Chapter 4

Practical Applications of \(N\text{-Acyl}, N\text{-alkyl}\text{-}\beta\text{-d-aldosylamines}

and \(N\text{-Acyl}, N\text{-alkyl}\text{-1-amino-1-deoxy-}\text{d-alditols}

4.1 Introduction

We synthesized the carbohydrate-derived surfactants described in Chapter 2 in order to investigate their potential use as (co-)surfactants in detergent systems. Their performance, foam capacity and foam stability, biodegradation, and biotoxicity have been determined.

The performance of the carbohydrate-derived surfactants in oily soil removal was determined by adding each to a typical laundry detergent (powder) formulation in mini-bottle tests. The results were compared to the performance of a benchmark formulation.

In order to determine their applicability, we further measured foamability and foam stability of the surfactants. Consumers often relate the presence of foam in wash water to the effectiveness of a detergent solution. The absence of extensive foam is associated, albeit incorrectly, with an absence of cleaning action. Therefore, detergents used for hand-wash should produce sudsy water. In contrast, high foamabilities may cause technical problems in washing machines.

Surfactants applied in detergents and other industrial and household cleaning products are large volume chemicals. After being used, they pass the waste water treatment plants (WWTP) and finally end up in the environment. It is therefore important that surfactants are biodegraded (completely) within the period they reside in a WWTP. Another important issue is the toxicity of these substances (if they are not fully degraded in the WWTP) and their degradation products. We determined biodegradability using closed-bottle tests and tested the influence of the surfactants on the growth of four different micro-organisms.

Each subject introduced in this chapter (performance, foamability and foam stability, biodegradation and biotoxicity) is preceded by introductory paragraphs in which some background information is given and the techniques are explained briefly.

4.2 Detergency

4.2.1 Trends in detergency

Surfactants have found applications in textiles and fibres (17%), cosmetics and pharmacy (7%), mining, flotation and oil production (7%), paints, plastics and resins (5%), food industry
(5%), pesticides (2%), and in the paper industry (2%). Their main application is in the washing and cleaning sectors (44%).

Table 1 shows the ingredients of common laundry detergent systems. The actual concentrations of the ingredients depend on the type of detergent: heavy or low duty, powder or liquid, compact or conventional. Surfactants are the most important components in detergents. Their main function consists of assisting in the soil removal process. Structures of some surfactants used in detergents are shown in Figure 1.

Table 1. Laundry detergent ingredients (phosphate-free).

<table>
<thead>
<tr>
<th>Component</th>
<th>Function</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surfactants:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- anionics (alkyl benzenesulfonates)</td>
<td>cleaning and foam formation</td>
<td>10-30</td>
</tr>
<tr>
<td>- alkylsulfates, alkyl ethersulfates</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- nonionics (fatty alcohol ethoxylates)</td>
<td></td>
<td>0-10</td>
</tr>
<tr>
<td>Builders/Cobuilders:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- zeolite</td>
<td>reduction of water hardness: complexation of Ca²⁺ and Mg²⁺ and ion exchange</td>
<td>20-40</td>
</tr>
<tr>
<td>- polycarboxylate</td>
<td>maintaining alkaline conditions</td>
<td>5-30</td>
</tr>
<tr>
<td>- sodium carbonate</td>
<td>alkalinity, corrosion inhibition</td>
<td>5-20</td>
</tr>
<tr>
<td>- sodium silicates</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bleaches:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- perborate, percarbonate</td>
<td>chemical oxidation of persistent stains</td>
<td>0-15</td>
</tr>
<tr>
<td>- activator</td>
<td>perborate bleaching at lower temperatures (TAED)</td>
<td>0-5</td>
</tr>
<tr>
<td>Enzymes (e.g., proteases)</td>
<td>removal of protein-based stains</td>
<td>0-3</td>
</tr>
<tr>
<td>Fluorescent whitening agents:</td>
<td>adherence to fibers (&quot;whiter look&quot;)</td>
<td>0.1-0.5</td>
</tr>
<tr>
<td>- stilbene derivatives</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Antiredeposition agents:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- sodium carboxymethylcellulose</td>
<td>keep din in suspension once it has been removed from a fabric</td>
<td>0-2</td>
</tr>
<tr>
<td>Filler</td>
<td>filler, ionic strength</td>
<td>0-20</td>
</tr>
<tr>
<td>- sodium sulfate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Other</td>
<td>perfumes, dyes, anti-dye transfer polymers, soil release polymers, cationic surfactants (fabric softeners), bleaching stabilizers, foam inhibitors (silicon oils, surfactants), solvents (water, alcohols, glycols)</td>
<td></td>
</tr>
</tbody>
</table>

¹ Phosphate-containing detergents still have a significant share in Europe and even predominate in Eastern Europe, Asia, Africa, Australia, and Latin America. ² Actual amounts depend on the type of detergent. ³-⁴⁻⁵⁻⁶⁻⁷

The cleaning properties of soaps (sodium or potassium neutralized fatty acids) were already known in antiquity. Prior to World War I, laundry detergents were mainly composed of
Practical Applications of N-Acy1,N-alkyl-PD-aldosylamines and N-Acy1,N-alkyl-1-amino-1-deoxy-d-alditols

Figure 1. Soap (1), tetrapropylenebenzene sulfonates (2), linear alkylbenzene sulfonates (3), alkylsulfates (4), and fatty alcohol ethoxylates (5).

Soaps. At the beginning of this century the limitations of soap (alkalinity and sensitivity to hard water) were recognized and the first successful synthetic surfactants (the fatty alcohol sulfates) were launched in 1928 to overcome these problems.10 In the 1930s, long chain alkylbenzene sulfonates (ABS) were introduced as detergents. These first alkylbenzene sulfonates were highly branched and nonbiodegradable.11 Tetrapropylenebenzene sulfonate (TPS) was the main component of synthetic laundry detergents until the 1960s. After a very hot summer, the nonbiodegradability of TPS resulted in large foam formations in sewage treatment plant and waterways. Subsequently, TPS was replaced by the linear alkylbenzene sulfonates (LAS). To date, LAS is the main surface-active ingredient of commercial laundry detergents.12

Due to their implication in the eutrophication of waterways, phosphates were either banned in most Western countries in the 1980s (e.g. Switzerland) or their concentrations were fixed to a limit (c. 5.5% of the detergent formulation).7,8,9 Their function was taken over by so-called zeolite-based builder systems. In large parts of the world, however, phosphate-containing detergents (sodium tripolyphosphate, STP) either still have a significant market share (Great Britain, France, Spain) or even predominate (Eastern Europe, Central and Southern Asia, Africa, Australia and Latin America)? In the early 1970s, liquid detergents were introduced.6,13 Currently, liquid detergents have a majority market share of 50-60% in the U.S., whereas in Europe the use of liquid detergents is only about 13%.13,14

In 1987, the KAO Corporation in Japan launched the first compact high-density powder and evoked a revolution in this field.6,13 Formulating concentrated liquid products creates all sorts of technical challenges, e.g. keeping the formulation stable. Developments in this field continue.15,16 Today, compacts have largely taken over the market in the Western world.6,13,15

In the 1990s carbohydrate-derived surfactants have emerged as the fastest growing type of surfactants. Especially alkyl polyglucosides and alkyl glucamides are being used in detergents,
their major application field being dish-washing detergents\textsuperscript{10,17-23} (see also Chapter 1). These surfactants show synergism with other surfactants and thus the total amount of active surfactants in formulations can be decreased. However, due to their high prices compared to LAS and alcohol ethoxylates, these surfactants still find limited application in laundry detergents.

The properties of carbohydrate-derived surfactants fit into current consumer requirements for detergents: environmentally friendly products and sensitive skin formulations, efficiency in cold water and reduced water levels, smaller volume detergent package for the ease of storage and above all else, value.\textsuperscript{"}  

\subsection{Mechanism of detergency}

Cleaning is a complex process due to the large variety of soils and substrates (\textit{e.g.} \textit{cloth}).\textsuperscript{24} There are generally two types of \textit{soil}.	extsuperscript{24,25} Liquid (oily) soil which may contain sebum (skin fats), fatty acids, oils, fatty alcohols, \textit{etc.}\textsuperscript{24} Solid or particulate soil often contain hydrophobic and hydrophilic carbon, skin protein, iron oxide, and clay \textit{particles}.\textsuperscript{24} Adhesion of both types of soil to cloth occurs mainly by van der Waals forces. Nonpolar soils are therefore more difficult to remove than polar soils, especially when the substrate is hydrophobic (\textit{e.g.}, polyester).\textsuperscript{"}

Solid soil is removed by wetting of the substrate and the soil followed by adsorption of surfactants at the interfaces. Water induces the formation of electrical double layers at the \textit{substrate/liquid} and \textit{particle/liquid} interfaces. Adhesion is decreased by repulsion stemming from the charges on substrate and particle which almost always have the same sign. Anionic surfactants are especially effective in increasing the mutual repulsion between substrate and particle.\textsuperscript{"} Adsorption of surfactants at interfaces reduces the interfacial tensions\textsuperscript{66} and consequently the work of adhesion is diminished. Adsorption is probably the major mechanism of soil removal by \textit{nonionics}.

The removal of oily soil is mainly accomplished by the "rollback" mechanism. The contact angle between the soil and fabric increases at the detergent interface and the liquid soil rolls up and becomes more \textit{globular}.\textsuperscript{25} Surfactant molecules align themselves at the surfaces of both fabric and soil, so that each is, in effect, covered with a layer in which hydrophilic groups are directed towards the detergent \textit{solution}.\textsuperscript{27} These layers will therefore attract water molecules, which push between the grease and the fabric and weaken their hold on each other. For both types of soil, agitation is needed to aid in the final release of the stain.\textsuperscript{"}

Soil, removed from the substrate, should remain suspended in the liquid. Redeposition of the soil onto another part of the substrate should be prevented. Solid soil is kept in suspension mainly by electrical (ionic, particularly anionic, surfactants) and steric barriers (nonionic
Practical Applications of N-Acyl,N-alkyl-β-D-aldosylamines and N-Acyl,N-alkyl-1-amino-1-deoxy-D-alditols surfactants) between the substrate and the soil. Special components are also added to the detergent formulation to create electrical and steric barriers (e.g. sodium carboxymethylcellulose in laundry detergents). Oily soil is suspended by micellar solubilization and by emulsification (see also section 6.4.1). The adsorption and solubilizing power of surfactants seem to correlate well with detergency.

4.2.3 Performance: mini-bottle tests

Carbohydrate-derived surfactants with a dodecyl chain were selected for the detergency tests because they show the lowest surface tension at the CMC in each series. Mini-bottle tests were kindly performed at Unilever Research Vlaardingen, The Netherlands. The effect of the addition of the surfactants (2.5%) to a standard powder formulation (a benchmark powder) was analyzed at 30°C. Table 2 shows the contents of the formulation. As nonionic carbohydrate-derived surfactants are not likely to replace the cheap and well performing NaLAS in the immediate future, we tested their applicability as cosurfactants (2.5%).

Table 2. Formulation, conditions and cloths used in the bottle tests

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Conditions</th>
<th>Stain and cloth</th>
</tr>
</thead>
<tbody>
<tr>
<td>24% NaLAS, 2.5% carbohydrate-derived surfactant, 21% STP, 20% sodium sulfate, 10% sodium carbonate, 9% disilicate up to 100% water</td>
<td>temperature 30°C, dosage 1 g L⁻¹, liquor: cloth = 20:1, hardness either 0 or 30 °FH, Ca:Mg = 3:1, with or without 6 ppm metal ions (Cu:Fe:Zn = 1:1:1)</td>
<td>fat-pigment on polyester-cotton (AS-9), kaolin-sebum on cotton (WFK 10D), kaolin-sebum on polyester-cotton (WFK 20D), kaolin-sebum on polyester (WFK 30D), red wine on cotton (EMPA 114), tea on cotton (BC1)</td>
</tr>
</tbody>
</table>

The mini-bottle test is a screening method that compares the influence of different ingredients under identical (optimized) conditions. The method has the advantage that various ingredients and conditions can be tested in one run. Test cloths (4x4 cm) with a stain are put in a PE bottle containing the detergent system in a liquor:cloth ratio of 20:1. The bottles are put in a (front loader automatic) washing machine for 10 to 15 minutes (main wash) at 30°C.

The total amount of detergent formulation in a dosage of 1 g/L is 0.840 g. The additional 0.160 g is reserved for possible additional ingredients such as enzymes, perfumes, or cosurfactants.

Prior to the washing process, the detergent is dissolved in the wash water, dissolution properties which might influence detergency are therefore excluded.
The performance of detergents under the conditions mentioned in Table 2 was determined from the reflectance of the cloth at 460 nm. A white cloth shows a reflectance of about 90 R units (460 nm). The performance of the formulation containing an additional 2.5% carbohydrate-derived surfactants was tested on three types of cloth (cotton, polyester-cotton, and polyester) with different stains under several conditions (in demineralized water (O°FH), in hard water (30°FH)b, with or without 6 ppm transition metal ions ("metals") added).

The reflectance of each cloth washed with the formulation containing carbohydrate-derived surfactant was measured and these reflectances were summed. The same was done for the cloths washed with the plain formulation. The sum of the reflectances of the cloths washed with plain formulation was subtracted from the sum of the reflectances of the cloths washed with the carbohydrate-containing formulation. These led to AR values which are shown in Figures 2-9. When an additional amount of NaLAS (2.5%) is added to the plain formulation, the gain in performance was very low: 0.3-0.5 AR units in case demineralized water is used (O°FH) and 0.5 for water of 30°FH; the performance versus concentration curve of NaLAS levels off after about 24%.

The error in the measurements is ±0.5 AR units. Consumer-perceivable is a change of 1.5 AR units.

4.2.4 Effects of the carbohydrate-derived surfactants on performance

Eight compounds were tested in demineralized water (O°FH), and in hard water (30°FH). The influence of metal ions was determined, except for NC2nC12 glucose, NC3nC12 glucose, and NC3nC12 lactitol. Figures 2-9 show the results for these eight carbohydrate-derived surfactants compared with the standard formulation. All surfactants show a positive influence on the performance in demineralized water without addition of metals. The effect is particularly large in the case of NC2nC12 glucitol (11.3 reflectance units better than the benchmark powder). When metals are added the performance decreases (except for NC2nC12 glucitol) compared to the standard formulation.

In water of 30°FH, the acetylated carbohydrate-derived surfactants have a positive effect on the performance compared to the benchmark powder (in case of NC2nC12 lactose and NC2nC12 lactitol the effect is positive even when metals are added). The propionylated compounds show a decrease in performance compared to the benchmark powder at 30°FH.

Table 3 shows that although the performance of NC2nC12 glucitol decreases at 30°FH compared to O°FH, the effect of this surfactant on persistent stains like red wine (EMPA 114) and tea (BC 1) is still highly positive. Furthermore, the carbohydrate-derived surfactants are

\[1°FH = 0.1 \text{ mM Ca}^{2+}.\]
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particularly effective when the cloth is made of polyester (WFK 30D, O°FH), which is more hydrophobic than the negatively charged cotton.

Overall, the monosaccharide surfactants show higher increases in performance at O°FH, because these derivatives have a relatively larger hydrophobic part compared to the lactose and lactitol surfactants and thus show better surface-active properties (lower critical micelle concentrations and a lower surface tension at the CMC).

Table 3. Influence on the performance of the carbohydrate-derived surfactants on separate stains.

<table>
<thead>
<tr>
<th></th>
<th>AS(^a)</th>
<th>WFK 10(^b)</th>
<th>WFK 20(^b)</th>
<th>WFK 30(^b)</th>
<th>EMPA 114(^b)</th>
<th>BC 1(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC(<em>2)nC(</em>{12}) glucose</td>
<td>+</td>
<td>0</td>
<td>0</td>
<td>+++</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NC(<em>2)nC(</em>{12}) glucose</td>
<td>0</td>
<td>+</td>
<td>++</td>
<td>++++</td>
<td>+</td>
<td>0</td>
</tr>
<tr>
<td>NC(<em>2)nC(</em>{12}) gluclitol</td>
<td>++</td>
<td>+</td>
<td>++</td>
<td>++++</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>NC(<em>2)nC(</em>{12}) glucitol</td>
<td>0</td>
<td>0</td>
<td>•</td>
<td>++++</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NC(<em>2)nC(</em>{12}) lactose</td>
<td>0</td>
<td>-</td>
<td>0</td>
<td>+++</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NC(<em>2)nC(</em>{12}) lactose</td>
<td>0</td>
<td>+</td>
<td>0</td>
<td>+++</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NC(<em>2)nC(</em>{12}) lactitol</td>
<td>+</td>
<td>+</td>
<td>0</td>
<td>+++</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>AS(^a)</th>
<th>WFK 10(^b)</th>
<th>WFK 20(^b)</th>
<th>WFK 30(^b)</th>
<th>EMPA 114(^b)</th>
<th>BC 1(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC(<em>2)nC(</em>{12}) glucose</td>
<td>0</td>
<td>0</td>
<td>+</td>
<td>+</td>
<td>0</td>
<td>++</td>
</tr>
<tr>
<td>NC(<em>2)nC(</em>{12}) glucose</td>
<td>0</td>
<td>0</td>
<td>+</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NC(<em>2)nC(</em>{12}) gluclitol</td>
<td>0</td>
<td>0</td>
<td>---</td>
<td>0</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>NC(<em>2)nC(</em>{12}) glucitol</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>---</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>NC(<em>2)nC(</em>{12}) lactose</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>++</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>NC(<em>2)nC(</em>{12}) lactose</td>
<td>+</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>NC(<em>2)nC(</em>{12}) lactitol</td>
<td>+</td>
<td>+</td>
<td>0</td>
<td>+</td>
<td>+</td>
<td>0</td>
</tr>
<tr>
<td>NC(<em>2)nC(</em>{12}) lactitol</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-</td>
<td>0</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^a\)--- = -3.5 \leq \Delta R \leq -2.5; -- = -2.5 \leq \Delta R \leq -1.5; -- = -1.5 \leq \Delta R \leq -0.5; 0 = -0.5 \leq \Delta R \leq +0.5; ++ = +0.5 \leq \Delta R \leq +1.5; +++ = +1.5 \leq \Delta R \leq +2.5; ++++ = +2.5 \leq \Delta R \leq +3.5 etc. \(^b\)For an explanation of the abbreviations of the cloth see Table 2.

Generally, the acetylated carbohydrate-derived surfactants show better results than the propionylated surfactants, although the latter have lower CMCs and \(\gamma_{CMC}\) values. This difference is particularly pronounced at 30°FH. Probably, the propionylated compounds are more susceptible to calcium and magnesium ions (although they do not precipitate). It is unclear how the sugar-OH complex formation with these cations and metals is influenced by
the addition of one methylene group in the short acyl side chain.\textsuperscript{29-32} We were not able to measure the binding capacity of these surfactants with a calcium selective electrode, due to adsorption of the surfactants to the (PVC) membrane of the electrode.

\begin{figure}
\centering
\includegraphics[width=0.45\textwidth]{figure1.png}
\caption{Effect of the addition of 2.5\% NC\textsubscript{12} to glucose on the performance of a standard formulation in mini-bottle tests.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=0.45\textwidth]{figure2.png}
\caption{Effect of the addition of 2.5\% NC\textsubscript{12} to glucose on the performance of a standard formulation in mini-bottle tests.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=0.45\textwidth]{figure3.png}
\caption{Effect of the addition of 2.5\% NC\textsubscript{12} to glucitol on the performance of a standard formulation in mini-bottle tests.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=0.45\textwidth]{figure4.png}
\caption{Effect of the addition of 2.5\% NC\textsubscript{12} to glucitol on the performance of a standard formulation in mini-bottle tests.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=0.45\textwidth]{figure5.png}
\caption{Effect of the addition of 2.5\% NC\textsubscript{12} to glucitol on the performance of a standard formulation in mini-bottle tests.}
\end{figure}
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Figure 6. Effect of the addition of 2.5% \( \text{NC}_2\text{nC}_{12} \) lactose on the performance of a standard formulation in mini-bottle tests.

Figure 7. Effect of the addition of 2.5% \( \text{NC}_3\text{nC}_{12} \) lactose on the performance of a standard formulation in mini-bottle tests.

Figure 8. Effect of the addition of 2.5% \( \text{NC}_2\text{nC}_{12} \) lactitol on the performance of a standard formulation in mini-bottle tests.

Figure 9. Effect of the addition of 2.5% \( \text{NC}_2\text{nC}_{12} \) lactitol on the performance of a standard formulation in mini-bottle tests.

4.2.5 Effects of the carbohydrate-derived surfactants on redeposition

The removed soil should stay in solution and redeposition of the soil on the cloth should be prevented. Clean polyester and cotton cloths were added to the mini-bottles to test the influence of the carbohydrate-derived surfactants on the redeposition of soil at 0°FH and 30°FH. The results were compared with the results for the benchmark powder (Figures 10 to 21). The higher the reflectance, the lower the redeposition on the cloth.

The surfactants do not have a large influence on the redeposition on both polyester and cotton at 0°FH compared to the benchmark powder. On polyester at 30°FH, \( \text{NC}_2\text{nC}_{12} \) glucitol,
increases redeposition. Again, NC\textsubscript{2}nC\textsubscript{12} glucitol, NC\textsubscript{2}nC\textsubscript{12} lactose, NC\textsubscript{2}nC\textsubscript{12} lactitol, and NC\textsubscript{3}nC\textsubscript{12} lactose show the same results on cotton at 30°FH.

There is no clear trend in the redeposition at 30°FH, but it is interesting to see that the surfactants that show the highest increase in performance, NC\textsubscript{2}nC\textsubscript{12} glucitol at 0°FH and NC\textsubscript{2}nC\textsubscript{12} lactose at 30°FH, also behave well in the redeposition tests (no influence on the redeposition at 0°FH and a decrease in redeposition at 30°FH) compared to the base powder.

Figure 10. Effect on redeposition on polyester at 0°FH.

Figure 11. Effect on redeposition on polyester at 0°FH.

Figure 12. Effect on redeposition on polyester at 0°FH.

Figure 13. Effect on redeposition on polyester at 30°FH.
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Figure 14. Effect on redeposition on polyester at 30°FH.

Figure 15. Effect on redeposition on polyester at 30°FH.

Figure 16. Effect on redeposition on cotton at 0°FH.

Figure 17. Effect on redeposition on cotton at 0°FH.

Figure 18. Effect on redeposition on cotton at 0°FH.

Figure 19. Effect on redeposition on cotton at 30°FH.
Figure 20. Effect on redeposition on cotton at 30°FH.  
Figure 21. Effect on redeposition on cotton at 30°FH.

4.3 Foam formation and foam stability\textsuperscript{33-39}

Excessive foaming of detergents in washing machines is undesirable. In contrast, abundant foam formation and high foam stabilities are required by consumers who use hand-wash protocols. This requirement is only for the consumer's eye; in reality good foaming properties do not imply good cleaning properties.

Foam is a dispersion of gas in liquid in which gas predominates.\textsuperscript{33} Stable foam lamellae can be formed when substances are present that lower the surface tension and that impart viscoelastic behavior on the surface.\textsuperscript{28} There are two types of foam. "Kugelschaum" is formed just above the liquid and the bubbles are spherical. Polyhedral foam is formed on top of the Kugelschaum due to drainage caused by gravity.\textsuperscript{33}

The amount of foam formed under a given set of conditions is a measure of foamability (the capacity to form foam). The decay of the foam volume over time is a measure of foam stability.\textsuperscript{40}

Anionic surfactants are generally good foamers. In contrast to the excellent foam production and stability of anionic surfactants, nonionics show less foam formation and stability.\textsuperscript{41-44} APGs are moderate foamers, but they are excellent foam stabilizers and have synergistic effects in combination with anionic surfactants.\textsuperscript{47}

The foamability and the stability of the foam formed were tested by means of the Ross-Miles technique for all eight carbohydrate-derived surfactants\textsuperscript{40,45,46} with a dodecyl chain. Ross and Miles developed this widely-used technique in 1941.\textsuperscript{44,47} A surfactant solution (200 mL) is poured quickly and from a 90 cm distance into a receiver filled with 50 mL of the same surfactant solution. As the solution pours into the receiver, foaming takes place.

The foamability and the foam stability of the pure surfactant solutions (0.5 g L\textsuperscript{-1}) were compared to NaLAS and Synperonic (an alcohol ethoxylate with an average composition of
The dependence of foaming properties on chain length was studied by measuring the foaming properties of the three acetylated glucitol derivatives (NC2nC8 glucitol, NC2nC10 glucitol and NC2nC12 glucitol). The two surfactants which showed promising performance, NC2nC12 glucitol (at 0°FH) and NC2nC12 lactose (at 30°FH), were subjected to conditions more closely related to applications. The influence of salts and soil on foam formation and foam stability were tested and compared to NaLAS solutions. Then we added 2.5% of NC2nC12 glucitol and NC2nC12 lactose to a standard formulation (NaLAS, 3 g/L, 10 g/L soil, 16 °FH) to investigate whether our surfactants could stabilize the foam formation under these conditions.

### 4.3.1 Foaming properties of pure solutions of carbohydrate-derived surfactants

Figure 22 shows the foaming properties of the glucose and glucitol derivatives, compared to NaLAS and syneronc (nonionic) at room temperature (22°C). The initial foam height was measured after 20 seconds. Obviously, NaLAS shows very good foaming properties, with a high initial height (almost 150 mm). The structure of the foam is quite open and remains stable for at least half an hour. The bubbles are relatively large and shiny compared to foams of the other surfactants. The initial foam height of syneronc is much less (about 80 mm) than was observed for NaLAS and the foam becomes hollow and collapses after 20 minutes.

![Figure 22. Foaming properties of glucose and glucitol derivatives, 0.5 g L⁻¹, 0°FH, 22°C.](image-url)

Both glucose derivatives show moderate initial foam heights and the foams collapse rapidly.
**NC₃nC₁₂** glucitol does not dissolve in water at room temperature. **NC₂nC₁₂** glucitol forms a very stable foam with a fairly high initial foam height. After a while, the foam in the middle section becomes more transparent, but the foam does not either collapse or hollow.

In Figure 23, the foam formation and stabilities of the lactose and lactitol derivatives are compared to **NaLAS** and synperonic. **NC₂nC₁₂** lactitol collapses rapidly and **NC₂nC₁₂** lactose collapses somewhat slower. **NC₃nC₁₂** lactose and **NC₃nC₁₂** lactitol have higher initial heights and form more stable foams than their acetylated counterparts. However, they do hollow out and the foam heights presented for these two derivatives are a bit misleading. The hole in the foam formed by **NC₃nC₁₂** lactitol has a larger cross section than the hole in the **NC₃nC₁₂** lactose solution.

![Figure 23](image)

**Figure 23. Foaming properties of lactose and lactitol derivatives, 0.5 g L⁻¹, 0°FH, 22°C.**

The dependence of foaming properties on the alkyl chain length is shown in Figure 24.**⁴⁸,⁴⁹** **NC₂nC₈** glucitol hardly foams and after 20 seconds almost all the foam formed has collapsed. Both **NC₂nC₁₀** and **NC₂nC₁₂** glucitol form stable foams. The foam of **NC₂nC₁₀** glucitol seems somewhat less stable than that formed by **NC₂nC₁₂** glucitol, the former becomes thinner and after a while, a few small holes appear. The initial height in case of the **NC₂nC₁₀** glucitol is higher. These results indicate that there might be an optimum in the relationship between foam height and chain length.** It should also be noted that the concentration of 0.5 g L⁻¹ is lower than the critical micelle concentration of **NC₂nC₈** glucitol, which is 7.4 g L⁻¹.**⁵
4.3.2 Influence of salts and soil on the foaming properties of the carbohydrate-derived surfactants

The foaming properties of $\text{NC}_2\text{nC}_{12}$ glucitol and $\text{NC}_2\text{nC}_{12}$ lactose, which performed well in the mini-bottle tests in demineralized water and water of $30^\circ$FH, respectively, were
investigated further. The influence of salt and soil was determined at 0°FH (NC\textsubscript{2}nC\textsubscript{12} glucitol) and at 30°FH (NC\textsubscript{2}nC\textsubscript{12} lactose) and compared with NaLAS (Figures 25 and 26). The salts and the dosage were the same as in a detergent composition, about 2 g L\textsuperscript{-1} which consisted of 0.5 g L\textsuperscript{-1} surfactant (24%) and 1.25 g L\textsuperscript{-1} base mix (sodium carbonate (10%), sodium sulfate (20%), STP (21%) and disilicate (9%)).

![Figure 26. Influence of soil on the foamability and foam stability of NC\textsubscript{2}nC\textsubscript{12} glucitol (0°FH, 22°C) and NC\textsubscript{2}nC\textsubscript{12} lactose (30°FH, 22°C).](image)

The glucitol derivative (at 0°FH) behaved the same with and without mix. The lactose derivative also showed nearly the same behavior with base mix (at 30°FH) and without base mix (0°FH). The initial foam height was somewhat higher when base mix was added, and the foam seemed to be stable for a longer period (10 minutes). However, in this case the foam became hollow after 5 minutes.

When both base mix and soil (20 g L\textsuperscript{-1}) were added, the foam formation and foam stability of NC\textsubscript{2}nC\textsubscript{12} glucitol (at 0°FH) behaved identically to the detergent composition with NaLAS. The initial appearance of the foam has a close resemblance to the foam formed by pure NaLAS (the bubbles are larger and it is shiny). After a while, the structure of the foam formed by NC\textsubscript{2}nC\textsubscript{12} glucitol becomes transparent. In the NaLAS-containing formulation, the foam with soil has relatively smaller bubbles and the foam is less glossy than without the soil. The middle section of the foam becomes transparent (after 10 minutes).

At 30°FH, the NaLAS-formulation (with base mix and soil) shows a low initial foam height and the foam collapses gradually. The foam formed by NC\textsubscript{2}nC\textsubscript{12} lactose (with base mix and soil) collapses even faster.
4.3.3 A practical application of $\text{NC}_3\text{nC}_{11}$ glucitol and $\text{NC}_3\text{nC}_{12}$ lactose

Nonionic carbohydrate-derived surfactants may find application as cosurfactants in detergents, but in the 
\textit{foreseeable} future, they will not replace the cheap and well \textit{performing} NaLAS. Therefore, we added 2.5\% of these surfactants (the same amount as used in the mini-bottle tests) to a standard \textit{formulation} of NaLAS to see whether these surfactants have a stabilizing effect on foam formation (Fig. 27). Addition of 2.5\% of $\text{NC}_3\text{nC}_{12}$ lactose does not stabilize the \textit{foam}, but rather destabilizes it slightly. However, the surfactant that showed good performance in the mini-bottle tests ($\text{NC}_3\text{nC}_{12}$ glucitol) also stabilizes the foam of the standard formulation. Figures 28 and 29 (taken after 20 minutes) clearly show this stabilization.

![Graph showing foam height over time with different surfactants](image-url)

\textbf{Figure 27.} Addition of 2.5\% $\text{NC}_3\text{nC}_{12}$ glucitol or $\text{NC}_3\text{nC}_{12}$ lactoses to a standard formulation of 3 g L$^{-1}$, 10 g L$^{-1}$ soil ($16^\circ\text{PH}, 22^\circ\text{C}$).
4.4 Biodegradability

The biodegradability of a substance indicates its ability to undergo microbial attack. Biodegradation can be described as the elimination of an organic compound from the ecosystem by metabolic activity of micro-organisms present in that system. Biodegradation can either be primary or ultimate. Primary or functional biodegradation is the biodegradation to the minimum extent necessary to change the identity of the compound. The ultimate biodegradation or mineralization is the conversion of the compound to CO₂, H₂O, and additional inorganic compounds if other elements than C, H, and O are present. Degradation to such an extent that undesirable properties of the compound (such as toxicity, foaming) are removed is deemed environmentally acceptable. From an ecological point of view only complete biodegradation is sufficient. Moreover, the compound should not only biodegrade fully but also rapidly. A compound that biodegrades fully, but very slowly, may persist in the environment for a long time. Therefore, the rate of degradation is one of the most important factors that influence the rate of biodegradation are the rate at which the organic substrate can be oxidized biochemically, the initial number of bacteria, and the acclimation of the
Practical Applications of N-Acyl,N-alkyl-β-D-aldosylamines and N-Acyl,N-alkyl-1-amino-1-deoxy-D-alditols

Micro-organisms. Biodegradability of hydrocarbons is impeded by branching and increasing chain length.50

In general, organic compounds are not completely degraded to CO₂, H₂O, and inorganic compounds. Part of the degraded surfactant will be used as a nutrient source and is built into the cells. This process should also be considered as biodegradation.

4.4.1 Biochemical oxygen demand

The technique we used to determine the ultimate biodegradability is based on the decrease in oxygen concentration of a surfactant solution containing micro-organisms from a WWTP. The decrease in oxygen concentration is due to oxidation of the surfactants by micro-organisms and is called the Biochemical Oxygen Demand (BOD). ""

This technique was initially used to determine the contribution of compounds released into the aquatic environment to eutrophication by measuring the amount of oxygen withdrawn from surface water after n days upon oxidation (contribution to eutrophication) of the compounds (NEN 6634).53 BOD measurements are now also used to determine the ultimate biodegradability of compounds. An incubation time is chosen of either five (BOD₅) or 28 days (BOD₂₈) and a compound is considered readily biodegradable if the amount of biodegradation is ≥ 60%.50,51 In our case, the BOD was measured after 20 days.

BOD is measured in a closed-bottle test.50,53 Each surfactant (2 mg L⁻¹) is added to a bottle with a low number of micro-organisms from a waste water treatment plant in a mineral nutrient solution that is saturated with oxygen. The surfactant is the only available carbon source. The bottles are closed in such a way that no air bubbles are introduced. After the incubation time in the dark at 20-21°C, the oxygen concentration is measured electrochemically.

The amount of biodegradation can be calculated by comparing the BOD with the Theoretical Oxygen Demand (TOD), the amount of oxygen in grams required for a complete oxidation of 1 g of a given compound. The percentage biodegradation is (BOD/TOD) × 100%.

For a compound with molecular formula CₙHₙOₙNₓ the TOD can be calculated according to the following equation (if the nitrogen is released as ammonia):50,54

\[
\begin{align*}
\text{TOD} &= \left[\left(\text{4c} + \text{h} - 2\text{O} - 3\text{n}\right) \cdot 8\right] / \text{M g/g} \\
\text{C}_{\text{n}}\text{H}_{\text{n}}\text{O}_{\text{n}}\text{N}_{\text{x}} + [2\text{c} + \left(\text{h}\cdot3\text{n}\right)/2 \cdot \text{O}] &= \text{c CO₂} + \left(\text{h}\cdot3\text{n}\right)/2 \text{H₂O} + \text{n NH₃}
\end{align*}
\]

Equation (1)

Oxidation of \(\text{NH}_4^+\) is inhibited by the addition of n-allylthiourea.
4.4.2 Extent of biodegradation of the carbohydrate-derived surfactants

Table 4 shows the extent of biodegradation of the carbohydrate-derived surfactants after 20 days. No clear trends can be observed between the different lengths of the alkyl chain. Therefore, the individual results for the different chain lengths per headgroup are not shown. The extent of biodegradation depends on the nature of the headgroup. The glucose-derived compounds are the least sensitive to microbial attack. The surfactants with a glucitol headgroup show the highest biodegradability. The glucitol-derived surfactants are followed by the surfactants with a lactose or lactitol headgroup. Most likely, microorganisms hydrolyze the \( \beta \)-glycosidic linkage between the galactose and glucose/glucitol fragments of the lactose/lactitol headgroup.

**Table 4.** Biodegradation of glucose-, glucitol-, lactose-, and lactitol-derived surfactants, and three reference compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Biodegradation after 20 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glucose-derived surfactant</td>
<td>30% (± 5%)</td>
</tr>
<tr>
<td>Glucitol-derived surfactants</td>
<td>45% (± 5%)</td>
</tr>
<tr>
<td>Lactose/lactitol-derived surfactants</td>
<td>35% (± 5%)</td>
</tr>
<tr>
<td>( C_{12}H_{25}N\left(CH_{3}\right)_2Br )</td>
<td>~ 70%</td>
</tr>
<tr>
<td>( C_{12}H_{25}(EO)_6 )</td>
<td>~ 70%</td>
</tr>
<tr>
<td>NaLAS</td>
<td>0%</td>
</tr>
</tbody>
</table>

We used dodecyltrimethylammonium bromide, hexaethylene glycol monododecylether and the sodium salt of dodecylbenzene sulfonate as reference compounds. Both dodecyltrimethylammonium bromide and hexaethylene glycol monododecylether can be termed readily biodegradable as they show a biodegradation of about 70% after 20 days. The results for NaLAS are striking. NaLAS is the main component in powder detergents and numerous studies on NaLAS have demonstrated that both primary and ultimate biodegradation occur rapidly under a variety of laboratory and field conditions. The accuracy of the closed-bottle tests was established by correct values of the standards (a solution mixture of glucose and glutamic acid). Moreover, the biodegradation tests of NaLAS were performed in duplicate twice and the inability to biodegrade was reproducible. The result obtained might be due to a different composition of the linear alkylbenzenesulfonate than the one applied in detergents.

We expected the carbohydrate-derived surfactants to be more easily degraded by microorganisms of a WWTP that are adapted to carbohydrate-derived compounds. We therefore
repeated the closed-bottle test for C_{12} lactose- and lactitol-derivatives with influent and effluent of the WWTP of AVEBE, a starch company. Indeed, the extent of biodegradation increases about 5%.

The biodegradation results of the carbohydrate-derived surfactants are in agreement with values for other nitrogen-containing, carbohydrate-derived surfactants.\textsuperscript{59,60} However, the biodegradation is not sufficient to classify the compounds as readily biodegradable. As the APGs are readily biodegradable, the difference in biodegradability is probably due to the amide functionality. The results from the closed-bottle tests performed with micro-organisms from the AVEBE WWTP show that biodegradation might improve if more time for adaptation of the micro-organisms would be provided.\textsuperscript{48,49,50,51} Also, the biodegradation will increase somewhat when a 28 days incubation period is selected.

This biodegradation test is an acceptancy test. Compounds that do not satisfy the 60\% requirement are not rejected immediately and further biodegradation tests are warranted.\textsuperscript{61}

4.5 Toxicity

Surfactants are surface-active agents and have the property of decreasing the surface tension of water. When detergents are drained into the aquatic environment, a critical situation arises for fish when the surface tension of water is reduced to 50 mN m\(^{-1}\). At this value, irreversible damage occurs at the skin epithelium of fishes’ gills.\textsuperscript{61} The lower the biodegradability, the higher toxicity towards fish. Primary biodegradation of surfactants (in which \textit{e.g.}, their property to reduce the surface tension is removed) can already lower the aquatic toxicity by two orders of magnitude. The most important factor in determining the aquatic environmental tolerance of a compound is therefore its biodegradability, followed by its toxicity.\textquoteleft" Compounds with a high acute toxicity, should be readily biodegradable in a short period. As already mentioned, the main ingredient in detergents until the 1960s was tetrapropylbenzyl sulfonate (TSP). Due to the branched alkyl chain, the compound was not biodegradable and was replaced by the linear alkylbenzenesulfonates (LAS). LAS is more toxic than TPS, but the LAS compounds biodegrade readily (producing much less toxic products).\textquoteleft"

Most tests to determine the aquatic toxicity of a compound are performed on fish, daphnia (water fleas), and additionally on bacteria and algae.\textsuperscript{62} The acute fish toxicities of most surfactants are in the range 1-10 mg L\(^{-1}\) (this is an LC\(_{50}\) value; a concentration at which 50\% of the fish do not survive)." Daphnia are generally about a factor of 5 - 7 less sensitive to surfactants than fish are. The effect of surfactants on bacteria is even smaller. Increasing the length of the alkyl chain of LAS increases the toxicity towards bacteria. Nonionic ethoxylated surfactants become less toxic upon increasing length of the polyethylene glycol residue."
As a first indication of the toxicity, we measured the influence of the carbohydrate-derived surfactants on the growth rate of micro-organisms (acute biotoxicity). The growth curves of micro-organisms in nutrient-rich media can be monitored by means of continuously measuring the optical density.

A general growth curve starts with an adaptation period at which the growth rate is zero. After this lag phase the growth rate gradually increases and reaches exponential growth. Eventually, the cell growth ceases and ultimately, cells decay due to the exhaustion of the limiting substrate necessary for cell growth. The toxicity is assessed during the phase of exponential growth. It is based on the time elapsed before a specific growth (difference in optical density) has been reached. The \( IC_{50} \) value (Inhibitory Concentration) of a surfactant is the concentration at which the growth rate is lower than 50% of the controls.

### 4.5.1 Acute biotoxicity tests of the carbohydrate-derived surfactants

We used four different micro-organisms for the biotoxicity tests, the *Saccharomyces cerevisiae* (a yeast), *Escherichia coli* (a gram - bacterium), *Pseudomonas putida* (a gram - bacterium), and *Bacillus subtilis* (a gram + bacterium).

The surfactant concentrations tested were 0, 1, 20, 100, 500, 1000, and 5000 mg L\(^{-1}\), respectively. We used the same reference compounds as for the biodegradation experiments (\(\text{NaLAS}, \text{dodecyltrimethylammonium bromide and hexaethylene glycol monododecylether}\)). The \( IC_{50} \) values are shown in Tables 5 and 6.

The carbohydrate-derived surfactants show inhibitory concentrations ranging from 20 to 5000 mg/L towards *P. putida* and *B. subtilis*. The \( IC_{50} \) values decrease with increasing chain length. The surfactants become more toxic just below and in the concentration range where they tend to form micelles. At these concentrations, they probably start to disrupt the cell membranes. The biotoxicities of the surfactants with a \( C_{12} \) alkyl chain are comparable to the biotoxicities of the reference compounds, which also have alkyl chains containing twelve carbon atoms.
Table 5. Biotoxicities of glucose- and glucitol-derived surfactants, and three reference surfactants.\(^a\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>(S.) cerevisae</th>
<th>(E.) coli</th>
<th>(P.) putida</th>
<th>(B.) subtilis</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{NC}_2\text{nC}_4) glucose</td>
<td>(&gt;5000)</td>
<td>5000</td>
<td>5000</td>
<td>5000</td>
</tr>
<tr>
<td>(\text{NC}_3\text{nC}_5) glucose</td>
<td>5000</td>
<td>5000</td>
<td>5000</td>
<td>5000</td>
</tr>
<tr>
<td>(\text{NC}<em>3\text{nC}</em>{10}) glucose</td>
<td>1000</td>
<td>1000</td>
<td>500</td>
<td>500</td>
</tr>
<tr>
<td>(\text{NC}<em>3\text{nC}</em>{10}) glucose</td>
<td>500</td>
<td>500</td>
<td>500</td>
<td>500</td>
</tr>
<tr>
<td>(\text{NC}<em>2\text{nC}</em>{12}) glucose</td>
<td>100</td>
<td>100(^b)</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>(\text{NC}<em>3\text{nC}</em>{12}) glucose</td>
<td>100</td>
<td>100(^b)</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>(\text{NC}_3\text{nC}_4) glucitol</td>
<td>(&gt;5000)</td>
<td>5000</td>
<td>5000</td>
<td>5000</td>
</tr>
<tr>
<td>(\text{NC}_3\text{nC}_4) glucitol</td>
<td>5000</td>
<td>5000</td>
<td>5000</td>
<td>5000</td>
</tr>
<tr>
<td>(\text{NC}<em>3\text{nC}</em>{10}) glucitol</td>
<td>500</td>
<td>500</td>
<td>500</td>
<td>500</td>
</tr>
<tr>
<td>(\text{NC}<em>3\text{nC}</em>{10}) glucitol</td>
<td>500</td>
<td>500</td>
<td>500</td>
<td>500</td>
</tr>
<tr>
<td>(\text{NC}<em>3\text{nC}</em>{12}) glucitol</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>(\text{NC}<em>3\text{nC}</em>{12}) glucitol(^c)</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>(\text{C}<em>{12}\text{H}</em>{25}\text{N}^+(\text{CH}_3)_3\text{Br}^-)</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>20</td>
</tr>
<tr>
<td>(\text{C}<em>{12}\text{H}</em>{25}(\text{EO})_6)</td>
<td>100</td>
<td>5000</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>NaLAS</td>
<td>500</td>
<td>500</td>
<td>100</td>
<td>20</td>
</tr>
</tbody>
</table>

\(^a\) The concentration at which the growth inhibition is exactly 50% lies between the value given in the tables and the next lower test concentration.\(^b\) 5000-100: Growth curve starts very slowly, followed by a rapid growth.\(^c\) 5000-500: The compound precipitates.

The effect on the growth is similar for all four micro-organisms in the case of the monosaccharide-derived surfactants. However, the lactose- and lactitol-derived surfactants with a \(\text{C}_{10}\) and a \(\text{C}_{12}\) alkyl chain are much less toxic towards \(S.\) cerevisae and \(E.\) coli than towards \(P.\) putida and \(B.\) subtilis. \(\text{NC}_2\text{nC}_{12}\) lactose, \(\text{NC}_3\text{nC}_{12}\) lactitol, \(\text{NC}_3\text{nC}_{12}\) lactose, and \(\text{NC}_3\text{nC}_{12}\) lactitol were tested at concentrations as high as 10 and 15 g L\(^{-1}\) and even at these high concentrations (much higher than would ever be encountered in waste water) the growth curves of \(S.\) cerevisae and \(E.\) coli were unaffected. The toxicity of the disaccharide-derived surfactants towards these two microorganisms \((S.\) cerevisae and \(E.\) coli\) is also much lower than that for the monosaccharide-derived surfactants. As already mentioned, the toxicity of polyethylene glycols towards bacteria also decreases with increasing headgroup size.
### Table 6. Biotoxicities of lactose- and lactitol-derived surfactants.

<table>
<thead>
<tr>
<th>Compound</th>
<th><em>S. cerevisae</em></th>
<th><em>E. coli</em></th>
<th><em>P. putida</em></th>
<th><em>B. subtilis</em></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IC₅₀ (mg L⁻¹)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NC₂₀C₄ lactose</td>
<td>&gt;5000</td>
<td>&gt;5000</td>
<td>5000</td>
<td>&gt;5000</td>
</tr>
<tr>
<td>NC₂₀C₄ lactose</td>
<td>&gt;5000</td>
<td>&gt;5000</td>
<td>5000</td>
<td>&gt;5000</td>
</tr>
<tr>
<td>NC₂₀C₄ lactose</td>
<td>&gt;5000</td>
<td>&gt;5000</td>
<td>500</td>
<td>5000</td>
</tr>
<tr>
<td>NC₂₀C₄ lactose</td>
<td>&gt;5000</td>
<td>&gt;5000</td>
<td>100</td>
<td>500</td>
</tr>
<tr>
<td>NC₂₀C₄ lactose</td>
<td>&gt;5000</td>
<td>&gt;5000</td>
<td>20</td>
<td>100</td>
</tr>
<tr>
<td>NC₂₀C₄ lactitol</td>
<td>&gt;5000</td>
<td>&gt;5000</td>
<td>5000</td>
<td>&gt;5000</td>
</tr>
<tr>
<td>NC₂₀C₄ lactitol</td>
<td>&gt;5000</td>
<td>&gt;5000</td>
<td>1000</td>
<td>5000</td>
</tr>
<tr>
<td>NC₂₀C₄ lactitol</td>
<td>&gt;5000</td>
<td>&gt;5000</td>
<td>500</td>
<td>500</td>
</tr>
<tr>
<td>NC₂₀C₄ lactitol</td>
<td>&gt;5000</td>
<td>&gt;5000</td>
<td>100</td>
<td>500</td>
</tr>
<tr>
<td>NC₂₀C₄ lactitol</td>
<td>&gt;5000</td>
<td>&gt;5000</td>
<td>20</td>
<td>100</td>
</tr>
</tbody>
</table>

*The concentration at which the growth inhibition is exactly 50% lies between the value given in the tables and the next lower test concentration.*

NaLAS shows considerable growth inhibition towards *P. putida* and *B. subtilis* far below its CMC (about 0.9 g L⁻¹). Dodecyltrimethylammonium bromide has IC₅₀ values far below its CMC value (which is about 1.9 g L⁻¹) for all four micro-organisms. As is the case for the lactose- and lactitol-derived surfactants, NaLAS and C₁₂H₂₅(EO)₆ show larger IC₅₀ values for *S. cerevisae* and *E. coli* than for *P. putida* and *B. subtilis*.

Matsumura et al. also determined the toxicity of a number of surfactants with a monosaccharide headgroup. In accordance with our results, they also found an increase in toxicity when the alkyl chain length is increased. Some compounds were less toxic towards *E. coli* than towards other bacteria, including the reference compounds (several ethoxylated dodecanols and tetradecanols).

#### 4.6 Conclusions

Three carbohydrate-derived surfactants show promising results in preliminary tests for their use as cosurfactants. NC₂₀C₄₆ glucitol would be a good cosurfactant in detergency products in
Brazil, for example, where tap water contains limited amounts of calcium and magnesium ions (2°FH). NC₂₆C₁₂ lactose and NC₂₆C₁₈ lactitol have potential as cosurfactants in hard water. In India, for example, the hardness of the water is very high (30°FH, or even higher). NC₂₆C₁₂ glucose shows good performance under both conditions (in demineralized water and in water of 30°FH), however, further tests are needed to see how the performance of this surfactant is influenced by the addition of metals.

NC₂₆C₁₂ glucitol and NC₂₆C₁₈ glucitol show high initial foaming heights and good foam stabilities. NC₂₆C₁₂ glucitol also stabilizes the foam formed by the standard detergent formulation in the presence of soil at 16°FH. These properties also make them interesting components for dish washing detergents.

In preliminary biodegradability tests, extents of biodegradation of 30-45% (depending on the nature of the headgroup) were found. These percentages are insufficient to award the surfactants the specification of readily biodegradable. Further research into their biodegradability and their biodegradation pathways is clearly warranted.

The surfactants show low to very low biotoxicity compared to the reference compounds used (NaLAS, dodecyltrimethylammonium bromide and hexaethylene glycol monododecylether).

In conclusion, these carbohydrate-derived surfactants have a pleasing potential as cosurfactants in detergency systems. Shortly before this thesis was written, Borculo patented applications of these surfactants in detergent systems.⁵⁵

4.7 Experimental

Materials. The carbohydrate-derived surfactants used in the experiments were synthesized as described in Chapter 2. Sodium dodecylbenzene sulfonate, sodium salt and dodecyltrimethylammonium bromide were purchased from Aldrich. Hexaethylene glycol monododecyl ether was purchased from Fluka. Synperonic A7 (alcohol ethoxylate C₁₂/E₀₇ on average, supplied from ICI) and the NaLAS used in the foam experiments were kindly provided by Unilever Research, Vlaardingen.

4.7.1 Performance (mini-bottle tests)
The performance of the carbohydrate-derived surfactants was determined at Unilever Research Vlaardingen (The Netherlands). Test cloths (4.4 cm) with a stain (Table 3) were put in a PE bottle containing the detergent system (Table 3) in a liquor/cloth ratio 20:1. The bottles were put in a washing machine for 10 minutes (main wash) at 30°C. The cloths were quickly rinsed twice and dried and the reflection was measured at 460 nm with a Minolta reflection spectrophotometer.

NC₂₆C₁₂ glucitol, NC₂₆C₁₂ glucitol, NC₂₆C₁₂ lactose, NC₂₆C₁₂ lactose, and NC₂₆C₁₂ lactitol were tested in demineralized water (0°FH), and in hard water (30°FH), both with and without 6 ppm
transient metal ions ("metals") added. \(\text{NC}_2\text{nC}_{12}\) glucose, \(\text{NC}_3\text{nC}_{12}\) glucose and \(\text{NC}_3\text{nC}_{12}\) lactitol were also tested in demineralized water (O°FH) and in hard water (30°FH). 1°FH = 0.1 mM Ca\(^{2+}\).

### 4.7.2 Foam formation and foam stability

The formation of foam and the stability of the foam was measured by means of the Ross-Miles method. Each time, 200 mL of a surfactant solution was poured into 50 mL of the same solution. The foam height was read after 20 seconds (initial foam height), 5, 10, 20, and 30 minutes. All measurements were performed in duplicate, the reproducability was good.

**Preparation of the solutions, pure solutions**

Solutions of 0.5 g L\(^{-1}\) surfactant in demineralized water (O°FH, 22°C) were prepared and measured.

**Solutions containing base mix**

\(\text{NC}_2\text{nC}_{12}\) glucitol (0.5 g L\(^{-1}\)), base mix (1.25 g L\(^{-1}\), containing 35% of STP, 16.7% of sodium carbonate, 33.3% of sodium sulfate and 15% of disilicate). Final composition of the solution: dosage ca. 2 g L\(^{-1}\), 24% of \(\text{NC}_2\text{nC}_{12}\) glucitol, 21% of STP, 10% of sodium carbonate, 20% of sodium sulfate and 9% of disilicate, demineralized water (0°FH, 22°C).

\(\text{NC}_2\text{nC}_{12}\) lactose (0.5 g L\(^{-1}\)), base mix (1.25 g L\(^{-1}\), containing 35% of STP, 16.7% of sodium carbonate, 33.3% of sodium sulfate and 15% of disilicate). Final composition of the solution: dosage ca. 2 g L\(^{-1}\), 24% of \(\text{NC}_2\text{nC}_{12}\) lactose, 21% of STP, 10% of sodium carbonate, 20% of sodium sulfate and 9% of disilicate, water (30°FH Ca:Mg = 3:1, 22°C).

**Solutions containing base mix and soil**

\(\text{NC}_2\text{nC}_{12}\) glucitol (0.5 g L\(^{-1}\)) or NaLAS, base mix (1.25 g L\(^{-1}\), containing 35% of STP, 16.7% of sodium carbonate, 33.3% of sodium sulfate and 15% of disilicate), soil 20 g L\(^{-1}\). Final composition of the solution: dosage ca. 2 g L\(^{-1}\), 24% of surfactant (\(\text{NC}_2\text{nC}_{12}\) glucitol or NaLAS), 21% of STP, 10% of sodium carbonate, 20% of sodium sulfate and 9% of disilicate, 20 g/L soil, demi water (0°FH, 22°C).

0.5 g/L \(\text{NC}_2\text{nC}_{12}\) lactose or NaLAS, 1.25/L g base mix (containing 35% STP, 16.7% sodium carbonate, 33.3% sodium sulfate and 15% disilicate) and soil 20 g L\(^{-1}\). Final composition of the solution: dosage ca. 2 g L\(^{-1}\), 24% of surfactant (\(\text{NC}_2\text{nC}_{12}\) lactose or NaLAS), 21% of STP, 10% of sodium carbonate, 20% of sodium sulfate and 9% of disilicate, soil 20 g L\(^{-1}\), water (30°FH, Ca:Mg = 3:1, 22°C).

**Solutions containing base mix, soil, and 2.5% of cosurfactant**

NaLAS (0.720 g L\(^{-1}\)), cosurfactant (0.075 g L\(^{-1}\), \(\text{NC}_2\text{nC}_{12}\) glucitol or \(\text{NC}_2\text{nC}_{12}\) lactose), base mix (1.80 g L\(^{-1}\), containing 35% of STP, 16.7% of sodium carbonate, 33.3% of sodium sulfate and 15% of disilicate) and soil (10 g L\(^{-1}\)). Final composition of the solution: dosage 3 g L\(^{-1}\), 24% of surfactant NaLAS, 2.5% of cosurfactant (\(\text{NC}_2\text{nC}_{12}\) glucitol or \(\text{NC}_2\text{nC}_{12}\) lactose), 21% of STP, 10% of sodium carbonate, 20% of sodium sulfate and 9% of disilicate, soil (10 g L\(^{-1}\)), water (16°FH, 22°C).

**Soil composition (AS-8)**

Filter cell (SiO\(_2\), 10 g L\(^{-1}\)), black indian ink (1 g L\(^{-1}\)), black iron oxide (0.5 g L\(^{-1}\)), yellow iron oxide (0.75 g L\(^{-1}\)), groundnut oil (20 g L\(^{-1}\)), emulsifier emulgator (12 g L\(^{-1}\)), carboxymethyl guar (12.5 g L\(^{-1}\)).
4.7.3 Biodegradation

The biodegradation experiments were performed according to the Dutch Standard: Water-Determination of biochemical oxygen demand after n days (BOD). Dilution and seeding method. NEN 6634; UDC 543.371:628.312.3, June 1991.

Stock solution

Demineralized water (20°C) was saturated with air. For each liter, 1 ml of the following aqueous solutions were added: phosphate buffer ($\text{KH}_2\text{PO}_4$ (8.5 g L$^{-1}$), $\text{K}_2\text{HPO}_4$ (21.75 g L$^{-1}$), $\text{Na}_2\text{HPO}_4.7\text{H}_2\text{O}$ (33.4 g L$^{-1}$), and 1.7 g L$^{-1}$ $\text{NH}_4\text{Cl}$, pH 7.2), magnesium sulphate solution ($\text{MgSO}_4.7\text{H}_2\text{O}$ (22.5 g L$^{-1}$)), calcium chloride solution (anhydrous $\text{CaCl}_2$ (27.5 g L$^{-1}$)), iron(III) chloride solution (anhydrous $\text{FeCl}_3.6\text{H}_2\text{O}$ (0.25 g L$^{-1}$)), and n-allylthiourea solution ($\text{C}_4\text{H}_7\text{N}_2\text{S}$ (2.5 g L$^{-1}$)). Influent and effluent were collected from the wastewater treatment plant of the city of Groningen, situated in Garmerwolde. The influent was filtered and had a chemical oxygen demand between 300 and 600 mg L$^{-1}$. Influent and effluent, both 2 mL per liter, were added to the air-saturated mineral solution.

Preparation

Bottles (content exactly known; ca. 300 mL) were filled half way with stock solution. A solution of test compound was prepared (concentration exactly known ca. 60 mg in 100 mL) and 1 mL was added to the stock solution. The final concentration was about 2 mg L$^{-1}$. The bottles were filled to the rim with stock solution and the oxygen concentration was measured electrochemically with an oxygen electrode (in mg L$^{-1}$, $t = 0$). The bottles were sealed with stoppers and care was taken that no air bubbles were closed in. All tests were performed in duplicate. Two controls (no addition of substrate) and two standard solutions (anhydrous glucose and anhydrous glutamic acid, final concentration of each 3 mg L$^{-1}$) were also included in the test. The bottles were placed in the dark at 20°C (± 1°C). After a time period of 20 days, the oxygen concentration was measured again ($t = 20$). The controls gave a decrease in oxygen concentration of ca. 1.30 mg L$^{-1}$. The BOD of the standards should give values of 200 ± 20 mg L$^{-1}$. We measured values of 250 ± 25 mg L$^{-1}$ for BOD$\text{D}_{20}$ of the standards. From the results of the control measurements and the standards, we can conclude that the test method is reliable.

Calculation of the biodegradability

The BOD was calculated from the difference in oxygen concentration at $t = 0$ and at $t = 20$ of the compound minus the average difference in oxygen concentration at $t = 0$ and $t = 20$ for the controls. The percentage biodegradation is ($\text{BOD/TOC} \cdot 100\%$. (TOC for $\text{C}_n\text{H}_m\text{O}_n\text{N}_w$: $[(4c + h - 20 - 3n) \cdot 8] / \text{M}$).

4.7.4 Biotoxicity

Saccharomyces cerevisiae was grown overnight (30°) in a PDB (potato dextrose broth) medium. Escherichia coli, Pseudomonas putida, and Bacillus subtilis were grown overnight (30°) in a TSB (trypoton soya broth) medium on a rotary shaker. Microtitre plates were filled with 250 $\mu$L diluted culture (initial optical density about 0.05). 100 $\mu$L surfactant solutions (final concentrations 0, 1, 20, 100, 500, 1000, and 5000 g L$^{-1}$) were added to the microtitre plates. The growth of the microorganisms was monitored at 30°C every 10 minutes for at least 15 hours by measuring the optical density using a Labsystems Bioscreen C apparatus. The curves were analyzed either with BioRTN or BioLink-Win software. The time needed to reach a difference in optical density from 0.15 to 0.50 was
compared to the cases where no surfactant was present in the medium (the controls). All measurements were performed twice in triplicate.

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4.8 References

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