Carbohydrate-derived surfactants containing an N-Acylated amine functionality

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Chapter 1

Nonionic Carbohydrate-Derived Surfactants and their Use in Industry

1.1 Aim of the research: surfactants from renewable sources

The name surfactant is a contraction of the term "surface-active agent". Surfactants are adsorbed at interfaces and change the properties of those interfaces; thus they are surface active. They have a dualistic character; they possess a headgroup, which by itself would be highly soluble in water, and a hydrophobic tail that tends to minimize water contact. The headgroup can be anionic (e.g., sulphate, sulfonate, phosphate, carboxylate), cationic (e.g., ammonium, alkyl substituted ammonium, pyridinium), zwitterionic (e.g., betain), or nonionic (polyglycol ether, carbohydrate). The tail consists of one or more alkyl chains which can be branched or unbranched and may be saturated or unsaturated.

Surfactants are large volume chemicals: their annual production exceeds 5 million tons worldwide. They are primarily used as cleaning agents in laundry and dish-washing applications. Surfactants are also applied in cosmetics and pharmaceuticals, in manufacturing textiles and fibers, in the food industry, in paints and plastics, in the paper industry, in pesticides, and in the oil production process. Their intrinsic interest, the large production, and their application justifies research into the structures, properties, and performance of surfactants as well as their impact on the environment (synthetic process, toxicity, and biodegradability).

Classic types of surfactants are produced from petrochemical raw materials. In the long term, fossil feedstocks will be exhausted and products based on renewable materials will become more important. Growing consumer demands for "natural" products have also directed the search for new surfactants towards renewable sources?

Therefore, our aim was to synthesize new surfactants based on renewables. We based our surfactants on carbohydrates, amines (which can be prepared from fatty acids), and acetic anhydride (which is prepared from natural acetic acid) or propionic anhydride. The surfactants should preferably be readily biodegradable and non-toxic and the syntheses should be possible on a large scale.

An additional benefit of applying carbohydrates is the creation of a new market for abundant agricultural products, such as starch. For the work described in this thesis glucose and lactose have been used. The former is prepared on a large scale by enzymatic hydrolysis of starch, whereas the latter is a unique carbohydrate only found in mammalian milk. The principle source of lactose is whey, the liquid that is a by-product in the production of cheese.
1.2 Aggregation behavior of surfactants

In water, surfactants adsorb at the air-water interface. At a certain concentration (the critical aggregation concentration), the surfactants form aggregates in water. The polar headgroups point towards water and the apolar alkyl chains stick together. This behavior arises from their dualistic character. Although water is the primary solvent in surfactant studies and applications, aggregation behavior is not restricted to water. There are also examples of the formation of aggregates in polar hydrogen-bonding solvents such as hydrazine, formamide, ethylene glycol, and ethyl ammonium nitrate.

In apolar solvents, the situation is reversed. The apolar alkyl chain is readily soluble and the polar headgroup is insoluble in apolar solvents. The surfactants do not adsorb at the air-apolar solvent interface as air is also apolar. However, in solution a reversed aggregation to inverted micelles is possible, but the process is much less cooperative than that in water. The headgroups stick together with traces of water in the inner core of the inverted micelles to avoid contact with the solvent. The alkyl chains point towards the apolar solvent and keep the aggregates in solution. Electrostatic interactions within the core provide the main driving force for the reversed aggregation. The size and structure of the inverted micelles depend on the nature of the surfactants and the apolar solvent. The amount of water present in the system is also an important factor and its presence may even be a prerequisite for the aggregation process.

The driving force for aggregation in water is related to the formation of a hydrophobic hydration shell around the hydrophobic moiety of the surfactant. Traditionally, it was thought that water undergoes a structural enhancement in the hydrophobic hydration shell which is expressed in the formation of stronger and/or more hydrogen bonds per unit volume. Upon aggregation, these shells overlap and structured water is released; this process is accompanied by a gain in entropy. A novel view is that in order not to sacrifice hydrogen bonds compared to bulk water, the hydrogen bonds of water in the hydrophobic hydration shells adjacent to the apolar moiety are predominantly oriented tangentially to the apolar surface. This leads to a loss of entropy. This tangential alignment does not lead to an appreciable enhancement of the three-dimensional hydrogen bond structure. At a certain surfactant concentration, the number of water molecules is not sufficient to form a complete hydrophobic hydration shell, which leads to interference and mutual obstruction of hydration shells. Hydrogen bonds are sacrificed and an increasing number of O-H bonds point towards the apolar surface. As a result, the tendency to form aggregates increases rapidly. Subsequently, the lost entropy upon formation of the tangentially oriented hydrogen bonds is regained.

Additional factors such as headgroup effects also play a role. Headgroups of ionic surfactants are equally charged and repel each other. Furthermore, an ionic headgroup will partially break down the hydrophobic hydration shell of the hydrophobic tail by its presence.
(and thus decrease the inclination to aggregate). Aggregation is also influenced by the counterions of ionic surfactants. By binding to the surfactant assembly counterions minimize headgroup repulsion. Nonionic surfactants aggregate at lower concentrations than ionic surfactants due to smaller headgroup repulsion. Repulsion between uncharged headgroups is due to hydration shell overlap and mainly of steric nature. Furthermore, in the case of nonionic surfactants, no counterions are involved.

Many techniques are available to determine the critical aggregation concentrations: surface tension, electrical conductivity in the case of ionic surfactants, NMR, and microcalorimetry. These techniques are all based upon a clear break near the CMC in the plot of a particular physical property versus the surfactant concentration. Extrapolation of the results at high and low concentration provides an intersection point, the CMC.

1.3 Surfactant types

Conventional surfactants contain one headgroup and one or two alkyl chains (types a and b in Figure 1). There are further interesting types of surfactants: bolaform and gemini surfactants.

Bolaamphiphiles (types c and d in Figure 1) are molecules which have a hydrophilic headgroup at both ends of a (long) hydrophobic chain. Compared to the case for single-headed surfactants, introduction of a second headgroup generally induces better solubilization in water, an increase in the critical aggregation concentration, and a decrease in aggregation number.

![Figure 1](image)

Figure 1. A single-chained surfactant (a), a double-chained surfactant (b), bolaamphiphiles (c and d) and gemini surfactants (e and f).
Menger introduced the term *gemini surfactants* in 1991 to describe surfactants possessing, in sequence, a long hydrocarbon chain, an ionic group, a rigid spacer, a second ionic group, and another hydrocarbon tail. Rosen extended the meaning of the word to all such "double-surfactants" regardless of the spacer (Figure 1, type e). Currently, all surfactants having two hydrophilic groups and two hydrophobic tails and a mirror plane or a C-2 axis are termed gemini surfactants, even if no spacer is present (Figure 1, type f). The majority of gemini surfactants reported so far possess ionic headgroups. This class of surfactants shows intriguing properties, including low CMCs, submicellar aggregation, markedly low surface tensions, good oil solubilization properties, and the formation of thread-like micelles.

### 1.4 Types of aggregates

Surfactants can form various types of aggregates (Figure 2). The type of aggregate that is preferred by a specific surfactant in water depends on its geometry and is described in the packing parameter:

\[
P = v \cdot (a_r \cdot l_0)^3
\]  

\(v\) is the volume of the hydrophobic tail, \(l_0\) is the critical chain length (which is slightly less than the length of the fully extended, all-trans, chain) and \(a_r\) is the optimal cross-sectional...
surface area of the headgroup. This cross-sectional area is an effective area and also includes electrical repulsion between ionic headgroups. Table 1 shows the relationship between the packing parameter of surfactants and the aggregates preferably formed in aqueous solution.

Table 1. The relation between surfactant geometry and preferred structure.

<table>
<thead>
<tr>
<th>Packing parameter $v \cdot (a_b \cdot l)^{1/3}$</th>
<th>$&lt; \frac{1}{3}$</th>
<th>$\frac{1}{3} \cdot \frac{1}{2}$</th>
<th>$\frac{1}{2} \cdot 1$</th>
<th>$-1$</th>
<th>$&gt;1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>effective shape of surfactant molecule</td>
<td>cone</td>
<td>truncated cone</td>
<td>truncated cone</td>
<td>cylinder</td>
<td>inverted truncated cone</td>
</tr>
<tr>
<td>preferred structure</td>
<td>spherical micelles</td>
<td>cylindrical micelles$^a$</td>
<td>flexible bilayers, vesicles</td>
<td>planar, bilayers</td>
<td>inverted micelles</td>
</tr>
</tbody>
</table>

A rough prediction for the type of aggregates (primarily valid for ionic surfactants) is that surfactants having a single alkyl chain form micelles and surfactants containing two alkyl chains form bilayers or vesicles (closed bilayers) in water.

The aggregate morphologies of bolaamphiphiles include spheres, large cylinders, small and large disks, and vesicles.$^b$ Inside these aggregates, the hydrophobic tail can be either folded or fully stretched.

The packing parameter has also been used to predict the aggregate morphologies of gemini surfactants. Generally, aggregates formed by dimeric (gemini) surfactants with short spacer lengths are less curved than those formed from the corresponding monomeric surfactants.$^b$ Aggregates formed by gemini surfactants include o.a. (long) thread-like micelles, spheroidal micelles and vesicles.$^b$

1.5 Conventional nonionic surfactants versus carbohydrate-derived surfactants

In petrochemical-based nonionic surfactants, the hydrophilic moiety is usually built from ethylene oxide.$^a$ Synthesis of polyoxyethylene alkyl ethers is relatively easy and inexpensive and these surfactants find many large-scale applications in e.g. detergents. In the future, the availability of petroleum will decrease and consequently, the price of petrochemical products such as ethylene oxide, the precursor of the hydrophilic part of the conventional nonionic surfactants, and fatty alcohols and substituted phenols, the main hydrophobic ingredients, will

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$^a$ The packing parameter approach has been criticized, and, as pointed out by Nagarajan, $a$, and $l$ are not independent.$^{24}$

$^b$ Cylindrical micelles have been given various names, e.g., worm-like micelles, rod-like micelles, elongated micelles, and thread-like micelles. We use the term thread-like micelles only for reasonably long cylindrical micelles.
Chapter 1

rise. More important in the short term is the growing demand of consumers for natural products. Therefore, the detergent industry is considering the replacement of classical petrochemicals by natural-based products. Of all detergent ingredients, 50 to 75% could be replaced by, e.g., starch-derived products.

Available and (relatively) cheap carbohydrates that can be used as raw material for surfactants include glucose, fructose, sucrose, maltose, cellobiose, and lactose. The atom that connects the carbohydrate-moiety and the hydrophobic chain can be either oxygen (ether, ester), or nitrogen (amine, amide). In principle, all hydroxyl groups of the carbohydrates can be linked to an alkyl chain, but the alkyl chain is mainly linked to the anomeric centre. Less common due to tedious synthetic routes are surfactants in which the alkyl chain and the carbohydrate moiety are connected through either a carbon-carbon bond or a sulfur link. Ames reviewed carbohydrate-derived surfactants in 1960. Miethchen and Peters updated this review in 1987.

Polyethylene oxide surfactants and carbohydrate-derived surfactants also differ in some physical and chemical properties. For example, the saturation concentration of conventional polyethylene oxide surfactants in lipophilic media is fairly high, which means that relatively high concentrations are needed for, e.g., solubilization, emulsification, and detergency.

Polyethylene oxide surfactants possess a cloud point. When aqueous solutions of these nonionic surfactants are heated, they suddenly become turbid. The temperature at which this occurs is called the cloud point. At a somewhat higher temperature, the solutions separate into two phases. One phase contains a very low concentration of surfactant approximately equal to the CMC. The other phase is surfactant-rich. The solubility gap of these systems is usually ascribed to partial dehydration of the headgroups. Carbohydrate-derived surfactants do not show this clouding phenomenon. The less sensitive phase behavior of the carbohydrate-based surfactants may result from the much stronger hydrophilicity of the glycoside moiety compared to that of the ethylene oxide units. Hence, the oxyethylene type of surfactants are suitable for technical processes which require change of emulsion types. Solutions of carbohydrate-derived surfactants are insignificantly affected by increasing the temperature, which makes them attractive for formulation work.

However, the solubility of carbohydrate-derived surfactants might cause a problem. These solubilities depend on the sizes of the headgroups and the tails. Carbohydrate-derived surfactants may display an unfavorable Krafft temperature. Below this temperature spontaneous crystallization of the solution occurs. (T_Krafft may also be described as the temperature at which the CMC equals the solubility of the surfactant.)

Carbohydrate-derived surfactants are extensively used in protein extraction from membranes.
1.6 Commercially produced carbohydrate-derived surfactants

Nonionic surfactants with a carbohydrate-derived headgroup are interesting because they are readily biodegradable, non-toxic, mild to the skin, and have synergistic effects in combinations with anionic surfactants. Applications are growing in the areas of foods, pharmaceuticals, cosmetics, and detergents.

Table 2. Application fields of industrially produced and used carbohydrate-derived surfactants.

<table>
<thead>
<tr>
<th>application field</th>
<th>sorbitan esters</th>
<th>sucrose esters</th>
<th>glucamides</th>
<th>APGs&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>detergents</td>
<td>X</td>
<td>X</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>cosmetics</td>
<td>X</td>
<td>X</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>food</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>other non-food</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Alkyl polyglucosides

Carbohydrate-derived surfactants produced and used on an industrial scale are (ethoxylated) sorbitan and sucrose fatty acid esters, fatty acid glucamides, and alkyl polyglucosides; Figure 3. Table 2 shows their application fields. An advantageous property of glucosides and amides over esters is that they are less sensitive to hydrolysis under alkaline conditions.

Figure 3. Commercially produced carbohydrate-based surfactants: sorbitan fatty acid ester (a), sucrose fatty acid ester (b), fatty acid glucamide (c), and alkyl polyglucoside (d).
16.1 Alkyl glucosides

Alkyl glucosides are the simplest carbohydrate-derived surfactants (Figure 4).\textsuperscript{72–83} They are well-studied and are the most important ingredients of the sugar-based surfactants with the largest worldwide production capacity, the alkyl polyglucosides. Depending on the synthetic route, the configuration at the anomeric center can either be \( \alpha \) or \( \beta \) (Figure 4).\textsuperscript{84} The glycosilation reactions used to synthesize specific alkyl glucosides (Koenigs-Knorr syntheses and modifications thereof) require expensive reagents and are rather time-consuming. They are, however, a necessary tool for the analytical description of the alkyl glucosides.\textsuperscript{84,85}

The physicochemical properties of both types of surfactants differ.\textsuperscript{73,75,76,86} For example, \( \beta \)-1-n-octyl-D-glucopyranoside is readily soluble in water and has a critical micelle concentration of \( 1.9 \times 10^{-2} \) M. By contrast, the \( \alpha \)-1-n-octyl-D-glucopyranoside is only sparingly soluble and has a CMC of \( 6.3 \times 10^{-3} \) M.\textsuperscript{75} Furthermore, \( \beta \)-1-n-octyl-D-glucopyranoside forms micelles in solution whereas \( \alpha \)-1-n-octyl-D-glucopyranoside forms very large, nonspherical assemblies.\textsuperscript{75} Molecular dynamic simulations on monolayers of \( \beta \)-1-n-decyl-D-glucopyranoside and \( \alpha \)-1-n-decyl-D-glucopyranoside show that the \( \beta \) compound forms a significantly larger number of hydrogen bonds between glucose units, whereas the \( \alpha \) compound compensates the smaller number of intersurfactant bonds by a larger number of hydrogen bonds to water.\textsuperscript{79} The tails of the \( \beta \)-1-n-decyl-D-glucopyranoside are able to pack more densely than those of the \( \alpha \) counterpart due to the different orientation of the headgroups with respect to the tails.\textsuperscript{79}

\( \beta \)-1-n-Octyl-D-glucopyranoside is widely used in biomembrane research for the extraction of water-insoluble membrane proteins without denaturation. It is preferred over other nonionic surfactants such as polyethylene glycol alkyl ethers because it has a very high CMC. Hence, it can easily be separated from the proteins by \textit{dialysis}.\textsuperscript{78}

On an industrial scale, alkyl polyglucosides (APGs) are synthesized by the Fischer synthesis (Scheme 1). The reaction is a specific acid-catalyzed acetalization. There are two variants. One is the direct synthesis, in which \textit{dry} glucose is allowed to react with a fatty alcohol. The solubility of glucose in alcohols declines sharply with increasing hydrocarbon chain length and for higher alcohols, the reaction mixture separates into two phases. The second variant overcomes this problem. The synthesis starts from glucose syrup, which is...
allowed to react with a low boiling alcohol such as n-butanol in the presence of an acidic catalyst to form butyl glucoside. Although the solubility of glucose syrup in butanol amounts to only a few percent, the solubility is greatly enhanced by the presence of butyl glucoside. In the second step, butylglucoside is trans-glycosylized with the fatty alcohol. The APGs produced are slightly colored and hence need final refining steps to meet application requirements.

The isolated product is a mixture of mono-, di-, and oligoglucosides (< 10% of tri- and higher oligoglucosides). The α-configuration is favored thermodynamically, but considerable amounts of β-product are also formed. Furthermore, the glucose moieties exist predominantly in the pyranose form, but appreciable amounts of furanosides (3-8%) are also found. The saccharide moieties are predominantly (1→4) and (1→6) linked. Most industrially prepared APGs have an average degree of polymerization (number of monosaccharide units) between 1.2 and 1.6. Although the common name for the products is alkyl polyglycosides, they are actually alkyl oligoglucosides.

Although the compounds had long been known, real interest was shown in the early 1980s, first by Procter and Gamble, soon followed by Kao (Japan), SEPPIC, Hüls AG, and Henkel. The first commercial production of APGs started in 1989 (Horizon). Today, the worldwide production capacity is estimated at 70,000 - 80,000 tons per year. Currently, APGs are by far the most important carbohydrate-derived surfactant.
Advantageous properties of APGs, such as being well tolerated by the skin, their high synergism with anionic surfactants, and their foam-stabilizing properties make them particularly beneficial for use in manual dishwashing detergents. Furthermore, they have a low toxicity and are completely biodegradable. Because they are non-toxic and tolerated well by the skin, APGs also have potential for use in cosmetics.

Up to now, APGs have found limited applications in laundry detergent compositions due to their relatively high prices compared to linear alkylbenzene sulfonates (ionic) and nonionic alcohol ethoxylates.

1.6.2 Sucrose esters

Carbohydrate-derived esters have a much older industrial tradition than APGs and glucamides. Sucrose fatty acid esters are prepared by transesterification of fatty acid methyl esters or triglycerides and sucrose, in aprotic solvents such as DMSO and DMF. The use of methyl esters is advantageous because the equilibrium can be forced towards the sucrose ester by distilling off the methanol as it is formed. Disadvantages of the process are the cost of the solvents and their high boiling points which makes them difficult to remove. The products obtained are complex mixtures and since only the monoesters show favorable surface active properties, elaborate purification steps are necessary.

Due to their tedious preparation and relatively high price, sucrose fatty acid esters have only been used as specialty surfactants in cosmetics, food, and pharmacy where dermatological and toxicological criteria are stringent. The annual world production is only about 2,000 tons.

1.6.3 Sorbitan esters

Sorbitan (anhydro sorbitol) esters are prepared by esterification of sorbitol with fatty acids under acidic conditions (Scheme 2). The cyclic ether structures are formed in situ by loss of water from sorbitol during the industrial esterification process, under the influence of heat or acidic reagents or both. The annual world production of sorbitan esters exceeds 10,000 tons. These products are known as "Spans" and are used as emulsifiers and solubilizers in food, cosmetics, and pharmaceuticals. The Spans become more water-soluble when polyoxyethylene chains are grafted onto the cyclic moiety. These products are known as Tweens or polysorbates and have found applications in the same fields.
1.6.4 Glucamides

The Mega compounds, short for N-alkanoyl-N-methylglucamine, have a linear headgroup derived from D-glucitol which is coupled via an amide linkage to an alkyl chain (Figure 5). They are synthesized by the reaction of N-methyl-D-(-)glucamine with a fatty acid.\textsuperscript{101,102} Megas are polyols, but like the alkyl glucosides, they do not show a cloud point.\textsuperscript{103,104} The nomenclature of these compounds is quite confusing. They have been called N-alkanoyl-N-methylglucamides, N-alkanoyl-N-methylglucamines, N-methyl-N-D-glucalkanamide, and 1-(alkanoylmethyl amino)-1-deoxy-D-glucitols.\textsuperscript{102,103,104-107} Aggregation properties of a number of Megas have been described in the literature.\textsuperscript{102,103,104,105,106,108} Recently, oleoyl-N-methylglucamide was synthesized enzymatically.\textsuperscript{109}

The Megas are part of the industrially produced fatty acid glucamides; in the latter, the alkyl group on the nitrogen is not restricted to methyl.\textsuperscript{110-120} Like APGs, glucamides show synergistic effects with other types of surfactants and due to their polyol structure, they have a low irritation potential. A disadvantage of glucamides is their affinity towards calcium ions. They always have to be formulated with sequestering agents in order to avoid precipitation. N-Methylauroylglucamine is applied in dish-washing compositions.\textsuperscript{88,121} The annual world production is about 5,000 tons per year. However, if N-methylglucamine is present either as a residue from the synthesis or as a metabolism product during biodegradation, N-Methylauroylglucamine may form an N-nitrosoamine which is suspected to be carcinogenic. Therefore, its toxicological properties have not yet been satisfactorily defined.\textsuperscript{88}
1.6.5 Aldo(bio)namides

An aldonamide (e.g., gluconamide, Figure 6a) is the amide of an aldonic acid (a carbohydrate in which the anomeric aldehyde functionality has been oxidized to a carboxylic acid). An aldonamide based on a disaccharide is often called aldobionamide (e.g., lactobionamide, Figure 6b, or maltobionamide). The alkylgluconamides are less soluble in water than $\beta$-1-$n$-alkyl-D-glucopyranosides. Pfannemiiller et al.\textsuperscript{122,123} showed that upon cooling a hot solution, $n$-alkyl gluconamides form gels in water at a concentration of only a few percent. Gel formation is favored by strong intermolecular hydrogen bonds between the carbohydrate residues. The gels consist of rope-like fibrillar structures with a right-handed helical twist.\textsuperscript{124,125} The helical growth is probably induced by the hydrogen bonds between the amide linkages in combination with one or several chiral centres of the carbohydrate-moiety. On standing at room temperature, water is continuously expelled from the gel and crystalline needles start to grow; the gel is thus a metastable state. The molecular conformations of the gluconamide headgroups and the alkyl chains in the helical micellar fibres (all-anti) were elucidated.\textsuperscript{126-132} Due to the methylation on nitrogen, Megas are much less prone to gel formation.

Micelle formation by some aldo(bio)namides has also been studied.\textsuperscript{133-136} Although applications of aldonamides in detergents have been claimed in patents, these compounds are not (yet) produced on an industrial scale.\textsuperscript{137-139}

The carbohydrate-derived surfactants under study in this thesis also contain an amide functionality. Structures and relevant references are given in section 1.9.

1.7 Bolaamphiphiles and gemini surfactants based on carbohydrates

Interest in nonionic bolaamphiphiles\textsuperscript{140-156} and gemini surfactants based on carbohydrates is increasing. Some bolaamphiphiles based on carbohydrates that have been described in the literature are shown in Figure 7. The structures clearly resemble monomeric carbohydrate-derived surfactants. Much attention has been paid to the way the amide containing
bolaamphiphiles pack in the crystal lattice.\textsuperscript{145,146,147,151,152,153,154} The packing is strongly stabilized by inter- and intramolecular hydrogen bonds between the carbohydrate moieties and the amide functionalities. Some aggregation properties of these bolaamphiphiles were also examined; they tend to aggregate when the structures contain a certain number of methylene groups in the hydrophobic moiety.\textsuperscript{145,147}

\[
\text{HO} \quad \text{HO} \quad \text{HO} \quad \text{N} \quad \text{(CH}_2\text{n}) \quad \text{H} \quad \text{H} \quad \text{OH} \quad \text{OH} \quad \text{OH}
\]

\[
\text{HO} \quad \text{HO} \quad \text{HO} \quad \text{O} \quad \text{N} \quad \text{(CH}_2\text{n}) \quad \text{H} \quad \text{H} \quad \text{OH} \quad \text{OH} \quad \text{OH}
\]

\[
\text{HO} \quad \text{HO} \quad \text{HO} \quad \text{(CH}_2\text{n}) \quad \text{O} \quad \text{N} \quad \text{OH} \quad \text{OH} \quad \text{OH}
\]

**Figure 7.** From top to bottom: "bis-gluconamide", "1-glucosamide bolaamphiphile", and \(\alpha,\omega\)-di-(1-O-D-mannityl)-alkane.

"1-D-glucamide bolaamphiphiles" (\(N,N'\)-bis(\(\beta\)-D-galactopyranosyl)alkane-\(\alpha,\omega\)-dicarboxarnide) produce solid-like fibrous assemblies upon cooling a hot aqueous solution. The nature of the assemblies strongly depends on whether the hydrocarbon chain has an odd or an even number of methylene groups.\textsuperscript{152}

Generally, bolaform surfactants are less effective surfactants than conventional surfactants, but they often display biological activity and some drugs are, in fact, bolaform surfactants.\textsuperscript{157} Bolaamphiphiles can span a membrane, having one headgroup on the outside of the membrane and one on the inside. The membranes of extremophiles (bacteria that live under extreme temperature and pH conditions), are stabilized in this way.\textsuperscript{158} The potential applications of bolaamphiphiles include the formation of ultrathin monolayer membranes, inclusion of functionalities into membranes, and disruption of biological membranes.\textsuperscript{159}

As already mentioned, the field of gemini surfactants (or dimeric surfactants) is quite new. Most reported physico-chemical results on gemini surfactants concern bisquaternary ammonium surfactants of the alkanediy1-a.\(\omega\)-bis(dimethylalkylammonium halide) type. They are referred to as \(m\)-s-\(m\), 2\(X^+\); \(s\) is the number of carbon atoms in the spacer and \(m\) is the number of carbon atoms in the alkyl chains. \(X\) stands for the counterion.

Recently, the first nonionic gemini surfactants were described by Castro et al.\textsuperscript{156} and by our group (Figure 8).\textsuperscript{160} The gemini surfactants reported by Castro possess very short alkyl chains. The gemini surfactants that we have prepared had not appeared in the nonpatent literature.
However, they have been described in a number of patents by Procter & Gamble in which they are claimed as components in laundry, cleaning, fabric, and personal care compositions.\textsuperscript{161-165} Some other gemini surfactants have also been claimed in the same fields,\textsuperscript{166-169} but in general, it is not yet clear what the added value of gemini surfactants will be and in what fields they can be applied. However, industry is closely monitoring the research that is being undertaken in this subject.

![Figure 8](image1.png)

**Figure 8.** 1,5-Bis[6-O-(n-butyl α-D-glucopyranoside)] glutarate prepared by Castro et al.\textsuperscript{156} (above) and the bis(N-alkanoyl-1-amino-1-deoxy-D-glucityl)alkanes prepared by our group.

1.8 Brief outline of the thesis

Following this introductory chapter, Chapter 2 describes the syntheses and physical properties of extensive series of carbohydrate-derived surfactants, namely \textit{N-acyl,N-alkyl-β-D-aldosylamines} and \textit{N-acyl,N-alkyl-1-amino-1-deoxy-D-alditols} (Figure 9).\textsuperscript{170-182}

![Figure 9](image2.png)

**Figure 9.** Structures of the monomeric surfactants under study in this thesis (Chapter 2 - 4).
Aggregation of these surfactants is described in Chapter 3. The lyotropic behavior of these $N$-acyl,$N$-alkyl-$\beta$-D-aldosylamines and $N$-acyl,$N$-alkyl-1-amino-1-deoxy-D-alditols is a first indication of their properties in aqueous solutions. Critical micelle concentrations have been determined both by drop tensiometry and microcalorimetry. Drop tensiometry not only yields the CMCs, but also the surface tension at the CMC. Furthermore, the size of the headgroups at the air-water interface can be calculated. Microcalorimetry also offers insight into the thermodynamics of micellization.

In Chapter 4, the applicability of $N$-acyl,$N$-alkyl-$\beta$-D-aldosylamines and $N$-acyl,$N$-alkyl-1-amino-1-deoxy-D-alditols as cosurfactants in laundry detergent systems is demonstrated by measurements of the increase in performance of a benchmark powder upon addition of 2.5% of our carbohydrate-derived surfactants in mini-bottle tests. Other important parameters are also commented on, such as the foaming power of the surfactants. Environmental issues are also dealt with, such as biodegradation and biotoxicity.

In Chapter 5, a series of nonionic gemini surfactants based on carbohydrates (Figure 8) is described. The gemini surfactants have tetradecanoyl chain lengths and spacers containing 6, 8, or 10 carbon atoms. Their aggregation is studied using electron microscopy. Furthermore, the rheological behavior of one of the gemini surfactants has been examined.

Chapter 6 deals with two other series of gemini surfactants. In one series, the geminis have decanoyl chains and a spacer length varying from 2 to 12 carbon atoms. In the other series, the spacer has a fixed length of 10 methylene groups. The alkanoyl chains range from pentanoyl to hexadecanoyl. Their aggregation is studied using electron microscopy. Their oil solubilization capacities are determined by measuring the amount of hexane and toluene that can be solubilized by the gemini aggregates in water.

In the final chapter, we estimate the costs of these surfactants were they to be prepared on an industrial scale.

1.9 References


Nonionic Carbohydrate-Derived Surfactants and their Use in Industry


Chapter 1


Chapter 1

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