

Short Communication

Molar mass determination of oligomeric ethylene oxide adducts using supercritical fluid chromatography and matrix-assisted laser desorption–ionization time-of-flight mass spectrometry

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Abstract

Supercritical fluid chromatography (SFC) and matrix-assisted laser desorption–ionization time-of-flight mass spectrometry [MALDI-MS (TOF)] are suitable, mutually complementary methods for characterizing oligomeric ethylene oxide adducts. While SFC is successfully applicable in the low-molecular-size range up to molar masses of *ca.* 1000 g/mol, MALDI-MS facilitates proper differentiation also in higher molar mass ranges. In the lower molar mass ranges down to approximately degree of polymerization $n = 6$, the problem of discrimination arises when MALDI-MS is applied; this problem is reduced considerably through the addition of lithium chloride instead of sodium or potassium ions, a measure which also eases identification of the molar peak. Provided that the ethylene oxide chain is known, it is also possible to definitely determine substituents in the molecule (*e.g.*, alkyl or arylalkyl chains). By-products, which may arise, for example, when water is split off during the reaction or during storage, can be detected.

1. Introduction

Oligomeric ethylene oxide adducts are of great significance in the chemistry of both surfactants and polymers. From scientific and economic points of view, it is necessary to know the composition and the oligomer distribution of these compounds and mixtures.

In the low-molecular-size range, gas chromatography (GC) can be applied as a method of analysis. High-temperature GC (HTGC) facili-

tates high-resolution analysis in the shortest of times; further, its use in conjunction with various detection and other methods such as GC–MS, GC–IR and GC–LC is both well tested and easy to implement [1].

Supercritical fluid chromatography (SFC) extends the molar mass range. An essential advantage over GC is that the compounds can be eluted at lower temperatures. This is of particular significance with respect to thermolabile components or compounds. Capillary SFC is the method of choice for the molar mass range 500–1000 g/mol [2]; reversed-phase high-perform-

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ance liquid chromatography (RP-HPLC, gradient elution) can be applied for higher molar mass ranges, *e.g.*, for separating polyethylene glycols up to a molar mass of 4500 g/mol [3].

Separation of substances with comparably high molar masses has also been achieved with capillary SFC by increasing the density (pressures up to 560 bar at 120°C) [4]. Hitherto, however, commercially available equipment has permitted pressures only up to *ca.* 400 bar. Unknown samples can be identified by coupling SFC with mass spectrometry (MS).

In order to facilitate the analysis of polar compounds using SFC, the addition of modifiers, *e.g.*, methanol or acetone, to the supercritical fluid carbon dioxide is recommended. In this instance detection can be implemented through the use of an evaporative light-scattering detector. In this work on the composition and purity of oligomeric ethylene oxide adducts, the chromatographic technique used was SFC with supercritical carbon dioxide and flame ionization detection (FID).

During the past few years, matrix-assisted laser desorption–ionization mass spectrometry (MALDI-MS) has proved a valuable complement to chromatography. This method is based on the principle that the dissolved specimen is mixed with a matrix and then crystallizes. The specimen is desorbed and ionized by laser incidence. The molar mass is determined by the time of flight (TOF) [5–11]. The aim of this investigation was to compare the information obtained through MALDI-MS (TOF) with that obtained by SFC with respect to the composition and purity of oligomeric ethylene oxide adducts.

2. Experimental

2.1. SFC

A Lee Scientific 602-D system with a fused-silica separation column (10 m × 50 μm I.D.) was used with SB-Biphenyl-30 as the stationary phase and CO₂ (SFC grade; Scott, Plumsteadville, PA, USA) as the mobile phase. FID at 380°C was applied. An integral restrictor was used and

the injection system was a switching valve with an internal loop (Valco) and timed split.

For the chromatograms shown in Fig. 1a–f the oven temperature was initially 100°C (5 min isothermal), then programmed at 1.6°C/min to 200°C. The pressure was initially 100 bar (5 min isobaric), then increased at 10 bar/min to 300 bar and at 5 bar/min to 400 bar, with 30 min isobaric at 400 bar. For the chromatograms shown in Fig. 1g–i the oven temperature was 130°C and the density was programmed from 0.25 to 0.55 g/ml in 42.86 min and from 0.55 to 0.7 g/ml in 27.27 min.

2.2. MALDI-MS

A Kratos Compact MALDI III system was used in the positive-ion mode with reflectron time-of-flight, and a 20 kV accelerating voltage. The matrix was dihydroxybenzoic acid (10 mg/ml in acetone).

2.3. Reference substances

The following series of substances were chosen for this study: defined polyethylene glycols (degree of hydroxyethylation $n = 4, 6, 8$); defined *n*-octylpolyethylene glycol ethers ($n = 3, 4, 6$); and defined *p*-isononylphenylpolyethylene glycol ethers ($n = 2, 6, 9$). These defined substances were prepared either by specific synthesis or by distillative isolation from homologous mixtures [2].

3. Results and discussion

For the molar mass range of the oligomeric ethylene glycols, alkylethylene glycol ethers and alkylarylethylene glycol ethers studied, SFC has shown itself to be the method of choice. The reference substances facilitate a precise assignment of the peaks in the distribution chromatogram (Fig. 1a–i). This is fundamental for the calculation of the molar masses for oligomeric mixtures [2]. In the case of hydroxyethylated *p*-isononylphenols, SFC provides not only for a separation according to the degree of hydroxy-

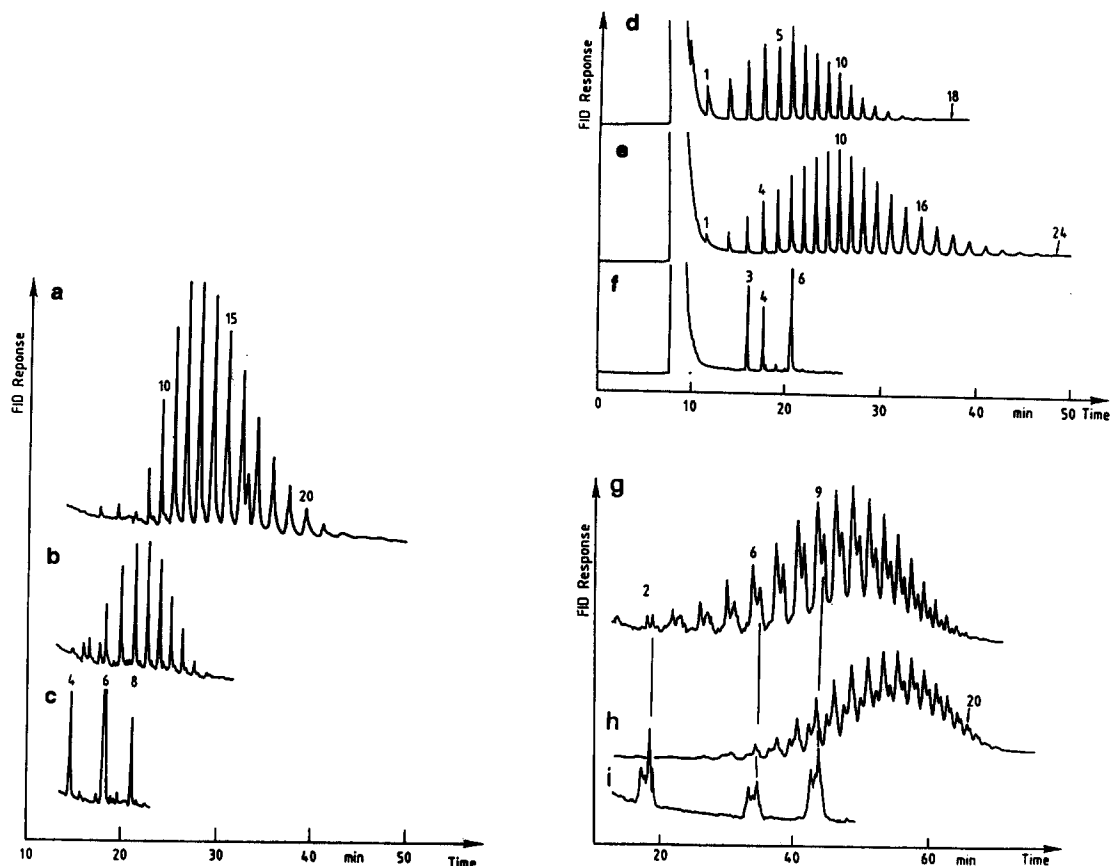


Fig. 1. SFC of (a) polyethylene glycol (PEG 600) (Polymer Laboratories, Church Stretton, UK), (b) polyethylene glycol (PEG 440) (Polymer Laboratories), (c) a mixture of reference substances (defined polyethylene glycols, $n = 4, 6, 8$), (d) *n*-octylpolyethylene glycol ether ($n = 5_{\text{statistical}}$), (e) *n*-octylpolyethylene glycol ether ($n = 10_{\text{statistical}}$), (f) a mixture of reference substances (defined polyethylene glycol ethers, $n = 3, 4, 6$), (g) *p*-isoalkylphenylpolyethylene glycol ether ($n = 10_{\text{statistical}}$), (h) *p*-isononylphenylpolyethylene glycol ether ($n = 13_{\text{statistical}}$) and (i) a mixture of reference substances (defined *p*-isononylphenylpolyethylene glycol ethers, $n = 2, 6, 9$).

ethylation but also according to the alkyl residues on the benzene ring. However, differentiations of this type become difficult where a branched nonylphenyl ethoxylate in the presence of, for example, octylphenyl ethoxylate is involved (Fig. 1g–i). Here MALDI-MS provides decisive information; it permits the exact determination of the lengths of the alkyl chains in the compound. Of course, branched chains cannot be differentiated from the corresponding linear chains, because the method only separates by mass. Both methods, SFC and MALDI-MS, complement each other to provide a solution to this analysis problem.

MALDI-MS provides outstanding differentiation in the higher molar mass range. While SFC for polyethylene glycol (PEG) 600, for example, facilitates the detection of components up to a degree of polymerization $n = 24$, MALDI-MS can differentiate up to a $n = 30$. In this molar mass range MALDI-MS is therefore superior to SFC. The reduced time required in comparison with an analysis by capillary SFC is also noteworthy.

A different picture is obtained in the molar mass range below *ca.* 500 g/mol. On application of MALDI-MS, a clear discrimination of the low-molar-mass components can be noted. In the

mass spectrum of the reference mixture tetra-, hexa- and octaethylene glycol (1:1:1), the peak for degree of polymerization $n = 6$ (molar mass 282 g/mol) shows only *ca.* 45% of the peak height to be expected in accordance with the mixture components as compared with $n = 8$ (molar mass 370 g/mol), and $n = 4$ (molar mass 194 g/mol) only shows *ca.* 4% as compared with $n = 8$ (Fig. 2a). The spectra show the molar peaks plus the mean molar mass of lithium (*ca.* 7 g/mol).

A similar result is obtained for a reference mixture of *n*-octyl(tri-, tetra- and hexa)ethylene glycol ethers (1:0.8:1). The peak for degree of polymerization $n = 4$ (molar mass 306 g/mol) shows only *ca.* 75% of the peak height to be expected in accordance with the mixture components as compared with $n = 6$ (molar mass 394 g/mol), and $n = 3$ (molar mass 262 g/mol) shows

only *ca.* 20%. As in SFC, so too the MALDI mass spectrum shows a small portion of $n = 5$ (molar mass 350 g/mol) (Fig. 2c).

The spectra usually show the molar peaks plus the molar mass of sodium (23 g/mol) and potassium (39 g/mol). Unless they have been specifically added, the sodium and potassium ions come from contaminants in the specimen and/or the matrix. Alternatively, the quality of the result can be influenced by adding a suitable salt [12]. The addition of lithium chloride suppresses the discrimination of the low-molar-mass components in the oligomeric mixture. While the mass spectrum of the octylpolyethylene glycol ether ($n = 5_{\text{statistical}}$) only begins at $n = 6$, the addition of lithium chloride makes it possible to also discern $n = 5$, 4 and 3. However, even in this preparation of the specimen, $n = 2$, 1 and 0, which are distinctly separated in SFC, are miss-

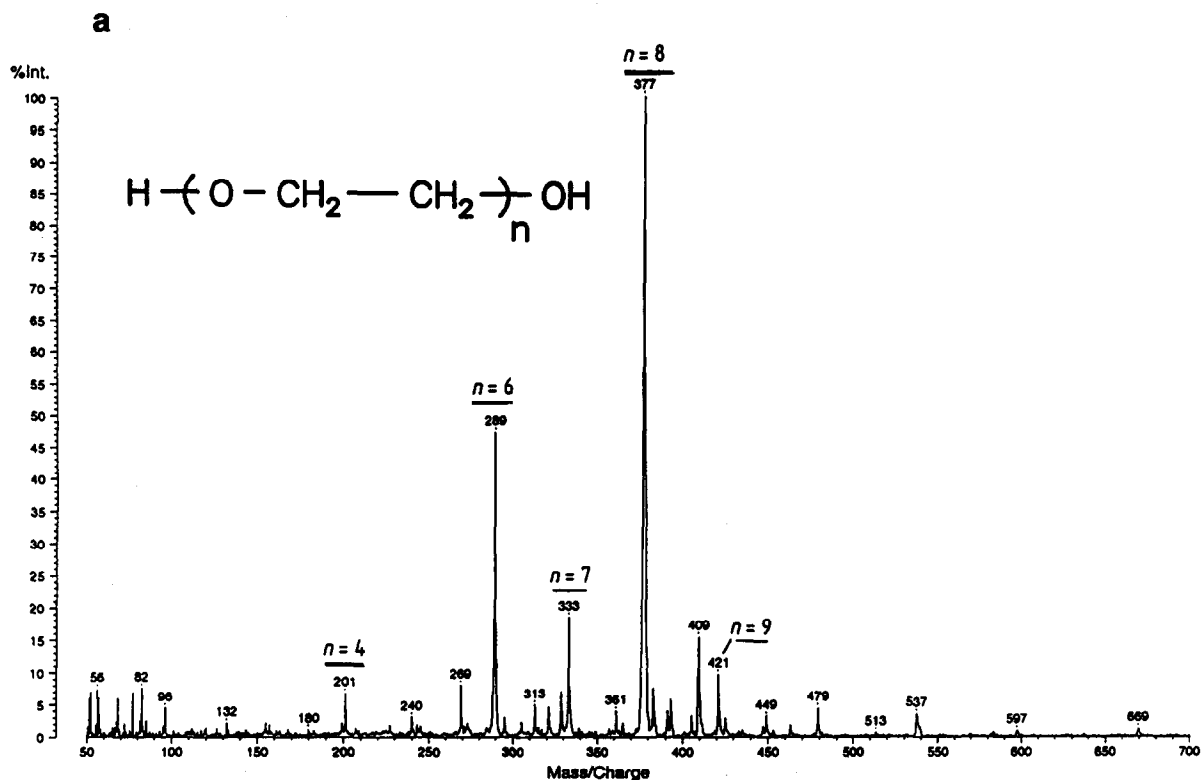


Fig. 2.

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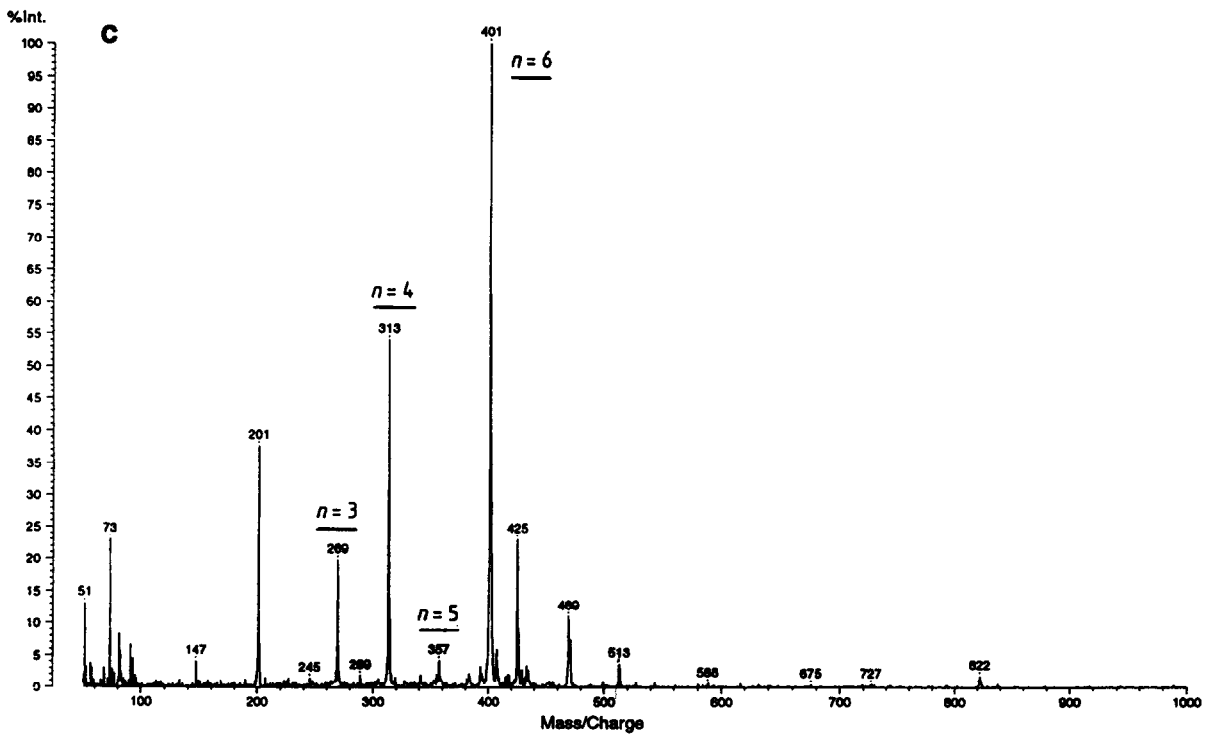
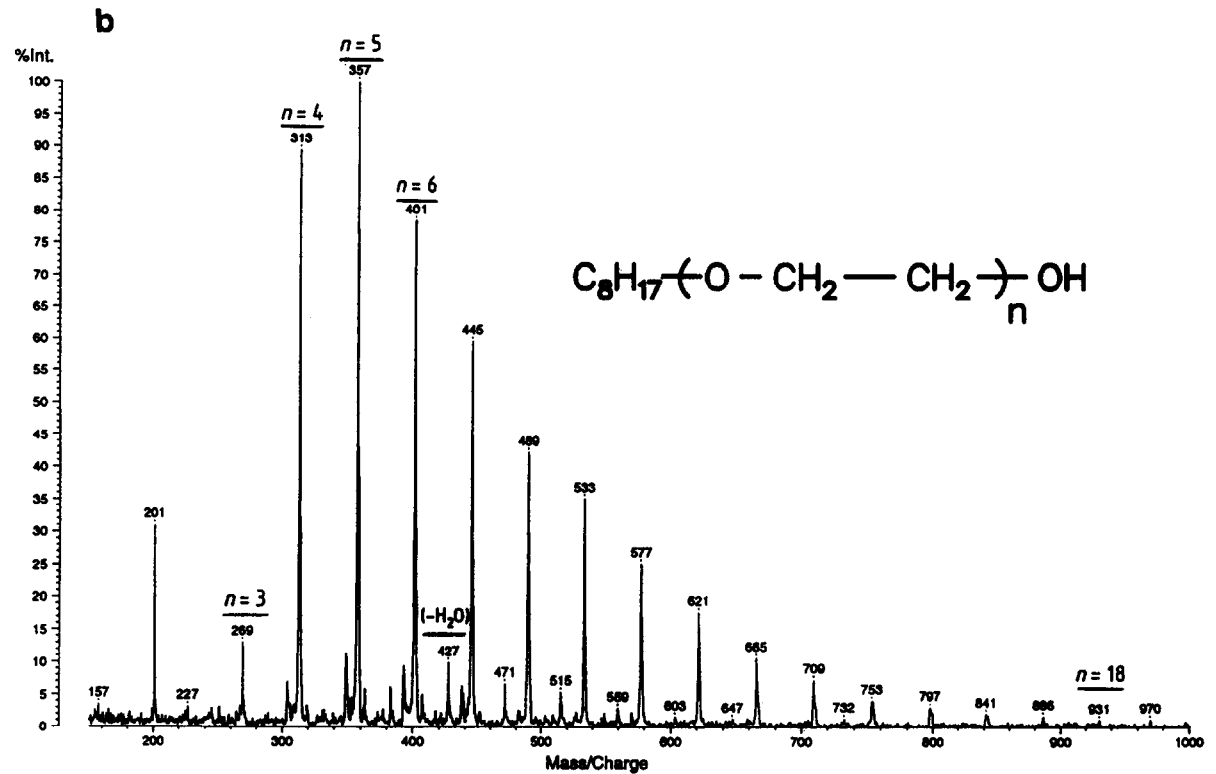


Fig. 2.

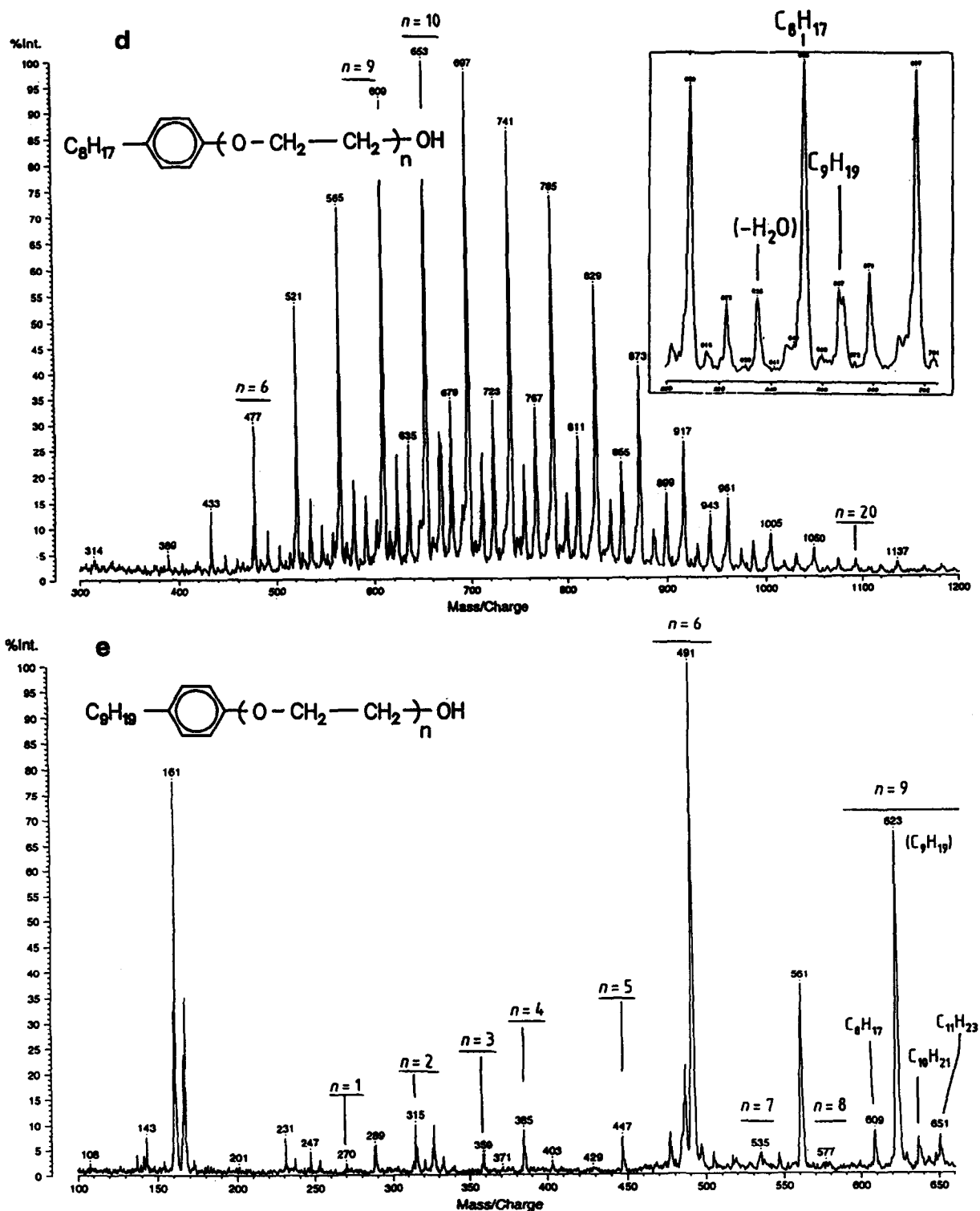


Fig. 2. MALDI mass spectra of (a) a mixture of reference substances (defined polyethylene glycols, $n=4, 6, 8$), (b) n -octylpolyethylene glycol ether ($n=5_{\text{statistical}}$), (c) a mixture of reference substances (defined n -octylpolyethylene glycol ethers, $n=3, 4, 6$), (d) p -isoalkylphenylpolyethylene glycol ether ($n=10_{\text{statistical}}$) and (e) a mixture of reference substances (defined p -isononylphenylpolyethylene glycol ethers, $n=2, 6, 9$).

ing in the MALDI mass spectrum, as a comparison between Fig. 2b with Fig. 1d shows. An essential advantage provided by the addition of lithium chloride is that sodium and potassium ions hardly appear, so that the spectra can be more easily interpreted. In the spectrum for octylpolyethylene glycol ether ($n = 5_{\text{statistical}}$), when lithium chloride is added a second distribution is identifiable, the molar masses of which are respectively 18 u per degree lower than for the regular n -degrees; this can be explained through mutual reactions with each other resulting in water splitting off (Fig. 2b). The maximum of this distribution is shown for molar mass 420 g/mol.

Through the application of MALDI-MS, it can be further shown that the mixture of the reference substances nonylphenyl ethoxylate with $n = 2, 6$ and 9 also contains components of all degrees $n = 1-9$; further, for example, for $n = 9$, it is found that the alkyl residue not only consists of a nonylic residue, but that there are also small portions of octyl, decyl and undecyl residues (Fig. 2e).

The mass spectrum of the p -iso-alkylphenylethoxylate ($n = 10_{\text{statistical}}$) clearly shows octylphenyl ethoxylate as the main component; a second distribution shows nonylphenyl ethoxylate with a 14 g/mol higher molar mass per degree. With addition of LiCl, the molar peak can be clearly interpreted. When LiCl is not used and sodium and potassium ions are present,

the presence of the latter hampers identification. The third distribution, on the other hand, again shows water split off (Fig. 2d). With MALDI-MS, this reaction can be clearly seen in specimens PEG 440 and p -isononylphenyl ethoxylate ($n = 14_{\text{statistical}}$).

4. References

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