Carbohydrate-derived surfactants containing an N-Acylated amine functionality

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
1998

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Citation for published version (APA):

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Chapter 7

Estimates of the Bulk Prices of the Carbohydrate-Derived Surfactants and Perspectives

7.1 Introduction

In Chapter 4, we showed that $N$-acyl,$N$-dodecyl-$\beta$-D-aldosylamines and $N$-acyl,$N$-dodecyl-1-amino-1-deoxy-D-alditols have potential as cosurfactants in, for example, laundry detergents. The gemini surfactants based on carbohydrates proved to be good oil solubilizers (Chapter 6). For the actual application of these surfactants on an industrial scale, the price-performance ratio is of great importance.

In this final chapter, bulk\(^a\) prices of the surfactants are estimated. The bulk prices of most chemicals needed for the production of the carbohydrate-derived surfactants can be found in the list of Chemical Prices (Chemical Market Reporter, November 1997). Prices of starting materials that were not available had to be estimated. There are several ways to estimate these prices. For example, acetic anhydride can be found in the price list (2.20 Hfl kg\(^{-1}\))\(^b\), but the price of propionic anhydride is not available. Acetic acid and propionic acid, however, are both provided by the Chemical Marketing Reporter. The ratio of the prices of acetic acid and propionic acid is 1.14. The price estimated for propionic anhydride is 2.20 \(\times\) 1.14 = 2.51 Hfl kg\(^{-1}\). Another approach, which leads to a rough estimate, is to divide the price of a chemical for use on a laboratory scale (found in e.g. the Fluka catalogue) by a factor of 10. For readily available compounds such as glucose monohydrate and lactose monohydrate, this factor is about 20 and 25, respectively. Most chemicals used as starting materials for the $N$-acyl,$N$-dodecyl-$\beta$-D-aldosylamines and $N$-acyl,$N$-dodecyl-1-amino-1-deoxy-D-alditols and the gemini surfactant 14-10-14 were available from the Chemical Prices list.

The cost of industrial processes is estimated at 0.50 Hfl kg\(^{-1}\) per reaction step for plain operations and 0.75 Hfl kg\(^{-1}\) if more complex or energy-consuming steps are involved (additional distillations etc.).\(^c\)

\(^{a}\) "Bulk" is defined here as multi-ton commercial production as (co)surfactant in detergent formulations.

\(^{b}\) The prices are converted to Dutch guilders (Hfl) per kilogram. One guilder is about $0.50.
Table 1 shows the calculation of the bulk prices of \( \text{NC}_2\text{nC}_{12} \) glucose and \( \text{NC}_3\text{nC}_{12} \) glucose. The process involves stirring glucose and dodecylamine in methanol. The product precipitates from the reaction mixture. The methanol can be reused. The acylation can be achieved with the appropriate anhydrides. The reaction mixture is neutralized with Dowex OH\(^{-}\) and the methanol is evaporated. The prices calculated are 6.10 Hfl kg\(^{-1}\) and 6.00 Hfl kg\(^{-1}\), respectively. Although propionic anhydride is more expensive than acetic anhydride, the price per kg of \( \text{NC}_3\text{nC}_{12} \) glucose is lower than the price of \( \text{NC}_2\text{nC}_{12} \) glucose, due to the higher molecular weight of the former. The price per mole of compound is higher for \( \text{NC}_3\text{nC}_{12} \) glucose. In industry the prices are, however, always given per kilogram of product.

The reaction solvent for \( \text{NC}_3\text{nC}_{12} \) lactose and \( \text{NC}_3\text{nC}_{12} \) lactose is 2-propanol-water. The removal of this reaction solvent requires more energy (due to the high boiling point of water) and therefore, the costs of the process are higher (estimation 0.75 Hfl kg\(^{-1}\)). Lactose is more expensive than glucose, but as the molecular weight of lactose is higher, \( \text{NC}_3\text{nC}_{12} \) lactose and \( \text{NC}_3\text{nC}_{12} \) lactose are cheaper (5.80 Hfl kg\(^{-1}\) and 5.90 Hfl kg\(^{-1}\), respectively, Table 2) because fewer moles of the relatively expensive alkylamine are required.

The first step in the preparation of \( \text{NC}_2\text{nC}_{12} \) glucitol, \( \text{NC}_3\text{nC}_{12} \) glucitol, \( \text{NC}_2\text{nC}_{12} \) lactitol, and \( \text{NC}_3\text{nC}_{12} \) lactitol is a reductive amination with Raney Ni. In the syntheses of our compounds (Chapter 2) we used \( \text{Pd}/\text{C} \) (5%). Raney Ni is also an efficient catalyst and much cheaper.

The carbohydrate, the dodecylamine (an excess) and Raney Ni are stirred at elevated \( \text{H}_2 \) pressure and temperatures (40°C and 70°C, respectively). After filtration (to remove the Raney Ni, which can be reused) the glucitol-derivatives precipitate from the reaction mixture upon cooling. The mother liquor (containing the excess of dodecylamine) can be reused. In case of the lactitol derivatives, the solvent has to be evaporated. Because of the relatively high molecular weight of lactose, the lactitol derivatives are slightly cheaper than the glucitol derivatives. Moreover, the lactitol derivatives can also be prepared in a one-pot synthesis. This might even further reduce the price of these compounds.
Table 1. Calculation of the bulk prices of $\text{NC}_3\text{nC}_{12}$ glucose and $\text{NC}_3\text{nC}_{12}$ glucose.

<table>
<thead>
<tr>
<th>Chemicals, processes</th>
<th>amount</th>
<th>price (Hfl kg$^{-1}$)</th>
<th>price (Hfl)</th>
<th>total costs (Hfl)</th>
<th>yield</th>
<th>price (Hfl kg$^{-1}$)</th>
<th>price (Hfl mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>glucose $\text{H}_2\text{O}$</td>
<td>1 kg (5.1 mol)</td>
<td>1.12</td>
<td>1.12</td>
<td>5.95</td>
<td>75%</td>
<td>4.50</td>
<td>1.56</td>
</tr>
<tr>
<td>dodecylamine</td>
<td>0.93 kg (5.1 mol)</td>
<td>4.00</td>
<td>3.73</td>
<td>6.10</td>
<td>2.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MeOH</td>
<td>20 L</td>
<td>0.45 (5% loss)</td>
<td>0.35</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>process</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>regeneration</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MeOH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

isolated 0.75 kg 5.1 mol = 3.83 kg 1.33 kg = price per kg: total costs 1.33 = 4.50 Hfl kg$^{-1}$

<table>
<thead>
<tr>
<th>Acetylation of $\text{nC}_{12}$ glucose</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{nC}_3\text{glucose}$</td>
</tr>
<tr>
<td>$(\text{CH}_3\text{CO}_2)\text{O}$</td>
</tr>
<tr>
<td>MeOH</td>
</tr>
<tr>
<td>Dowex OH$^-$</td>
</tr>
<tr>
<td>process</td>
</tr>
<tr>
<td>regeneration</td>
</tr>
<tr>
<td>MeOH</td>
</tr>
</tbody>
</table>

isolated 0.95 kg 3.83 = 3.64 mol = 1.42 kg 1.42 kg = price per kg: total costs 1.42 = 6.10 Hfl kg$^{-1}$

<table>
<thead>
<tr>
<th>Propionylation of $\text{nC}_{12}$ glucose</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{nC}_3\text{glucose}$</td>
</tr>
<tr>
<td>$(\text{CH}_3\text{CH}_2\text{CO}_2)\text{O}$</td>
</tr>
<tr>
<td>MeOH</td>
</tr>
<tr>
<td>Dowex OH$^-$</td>
</tr>
<tr>
<td>process</td>
</tr>
<tr>
<td>regeneration</td>
</tr>
<tr>
<td>MeOH</td>
</tr>
</tbody>
</table>

isolated 0.95 kg 3.83 = 3.64 mol = 1.47 kg 1.47 kg = price per kg: total costs 1.47 = 6.20 Hfl kg$^{-1}$

$^a$Amount of acetic acid to be neutralized: $(4.59 \times 2) - 3.83 = 5.4$ mol. Dowex OH$^-$ can neutralize 4.4 meq g$^{-1}$, thus at least 1.2 kg of Dowex is needed. $^b$For the regeneration of Dowex at least 1.5 $\times$ 4.4 = 6.6 mol of NaOH is needed. We calculated the price of 10 mol of NaOH (1.50 Hfl kg$^{-1}$).
Table 2. Calculation of the bulk prices of NC<sub>12</sub>nC<sub>12</sub> lactose and NC<sub>3</sub>nC<sub>13</sub> lactose.

<table>
<thead>
<tr>
<th>Synthesis of nC&lt;sub&gt;12&lt;/sub&gt; lactose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemicals, processes</td>
</tr>
<tr>
<td>lactose:H&lt;sub&gt;2&lt;/sub&gt;O</td>
</tr>
<tr>
<td>dodecylamine</td>
</tr>
<tr>
<td>2-propanol</td>
</tr>
<tr>
<td>process&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>regeneration</td>
</tr>
<tr>
<td>excess amine</td>
</tr>
<tr>
<td>isolated 0.75 × 2.78 = 2.08 mol ≈ 1.06 kg = price per kg: total costs / 1.06 = 4.40 Hfl kg&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Acetylation of nC&lt;sub&gt;12&lt;/sub&gt; lactose</th>
</tr>
</thead>
<tbody>
<tr>
<td>nC&lt;sub&gt;12&lt;/sub&gt; lactose</td>
</tr>
<tr>
<td>(CH&lt;sub&gt;3&lt;/sub&gt;CO&lt;sub&gt;2&lt;/sub&gt;)O</td>
</tr>
<tr>
<td>MeOH</td>
</tr>
<tr>
<td>Dowex OH&lt;sup&gt;−&lt;/sup&gt;</td>
</tr>
<tr>
<td>process</td>
</tr>
<tr>
<td>regeneration</td>
</tr>
<tr>
<td>MeOH</td>
</tr>
<tr>
<td>isolated 0.95 × 2.08 = 1.98 mol ≈ 1.12 kg = price per kg: total costs / 1.12 = 5.85 Hfl kg&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Propionylation of nC&lt;sub&gt;12&lt;/sub&gt; lactose</th>
</tr>
</thead>
<tbody>
<tr>
<td>nC&lt;sub&gt;12&lt;/sub&gt; lactose</td>
</tr>
<tr>
<td>(CH&lt;sub&gt;3&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;2&lt;/sub&gt;)O</td>
</tr>
<tr>
<td>MeOH</td>
</tr>
<tr>
<td>Dowex OH&lt;sup&gt;−&lt;/sup&gt;</td>
</tr>
<tr>
<td>process</td>
</tr>
<tr>
<td>regeneration</td>
</tr>
<tr>
<td>MeOH</td>
</tr>
<tr>
<td>isolated 0.95 × 2.08 = 1.98 mol ≈ 1.16 kg = price per kg: total costs / 1.16 = 5.90 Hfl kg&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Including regeneration of the reaction medium (2-propanol-water).  
<sup>b</sup> Amount of acetic acid to be neutralized: (2.50 × 2) - 2.08 = 2.92 mol. Dowex OH<sup>−</sup> can neutralize 4.4 meq g<sup>-1</sup>, thus at least 0.66 kg of Dowex is needed.  
For the regeneration of Dowex at least 0.75 × 4.4 = 3.3 mol of NaOH is needed. We calculated the price of 5 mol of NaOH (1.50 Hfl kg<sup>-1</sup>).
### Table 3. Calculation of the bulk prices of NC<sub>n</sub>C<sub>12</sub> glucitol and NC<sub>n</sub>C<sub>12</sub> glucitol.

#### Synthesis of nC<sub>12</sub> glucitol

<table>
<thead>
<tr>
<th>Chemicals, processes</th>
<th>amount</th>
<th>price (Hfl kg&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>price (Hfl)</th>
<th>total costs (Hfl)</th>
<th>yield</th>
<th>price (Hfl kg&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>price (Hfl mol&lt;sup&gt;-1&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>glucose-H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>1 kg (5.1 mol)</td>
<td>1.12</td>
<td>1.12</td>
<td>6.05</td>
<td>95%</td>
<td>3.55</td>
<td>1.25</td>
</tr>
<tr>
<td>dodecylamine</td>
<td>0.93 kg (5.1 mol)</td>
<td>4.00</td>
<td>3.73</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MeOH</td>
<td>10 L</td>
<td>0.45 (5% renew)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.20</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raney Ni</td>
<td>50 g</td>
<td>50 (10% loss)</td>
<td>0.25</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>process&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
<td></td>
<td>0.75</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Isolated 0.95 × 5.1 = 4.85 mol ≈ 1.69 kg → price per kg: total costs 1.69 = 3.55 Hfl kg<sup>-1</sup>.

#### Acetylation of nC<sub>12</sub> glucitol

| nC<sub>12</sub> glucitol | 1.69 kg (4.85 mol) | 6.05 | 9.25 | 95% | 5.15 | 2.00 |
| (CH<sub>3</sub>CO)O | 0.59 kg (5.82 mol) | 2.20 | 1.30 |
| MeOH | 20 L | 0.45 (5% loss) | 0.35 |
| Dowex OH<sup>-</sup> | 2.0 kg<sup>c</sup> | no loss | 0.80<sup>d</sup> |
| process | | | 0.50 |
| regeneration of MeOH | | | 0.25 |

Isolated 0.95 × 4.85 = 4.60 mol ≈ 1.80 kg → price per kg: total costs 1.80 = 5.15 Hfl kg<sup>-1</sup>.

#### Propionylation of nC<sub>12</sub> glucitol

| nC<sub>12</sub> glucitol | 1.69 kg (4.85 mol) | 5.95 | 9.78 | 95% | 5.25 | 2.15 |
| (CH<sub>3</sub>CH<sub>2</sub>CO)O | 0.77 kg (5.82 mol) | 2.50 | 1.93 |
| MeOH | 20 L | 0.45 (5% loss) | 0.35 |
| Dowex OH<sup>-</sup> | 2.0 kg<sup>c</sup> | no loss | 0.80<sup>d</sup> |
| process | | | 0.50 |
| regeneration of MeOH | | | 0.25 |

Isolated 0.95 × 4.85 = 4.60 mol ≈ 1.86 kg → price per kg: total costs 1.86 = 5.25 Hfl kg<sup>-1</sup>.

<sup>a</sup> The Raney Ni can be filtered off and the compound precipitates from the reaction solvent when cooled. The mother liquor can be reused. <sup>b</sup> The methanol will have to be renewed after a certain number of cycles. <sup>c</sup>Amount of acetic acid to be neutralized: (5.82 × 2) - 4.85 = 6.79 mol. Dowex OH<sup>-</sup> can neutralize 4.4 meq<sup>g</sup>, thus at least 1.5 kg of Dowex is needed. <sup>d</sup> For the regeneration of Dowex at least 2 × 4.4 = 8.8 mol of NaOH is needed. We calculated the price of 13 mol of NaOH (1.50 Hfl kg<sup>-1</sup>).
Table 4. Calculation of the bulk prices of NC\textsubscript{12} lactitol and NC\textsubscript{12} lactitol.

<table>
<thead>
<tr>
<th>Chemicals, processes</th>
<th>amount</th>
<th>price (Hfl kg\textsuperscript{-1})</th>
<th>price (Hfl)</th>
<th>total costs (Hfl)</th>
<th>yield</th>
<th>price (Hfl kg\textsuperscript{-1})</th>
<th>price (Hfl mol\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>lactose H\textsubscript{2}O</td>
<td>1 kg (2.78 mol)</td>
<td>1.20</td>
<td>1.20</td>
<td>4.70</td>
<td>95%</td>
<td>3.50</td>
<td>1.80</td>
</tr>
<tr>
<td>dodecylamine</td>
<td>0.51 kg (2.78 mol)</td>
<td>4.00</td>
<td>2.05</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MeOH</td>
<td>10 L</td>
<td>0.45 (5% loss)</td>
<td>0.20</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raney Ni</td>
<td>50 g</td>
<td>50 (10% loss)</td>
<td>0.25</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>process\textsuperscript{a}</td>
<td></td>
<td></td>
<td></td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

isolated 0.95 \times 2.78 = 2.64 mol \approx 1.35 kg \Rightarrow \text{price per kg: total costs / 1.35 = 3.50 Hfl kg}\textsuperscript{-1}

<table>
<thead>
<tr>
<th>Acetylation of nC\textsubscript{12} lactitol</th>
</tr>
</thead>
<tbody>
<tr>
<td>nC\textsubscript{12} lactitol</td>
</tr>
<tr>
<td>(CH\textsubscript{3}CO\textsubscript{2})O</td>
</tr>
<tr>
<td>MeOH</td>
</tr>
<tr>
<td>Dowex OH\textsuperscript{-}</td>
</tr>
<tr>
<td>process</td>
</tr>
<tr>
<td>regeneration</td>
</tr>
<tr>
<td>MeOH</td>
</tr>
</tbody>
</table>

isolated 0.95 \times 2.64 = 2.51 mol \approx 1.39 kg \Rightarrow \text{price per kg: total costs / 1.39 = 4.90 Hfl kg}\textsuperscript{-1}

<table>
<thead>
<tr>
<th>Propionylation of nC\textsubscript{12} lactitol</th>
</tr>
</thead>
<tbody>
<tr>
<td>nC\textsubscript{12} lactitol</td>
</tr>
<tr>
<td>(CH\textsubscript{2}CH\textsubscript{2}CO\textsubscript{2})O</td>
</tr>
<tr>
<td>MeOH</td>
</tr>
<tr>
<td>Dowex OH\textsuperscript{-}</td>
</tr>
<tr>
<td>process</td>
</tr>
<tr>
<td>regeneration</td>
</tr>
<tr>
<td>MeOH</td>
</tr>
</tbody>
</table>

isolated 0.95 \times 2.64 = 2.51 mol \approx 1.42 kg \Rightarrow \text{price per kg: total costs / 1.42 = 5.00 Hfl kg}\textsuperscript{-1}

\textsuperscript{a} The Raney Ni can be filtered. The methanol has to be removed by distillation. The excess of dodecylamine can be recovered by extraction of the crude product with hexane.

\textsuperscript{b} Amount of acetic acid to be neutralized: (3.17 \times 2) - 2.64 = 3.7 mol. Dowex OH\textsuperscript{-} can neutralize 4.4 meq NaOH, thus at least 0.85 kg of Dowex is needed.

\textsuperscript{c} For the regeneration of Dowex at least 1 \times 4.4 = 4.4 mol of NaOH is needed. We calculated the price of 6.5 mol of NaOH (1.50 Hfl kg\textsuperscript{-1}).
73 Calculated bulk prices of the carbohydrate-derived surfactants compared with bulk prices of commercially available surfactants

The calculated bulk prices of the carbohydrate-derived surfactant are in the range of 4.90 - 6.10 Hfl kg\(^{-1}\). The best performing surfactants (NC\(_2\)\(_n\)C\(_{12}\) glucitol and NC\(_2\)\(_n\)C\(_{12}\) lactose, Chapter 4) will cost 5.15 Hfl kg\(^{-1}\) and 5.80 Hfl kg\(^{-1}\), respectively. If cruder starting materials would be used, the prices might even be reduced (e.g., cocoamine instead of dodecylamine). Table 5 shows the bulk prices of some commercially available surfactants. The prices of the surfactants we synthesized are in the same range as those of the carbohydrate-derived surfactants which are already produced on an industrial scale (alkylpolyglucosides, APGs, and glucamides, see also Chapter 1). However, they are 2 - 4 times more expensive than the major petroleum-based anionic and nonionic surfactants. In the detergency tests described in Chapter 4, only 2.5\% of NC\(_2\)\(_n\)C\(_{12}\) glucitol and NC\(_2\)\(_n\)C\(_{12}\) lactose already gave appreciable increases in performance. Taking account of the calculated bulk prices, these carbohydrate-derived surfactants are promising cosurfactants. Costs for applications in, for example, cosmetics would likely be significantly higher owing to higher standards of purity.

Table 5. Bulk prices of some commercially available surfactants.

<table>
<thead>
<tr>
<th>commercial surfactants</th>
<th>guideline to prices (Hfl kg(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaLAS</td>
<td>1.3 - 1.6</td>
</tr>
<tr>
<td>Nonionics (e.g. C(_{12})E(_7))</td>
<td>1.9</td>
</tr>
<tr>
<td>alkylether sulfates</td>
<td>2.4 - 2.7</td>
</tr>
<tr>
<td>APG</td>
<td>4.5</td>
</tr>
<tr>
<td>Glucamides</td>
<td>4.5 - 5.5</td>
</tr>
<tr>
<td>Sodium dodecyl sulfate</td>
<td>2.7</td>
</tr>
</tbody>
</table>

\(^{6}\)A profit margin should be added to the calculated bulk prices of the carbohydrate-derived surfactants presented in this thesis.
7.4 Calculated bulk price of gemini surfactant 14-10-14

Table 6 shows the calculation of the bulk price of gemini surfactant 14-10-14. The price of \(\alpha,\omega\text{-diaminododecane}\) was estimated from the price of decanedioic acid (8.8 Hfl kg\(^{-1}\)).\(^d\) Tetradecanoic anhydride can be prepared from myristic acid and acetic anhydride.\(^c\)

The price is about twice the price of the monomeric carbohydrate-derived surfactants (11.35 Hfl kg\(^{-1}\)). Although the estimated bulk price is high, these gemini surfactants can probably still compete with conventional surfactants, e.g., in enhanced oil recovery, due to their high oil solubilization efficiency (Chapter 6).

Table 6. Calculation of the bulk prices of gemini surfactant 14-10-14.

<table>
<thead>
<tr>
<th>Chemicals, processes</th>
<th>amount</th>
<th>price (Hfl kg(^{-1}))</th>
<th>price (Hfl)</th>
<th>total costs (Hfl)</th>
<th>yield</th>
<th>price (Hfl kg(^{-1}))</th>
<th>price (Hfl mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>glucose-H(_2)O</td>
<td>1 kg (5.1 mol)</td>
<td>1.12</td>
<td>1.12</td>
<td>6.71</td>
<td>90%</td>
<td>5.90</td>
<td>2.90</td>
</tr>
<tr>
<td>diaminododecane</td>
<td>0.44 kg (2.55 mol)</td>
<td>10</td>
<td>4.39</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MeOH</td>
<td>10 L</td>
<td>0.45 (5% renew)(^b)</td>
<td>0.20</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raney Ni</td>
<td>50 g</td>
<td>50 (10% loss)</td>
<td>0.25</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>process(^a)</td>
<td></td>
<td></td>
<td>0.75</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

isolated: 0.90 \(\times\) 2.30 = 2.07 mol \(\Rightarrow\) price per kg: total costs 1.90 = 12.00 Hfl kg\(^{-1}\)

| Acylation of bola 10 |       |                         |                |               |       |                     |
|----------------------|--------|--------------------------|-------------|------------------|-------|------------------------|--------------------------|
| bola 10              | 1.14 kg (2.30 mol) | 6.71 | 22.81 | 90% | 12.00 | 11.05 |
| \(\text{C}_{14}\text{-anhydride} \) | 3.02 kg (6.90 mol) | 5.00 | 15.10 |
| process\(^c\)        |       |                         | 1.00 |

isolated: 0.90 \(\times\) 2.30 = 1.90 kg \(\Rightarrow\) price per kg: total costs 1.90 = 12.00 Hfl kg\(^{-1}\)

\(^a\) The Raney Ni can be filtered off and the compound precipitates from the reaction solvent when cooled. The mother liquor can be reused. \(^b\) The process includes stirring of the reaction mixture (0.30 Hfl kg\(^{-1}\)), evaporation of the reaction solvent (which can be reused, 0.50 Hfl kg\(^{-1}\)) and continuous extraction of the crude product with hexane.

\(^d\) Reaction of 1,10-decanedicarboxylic acid with ammonia leads to the diamide and subsequent catalytic hydrogenation gives the aminodecane.

\(^c\) Pure myristic acid costs 3.75 Hfl kg\(^{-1}\); a mixture of fatty acids with an average chain length of 14 carbon atoms will be cheaper.
Estimates of the Bulk Prices of the Carbohydrate-Derived Surfactants and Perspectives

7.5 Conclusions

In Chapter 1 we formulated the aim of this research project: the synthesis of readily biodegradable, nontoxic surfactants based on renewables, by synthetic pathways that would be applicable on a large scale. We prepared $N$-acyl-$N$-alkyl-$\beta$-D-aldosylamines and $N$-acyl,$N$-alkyl-1-amino-1-deoxy-D-alditols by straightforward reaction routes (Chapter 2). Preliminary tests indicate that the compounds are nontoxic (Chapter 4). The extent of biodegradation was insufficient, however, more extensive tests need to be performed to draw definite conclusions on the biodegradability of the compounds. Chapter 4 also shows that some of the carbohydrate-derived surfactants considerably increase the performance of a standard laundry detergent formulation. Furthermore, the estimated bulk prices show a reasonable price, especially with respect to their use as cosurfactants.

The bis($N$-alkanoyl-1-amino-1-deoxy-D-glucityl)alkanes show a high oil-solubilization capacity. The syntheses of these carbohydrate-derived gemini surfactants do not imply tedious reaction steps and the price-performance ratio seems to be reasonable. Therefore, we have reached our aim, except for the ready biodegradability of the compounds.

In Chapter 2 we formulated an additional aim: insights into the structure-property relationships by introducing small structural changes in order to devise tailor-made materials. Chapters 3, 5, and 6 show that the physical and chemical properties and aggregation behavior of the $N$-acyl,$N$-alkyl-$\beta$-D-aldosylamines and $N$-acyl,$N$-alkyl-1-amino-1-deoxy-D-alditols, and of the bis($N$-alkanoyl-1-amino-1-deoxy-D-glucityl)alkanes follow consistent trends, and the behavior can thus be predicted. Although general trends are also observed in the relationship between the structure and the practical performance of the surfactants (in detergency tests in case of the former surfactants and in oil solubilization experiments in case of the gemini surfactants), this interrelation is more complex.

7.6 Reference