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On-line HPLC ^{1}H NMR coupling for the analysis of fatty alcohol ethoxylates

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Summary

The characterisation of fatty alcohol ethoxylate based surfactants by on-line LC-NMR coupling is described. Different surfactant mixtures were separated by a mixed exclusion-adsorption method of liquid chromatography and simultaneously characterised by ^{1}H-NMR spectroscopy. Information about the degree of oligomerisation of the ethylene oxide chain and the chemical structure of the endgroups can be obtained in a one-step experiment.

Introduction

Nuclear magnetic resonance (NMR) spectroscopy is one of the most powerful non invasive techniques to achieve unambiguous structural information on almost all sample classes, including highly polar or ionic compounds as well as sensitive samples. The hyphenation of liquid chromatography (LC) techniques with NMR spectroscopy combines the efficient separation of complex mixtures on-line with structural identification (1). Hyphenation of high performance liquid chromatography (HPLC) and NMR has many advantages over conventional off-line separation. In most cases off-line techniques are laborious and time-consuming, including working up the samples for re-dissolving in deuterated solvents, and subsequent recording of NMR spectra. Hyphenated experiments enable the simultaneous separation and ^{1}H NMR detection in a closed system (2). However, only few examples of this powerful hyphenated technique in polymer analysis are reported up to now (3).

Technical fatty alcohol ethoxylates (FAE) are prepared by ionic polymerization of ethylene oxide, using a fatty alcoholate as the starter. In addition to the formation of the desired α-alkoxy-ω-hydroxy polyethylene oxide (PEO), the polymerization process is known to lead to a number of by-products such as polyethylene glycol (PEG), cyclic oligomers, and α,ω-dialkoxy PEO. Accordingly, the reaction products consist of more than one ethylene oxide homologous series, differing in the type of the endgroup.

A separation of FAE with respect to the endgroups can be achieved by different means of interaction chromatography (4,5). Using typical stationary phases for reversed phase chromatography and binary eluents, e.g. acetonitrile-water or methanol-water, the different functionality fractions are isolated regardless of the molar mass distribution. The analysis of a technical PEO by coupling a functionality type separation and ^{1}H-NMR has been published recently (6).

Experimental

Materials

The FAE samples under investigation were technical products of BASF AG, Ludwigshafen. For all HPLC separations, acetonitrile (ACN), (LiChrosolv gradient grade, Merck, Darmstadt, Germany) and [$^2H_2$]water 99.9 % (Deutero GmbH, Herresbach, Germany) were used.

Chromatography

Separations were carried out under ambient conditions using a Merck Lichrograph L-6200A intelligent pump and a Hewlett-Packard refractive index (RI) detector 1037A (Waldbronn, Germany). For all experiments, a flow rate of 0.5 ml/min was used and the separation was monitored by RI. The eluent was an isocratic mixture of acetonitrile-deuterium oxide (70:30). Chromatography was performed on a Nucleosil-5 C_{18} column (125 mm × 4.0 mm, Macherey-Nagel, Düren, Germany). 50 µl of sample solution (20mg/ml) were injected.

LC-NMR

The experimental set-up for LC-NMR experiments has been described in detail elsewhere (7). NMR spectra were recorded by use of a Bruker ARX 400 spectrometer (Bruker, Rheinstetten, Germany) equipped with an LC-probe matched with a radio frequency (rf) coil selective for protons and a detection cell of 120 µl volume. The ^2H resonance of the eluent D_2O was used for field-frequency lock. The NMR spectra were recorded at 300 K. During the separation 64 FIDs with a total acquisition time of 5.4 s per FID were recorded. For each FID 16 transients with 4096 complex data points and a spectral width of 6024 Hz were accumulated. The spectrum was centred on the acetonitrile methyl resonance. Suppression of the solvent methyl resonance was achieved by application of a NOESY-type pulse train with a presaturation time of 900 ms during the relaxation time and of 80 ms during mixing time. Data were treated as a pseudo 2D NMR matrix (F_1 = retention time) and processed with XWINNMR® software. A phase sensitive Fourier transformation was performed in the F_2 direction only. Prior to Fourier transformation, a shifted sine bell function (shift 2.0) was applied to the FID in F_2 only.

Results and discussion

The present samples are mixtures of PEG and FAE with different endgroups. In agreement with previous investigations, the functionality type separation shall be carried out on a Nucleosil RP-18 stationary phase using acetonitrile-deuterium oxide as the eluent. The optimum conditions for such a separation correspond to a mixed exclusion-adsorption mechanism which can be established, e.g. using an eluent of acetonitrile-deuterium oxide 70:30 % by volume.

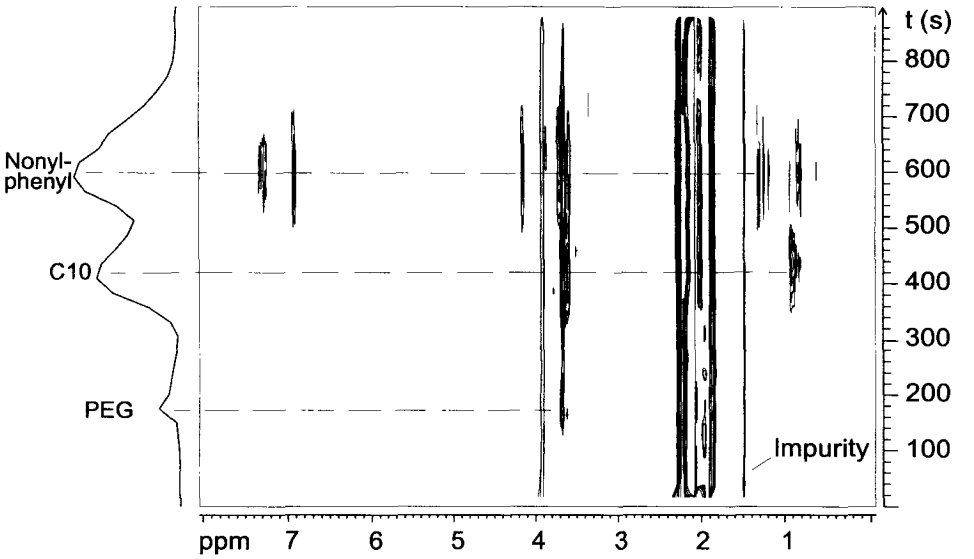

Figure 1. Contour plot of chemical shift vs. retention time and reconstructed chromatogram of sample 1

The analysis of a typical mixture comprising three components is shown in Fig. 1 as an NMR chromatogram. In such a representation the ^{1}H NMR frequency domain is in the horizontal dimension and the chromatographic separation time is in the vertical dimension. The chromatogram along the F_1-axis was reconstructed by a summation over the ^{1}H NMR signal intensities. Although such a reconstruction suffers from a small number of data points, the separation of the sample into three components is readily recognizable.

Due to the high price, in LC-NMR protonated solvents are used instead of deuterated solvents. Therefore, one drawback of LC-NMR is the presence of strong resonance signals of the LC eluent. Several pulse techniques have been successfully introduced to reduce the intensity of the solvent signals, however in all cases residual solvent signals are still present. These relate to the proton signals of acetonitrile at 1.8 to 2.2 ppm and of water at 3.9 ppm. Beside these remaining signals, the characteristic spectral regions of the oxyethylene resonances and the resonances of the endgroups are free for interpretation. In particular, all three components exhibit NMR signals at about 3.7 ppm, which can be attributed to the protons of -CH_2O- groups. Accordingly, it can be assumed that all three elution peaks are due to ethylene oxide oligomers (repeat unit -CH_2CH_2O-).

Figure 2 illustrates the NMR spectra extracted from the contour plot at the corresponding chromatographic peak maxima. It is evident that the sample components are polyethylene oxides with different endgroups. The analysis of the aliphatic and the aromatic part of the spectrum gives evidence about the chemical structure of the end-

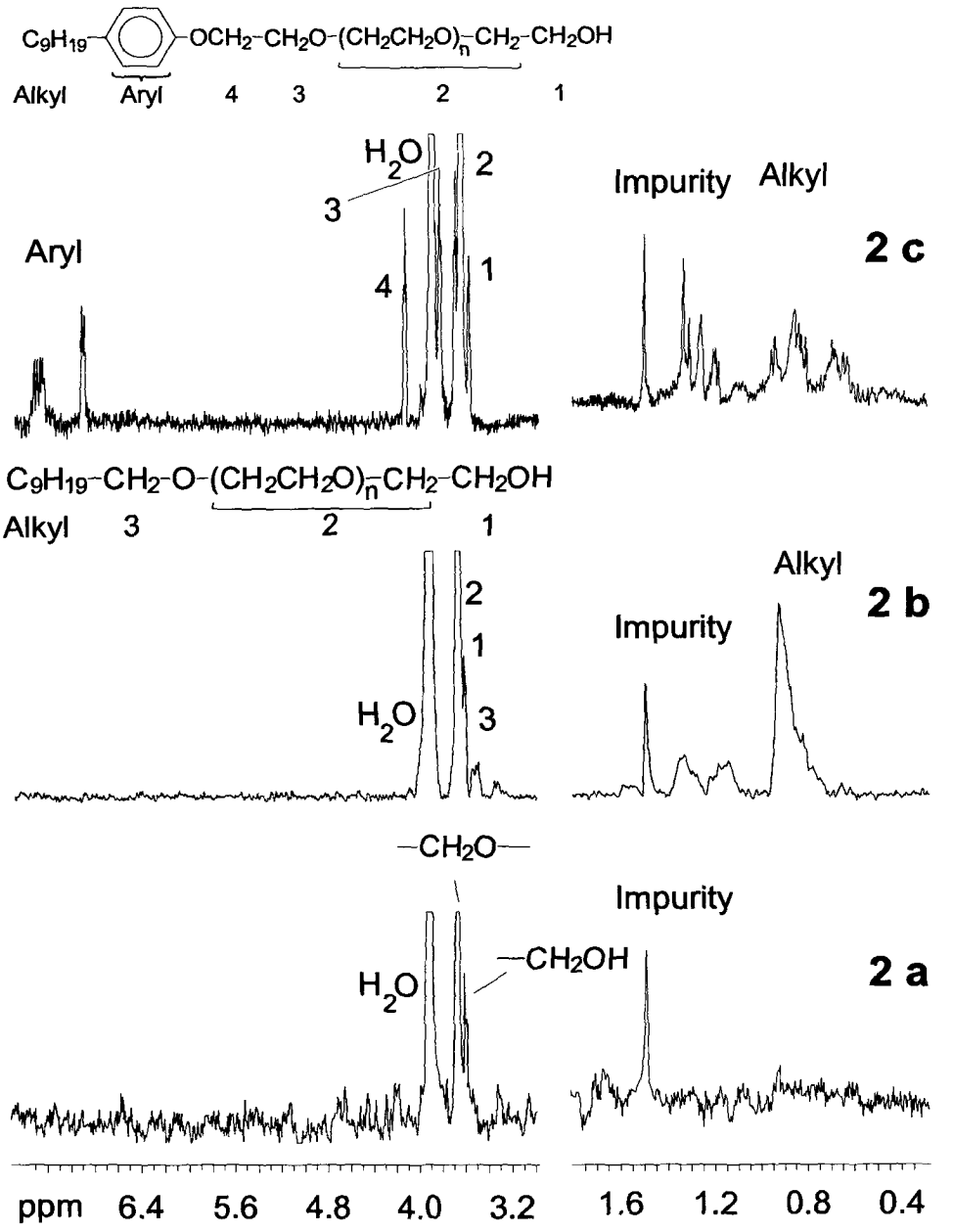

Figure 2. NMR spectra of the three components of sample 1 extracted from the contour plot in Fig. 1

groups including their linearity or branching. The ratios of the integrals of the oxyethylene region (-CH_2O-) to the terminal -CH_2OH group reveal the degree of oligomerisation. Peak 1 (Fig. 2a) does not contain an aliphatic or aromatic endgroup and can be assigned to PEG which is known to be present as an unwanted by-product. Peak 2 (Fig. 2b) is shown to contain an aliphatic decyl endgroup with an average of three methyl, four methylene and two methine groups as can be determined by integrating the aliphatic region. Peak 3 (Fig. 2c) exhibits aromatic protons in addition to the aliphatic protons and can be assigned to an average structure of nonylphenol-terminated polyethylene oxide. The complexity of the aromatic proton signals and the aliphatic methyl signals indicate that different substitution patterns at the endgroup are present in this fraction.

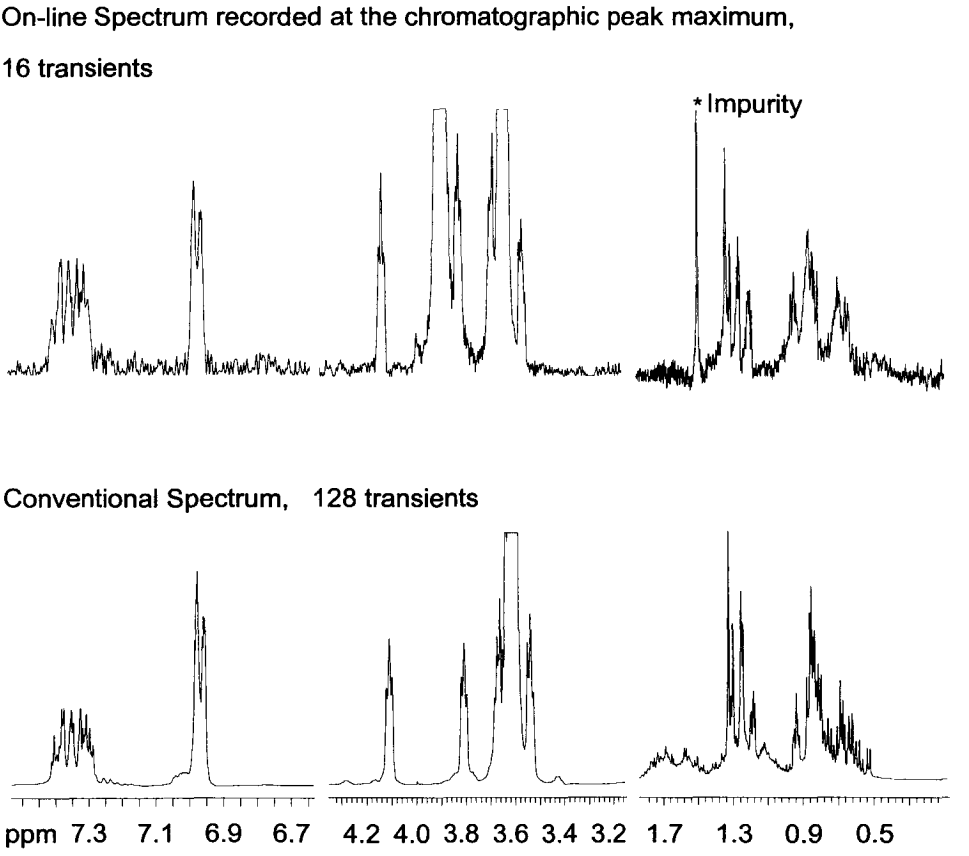

Figure 3. Comparison of on-line and conventional NMR spectra of the nonylphenol PEO fraction of sample 1

Figure 3 depicts a comparison of on-line and conventional NMR spectra of the nonylphenyl PEO fraction. Both spectra show a good agreement in their information content. The substitution pattern at the aromatic ring can be assigned as para-substitution. The integration ratio and the chemical shifts confirm this statement. The

splitting of the aromatic signal at 7.3 ppm indicates that the nonyl group is heterogeneous in configuration. This effect of diversity in the side chain is even more evident in the aliphatic part of the spectrum.

The contour map of the separation of a three component system of PEG, decyl and dodecyl FAE is shown in Figure 4. Information about differences in the aliphatic endgroups arise directly from the on-line spectrum, the degree of branching can be determined by integrating the resonance signals of the aliphatic region. Whereas the decyl substituent is branched, the dodecyl chain is linear. This follows directly from the comparison of the integration ratios of methyl groups versus methylene groups. Methine groups have not been observed for the dodecyl FAE component.

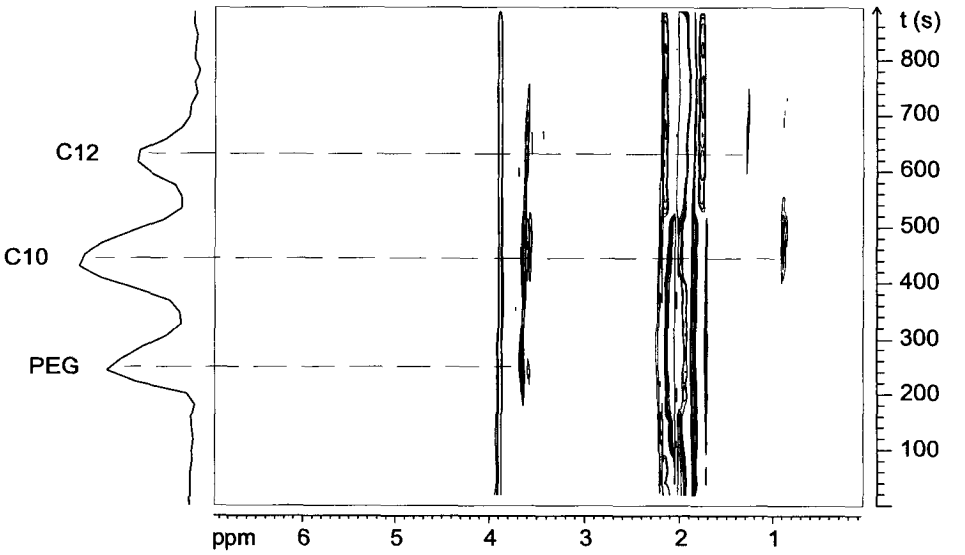

Figure 4. Contour plot of chemical shift vs. retention time and reconstructed chromatogram of sample 2

Table 1. α-Hydroxy-ω-alkoxy(aryloxy) FAE structural information obtained by on-line LC-NMR

Sample	Components	n	Alkoxy(aryloxy) Endgroup
1	PEG	4	---------
	C10-PEO	9	$-(CH_2)_5-CH(CH_3)-CH(CH_3)_2$
	Nonylphenyl-PEO	9	$-C_6H_4-C_9H_{19}$ isomeric mixture
2	PEG	6	---------
	C10-PEO	9	$-(CH_2)_5-CH(CH_3)-CH(CH_3)_2$
	C12-PEO	11	$-(CH_2)_{11}-CH_3$

n = average degree of oligomerisation

In conclusion, it has been shown that on-line HPLC NMR coupling provides excellent structural information on complex polymer systems. Running one single on-line experiment, information on the number of components, their chemical composition and substitution pattern can be obtained. The degree of oligomerisation of each component is accessible, thus providing a true two-dimensional information in the coordinates chemical composition and molar mass, see Table 1 for a summary of the results.

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