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Journal of Chromatography A, 952 (2002) 149–163

JOURNAL OF CHROMATOGRAPHY A

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Liquid exclusion–adsorption chromatography, a new technique for isocratic separation of nonionic surfactants IV. Two-dimensional separation of fatty alcohol ethoxylates with focusing of fractions

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Received 18 October 2001; received in revised form 18 January 2002; accepted 18 January 2002

Abstract

Fatty alcohol ethoxylates can be analyzed using a combination of liquid chromatography under critical conditions as the first dimension and liquid exclusion–adsorption chromatography as the second dimension. Transfer of fractions from the first to the second dimension is achieved using the full adsorption–desorption (FAD) technique. The peaks of interest in the first dimension are trapped on a short precolumn before injecting them into the second dimension. Full adsorption is achieved by increasing the water content in the mobile phase before the FAD column. When the fractions are desorbed by switching to the mobile phase of the second dimension, they are focused and reconcentrated. In this way, a full resolution of oligomers is achieved. As both dimensions are run in isocratic mode, density and refractive index detection can be applied, which allows an accurate quantitation.

Keywords: Liquid exclusion–adsorption chromatography; Liquid chromatography under critical conditions; Fatty alcohol ethoxylates; Ethoxylates; Alcohol ethoxylates; Surfactants

1. Introduction

Fatty alcohol ethoxylates (FAEs) are commonly used as nonionic surfactants. The oligomer distribution of these products depends on the conditions applied in the ethoxylation reaction (catalyst, temperature, etc.). FAEs based on pure fatty alcohols contain one polymer homologous series, hence they can be sufficiently characterized by one-dimensional HPLC. Technical samples are, however, based on technical fatty alcohols, which mostly contain considerable amounts of other fatty alcohols, and typically consist of at least two polymer homologous series.

The producer of such surfactants, who knows the purity or composition of his starting material, is mainly interested in the overall degree of ethoxylation, and assumes that all polymer homologous series in his sample have the same oligomer distribution.

In the analysis of unknown surfactant samples, the oligomer distribution of the individual polymer homologous series must be determined, as it may well be the case, that different FAEs with similar HLB value, but different functionality and oligomer distribution have been mixed. Consequently, their

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0021-9673/02/$ – see front matter
PII: S0021-9673(02)00076-6

full characterization requires a two-dimensional separation (according to functionality and molecular mass distribution).

As has been discussed in previous papers [1–3], different modes of liquid chromatography can be applied in the analysis of nonionic surfactants. These techniques may also be combined to achieve multi-dimensional separations:

(i) Size-exclusion chromatography (SEC) separates according to molecular size (not actually molecular mass!). It is always performed in isocratic mode, typically in pure solvents. SEC has a low separation efficiency, but allows an accurate quantification.

(ii) Liquid adsorption chromatography (LAC) separates according to chemical composition and to molecular mass [4]. In principle, LAC can be performed using isocratic or gradient elution, but samples with higher molecular mass typically require gradients [5–7]. High resolution can be achieved by gradient LAC; the quantitative reliability is, however, questionable because of detection problems [8–12].

(iii) Liquid chromatography at the critical adsorption point (CAP), often also called LC under critical conditions (LCCC) [13–18], is run at a special temperature and mobile phase composition, at which the polymer chain (or one block) becomes chromatographically invisible: all chains with the same repeating unit elute at the same elution volume (regardless of their length). In this case, a separation according to structural units other than the repeating unit (e.g. end groups) can be achieved. LCCC is run under isocratic conditions, but typically in mixed mobile phases.

(iv) Liquid exclusion–adsorption chromatography [2] allows a baseline separation of the individual oligomers up to 20–25 ethylene oxide units under isocratic conditions. In LEAC, a mobile phase composition is applied, in which the hydrophobic part is adsorbed, while the oxyethylene chain is still in the exclusion regime, where no interaction between the molecule's polyether part and the stationary phase takes place. The individual oligomers are eluted in order of decreasing molecular mass (as in SEC, but far behind the void volume of the column!). LEAC allows a satisfactory separation of the individual ethoxylate oligomers under isocratic conditions, which makes quantitation much easier [3] than in gradient LAC.

The typical approach in the analysis of FAEs by two-dimensional liquid chromatography employs LCCC on a reversed-phase column in the first dimension (under critical conditions for polyoxyethylene), which allows a separation of the individual series of ethoxylates. In the second dimension, SEC, gradient LAC, or LEAC can be applied.

The crucial point in two-dimensional LC is always the transfer of fractions from the first dimension to the second one. In this paper, a new approach is presented, which uses a reconcentration step on a small storage column.

1.1. Transfer of fractions from the first to the second dimension

Obviously, a direct transfer between non-miscible mobile phases is not possible, as would be the case with typical reversed-phase eluents (such as methanol–water) and organic SEC eluents (as $CHCl_3$).

On the other hand, aqueous mobile phases from the first dimension (LCCC on a reversed-phase column) can destroy the separation in the second dimension (typically LAC on a normal-phase column).

Both problems can be solved by performing LCCC in the first dimension on a semi-preparative scale, collecting fractions from which the mobile phase is evaporated, and re-dissolving them in the mobile phase used in the second dimension [19,20]. This procedure is, however, laborious and subject to various kinds of errors in sample handling. Moreover, impurities in the mobile phase of the first dimension are enriched, which is especially dangerous for broad peaks.

The worst problem arises, however, from dilution and peak dispersion: The fractions appearing at higher elution volumes in the first dimension, cannot be injected directly into the second dimension because of their too large volumes. Dividing these peaks into sufficiently narrow slices is not a good alternative, either, because this requires a lot of unnecessary chromatograms in the second dimension, which is time-consuming, and causes detection problems because of high dilution.

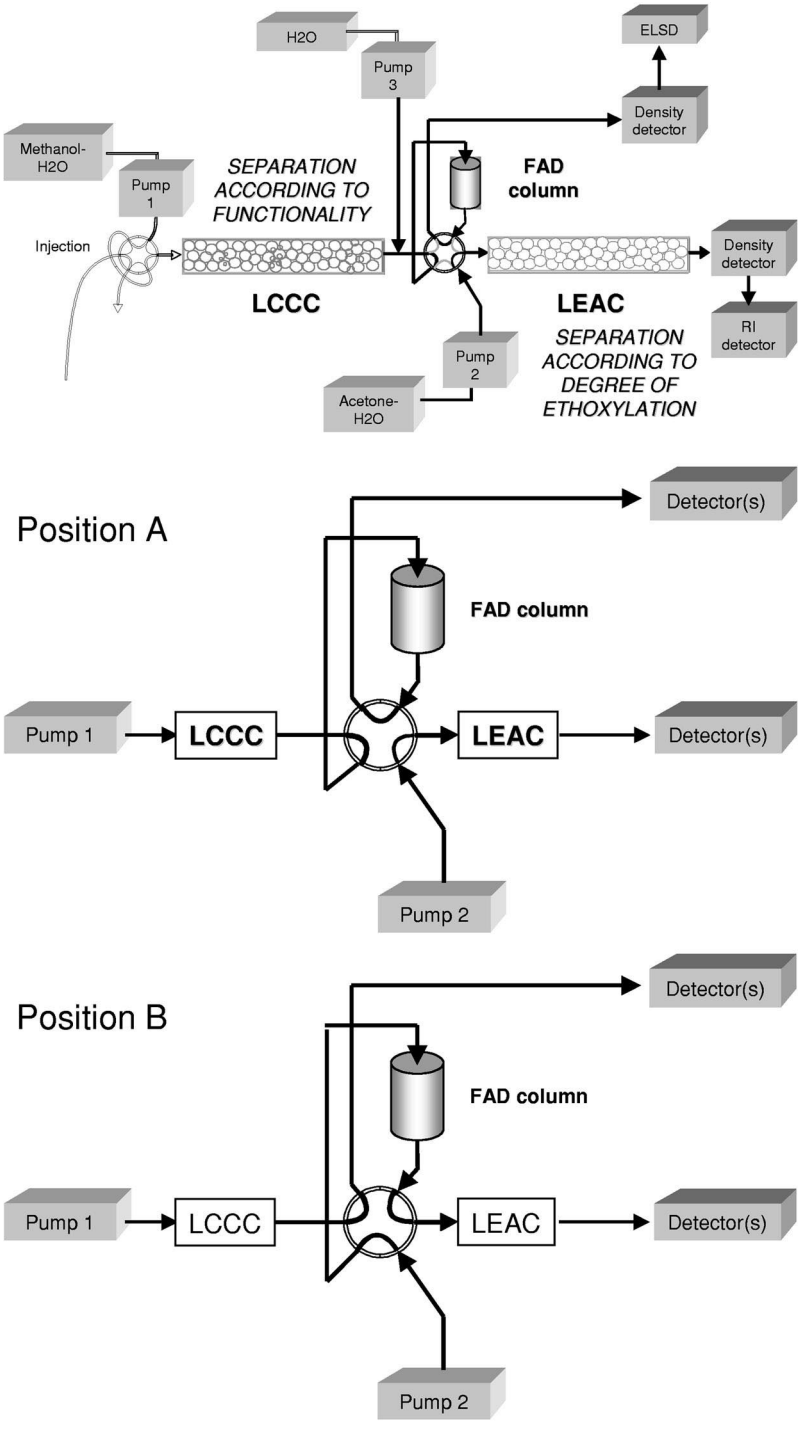

Fig. 1. (a) Experimental set-up for two-dimensional LC with a combination of LCCC as the first and LEAC as the second dimension and FAD for focusing of fractions. (b) Trapping of a fraction on the FAD column in the first dimension. (c) Injection of trapped fractions from the FAD column onto the second dimension.

Another problem concerns column dimensions and flow-rate: in the first dimension, a very low flow-rate must be applied, which allows running an entire chromatogram in the second dimension, while filling the storage loop in the first dimension. Consequently, small columns and high flow-rates are required in the second dimension, which limits the separation efficiency.

A solution to these problems can be the complete adsorption on a small column after the LCCC column, and subsequent elution with a different (strong) solvent. In this case, peaks are focused again and appear at the inlet of the column of the second dimension as very narrow zones.

Such a full adsorption–desorption (FAD) technique has been described by Berek and coworkers in several papers [21–27]. This approach works well for higher polymers, as retention increases exponentially with the number of repeat units: even a small change in polarity of the stationary phase between separation column and FAD column leads to complete adsorption on the latter.

In the case of oligomers, such as FAEs, there are, however, some limitations: If a reversed-phase column is used in the first dimension to separate the individual series of ethoxylates according to the hydrophobic alkyl groups (at the CAP for polyoxyethylene), it is hard to imagine, which kind of stationary phase could be so much more hydrophobic to adsorb a fraction completely.

The only way to achieve this goal is a change in polarity of the mobile phase (after the LCCC column) by increasing its water content. This can easily be done using another pump (delivering water), which is connected to the solvent stream between the outlet of the LCCC column and the FAD column (Fig. 1). When such a trapped fraction is eluted from the FAD column, it still contains a considerable amount of water. Consequently, the second dimension can neither be SEC in a typical organic solvent, nor gradient LAC on a normal-phase column: the water eluting from the FAD column would terminate the separation in the second dimension.

This problem can be overcome by using LEAC in the second dimension, the only chromatographic mode which tolerates rather high water concentrations: In LEAC, the water peak always runs in front of the ethoxylate peaks, hence it does not influence the separation of the latter.

In this paper, the scope and limitations of this approach will be evaluated.

2. Experimental

These investigations were performed using the density detection system DDS70 (Chromtech, Graz, Austria), which has been developed by our group. Data acquisition and processing were performed using the software package CHROMA, which has been developed for the DDS 70. Both columns and density cells were placed in a thermostatted box, in which a constant temperature of 25.0 °C was maintained for all measurements.

In LCCC, a flow-rate of 0.5 ml/min was maintained with an ISCO 2350 HPLC pump (ISCO, Lincoln, NE, USA). A Zorbax 300 C_{18} column (150×4.6 mm, 3.5 μm, 300 Å) was used for all measurements. A Guard-Pak precolumn module (''Butterfly'') containing a μBondapak C_{18} cartridge (3×4.6 mm, Waters, Milford, MA, USA) was used for focusing of fractions.

Samples were injected using a VICI injector (Valco Europe, Schenkon, Switzerland) with a 100-μl sample loop. A Sedex 45 evaporative light scattering detection (ELSD) apparatus (Sedere, Vitry sur Saine, France) was connected to the DDS 70. Nitrogen was used as the carrier gas, the pressure at the nebulizer was set to 1.0 bar and the temperature of the evaporator to 30 °C.

In LEAC, the mobile phase was delivered by a Jasco 880 PU pump (Japan Spectroscopic Co., Tokyo, Japan) at a flow-rate of 0.5 ml/min. A Prodigy 5 μm ODS(3) column (250×4.6 mm, pore diameter 100 Å, series 185970, from Phemonenex, Torrance, CA, USA) was used in all measurements. A Bischoff 8110 refractive index (RI) detector (Bischoff, Leonberg, Germany) was connected to the DDS 70.

Both dimensions were coupled using a six-port two-position valve with an electric actuator (EC6W, from Valco Europe, Schenkon, Switzerland).

Fig. 1 shows the experimental set-up. The positions of the switching valve and the corresponding mobile phase streams are shown in Fig. 1b,c.

The solvents (methanol and water, both HPLC grade) were purchased from Riedel-de Haen, Seelze, Germany). The following polydisperse FAE samples

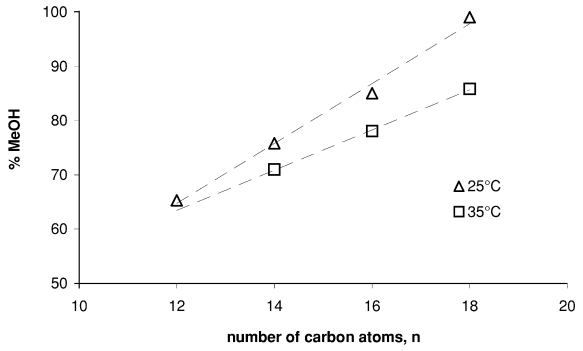

Fig. 2. Cloud points of fatty alcohols in methanol–water at different temperatures.

were used in these investigations (specifications given by the producer): Brij 30: poly(ethylene glycol) dodecyl ether, main component: tetra(ethylene glycol) dodecyl ether (Fluka, Buchs, Switzerland); Dehydol TA 5 (Henkel, Germany). Monodisperse monoalkyl ethers of oligo(ethylene glycols) as well as poly(ethylene glycol) (PEG) and fatty alcohols were also purchased from Fluka.

Cloud points were determined by the following procedure: Samples were dissolved in pure methanol at concentrations of 8–9 g/l and titrated with water at 25.0 and 35.0 °C.

3. Results and discussion

As shown schematically in Fig. 1a, fractions are trapped by increasing the water content of the mobile phase after the LCCC column: when the peak of interest leaves the LCCC column, pump 3 adds water to the eluent to yield a mobile phase composition, in which the fraction is completely adsorbed on the FAD column or even precipitated. The mobile phase composition is controlled by the relative flow-rates of pumps 1 and 3.

The first question concerned the solubility of the individual oligomers, which determines the trapping mechanism: precipitation or adsorption. Hence we have determined the cloud points of the fatty alcohols and some selected monodisperse oligomers. The results are shown in Figs. 2 and 3. As can be seen from Fig. 2, the methanol content at the cloud point increases with the carbon number of the fatty alcohol. Within the individual series of ethoxylates it decreases with increasing number of ethylene oxide (EO) units (Fig. 3). No clouding was observed for the hexa-ethoxlyates at any methanol content larger than 20%. For practical reasons, titration was stopped at this point.

Consequently, $C_{14}EO_6$ would be trapped by adsorption at a mobile phase composition of 42.5% methanol (corresponding to equal flow-rates of pumps 1 and 3), while $C_{14}EO_2$ should be precipitated, as is indicated by the dotted horizontal line.

In order to evaluate the influence of the trapping mechanism, we analyzed the monodisperse oligomers on the Zorbax column in 85% methanol with coupled density detection and ELSD. Then the

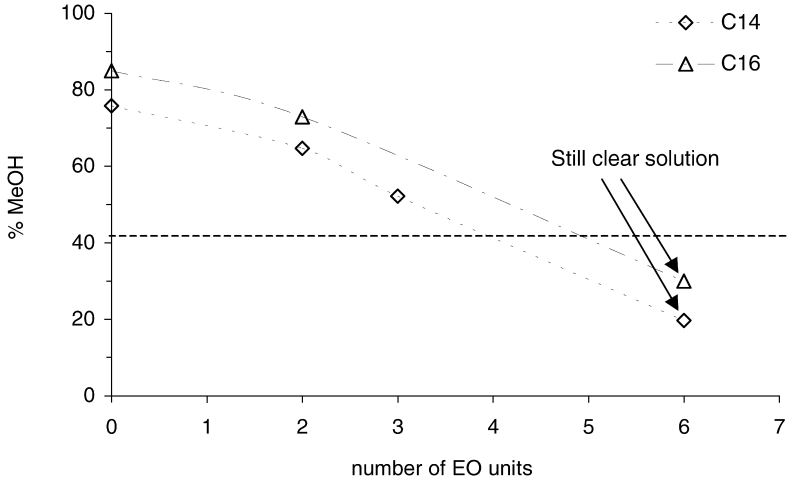

Fig. 3. Cloud points of oligo(ethylene glycol) monoalkylethers in methanol–water at 25 °C.

analysis was repeated and the analyte peaks trapped as a small band at the head of the enrichment column by switching on pump 3 for several minutes. The flow-rates for both pumps were 0.5 ml/min. When pump 3 was switched off, the trapped fraction was eluted as a much narrower peak compared with that obtained without trapping. The change in the mobile phase composition can be seen from the density trace.

Figs. 4 and 5 show the comparison of the chromatograms obtained for $C_{14}EO_2$ and $C_{14}EO_6$ with and without trapping. As can be seen, the peak is much narrower after trapping in both cases, and there is no difference in peak shape and width, regardless of the mechanism of trapping (adsorption for $C_{14}EO_6$ and precipitation for $C_{14}EO_2$). As the trapping mechanism remains without any influence on results, the term FAD will be used throughout the following text. When pump 3 is run at a flow-rate of 0.1 ml/min (which corresponds to a mobile phase composition of 70% methanol), the water content of the mobile phase is too low for complete retention on the precolumn and a part of the fraction to be trapped breaks through, as can be seen from Fig. 6. When pump 3 is switched off again, the rest of the sample is eluted.

In order to quantify the efficiency of the trapping procedure, we performed the same measurements (as illustrated in Fig. 7a–d)

(i) without column and FAD column (injection valve→bypass→density detector→ELSD) (Fig. 7a);
(ii) without column (injection valve→bypass→FAD column→density detector→ELSD) (Fig. 7b);
(iii) entire system (injection valve→column→FAD column→density detector→ELSD) (Fig. 7c).

During the process of sample trapping, the analyte of interest is focused as a narrow band at the head of the FAD column, and the variance (in ELSD) is quite the same, irrespective of whether the trapping mechanism is adsorption or precipitation (Table 1 and Figs. 4 and 5).

As the variance in density detection (i.e. directly after the FAD column) cannot be determined after

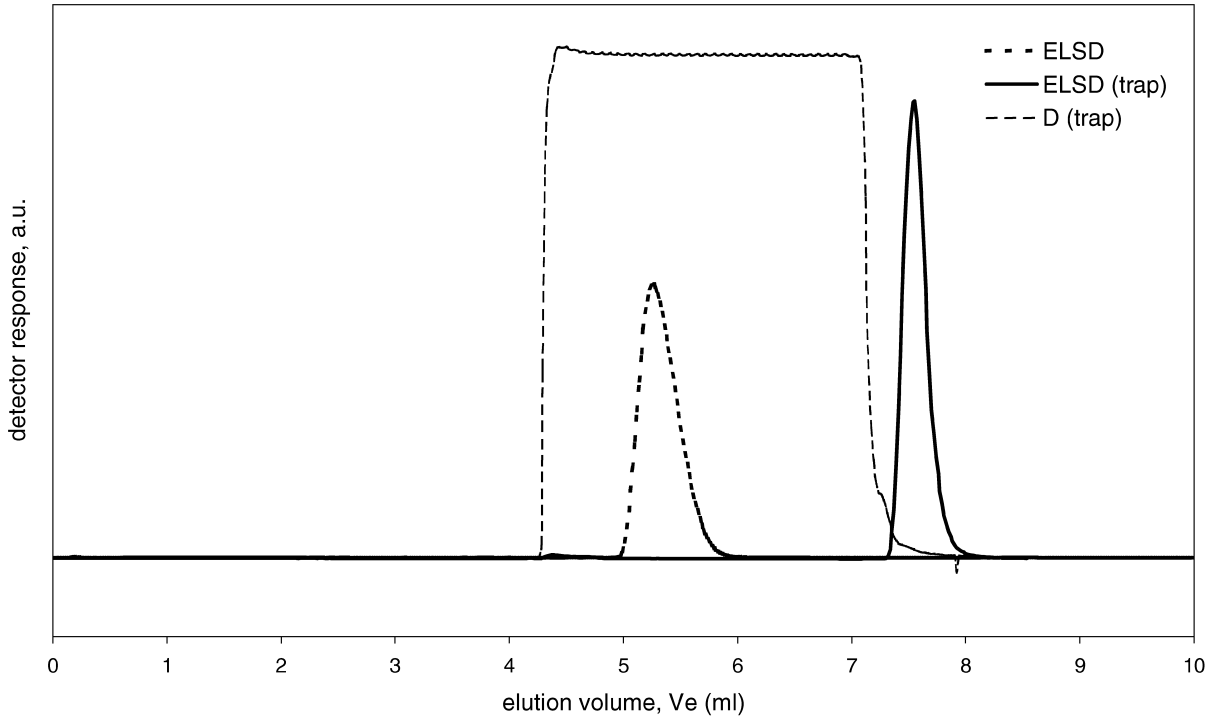

Fig. 4. Trapping of $C_{14}EO_2$.

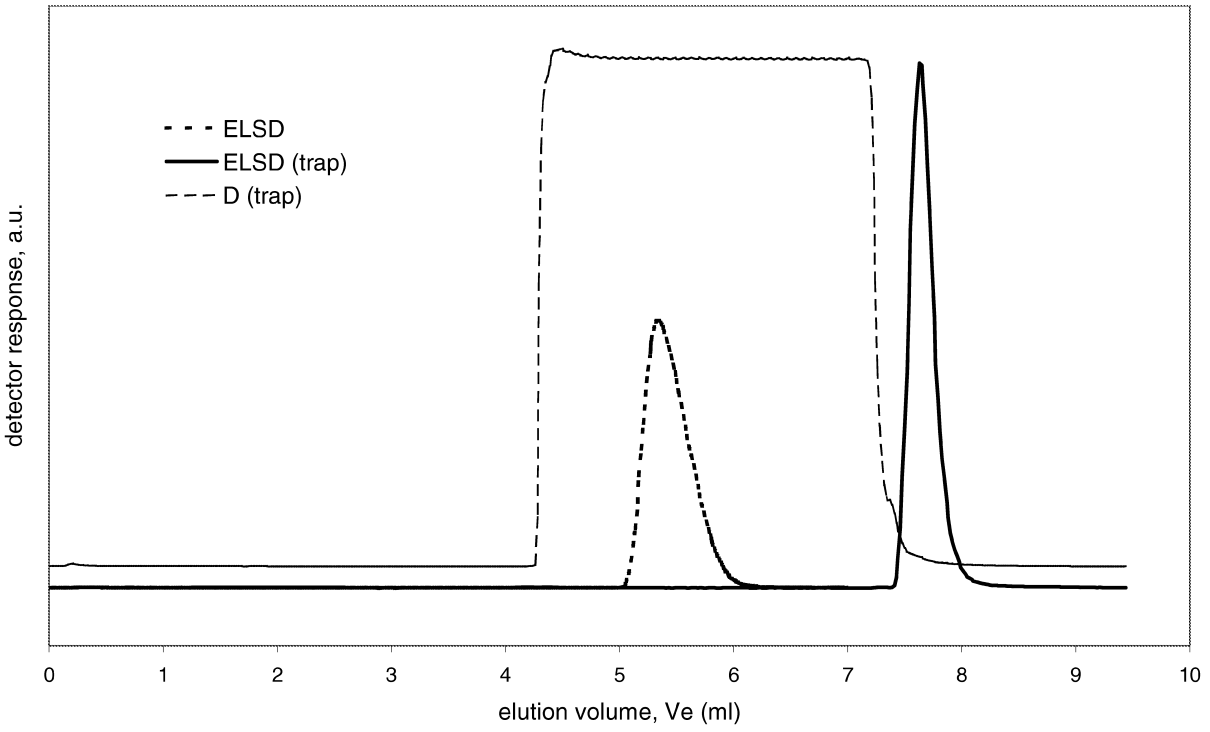

Fig. 5. Trapping of $C_{14}EO_6$.

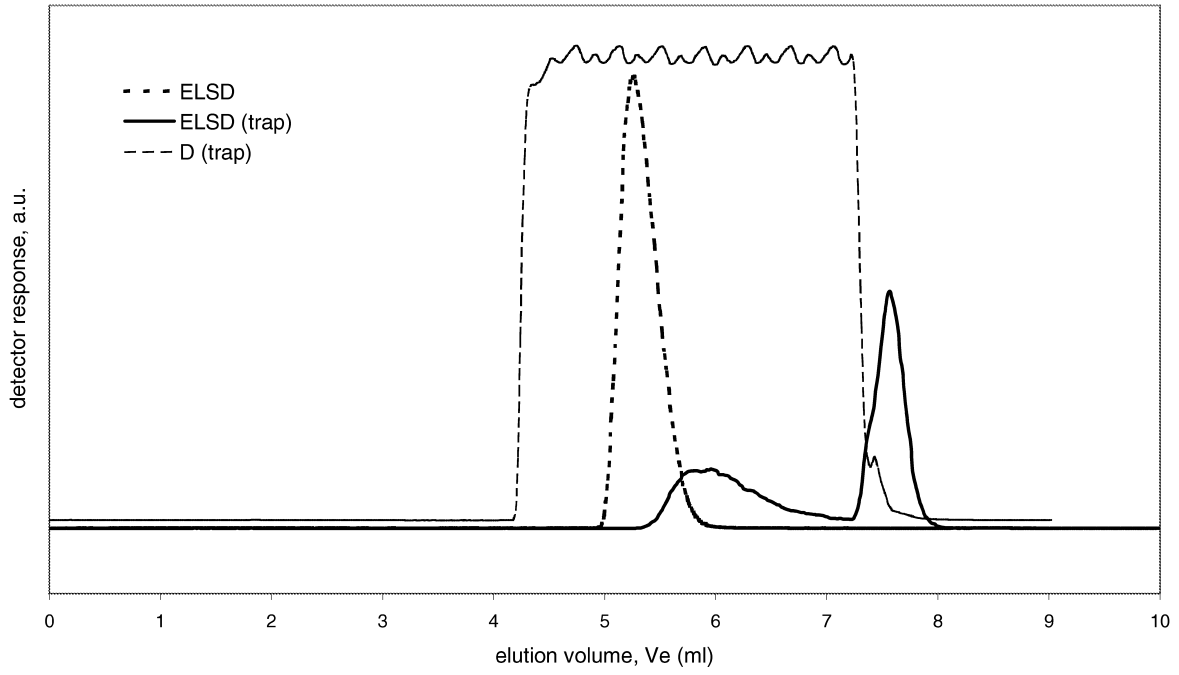

Fig. 6. Insufficient change in mobile phase composition: $C_{14}EO_6$ breaks through, when the flow-rate of pump 3 is set at 0.1 ml/min, corresponding to 70% (w/w) methanol in the final eluent reaching the FAD column.

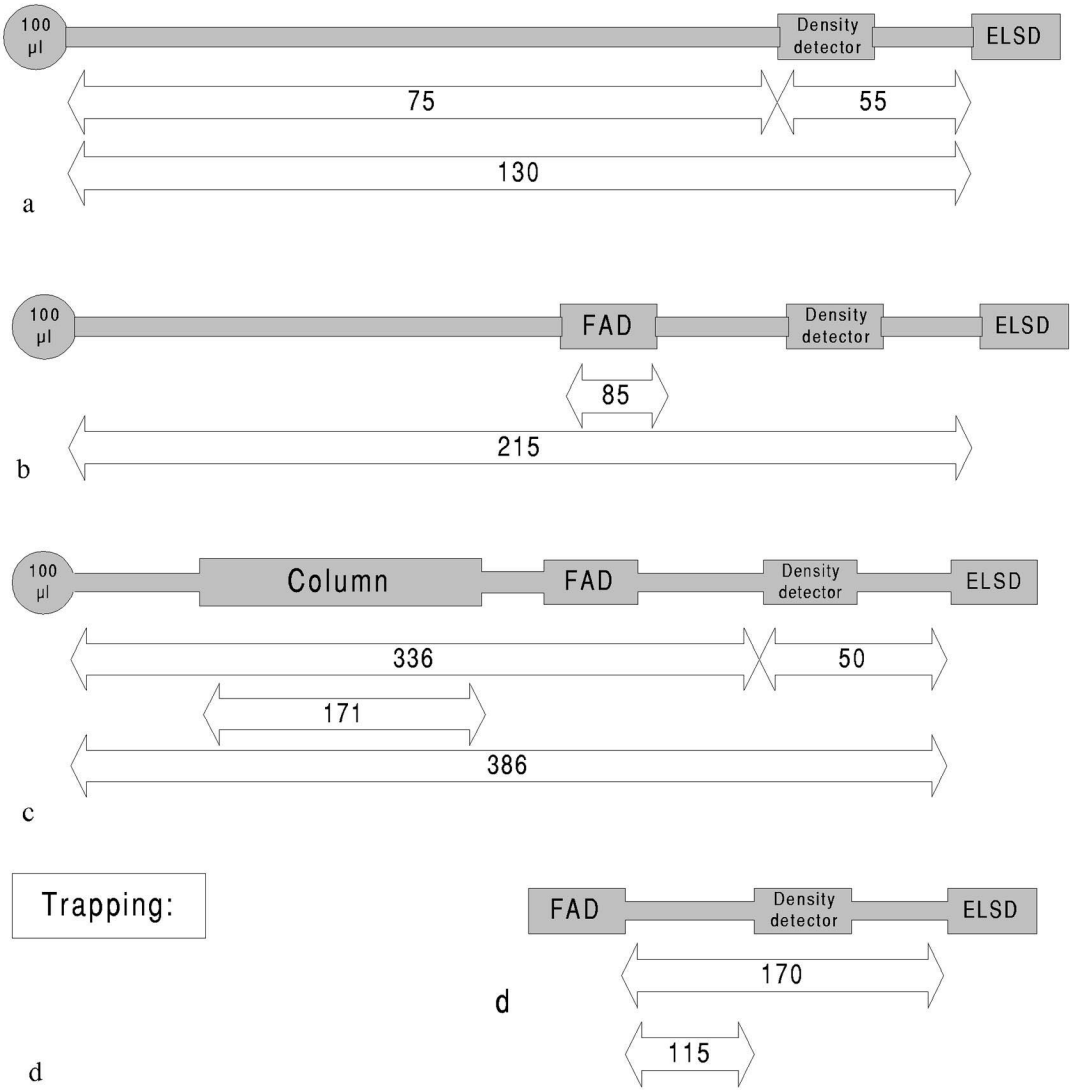

Fig. 7. Variances (in s^2) of the $C_{14}EO_2$ peak in individual parts of the system.

Table 1
Variance of ELSD peaks

LCCC column	Variance of ELSD peak (s^2)	
	$C_{14}EO_2$ (precipitation)	$C_{14}EO_6$ (adsorption)
Yes	176.89	200.51
No	166.67	169.50

trapping, it must be calculated from the ELSD peak after trapping (170 s^2) and the difference in the variances in density and ELS detection without trapping (55 s^2), which yields a value of 115 s^2 (Fig. 7d).

The next question concerned the capacity of the FAD column and the time at which a fraction breaks through. This was checked by repeated injections of

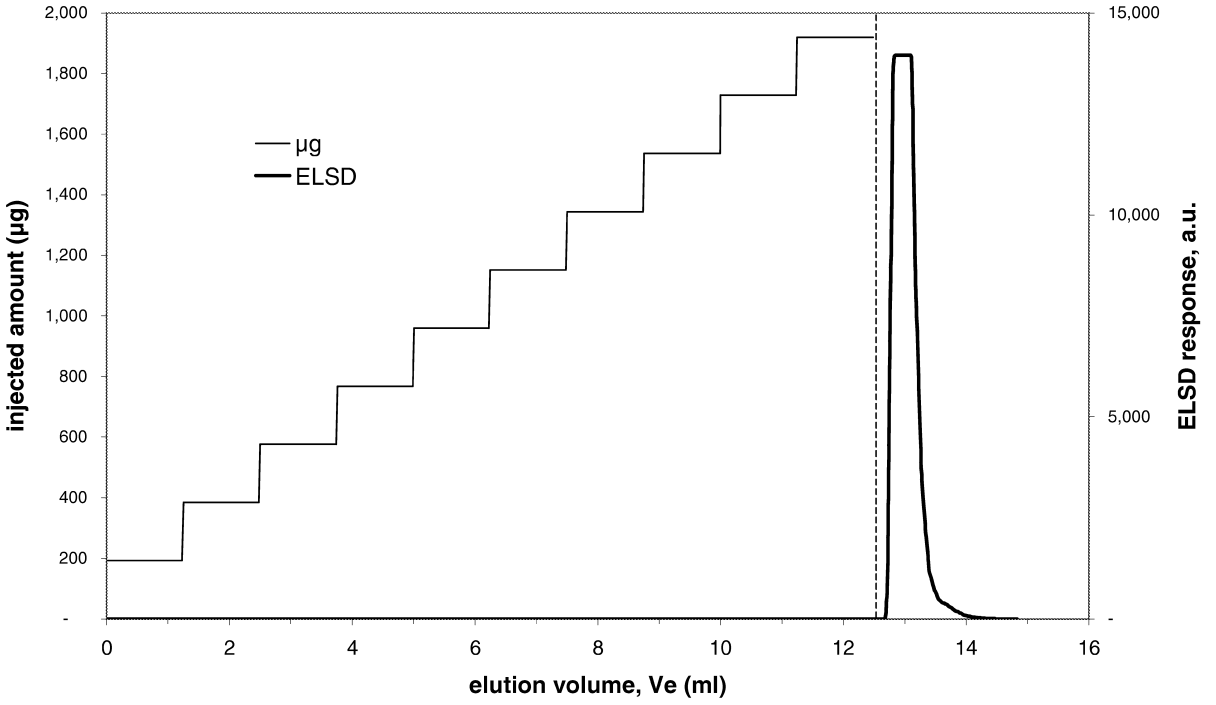

Fig. 8. Capacity of the FAD column: 10 injections of $C_{14}EO_6$ (without LCCC column). Flow-rate of pump 3: 0.5 ml/min, corresponding to a mobile phase composition required for complete trapping: 42.5% (w/w) methanol.

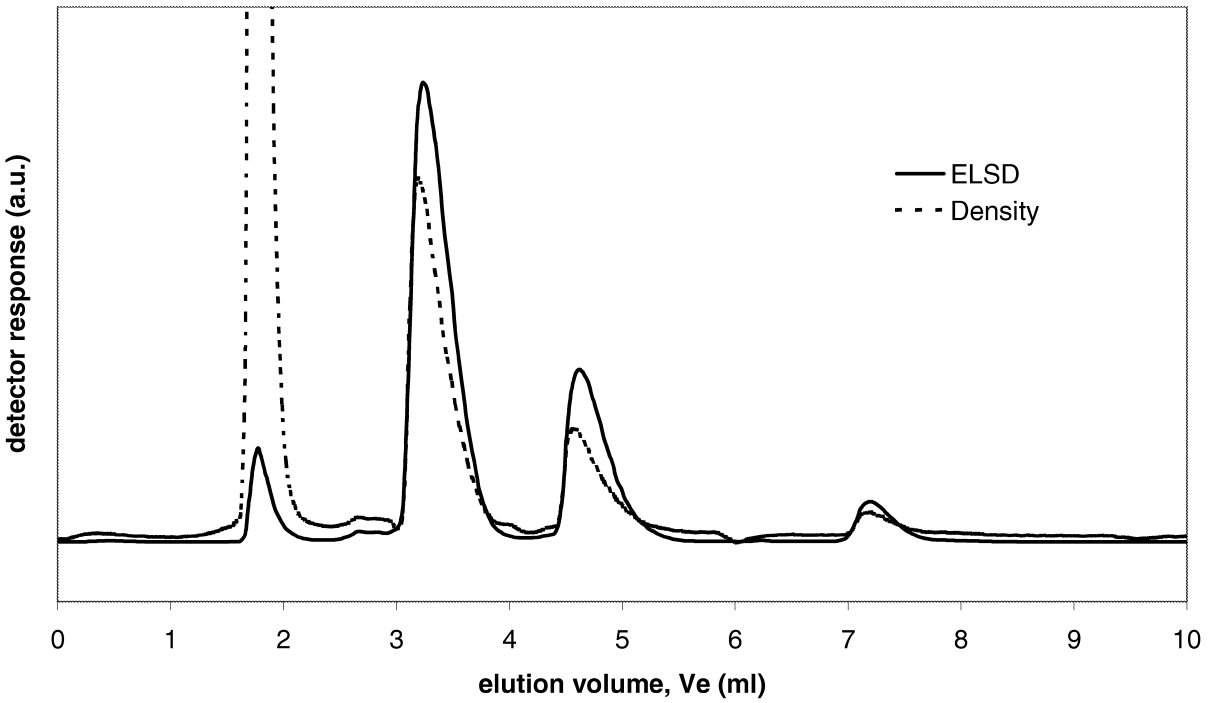

Fig. 9. LCCC of Brij 30 on Zorbax 300 C_{18} in methanol–water (85:15, w/w) with density detection and ELSD.

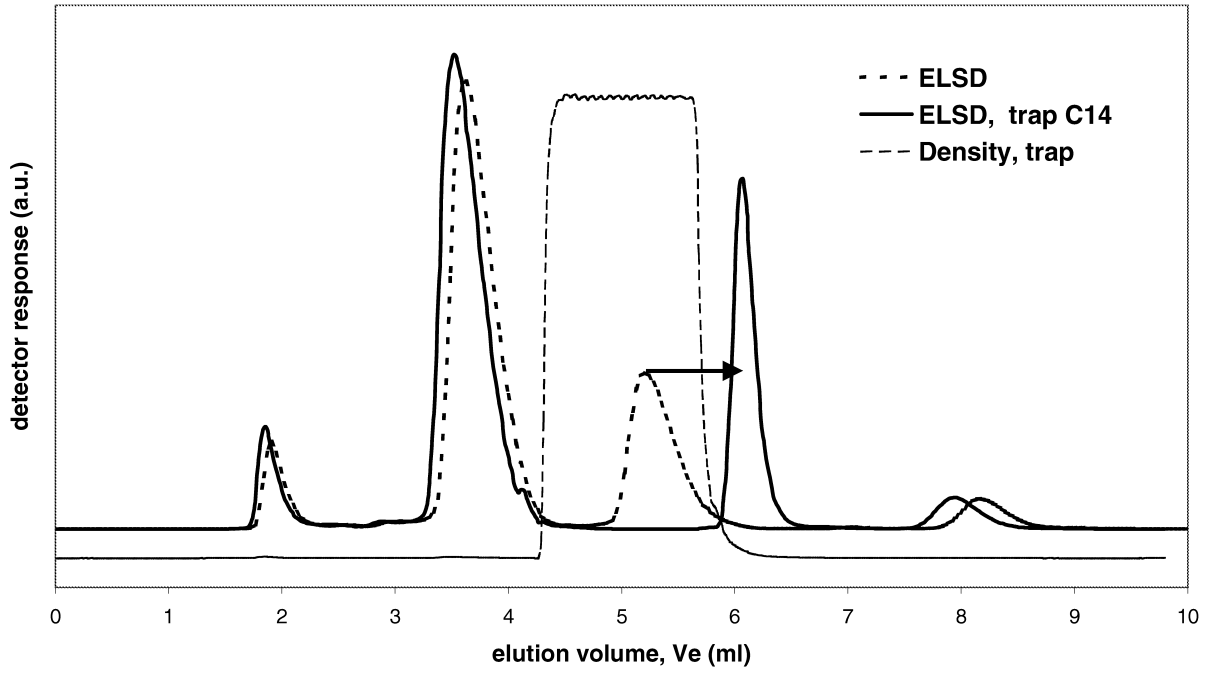

Fig. 10. Trapping of the C_{14} fraction of Brij 30: same conditions as in Fig. 9; flow-rate of pump 3: 0.5 ml/min.

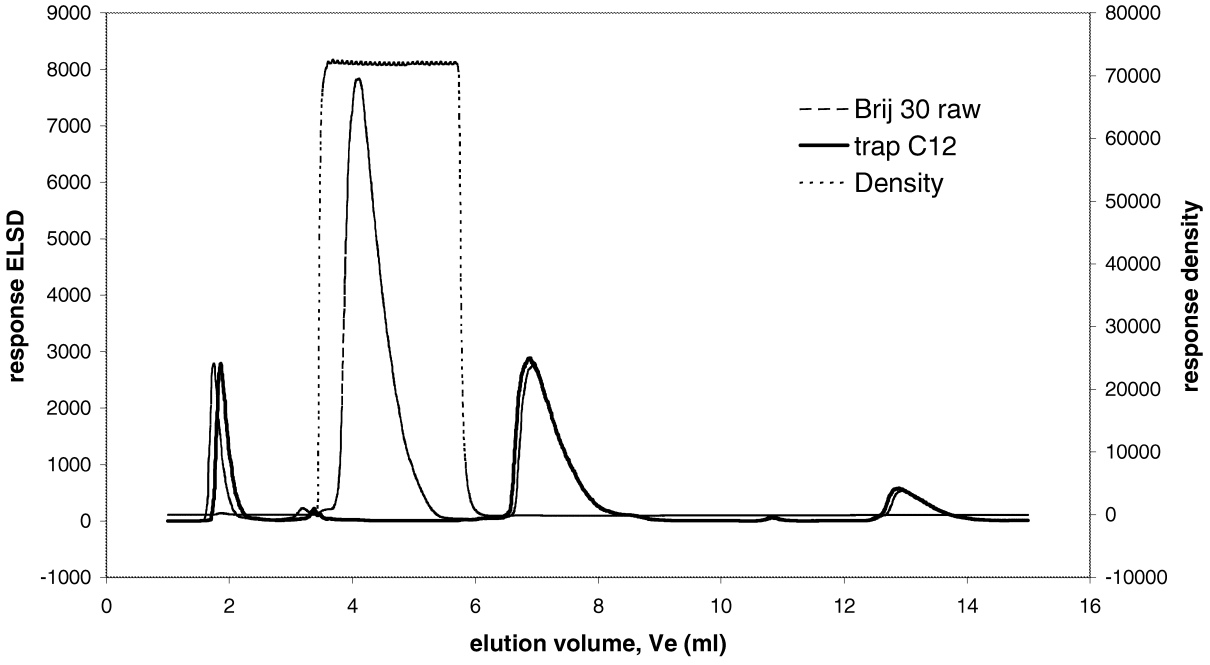

Fig. 11. Transfer of the C_{12} fraction of Brij 30 from LCCC to LEAC. Chromatographic conditions as in Fig. 9.

the same concentration (1.92 g/l) of $C_{12}EO_6$ (which stays soluble in the mobile phase used for trapping) directly on the FAD column (without any LCCC column. With both pumps running at equal flow-rates (0.5 ml/min), which means at a mobile phase composition of 42.5% (w/w) methanol on the FAD column, even after 10 injections (corresponding to an overall amount of 1.92 mg) no material breaking through could be detected by the ELSD, as can be seen in Fig. 8. When pump 3 was switched off again, the trapped material appeared as a quite narrow peak in spite of the too high concentration, which overloaded the ELSD.

The efficiency of this technique is illustrated by the following figures: Fig. 9 shows the density and ELSD traces of a chromatogram of Brij 30, a polydisperse FAE, which consists of ethoxylates with C_{12}, C_{14}, and C_{16} end groups, without the FAD column (position B).

Fig. 10 shows an overlay of two chromatograms of the same sample, but with the FAD column (position A) under otherwise identical conditions. The dotted line is the ELSD trace of the chromatogram without trapping (which looks quite the same as that in Fig. 9, only the retention volumes are somewhat larger). For the second chromatogram in Fig. 10, density (dashed) and ELSD trace (solid line) are shown. At an elution volume of 4.3 ml, pump 3 was switched on, which caused a dramatic density change in the eluate (according to the much higher water content). In this mobile phase composition (42.5 instead of 85% (w/w) of acetone), the C_{14} fraction was trapped on the FAD column. At 5.7 ml pump 3 was switched off again, and the density of the mobile phase dropped rapidly to the original value. Now the C_{14} fraction started to move again and was focused considerably, when compared to its width without trapping.

Fig. 11, shows a comparison of two chromatograms obtained with the FAD column without and with trapping of the C_{12} fraction. The ELSD traces in both chromatograms without and with trapping

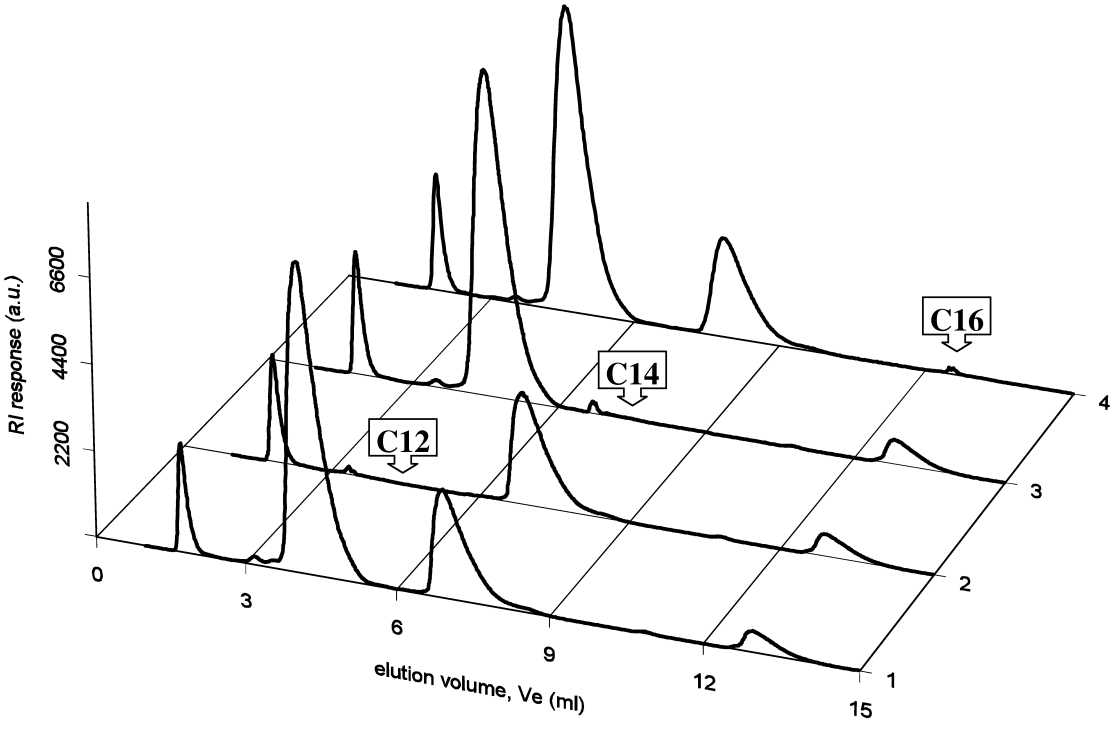

Fig. 12. LCCC of Brij 30 with transfer of fractions to LEAC. Conditions as above, detection: ELSD. 1, Original chromatogram; 2, transfer of C_{12} fraction; 3, transfer of C_{14} fraction; 4, transfer of C_{16} fraction.

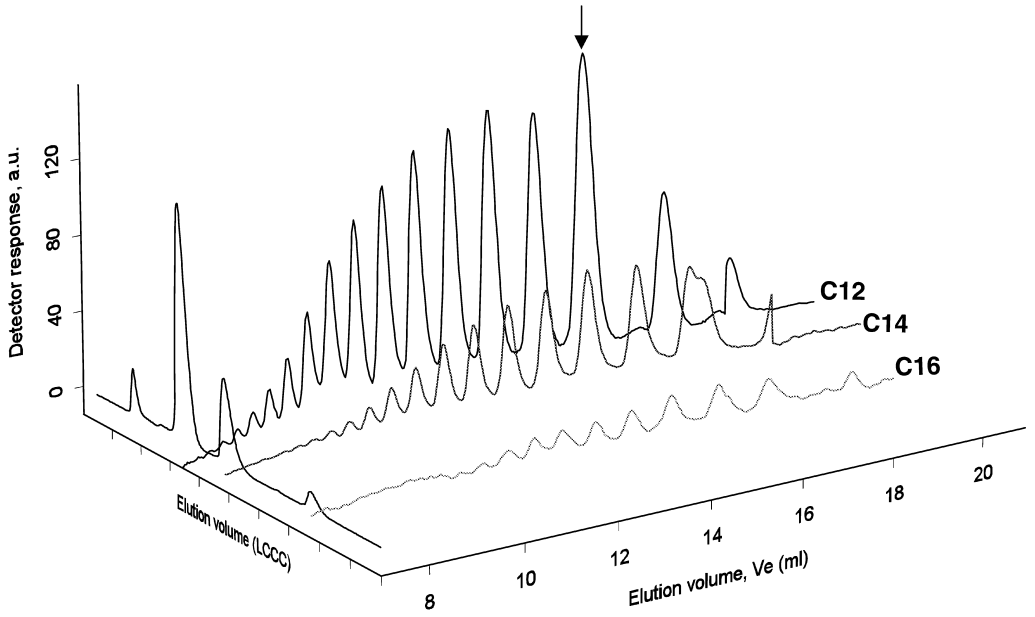

Fig. 13. Two-dimensional separation of Brij 30. First dimension (LCCC) on Zorbax 300 C_{18} in methanol–water (85:15, w/w) with ELSD. Second dimension (LEAC) on Prodigy ODS3 in acetone–water with different acetone contents (C_{12}: 65%, C_{14}: 70%, C_{16}: 75%). Detection: RI.

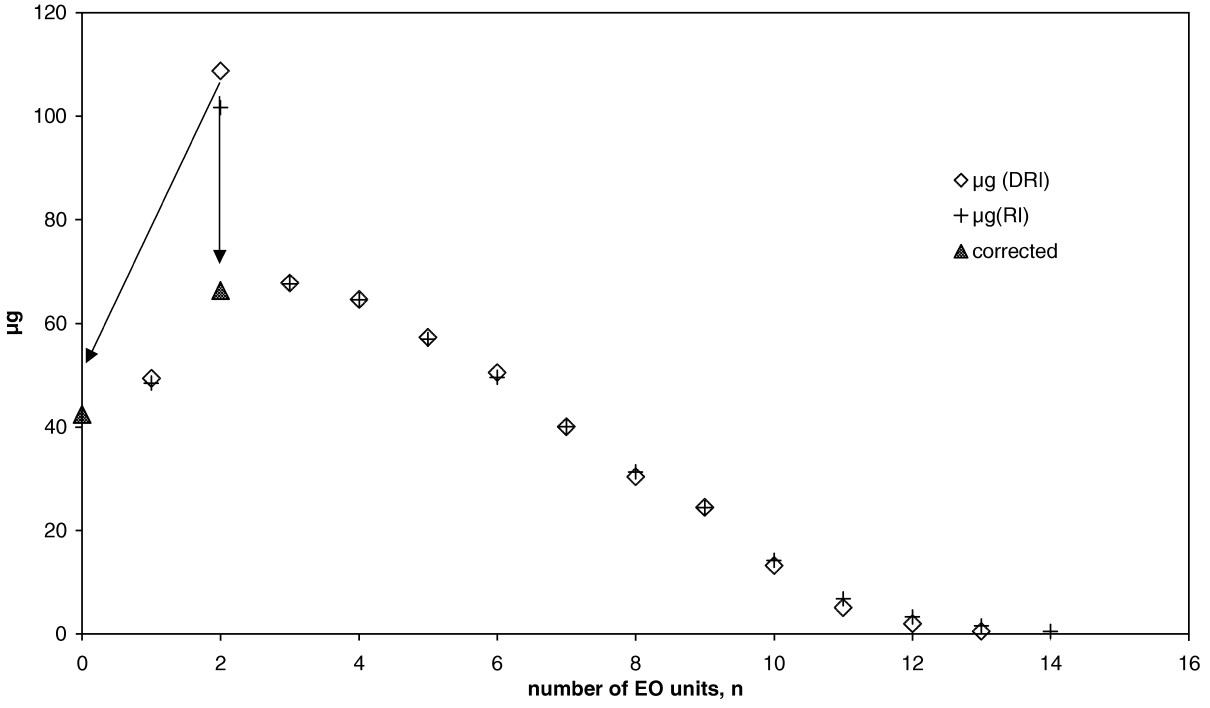

Fig. 14. Quantification of the C_{12} fraction in LEAC. The peak marked with an arrow in Fig. 13 was separated into the components fatty alcohol and $C_{12}EO_2$ using Eq. (1).

really coincide for all the other fractions. Only where the C_{12} fraction would have been in the original chromatogram, there is only baseline in the ELSD trace of the first dimension, when the fraction is trapped and transferred to the second dimension. Again the change in mobile phase composition can be seen from the density trace (dotted line).

In Fig. 12, a stacked representation of four chromatograms (numbers on the right side) is shown: Chromatogram 1 was obtained without trapping. In chromatograms 2–4, one fraction each (C_{12}, C_{14}, C_{16}) was transferred to the second dimension, and at the position indicated by the arrows no material was eluted in the first dimension. The very small peaks appear slightly in front of the trapped fractions. Their nature is not completely clear (eventually C_{10}, etc.).

In Fig. 13, the original chromatogram is shown on the LCCC axis (i.e. that without trapping), while the individually (trapped) fractions are shown on the LEAC axis: well resolved chromatograms were obtained for the individual homologous series in the second dimension (LEAC).

The main problem in these separations is the fact that the peaks of the fatty alcohol and the diethoxylate overlap under these conditions [28]. While all other oligomers can be determined with good quantitative accuracy from the RI trace alone, dual detection [3] is required for this peak, which is marked with an arrow in Fig. 13.

The amounts of fatty alcohol and the diethoxylate can be calculated using Eq. (1):

$$m_i = F \cdot \frac{x_R f_{D,j} - x_D f_{R,j}}{f_{D,i} f_{R,j} - f_{R,i} f_{D,j}} \quad (1)$$

where m_i is the mass of the individual oligomer (with $n_{EO} = 0$ or 2), F is the flow-rate, x_D and x_R are the peak areas in density and RI detection, $f_{D,i}$, $f_{D,j}$, $f_{R,i}$, $f_{R,j}$ are the corresponding response factors in density and RI detection for these oligomers [1].

The effect of this procedure can be seen in Fig. 14: The peak of the diethoxylate, which also contains the fatty alcohol, would be strongly overestimated. If their correct amounts are calculated using Eq. (1), a reasonably smooth distribution is obtained.

Fig. 15 shows the oligomer distribution for the

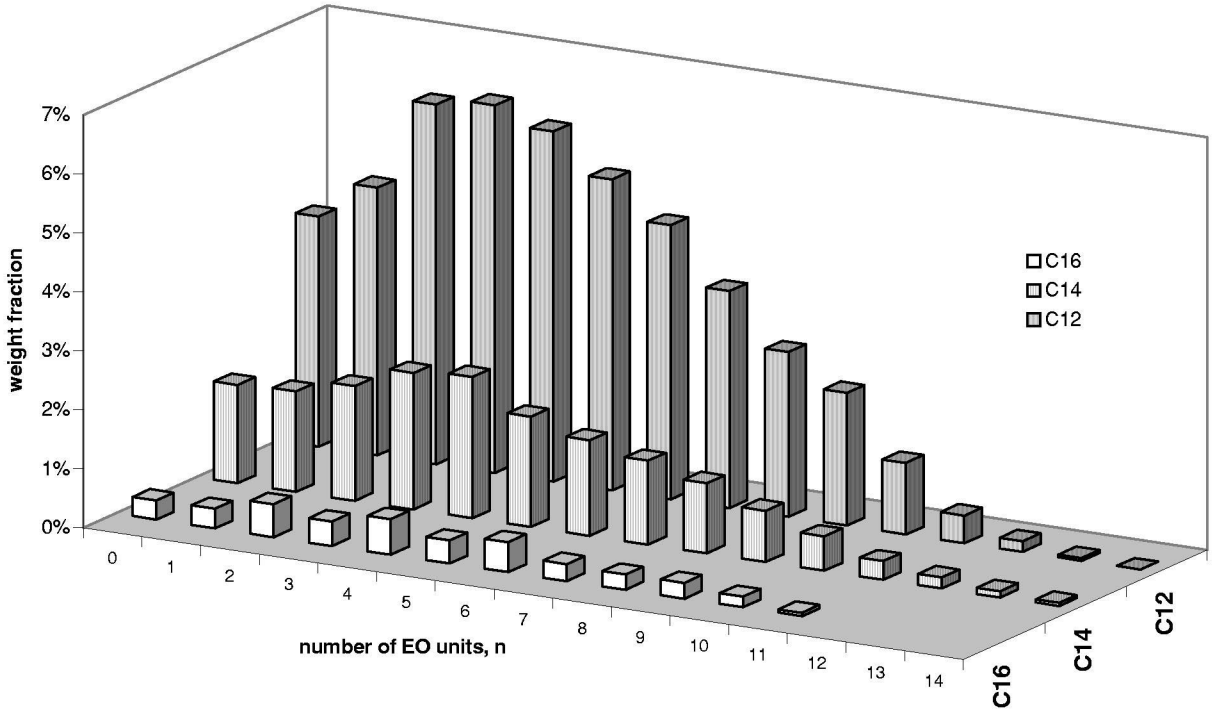

Fig. 15. Mapping of Brij 30 from the data shown in Figs. 13 and 14.

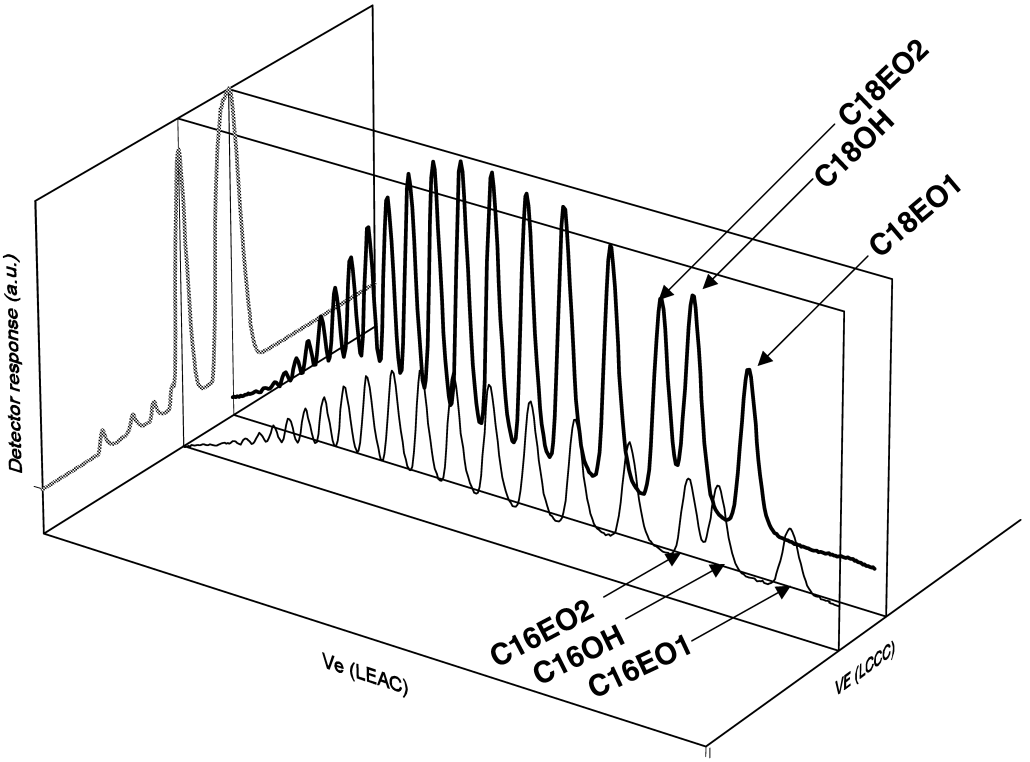

Fig. 16. Two-dimensional separation of Dehydol TA5. First dimension (LCCC) on Zorbax 300 C_{18} in methanol–water (90:10, w/w) with ELSD. Second dimension (LEAC) on Prodigy ODS3 in acetone–water with different acetone contents (C_{16}: 75%, C_{18}: 80%). Detection: RI.

entire sample, which was determined from the data shown in Fig. 13 using the same procedure.

This result is in good agreement with the one obtained by the procedure described recently [1] (with isolation of the individual fractions). When changing the mobile phase composition, the same technique can also be applied to FAE samples with longer hydrophobic groups.

Fig. 16 shows a two-dimensional separation of Dehydol TA5, which contains mainly C_{16} and C_{18} ethoxylates. In this case, the fatty alcohol and the diethoxylate are sufficiently resolved to be determined directly from RI detection.

4. Conclusions

A combination of LCCC as the first dimension and LEAC with coupled density and RI detection in the second dimension can be successfully applied in the characterization of fatty alcohol ethoxylates. The fractions from LCCC can be focused and reconcentrated on a short FAD column prior to injecting them in the second dimension. Optimization of the separation in the second dimension leads to different mobile phase compositions for the individual fractions. In order to save time in routine analysis, it is feasible to analyze the same homologous series of ethoxylates for several samples in the same mobile phase before changing the mobile phase composition in LEAC, which will require some time for equilibration. Basically, no detection is required in the first dimension. Using ELSD, one can make sure that trapping of the LCCC fractions on the FAD column is complete.

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