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Journal of Chromatography A, 910 (2001) 207–216

JOURNAL OF CHROMATOGRAPHY A

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Liquid exclusion–adsorption chromatography: new technique for isocratic separation of nonionic surfactants I. Retention behaviour of fatty alcohol ethoxylates

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Received 3 August 2000; received in revised form 21 November 2000; accepted 28 November 2000

Abstract

A new technique of liquid chromatography is described, which allows a baseline separation of fatty alcohol ethoxylates with 15–20 ethylene oxide units under isocratic conditions. The new method is based on a combination of two different chromatographic modes for the individual structural units: size exclusion for the poly(oxyethylene) chain and adsorption interaction for the hydrophobic end fragments. A theory is provided for this mixed exclusion–adsorption mode of liquid chromatography. Chromatographic data are found to be in a good agreement with this theory. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Liquid exclusion–adsorption chromatography; Fatty alcohols ethoxylates; Non-ionic surfactants

1. Introduction

Ethoxylates of fatty alcohols, fatty acid methyl esters and alkylphenols can be used in many fields: according to the hydrophilic nature of the polyoxyethylene chain, they may be used as nonionic surfactants, the most important of which are fatty alcohol ethoxylates (FAEs). These products often consist of different polymer homologous series (based on the purity of the starting materials). Hence their full characterization requires the independent determination of two distributions: molar mass (MMD) and type of functionality (FTD).

Basically, the following chromatographic techniques can be applied, which differ in the stationary and mobile phases used, and thus in the separation mechanism.

- Gas chromatography (GC) is limited to the lowest oligomers [1].
- Supercritical fluid chromatography (SFC) [1–3] is suitable in the analysis of polymers and oligomers, but it is not — or not yet — a common routine technique, despite the fact, that its efficiency is often considerably higher than that of liquid chromatography. A special case is chromatography in subcritical or enhanced fluidity mobile phases [4,5]. In such phases, similar separation mechanisms can be observed as in liquid chromatography [3,5–10].
- Liquid chromatography (LC, HPLC) is the most frequently used technique in the separation of

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0021-9673/01/$ – see front matter
PII: S0021-9673(00)01215-2

polymers and oligomers. It can be performed with standard instrumentation and allows variations in separation mechanism and detection.

Basically, there are three limiting cases in the separation mode, which may be observed as well in LC as also in SFC.

1. Size-exclusion chromatography (SEC) separates according to the hydrodynamic volume, which corresponds to the size of the entire molecule. With an appropriate calibration, SEC may be used to determine the molar mass distribution (MMD) [6,7]. As the elution volumes are related to log *M*, only the lowest oligomers can be reasonably separated. SEC is always performed in isocratic mode, typically in pure solvents. This allows the use of refractive index (RI) and density detection, thus making an accurate quantitation possible.
2. Interaction chromatography (IC), liquid adsorption chromatography (LAC) separates according to the number of structural units capable of being adsorbed on the stationary phase: this may be the repeating units, the end groups, or both. In principle, LAC can be performed using isocratic or gradient elution, but samples with higher molar mass typically require gradient elution [8–20]. As retention increases exponentially with the number of repeating units, higher oligomers will be very strongly retained, hence gradient elution has to be applied in most cases. While alkyl phenol ethoxylates can be detected in UV, this is not possible for samples, which do not contain a chromophoric group, such as FAEs and fatty acid methyl ester ethoxylates (FAMEEs): in this case, the evaporative light scattering detector (ELSD) is the only choice. Unfortunately, quantitation with an ELSD is a difficult task, if possible at all [12,21–25].
3. LC at the critical point of adsorption (often also called LC under critical conditions; LCCC, or LC at the critical adsorption point, LCCAP) [26–35] is the limiting case between SEC and LAC: at a special temperature and mobile phase composition, the entropic and enthalpic contributions compensate each other. Under these conditions, all chains with the same repeating unit elute at the same elution volume (regardless of their length), which means that the polymer chain (or one block) becomes chromatographically invisible. Hence a separation according to a structural units other than the repeating unit (end groups, one block in a copolymer etc.) can be achieved. Obviously, LCCC is run under isocratic conditions, but typically in mixed mobile phases.

In the case of nonionic surfactants molecules — such as FAEs — one may separate the individual oligomeric series of ethoxylates according to their hydrophobic end group on a reversed-phase column at the CAP for the poly(oxyethylene) chain.

Similar ideas are true when applied to diblock copolymers (for which FAEs are a good example): using LCCC one may separate amphiphilic diblocks with respect to the length of the polar block at the CAP for the non-polar one on a normal-phase column, and with respect to the length of the less polar block at the CAP for the more polar one on a reversed-phase column [29,36–41].

The basic requirements in the separation of nonionic surfactants by LCCC (according to the hydrophobic groups) are

- Elution of ethoxylate chain sufficiently close to the critical point of adsorption.
- Sufficient resolution of hydrophobes.

It is not always possible to achieve a perfect compensation of entropic and enthalpic effects under conditions, which allow a separation of hydrophobes (such as fatty alcohols, etc.).

In some systems no critical point is observed at all. On the other hand, there are also systems, where k' is close to zero over a wide range of mobile phase composition. This is the case with many C_{18} packings in methanol–water. This allows a fine tuning in order to optimize the separation, as will be shown in another paper.

In other systems the critical point of adsorption for EO is found at a mobile phase composition, in which fatty alcohols (and also the lower oligomers of FAEs) are insoluble or very strongly adsorbed on the stationary phase. This is the case on C_{18} columns in acetone–water, where the critical point of adsorption is typically between 25 and 35 wt.% of acetone.

A reasonable methylene selectivity is, however, found in this system at a much higher acetone content of the mobile phase, where the polyoxyethylene chain should be clearly in the exclusion regime.

The basic idea of this paper was, to utilize this situation for a separation of ethoxylate oligomers in isocratic mode.

As a first step, such a method should be developed

for single hydrophobe ethoxylates; in the next step, FAE samples with a polydispersity in the hydrophobic part should be analyzed. This paper deals with the optimization of chromatographic conditions; the quantitative aspects will be discussed in part 2 of this series.

2. Experimental

These investigations were performed using the density detection system DDS70 (Chromtech, Graz, Austria), which has been developed in our group [42,43].

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 temperature of 25.0°C was maintained for all measurements in systems A and B, while in system C the measuring temperature was 35.0°C.

In system A, the mobile phase was delivered by a Jasco 880 PU pump (Japan Spectrosopic, Tokyo, Japan) at a flow-rate of 0.5 ml/min. Samples were injected manually using a Rheodyne 7125 injection valve (Rheodyne, Cotati, CA, USA) equipped with a 50-μl loop. A Bischoff 8110 RI detector (Bischoff, Leonberg, Germany) was connected to the DDS 70. Columns were connected to two column selection valves (Rheodyne 7060): a Prodigy 5-μm ODS(3) column (250×4.6 mm, pore diameter 100 Å, ser. no. 185970, from Phemonenex, Torrance, CA, USA) was used in all measurements.

In system B, 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 0.5 ml/min in all measurements. Samples were injected using a Spark 125 autosampler equipped with a 20-μl loop. A Spherisorb S5 W column (250×4.6 mm, 5 μm, 80 Å) was used in all LAC measurements. In gradient elution, mobile phase A was pure acetone, mobile phase B was acetone–water (80:20, w/w). The following gradient profile was used: start 100% A, delay time 7.0 min, then in 2 min to 85% A, in 30 min to 0% B, 5 min constant at 100% B, then within 1 min back to 100% A. A Sedex 45 ELSD (Sedere, France) was connected to the DDS 70. Nitrogen was used as carrier gas, and the pressure at the nebulizer was set to 1.0 bar, the temperature of the evaporator to 30°C.

In system C, the following semipreparative columns were used, which were connected to two column selection valves (Rheodyne 7060): Spherisorb ODS2 (250×10 mm, 5 μm, 80 Å) from PhaseSep (Deeside, Clwyd, UK) Sphereclone 5 μm ODS (2), 250×10 mm, ser. no. 185968 (Phemonenex) A flow-rate of 2.0 ml/min was maintained with an LDC Constametric IIG HPLC pump (from Milton Roy, Riviera Beach, FL, USA). A Sicon LCD 201 RI detector was combined with the DDS70. An Advantec 2120 fraction collector was used in the fractionations (Advantec, Dublin, CA, USA).

All solvents were HPLC grade. Acetone was purchased from Roth (Karlsruhe, Germany), methanol and water from Riedel-de Haen (Seelze, Germany).

The following polydisperse FAE samples were used in these investigations (specifications given by the producer: Fluka, Buchs, Switzerland): Brij 30: polyethyleneglycol dodecyl ether, main component: tetraethylene glycoldodecyl ether; Brij 52: polyethyleneglycol hexadecyl ether, main component: diethyleneglycolhexadecyl ether; Brij 56: polyethyleneglycol hexadecyl ether, main component: decaethylene glycol hexadecyl ether; Brij 72: polyethyleneglycol octaadecyl ether, main component: diethyleneglycol octadecyl ether; Brij 76: polyethyleneglycol octaadecyl ether, main component: decaethyleneglycol octadecyl ether.

Monodisperse samples (C_{12} to C_{18} monoalkylethers of di- to octaethylene glycol) as well as PEG and fatty alcohols were purchased from Fluka.

The determination of interstitial volume V_i and pore volume V_p was performed in tetrahydrofuran (HPLC grade, Baker, Phillipsburg, NJ, USA) using polystyrene standards in a molecular-mass range of 500–200 000 and ethyl benzene (all from Fluka).

3. Theoretical considerations

The elution volume of a species in liquid chromatography is known to be:

$$V_e = V_i + KV_p \quad (1)$$

where V_i denotes the interstitial volume (i.e. the volume of the solvent outside the particles of the packing), $V_0 = V_i + V_p$ is the void volume (V_p being the entire pore volume), and K is the distribution coefficient relevant to the change in Gibbs free energy, which results from the changes in enthalpy and entropy.

The theory of ideal SEC has been developed by Casassa [44,45]. According to this theory, in ideal SEC, which is governed solely by entropy, the equilibrium constant K_{SEC} is dependent on only one parameter, the molecule-to-pore size ratio R/d, where R is the radius of gyration, and d is the pore diameter.

For small molecules and wide pores ($R/d \ll 1$) K_{SEC} has the form:

$$K_{SEC} \approx 1 - \frac{2}{\sqrt{\pi}} \cdot \frac{R}{d} \quad (2)$$

For Gaussian chains (with $R \propto \sqrt{M}$) this gives:

$$K_{SEC} \approx 1 - C\sqrt{M} \quad (3)$$

- Large molecules, which have no access to the pores (exclusion limit) are eluted at V_i: for $R/d \gg 1$ (very big molecules, small pores) K_{SEC} is close to zero.
- Small molecules, which have access to almost the entire pore volume V_p, will appear near the void volume $V_0 = V_i + V_p$.
- At $R/d > 1$ K_{SEC} is exponentially decreasing function of molar mass M: large molecules are eluted before small ones with an elution volume V_e between V_i and V_0, which is determined by $K_{SEC.}$. More accurate formulae describing a cross-over between these two asymptotes can be found in [44,45].

In SEC, no sample component should be eluted at a volume larger than the void volume V_0.

In LAC, where the interactions between the sample and the stationary phase determine retention, elution volumes are larger than V_0. The theory of interactive chromatography of homopolymers (more general that the SEC theory but based on the same polymer and pore model) has been developed by Gorbunov and Skvortsov [46,47]. The general theory accounted for adsorption interactions, and apart from R and d parameters an additional parameter appeared in the theory, namely the parameter of adsorption interactions, c.

In SEC c is negative: ideal SEC with no adsorption interactions corresponds to large negative $c \to \infty$ (in this case the general theory reduces to Casassa's equations). To describe LAC, c should be taken as positive. The parameter c can be estimated by comparing the theory with experimental LAC data [15,48,49].

In the case of rather strong adsorption, $cR \gg 1$, it follows from the general theory:

$$K \approx \frac{2}{cd} \exp(c^2 R^2) \quad (4)$$

which means that the distribution coefficient should increase exponentially with M.

The special case of $c = 0$ is called the critical adsorption point (CAP), or adsorption threshold point. At this point corresponding to weak attractive interactions entropic and enthalpic phenomena compensate each other, and $K = 1$ (the retention factor $k' \equiv V_e/V_0 - 1 = 0$) regardless the number of repeating units in the chain. As a result all polymeric homologues of a polydisperse sample are eluted in a narrow peak at $V_e = V_0$. If a polymer contains end groups, which can interact strongly with the stationary phase, the peak will be shifted towards higher elution volumes, and a separation according to nature and number of end groups can be achieved. In this case K will be >1 ($k' > 0$), but both K and k' should show no dependence on molar mass.

In the case of two-block structures (such as FAEs), each part of the molecule can be assigned a different value of the adsorption interaction parameter, c: c_A for the alkyl group, and c_B for the poly(oxyethylene) chain.

If a surfactant is to be separated according to the hydrophobic groups, one should find conditions, where $c_B = 0$ (critical point of adsorption for EO) and $c_A > 0$ (alkyl groups can be separated by adsorption).

One might speculate, that a positive value of c_A (alkyl groups in adsorption regime) and a sufficiently negative value of c_B(PEG in exclusion regime) should lead to a situation where the individual oligomers should be eluted in SEC order, but far beyond V_0. This follows from the general theory of

interactive chromatography of two-block copolymers which has been developed in previous communications [15,50].

Let us first consider one specific case, for which the theory gives very simple formulae [15,50], namely the situation of ideal SEC regime for block B (PEG), and strong adsorption for alkyl block A. Both blocks are assumed as Gaussian chains with the radii of gyration R_B and R_A, which are much smaller than the pore radius d. The theoretical result for this specific case may be written in the form:

$$K_{AB} \approx K_B \cdot Y(c_B R_A) \quad (5)$$

where $K_B \gg 1$ is the distribution coefficient of an adsorbing chain B (K_B having the form of Eq. (4)), and a special mathemathic function Y is defined as $Y(x) \equiv \exp(x^2) \cdot \mathrm{erfc}(x)$.

For small length of the EO chain B (small R_A) formula (5) can be simplified:

$$K_{AB} \approx K_B(1 - \frac{\sqrt{\pi}}{2} c_B R_A) = K_B(1 - \tilde{C}\sqrt{M_A}) \quad (6)$$

Formula (6) shows the same elution order as in SEC (see Eq. (3)), but the values of K are more than unity, which is characteristic of LAC mode.

This is why we apply the term liquid exclusion–adsorption chromatography (LEAC) to such a type of chromatographic separation.

When the PEG block is big enough ($R_A c_B \gg 1$), K_{AB} tends to zero as R_A^{-1}:

$$K_{AB} \approx \frac{K_B}{\sqrt{\pi}} \cdot \frac{1}{R_A c_B} \quad (7)$$

and we see again both similarity with and difference from SEC: in SEC K also tends to zero, but exponentially.

It is interesting to note that the pore size dependence of the distribution coefficient in LEAC is very different to that in SEC. According to Eq. (2), K_{SEC} increases with d, while the theory for LEAC gives just opposite dependence $K_{AB} \approx K_B \approx d^{-1}$, which is characteristic of adsorption chromatography (see Eq. (4)).

To analyze a crossover behavior in-between the regimes of Eq. (6) and Eq. (7), as well as the more complicated situation of the not perfectly ideal SEC mode for the EO block, one may use the general theory [15,50].

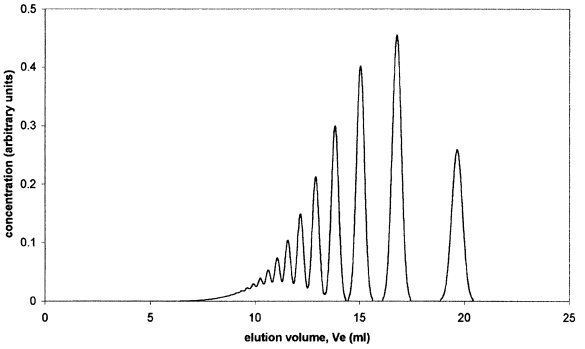

Fig. 1. Simulation of a LEAC separation of a fatty alcohol ethoxylate. Column parameters used in the simulation: pore diameter 6.8 nm, pore volume 0.86 ml, void volume 2.4 ml, efficiency: 5000. Sample parameters: diblock, composed of the structural units EO ($M_w = 164$, $M_w/M_n = 1.6$, $c = -6.0$) and CH_2 ($M_w = 224$, $M_w/M_n = 1.0$, $c = 3.6$).

There is another way to visualize complicated theoretical solutions. In a recent paper [51] a special software for simulation of chromatograms of homopolymers on the base of the general theory of interactive chromatography has been described. The program uses a few parameters, which describe the column, the polymer to be analyzed and its interaction parameters.

Now this 'virtual chromatograph' can also deal with two-block copolymers — we incorporated the theory of Refs. [15,50] in this software. With a rough estimate of the required parameters, a chromatogram could be expected, in which the individual oligomers would be resolved to the baseline, as is shown in Fig. 1.

The question now was whether a system with such parameters could be found in practice.

4. Results and discussion

As the first step, we analyzed several single hydrophobe surfactants, which consist (mainly) of one homologous series. The functionality if these products was evaluated by LCCC in methanol water (details will be given later on).

- Brij 52 and 56 are based on hexadecanol (with traces of octadecanol).

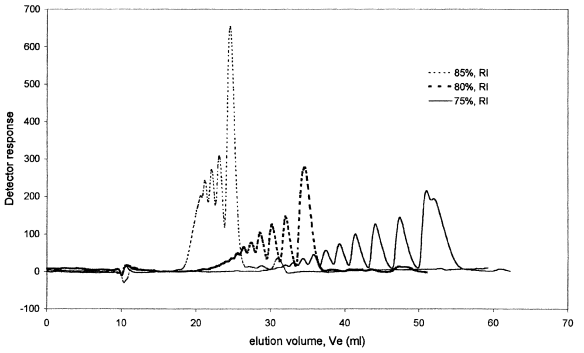

Fig. 2. Chromatograms of Brij 52, as obtained on Sphereclone ODS(2) in acetone–water mobile phases of different composition (other chromatographic conditions: see system C).

- Brij 72 and 76 are based on octadecanol (with traces of hexadecanol).

In Fig. 2, three chromatograms of Brij 52 are shown, which were obtained on the semipreparative Sphereclone ODS(2) column. Obviously, the peak pattern is very similar as in the simulated chromatogram. As expected, elution volumes and resolution increase with decreasing acetone content. The order of peaks was also the predicted one, as could be proven by injection of monodisperse ethoxylates. Surprisingly, a double peak appears at 75% acetone in the mobile phase.

If the same sample is analyzed on the Prodigy ODS(3) column in 80% acetone (Fig. 3), the situation becomes clear: while all other peaks have a positive sign in density and RI detection, peak 15 is positive in RI and negative in density detection, which indicates, that it should be the fatty alcohol, which is eluted before the monoethoxylate. Indeed, these peaks could be identified by injection of the fatty alcohols and monodisperse ethoxylates.

This effect is obviously stronger on the Prodigy column, while on the semipreparative Sphereclone ODS(2) column the fatty alcohol and the monoethoxylate merge into one peak.

The same behaviour is also found on the Prodigy column for Brij 72, as can be seen from Fig. 4: all peaks are separated to the baseline, and the fatty alcohol is again in front of the monoethoxylate.

This behaviour can easily be explained: the fatty alcohol does not belong to the same homologous series as the ethoxylates. When it is adsorbed on the stationary phase, the polar hydroxy end group pulls the adjacent methylene group(s) out of the adsorption layer, as is shown in Fig. 5.

Again we used a simulation to demonstrate the reason for this behaviour: The FAEs were regarded as two-block copolymer with the components $(CH_2)_n$ and $(EO)_m$, and the fatty alcohol as a two-block molecule with the components $(CH_2)_{n-2}$ and $-CH_2-CH_2-OH$ (Fig. 6). By choosing a slightly smaller adsorption interaction parameter for the $-CH_2-CH_2-OH$ unit (compared to the one of the methylene unit), the peak really appears between the mono and diethoxylate, as can be seen from Fig. 7.

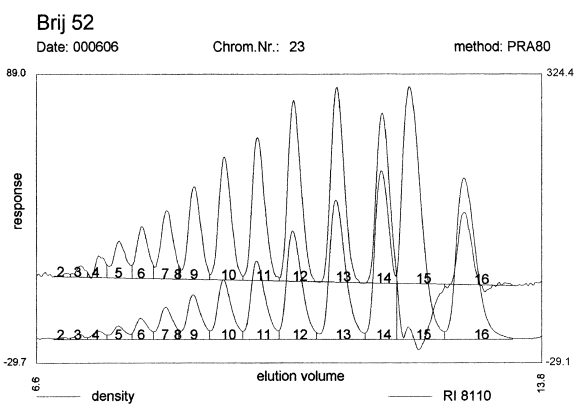

Fig. 3. Chromatogram of Brij 52, as obtained on Prodigy ODS(3) in acetone–water (80 wt.% acetone, other chromatographic conditions: see system A).

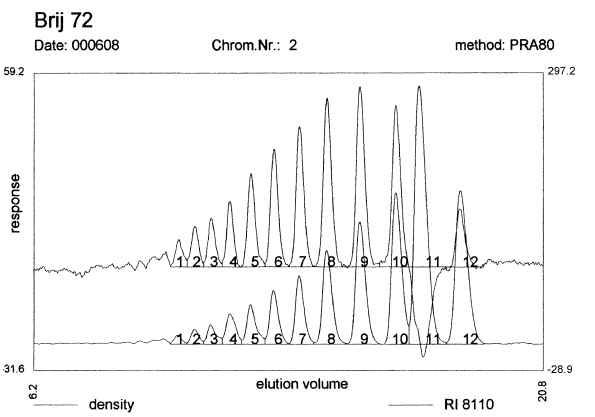

Fig. 4. Chromatogram of Brij 72, as obtained on Prodigy ODS(3) in acetone–water (80 wt.% acetone, other chromatographic conditions: see system (A).

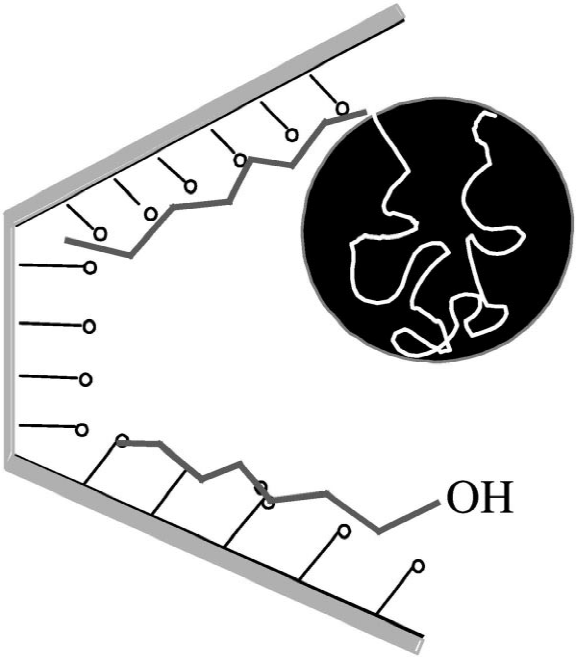

Fig. 5. Schematic representation of the different chromatographic behaviour of FAEs and fatty alcohols in a porous stationary phase.

A similar effect can be observed at, or close to, the CAP: in mobile phases composed of methanol and water, the fatty alcohol appears always slightly before the peak of the ethoxylates, even when the composition of the mobile phase corresponds to the CAP for the poly(oxyethylene) chain. This effect can be utilized in the analysis of FAE, especially on stationary phases with a ''critical plateau'', as will be demonstrated in another paper.

As a practical example, we separated Brij 72 by LCCC on the Spherisorb ODS2 column in 95%

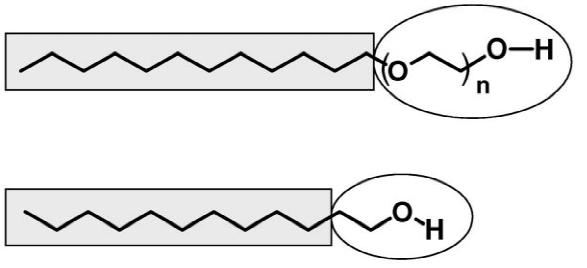

Fig. 6. Models used in the simulation of LEAC: FAEs (top), fatty alcohol (bottom).

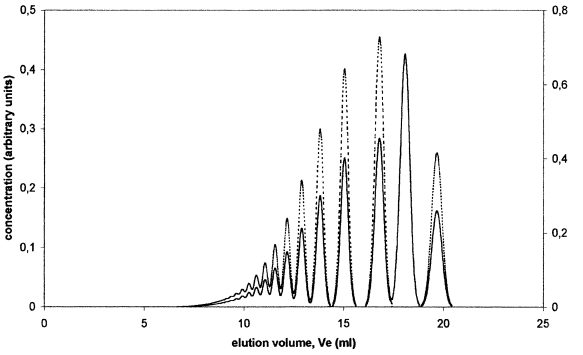

Fig. 7. Simulation of a LEAC separation of a 1:0.4 mixture (solid line) of fatty alcohol ethoxylate (dotted line) and fatty alcohol. Column parameters used in the simulation as in Fig. 1: pore diameter 6.8 nm, pore volume 0.86 ml, void volume 2.4 ml, efficiency: 5000. Sample parameters for FAEs as in Fig. 1: diblock, composed of the structural units EO ($M_w = 164$, $M_w/M_n = 1.6$, $c = -6.0$) and CH_2 ($M_w = 224$, $M_w/M_n = 1.0$, $c = 3.6$). Sample parameters for the fatty alcohol: diblock, composed of the structural units CH_2 CH_2OH ($M_w = 45$, $M_w/M_n = 1.0$, $c = -6.0$) and CH_2 ($M_w = 196$, $M_w/M_n = 1.0$, $c = 1.4$).

methanol, and collected fractions in such a way that the fatty alcohol was separated from the ethoxylates. When the ethoxylate fraction was again analyzed by LEAC on the Prodigy column, the alcohol peak had almost disappeared, as can be seen from Fig. 8.

The new technique can as well be applied to samples with a higher degree of ethoxylation, as can be seen from Fig. 9, which shows a chromatogram of Brij 76. Again the fatty alcohol appears in front of the monoethoxylate, as is indicated by the arrows in

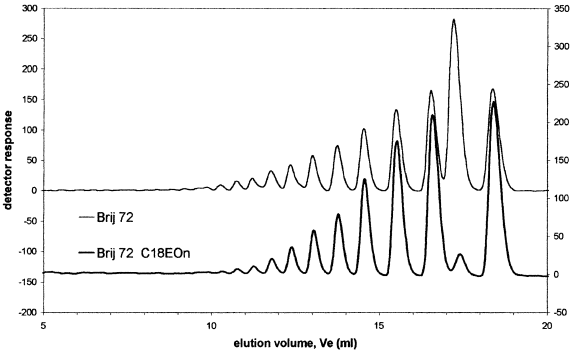

Fig. 8. Chromatograms of Brij 72 and the C_{18} ethoxylate fraction (from LCCC on ODS2 in methanol–water, 95:5), as obtained on Prodigy ODS(3) in acetone–water (80 wt.% acetone, other chromatographic conditions: see system (A).

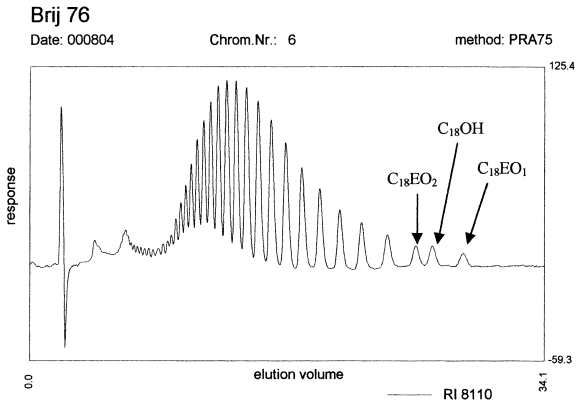

Fig. 9. Chromatogram of Brij 76, as obtained on Prodigy ODS(3) in acetone–water (75 wt.% acetone, other chromatographic conditions: see system A).

Fig. 9. About ten peaks are resolved almost to the baseline, for the higher oligomers the resolution is not that good.

In the analysis of surfactants with more than one homologous series, a two-dimensional separation is necessary (details will be given in part 2 of this series). In a chromatogram of Brij 30 (which contains ethoxylates of dodecanol, tetradecanol and hexadecanol), the individual series of peaks overlap (Fig. 10). When this sample is fractionated by LCCC in 90% methanol in the first dimension, the individual series of ethoxylates and the corresponding fatty alcohols can be separated, and well resolved chromatograms are obtained from LEAC in the second dimension. The fatty alcohols (which are marked by the arrows in the chromatogram of the raw product) have been removed in the first dimension.

Fig. 11 shows that the type of experimental dependencies is in reasonable agreement with theoretical formulae (6,7). When the equilibrium constant K is plotted vs. the square root of the degree of ethoxylation, straight lines are obtained for the individual polymer homologous series up to a chain length of 10–15 EO units. The slope of these lines depends on the length of the alkyl group, and all lines have an intersection point at a degree of ethoxylation of about 30–35. According to Eq. (6) this point is a function only of adsorption interaction parameter of alkyl groups, c_B, $R_A^* \sqrt{\pi}/2 \cdot c_B^{-1}$. Hence the parameter c_B can be easily obtained from the chromatographic data.

For comparison, FAE samples were also analyzed by gradient LAC with ELSD. Fig. 12 shows such a chromatogram of Brij 52. The peaks are very well resolved, but in the lower molecular region, detection problems are obvious: the fatty alcohol, which is a major component of the sample, is almost invisible, and the lower ethoxylates are also strongly underestimated. This becomes also clear from the number of visible peaks: while 15 peaks appear in LEAC (plus the solvent peak), gradient LAC with ELSD sees four peaks less!

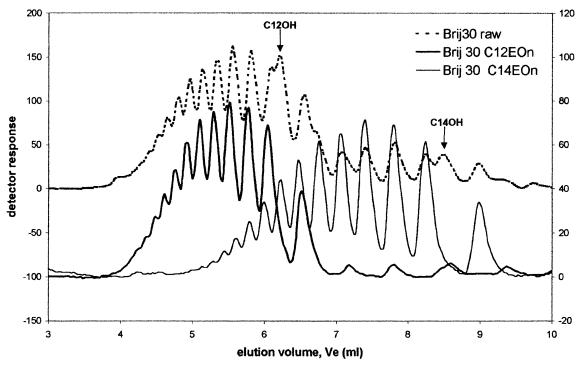

Fig. 10. Chromatograms of Brij 30 and the C_{12} and C_{14} ethoxylate fraction (from LCCC on ODS2 in methanol–water, 90:10), as obtained on Prodigy ODS(3) in acetone–water (75 wt.% acetone, other chromatographic conditions: see system A).

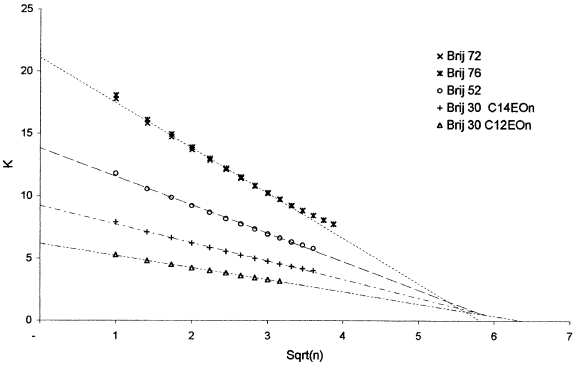

Fig. 11. Equilibrium constants as a function of $\sqrt{n}$ for different polymer homologous series of FAE, as obtained on Prodigy ODS(3) in 80% acetone (other chromatographic conditions: see system A).

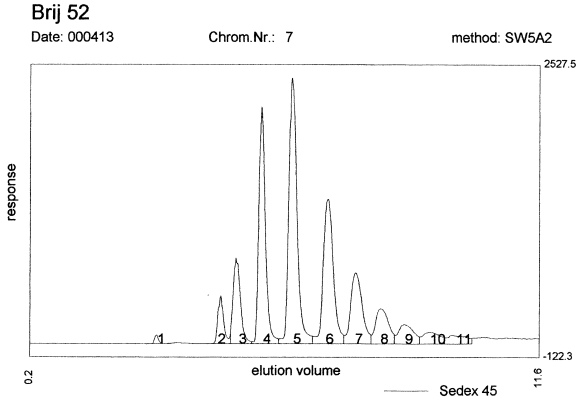

Fig. 12. Separation of Brij 52 by gradient LAC on Spherisorb S5W with ELSD (other chromatographic conditions: see system B).

A more detailed study on quantitatitive aspects will be described in part 2 of this series.

5. Conclusions

A combination of size exclusion (for the ethoxylate chain) and adsorption mode (for the end groups) can be used to separate fatty alcohol ethoxylates with isocratic elution. Compared to SEC, the resolution of the individual oligomers is much better, compared to gradient LAC, the new technique is superior with respect to quantitation, as it allows the use of RI and density detection instead of ELSD.

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