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Application of chemical ionisation in comprehensive GCxGC-qMS for characterization of fatty alcohol alkoxylate copolymers in the low molecular range up to 700 Da

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Introduction

The class of fatty alcohol alkoxylates describes surfactants that are synthesised by reaction of fatty alcohols with alkoxides like ethylene oxide or propylene oxide respectively a combination of both as copolymers. Such alkoxylates are used for example as nonionic surfactants in home and industrial cleaning and washing agents. They have important properties like foam supression, foam control and wetting effects in these products. In this context chemical characteristics of such alkoxylate copolymers like the degree of alkoxylation, the arrangement of building blocks (random or block polymerisation), the type of the starter and endcapping often play an important role.

The analysis of these characteristics is challenging because in many cases such copolymers possess high polydispersity and a large number of constitutional isomers depending on the degree of alkoxylation. Furthermore the alkoxylates occur often in a complex multicomponent matrix.
Here we present a method for the characterization of fatty alcohol alkoxylates in the low molecular range based on comprehensive two-dimensional gas chromatography – mass spectrometry with electron and chemical ionisation. This method also allows the detailed analysis of the alkoxylates in a complex matrix like modern detergents.

Results

The used GCxGC-qMS system for these investigations was a Shimadzu GC 2010 gas chromatograph and a GCMS QP 2010 Plus. Isobutane was used as CI gas. The GC-carrier gas was helium and a ZX1 LN2 cooled loop modulator from Zoex was used as the cryo-interface. For the first dimension a nonpolar column (ZebronTM ZB-5HT Inferno; 30 m x 0.25 mm x 0.25 µm from Phenomenex) and for the second dimension a moderately polar column (BPX50; 1 m x 0.15 mm x 0.15 µm from SGE) was used.

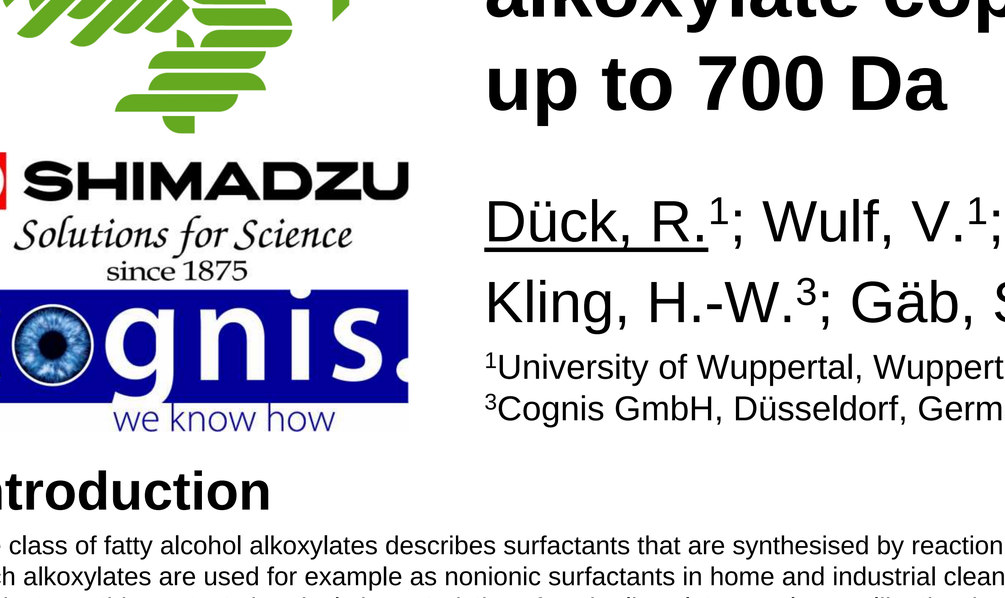

Figure 1: GCxGC chromatogram of a commercial cleaner containing fatty alcohol alkoxylates
Abbreviations: FA = fatty alkohol; FS = fatty acid; FAEO = ethoxylated fatty alkohols; FAPOEO = fatty alkohol block-co-polymers (propoxylated and ethoxylated); APG = alkyl polyglucosides

Sample preparation: 50 mg of the technical product was silylated with 2 ml of a BSTFA / MSTFA mixture (5:1; v/v). The derivatisation was carried out for 1 h at 80 °C.

Figure 2: Extracted chromatogram of the fatty alcohol alkoxylate spots from chromatogram in figure 1 (propoxylate-ethoxylate block-co-polymer) in CI mode and the assigned structures of different monomer sequences for the second degree of alkoxylation
Abbreviations: PO' = main isomer resulting from nucleophile ring opening reaction of propylene oxide; PO'' = co-isomer resulting from nucleophile ring opening reaction of propylene oxide

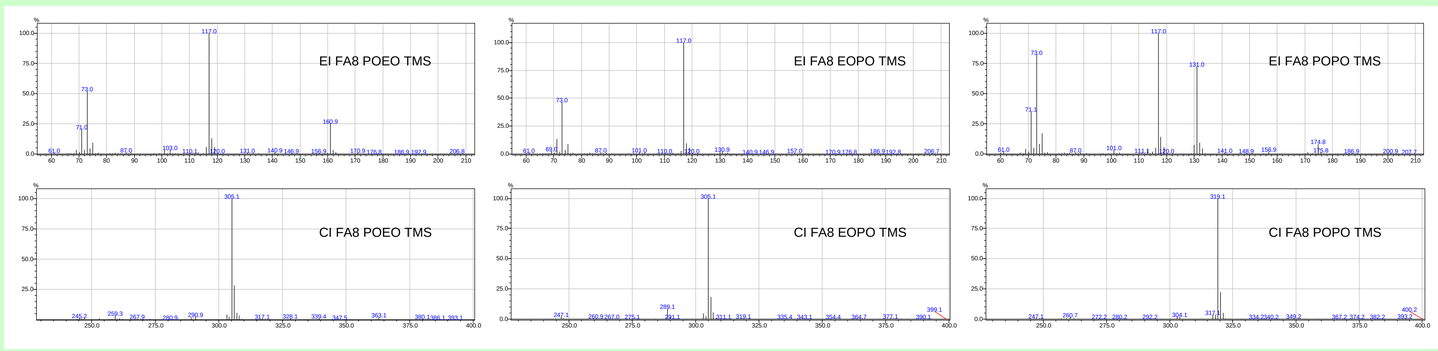

Figure 3: Comparison of mass spectra (EI-qMS, above and CI-qMS, below) of the C8 based fatty alcohol alkoxylates co-polymer (POEO / EOPO / POPO) spots

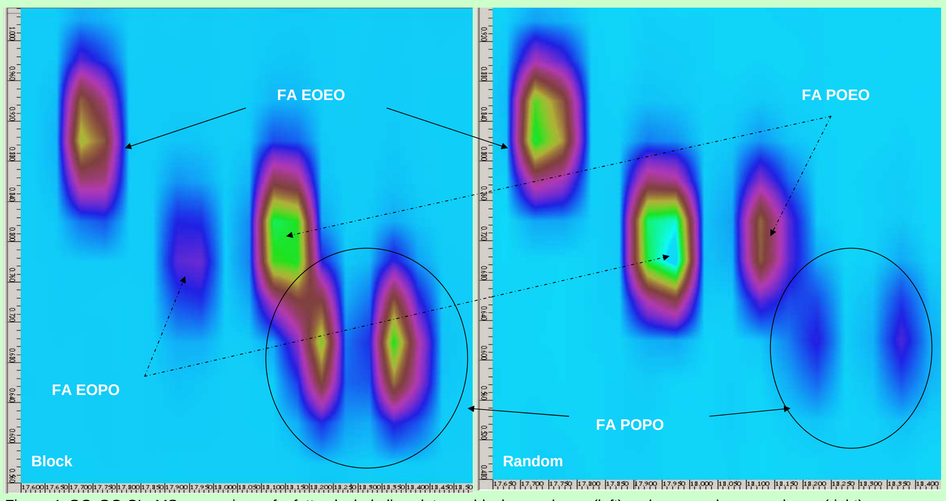

Figure 4: GCxGC-CI-qMS comparison of a fatty alcohol alkoxylat as a block-co-polymer (left) and as a random-co-polymer (right)

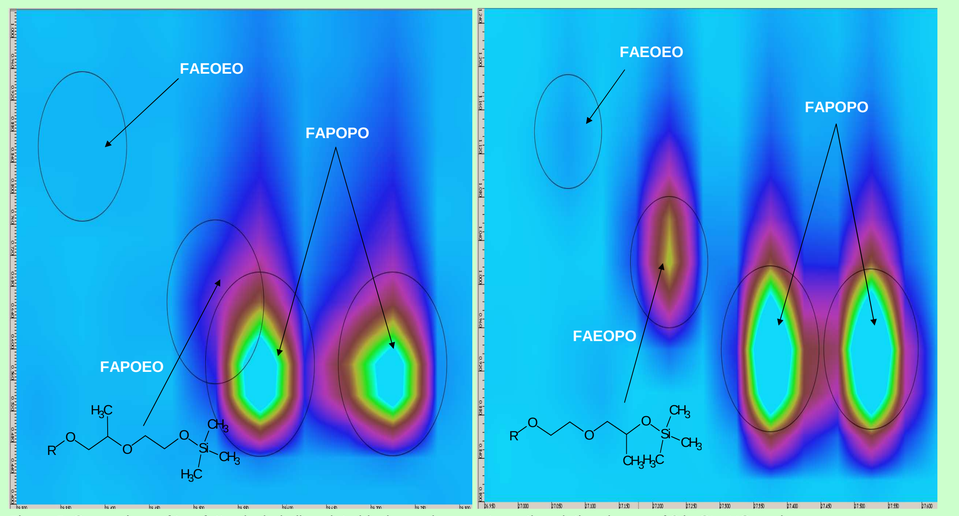

Figure 5: Comparison of two fatty alcohol alkoxylate block-copolymers at an ethoxylation degree of 2 in CI-qMS mode
left = product polymerisation started with propylene oxide (POEO) right = product polymerisation started with ethylene oxide (EOPO)

Discussion and Conclusions

The combination of two different ionisation techniques (EI, CI) in connection to GCxGC is a powerful tool to analyse complex technical products and product mixtures and in addition to characterise and identificate the structures of some components.

The technical mixture (GCxGC chromatogram shown in figure 1) contains different oleochemical based ingredients like fatty acids, fatty alcohols and nonionic surfactants as alkylpolyglucosides, fatty alcohol ethoxylates and fatty alcohol alkoxylates. The copolymer nonionic surfactants (fatty alcohol alkoxylates) are even more complex than the pure ethoxylates. Only with a combination of EI and CI the exact identification and the building block characterisation is realisable (figure 2, 3).
Due to that it is also possible to differentiate between block and random copolymerisation. A block-co-polymer for example shows a larger peak area for the FA-POPO-product spot in contrast to the random-co-polymer. In the opposite the FA-EOPO product spot is much more distinctive as the spot in the random-co-polymer (figure 4). Furthermore it is also possible to identify the starter building block within a block-co-polymer group. The FA-EOPO product spot arises in a higher concentration if the polymerisation is started with ethylene oxide than the product with a PO starting block (figure 5).

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