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Liquid exclusion adsorption chromatography, a new technique for isocratic separation of nonionic surfactants III. Two-dimensional separation of fatty alcohol ethoxylates

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Abstract

A quantitatively accurate mapping of lower fatty alcohol ethoxylates can be achieved using a combination of liquid chromatography under critical conditions as the first dimension and liquid exclusion–adsorption chromatography as the second dimension. With coupled density and refractive index detection in both dimensions, the contribution of preferential solvation can also be estimated. In most cases, however, the use of refractive index detection alone also yields satisfactory results.

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

1. Introduction

Ethoxylates of fatty alcohols and alkylphenols are used in many fields. According to the hydrophilic nature of the polyoxyethylene chain, they are in widespread use as nonionic surfactants. Fatty alcohol ethoxylates (FAEs) typically consist of different polymer homologous series, hence their full characterization often requires a two-dimensional separation (according to functionality and molecular mass distribution).

As has been discussed in Part 1 of this series [1], different modes of liquid chromatography can be applied in the analysis of nonionic surfactants. These techniques may also be combined to achieve multidimensional 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.

(ii) Liquid adsorption chromatography (LAC) separates according to chemical composition and to molecular mass [2]. In principle, LAC can be performed using isocratic or gradient elution, but samples with higher molecular mass typically require gradients [3–5].

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(iii) Liquid chromatography at the critical point of adsorption (often also called LC under critical conditions; LCCC) [6–11] is run at a special temperature and mobile phase composition, at which all chains with the same repeating unit elute at the same elution volume (regardless their length), which means, that the polymer chain (or one block) becomes chromatographically invisible. In this case, a separation according to structural units other than the repeating unit, e.g. with respect to end groups etc., can be achieved. LCCC is also run under isocratic conditions, but typically in mixed mobile phases.

(iv) Liquid exclusion–adsorption chromatography (LEAC, which has been described previously [1]) allows a baseline separation of the individual oligomers up to 20–25 ethylene oxide units under isocratic conditions. In LEAC, the mobile phase composition is adjusted in such a way, that the hydrophobic part is adsorbed, while the oxyethylene chain is still in the exclusion regime, i.e. no interaction between the molecules polyether part and the stationary phase takes place, and the individual oligomers are eluted in the order of decreasing molecular weight as typical in SEC, but far behind the void volume of the column. A similar behaviour has also been observed in other systems [12–14], which indicates, that this technique can be applied to block copolymers in general.

All of these techniques have advantages and disadvantages, as is shown in the following table.

Method	Pro	Contra
SEC	Mechanism well understood Accurate quantitation using dual detection [15]: chemical composition along molecular mass distribution (MMD) [16,17].	Low efficiency: Resolution limited by column length. No separation of oligomers with higher degree of ethoxylation.
LAC	Excellent resolution: Baseline separation for 30 and more ethoxylate oligomers possible. Hydrophobic structural elements do not influence the separation considerably	High selectivity typically requires gradient elution for higher ethoxylates: Detection of samples without chromophores only by evaporative light scattering detection problems with quantitation.
LCCC	Separation of individual polymer homologous series according to functionality (regardless the MMD)	Problems with quantitation: each peak contains a fraction with unknown composition and response factor
LEAC	Baseline separation of individual oligomers up to 20–25 EO units under isocratic conditions easy quantitation using bulk property detectors (refractive index, density) [18].	Overlap of individual polymer homologous series: applicable only to single hydrophobe samples or fractions from LCCC

In principle, lower FAEs can be separated on normal-phase (silica) columns in 2-propanol–water or acetone–water mobile phases under isocratic conditions [19]. The main drawback of this technique is, that the fatty alcohol and the lowest ethoxylates (n=1–2) are not resolved even in a mobile phase composition, at which the oligomers with 5–10 EO units elute as broad, asymmetric peaks. Consequently, higher ethoxylates can only be analyzed with gradient elution.

In the analysis of FAE by two-dimensional liquid chromatography, the most feasible approach is a combination of LCCC on a reversed-phase column (under critical conditions for polyoxyethylene) as the first dimension, which allows a separation of the individual series of ethoxylates, and the subsequent separation of the fractions thus obtained according to the number of EO units. In the second dimension, SEC, gradient LAC, or LEAC can be applied. While SEC has a low separation efficiency, but allows an accurate quantification, high resolution can be achieved by gradient LAC, quantitative reliability is, however, questionable because of detection problems [20–24]. On the other hand, LEAC allows a satisfactory separation of the individual ethoxylate oligomers under isocratic conditions, which makes quantitation much easier (Part II of this series [18]).

In this paper, FAEs were analyzed by two-dimensional LC with LCCC as the first and LEAC as the second dimension.

2. Experimental

These investigations were performed using the density detection system DDS70 (Chromtech, Graz, Austria), which has been developed in our group [25,26].

Each system was connected to a MS-DOS computer via the serial port. Data acquisition and processing was performed using the software package CHROMA, which has been developed for the DDS 70. The columns and density cells were placed in a thermostatted box, in which a constant temperature was maintained for all measurements: 25.0°C on systems A and B, 35.0°C on system C, and 30.0°C an system D.

In system A (LEAC), the mobile phase was delivered by a Jasco 880 PU pump (from Japan Spectrosopic Company, 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, No. 185970; Phemonenex, Torrance, CA, USA) was used in all measurements. Samples were injected manually using a Rheodyne 7125 injection valve (Rheodyne, Cotati, CA, USA) equipped with a 50-μl loop. A Bischoff 8110 refractive index (RI) detector (Bischoff, Leonberg, Germany) was connected to the DDS 70.

In system B (gradient LAC), the mobile phase was delivered by an ISCO 2350 HPLC pump and an ISCO 2360 gradient programmer (ISCO, Lincoln, NE, USA). The flow-rate was 1.0 ml/min in all measurements. Samples were injected using a Spark 125 autosampler equipped with a 20-μl loop. A Waters Spherisorb silica column (5 μm, 80 Å, 250× 4.0 mm) was used in all LAC measurements. Similar conditions as described in an application note by Waters (Ref. SPH/17) were chosen: mobile phase A was pure ethyl acetate (instead of ethyl acetate–water, 99:1), mobile phase B was acetone–water (80:20, w/w) (instead of 90:10). The following gradient profile was used: start 100% A, delay time 3.5 min, then in 20 min to 100% B, then within 1 min back to 100% A. A Sedex 45 evaporative light scattering detection (ELSD) apparatus from Sedere, Vitry sur Saine, France was connected to the DDS 70. Nitrogen was used as the carrier gas, and the pressure at the nebulizer was set to 1.0 bar and the temperature of the evaporator to 30°C.

In system C (LCCC), a flow-rate of 2.0 ml/min was maintained with an LDC Constametric IIG HPLC pump (Milton Roy, Riviera Beach, FL, USA). A semi-preparative column was used for all measurements: Spherisorb ODS2 (250×10 mm, 5 μm, 80 Å) from PhaseSep (Deeside, UK). A SICON LCD 201 RI detector was combined with the DDS70. An Advantec SF 2120 fraction collector (Advantec, Dublin, CA, USA). was used for sampling of different fractions. The solvents (methanol and water, both HPLC grade) were purchased from Riedel–de Haen (Seelze, Germany).

In system D (SEC) a flow-rate of 1.0 ml/min was maintained with a Gynkotek 300C pump (Gynkotek,

Germering, Germany). Samples were injected using a VICI injector (from Valco Europe, Schenkon, Switzerland) with a 100-μl sample loop. A column packed with PLgel 100 Å (5 μm, 600×7.6 mm), from Polymer Labs., Church Stretton, UK, was used in all measurements. The mobile phase was chloroform (HPLC grade, stabilized with 2-methylbutene, from Mallinckrodt, Paris, KY, USA). Sample concentrations were 3.0–10.0 g/l. The DDS 70 was coupled to an ERC 7512 RI detector (ERMA, Japan/INULA, Vienna, Austria).

The following polydisperse FAE samples were used in these investigations (specifications given by the producer: Fluka, Buchs, Switzerland): Brij 30: polyethylene glycol dodecyl ether, main component: tetraethylene glycol dodecyl ether; Brij 52: polyethylene glycol hexadecyl ether, main component: diethylene glycol hexadecyl ether; Brij 76: polyethylene glycol octaadecyl ether, main component: decaethylene glycol octadecyl ether.

Monodisperse monoalkylethers of oligoethylene glycols as well as PEG and fatty alcohols were also purchased from Fluka.

3. Results and discussion

The main problem in the analysis of non-ionic surfactants is quantitation: the response factors of all detectors depend strongly on chemical composition (i.e. the relative length of the hydrophobic and the hydrophilic part), hence they vary with the degree of ethoxylation. For single hydrophobe surfactants (containing only one polymer homologous series), simple algorithms can be applied to compensate for this dependence [17,27].

Technical samples are, however, based on technical fatty alcohols, which mostly contain considerable amounts of other fatty alcohols, hence these samples typically consist of at least two polymer homologous series.

As a full separation of all oligomers (of all series) cannot be achieved by one-dimensional chromatography, one may think of separation exclusively according to the degree of ethoxylation and a detector, the sensitivity of which does not depend on the alkyl end group.

A commonly used approach is the analysis of FAE by normal-phase LAC with gradient elution and an ELSD system. Assuming that ELSD obeys to the mass detection principle, constant response factors for all oligomers should be expected (regardless their chemical composition), which is obviously not correct, as can be seen from the following figures.

We selected two FAE samples with similar MMD, as was shown by SEC (Fig. 1). By separate integration of the fatty alcohol peak, the alcohol content

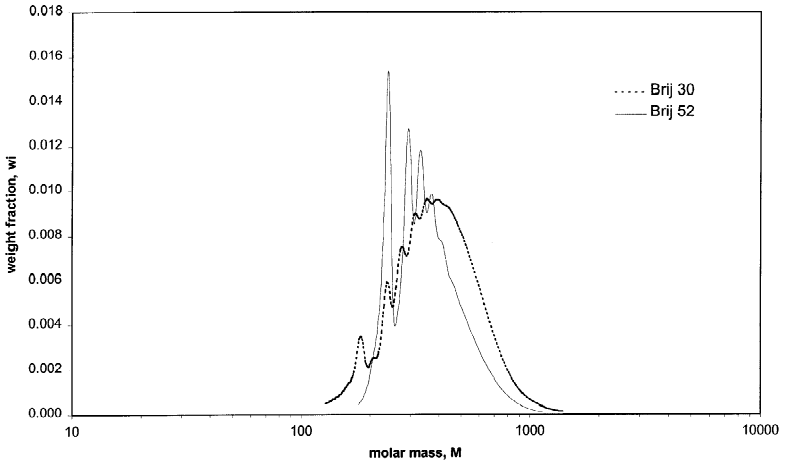

Fig. 1. Molecular mass distribution (MMD) of two fatty alcohol ethoxlates, as obtained from SEC with density and RI detection on PLgel 100 Å in $CHCl_3$ (system D).

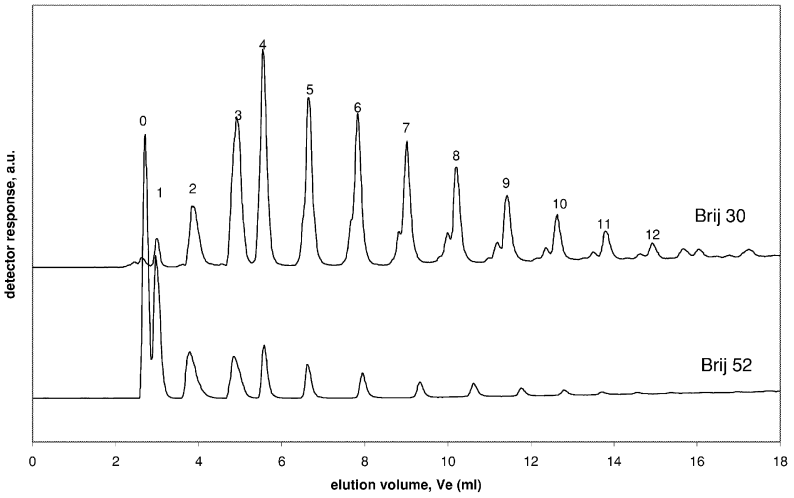

Fig. 2. Gradient LAC of the same FAE samples as in Fig. 1. Chromatographic conditions are given in Section 2 (system B).

was determined: 22.9% in Brij 52 and 7.9% in Brij 30. This agrees quite well with the data from LCCC, as will be shown later on.

Fig. 2 shows two chromatograms of Brij 30 and Brij 52. In both chromatograms, the individual oligomers are well resolved. In the chromatogram of Brij 30, a second series of peaks (C_{14}) appears in front of the main peaks (C_{12}) at higher degree of ethoxylation. Peaks were identified by spiking with monodisperse oligomers.

Obviously, the ELSD overestimates the fatty alcohol and the monoethoxylate in the C_{16} series of Brij 52, while it does not detect the C_{12} fatty alcohol and its monoethoxylate in Brij 30, the latter sample mainly consisting of C_{12} fatty alcohol ethoxylates and only minor amounts of the C_{14} series, which however are responsible for the small peaks in Brij 30. Consequently, no quantitation is possible with ELSD for the lower oligomers in samples containing considerable amounts of the C_{12} and C_{14} series.

As we have shown previously [1], the problem with gradient elution, which requires the ELSD, can be avoided by using LEAC which is run in the isocratic mode, thus allowing density and RI detection.

Unfortunately, there is a limitation in the analysis of technical surfactants: LEAC works only well with single hydrophobe ethoxylates, hence one has to separate the individual series of ethoxylates in a first dimension with respect to the length of the hydrophobic end groups by LCCC, before they may be analyzed by LEAC.

The problem is rather the quantitation in the first dimension: in the case of LCCC, each peak contains an unknown amount of an entire polymer homologous series with unknown chemical composition and MMD, plus an unknown amount of solvent from preferential solvation, which also depends on molecular mass and chemical composition [28]. Quantitative determination is effected in accordance to previously published papers [15,29,30]. If the average composition of a fraction i is known from the second dimension, the average response factor $f_{i,j}$ of the detector j in the first dimension (density and RI) is calculated from the response factors $f_{A,j}$ and $f_{B,j}$ of the detector j for each component and the weight fraction w_A of component A (fatty alcohol) and from these data the correct amount of the fraction as well as the contribution of preferential solvation.

The average response factor f_i of the detector j (density and RI) for a fraction in the first dimension can be calculated from the response factors $f_{A,j}$ and $f_{B,j}$ of each component and the weight fraction w_A of component A:

$$f_{i,j} = f_{B,j} + w_A(f_{A,j} - f_{B,j}) \quad (1)$$

The mass m_p of the fraction i is given by:

$$m_p = F \cdot \frac{x_D f_{S,R} - x_R F_{S,D}}{f_{i,D} f_{S,R} - f_{i,R} f_{S,D}} \quad (2)$$

wherein F is the flow-rate, x_D and x_R are the peak areas in density and RI detection $f_{i,D}$, $f_{i,R}$, $f_{S,D}$, and $f_{S,R}$ are the corresponding true response factors for the polymer and the solvent (which are obtained, when the samples are injected directly into the detectors).

The amount m_S of solvent (in this case water) from preferential solvation is given by:

$$m_S = F \cdot \frac{x_R f_{i,D} - x_D f_{i,R}}{f_{i,D} f_{S,R} - f_{i,R} f_{S,D}} \quad (3)$$

In the second dimension (LEAC) the same algorithm can also be applied, but with a major difference: in LEAC, there is no need to use average response factors, as the peaks contain monodisperse oligomers, for which the individual response factors can be determined. As the response factors of RI and density detector are closely related to specific properties (refractive index increment and apparent specific volume, respectively), their dependence on molecular mass is given by the relation [27]:

$$f_i = f_\infty + \frac{K}{M_i} \quad (4)$$

wherein f_i is the response factor of a molecule with the molecular mass M_i, f_∞ is the response factor of a chain with infinitely high degree of polymerization), and K is a constant describing the influence of the end groups, which can be determined by linear regression.

(i) Using dual detection and Eqs. (2) and (3), the correct amount of each oligomer as well as the contribution of preferential solvation can be determined. Alternatively, one may use the apparent response factors, which already contain the contribution of preferential solvation.

(ii) Under the assumption, that the contribution of preferential solvation does not depend on concentration, the weight fractions w_A and w_B $(=1-w_A)$ of component A and B (fatty alcohol and ethylene oxide) and from these data the amount of each oligomer can be obtained from the areas $x_{i,j}$ and the corresponding apparent response factors $f_{i,j}$:

$$\frac{1}{w_A} = 1 - \frac{\left(\frac{x_{i,D}}{x_{i,R}} \cdot f_{R,A} - f_{D,A}\right)}{\left(\frac{x_{i,D}}{x_{i,R}} \cdot f_{R,B} - f_{D,B}\right)} \quad (5)$$

$$m_i = \frac{x_{i,R}}{w_A \cdot (f_{R,A} - f_{R,B}) + f_{R,B}} \quad (6)$$

(iii) As the response factor of water is rather small in RI detection, reliable results can also be obtained by using RI detection alone in the second dimension, as will be reported in the following section.

In LCCC, fatty alcohols are eluted slightly in front of the ethoxylate peaks even at the critical adsorption point (CAP) on ODS columns in methanol–water, which is typically found between 95 and 97% (w/w) of methanol (depending on the type of the stationary phase). However, if the mobile phase composition is slightly changed in a way, that the ethylene oxide (EO) units are very slightly adsorbed, but the fatty alcohol ethoxylates are still eluted in a sufficiently narrow peak, the fatty alcohol can be separated from the ethoxylates (on most columns, this can be effected at approximately 90% (w/w) of methanol). In this case, the fatty alcohol can be determined directly from RI detection (which is almost not affected by preferential solvation, as the response factor of water is very small in RI detection).

Fig. 3. shows a separation of Brij 30 on the semipreparative column in methanol–water (90:10). As can be seen, the fatty alcohols (peaks 3, 5, and 7) are eluted in front of the corresponding ethoxylate peaks (4, 6, and 8). If polyethylene glycol is present in the sample (originating from a chain transfer reaction), it will be eluted at the column void volume (peak 1). The nature of peak 2 is not clear, because it is too small to be identified (most probably, it contains traces of a C_{10} fraction).

The amounts of the fatty alcohol in the sample was determined directly from the peak areas of RI detection (using the apparent response factors due to the extensive independence of RI detection on preferential solvation) as well as from dual detection (Eq. (2), with the true response factors), thus accounting for preferential solvation. The sum of the relative compositions of the fatty alcohols calculated on the basis of the RI trace (apparent response factor) and dual detection (true response factor) was com-

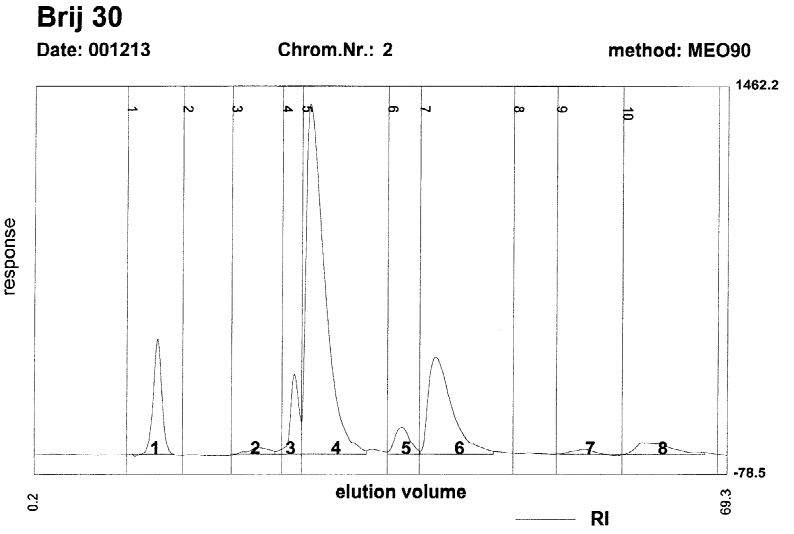

Fig. 3. Semipreparative LCCC of Brij 30 on a Spherisorb ODS 2 column (system C) in methanol–water (90:10, w/w). Fraction numbers, top row; peak numbers, bottom row.

pared to the result from dual detection SEC. As can be seen from Table 1, the results agree quite well.

The material eluted within peaks 3–8 was collected, the mobile phase evaporated in vacuum, and the residues analyzed by LEAC and SEC in the second dimension.

If the same mobile phase composition (70%, w/w, acetone) is used in LEAC for all fractions, the C_{16} series elutes at rather high retention times, while the C_{12} counterparts are not perfectly resolved, as can be seen from Fig. 4.

A much better separation of the individual oligomers can be achieved, if the C_{12} fraction is analyzed in 65% acetone, the C_{14} fraction in 70% acetone, and the C_{16} fraction in 75% acetone, as can be seen in Fig. 5.

Table 1
Fatty alcohol content of Brij 30, as determined by dual detector SEC and LEAC

	Fatty alcohol (%)		
	SEC	RI, app.	Dual true
$C_{12}OH$		5.3	4.8
$C_{14}OH$		3.2	3.0
$C_{16}OH$		0.7	0.8
% Total ROH	7.9%	9.2	8.6

A satisfactory separation was also achieved for the small amounts of the C_{16} ethoxylates present in this sample, as is shown in Fig. 6: all oligomers show well separated peaks with both detectors, and only the peak of the monoethoxylate is almost invisible in density detection (as its response factor is very small), while all peaks are appropriately considered in RI detection.

The true and apparent response factors $f_{i,j}$ of the individual oligomers were determined by linear regression from the available monodisperse oligomers (C_nEO_{2-6}), poly(ethylene glycol) (PEG) 6000

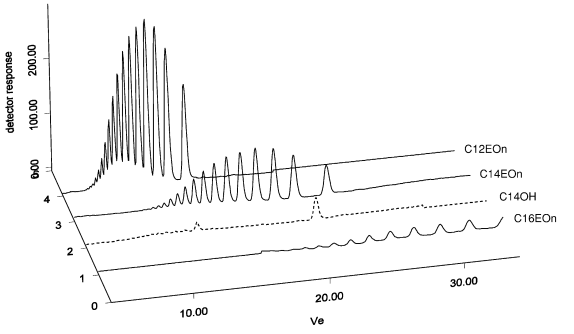

Fig. 4. Chromatograms of fractions 5, 6, 7, and 10 from Fig. 3, as obtained by LEAC on a Prodigy ODS3 column (system A) in acetone–water (70:30, w/w).

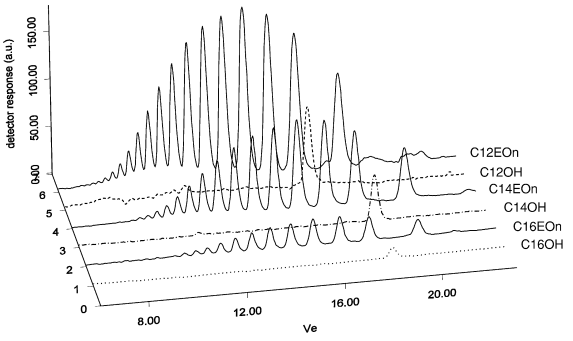

Fig. 5. Chromatograms of fractions 5–10 from Fig. 3, as obtained by LEAC on a Prodigy ODS3 column (system A) in acetone–water. Mobile phase composition: (65:35, w/w) for the C_{12} series, (70:30, w/w) for the C_{14} series, (75:25, w/w) for the C_{16} series.

and the corresponding fatty alcohol using Eq. (4). PEG 6000 was chosen as sufficiently high-molecular-mass sample, the response factor of which should be close to that of the repeating unit (f_∞ in Eq. (4)).

With the individual response factors thus obtained, the oligomer distribution was calculated in three different ways:

(A) Apparent response factors, RI alone.

(B) Density+RI, apparent response factors, according to Eqs. (5) and (6).

(C) Density+RI, true response factors, according to Eq. (2).

The results for the C_{16} fraction are shown in Fig. 7: regardless the calculation method, the same distribution is obtained.

The reproducibility is also good, as can be seen from Fig. 8: The oligomer distribution of the C_{12}-ethoxylates obtained from different two-dimensional separations agrees very well and the ethylene oxide content (w_{EO}) of this fraction in four separations was 49.2±0.5%.

The molecular mass averages M_w (weight-average) and M_n (number-average) and the average composition of the individual ethoxylate fractions are given in Tables 2 and 3: From the chemical composition, the response factors of each fraction in LCCC could be calculated (using Eq. (1)), and therefrom (using Eq. (2)) the amount of the ethoxylate fractions. Again, we compared three different calculation methods, and found good agreement between all of them. Obviously, the amount of PEG can only be determined from dual detection using Eq. (2). In Fig. 9, the weight fractions of PEG, the fatty alcohols, and the ethoxylates in Brij 30, as obtained from five LCCC separations, are shown. With the correct amount of the ethoxylate fractions, the weight fractions of all individual oligomers in the sample can be determined, as is shown in Fig. 10.

The technique can also be applied to samples containing only very small amounts of a second polymer homologous series, as is the case with Brij 52. This sample consists mainly of the C_{16} series and traces of the C_{18} series, as can be seen from Fig. 11:

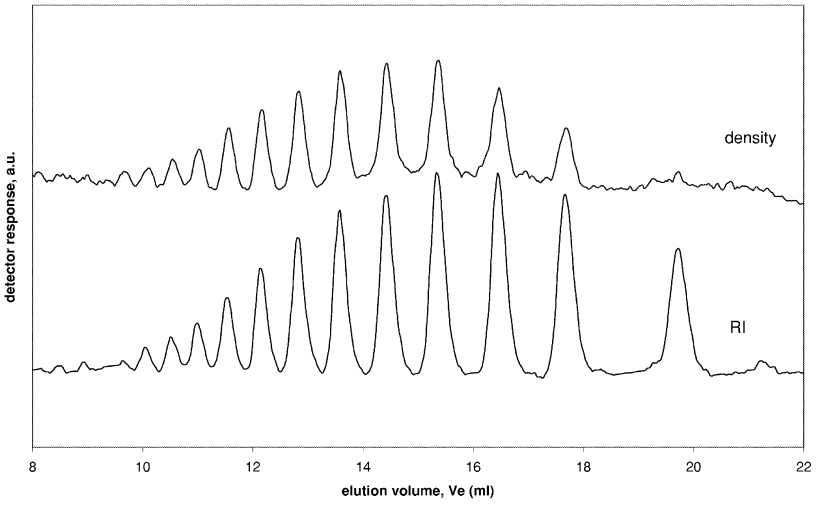

Fig. 6. LEAC of the $C_{16}EO_n$ series (fraction 8 from Fig. 3).

the fatty alcohols (peaks 2 and 4) are separated from the ethoxylates (peaks 3 and 5). Direct integration of peaks 2 and 4 yields 24.10% for $C_{16}OH$ and 1.31% for $C_{18}OH$.

Fractions 5, 6 and 10 (corresponding to peaks 2, 3, and 5) were analyzed by LEAC and the chromatograms thus obtained compared to that of the raw sample. The results are shown in the following figures: the C_{16} alcohol as well as the C_{18} fraction has been successfully removed from the C_{16}-ethoxylates (Fig. 12). Despite the small amount of C_{18}-ethoxylates present in this sample, a reasonable chromatogram could be obtained for fraction 10 corresponding to peak 5 in Fig. 11, as shown in Fig. 13.

Table 2
Molecular mass averages M_w and M_n and the average composition of the individual ethoxylate fractions, as determined by LEAC

	C_{12}	C_{14}	C_{16}
M_w	402	439	445
M_n	366	401	415
M_w/M_n	1.099	1.096	1.070
$w(EO)_{av}$ (%)	49.2	46.6	41.7

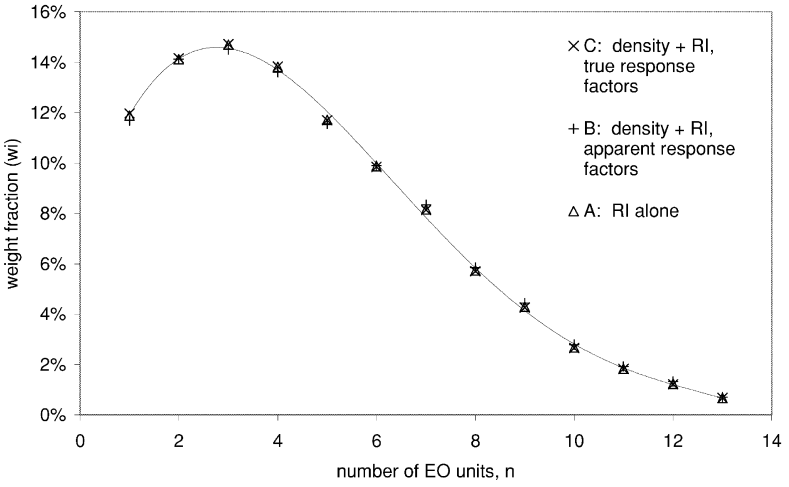

Fig. 7. Oligomer distribution of the $C_{16}EO_n$-fraction from Fig. 3, as obtained using three different methods of calculation.

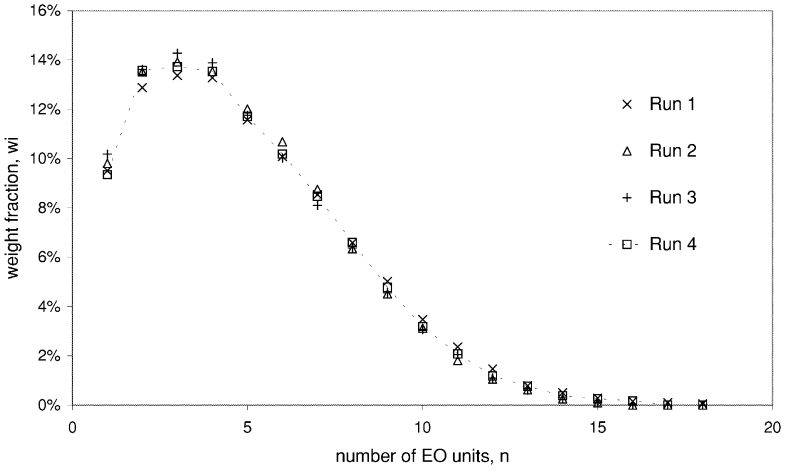

Fig. 8. Reproducibility of coupled LCCC–LEAC: oligomer distribution of the $C_{12}EO_n$ fraction of Brij 30; as obtained from four different two-dimensional separations.

Table 3
Molecular mass averages M_w and M_n and the average composition of the individual ethoxylate fractions, as determined by dual detector SEC

	C_{12}	C_{14}	C_{16}
M_w	395	432	471
M_n	352	388	418
M_w/M_n	1.122	1.113	1.128
w(EO) (%)	44.5	42.8	41.4

Using the same procedure as above, a full characterization of this product with respect to the ethoxylate content can be obtained, as is shown in Fig. 14.

There are, however, some limitations of this technique: for samples with a higher degree of ethoxylation, which contain only small amounts of a second polymer homologous series, a full separation of all oligomers cannot easily be achieved, as can be

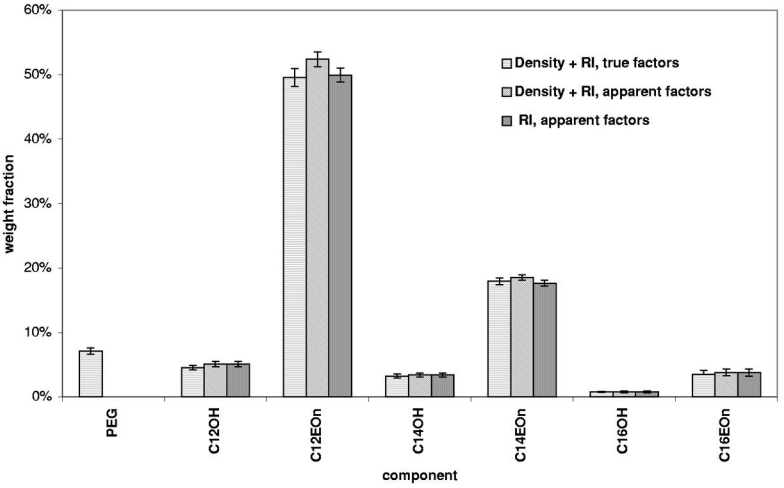

Fig. 9. Reproducibility of LCCC. Mass fractions were determined using three different methods of calculation.

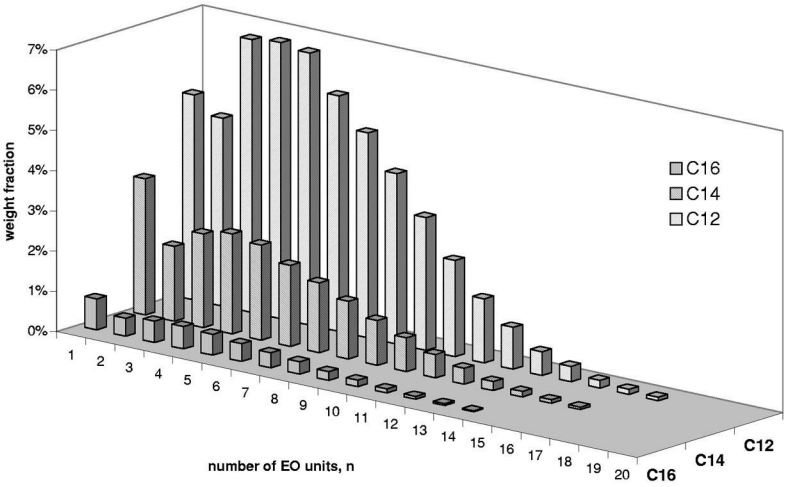

Fig. 10. Mapping of Brij 30 with full separation of all individual oligomers.

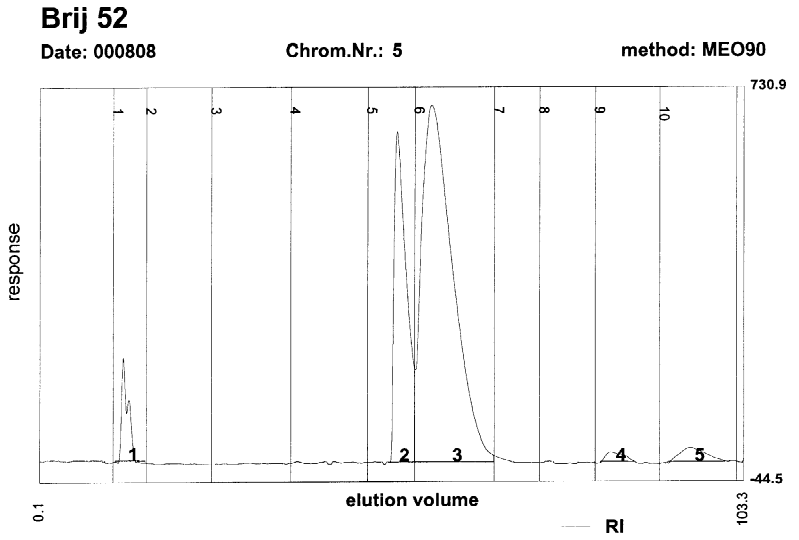

Fig. 11. Semipreparative LCCC of Brij 52 on a Spherisorb ODS 2 column (system C) in methanol–water (90:10, w/w). Fraction numbers, top row; peak numbers, bottom row.

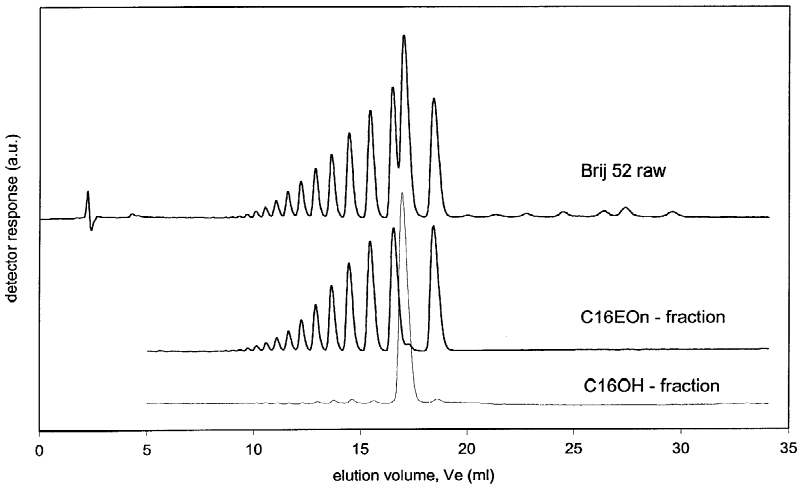

Fig. 12. Chromatograms of raw Brij 52 and the fractions 5 and 6 (peaks 2 and 3, respectively) from Fig. 11, as obtained by LEAC on a Prodigy ODS3 column (system A) in acetone–water (75:25, w/w).

seen from the following example. Fig. 15 shows a LCCC separation of Brij 76, in which two series of ethoxylates are observed: mainly C_{18} (peak 4) and a small amount of C_{16} (peak 3). According to the higher degree of ethoxylation, no fatty alcohol peak appears in front of the ethoxylates. When peak 3 (fraction 3) and peak 4 (fractions 5–8) were analyzed by LEAC (Fig. 16), reasonable chromatograms were obtained for both series, in which the fatty alcohol is still present, but in very small amounts. A full separation of the higher oligomers is, however, not achieved. Anyway, the result thus obtained will be sufficient for most purposes, as it provides more reliable quantitative information with respect to both oligomer distribution and non-reacted fatty alcohol than gradient LAC with ELS detection.

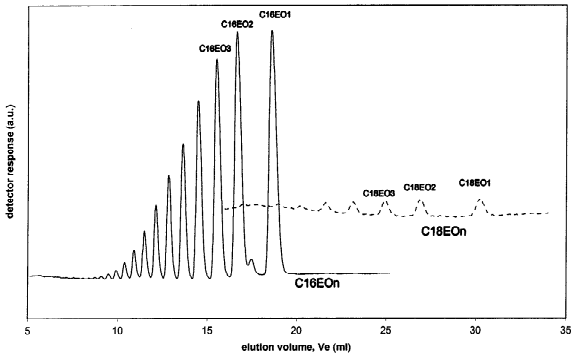

Fig. 13. Chromatograms of fractions 6 and 10 (peaks 3 and 5, respectively) from Fig. 11, as obtained by LEAC on a Prodigy OD53 column (system A) in acetone–water (75:25, w/w).

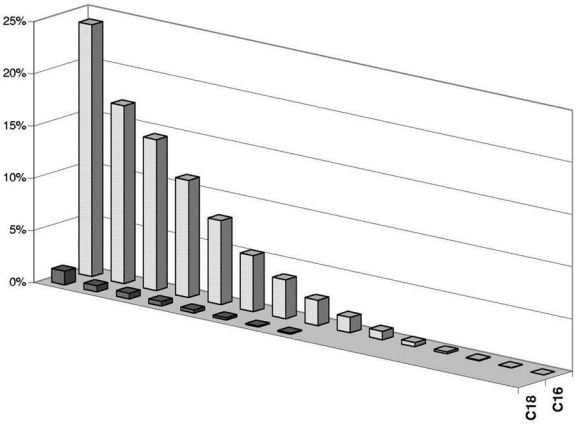

Fig. 14. Mapping of Brij 52 with full separation of all individual oligomers.

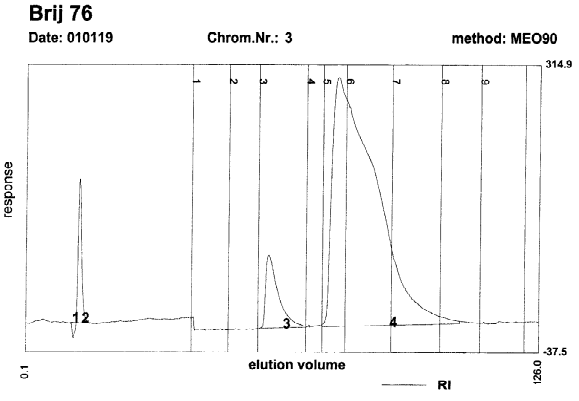

Fig. 15. Semipreparative LCCC of Brij 76 on a ODS 2 column (system C) in methanol–water (90:10, w/w). Fraction numbers, top row; peak numbers, bottom row.

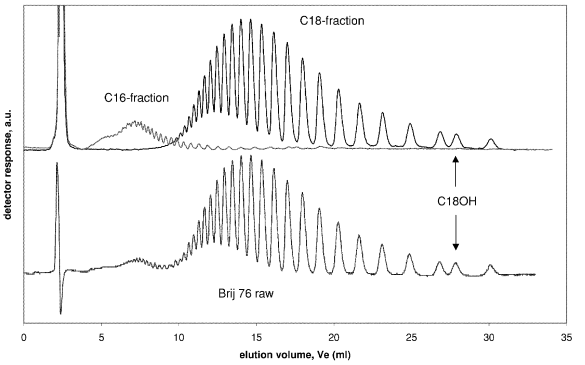

Fig. 16. Chromatograms of raw Brij 76 and the peaks 3 and 4 (fractions 3 and 5–8) from Fig. 15, as obtained by LEAC on a Prodigy ODS3 column (system A) in acetone–water (75:23, w/w).

4. Conclusions

Using LCCC with coupled density and RI detection in the first dimension and subsequent analysis of the fractions by LEAC in the second dimensions with density and RI detection a quantitatively accurate full characterization of fatty alcohol ethoxylates can be achieved (at least for samples with low to medium degree of ethoxylation). The contribution of preferential solvation can also be estimated. In most cases, the use of RI detection alone yields also accurate results.

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