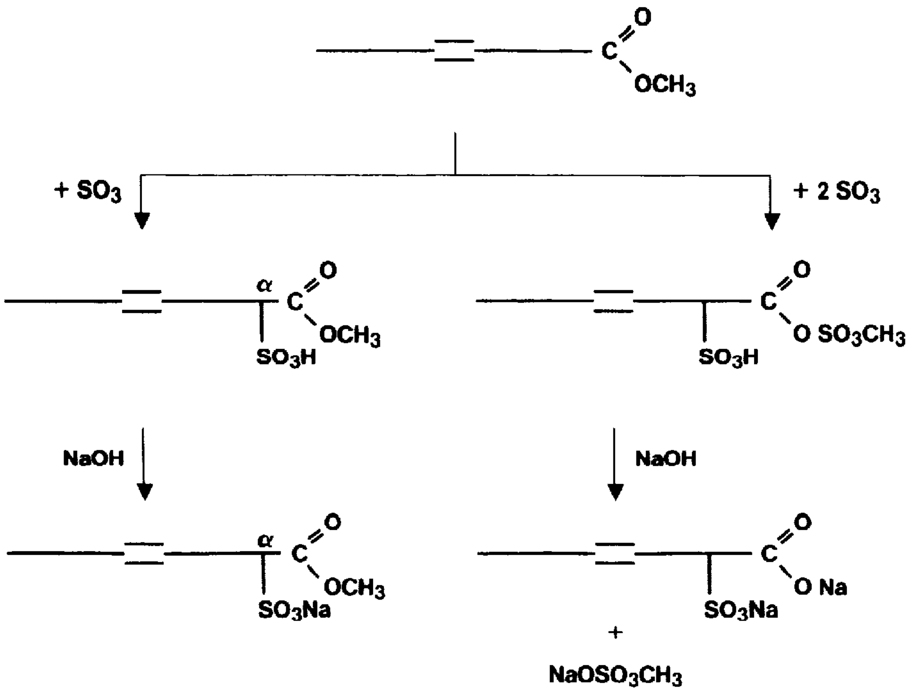


Figure 11. Sulphonation of oleic acid methyl ester: side reactions.

Main products	internal alkene and hydroxy alkene sulphonates (sodium salts)
By-products	oleic acid sulphonate di-sodium salts sodium α-sulpho oleic acid methyl ester sodium sulphate sodium methyl sulphate

Figure 12. Products formed in the synthesis of oleic acid methyl ester sulphonates.

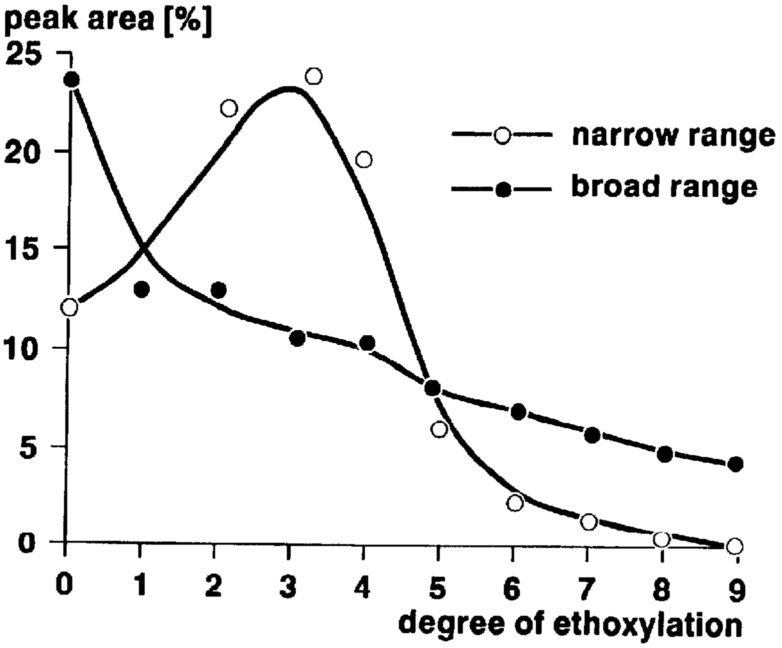


Figure 13. Homologue distribution in the ethoxylation of decanol with 3 moles of ethylene oxide: narrow distribution produced with a barium salt of a substituted fatty acid as catalyst, broad distribution with sodium methylate as catalyst.

The formation of dioxane during the sulphonation of fatty alcohol ethoxylates with a narrow range of homologue distribution is also reduced.

Further product innovations can be expected, thus increasing the demand for fatty alcohol ethoxylates.

Because of the current interest in obtaining surfactants largely from natural starting materials for ecological reasons, carbohydrates, (starch, sugar, *etc.*), as renewable biological products, are gaining more and more importance along with natural oils and fats for this purpose (Semel *et al.*, 1983; Kleinhaub, 1988 and Lichtenthaler, 1990).

The increase in using of these materials is, of course, dependent on finding suitable technologies.

Of the approximately 20 million tonnes of renewable chemical raw materials which are used world-wide each year, carbohydrates account for about 15% (against 55% for oils and fats). Glucose (Hickson, 1977), sucrose (Khan, 1983), and sorbitol (from the hydrogenation of glucose) are typical polyhydroxy compounds of natural origin, with virtually unlimited availability, high purity and good ecological and toxicological characteristics; compared to ethylene oxide they represent inexpensive solubility-promoting constituents for surfactants (*Figure 14*).

Increasing environmental concerns and preference for renewable raw materials generated interest in linking the two groups of such raw materials - oils and fats, and carbohydrate. Surfactants in which a longer alkyl residue (C_8–C_{22}) is rendered hydrophilic by means of carbohydrate instead of ethylene oxide have been the subject of intensive tests for decades (Ames, 1960).

A carbohydrate molecule and the alkyl chain can be linked by means of ester, ether, amide or amine bridges (*Figure 15*).

Sorbitol fatty acid esters (*Figure 16*) are among the best known carbohydrate surfactants (Falbe, 1987); they can be obtained by the esterification of sorbitol. As emulsifiers they occupy an established place in goods, cosmetics, pharmaceuticals and numerous other industrial applications. The hydrophilicity of sorbitol esters, can be increased by ethoxylation. More than 10 000 tonnes of (ethoxylated) sorbitol esters are produced world-wide each years.

In the 1960, strong interest was aroused in the fatty acid esters of sucrose (Desai *et al.*, 1983; Hunt, 1961) (*Figure 16*).

Sucrose mono fatty acid esters, especially, are surface active substances with interesting charac-

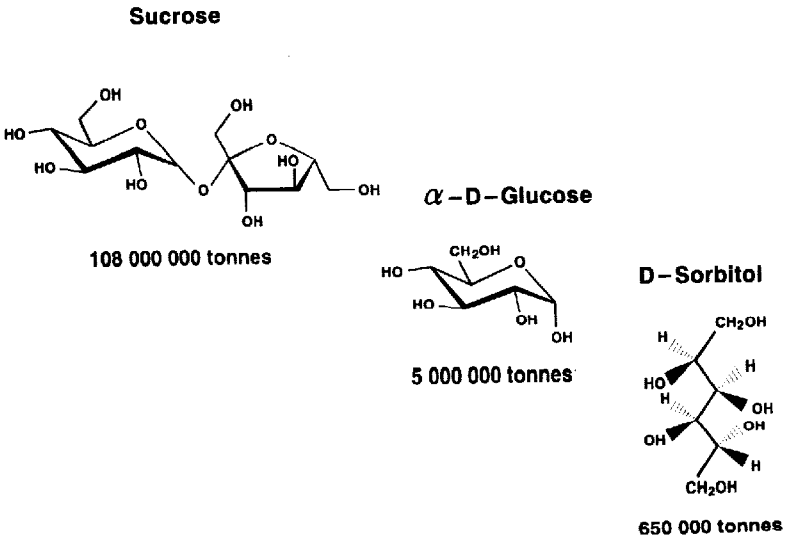


Figure 14. Structures and annual world production of low molecular weight carbohydrates which can be used as hydrophilization agents in the synthesis of surfactants.

teristics. Sucrose monoesters with acyl radicals of chain length C_{14} to C_{18} show optimal detergency (Manneck, 1962). The insertion of a single longer chain fatty acyl residue into a specific position in the polyvalent sucrose molecule is not a practical possibility thus far. Complex mixtures are always obtained whether polar solvents (DMF, DMSO) are used or not. Sucrose mono fatty acid esters can only be isolated from unreacted sucrose and higher acylated sugar by costly refining operations. The organic solvents used also have to be removed to below the critical concentration limits. As a result, the sucrose mono fatty acid esters, although interesting with regard to surfactant properties, cannot be produced economically to compete with other high-volume surfactants.

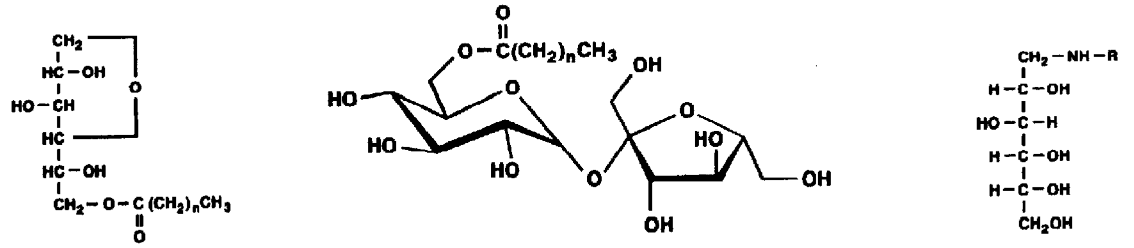
Consequently, their use (about 2000 tonnes per annum world-wide) has been restricted to special applications in cosmetics (Desai *et al.*, 1983; Hunt, 1961), the food industry and pharmaceuticals, where their outstanding toxicological characteristics – they are non-poisonous, non-irritating and non-sensitizing – are particularly advantageous.

Fatty alkyl glucamines and fatty acyl glucamides (*Figure 16*), which are obtained by reductive amination of reducing sugars such as glucose with alkylamines, or by the amidation of fatty acid methyl esters with glucamines, have been known for a long time and have recently attracted great interest (Kelkenberg, 1988).

This was a result of improvement in the technology for producing the fatty alkyl glucamines.

Carbohydrate-derived surfactants		
sugar unit	**linkage**	**hydrophobic group**
Sucrose	$-O-\overset{O}{\overset{\|}{C}}-$	**fatty alkyl chain**
Glucose	$-O-$ $-NH-\overset{O}{\overset{\|}{C}}-$	
Sorbitol	$-NH-$	

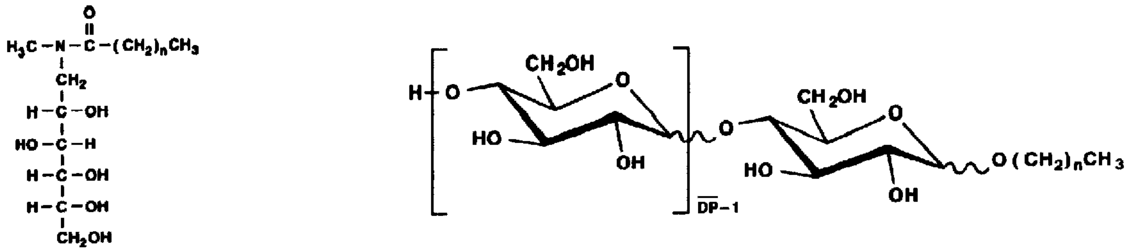
Figure 15. Possible types of linkage between carbohydrate molecules and alkyl groups.



Sorbitol fatty acid esters

Sucrose fatty acid monoesters

N-Fatty alkyl-glucamines



Fatty acyl glucamides

Alkylpolyglucosides

Figure 16. Types of surfactant based on carbohydrates.

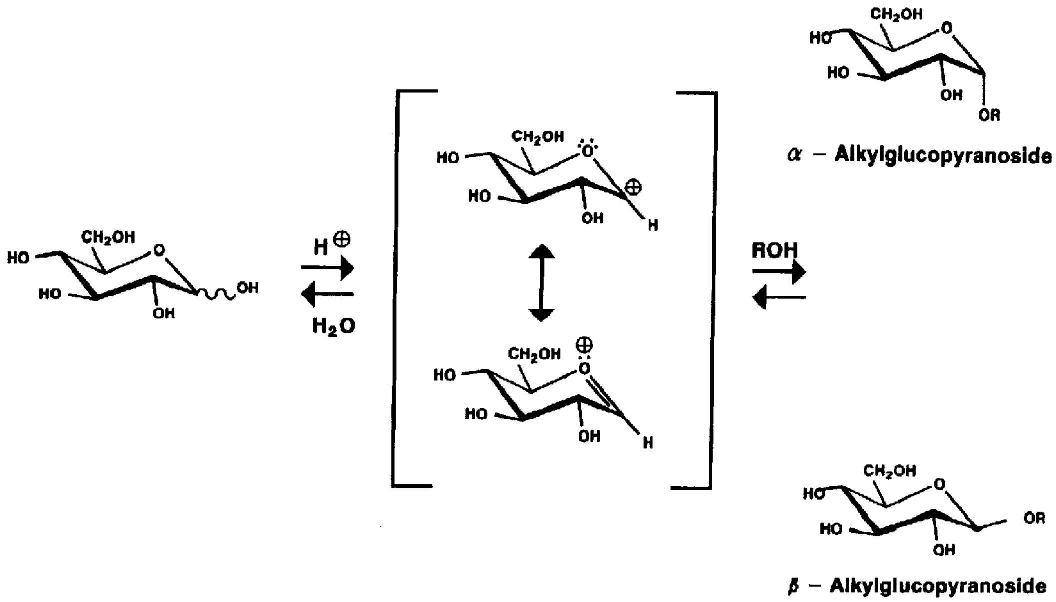


Figure 17. Mechanism of the Fischer synthesis of glucosides.

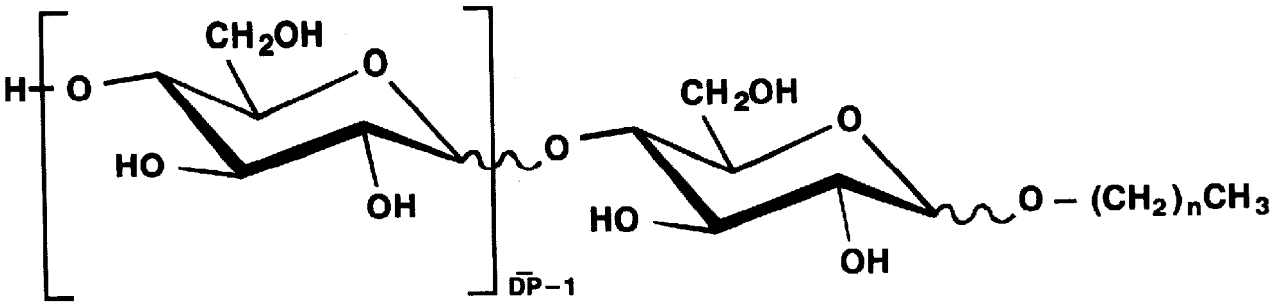


Figure 18. Generalized structure of alkylpolyglycosides (APG).

For the surface active fatty alkyl glucamines (quaternary) and fatty acyl glucamides, different applications are described in cosmetics (for hair care, as thickeners, for the improvement of the skin compatibility of co-surfactants) and in weak-foaming rinsing and cleaning agents (Kelkenberg, 1988) and, only recently, as surfactants in detergents and dish washing agents.

Sugar ethers, another class of non-ionic surfactants, can also be derived from sugars. Alkyl glycosides (Ames, 1960) are particularly important. On account of the availability and price of glucose, alkyl glucosides are of special interest.

Structurally alkyl monoglucosides are monocyclic acetals which can have two isomeric forms (Overend, 1972). Alkyl glucosides of low molecular alcohols (< C4) are easily obtained by the Fischer synthesis. Here, D-glucose reacts in its semiacetal form with the alcohol used by forming the full acetal structure; a mixture of the α– and β–alkyl glucosides results. Acetalization occurs in the presence of strong acids. By splitting off water the protonation of the anomeric hydroxyl group yields a stabilized carbonium ion as an intermediate, which reacts with alcohol and forms the two isomeric alkyl glucosides (*Figure 17*).

If on average two or more glucose units are condensed with an alcohol molecule, the resulting compounds are referred to as alkyl polyglucosides (APG) (Hughes, 1970) (*Figure 18*). The mean number of condensed glucose units is termed the degree of glucosidation or degree of polymerization (DP).

The surfactant characteristics (Ames, 1960) of glucosides of longer chain alcohols, *e.g.* fatty alcohols, have already been recognized for many decades. However, these glucosides could only be prepared by means of the costly and industrially unattractive Königs-Knorr synthesis (Havlinova *et al.*, 1978).

The process which proved successful for the industrial production of surface active alkyl polyglucosides was based on the Fischer synthesis. The development began about twenty years ago and the last 10 years have been relatively eventful. Two main process variants (Jeffrey, 1983) were developed and described in the patent literature; they allow the production of alkyl polyglucosides with surfactant characteristics and the quality (light-coloured and colour-stable) which is demanded by the detergent industry. The following problems had to be solved.

- Slow conversion of the reactants because of the insolubility of the glucose in fatty alcohols.
- Suppression of by-product formation (polymerization of glucose, formation of coloured substances).
- Removal of excess fatty alcohol.

In the transglucosidation process glucose is reacted with a fatty alcohol under acidic conditions in the presence of a C_3 or C_4 alcohol (*e.g.* n-butanol) or diol (*e.g.* propylene glycol) (*Figure 19*).

The intermediate low molecular weight alkyl glucoside is miscible with the fatty alcohol and the transglucosidation agent, and the long chain APG is formed in an exchange reaction.

The equilibrium is shifted towards the product by the removal of the water produced in the reaction by distillation and of the excess of solubility promoter and/or transglucosidation agents. After neutralization of the acid catalyst, the excess of fatty alcohol is removed during further distillation.

In a more direct version of the process the fatty alcohol is reacted with glucose under acid catalysis without a solubility promoter. The reactants used must be anhydrous or (as in the case of glucose monohydrate) they must be dehydrated before the reaction; the removal of water formed in the reaction must be controlled precisely. The resulting technical APGs are complex mixtures of α-(β)- alkylmono (di)- and alkyl polyglucopyranosides and -furano-sides (*Figure 19*).

The oligomer distribution is similar with both variants of the synthesis, and is determined by the ratio of glucose and fatty alcohol. Although the APGs are non-ionic surfactants, they differ from ethoxylated fatty alcohols. In contrast to known fatty alcohol polyglycol ethers the APGs and sugar esters are solid non-ionic surfactants.

In the fatty alcohol ethoxylates, an asymmetrical or a restricted homologue distribution can be obtained, depending on the degree of ethoxylation and on the catalyst (*Figure 13*). The surfactant APGs obtained through the Fischer synthesis show a lower DP, thus causing an asymmetrical oligomer distribution (*Figure 20*).

Above 70°C APGs form a liquid-crystal phase (Jeffrey, 1983). They foam more strongly than the common non-ionic surfactants, and they are compatible with different washing ingredients (Hughes, 1970). Furthermore, APGs show synergistic interaction with many industrial surfactants, which results in a clear reduction of surfactant consumption in formulations without loss of performance (Andree *et al.*, 1991). APGs are skin-friendly surfactants with very favourable ecological and toxicological properties (Jeffrey, 1983; Putnik *et al.*, 1986).

Depending on the method of production and their lipophilic nature, the range of application of carbohydrate esters as emulsifiers is either broad (sorbitol fatty acid esters) or narrow (sucrose fatty acid esters). For these reasons, and because of a lack of economic technologies, an advance into the detergent range is not possible.

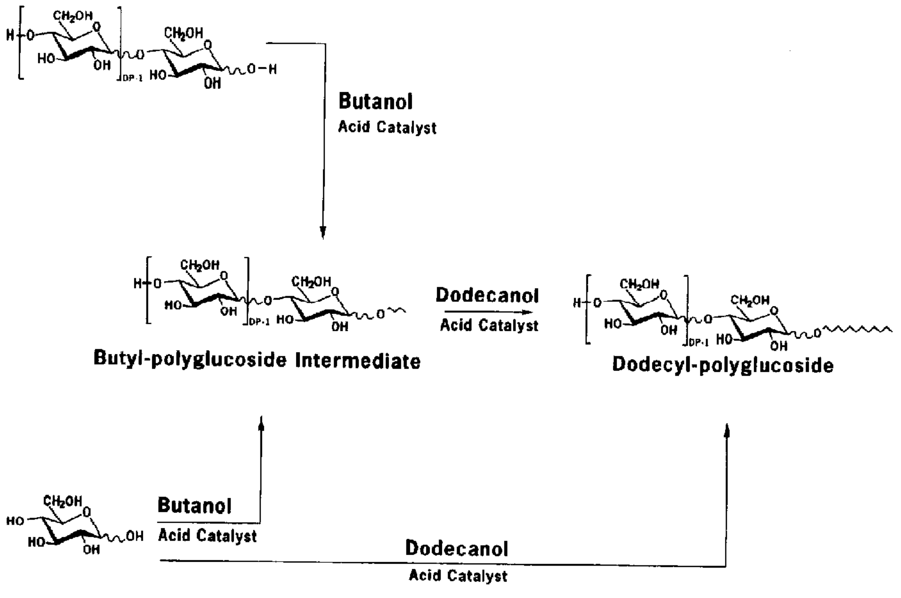


Figure 19. Reaction mechanisms in the synthesis of APGs.

In the case of the APGs, economic manufacturing processes and the property profile guarantee a broad range of applications in washing, rinsing and cleaning agents and in emulsifiers. Because of their compatibility with human mucosae, their absence of oral toxicity and their metabolism, they are also interesting surfactants for cosmetic formulatios and food additives.

The large number of patent applications of different companies in the detergent industry, the application of APGs in branded products and the launching of different APG-containing test products in the European and American markets show the importance of this new class of surfactants. In the form of APGs, carbohydrate surfactants have for the first time entered the group of leading, high-volume surfactants.

Summary and outlook

$C_{16/18}$ fatty alcohol sulphates and $C_{16/18}$ ester sulphonates are available for utilization in detergents in powder form as oleochemical anionic surfactants which can be produced in a large scale. Their success in the market will be determined mainly by economic factors with respect to the individual surfactant and the overall system. So far, no individual fatty chemical surfactant has been found which has the 'all-round-characteristics' and thus the broad range of possible applications of linear alkylbenzenesulphonates (LAS). This explains why a great effort was made to find a type of surfactant with a better solubility in water (i-ester sulphonates and oleic acid sulphonates) than $C_{16/18}$ fatty alcohol sulphates and $C_{16/18}$ ester sulphonates, which are not particularly suitable for liquid products because of their low solubility in water.

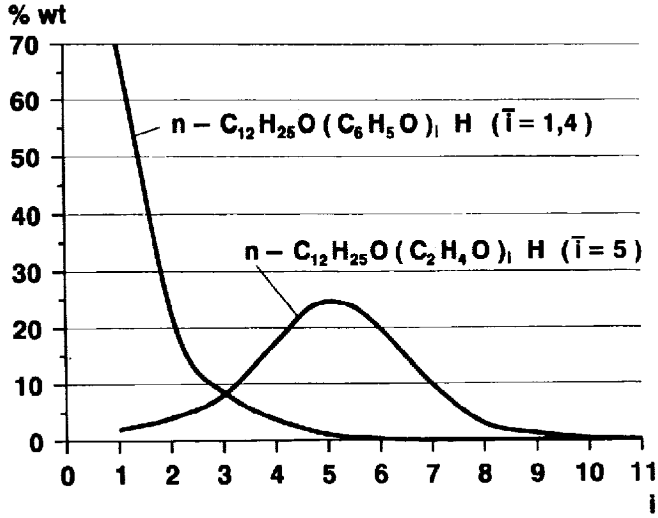


Figure 20. Comparison of the homologue distribution in fatty alcohol ethoxylates and APGs.

For the development of new non-ionic surfactants, naturally-occurring substances will have to be taken into consideration for ecological reasons, *e.g.* by replacing the polyethyleneglycol groups in the fatty alcohol ethoxylates with a hydrophilic substance that occurs naturally. The APGs represent one step in this direction. In the end such developments might lead to pure biosurfactants being produced by microorganisms from biomass.

This report on recent work on oleochemical surfactants has revealed the great potential of natural oils and fats for the development of such materials; this will certainly lead to a further increase in the world prodction of surfactants. The trend will be further supported by the increase in the amounts of palm oil, palm stearin and palm kernel oil which are produced in South East Asia, especially in Malaysia. The chain length distribution of the fatty acids ($C_{16/18}$, $C_{12/14}$) and the high quality of these oleochemical raw materials are an additional contribution to the encouraging future of oleochemical surfactants.

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