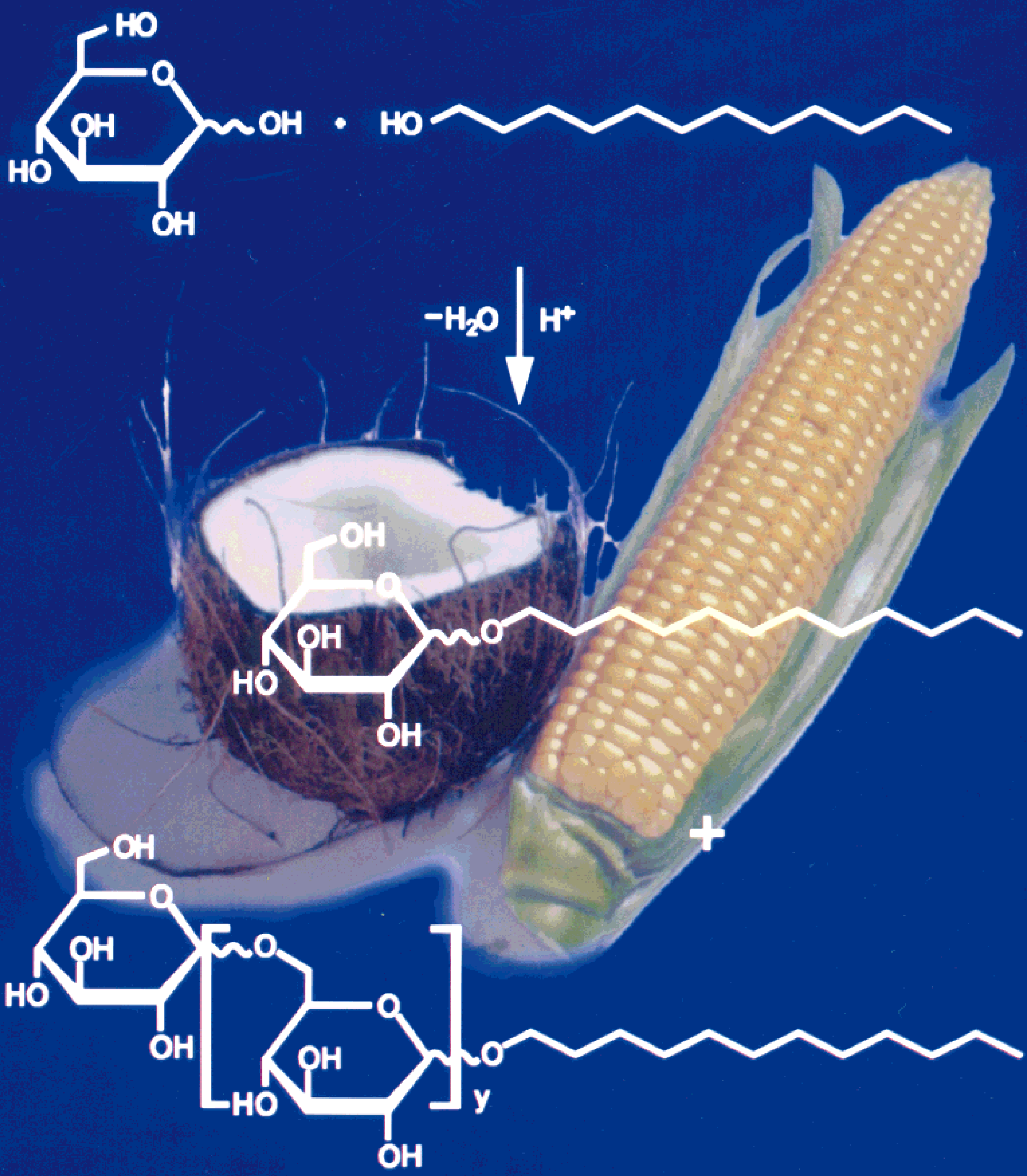

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Coconut oil and corn starch are the raw materials in the technical synthesis of alkyl polyglycosides.

Alkyl Polyglycosides—Properties and Applications of a new Class of Surfactants

Wolfgang von Rybinski* and Karlheinz Hill*

The development of surfactants based on carbohydrates and vegetable oils is the result of a product concept based on the exclusive use of renewable resources. While oils and fats have been known for a long time as suitable raw materials for the production of surfactants such as soap, alkyl sulfate, and alkyl ether sulfate, their derivatization with a carbohydrate molecule as the hydrophilic moiety has just recently become possible on a large industrial scale. The resulting sugar-surfactants sucrose esters, sorbitane esters, *N*-methyl glucamides, and alkyl polyglycosides are based on carbohydrate raw materials, which are available on the world market in large quantities and at competitive prices: sucrose, glucose, and sorbitol.[1] The selective functionalization of sucrose or sorbitol to construct an ideal amphiphilic structure cannot be achieved by simple chemical processes due to the polyfunctionality of the molecules and the relatively small differences in the reactivity of the hydroxyl groups. As a result the products on the market are predominantly composed of a mixture of mono-, di-, and triesters and are used in special applications only, for example as emulsifiers in foods and cosmetics and, in case of the sorbitan esters, in technical fields like explosives and emulsion polymerization. Glucose is the carbohydrate raw material of choice for selective derivatization. The reaction with alcohols leads to alkyl glucosides. *N*-methyl glucamides are formed by reductive amination and subsequent acylation. Both products have proved to be high-performance surfactants for detergents, and one company at present exclusively uses *N*-methyl glucamides. Alkyl glucosides have a broader application spectrum and are used as well in cosmetic products, as surfactants for industrial cleaners, and in agricultural applications. Based on the annual production figures they can be considered as the most important sugar-surfactant today. The following survey on alkyl glucosides covers various aspects on synthesis, industrial production, physico-chemical properties, ecotoxicological evaluation, and selected fields of application.

Keywords: glucosides · interfaces · surface chemistry · surfactants

1. Developments in Industry

Alkyl glucosides—or alkyl polyglycosides as the industrially manufactured products are widely known—are a classic example of products which, for a long time, were of academic interest only. The first alkyl glucoside was synthesized and identified by Emil Fischer more than 100 years ago. The first patent application describing the use of alkyl glucosides in detergents was filed in Germany some 40 years later.[2] Another 40 to 50 years went by before research groups in various companies redirected their attention to alkyl glucosides and developed technical processes for the production of alkyl polyglycosides (Scheme 1).

In the course of this development, Fischer's early work, which involved the reaction of glucose with hydrophilic alcohols such as methanol, ethanol, glycerol, etc., was applied to hydrophobic alcohols with alkyl chains from C_8 to C_{16}, the typical fatty alcohols. Not pure alkyl monoglucosides but a complex mixture of alkyl mono-, di-, tri-, and oligoglycosides are produced in the industrial processes. Because of this, the industrial products are called alkyl polyglycosides. The products are characterized by the length of the alkyl chain and the average number of glucose units linked to it, the degree of polymerization (DP).

Rohm & Haas (Philadelphia, USA) was the first to market an octyl/decyl ($C_{8/10}$) polyglycoside in commercial quantities in the late 1970s, followed by BASF (Ludwigshafen, Germany), and later SEPPIC (Paris, France). However, owing to the unsatisfactory performance of this short-chain version as a surfactant and its poor color quality, applications were limited to few market segments, for example industrial bottle cleaning. The product quality of such short-chain alkyl polyglyco-

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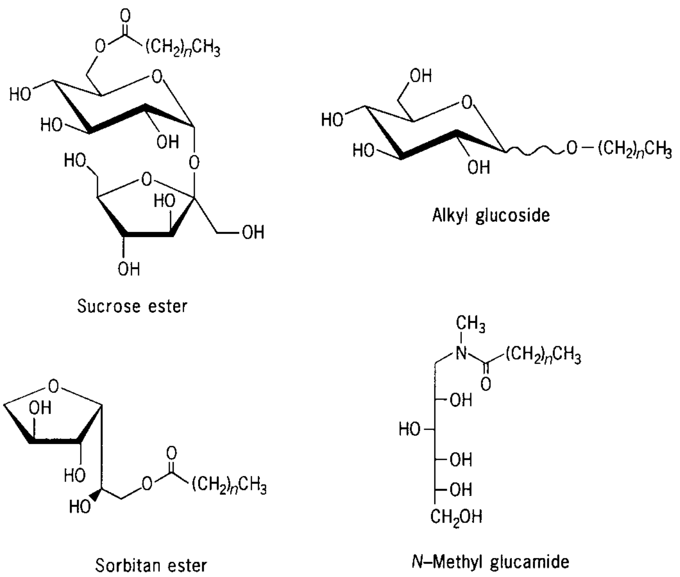

Scheme 1. Commercially produced carbohydrate-based surfactants.

sides has been improved in the last few years, and new types of octyl/decyl polyglycoside are currently being offered by various companies, among them, Akzo Nobel (Stenungsund, Sweden), BASF, Henkel (Düsseldorf, Germany), ICI (Middlesborough, U.K.), SEPPIC, and Union Carbide (Danbury, USA).

At the beginning of the 1980s, several companies started programs to develop alkyl polyglycosides in the longer dodecyl/tetradecyl alkyl chain range ($C_{12/14}$-alkyl polyglycoside) for application in the cosmetics and detergent industries. According to the number of patent applications,[3] the following companies made the major efforts: Procter & Gamble (Cincinnati, USA), Henkel, Horizon (a division of A. E. Staley Manufacturing Company in Decatur, USA, which was acquired by Henkel later), Hüls (Marl, Germany), Kao (Tokyo, Japan), and SEPPIC. In 1988/1989 Henkel built a pilot plant to manufacture alkyl polyglycosides (APG surfactants) in Crosby, USA, with a capacity of 5000 t per year. Between 1990 and 1992 other companies announced their intention to build up industrial plants for the manufacturing of alkyl polyglycosides, among them Hüls, ICI, Kao, and SEPPIC. The final breakthrough in the commercial exploitation of alkyl polyglycosides was reached in 1992 with the inauguration of a production plant for APG surfactants with an annual capacity of about 25000 t by Henkel in Cincinnati, USA and in 1995 with the opening of a second plant of equal capacity by Henkel in Düsseldorf, Germany.[2d]

2. Synthesis of Alkyl Polyglycosides

2.1. Glycosylation Reactions

In the synthesis of glycosides, a polyfunctional sugar component is combined with a nucleophile such as an alcohol, a carbohydrate, or a protein. The broad synthesis potential of this reaction, which is very common in nature, has recently been reviewed in articles by R. R. Schmidt and P. Sinaÿ, as well as K. Toshima and K. Tatsuta.[4]

Selective glycosylation reactions require special activation methods, the use of protective groups, or selective catalysis by enzymes. A selection of the many routes to glycosides is shown in Scheme 2 in a generalized way; the effect of

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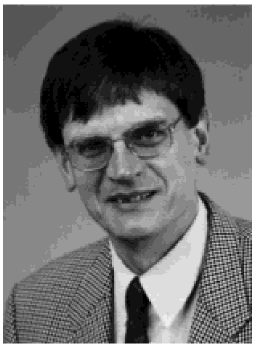
W. von Rybinski


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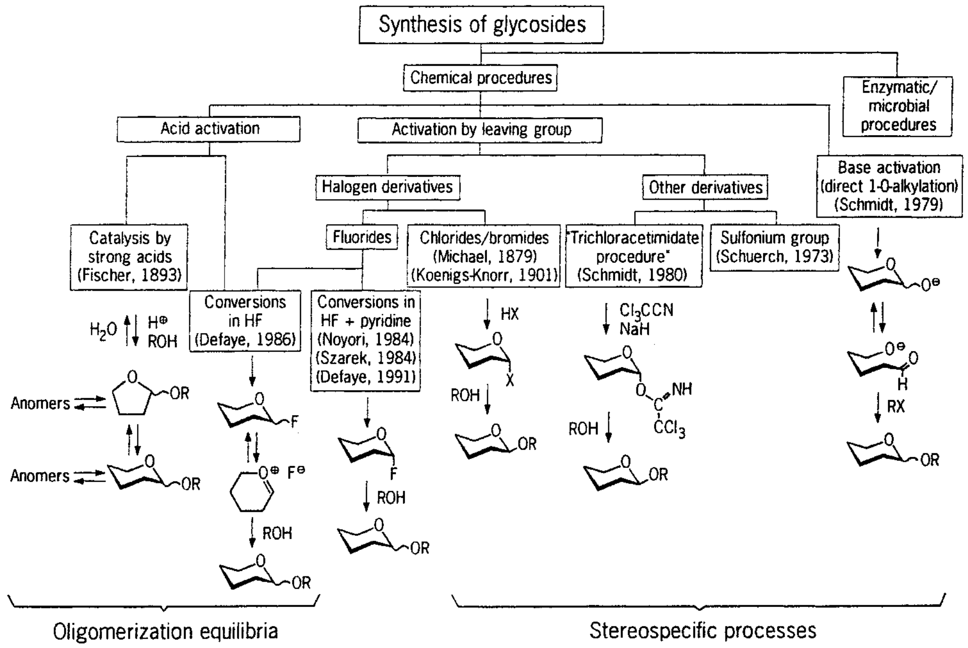
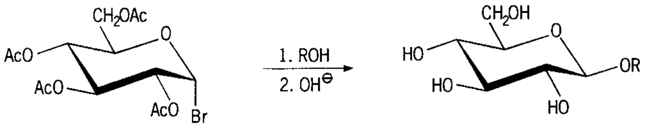
Karlheinz Hill, born 1955 in Bayreuth (Germany), studied Chemistry at the University of Würzburg. After receiving his Ph.D. under the supervision of W. Adam in 1984 he spent one and a half years as a post-dococtoral fellow in the Structural Chemistry group of M. Lahav at the Weizmann Institute in Rehovot (Israel). In 1986 he joined Henkel KGaA in Düsseldorf and worked three years in the organic chemistry research group in the field of alkyl polyglycosides. The next two years he spent at the Henkel Research Corporation in Santa Rosa, California, working on carbohydrate derivatives. After returning to Düsseldorf he was involved in various projects in the chemical research division, focusing on organic chemistry, oleochemistry, and surfactants. In 1995 he was appointed head of Research Oleochemistry, and since 1998 he is head of Research Chemical Products at Henkel. He is a member of the German Society for Fat Research (DGF), where he is responsible for the Oleochemistry division.

neighboring groups on the stereoselectivity of the reaction is not considered.[4, 5] In principle, enzymatic or microbial procedures, by virtue of their selectivity, can replace complicated chemical protection and deprotection steps where regioselective formation of glycosides is required. Nevertheless, the use of enzymes in glycoside synthesis has not yet been widely enough investigated, and applications are presently limited to the laboratory.[6] Owing to problems of availability of suitable enzyme systems and the high manufacturing costs anticipated, enzymatic syntheses of alkyl glycosides are not yet ready for upgrading to the industrial level, and chemical procedures are preferred. In general, chemical glycosylations may be divided into two processes: those leading to complex oligomer equilibria in acid-catalyzed glycosyl exchange reactions (Fischer glycosylation[2a] and reactions in hydrogen fluoride (HF)[7, 8] with unprotected carbohydrate molecules) and kinetically controlled, irreversible, mostly stereoselective substitution reactions on suitably activated carbohydrate substrates.[9–13] Procedures of the second type may result in the formation of exclusive products rather than of complex reaction mixtures, especially when combined with protective group techniques. Carbohydrates may be activated at the anomeric carbon by leaving groups (for example, halides,[7–10] the sulfonium group,[11] or the trichloroacetimidate group[12]) or by base activation.[13]



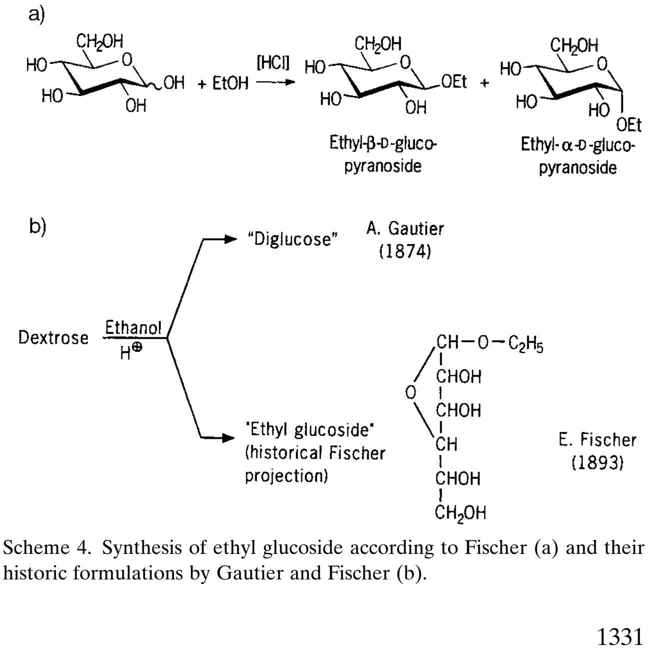
Scheme 2. Overview of glycosylation reactions.

The history of synthetic routes that eventually led to glycosides began in 1870, when M. A.Colley[14] reported the synthesis of "acetochlorohydrose" by reaction of dextrose (glucose) with acetyl chloride. Tetra-*O*-acetyl-glucopyranosyl halides (acetohaloglucoses) were later found to be useful intermediates for the stereoselective synthesis of pure alkyl glucoside anomers. In 1879 Arthur Michael[9] succeeded in preparing well-defined, readily crystallizable aryl glucosides starting from Colley's intermediate and phenolates. The crucial application of Michael's synthesis to a broad range of carbohydrates and hydroxylic aglycons occurred in 1901, when W. Koenigs and E. Knorr introduced an improved stereoselective glycosylation process (Scheme 3).[10] The reaction, which takes place in the presence of silver or mercury promotors, involves an S_N2 substitution at the anomeric carbon and proceeds stereoselectively with inversion of configuration, producing, for example, the β-glucoside from the α anomer of the acetobromoglucose intermediate.



Scheme 3. Stereoselective synthesis of glycosides according to Koenigs–Knorr. R = alkyl.

A fundamentally different approach to the synthesis of alkyl glucosides was chosen by Emil Fischer in 1893, when he discovered the acid-catalyzed reaction of glycoses with alcohols (Scheme 4a). This process is now well known as the "Fischer glycosylation". Any historical account should nevertheless also include A. Gautier's first reported attempt, in 1874, to convert dextrose with anhydrous ethanol in the presence of hydrochloric acid. Due to a misleading elemental analysis, Gautier believed he had obtained a "diglucose".[15] Fischer later demonstrated that Gautier's "diglucose" was in fact mainly ethyl glucoside. The structure of ethyl glucoside was defined correctly by Fischer—as the furanosidic "Fischer projection" (Scheme 4b).[2a] In fact, the Fischer glycosylation



Scheme 4. Synthesis of ethyl glucoside according to Fischer (a) and their historic formulations by Gautier and Fischer (b).

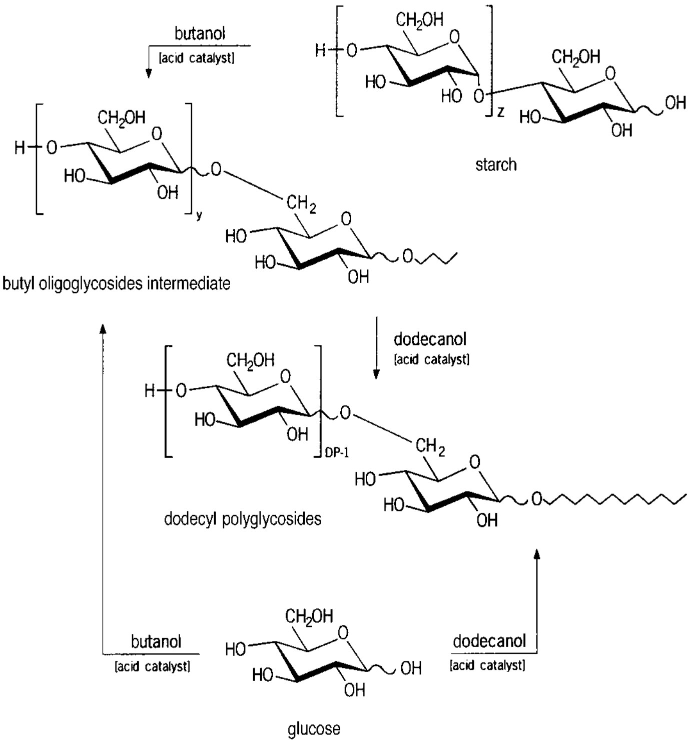
is an equilibrium reaction that on passing through kinetically favored furanoside stages leads to complex product mixtures dominated by pyranosides. The polyfunctionality of the carbohydrates cause the formation of randomly linked glycoside oligomers (isomaltosides, maltosides, maltotriosides, etc.) besides α- and β-anomers of pyranosides and furanosides (α:$\beta \approx 2$:1 in product mixtures from technical processes).[16] Accordingly, individual molecular species are not easy to isolate from Fischer reaction mixtures. After some improvement of this synthesis method, Fischer subsequently adopted the Koenigs-Knorr synthesis for his investigations.[17] Using this process, E. Fischer and B. Helferich were the first to report the synthesis of a long-chain alkyl glucoside exhibiting surfactant properties in 1911.[17c] Other research groups have applied modifications of this method in the recent past to investigate the product properties of these sugar-surfactants further.[10b, 18]

2.2. Technology for the Manufacture of Long-Chain Alkyl Polyglycosides

Any production process suitable for use on an industrial scale must satisfy several criteria. The ability to produce products with suitable performance properties under economically viable technical conditions is the most important. Some other aspects are the minimizing of side reactions, waste, and emissions. The technology should be flexible enough to allow properties and qualities to be adapted to dynamic market requirements. As far as the industrial production of alkyl polyglycosides is concerned, processes based on the Fischer synthesis have been successfully adopted. Development work over the past decade has enabled the efficiency of this synthesis route to be increased to a level where it has finally become attractive for industrial application, especially with regard to product quality and process economy. Modern production plants built on the basis of the Fischer synthesis are the embodiment of low-waste, virtually emission-free technologies. Another advantage of the Fischer synthesis is that the ratio of alkyl monoglycosides to alkyl oligoglycosides can be precisely controlled over a wide range by adjusting the amounts of glucose and fatty alcohol in the reaction mixture. Relevant performance properties, for example hydrophilicity, can thus be adapted to meet requirements of specific applications without further purification of the final product mixture or isolation of one component.[5]

In a technical process either a polymeric form of glucose such as starch or glucose syrup with low dextrose equivalent (DE), or monomeric glucose (anhydrous or as the monohydrate) can be used. Fatty alcohols can be obtained either from petrochemical sources (synthetic fatty alcohols) or from natural, renewable resources such as fats and oils, after splitting of the triglycerides with methanol and subsequent hydrogenation of the corresponding fatty acid methyl esters (natural fatty alcohols). Due to its fatty acid composition coconut and palm-kernel oil are the preferred raw materials for the production of dodecanol/tetradecanol blends. The typical ratio formed is 70:30 (hexadecanol < 5%).[5, 19]

Depending on the type of carbohydrate used, all manufacturing processes for the Fischer synthesis of alkyl polyglycosides can be attributed to two process variants, namely direct synthesis[20] and the transacetalization process (Scheme 5).[21] In either case, the reaction can be carried out in batches or continuously.[20c, 22] The two-stage transacetalization process is applied if oligo- and polyglycoses are used and involves more equipment than the direct synthesis. In the first stage the carbohydrate reacts with a short-chain alcohol (for example, n-butanol or propylene glycol); polymeric carbohydrates require depolymerization. In the second stage the short-chain alkyl glycoside is transacetalized with a long-chain alcohol ($C_{12/14}OH$) to form the final alkyl polyglycoside. The necessary depolymerization of the polymeric glycose starting materials requires temperatures of > 140°C. Depending on the alcohol used, this can create correspondingly higher pressures, which impose more stringent demands on equipment and can lead to higher plant cost. If the molar ratios of carbohydrate to alcohol are identical, the oligomer distribution obtained in the transacetalization process is basically the same as in the direct synthesis.



Scheme 5. Reaction pathways for the industrial production of dodecyl polyglycoside.

In the following, the one stage process (direct synthesis) for the manufacturing of dodecyl/tetradecyl polyglycoside is discussed in detail.[20] In this case glucose is suspended in excess fatty alcohol (2-6 mol), and the reaction is carried out at a temperature of 100-120°C in the presence of an acidic catalyst, typically a sulfonic acid. After removal of water as by-product (1 equiv relative to glucose) under vacuum, the product mixture comprises alkyl mono-, alkyl oligo-, and alkyl polyglycosides. The (average) degree of polymerization (DP) for such an alkyl polyglycoside is largely dependent on the ratio of glucose to alcohol in the reaction mixture and can be calculated from the mole percent *p* of the respective oligomeric species *n* in the glycoside mixture. The composition of a typical product is shown in Figure 1. Several analytical methods have been developed recently to identify and characterize the individual species in the alkyl polyglycoside.[23] The chromatogram of a high-temperature GC analysis of dodecyl/tetradecyl polyglycoside is shown as an example (Figure 2).

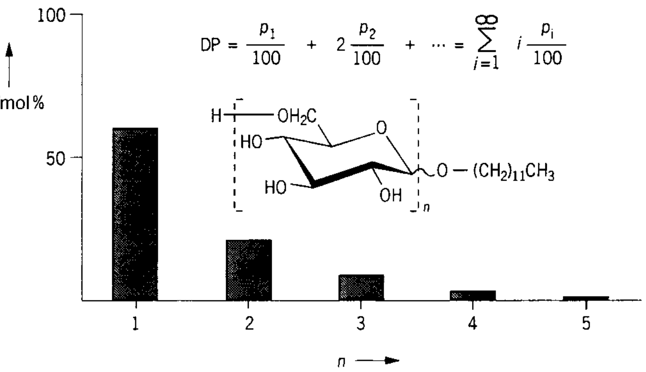


Figure 1. Typical distribution of oligomers in dodecyl polyglycoside (DP = 1.3).

Under the conditions of the acid-catalyzed syntheses of alkyl polyglycoside, secondary products such as glucose polymers,[24] ethers, and colored impurities, are formed. Glucose polymers are substances of undefined structure formed in the course of the synthesis through the polymerization of glycopyranoses. The type and concentration of the substances formed by secondary reactions are dependent on process parameters such as temperature, pressure, reaction time, and catalyst, which have to be adjusted and controlled exactly.[19]

The Fischer glycosylation may be described as a process in which, in a first step, the dextrose reacts relatively quickly, and an oligomer equilibrium is reached. This step is followed by slow degradation of the alkyl polyglycoside. In the course of the degradation, which consists of dealkylation and polymerization steps, the thermodynamically more stable glucose polymer is formed irreversibly in increasing concentrations. Reaction mixtures that have exceeded an optimal reaction time may be described as overreacted. If the reaction is terminated too early, the resulting reaction mixture contains a significant amount of residual glucose (Figure 3). As catalysts, any acids with sufficient strength are suitable for this purpose such as sulfuric acid, *p*-toluenesulfonic acid, alkylbenzenesulfonic acid, and sulfosuccinic acid.[25] The reaction rate is dependent on the acidity and the concentration of the acid in the alcohol.[26] Secondary reactions that are also catalyzed by acids such as the formation of glucose polymers mainly take place in the polar phase (traces of water) of the heterogeneous reaction mixture and can be reduced by using hydrophobic acids such as alkylbenzene sulfonic acids, which, through the length of their alkyl chain, mainly dissolve in the less polar phase of the reaction mixtures.

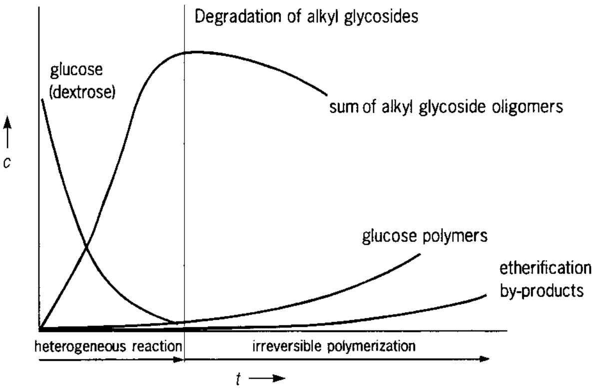


Figure 3. Course of reaction of the technical glycosylation process (dodecyl polyglycoside).

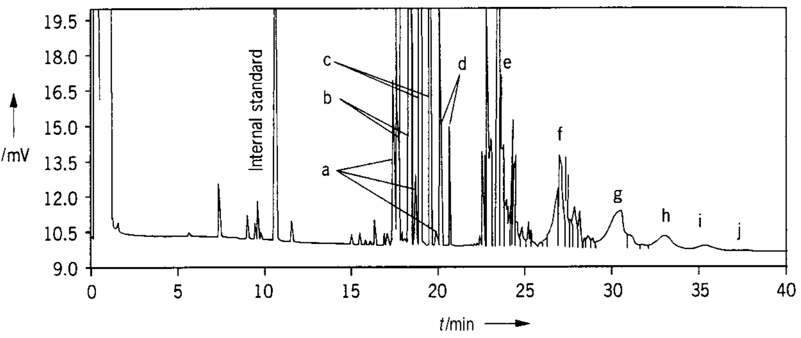
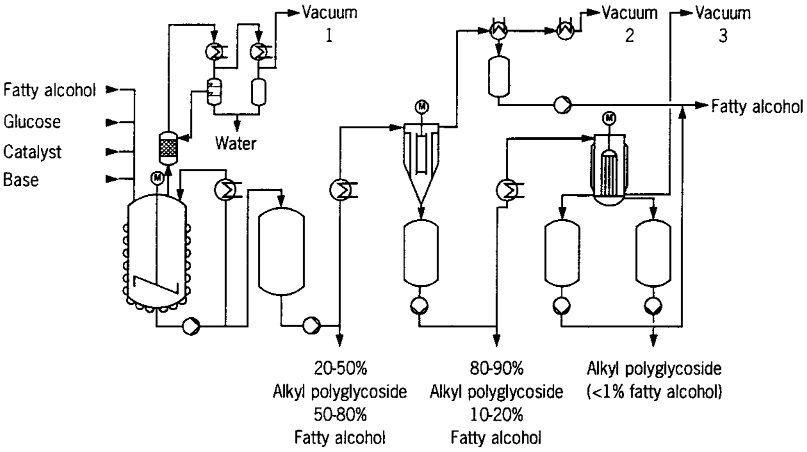


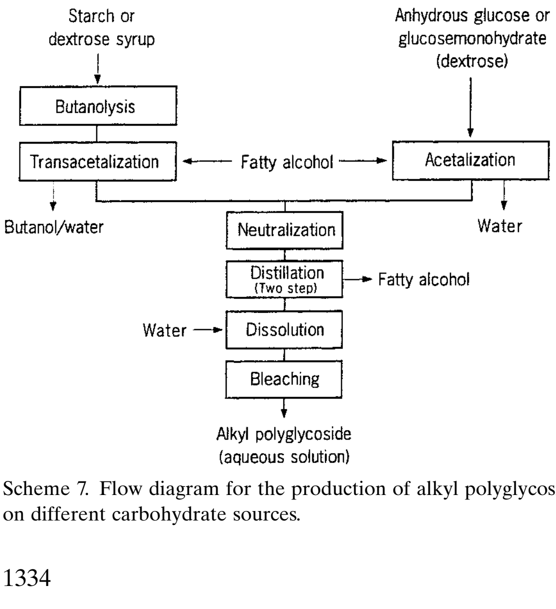
Figure 2. Chromatogram of the high-temperature GC analysis of dodecyl/tetradecyl polyglycoside. a) $C_{12/14/16}$ furanosides, b) C_{12} monoglycosides, c) C_{14} monoglycosides, d) C_{16} monoglycosides, e) diglycosides, f) triglycosides, g) tetraglycosides, h) pentaglycosides, i) hexaglycosides, j) heptaglycosides (detection: FID, 420°C; hydrogen 30 mL min^{-1}, air 300 mL min^{-1}. Duran glass capillary column, 10 m × 0.53 mm ID, SIMDIS; injection: on column, 1 µL; carrier gas: hydrogen 20 mL min^{-1}; temperature program: 70°C [4 min], heating rate 10°C min^{-1} to 400°C [12 min]).

After the reaction the acidic catalyst is neutralized by a suitable base, for example sodium hydroxide or magnesium oxide. The neutralized reaction mixture is a yellowish solution containing less than 1% of residual glucose and 50 to 80% fatty alcohol, depending on the fatty alcohol excess used. The fatty alcohol is removed by continuous vacuum distillation to 1% or below. To minimize the formation of unwanted pyrolysis products or discoloring components during distillation, thermal stressing and residence time of the target product are kept as low as possible. No monoglycoside should enter the distillate, because the distillate is recycled in the reaction as pure fatty alcohol. In case of dodecyl/tetradecyl polyglycoside these requirements are largely satisfied by multistage distillation. It is important to note that there is a distinct increase in viscosity with decreasing fatty alcohol content. This significantly impairs heat and mass transport in the last distillation stage. Accordingly, thin-layer or short-path evaporators are preferred.[20a, 27] In these evaporators, the mechanically moved film provides for high specific evaporation efficiency and a short product residence time, and at the same time a good vacuum. The end product after distillation is an almost pure alkyl polyglycoside, which accumulates as a solid with a melting range of 70 to 150°C. Scheme 6 summarizes the main process steps for the synthesis of alkyl polyglycosides.



Scheme 6. Industrial-scale glycosylation process for the direct reaction of glucose with fatty alcohol (dodecanol/tetradecanol).

After removal of the fatty alcohol, the alkyl polyglycoside active substance is directly dissolved in water to form a highly viscous 50 to 70% alkyl polyglycoside paste. In subsequent refining steps this paste is worked up into a product of satisfactory quality in accordance with performance-related requirements. These refining steps may comprise bleaching of the product, the adjustment of product characteristics such as pH value and active substance content, and microbial stabilization.[20a] The patent literature includes many examples of reductive[28a] and oxidative bleaching[28b–f] and of two-stage processes of oxidative bleaching and reductive stabilization.[29] For example, treatment with hydrogen peroxide under alkaline conditions leads to a colorless product, which is stable during long storage—an important requirement for high-quality applications in consumer-friendly market products. Scheme 7 summarizes the individual steps of the industrial production of dodecyl/tetradecyl polyglycoside.



Scheme 7. Flow diagram for the production of alkyl polyglycosides based on different carbohydrate sources.

3. Physicochemical Properties of Alkyl Polyglycosides

The favorable performance properties of surfactants, in particular interfacial properties and behavior in solutions (for example, phase behavior), are essentially attributable to specific physicochemical effects.[30] Alkyl polyglycosides were found to possess remarkable properties which, in some cases, differ clearly from those of other nonionic surfactants. The results obtained so far are summarized in the following sections. Significant differences in relation to the behavior of fatty alcohol ethoxylates in particular are highlighted.

3.1. Interfacial Properties

The surface tension of alkyl (poly)glycosides was investigated as a function of the alkyl chain and the degree of polymerization (DP) on samples differing in purity. Shinoda et al.[31] and Böcker et al.[18c] determined the critical micelle concentration (cmc) and the surface tension values at the cmc from surface tension/concentration curves. A few selected values are set out in Table 1. Figure 4 shows the surface tension as a function of concentration for three alkyl monoglycosides (C_nG_1, G = number of glycoside units) and a technical $C_{12/14}$ APG at 60°C.[32] The cmc values of the pure alkyl monoglycosides and the technical alkyl polyglycosides are comparable with those of typical nonionic surfactants and decrease distinctly with increasing alkyl chain length. The alkyl chain length has a far stronger influence on the cmc than the number of glucoside groups of the APG.

Table 1. Critical micelle concentrations c_M from surface tension measurements.

Substance	T [°C]	c_M [mol L^{-1}]	Ref.
β-D-C_8G_1	25	2.5×10^{-2}	[31]
C_8G_1	25	1.8×10^{-2}	[32]
β-D-$C_{10}G_1$	25	2.2×10^{-3}	[31]
β-D-$C_{12}G_1$	25	1.9×10^{-4}	[31]
$C_{12}G_1$	25	1.7×10^{-4}	[32]

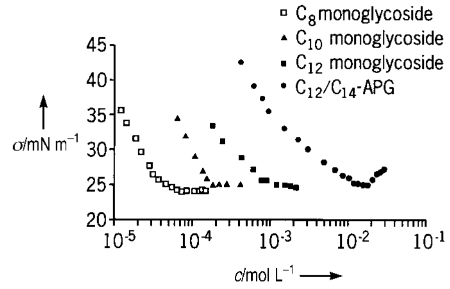


Figure 4. Static surface tension σ of alkyl glycosides with different alkyl chain lengths as a function of the concentration c in distilled water at 60°C.

A mixture of APG and fatty alcohol sulfate (FAS) was used as example to investigate the surface tension behavior of surfactant mixtures of APG and anionic surfactants.[32] The values of the mixtures are near the curve for APG even despite a high anionic surfactant content. This corresponds to the normally observed behavior of mixtures of anionic and nonionic surfactants differing considerably in their cmc values.[33] A weak attractive interaction between these surfactants can be derived on the basis of Rosen's theory.[34] Similar results are reported for mixtures of alkyl polyglycosides and alkyl benzenesulfonates.[35]

Figure 5 shows the dynamic surface tension as a function of time for the same surfactant solutions at a concentration of 8×10^{-4} moles L^{-1} at 40°C.[36] The curve of the pure FAS falls more quickly for short times than that of pure APG: the FAS thus diffuses more quickly to the surface of the liquid than the APG with the same alkyl chain length. The mixtures of both surfactants reach lower surface tensions than the pure surfactants. It should be noted that surfactants of technical purity were compared with one another in these investigations. This factor can be important in the interpretation of the results of dynamic surface tension measurements, because the individual components of the technical surfactants can have a different affinity for the surface.[37]

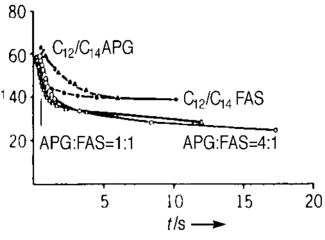


Figure 5. Static surface tension σ of $C_{12/14}$ APG and $C_{12/14}$ FAS and 1:1 and 4:1 mixtures thereof as a function of the time at 40°C and a concentration of 8×10^{-4} mol L^{-1}.

The interfacial tension between various APGs and three oils (decane, isopropyl myristate, and 2-octyl dodecanol) differing in structure and polarity was investigated by Kutschmann et al.[38] The influence of oil polarity is clearly illustrated in Figure 6. The interfacial tension between aqueous solutions of alkyl monoglycosides and the three oils is plotted against the logarithm of the surfactant concentration. For each oil there is a pronounced break and a constant plateau value, which decreases in the order decane > isopropyl myristate > octyl dodecanol. For C_8G_1 the break occurs at approximately the same concentration of the surfactant in the water phase for all three oils. The corresponding curves for $C_{12}G_1$ are shown in Figure 13b. For isopropyl myristate and octyl dodecanol, the break of the isotherm distinctly shifts towards higher concentrations of the surfactant. Also, the position of the plateau value lies at far higher values for octyl dodecanol than for the other two oils: the cmc apparently shifts towards higher values with increasing oil polarity. This effect is more pronounced, the longer the alkyl chain length of the glucoside. One possible explanation for this is the increase in the solubility of the surfactant in the oil phase with increasing alkyl chain length and, hence, hydrophobicity or increasing polarity of the oil.

Figure 7 shows the plateau values γ_c of the interfacial tension between C_nG_1 homologues as well as various technical APGs and the three oils as a function of the chain length of the surfactant. For decane/water and IPM/water mixtures, γ_c decreases with increasing alkyl chain length and, hence, increasing hydrophobicity of the surfactant. By contrast, the curve of the octyl dodecanol/water system has a pronounced minimum in the case of $C_{10}G_1$ and increases steeply with increasing alkyl chain length. Since $C_{12}G_1$ is highly oil-soluble in the octyl dodecanol/water system, optimum affinity for the oil phase in this system is actually achieved in the case of $C_{10}G_1$.

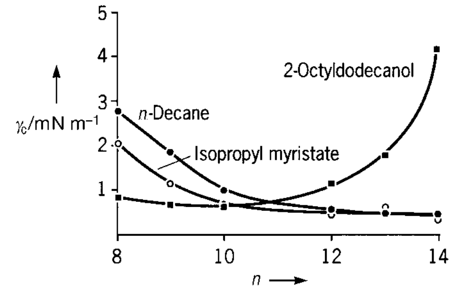


Figure 7. Plateau values of the interfacial tension γ_c in three different oil/water systems as a function of the alkyl chain length of the surfactant n at 60°C.

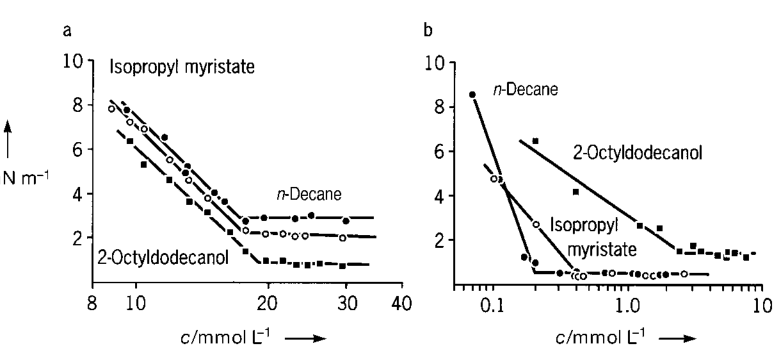


Figure 6. Influence of alkyl glycosides C_8G_1 (a) and $C_{12}G_1$ (b) on oil/water interfacial tension γ for three different oils as a function of the initial concentration c of the surfactant in the water phase.

Similarly to the liquid/gas and liquid/liquid interfaces, surfactants also influence the interface of liquid systems with solid substrates by virtue of their amphiphilic structure. This affects, for example, dispersions of solids in liquids,[39] washing and cleaning processes,[40] and the processing of ores.[41] The systematic dependence of adsorption on the structure of nonionic surfactants has been summarized.[42] Nickel et al.[43] report on the adsorption of alkyl glycosides onto various types of solids and demonstrate a connection with the dispersion of solids.

Figure 8 shows the adsorption behavior of $C_{10}G_1$ for graphitized carbon black at 22°C.

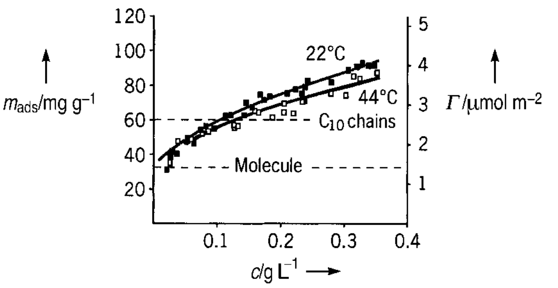


Figure 8. Adsorbed amount m_{ads} and surface concentration Γ of $C_{10}G_1$ on graphitized carbon black as a function of the surfactant concentration c in water at 22°C and 44°C.

The adsorption isotherms are characterized by a very steep initial slope. This behavior is indicative of a high affinity of the alkyl glycosides for this solid surface. In addition to the adsorption curve, the theoretical values for monolayers on horizontal and vertical arrangements are indicated. The adsorption volume corresponding to a monomolecular layer with a vertical arrangement of the alkyl chain is exceeded at a concentration of around 0.15 g L^{-1}. The dependence of adsorption on temperature is very weak. The 22°C curve is slightly above the 45°C curve.

Comparison with the adsorption behavior of $C_{10}E_4$ (E = number of oxyethylene glycol groups) on graphitized carbon black at three temperatures (Figure 9) shows clear differences between the surfactant types. A marked dependence on temperature in the upper concentration range can be seen for the fatty alcohol ethoxylate. In contrast to the alkyl glycosides, adsorption increases with increasing temperature. The critical parameter for the dependence of the adsorption of $C_{10}E_4$ on temperature is clearly the cloud point ($T_c = 20°C$). The adsorption of $C_{10}E_4$ increases dramatically at temperatures above T_c. On the other hand, however, a C_8E_4 with a cloud point of 40°C also shows significant dependence of adsorption behavior on temperature below the cloud point.[42]

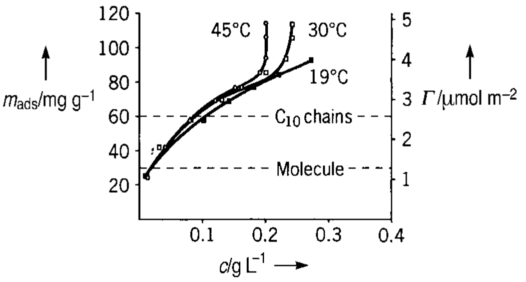


Figure 9. Adsorbed amount m_{ads} and surface concentration Γ of $C_{10}E_4$ on graphitized carbon black as a function of the surfactant concentration c in water at 19°C, 30°C, and 45°C.

The influence of surface quality is even clearer on hydrophilic surfaces. Smith et al.[44] studied the adsorption of technical APGs with different chain lengths on titanium dioxide. It is known from adsorption studies that lauryl polyglycol ethers are not adsorbed onto the surface of titanium dioxide particles.[45] The reason was assumed to be that the ether bonds of the nonionic surfactants preferentially form hydrogen bonds with the unbound water molecules than with the hydroxyl groups of the polar titanium dioxide surface. Alkyl glycosides show different behavior on polar solid surfaces.

The adsorption isotherms of three technical alkyl polyglycosides on titanium dioxide are shown in Figure 10. In the identical concentration range investigated, the shapes of the isotherms differ with the chain length of the alkyl polyglycoside mixtures. In the case of the short-chain $C_{8/10}$ alkyl polyglycoside, the amount adsorbed is almost linearly dependent on the concentration, whereas a tendency towards a pronounced S form of the isotherms is observed with increasing alkyl chain length. A similar isotherm form is also observed for the adsorption of anionic surfactants onto polar solids, for example sodium dodecyl sulfate (SDS) onto titanium dioxide[46] and aluminium oxide.[47] By way of explanation, it was stated in these examples that individual surfactant molecules with the polar head directed towards the surface are adsorbed by an acid/base interaction of the basic OH groups of the surface with the SDS anion. If the concentration of the surfactants in solution is increased, two-dimensional aggregates—often referred to as "hemimicelles"[48]—are formed by hydrophobic interactions of the alkyl chains. Such interactions lead to a marked increase in the quantities adsorbed. A similar mechanism can also be postulated for the adsorption of alkyl polyglycosides with relatively long alkyl chains. The hydroxyl groups of the surfactant have a slightly acidic character and are capable of forming hydrogen bonds with the hydroxyl groups of the titanium dioxide surface. If a sufficient number of alkyl glycoside molecules is adsorbed onto the surface, other molecules are adsorbed onto the surface through an interaction of the alkyl chains. This leads to surface coverages above a theoretical monolayer, which is confirmed by the adsorption measurements. The effects of adsorption on the dispersion of pigments in aqueous solutions of alkyl polyglycosides and the rheology of dispersions were described by Nickel et al.[43] and by Smith et al.[44]

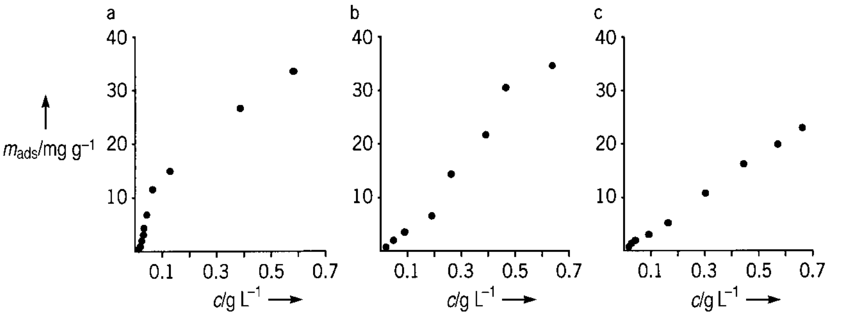


Figure 10. Adsorbed quantity m_{ads} of APGs $C_{12/14}$ (a), $C_{9/11}$ (b), and $C_{8/10}$ (c) on titanium dioxide (R-960) as a function of the surfactant concentration c in water at 25°C.

3.2. Phase Behavior

In contrast to systematic studies of fatty alcohol ethoxylates, only a few studies have hitherto been conducted into the phase behavior of alkyl polyglycosides. For a pure short-chain *n*-octyl-β-D-glucoside, the phase diagram was investigated in detail by Nilsson and Söderman[49] and Sakya et al.[50] The phase sequence is illustrated in Figure 11. At low temperatures, a hexagonal, a cubic, and finally a lamellar phase are observed with increasing surfactant content. The phase diagram of the $C_{12/14}$ alkyl polyglycoside/water system (Figure 12) differs clearly from that of a short-chain alkyl polyglycoside.[49] At low temperatures, a region corresponding to a solid/liquid region below the Krafft point is formed over a wide concentration range. With an increase in temperature, the system changes into an isotropic liquid phase. Since crystallization is kinetically retarded to a considerable extent, this phase boundary changes position with the storage time. At low concentrations the isotropic liquid phase changes above 35°C into a two-phase region of two liquid phases, as is normally observed with nonionic surfactants.[51] At concentrations above 60% by weight, a sequence of liquid crystalline phases is formed at all temperatures. Investigations into the structure of the liquid crystalline phases were conducted by Platz et al.[52] According to these investigations, there are three different lamellar regions in concentrated $C_{12/14}$ APG solutions: $L_{\alpha l}$, $L_{\alpha l\text{-}h}$, and $L_{\alpha h}$. Polarization microscopy shows that there are three different textures.

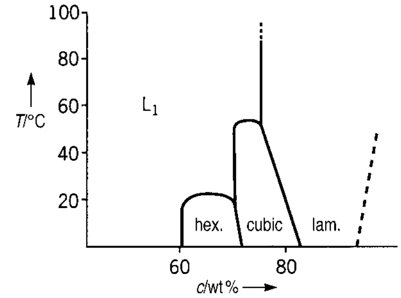


Figure 11. Phase diagram of *n*-octyl-β-D-glucoside in water.

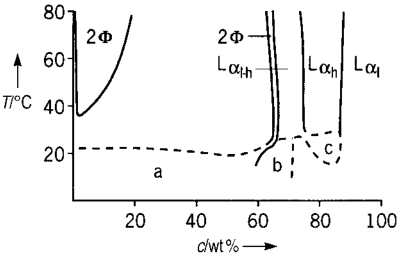


Figure 12. Phase diagram of $C_{12/14}$ alkyl polyglycoside in water.

The influence of the degree of polymerization (DP) of alkyl polyglycosides on their phase behavior was described by Fukuda et al.[53] The region in which the liquid crystalline phases occur is only slightly dependent on concentration with a greater expansion in the case of alkyl polyglycosides with a higher DP. The two APGs with a low DP have a two-phase region (see also Figure 12) at low concentrations, which is reminiscent of the clouding phenomena of nonionic surfactants of the ethylene oxide type.[50] Balzer[54] investigated the clouding phenomena in dependence upon various parameters. He showed that the two-phase region is influenced to a far greater extent by the length of the alkyl chain than in the case of alkyl polyglycol ethers. If increasing quantities of $C_{10/12}$ alkyl polyglycoside are added to $C_{12/14}$ alkyl polyglycoside, the initially broad miscibility gap becomes gradually narrower (Figure 13), the separation zone separates from the Krafft point curve, and a lower separation point becomes visible. Accordingly, the dependence of the clouding effect for alkyl polyglycoside is comparable with that of alkyl polyglycol ethers, although the dependence on chain length is extremely strong for alkyl polyglycosides. In order to shift the cloud point from 25°C to 90°C, it is sufficient to change the alkyl chain length from $C_{11.5}$ to $C_{11.2}$. In the case of alkyl polyglycol ethers, a corresponding change in chain length would signify a change in the cloud point of only 2°C. An equally strong influence on the cloud point is observed when the degree of polymerization is changed.[53]

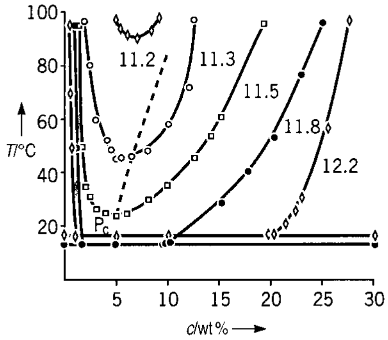


Figure 13. Phase diagrams of alkyl polyglycosides (DP = 1.3) for different alkyl chain lengths in the concentration range to 30 wt%.

If small quantities of electrolyte are added to alkyl polyglycosides, clouding phenomena are also observed with relatively short-chain alkyl polyglycosides.[53] In this case, the electrolyte effect is far more clearly pronounced than in the case of alkyl polyglycol ethers, for which the influence of salt type and concentration has long been known.[55] The behavior of alkyl polyglycosides resembles mixtures of alkyl polyglycol ethers and anionic surfactants.[56]

The addition of fatty alcohols as a third component to alkyl polyglycoside/water mixtures leads to the appearance of different lamellar phases over the entire concentration range.[51] This behavior is typical of the influence of fatty alcohols on the phase behavior of binary surfactant/water systems.[57] Figure 14 shows the phase diagram determined for the addition of hexanol to various mixtures of $C_{12/14}$ alkyl polyglycoside and water. Three L_α phases can be seen: $L_{\alpha l}$, $L_{\alpha h}$, $L_{\alpha l\text{-}h}$. The almost linear trend of the phases as a function of the alkyl polyglycoside and hexanol concentration indicates that the structure formed depends primarily on the alkyl polyglycoside/alcohol ratio. The quantity of alcohol that has to be added to ensure that a certain phase is formed decreases drastically with increasing alkyl chain length of the alcohol.

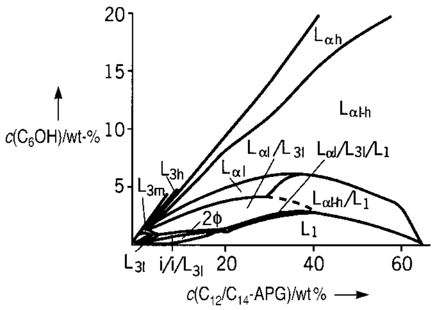


Figure 14. Phase diagram of the $C_{12/14}$ alkyl polyglycoside/hexanol/water system at 25°C.

In principle, the phase sequences observed with mixtures of alkyl polyglycosides and anionic surfactants, which are of particular importance in practice, are similar to those observed with the ternary systems of alkyl polyglycoside, alcohol, and water.[52] The $L_{\alpha l}$ phase disappears on the addition of fatty alcohol sulfates, and the $L_{\alpha l\text{-}h}$ region becomes very dominant. The phases that in addition contain ionic surfactants appear optically more transparent and have a higher viscosity and elasticity than systems consisting solely of alkyl polyglycoside and alcohol. Yield points, which increase considerably with increased concentration of fatty alcohol sulfate, are obtained in the $L_{\alpha l\text{-}h}$ and L_{3m} phases of these systems. Dilute lamellar phases can only be obtained in $C_{12/14}$ alkyl polyglycoside solutions on addition of fatty alcohol. Fatty alcohol has to be added for steric reasons. Anionic surfactants have large head groups. Accordingly, in the case of systems containing fatty alcohol sulfates, relatively large quantities of fatty alcohol are required to obtain a lamellar structure. This explains why the lamellar phases in these systems are displaced towards higher fatty alcohol concentrations. It is interesting that the repulsive forces between the charged lamellae and hence the elastic shear moduli are far greater than in uncharged systems. Relatively large viscous and elastic moduli were observed with all the anionic surfactants investigated.

The addition of anionic surfactants also has an influence on the clouding phenomena. The cloud points are considerably increased by small quantities of alkyl sulfates. According to Balzer,[54] small quantities of alkyl sulfate lead to a change in the electrical charge of the alkyl polyglycoside micelles. This results in a greater repulsive interaction between the micelles and leads to a distinct increase in the cloud point.

3.3. Ecological Evaluation, Toxicology, and Dermatological Properties

Alkyl polyglycosides are mostly used in dishwashing and laundry detergents, cosmetics, and cleaning products, which are discharged into domestic wastewater after use and thus enter the aquatic environment. Generally, the environmental fate of surfactants is inextricably linked with their biodegradation behavior. Thus, quick and complete biodegradability is the most important requirement for an environmentally compatible surfactant. The environmental impact of chemicals lies mainly in their ecotoxicity, which is relatively high in the case of surfactants because of their surface activity and the resulting effects on biological membranes. According to broadly accepted risk assessment schemes for chemical substances,[58] environmental compatibility requires proof that the use of the chemical will not result in environmental concentration levels higher than the ecotoxicological no-effect concentration.

The biodegradation tests with alkyl polyglycosides were carried out by internationally used and accepted standard methods.[59] The group of discontinuous tests is relatively simple in terms of design but has a high stringency, which, in the case of positive results, allows general conclusions to be drawn as to biodegradability in aquatic and terrestrial environments.[60] The group of continuous activated sludge tests mainly comprises those tests that simulate the biodegradation process in a municipal sewage treatment plant.

The biodegradability assessment of chemicals normally starts with screening tests. Although alkyl polyglycosides are nonionic surfactants, the routine analytical procedure used to follow the (primary) degradation of nonionic surfactants, namely measurement of bismuth-active substance (BiAS) removal,[61] cannot be applied, because alkyl polyglycosides do not react as BiAS. Only nonionic surfactants with a polygylcol ether chain form a complex with the barium ion of the added barium iodo bismuthate. Thus, legal biodegradability requirements in Europe for nonionics ($\geq 80\%$ BiAS removal) do not apply to this group of surfactants. However, the OECD ready biodegradability tests (OECD 301 series)[61] represent a group of broadly applicable screening tests which form the basis for the biodegradability evaluation of most chemicals. These tests determine the ultimate biodegradation of the test compound, that is, the microbial transformation of the parent test substance into the final products of the degradation process such as carbon dioxide, water, and assimilated bacterial biomass. $C_{12/14}$ alkyl polyglycoside was tested in three different ready biodegradability tests, the Closed Bottle Test (OECD 301 D), the Modified OECD Screening Test (OECD 301 E), and the DOC Die Away Test (OECD 301 A). The results obtained reflect a very high degree of ultimate biodegradation over the 28-day test period in all tests.[59] The Closed Bottle Test, which is the most exact of all OECD 301 tests,[62] reached mineralization levels of 88% (test concentration 2 $\text{mg}\,\text{L}^{-1}$) and 72% (5 $\text{mg}\,\text{L}^{-1}$), thus far exceeding the OECD limit for the label "ready biodegradability" (60% biological/chemical oxygen demand (BOD/COD)). The "10-day time window" was also easily fulfilled.[59] To sum up, the results of various OECD ready biodegradability tests show unequivocally that alkyl polyglycosides are readily biodegradable and, according to the conclusions of the OECD,[60] will undergo rapid and complete biodegradation in the environment.

Today, defined test strategies[63, 64] are available for characterizing biological properties. After toxicological safety screening, they provide for the direct testing of effects on the skin of volunteers and have also been applied comprehensively to alkyl polyglycosides. Dermatologically, alkyl polyglycosides represent a new class of very mild surfactants, which, depending on the type of product, are eminently suitable for use as sole surfactant or cosurfactant in the formulation of particularly gentle products. Optimized dermatological compatibility for many cleaning products can be achieved through careful choice of the chain length, the degree of polymerization, the vehicle or solvent, and the particular formulation.

The object of toxicological studies is to assess the harzard potential of chemical products in order—on the basis of these findings—to assess the risks to the health of the user and to prevent possible adverse effects, even after improper use. The main concern of these studies is to determine the toxic potential of a substance and often involves conditions that considerably exceed normal exposure levels. Toxicological studies thus provide information on the inherent toxicological potential of chemical substances. An assessment of the actual risks is only possible if the corresponding exposure conditions, that is, the mode of application, duration, and frequency of contact are included in these considerations. If these principles are disregarded by arbitrarily equating hazard with risk, wrong conclusions will inevitably be drawn.

The toxicological safety strategy for chemical products should be based on the following objectives:

- Correct handling should rule out unwanted side effects.
- Foreseeable improper use should not cause serious health damage.
- Even long-term exposure as a result of long environmental residence times should not involve any health risk.

Alkyl polyglycosides varying in chain length and purity have been subjected to the most relevant toxicological tests necessary for a sound risk assessment. On the basis of the information available, alkyl polyglycosides are not considered as toxic or harmful in acute toxicity tests, but in high concentrations have to be classified as irritating to the skin and eyes. In addition, sensitizing effects are unlikely to occur. A NOAEL (NOAEL = no observed adverse effect level) of 1000 mg kg^{-1} body weight can be estimated for toxicity after repeated oral application. In vitro tests indicated that alkyl polyglycosides have no potential for gene and chromosome mutations.

Safety in use and handling also includes foreseeable improper use such as the accidental swallowing of cosmetic products by children. By virtue of their low acute oral toxicity, alkyl polyglycosides do not contribute to the toxicity of cosmetic and other household products. The acute oral toxicity values (LD_{50}) are of the order of several grams per kilogram body weight. In other words, it is virtually impossible to be seriously poisoned by these products.[64]

4. Applications

Due to their physico-chemical properties, alkyl polyglycosides show interesting effects for various applications. Specific examples will be given in the following sections.[64]

4.1. Microemulsions

Various parameters determine whether ternary systems of water, oil, and nonionic surfactants can form microemulsions. Microemulsions of oil, water, and ethoxylated nonionic surfactants have become particularly interesting.[65, 66] One characteristic of these systems of oil, water, and ethoxylated nonionic surfactant is their pronounced dependence on temperature, which is the basis of the known phase inversion temperature (PIT) phenomenon.[65–67] Due to the fact that the phase behavior of simple binary alkyl polyglycoside/water mixtures shows only comparatively weak temperature effects[68, 69] no temperature-dependent phase inversion can be expected to occur in alkyl polyglycoside-containing emulsions.

Alkyl polyglycosides react similarly to anionic surfactants on the addition of cosolvents that increase the solubility of the surfactant in the oil phase. In the decane/water/APG system the addition of the cosolvent isobutanol results in a drastic reduction in the interfacial tension between oil and aqueous phase, and, hence, in the formation of a third phase, the microemulsion.[70] As expected, the range in which this three-phase microemulsion exists is only slightly dependent on temperature and, in contrast to anionic surfactants, is also hardly affected by electrolytes.[70] Systematic investigations of the phase behavior confirm these initial results for a number of simple hydrocarbons from hexane to hexadecane and aromatics.[71, 72]

Figure 15 shows the known microemulsion phases (in the literature named as "Kahlweit" fish[65] because of the shape) in a pseudoternary phase diagram. With small alkyl polyglycoside content of 5 to 25 % and small pentanol content of 3 to 10%, three-phase microemulsions are formed. Of greater interest for practical applications are single-phase microemulsions, which are formed with an alkyl polyglycoside content of >25% and a pentanol content of 10% in the system. Figure 15 includes the—almost identical—results for two different alkyl polyglycosides, namely a high-purity C_{10} monoglycoside and a $C_{10/12}$ alkyl polyglycoside of technical purity with an average degree of polymerization of 1.3. In the technical product, the slightly increased degree of polymer-

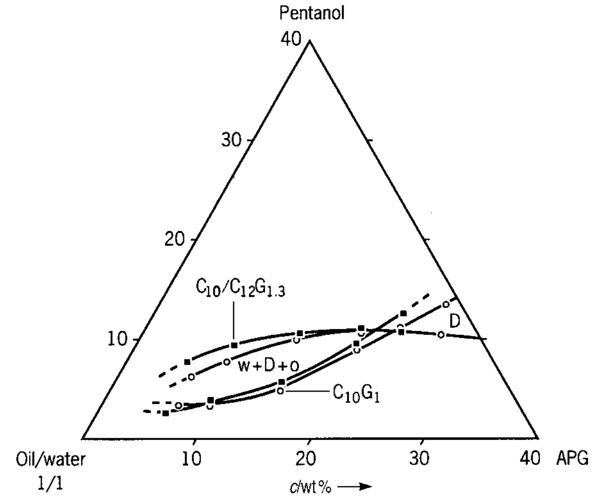


Figure 15. Pseudoternary phase diagram for the systems dodecane/water (1/1), pentanol, C_{10} monoglycoside ($C_{10}G_1$), and $C_{10/12}$ alkyl polyglycoside (DP = 1.3; $C_{10}/C_{12}G_{1.3}$) at 40°C.

ization evidently compensates for the somewhat longer alkyl chain length cut. Another way of achieving balanced hydrophilic/lipophilic properties is to combine the hydrophilic emulsifier alkyl polyglycoside with a hydrophobic coemulsifier.

Representation of the microemulsion phases as a function of formulation parameters (for example, temperature for systems containing fatty alcohol ethoxylate) and emulsifier concentration[65, 73] has been successful as an aid for establishing practical formulations. A basically similar picture emerges for emulsions of oil, water, and an emulsifier mixture of alkyl polyglycoside and a hydrophobic coemulsifier: instead of temperature as the formulation parameter, the mixing ratio of alkyl polyglycoside to hydrophobic coemulsifier is varied.[74] In the case of the specific emulsifier mixing ratio of 1:1, the system of dodecane, water, $C_{12/14}$ alkyl polyglycoside, and sorbitan monolaurate (SML) as hydrophobic coemulsifier forms microemulsions (Figure 16). The emulsions formed with a relatively large SML content are water-in-oil (w/o) emulsions while the emulsions formed with a relatively large alkyl polyglycoside content are oil-in-water (o/w) emulsions. By varying the overall emulsifier concentration, a "Kahlweit" fish again appears in the phase diagram with three-phase microemulsions in its body and a single-phase microemulsion in its tail.

The similarity between alkyl polyglycosides and fatty alcohol ethoxylates is not confined to phase behavior but also applies to the interfacial tension of the emulsifier mixture. With an alkyl polyglycoside/SML ratio of 4:6, the hydrophilic/lipophilic properties of the emulsifier mixture are balanced, and the interfacial tension is minimal. It is remarkable that the alkyl polyglycoside/SML mixture produces a very low minimum interfacial tension value (around $10^{-3}\,mN\,m^{-1}$) which, once again, is lower by one order of magnitude than that observed in the case of the fatty alcohol ethoxylate system.[33, 65, 75]

In the case of the alkyl polyglycoside-containing microemulsion, the high interfacial activity is attributable to the fact that the hydrophilic alkyl polyglycoside with the large polyglycoside head group is present in exactly the right mixing ratio with the hydrophobic coemulsifier SML with its small head group at the oil/water interface. In contrast to ethoxylated nonionic surfactants, hydration and hence the effective size of the head group are hardly dependent on temperature,[54, 70, 76] an attribute that can be utilized for formulating temperature-stable microemulsions.[77]

In order to be able to use alkyl polyglycoside microemulsions for industrial or cosmetic applications, tailor-made formulations with certain desirable performance properties are necessary. Figure 17 shows the pseudoternary phase triangle of a five-component system of cosmetic raw materials, which may serve as a model system for foaming and simultaneous refatting body-care formulations.[78] The water content is a constant 60%, the oil component is dioctyl cyclohexane. In this example, the hydrophilic emulsifier is a 5:3 mixture of alkyl polyglycoside and a fatty alcohol ether sulfate (FAES), which, as a high-foaming anionic surfactant, forms the basis of many body-care formulations. Although sorbitan monolaurate (SML) was chosen as the hydrophobic coemulsifier in this case, other coemulsifiers (for example glycerol monooleate[35]) are, in principle, also suitable.

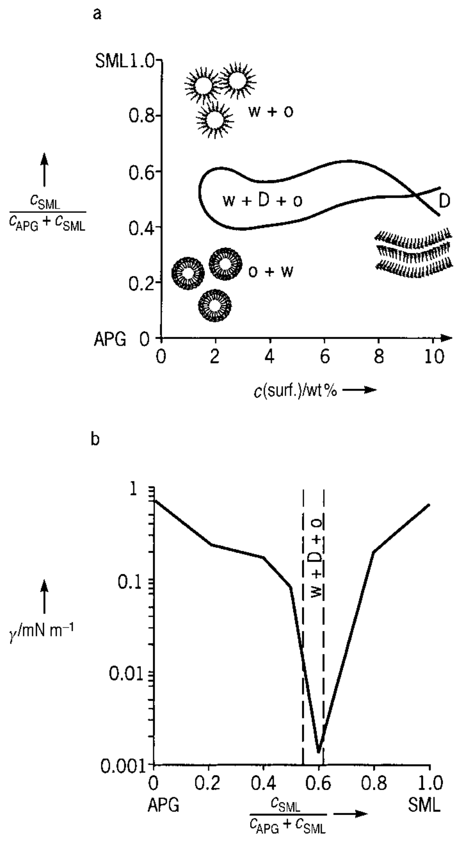


Figure 16. a) Dependence of the phase behavior of the system dodecane/water (1:1), $C_{12/14}$ APG, sorbitan monolaurate upon the ratio of APG to SML as a function of the total surfactant concentration. b) Dependence of the interfacial tension of the system dodecane/water (1:1), $C_{12/14}$ APG, sorbitan monolaurate in dependence upon the ratio of APG to SML for a total surfactant concentration of 1.5 wt%.

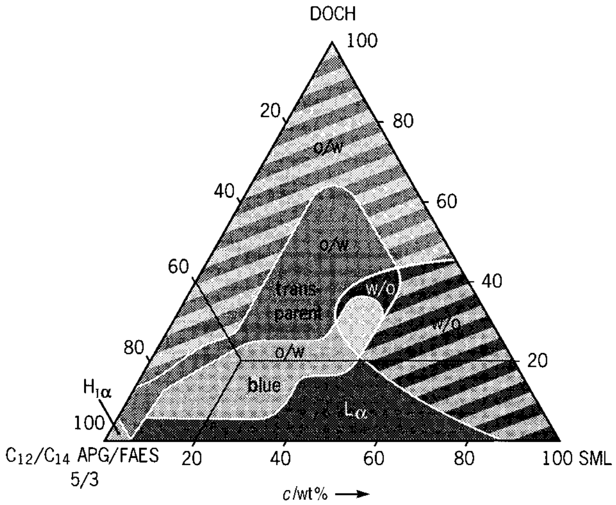


Figure 17. Pseudoternary phase diagram for emulsion systems of 60 wt% water with dioctyl cyclohexane (DOCH), sorbitan monolaurate (SML), and a FAES/APG mixture (sodium laureth sulfate:$C_{12/14}$ APG = 3:5) at 25°C.

Accordingly, the indicated formulation in the blue o/w emulsion range contains 15 % alkyl polyglycoside, 9 % FAES, 8 % SML, 8 % dioctyl cyclohexane, and 60 % water.

Starting out from an oil-free and coemulsifier-free system, a 40 % alkyl polyglycoside/FAES mixture in water is present as a viscous hexagonal liquid crystal ($H_{1\alpha}$). Even the replacement of a small part of the alkyl polyglycoside/FAES mixture by the hydrophobic cosurfactant SML is sufficient to allow a low-viscosity lamellar phase (L_α) to be formed. If the SML content is increased, the lamellar phase remains intact whereas the viscosity increases considerably and reaches levels that are even above those of the hexagonal phase. Like the hexagonal phase, the lamellar phases are also non-Newtonian, in other words their viscosity decreases with increasing shear rate.

The two liquid crystals react very differently to the addition of oil. Whereas the hexagonal liquid crystal is only capable of solubilizing very small quantities of oil, the range in which the lamellar phase exists extends far towards the oil corner. The ability of the lamellar liquid crystal to incorporate oil increases distinctly with increasing SML content. Solubilization of the oil leads to an increase in the lamellar layer spacing, which was measured by small angle X-ray scattering. Accordingly, the oil molecules are incorporated in the hydrophobic interior of the lamellar layers and not in the palisade layer parallel to the emulsifier molecules.

With a relatively high proportion of oil, blue emulsions or transparent microemulsions are formed. With a high percentage of SML (more than 50 % in the emulsifier mixture), these emulsions are of the w/o type. For an optimal mixing ratio of hydrophilic alkyl polyglycoside/FAES compound to hydrophobic SML, the range in which a transparent microemulsion exists extends very far towards the oil corner: a maximum of 60 % of dioctyl cyclohexane can be microemulsified. The microemulsions have low viscosities and are substantially Newtonian, the w/o microemulsions having slightly higher viscosities than the o/w microemulsions.

4.2. Detergents and Cleaners

Alkyl polyglycosides are used in manual dishwashing detergents as well as all-purpose cleaners and laundry detergents. Alkyl polyglycosides show pronounced synergisms with the three primary surfactants linear alkyl benzene sulfonate (LAS), secondary alkane sulfonate (SAS), and fatty alcohol sulfate (FAS). These synergisms are far more pronounced (Figure 18) than those observed with fatty alcohol ether sulfate (FAES). In contrast to alkyl polyglycosides, other nonionic surfactants such as fatty alcohol polyethylene glycol ether (FAEO) do not show any synergisms with FAES. The synergistic interactions of alkyl polyglycosides with the various primary surfactant systems enables the formulation of even more effective products for the same active substance content or the reduction of the active substance content without affecting the performance level.

Although foam volume and foam structure both in the dishwashing liquor and under running water do not directly determine product performance, they are expected by the consumer and thus lead to purchasing decisions. In APGs the product developer has a nonionic surfactant that improves the foam properties of the product. Both foam height and foam stability under mechanical influence can be investigated by suitable methods. The test results obtained with various commercial concentrates, even in the presence of soil, are set out in Figure 19. The results show that the APG-containing dishwashing detergent produces an elastic foam which is relatively unaffected by soil.

Because of the broad range of soil types found in the home, all-purpose cleaners have to perform efficiently against both emulsifiable oil- and fat-containing soils and against disper-

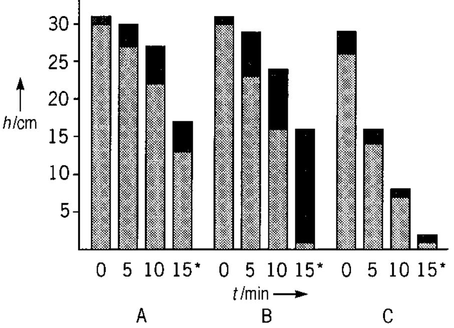


Figure 19. Foaming behavior of concentrated manual dshwashing detergents. Test method: stress stability of foam; concentration of the product 1 gL^{-1}; $T = 50°C$, water hardness 16°d. h = foam height; A = APG-containing concentrate, B = glucamide-containing concentrate, C = SAS-based concentrate, * = with mechanical impact. Dark gray column: foam height without soil; light gray column: foam height on addition of vegetable oil.

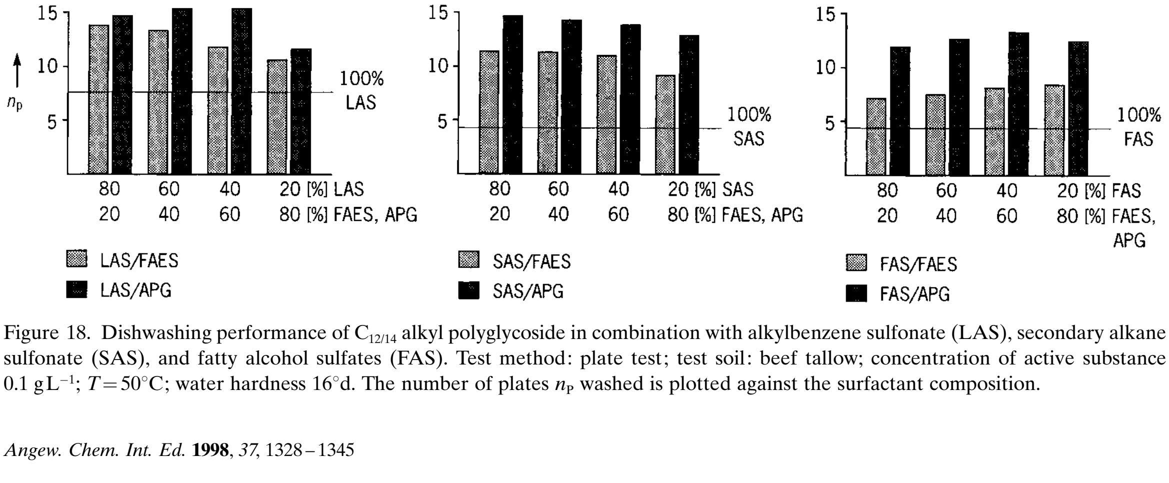


Figure 18. Dishwashing performance of $C_{12/14}$ alkyl polyglycoside in combination with alkylbenzene sulfonate (LAS), secondary alkane sulfonate (SAS), and fatty alcohol sulfates (FAS). Test method: plate test; test soil: beef tallow; concentration of active substance 0.1 gL^{-1}; $T = 50°C$; water hardness 16°d. The number of plates n_P washed is plotted against the surfactant composition.

sible solid soil particles. Alkyl polyglycosides themselves have an excellent cleaning performance, which can be determined, for example, in accordance with the IPP quality standard.[79] The cleaning performance can be further increased by small additions of anionic surfactants and/or polymeric boosters. Thus, it is possible to formulate products comparable in cleaning performance to the market leaders at significantly lower surfactant contents. All-purpose cleaners with particularly good skin compatibility should be slightly acidic rather than alkaline. Alkyl polyglycoside is a surfactant of which the high cleaning performance level is hardly affected by changes in the pH value. Consumers today prefer all-purpose cleaners with moderate or low foaming behavior. The foaming capacity of alkyl polyglycoside-containing cleaners can readily be reduced by using small quantities of soaps or increased by adding small quantities of anionic surfactants. Alkyl polyglycoside has proved to be the problem solver in the formulation of concentrated all-purpose cleaners with excellent ecological compatibility. With alkyl polyglycosides, it is possible to formulate concentrates which have a correspondingly higher content of builders and perfume oils without having to use large quantities of solubilizers (hydrotropes).

The alkyl polyglycosides used in detergent formulations are those with an alkyl chain length of $C_{12/14}$ and a DP value of around 1.42. As a nonionic surfactant, they are particularly effective against fatty soils. Optimized surfactant systems generally based on mixtures of anionic and nonionic surfactants are used in modern detergent formulations. Alkyl polyglycosides occur in these surfactant mixtures preferably as so-called cosurfactants, which have the property of complementing or improving quantitatively the washing performance of the predominant surfactants. Besides performance, the aesthetics play an important part for a detergent. Wool detergents, for example, are intended to produce a rich, stable foam. The consumer associates performance and care with foam. For machine washing, the correct foam height on the one hand determines textile care, because the mechanical action on the wash load is reduced. On the other hand, foam may cause a distinct reduction of the detergency performance. Alkyl polyglycosides in conjunction with anionic surfactants may alter the foaming behavior of the formulations.

APGs were first used in liquid laundry detergents in 1989. The hydrotropes—which do not contribute to cleaning—can be partially replaced by alkyl polyglycosides. Alkyl polyglycosides surprisingly have a positive influence on the low-temperature and storage stability of such formulations. In addition, triethanolamine soaps have been successfully replaced by the similarly acting sodium/potassium soaps.[80] The diethanolamine contamination of triethanolamine, which may cause the formation of nitrosamines, was thus avoided. In addition, as sodium soaps are less expensive, a net result of the use of alkyl polyglycosides is a price advantage for the formulation. Washing tests show that these new formulations outperform their predecessors (Figure 20). Whereas in the case of liquid heavy duty detergents containing optical brighteners and enzymes, the emphasis is on performance, the aspect of textile care is more dominant in the case of specialty detergents. Liquid specialty detergents are formulated with pH values less than or equal to 8.5. In order to avoid shifts in color, optical brighteners are avoided in the formulations.[81]

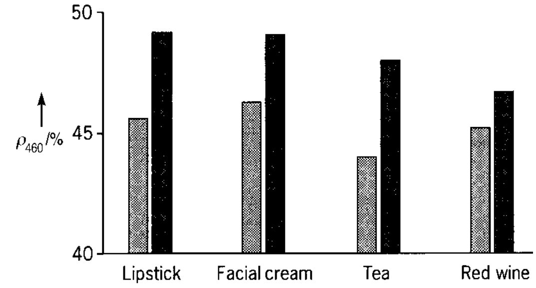


Figure 20. Washing performance of heavy-duty detergents. Test method: washing machine concentration: 180 mL per wash load (Miele-W-760 washing machine), 60°C, water hardness 16°d. The reflectance ρ at 460 nm is plotted against the type of soil; light gray column: triethanolamine soaps; dark gray column: sodium soaps.

The storage stability of enzymes in liquid formulations is smaller than in powders. On account of the high surfactant content of certain formulations, the enzymes are partly deactivated and slowly lose their initial activity upon storage. In order to improve the storage stability of enzymes such as proteases, lipases, amylases, and/or cellulases in liquid detergents, stabilizers (borates, phosphates, or special esters) are added, and the surfactant systems are adapted. The storage stability of enzymes in liquid detergents can be distinctly improved by the use of alkyl polyglycosides (Figure 21). The alkyl polyglycosides have the advantage over the otherwise typical stabilizers of enhancing the washing result.

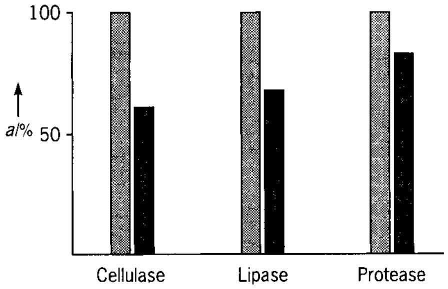


Figure 21. Stability of enzymes in liquid detergents. Test method: relative enzymatic activity a after storage for 56 days at room temperature. Formula: heavy-duty liquid detergent, 42 % surfactants, pH = 8. Light gray column: formulation with 5 wt.% $C_{12/14}$ APG; dark gray column: formulation without $C_{12/14}$ APG.

Quantitatively the largest group, namely the heavy duty powder detergents, are based on formulations that remove virtually all the soil types normally encountered. Particular emphasis is placed on washing performance. For this reason, these detergents have a distinctly higher alkalinity (pH value in the range from pH 9.5 to 10.5) to greatly improve soil removal. In addition, heavy duty detergents are provided with a bleaching system. Bleachable stains such as tea, coffee, red wine, etc., are thus effortlessly removed. Fat- and oil-containing soils such as sebum, olive oil, lipstick, and facial cream are difficult to remove, particularly at low temperatures. By using alkyl polyglycosides in powder detergents, these stains in particular can be removed considerably more effectively.

4.3. Personal Care Products

Over the past decade, progress in the development of raw materials for personal-care products has mainly occurred in three areas:

- mildness and protection for the skin
- high-quality standards by minimization of by-products and trace impurities and
- ecological compatibility.

At the same time, the variety of parameters relevant for a new raw material has increased, and their detection by subjective and objective methods has become more precise. In the cosmetic field alkyl polyglycosides show interesting properties. For example, addition of alkyl polyglycosides modifies the rheology of concentrated surfactant mixtures, so that pumpable and readily dilutable concentrates containing up to 60% active substance can be prepared. These concentrated blends of several components may be generally used as cosmetic raw materials or specifically as core concentrates in the production of cosmetic formulations (for shampoos, shampoo concentrates, shower baths, foam baths etc).

The compositions are based on anionics such as alkyl ether sulfate, betaines, and/or nonionic surfactants, and are more gentle on the eyes and the skin than conventional systems. At the same time, they show excellent foam, viscosity, and processing properties. Super concentrates are preferred for economic reasons insofar as they are easier to handle and dilute without containing hydrotropes.

A simple characteristic example is the compound of standard ether sulfate and $C_{12/14}$ alkyl polyglycoside in a ratio of 2:1. Alkyl polyglycoside disrupts the formation of the highly viscous hexagonal phase of the ether sulfate, which, in turn, inhibits the crystallization of alkyl polyglycoside (Figure 22). The mixture is pumpable above 15°C and can be cold-processed with normal mixing units. On dilution, the viscosity passes through a flattened broad maximum at 40–45%.[78] Foaming is an essential quality feature of cosmetic cleansing formulations. Alkyl polyglycosides foam considerably better than fatty alcohol ethoxylates, the foam volume increasing with increasing percentage of short carbon chains in the alkyl polyglycosides. They are comparable with betaines and sulfosuccinates but do not match the initial foam behavior or foam volume of alkyl ether sulfates.[82–84]

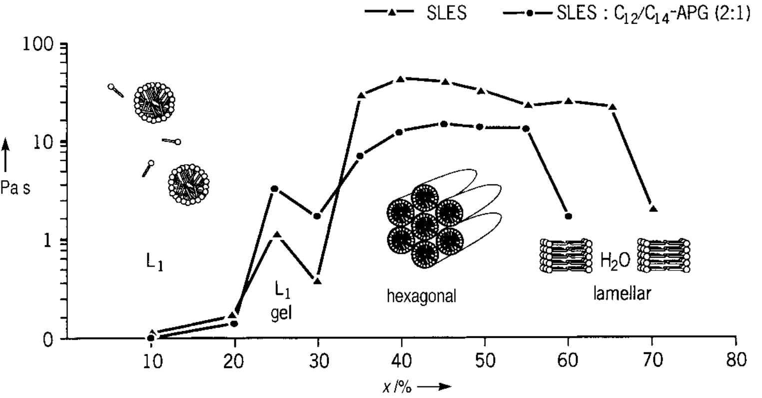


Figure 22. Rheology of standard sodium lauryl ether sulfate (SLES) and C_{12}/C_{14} alkyl lauryl ether polyglycoside in admixture, superimposed on a plot of the viscosity η of the surfactants against the proportion of surfactant in the mixture.

On the other hand, alkyl polyglycosides can stabilize the foam of anionics in hard water and in the presence of sebum, so that up to 20% of surfactant can be saved for the same foaming power.[82, 84] The structure of the foams of alkyl ether sulfates and alkyl polyglycosides was investigated by image analysis and provides a basis for understanding the observed properties.[82, 84] Alkyl polyglycoside foam consists of finer bubbles and is more creamy than alkyl ether sulfate foam (Figure 23).

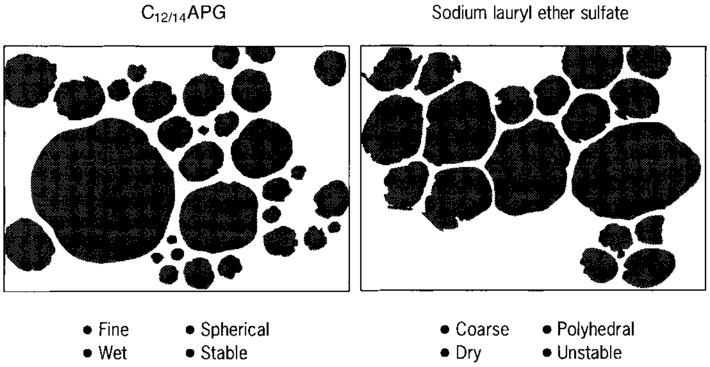


Figure 23. Foam structure of lauryl glycoside and sodium lauryl ether sulfate after 15 min (magnification 30 ×).

Alkyl polyglycosides with carbon chains longer than $n = 12$ assist the build-up of rodlike mixed micelles in solutions of anionics and thus make a considerable contribution towards increasing viscosity.[82, 85] This effect is somewhat weaker in standard ether sulfate formulations than with alkanolamides, but is more pronounced with sulfosuccinates and highly ethoxylated alkyl ether sulfates, which are very difficult to thicken with alkanolamides. Alkyl polyglycoside formulations without anionics can best be thickened by adding polymeric thickeners such as xanthan gum, alginate, polyethoxylated esters, carbomers, etc.

The mildness of alkyl polyglycosides is also reflected in a caring effect on damaged hair. The tensile strengths of permed hair tresses are reduced far less by treatment with alkyl polyglycosides solutions than by standard ether sulfate solutions.[82, 84] Direct proof of the adsorption of alkyl polyglycosides onto hair can be qualitatively provided by the XPS technique (X-ray photoelectron spectroscopy). Hair tresses were divided into two halves; both surfactants can be detected on the hair surface by XPS. If the process is repeated several times, no change in the XPS signals is observed in case of ether sulfate between treated and untreated hair. By contrast, slightly increased oxygen contents are measured for alkyl polyglycosides. This result shows that alkyl polyglycoside is more substantive to the hair than standard ether sulfate. The substantivity of surfactants to hair influences combability.

In addition to the mentioned fields of application and the formulation of emulsions and microemulsions alkyl polyglycosides may also be used in soaps, syndets (synthetic detergents), and toothpastes. $C_{12/14}$ alkyl polyglycoside was found to be an effective booster for special antibacterial agents such as chlorohexidine. In the presence of alkyl polyglycoside, the quantity of bactericidal agent can be reduced to about one quarter without losing any bactericidal activity.

5. Summary

By virtue of their physico-chemical parameters and their performance profile alkyl polyglycosides are a new class of environmentally favorable nonionic surfactants, which represent new concepts in performance, compatibility, and care for various consumer products. Alkyl polyglycosides are multifunctional raw materials that are beginning to make their mark on modern formulation techniques and represent a trend-setting innovation.

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[1] a) M. Biermann, F. Lange, R. Piorr, U. Ploog, H. Rutzen, J. Schindler, R. Schmid in *Surfactants in Consumer Products—Theory, Technology and Application* (Ed.: J. Falbe), Springer, Berlin, **1986**, pp. 99–105; b) H. Baumann, M. Biermann in *Nachwachsende Rohstoffe, Perspektiven für die Chemie* (Eds.: M. Eggersdorfer, S. Warwel, G. Wulff), VCH, Weinheim, **1993**, pp. 33–55; c) P. Jürges, A. Turowski in *Perspektiven Nachwachsender Rohstoffe in der Chemie* (Ed.: H. Eierdanz), VCH, Weinheim, **1996**, pp. 61–70; d) H. Kelkenberg, *Tenside Surfactans Deterg.* **1988**, *25*, 8–13.

[2] a) E. Fischer, *Ber. Dtsch. Chem. Ges.* **1893**, *26*, 2400–2412; b) H. Th. Böhme AG, DRP 593422, **1931**; c) H. Th. Böhme AG, DRP 611055, **1933**; H. Bertsch, G. Rauchalles (H. Th. Böhme AG), US-A 2049758, **1933** [*Chem. Abstr.* **1936**, *30*, 6582(5)]; d) J. Knaut, G. Kreienfeld, *Chimica Oggi* **1993**, 41–46.

[3] a) B. Fabry in Lit. [3b], pp. 211–223; b) *Alkyl Polyglycosides—Technology, Properties and Applications* (Eds.: K. Hill, W. von Rybinski, G. Stoll), VCH, Weinheim, **1997**.

[4] a) R. R. Schmidt, *Angew. Chem.* **1986**, *98*, 213–236; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 212; b) R. R. Schmidt in *Comprehensive Organic Synthesis, Vol. 6* (Ed.: E. Winterfeldt), Pergamon, Oxford, **1991**, pp. 33–64; c) P. Sinaÿ, *Pure Appl. Chem.* **1991**, *63*, 519; d) K. Toshima, K. Tatsuta, *Chem. Rev.* **1993**, *93*, 1503–1531.

[5] a) P. Schulz, *Chimica Oggi* **1992**, 33–38; b) M. Biermann, K. Schmid, P. Schulz, *Starch/Stärke* **1993**, *45*, 281–288.

[6] a) F. Wagner, S. Lang, *Proceedings 4th World Surfactants Congress, Vol. 1*, Barcelona (Spanien), **1996**, pp. 124–137; b) H. Waldmann, *Nachr. Chem. Tech. Lab.* **1992**, *40*, 828–834; c) D. G. Drueckhammer, W. J. Hennen, R. L. Pederson, C. F. Barbas III, C. M. Gautheron, T. Krach, C.-H. Wong, *Synthesis* **1991**, 499–525; d) E. N. Vulfson, R. Patel, J. E. Beecher, A. T. Andrews, B. A. Law, *Enzyme Microb. Technol.* **1990**, *12*, 950–954; e) K. Krohn, *Nachr. Chem. Tech. Lab.* **1987**, *25*, 930–935; f) K. G. I. Nilsson, *Trends Biotechnol.* **1988**, *6*, 256–264.

[7] a) J. Defaye, C. Pedersen, *Zuckerindustrie* **1991**, *116*, 271–276; b) J. Defaye, E. Wong, C. Pedersen (Beghin-Say S.A.), FR-B 2567891, **1984** [*Chem. Abstr.* **1986**, *105*, 227221h].

[8] a) M. Hayashi, S. Hashimoto, R. Noyori, *Chem. Lett.* **1984**, 1747–1750; b) W. A. Szarek, G. Grynkiewicz, B. Doboszewski, G. W. Hay, *ibid.* **1984**, 1751–1754.

[9] A. Michael, *Am. Chem. J.* **1879**, *1*, 305–316.

[10] a) W. Koenigs, E. Knorr, *Ber. Dtsch. Chem. Ges.* **1901**, *34*, 957–981; b) P. Rosevear, T. Van Aken, J. Baxter, S. Ferguson-Miller, *Biochemistry* **1980**, *19*, 4108–4115.

[11] A. C. West, C. Schuerch, *J. Am. Chem. Soc.* **1973**, *95*, 1333–1335.

[12] R. R. Schmidt, J. Michel, *Angew. Chem.* **1980**, *92*, 763–764; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 731.

[13] R. R. Schmidt, M. Reichrath, *Angew. Chem.* **1979**, *91*, 497–499; *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 466.

[14] M. A. Colley, *Ann. Chim. Phys. IV* **1870**, *21*, 363–377.

[15] A. Gautier, *Bull. Soc. Chim.* **1874**, *22*, 145–147.

[16] a) B. Capon, *Chem. Rev.* **1969**, *69*, 407–498; b) R. J. Ferrier, *Fortschr. Chem. Forsch.* **1970**, *14*, 389–429.

[17] a) E. Fischer, L. Beensch, *Ber. Dtsch. Chem. Ges.* **1894**, *27*, 2478–2486; b) E. Fischer, *ibid.* **1895**, *28*, 1145–1167; c) E. Fischer, B. Helferich, *Justus Liebigs Ann. Chem.* **1911**, *383*, 68–91.

[18] a) D. E. Koeltzow, A. D. Urfer, *J. Am. Oil Chem. Soc.* **1984**, *61*, 1651–1655; b) A. J. J. Straathof, H. van Bekkum, A. P. G. Kieboom, *Starch/Stärke* **1988**, *40*, 229–234, 438–440; c) T. Böcker, J. Thiem, *Tenside Surfactans Deterg.* **1989**, *26*, 318–324.

[19] R. Eskuchen, M. Nitsche in Ref. [3b], pp. 9–22.

[20] a) K. Hill, W. Wuest, J. Wollmann, M. Biermann, H. Rossmaier, R. Eskuchen, A. Bruns, G. Hellmann, K. H. Ott, W. Winkle, K. Wollmann (Henkel KGaA), DE-B 3833780, EP-B 0437460, **1988** [*Chem. Abstr.* **1990**, *113*, 99889]; b) S. Schmidt (Hüls AG), EP-B 0495174, **1991** [*Chem. Abstr.* **1992**, *117*, 194056]; c) M. J. Bergfeld, J. Seifert (Akzo Nobel N.V.), EP-B 0617045, **1994** [*Chem. Abstr.* **1995**, *122*, 217198]; d) N. Ripke (Hüls AG), DE-B 4006192, EP-B 0448799, **1990** [*Chem. Abstr.* **1991**, *115*, 235219]; e) G. Wolf, H. Wolf (BASF AG), DE-B 4227752, WO-A 9404544, **1992** [*Chem. Abstr.* **1994**, *120*, 271067].

[21] a) M. Biermann, K. Hill, W. Wuest, R. Eskuchen, J. Wollmann, A. Bruns, G. Hellmann, K. H. Ott, W. Winkle, K. Wollmann (Henkel KGaA), DE-B 3723826, EP-B 0301298, **1987** [*Chem. Abstr.* **1989**, *110*, 195187]; b) A. Oberholz, J. Kahsnitz, S. Schmidt (Hüls AG), EP-B 0482325, **1990** [*Chem. Abstr.* **1992**, *117*, 29138]; c) R. W. P. Short (Staley A.E. Mfg. Co.), EP-B 0099183, **1982** [*Chem. Abstr.* **1984**, *101*, 7592]; d) P. Schulz, R. Eskuchen (Henkel KGaA), DE-B 4138250, WO-B 9310133, **1991** [*Chem. Abstr.* **1993**, *119*, 252610].

[22] W. Ruback, S. Schmidt in *Carbohydrates as Organic Raw Materials III* (Eds.: H. van Bekkum, H. Röper, A. G. J. Vorhagen), VCH, Weinheim, **1996**, pp. 231–253; b) J. Kahsnitz, S. Schmidt, A. Oberholz (Hüls AG), EP-B 0514627, **1991** [*Chem. Abstr.* **1993**, *118*, 255256].

[23] a) H. Waldhoff, J. Scherler, M. Schmitt, J. R. Varvil in Ref. [3b], pp. 23–38; b) N. Buschmann, F. Hülskötter, A. Kruse, S. Wodarczak, *Fett/Lipid* **1996**, *98*, 399–402; c) R. Spilker, B. Menzebach, U. Schneider, I. Venn, *Tenside Surfactants Deterg.* **1996**, *33*, 21–25; d) N. Buschmann, S. Wodarczak, *ibid.* **1995**, *32*, 336.

[24] a) Y.-Z. Lai, F. Shafizadeh, *Carbohydr. Res.* **1974**, *38*, 177–187; b) G. R. Ponder, G. N. Richards, *ibid.* **1990**, *208*, 93–104.

[25] a) J. E. Davis, J. C. Letton (Procter and Gamble Co.), US-A 504647, EP-B 0132043, **1983** [*Chem. Abstr.* **1985**, *102*, 149713]; b) P. M. McCurry, W. Kozak, C. Pickens (Henkel KGaA), WO-A 9007516, **1990** [*Chem. Abstr.* **1991**, *114*, 122966]; c) P. M. McCurry, Jr., R. Eskuchen, P. Schulz (Henkel KGaA), US-A 5478930, **1993** [*Chem. Abstr.* **1996**, *124*, 235583]; d) J. C. Letton (Procter and Gamble Co.), US-A 536472, EP-B 0132046, **1983** [*Chem. Abstr.* **1985**, *102*, 149712], e) K. Hill, M. Wenthen, H.-P. Köhler (Henkel KGaA), DE-B 3927919, **1989** [*Chem. Abstr.* **1991**, *114*, 145865].

[26] a) K. Böge, Dissertation, Universität Göttingen, **1993**; b) K. Böge, L. F. Tietze, *Fett/Lipid* **1998**, *100*, 36–41.

[27] W. Johannisbauer, H. Koerner, M. Nitsche (Henkel KGaA), DE-B 3932173, **1989** [*Chem. Abstr.* **1991**, *115*, 29834].

[28] a) A. Yamamuro, M. Amau, T. Fujita, K. Aimono, A. Kimura (Kao Corp.), EP-B 0388857, **1989** [*Chem. Abstr.* **1991**, *114*, 185923]; b) H. Lueders (Hüls AG), EP-B 0306650, **1987** [*Chem. Abstr.* **1989**, *111*, 60020]; c) N. Ripke, P. Hofmann (Hüls AG), EP-B 389753, **1989** [*Chem. Abstr.* **1991**, *114*, 64792]; d) P. Schulz, S. Mueller, S. Hammelstein, K. Neary (Henkel KGaA), DE-B 3940827, WO-A 9109043, **1989** [*Chem. Abstr.* **1991**, *115*, 136640]; e) M. Weuthen, A. Werdehausen, W. Wuest, G. Panthel, U. Hees (Henkel KGaA), DE-B 4142592, WO-A 9313113, **1991** [*Chem. Abstr.* **1994**, *120*, 57222]; f) P. M. McCurry, Jr., J. D. Beaulieu (Henkel Corp.), US-A 5432275, **1994** [*Chem. Abstr.* **1995**, *123*, 290263].

[29] H. Sawada, H. Nagumo, T. Koike, A. Kimura, A. Yamamuro (Kao Corp.), EP-B 0387913, **1989** [*Chem. Abstr.* **1991**, *114*, 143902].

[30] D. Nickel, H. D. Speckmann, W. von Rybinski, *Tenside Surfactants Deterg.* **1995**, *32*, 470 – 474.

[31] K. Shinoda, T. Yamaguchi, R. Hori, *Bull. Chem. Soc. Jpn.* **1989**, *34*, 237 – 241.

[32] D. Nickel, C. Nitsch, P. Kurzendörfer, W. von Rybinski, *Progr. Colloid Polym. Sci.* **1992**, *89*, 249 – 252.

[33] F. Jost, H. Leiter, M. J. Schwuger, *Colloid Polym. Sci.* **1988**, *266*, 554 – 561.

[34] B. Y. Zhu, M. J. Rosen, *J. Colloid Interface Sci.* **1984**, *99*, 435 – 442.

[35] R. Wüstnek, G. Wasow, *Tenside Surfactants Deterg.* **1996**, 33, 130 – 137

[36] R. Hofmann, D. Nickel, W. von Rybinski, *Tenside Surfactants Deterg.* **1994**, *31*, 63 – 66.

[37] R. Miller, K. Lunkenheimer, *Colloid Polym. Sci.* **1986**, *264*, 273 – 276.

[38] E. M. Kutschmann, G. H. Findenegg, D. Nickel, W. von Rybinski, *Colloid Polym. Sci.* **1995**, *273*, 565 – 571.

[39] *Technological Applications of Dispersions* (Ed.:R. B. McKay), Marcel Dekker, New York, **1994.**

[40] M. J. Schwuger, *J. Am. Oil Chem. Soc.* **1982**, *59*, 258 – 264.

[41] *Surface Chemistry of Froth Flotation* (Ed.: J. Leja), Plenum, New York, **1982**.

[42] W. von Rybinski, M. J. Schwuger in *Nonionic Surfactants Physical Chemistry* (Ed.: M. J. Schick), Marcel Dekker, New York, **1987**, pp. 45 – 107.

[43] D. Nickel, W. von Rybinski, E. M. Kutschmann, C. Stubenrauch, G. H. Findenegg, *Fett/Lipid* **1996**, *98*, 363 – 369.

[44] G. A. Smith, A. L. Zulli, M. D. Grieser, M. C. Counts, *Colloids Surf. A* **1994**, *88*, 67 – 73.

[45] S. Fukushima, S. Kumagai, *J. Colloid Interface Sci.* **1973**, *42*, 539 – 544.

[46] C. Ma, Y. Xia, *Colloids Surf.* **1992**, *68*, 171 – 177.

[47] P. Chandar, P. Somasundaran, N. J. Tarro, *J. Colloid Interface Sci.* **1987**, *117*, 31 – 46.

[48] A. M. Gaudin, D. W. Fuerstenau, *Trans. Am. Inst. Min. Eng.* **1955**, *202*, 958.

[49] F. Nilsson, O. Söderman, *Langmuir* **1996**, *12*, 902 – 908.

[50] P. Sakya, J. M. Seddon, R. H. Templer, *J. Phys. II* **1994**, *4*, 1311 – 1331.

[51] R. A. Mackay in *Nonionic Surfactants: Physical Chemistry* (Ed.: M. J. Schick), Marcel Dekker, New York, **1987**, pp. 297.

[52] G. Platz, C. Thunig, J. Pölicke, W. Kirchhoff, D. Nickel, *Colloids Surf. A* **1994**, *88*, 113 – 122.

[53] K. Fukuda, O. Södermann, B. Lindman, K. Shinoda, *Langmuir* **1993**, *9*, 2921 – 2925.

[54] D. Balzer, *Langmuir* **1993**, *9*, 3375 – 3384.

[55] M. J. Schick, *J. Colloid Sci.* **1962**, *17*, 801 – 813.

[56] L. Marszall, *Langmuir* **1988**, *4*, 90 – 93.

[57] G. Platz, C. Thunig, H. Hoffmann, *Ber. Bunsen-Ges. Phys. Chem.* **1992**, *96*, 667 – 677.

[58] EEC, Commission Regulation (EC) No. 1488/94, 24th June 1994, *Off. J. Europ. Comm. L 161*, 29th June 1994.

[59] J. Steber, W. Guhl, N. Stelter, F. R. Schröder in Ref. [3b], pp. 177 – 190.

[60] *OECD Guidelines for the Testing of Chemicals, Volume 1, Section 3: Degradation and Accumulation*, OECD, Paris, **1993**.

[61] EEC, Council Directive, 31st March, 1982 (82/242/EEC), *Off. J. Europ. Comm. L 109*, 22nd April, 1982.

[62] EEC, Guidance Document of the Competent Authorities for the Implementation of Directive 79/831/EEC, Doc. XI/861/86 final.

[63] a) W. Matthies, *Parfüm. Kosmet.* **1992**, 73, 80; b) COLIPA, *Cosmetic Product Guidelines for the Assessment of Human Skin Compatibility*, Brüssel, **1995**.

[64] W. Aulmann, W. Sterzel in Ref [3b], pp. 151 – 167.

[65] M. Kahlweit, R. Strey, *Angew. Chem.* **1985**, *97*, 655 – 669; , *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 654 – 668.

[66] K. Shinoda, H. Kunieda in *Encyclopedia of Emulsion Technology, Vol. 1* (Ed.: P. Becher), Marcel Dekker, New York, **1983**, pp. 337 – 367.

[67] T. Förster, W. von Rybinski, A. Wadle, *Adv. Colloid Interface Sci.* **1995,** *58*, 119 – 149.

[68] G. G. Warr, C. J. Drummond, F. Grieser, B. W. Ninham, D. F. Evans, *J. Phys. Chem.* **1986**, *90*, 4581 – 4586.

[69] W. D. Clemens, *Ber. Forschungszentrum Jülich* **1994**, 3028.

[70] D. Balzer, *Tenside Surfactants Deterg.* **1991**, *28*, 419 – 427.

[71] M. Kahlweit, G. Busse, B. Faulhaber, *Langmuir* **1995**, *11*, 3382 – 3387.

[72] H. Kahl, K. Kirmse, K. Quitzsch, *Tenside Surfactants Deterg.* **1996**, *33*, 26 – 32.

[73] T. Förster, B. Guckenbiehl, H. Hensen, W. von Rybinski, *Progr. Colloid Polymer Sci.* **1996**, *101*, 105.

[74] G. H. Findenegg, as yet unpublished.

[75] R. Aveyard, B. P. Binks, P. D. I. Fletcher, *Langmuir* **1989**, *5*, 1210 – 1217.

[76] R. Hofmann, D. Nickel, W. von Rybinski, G. Platz, J. Pölike, Ch. Thunig, *Progr. Colloid Polymer Sci.* **1993**, 93, 320.

[77] T. Förster, B. Guckenbiehl, A. Ansmann, H. Hensen, *Proceedings Forum Cosmeticum*, Salzburg (Austria), **1996**.

[78] T. Förster, H. Hensen, R. Hofmann, B. Salka, *Cosmet. Toiletries* **1995**, *110*, 23 – 29.

[79] IPP Quality Standard, *Seifen Oele Fette Wachse* **1986**, *112*, 371.

[80] K. Schwadtke, E. Smulders, E. Sung (Henkel KGaA) DE-A 3920480, **1989**.

[81] R. Puchta, P. Krings, H. M. Wilsberg, *Seifen Oele Fette Wachse* **1990**, *116*, 241 – 244.

[82] P. Busch, H. Hensen, H.-U. Krächter, H. Tesmann, *Cosmet. Toiletries Manuf. Worldwide* **1994**, 123.

[83] K. H. Schrader, *Euro Cosmetics* **1994**, 18.

[84] P. Busch, H. Hensen, H. Tesmann, *Tenside Surfactants Deterg.* **1993**, *30*, 116.

[85] B. Salka, *Cosmet. Toiletries* **1993**, 108, 89.