Natural surfactants

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Abstract

The ever-increasing environmental concern about surfactants triggers an interest in natural surfactant. This review, which has an emphasis on work published since 1998, covers three categories of natural surfactants: amphiphiles produced by yeast or bacteria, amphiphiles containing a natural polar headgroup and amphiphiles containing a natural hydrophobic tail. Microorganisms produce both high molecular weight and low molecular weight surfactants. Only the low molecular weight compounds are included in the review. Sugars and amino acids are the two most important examples of surfactant polar headgroups of natural origin. The research is particularly intense in the area of sugar surfactants and the review covers three types: alkylglucosides, alkylglucamides and sugar esters. Surfactants based on two types of natural hydrophobic tails are included: fatty acid monoethanolamides and sterol ethoxylates. Routes of preparation as well as physico-chemical properties are discussed for the surfactants prepared by organic synthesis. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The term ‘natural surfactant’ is not unambiguous. Taken strictly a natural surfactant is a surfactant taken directly from a natural source. The source may be of either plant or animal origin and the product should be obtained by some kind of separation procedure such as extraction, precipitation or distillation. No organic synthesis should be involved, not even as an after-treatment. There are in fact not many surfactants in use today that fulfil these requirements. Lecithin, obtained either from soybean or from egg yolk, is probably the best example of a truly natural surfactant.

The main reason why natural surfactants in the real sense of the word are so scarce is not a lack of availability. Amphiphiles are abundant in both the plant and the animal kingdom where they are often referred to as polar lipids. In biological systems the surface active agents are used in very much the same way as surfactants are employed in technical systems: to overcome solubility problems, as emulsifiers, as dispersants, to modify surfaces, etc.

The factor that works against production of truly natural surfactants is the cost of work-up. The products are usually present in small quantities and the separation process tends to be tedious. In most instances the cost of separation/isolation will by far exceed the manufacturing cost of equivalent synthetic surfactants.

The unfavorable cost situation for truly natural surfactants may change if fermentation processes can be developed that yield biosurfactants in high yields. Both yeast and bacteria can be efficient producers of surface active agents and there is considerable current interest in biotechnological processes for production of amphiphilic compounds. These substances can be either low molecular weight, such as acylated...
oligosaccharides, or high molecular weight, most often lipopolysaccharides. So far most interest has focused on the high molecular weight products, with *Emulsan*, a highly charged heterolipopolysaccharide with a molecular weight of approximately $10^6$, as the prime example [1].

The term ‘natural surfactant’ is often used in a broader sense than that discussed above, however. Surfactants synthesized from natural raw materials are usually referred to as natural surfactants. Proper examples of surfactants belonging to this category are fatty acid esters of sugars and fatty acid esters or amides of amino acids. It is, in fact, common practice to be even more generous in the use of the term ‘natural surfactant’. A surfactant with one of the main building blocks, the polar headgroup or the hydrophobic tail, obtained from a natural source is often referred to as a natural surfactant. For example, alkyl glucosides which are prepared from a ‘natural’ sugar unit and a ‘non-natural’ fatty alcohol are often regarded as natural surfactants. (So-called ‘natural fatty alcohols’ should not be seen as natural starting materials, although this is often done. Fatty alcohols derived from coconut oil and other triglycerides are made by two consecutive chemical reactions: methanolysis of the triglyceride followed by reduction of the methyl ester.)

In this review the term ‘natural surfactant’ is used in its broadest sense. The paper covers true natural surfactants prepared by fermentation, synthetic surfactants with a natural polar head group and synthetic surfactants with a natural hydrophobic tail. Only low molecular weight surfactants with a well-defined structure are included. The ‘natural surfactants’ used to treat the respiratory distress syndrome, a chapter of its own, are in reality mixtures of amphiphiles with structures not fully elucidated [2] and are, hence, not covered. The review is organized correspondingly.

2. Surfactants prepared by fermentation

2.1. Acylpolyols

Acylpolyols prepared by fermentation are usually hydroxy fatty acids connected to disaccharides by ester bonds. They are extracellular compounds produced by actinomycetes such as *Mycobacterium*, *Corynebacterium*, and *Brevibacterium* [3]. The acylpolyols are abundant in bacterial cell walls. A typical example of an acylpolyol is the trehalose ester shown in Fig. 1.

2.2. Glycolipids

Glycolipids are usually hydroxy fatty acids attached to a sugar via a glycosidic bond. Sophorolipids and rhamnolipids are well known examples, produced by *Candida* and by *Pseudomonas*, respectively [4,5]. Fig. 2 shows a cyclic and an acyclic sophorolipid. Rhamnolipids are attractive in that they can be efficiently produced during growth on either hydrocarbon or carbohydrates as the sole carbon source. There has been considerable interest in the molecular genetics of rhamnolipids and this topic has recently been reviewed in this journal [6].

A sucrose lipid produced by *Serratia marcescens* has recently been isolated and characterized [7•]. The product was found to be an excellent emulsifier for a

![Fig. 1. A trehalose ester.](image)

![Fig. 2. A cyclic and an acyclic sophorolipid.](image)
wide range of hydrocarbons including crude oil. It has been suggested as a surfactant for cleaning of oil tanks.

2.3. Acylpeptides

Acylpeptides or lipopeptides, are usually cyclic compounds based on a hydroxy acid and a short peptide chain. By far the most studied compound is *Surfactin*, produced from *Bacillus subtilis* [8,9]. Acylpeptides, such as Surfactin and Lichenysin produced by *Bacillus licheniformis*, are efficient amphiphiles when it comes to surface tension reduction, etc. Surfactin is one of the few biosurfactants that has found commercial use. It is used in a variety of pharmacological applications [10]. The formula of Surfactin is shown in Fig. 3. Surfactin and rhamnolipids are the only two biosurfactants for which there is any regulatory information and the molecular genetics of Surfactin has recently been reviewed [6].

3. Surfactants based on a natural polar headgroup

3.1. Sugar as polar headgroup

Various types of sugars or polyols derived from sugar have been used as surfactant polar headgroup for many years. Sorbitane alkanoates and ethoxylated sorbitane alkanoates, well known under the trade names of *Span and Tween*, respectively, have been around for a long time. In recent years there has been a focus on three classes of surfactants with sugar or a polyol derived from sugar as polar headgroup: alkyl polyglycosides (APGs), alkyl glucamides and sugar esters. Representative structures of the three surfactants are shown in Fig. 4.

There is currently a very strong interest in exploring alkyl polyglycosides (APGs) as surfactant for several types of applications. APGs are synthesized by direct reaction of glucose with fatty alcohol, using a large excess of alcohol in order to minimize sugar oligomerization. Alternatively, they are made by transacetalization of a short chain alkyl glucoside, such as ethyl or butyl glucoside, with a long chain alcohol. An acid catalyst is used in both processes. Either glucose or a degraded starch fraction is used as starting material. Fig. 5 illustrates the synthesis. Alkyl...
glucosides can also be made by enzymatic synthesis, using \( \beta \)-glucosidase as catalyst which yields only the \( \beta \)-anomer (and gives low yield). The corresponding \( \alpha \)-anomer can more readily be obtained by \( \beta \)-glucose-
sidase catalyzed hydrolysis of the racemate. There are considerable differences between the \( \alpha \beta \) mixture ob-
tained by organic synthesis and the pure enantiomers obtained by the bio-organic route. The \( \beta \)-anomer of \( n \)-octyl glucoside has found use as a surfactant in biochemical work.

Alkyl glucosides are stable at high \( \mathrm{pH} \) and sensitive to low \( \mathrm{pH} \) where they hydrolyze to sugar and fatty alcohol. A sugar unit is more water-soluble and less soluble in hydrocarbons than the corresponding poly-

oxethylene unit; hence, APGs and other polyol-based surfactants are more lipophobic than their polyox-
ethylene-based surfactant counterparts [11]. This makes the physico-chemical behavior of APG surfac-

tants in oil-water systems distinctly different from that of conventional non-ionics. Furthermore, APGs do not show the pronounced inverse solubility vs. temperature relationship that normal non-ionics do. This makes an important difference in solution behavior between APGs and polyoxethylene-based surfac-

tants. The main attractiveness of APGs lies in their favorable environmental profile: the rate of biodegra-
dation is usually high and the aquatic toxicity is low [12,13]. In addition, APGs exhibit favorable dermato-

gical properties, being very mild to skin and eye [14]. The mildness makes this surfactant class attrac-
tive for personal care products but APGs have also found a range of technical applications.

APGs have been the topic of several excellent overviews [15–18]. In addition, the physico-chemical properties of APGs, as well as other polyhydroxyl-

based surfactants, have recently been reviewed in this journal [19]. Only a few brief notes on recent develop-

ments in the field will therefore be given here.

The solution behavior of APGs, both anomic mixtures, prepared by organic synthesis, and pure enantiomers have been studied in detail [20*,21–23]. The micellar phase region is usually large and at higher concentrations the normal pattern of liquid crystalline phases appears. It interesting to note, as was described in a previous review [19], that some APG surfactants exhibit a miscibility gap in the micel-

lar region. As with polyoxethylene-based non-ionics two micellar phases appear in this region, one dilute and one concentrated. For a pure decyl glucoside surfactant it was found that the dilute phase consisted of micelles of aggregation number in the range 200–400 while the concentrated phase contained larger aggregates, probably branched micelles that formed a network through entanglement [20]. A char-

acteristic feature of the liquid crystalline region which appears at higher surfactant concentration is that the
borders between the different crystalline phases in a temperature vs. surfactant concentration diagram are almost vertical, indicating a temperature-independent behavior. This is very different from the behavior of polyoxylene-based non-ionics.

Mixed micelle formation of two APGs with differ-

cent length of the alkyl chain with both anionic and cationic surfactants have been studied [24*]. The ex-
perimental data were fitted to Rubingh’s model for non-ideal mixed micelle formation [25]. A value of the
interaction parameter, \( \beta \) is obtained and the value of \( \beta \), positive or negative, indicates whether there is a repulsive or an attractive interaction involved in the formation of mixed micelles between the two surfac-
tant types. Combination of an APG with the cationic surfactant dodecyltrimethylammonium bromide gave a value of the \( \beta \)-parameter of \(-4.1\) indicating rather strong attractive interaction. The combination of the same APG with the anionic surfactant sodium dode-
cylsulfate gave a \( \beta \)-value of \(-2.3\), indicative of a smaller attraction. These results are interesting and not easily explained. They tend to support the view, proposed by several workers, that APGs carry a negative net charge, the origin of which is unclear [24*]. It is interesting that whereas a combination of an APG and an alcohol ethoxylate gave a value of the \( \beta \)-parameter of zero, the same APG when combined with another alkyl glycoside, an alkyl maltoside of the same alkyl chain length (C10) gave a \( \beta \)-value of \(-2.0\). This attractive interaction was tentatively explained as due to favorable packing of the headgroups of the two surfactants [24*].

The majority of work on glycoside surfactants has been made on alkyl glucosides, i.e. surfactants based on glucose or slightly oligomerized glucose as polar headgroup. Recently, alkyl maltosides have been studied with a specific focus on its behavior in mixed micelles together with anionic and non-ionic surfac-
tants [26,27]. A combination of a decyl maltoside with sodium dodecylbenzene sulfonate gave a value of the \( \beta \)-parameter of \(-2.1\) which can be compared with the value of \(-3.3\) for a combination of an alcohol ethoxy-
late, octa(ethylene glycol)monodecyl ether (C10E8) with the same anionic surfactant. A combination of the alkyl maltoside with the alcohol ethoxylate gave a very small \( \beta \)-value (\(-0.3\)). A synergistic effect with regard to surface tension reduction was also found for combinations of either of the non-ionic surfactants and sodium dodecylbenzene sulfonate. Thus, the re-
results obtained with the maltoside surfactant agree very well with those previously obtained with glucoside surfactants of the same alkyl chain length. A full explanation of the results still remains, however.

Alkyglucamides (see Fig. 4), or more strictly named as \( N \)-alkanoyl-N-methylglucamines, are commercially important products. The product sold in large quanti-
ties for the detergent sector is \(N\)-dodecanoyl-\(N\)-methylglucamines, i.e. the C12-derivative. The product is prepared from glucose, methyl amine, hydrogen and methyl laurate by a two-step reaction.

Alkylglucamides have been the subject of an extensive review recently [28]. Few major investigations on this surfactant class seem to have been made recently. In a paper by Zhu et al. a glucamide was compared with polyol surfactants of similar structure, a xylamide and a glyceramide, all having a C12 alkyl chain [29\*]. The glucamide has four hydroxyl groups in the polar head, the xylamide three and the glyceramide one. This was reflected both in the area per molecule values and the CMC values which were 30, 28 and 26 \(\text{Å}^2\) and 0.347, 0.331 and 0.234 mM, respectively.

There is considerable current interest in sugar esters (see Fig. 4) and a recent review covers the topic until 1998 [30]. Esters of glucose can be made either by enzymatic synthesis, using a lipase catalyst, or by an organic chemical route. Using the right enzyme the bio-organic route can give esterification almost exclusively at the 6-position of the sugar moiety. The organic synthesis requires extensive use of protecting groups to obtain high selectivity. Selective enzymatic synthesis of other sugar esters than glucose esters have been difficult to achieve without the use of protective groups. Starting from sugar acetals and fatty acids, monoesters of sugars were obtained in good yield, after a deprotection step, from several starting materials, both mono- and disaccharides [31,32].

The advantage of the organic synthesis over the enzymatic route is that the sugar unit can be varied at will. The group of Drummond has recently made important contributions in this area with a specific focus on degradation mechanisms [33*], but also covering physico-chemical behavior [36*]. A series of sugar ester surfactants were synthesized having different headgroup size (glucose, sucrose and raffinose, consisting of one, two and three anhydroglucose rings, respectively) and with C12 and C16 acyl chains. Sulfonated sugar esters were also prepared. It was found that all unsubstituted sugar esters degraded rapidly. Variations in the sugar headgroup size or the acyl group chain length did not significantly affect the biodegradability. The anionic derivatives degraded more slowly, however [33*].

A detailed study on the mechanism of biodegradation of the unmodified and the sulfonated sugar esters showed that sucrose laurate biodegradation occurs via initial ester hydrolysis. The sucrose \(\alpha\)-sulfonyl laurate, on the other hand, degrades by initial alkyl chain oxidation. This indicates that the ester hydrolysis pathway is blocked by the sulfonyl group adjacent to the ester bond so that biodegradation is forced to proceed via the slower alkyl chain oxidation pathway [34**]. An ethyl substituent in \(\alpha\)-position instead of the sulfonate group also slowed down the biodegradation rate, probably for the same reason. The two degradation routes are shown in Fig. 6.

Base catalyzed hydrolysis was also investigated. Similar to the results from the biodegradation, the unsubstituted sugar esters degraded faster than the derivatives with either a sulfonate or an ethyl group in the \(\alpha\)-position. The difference in hydrolysis rate between the three surfactants sucrose laurate, sucrose \(\alpha\)-sulfonyl laurate and sucrose \(\alpha\)-ethyl laurate, varied with temperature. It was concluded that at higher temperature, when steric hindrance is the dominant factor, hydrolysis of \(\alpha\)-sulfonyl laurate is slowest. By contrast, at lower temperature, when activation energy is more important, hydrolysis is faster in the presence of an electron-withdrawing \(\alpha\)-sulfonyl group than in the presence of an electron-attracting \(\alpha\)-ethyl group [35].

Dimeric and trimeric sugar ester surfactants have been synthesized by a combination of enzymatic and organic chemical methods [37**]. An impressive series of products were prepared with different spacer units between the sugar rings. For instance, a dimeric (gemini) glucose ester with C12 acyl chains attached at positions 6 of the two anhydroglucose units and with the two moieties connected via a six carbon spacer was prepared in high yield. The product is shown in Fig. 7.

### 3.2. Amino acid as polar headgroup

Amino acids and short peptides constitute an alternative to sugars as a natural polar headgroup for surfactants. Several amino acids have been investigated for this purpose with the majority of papers dealing with basic amino acids such as arginine and lysine from which cationic surfactants can easily be prepared. Most synthetic procedures are based on organic synthesis but enzymatic processes have also been explored [38,39]. Arginine-based surfactants have recently been reviewed [40].

Arginine surfactants, such as \(N\)-dodecanoylarginine methyl ester salt are conveniently prepared by reaction between the oil soluble dodecanoic acid and the water soluble arginine methyl ester hydrochloride using di-cyclohexylcarbodiimide as condensing agent. The reaction is normally carried out in an aprotic, polar solvent such as dimethylformamide (DMF). The reaction is performed at room temperature and works well in a laboratory scale. However, DMF is an unsuitable solvent for large scale operations, partly due to cost and toxicity and partly due to difficulties in removing it from the product by simple vacuum evaporation. An alternative process, using a high-internal-phase-ratio emulsion, has been investigated
Fig. 6. Degradation pathways of a sugar fatty acid ester (from Baker et al. [34] with permission).

Fig. 7. A sugar fatty acid gemini surfactant (from Gao et al. [37] with permission).

for the synthesis [41**]. Such emulsions can be formulated with a large amount, sometimes above 99%, of internal phase and with very low amount of surfactant, often less than 0.5%. The structure of water-in-oil emulsions of this type is that of closed-packed water droplets of a broad size distribution separated by a thin film of the continuous oil phase. The viscosity is usually high and such emulsions are sometimes referred to as gel emulsions. It was demonstrated that the concentrated emulsions were good reaction media with yields equivalent to those obtained in DMF. The yield depended on the water-to-oil ratio. Too high water content at constant surfactant concentration gave large water droplets with corresponding small interfacial area which was found to be unfavorable.

A papain-catalyzed synthesis of arginine-based surfactants have been reported [42,43]. Papain deposited on a solid support was used as catalyst for the amide and ester bond formation between arginine methyl ester and various long-chain alkyl amines and fatty
alcohols in organic solvent. High yield of arginine amide was obtained from reaction in acetonitrile. For the synthesis of the arginine fatty acid ester the best yield was obtained in a solvent-free system kept at a temperature above the melting temperature of the fatty alcohol.

Using a combination of organic and bioorganic synthesis arginine-based gemini surfactants have been synthesized by the group of Infante [44] and the solution properties have been investigated [45]. The gemini surfactants consisted of two \(N\)-acylarginine moieties connected via the arginine carboxyl groups by a diamino spacer molecule, such as 1,3-diaminopropane or 1,3-diamino-2-hydroxypropane. A \(N\)-acyl-L-arginine alkyl ester was used as starting material. This compound was first reacted with the diamino spacer to form the amino-amide, i.e. the spacer reacted with one of its amino group to form a \(N\)-acyl-L-arginine amide. In a second step, catalyzed by papain, the free amino group reacted with another molecule of \(N\)-acyl-L-arginine alkyl ester to form the diamide product. Overall yields of the order of 65% were reported.

A series of tryptophan-based surfactants have been synthesized [46]. The surfactants were synthesized by reaction of tryptophan with the epichlorohydrine adduct of a fatty alcohol, as shown in Fig. 8. The series of surfactants based on fatty alcohols with from 9 to 16 carbon atoms was evaluated with respect to CMC, surface tension at CMC and area per molecule at the air–water interface. The results are summarized in Table 1. As can be seen, the CMC values are low, considerably lower than for simple alkanoate surfactants of the same hydrocarbon chain length. For instance, sodium laurate has a CMC of 20 mM to be compared with the value of 0.038 mM of the C12 surfactant of Table 1. The surface tension values are generally low, as expected for these hydrophobic surfactants. The areas per molecule are within the expected range, the increase in area for the shorter chain length surfactants most probably reflecting a less ordered packing at the surface.

The amino acid-based surfactants are possible candidates for pharmaceutical applications and the hemolytic action of some lysine-based anionic surfactants has been investigated. The surfactants were salts
of Nₙ,Nₙ-dialkanoyl lysine. In one series of experiments the alkyl chain lengths were varied [47]. In another work the surfactant was Nₙ,Nₙ-octanoyl lysine and the counterion was varied [48]. As expected, the hemolytic activity depended on the alkyl chain length and on the choice of counterion. With lysine as counterion to the lysine-based anionic surfactant a protective effect against hypotonic hemolysis was obtained.

4. Surfactants based on a natural hydrophobic tail

4.1. Fatty acid as hydrophobic tail

Fatty amide ethoxylates are easily prepared by ethoxylation of the fatty amide monoethanolamide. The ethanolamide, in turn, is prepared by aminolysis of the fatty acid methyl ester by ethanolamine. The fatty amide ethoxylates are of interest as an alternative to fatty alcohol ethoxylates for several reasons: (i) they biodegrade readily to fatty acid and amino-terminated poly(ethylene glycol); (ii) the amide bond in the structure may improve surfactant packing due to hydrogen bond formation; and (iii) double bonds in the fatty acid chain can be preserved in the product (although during the ethoxylation step 1,3-cis, cis-double bonds undergo migration to conjugated trans, cis structures).

A series of fatty amid ethoxylates, all based on C₁₈ fatty acids but with varying number of double bonds, has been synthesized and evaluated with regard to the effect of the amide bond and the double bonds on physico-chemical properties [49, 50]. Surfactants with different polyoxyethylene chain lengths were prepared and the corresponding saturated fatty alcohol ethoxylates, stearyl ethoxylates, were used as references. It was found that the presence of the amide group led to a decrease in CMC, possibly due to hydrogen bond formation. The surface tension at the CMC was higher when an amide bond was present, however, which was assumed to reflect the increase in size of the polar group (decrease in the critical packing parameter value) which is unfavorable for close alignment of surfactant molecules at the air–water interface. The same effect was seen in adsorption at a hydrophobic, solid surface, as studied by ellipsometry.

The presence of unsaturations in the hydrophobic tail gave an increase in CMC. This may partly be due to the surfactants becoming more hydrophilic and partly to the increased bulkiness of the chains rendering packing into closed aggregates and formation of hydrogen bonds between amide groups more difficult. The presence of one double bond, cis (oleyl) or trans (elaidyl), did not much affect the molecular cross-sectional area at the surface. Two double bonds gave much larger areas, as can be seen from Fig. 9.

Self-diffusion NMR was used to study the effect of temperature and surfactant concentration on the size of the surfactant aggregates. It was found that at both

![Fig. 9. Area per molecule for a series of fatty amide ethoxylates with 10, 15 or 20 oxyethylene units. The number of double bonds in the acyl chain vary from zero (stearyl) to one, cis (oleyl) and one, trans (elaidyl) to two (linoleyl). Stearyl alcohol ethoxylates (C18En) are included as references.](image-url)
high and low surfactant concentration the hydrodynamic radius of a stearyl amide ethoxylate was somewhat larger than the radius of the stearyl alcohol ethoxylate with the same number of oxyethylene units. For the higher surfactant concentration, where the micelles are non-spherical, this may be due to the larger polar headgroup size of the amide surfactants (see discussion above) giving slightly less elongated micelles. The results are more difficult to rationalize for the low surfactant concentration where both amphiphiles give spherical micelles.

4.2. Sterol as hydrophobic tail

Sterol-based surfactants have been reviewed recently [51] and a new review is in progress [52]. Sterol-based surfactants are of interest because of the large hydrophobic group of fully natural origin which, due to its rather planar four ring structure, may induce good packing at interfaces. Two recent papers deal with phytosterol ethoxylates [53,54]. Phytosterols are sterols of plant origin and their structure is similar to that of cholesterol, the prime example of sterols from animal sources. The sterols contain a secondary hydroxyl group that can be ethoxylated. The alcohol is sterically hindered, however, and the reaction with ethylene oxide is not straightforward. The best procedure seems to be to start the ethoxylation with a Lewis acid catalyst, cease the reaction after 3–5 mol of ethylene oxide have been added, and continue with KOH as initiator [55]. The structure of a representative sterol ethoxylate is shown in Fig. 10.

Surface tension plots of a series of phytosterol ethoxylates with 10, 20 and 30 oxyethylene units showed that (i) the CMC values were very low; and (ii) the CMC increased with increasing polyoxyethylene chain length. The latter, which has previously been observed by others as accounted for in Folmer et al. [53,54], is unexpected and is difficult to explain. The values are collected in Table 2. Another interesting observation is that the time to reach surface tension equilibrium is very long, more than 2 h. The decay of surface tension with time is shown in Fig. 11. Most likely, the long equilibrium time is due to exchange reactions of sterol ethoxylates with varying polyoxyethylene chain length at the air–water interface and to slow conformational changes of individual molecules at the surface. The multiring structure of sterols is rigid and the time required to adapt a favorable conformation at an interface may be long.

The phase behavior of the sterol ethoxylates has been studied in some detail [53,54]. Fig. 12 shows phase diagrams for phytosterols with 5, 10, 20 and 30 oxyethylene units. The surfactant having 10 oxyethylene units gives a lamellar phase over a very wide concentration range at elevated temperature. The phase diagrams of the more hydrophilic surfactants with large headgroups are dominated by hexagonal and cubic phases. The high thermal stability of the liquid crystalline phases is noteworthy. It is particularly striking to see a cubic phase for a non-ionic surfactant that extends above 100°C. Cubic phases are normally seen as being trapped in a three-dimensional lattice with no possibility of movement. Usually when the temperature is increased a cubic structure therefore melts at a relatively low temperature. The high thermal stability of the cubic phase formed by the ethoxylated sterols is probably related to an efficient packing of the sterol moieties. Self-diffusion NMR measurements of samples from within the cubic

![Fig. 10. β-Sitosterol ethoxylates.](image)

![Fig. 11. Surface tension for phytosterol with 20 oxyethylene units as a function of time at fixed concentration (3.44 × 10⁻⁶ M) from Folmer et al. [53] with permission.](image)
5. Conclusions

The review has covered work performed in recent years in three areas, i.e. surfactants produced from bacteria and yeast, surfactants based on either sugar or amino acid as polar headgroup, and surfactants based on either fatty acid or sterol as hydrophobic tail. All three areas are important and subject to considerable research activity. The natural surfactants obtained by these approaches are generally well characterized and the performance are up to the standards of conventional surfactants. The biotechnologically produced surfactants suffer from high cost due to relatively low yield in the fermentation and cumbersome work-up procedures. The surfactants based on either a natural polar headgroup or a natural hydrophobic tail show great promise for the future.

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References and recommended reading

- of special interest
- of outstanding interest


Sucrose lipids with excellent ability to emulsify hydrocarbons, including crude oil, were produced. The surfactant was a mixture of two hydroxyalkanoic acid esters of sucrose.

Formation of micelles in mixtures of alkylglycosides and a conventional surfactant was studied. A strong negative value of the inter-{\it H}19 {\it G1}-alkylglucoside/water system. A phase diagram and NMR self-diffusion study. Langmuir 1998;14:6396–6404.

The paper discusses the mechanism behind the liquid–liquid phase separation that occurs in the micellar region; this region is split into one concentrated and one dilute phase, both containing micelles.

Formation of micelles in mixtures of alkylglucosides and a conventional surfactant was studied. A strong negative value of the interaction parameter, $\beta$, indicating attractive interaction, was obtained for the mixture of alkylglucoside and the cationic surfactant. A somewhat smaller negative $\beta$-value was obtained for the mixture of a glucoside surfactant with the anionic surfactant. No interaction was seen for the alkylglucoside–alcohol ethoxylate mixture.

A series of sugar esters with different sized sugar headgroups were synthesized by a combination of enzymatic and alternative surfactants to aprotic, polar solvents such as dimethylformamide with dodecylbenzene sulphonate-2. Interaction of mixed micelles. J Colloid Interface Sci 2000;222:1531–1539.


A highly concentrated water-in-oil emulsion was used as a reaction medium for acylation of arginine methyl ester with dodecanoic acid. It was demonstrated that such emulsions should be seen as an alternative to aprotic, polar solvents such as dimethylformamide and also to microemulsions.


The effect of the alkyl chain length, headgroup polymerization and anomeric configuration of a series of sugar esters on physico-chemical properties were investigated.


An impressive series of gemini sugar surfactants (and some trimeric surfactants) were synthesized by a combination of enzymatic and organo-chemical routes.


A highly concentrated water-in-oil emulsion was used as a reaction medium for acylation of arginine methyl ester with dodecanoic acid. It was demonstrated that such emulsions should be seen as an alternative to aprotic, polar solvents such as dimethylformamide and also to microemulsions.


A new type of tryptophan-based surfactants were synthesized and characterized with respect to CMC, surface tension and area per molecule at the air–water interface. The tryptophane surfactants showed very low CMC values.


A series of fatty acid monoethanolamide ethoxylates with varying number of double bonds in the acyl chain and with varying number of oxylethane groups in the polar headgroup was investigated. The influence of the amide bond and of the unsaturations on adsorption at the air–water interface and on self-assembly was investigated.


A series of fatty acid monoethanolamide ethoxylates with varying number of double bonds in the acyl chain and with varying number of oxylethane groups in the polar headgroup was investigated. The influence of the amide bond and of the unsaturations on adsorption at a hydrophobic solid surface and on micellization was investigated by ellipsometry and by NMR.


A series of sterol ethoxylates was investigated. It was found that the time to reach equilibrium surface tension was very long, more than two hours. This probably reflects both exchange reactions at the surface and a slow reorientation of molecules at the air–water interface.

54 Folmer BM, Nydén M. Structure and dynamics in the micellar and cubic phase of an ethoxylated phytosterol surfactant. Langmuir (submitted).