Methyl ester ethoxylates
An approach to use renewable raw materials

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ABSTRACT: Today’s consumers’ expectations for a detergent are diverse. On one hand the purchasing price, and on the other hand excellent washing performance at low temperatures based on renewable raw materials and environmentally friendly production processes. Within this context we carried out a study focusing on the synthetic use of renewable Fatty Acid Methyl Esters and the properties and applications of the final products, namely Methyl Ester Ethoxylates.

INTRODUCTION
Renewable surfactants are a hot topic in modern formulations of liquid detergents thanks to their biodegradability, low ecotoxicity and favourable carbon footprint. Latest developments are high concentrated liquid laundry detergents, whose main components are anionic and non-ionic surfactants. Among the non-ionic surfactants AE7 is the most common workhorse. These alkyl ethoxylates are either derived from fatty alcohols (oleo chemical based) or synthetic alcohols (petrochemical based). Our approach to help preserving natural fossil raw materials was initiated by the launch of our Greenbentin™ product line, whose products are based on at least 30 w/w % of renewable raw materials. In this regard we carried out a study focusing on the synthetic use of renewable Fatty Acid Methyl Esters (FAME), which develop very early during the refinement process. Methyl Ester Ethoxylates (MEE) have been known for approximately 20 years. MEEs consist of three structural moieties, namely the fatty acid part, the PEG-chain, and the methyl end-group. Hence MEEs can be synthesized by four different methods:
I. Ethoxylation of fatty acid and subsequent methylation
II. Esterification of fatty acid with MPEG
III. Transesterification of fatty acid methyl ester (FAME) with MPEG
IV. Direct Ethoxylation of fatty acid methyl ester (FAME)

The different surfactant properties arising from the different synthetic routes will be published elsewhere. From economical point-of-view, III. and IV. are suited best for industrial purposes (Scheme 1).

From the early days we know that the direct ethoxylation of FAME is negligible in the presence of conventional catalysts such as potassium hydroxide, sodium hydroxide or sodium methoxide. Hence a lot of special catalysts have been developed by individual companies and groups (17, 18). The most relevant facts on MEE from this time can be summarized as follows (19-21):
• MEEs are low foaming non-ionic surfactants compared to FAEs.
• They show limited stability in the presence of inorganic acids and bases (pH 3-9).
• Wetting is comparable to FAEs of equivalent alkyl chain length.
• Nearly no gel formation observed.
• CMC can be adjusted either by the alkyl chain length or the degree of ethoxylation (a).
• Cloud point can be raised by a higher degree of ethoxylation.
• Due to the special catalysts MEEs show a narrow homologue distribution.
• Filtration of the final product is difficult.

Thus the aim of this paper is to show that based on state-of-the-art technology (12, 22) the direct ethoxylation of renewable Fatty Acid Methyl Esters under industrial conditions yields a non-ionic surfactant, which is ideally suited for liquid detergents and general purpose cleaners. The outstanding surfactant properties of MEEs in comparison to the benchmark will be presented in this paper as well.

EXPERIMENTAL SECTION
Synthetic part
The two MEEs, namely Greenbentin-MLS/070 and Greenbentin-MLS/100, are based on a palm cut methyl ester with a degree of ethoxylation of approximately 7 and 10 mol. Samples have been prepared on production scale
using Kolb’s patented technology (22), which is based on a doped heterogeneous catalyst system. Specifications of both samples in comparison to the benchmark AE7 are summarized in Table 1.

**Table 1. Typical specifications of MEE types in comparison to AE7**

<table>
<thead>
<tr>
<th>Property</th>
<th>Greenbentin-MLS/070</th>
<th>Greenbentin-MLS/100</th>
<th>AE7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Liquid, clear</td>
<td>Liquid, clear</td>
<td>Liquid, clear</td>
</tr>
<tr>
<td>Cloud point <strong>°C</strong></td>
<td>approx. 55.0</td>
<td>approx. 62.9</td>
<td>approx. 70.5</td>
</tr>
<tr>
<td>Saponification number [mg/kg]</td>
<td>approx. 100</td>
<td>approx. 75</td>
<td>–</td>
</tr>
<tr>
<td>Solidification point [°C]</td>
<td>approx. –7</td>
<td>approx. 2</td>
<td>approx. 15</td>
</tr>
<tr>
<td>pH</td>
<td>4.7</td>
<td>4.7</td>
<td>6.7</td>
</tr>
<tr>
<td>Foaming behaviour:</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 2. Wetting times on cotton for MEE types in comparison to AE7**

<table>
<thead>
<tr>
<th>MEE Type</th>
<th>Greenbentin-MLS/070</th>
<th>Greenbentin-MLS/100</th>
<th>AE7</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 μL</td>
<td>&gt;300</td>
<td>&gt;300</td>
<td>186</td>
</tr>
<tr>
<td>0.5 μL</td>
<td>139</td>
<td>117</td>
<td>45</td>
</tr>
<tr>
<td>1.0 μL</td>
<td>138</td>
<td>276</td>
<td>88</td>
</tr>
</tbody>
</table>

**Surfactant properties**

In the following paragraph the surfactant properties of the Greenbentin-MLS types are discussed in comparison to AE7.

**a. CMC, surface tension and solubility:** We determined the solubility of both MEEs in comparison to AE7. Greenbentin-MLS types are based on a palm cut methyl ester with a carbon chain distribution, which exceeds the C12-C14 carbon chain of AE7 by far. This difference has a small effect on the solubility. AE7 yields a clear, soluble and homogeneous solution in water (0.1-10 g/L), while both MEE types show at high concentration (>10 g/L) a slight opaque to turbid aspect, indicating a limited solubility at higher concentrations. AE7 yields a static surface tension [EN 14370] of approx. 28.4 mN/m. In consideration of the fact that MEE is an ester ethoxylate, static surface tensions in the range of 30 mN/m are very good results (MLS/070: 30.5 mN/m; MLS/100: 31.5 mN/m). Both MEE-types show no dynamic contact angle on polyamide. The CMC of the MEEs in comparison to AE7 is shown in Figure 1. While MLS/070 and AE7 yield an identical CMC of 13 mg/L, MLS/100 shows an even lower CMC of 8 mg/L.

**b. Wetting Times:** We determined the wetting times on cotton using the Draves-Test (ISO 8022). The results in comparison to AE7 are summarized in Table 2. The differences in wetting in comparison to AE7 are based on the differences in the carbon chain distribution. AE7 predominantly consists of C12 and C14, while the investigated MEEs consist of a carbon chain ranging from C10 to C18. Furthermore, a minor part of C18:1 and C18:2 is present. The carbon chain distribution of the MLS-types is perfectly balanced in order to ensure good wetting in combination with good flotation and washing performance.

**c. Foaming behaviour:** We investigated the foaming behaviour of both MLS-types in comparison to AE7 at temperatures of 25 and 50°C using the beating method with perforated disks (EN 12728). The results are visualized in Figure 2.

The two MEE-types exhibit due to the terminal methyl group and the relatively long alkyl chain in comparison to AE7 a significantly lower foaming behaviour. Greenbentin™-MLS/100 shows a higher initial foam height at 25 and 50°C than MLS/070. This is in agreement with the higher degree of ethoxylation of MLS/100. At 50°C both MEE-types show nearly equivalent foam levels after 5 minutes.
d. Gel Forming Behaviour: In order to determine the gel forming behaviour, both MEE-types and AE7 have been mixed in different ratios with deionised water. The results observed at 25°C are visualized in Figure 3. It is known that the benchmark forms a gel phase over a broad range (40-80 weight % surfactant in water). In contrast, both MEEs show only minor gel forming behaviour. Surprisingly, Greenbentin™-MLS/070 exhibits phase separation over a medium range (10-50 weight % surfactant in water). The fact that gel formation occurs over a small range exclusively make both MEE-types ideally suited for detergent compositions.

CONCLUSION

We investigated the applicability of MEE-types for the use in liquid detergents and all purpose cleaners. In order to get significant results MEEs have been benchmarked with AE7. The two MEE-types used in this study, namely Greenbentin™-MLS and 100, are produced on industrial scale using state-of-the-art technology. The results can be summarized as follows:

- MEE can be synthesized by four different techniques of which the direct ethoxylation is suited best for industrial purposes.
- The synthetic routes have influence on the application/performance of the product.
- Methyl esters from natural feedstock are interesting raw materials.
- The MEEs presented in this publication are 100 percent biodegradable and exhibit an insignificant aqua toxicity.
- The Greenbentin™-MLS-types are compatible to enzymes used in liquid detergents.
- They are stable in the presence of organic bases (amines).
- MEEs have a low tendency to form gels.
- Due to their terminal methyl group MEEs are low foaming.
- The carbon chain distribution of the MLS-types is perfectly balanced in order to ensure good wetting in combination with good flotation and washing performance. Consequently, the observed wetting times are moderate in comparison to AE7.
- The static surface tension and solubility of the MEEs is good, the CMC equivalent to AE7 or even lower.

We believe that MEEs have interesting properties, which e.g. can be tuned by the synthetic route. 20 years after their first introduction MEEs are more of interest than ever. MEEs are ideally suited for all purpose cleaner, detergent powders and especially for liquid detergents. It is an alternative to AE7 and due to their special properties one way to reduce washing temperature, and consequently a way to save energy.

REFERENCES AND NOTES

a. CMC stands for Critical Micelle Concentration. The CMC is one of the most relevant parameters for surfactants. E.g. a) Surfactants yield optimal cleaning performance above CMC. b) The optimal amount of an emulsifier at constant temperature is CMC dependent.

10. B.E.A. Leach, J.C.P. Lin et al., Vista Chemical Company (Houston, TX), USA, 1993.
Leading technologies for detergent, surfactant, chemical and oleochemical industries

**SURFACANTs**
- Anionics
  - Sulphonation / Sulphonation
  - Vacuum Neutralization
  - Drying
- Non Ionics
  - Ethoxylation / Propoxylation
  - Alkylamides
  - Amphotericis & Cationics
  - Betaines
  - Ethoxylates
  - Ammonoxides

**DETERGENTS**
- Powder
  - Spray Drying Tower process
  - NTD (non tower / agglomeration) process
- Liquids
  - Batch / Continuous

**OLEOCEMICALS**
- Fatty Acids
- Fatty Alcohols
- Methylesters
- Glycerine
- Biodiesel

**ORGANIC CHEMICALS**
- Linear Alkyl Benzene
- Ethyl Alcohol
- Starch & Yeast
- Fatty Amines

**INORGANIC CHEMICALS**
- Sodium Silicate
- Sulphuric Acid
- Sodium & Potassium Sulphate
- Zeolite
- Sodium Tripolyphosphate
- Single & triple Superphosphates
- Phosphoric Acid
- NPK
- PAC (Poly Aluminium Chloride)

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