

Liquid chromatography of polyoxyethylenes under critical conditions: A thermodynamic study

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Abstract

Polyethylene glycols (PEG), fatty alcohol ethoxylates (FAE) and fatty acid polyglycol esters were analyzed by liquid chromatography under critical conditions (LCCC) on typical reversed phase columns in mobile phases consisting of methanol–water and acetone–water in the region of the critical adsorption point (CAP) for the oxyethylene unit. Critical conditions can be adjusted by varying the mobile phase composition or temperature. In methanol–water the temperature dependence is almost negligible, while it is much more pronounced in acetone–water. Critical conditions for the oxyethylene unit were realized on octadecyl phases in methanol–water containing 85.8 wt.% methanol and in acetone–water at 89.6 wt.% acetone. In the van't Hoff plots the logarithm of the distribution coefficient was plotted versus the reciprocal temperature. In all plots straight lines were found, from slope and intercept of which the entropy and enthalpy changes were calculated. The relation of the thermodynamic parameters $-\Delta G/RT$, $-\Delta H/RT$, and $\Delta S/R$ to the numbers of A and B chain units in block copolymers AB and BAB at the CAP for A is studied both theoretically and experimentally. Various approaches for obtaining the critical temperature are discussed.

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1. Introduction

Liquid chromatography at the critical condition (LCCC) is a very useful technique in the analysis of functional polymers and block copolymers, because in this mode of chromatography a separation according to a particular end group (or block) is not influenced by the length of the main chain (or the other block).

A critical adsorption point (CAP) was described for the first time almost 30 years ago by Russian groups [1,2], who reported the transition from size exclusion chromatography (SEC) to liquid adsorption chromatography (LAC) by changing the mobile phase composition (or temperature). This transition happens at the CAP, and for high molar mass polymers possesses features of the first order phase transition [3].

In SEC mode, where interactions with the stationary phase should be absent, homopolymers elute before the void volume $V_0 = V_i + V_p$, and retention decreases with increasing of molar mass M .

In LAC mode, where the separation is based on adsorption interactions, all molecules elute after the void volume and retention exponentially increases with M . At the CAP the retention of a homopolymer A becomes independent on molar mass and all polymer chains elute at the void volume.

The interaction of a homopolymer with a stationary phase can be described in terms of the interaction parameter c [4], which is relevant to the change in the free energy of the 'polymer segment/solvent/adsorbent' system, χ_s , when a statistical element (Kuhn segment) of a polymer chain makes a contact with the pore wall. In the vicinity of the CAP c is proportional to the deviation of χ_s from its critical value χ_{sc} : $c \propto (\chi_s - \chi_{sc})/RT$ [5]. It must be mentioned, that this holds strictly just for a homopolymer, in which the influence of the end groups can be neglected.

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The interaction parameter c is negative in size exclusion mode, positive in LAC mode, and zero at the CAP. The interaction parameter can be obtained from the experimental data on the chromatography of polymer homologues of various molar mass [4,6].

If a group B is attached to the A chain, the elution volume of AB corresponds to that of the group B. The same is true for block copolymers AB, as has been pointed out previously [7–9].

An interaction of a diblock AB with the stationary phase can be characterized by two interaction parameters c_A and c_B [7]. Under the critical condition for A $c_A = 0$, while c_B may be different.

- If c_B is negative, B elutes in the SEC mode, and for AB $V_e < V_0$, which is especially useful in the analysis of copolymers, in which B is high molecular.
- If c_B is positive, B elutes in LAC mode. As LCCC works only in a special mobile phase composition, the value of c_B must allow an isocratic separation of B.
- In this paper, we shall focus on the case of positive c_B , when all AB chains elute as narrow peaks (regardless the length of A) at the elution volume V_B of the block B (at $V_e = V_B > V_0$).

The situation becomes more complicated for BAB polymers with two adsorbing end blocks ($c_B > 0$). Even at the CAP for A ($c_A = 0$), such molecules elute not as narrow peaks, but are separated according to the size of the critical block with an elution order like in SEC: the smallest oligomer elutes at the highest volume. This is due to a correlation in the adsorption of blocks B; the extent of this correlation is dependent of the length of the A chain [9,10].

Basically, critical conditions can be adjusted by variation of mobile phase composition and temperature. In practice, the temperature range applicable in liquid chromatography is limited (e.g. by the boiling point of the solvents and the thermal stability of the sample and the column), while the solvent composition can be varied freely, at least as long the sample is soluble.

Depending on the solvent system and the samples to be analyzed, adjustment of critical conditions can be difficult: for high molecular-weight polymers small deviations of the interaction conditions from CAP have tremendous effects, hence the CAP has to be adjusted very precisely.

At the CAP entropic and enthalpic contributions into the change of the Gibbs energy of a linear homopolymer compensate each other exactly [3], therefore the critical point may be also considered as the entropy–enthalpy compensation point. However, for other types of polymers the conceptions of the critical and compensation point seem to be rather different. We shall demonstrate this difference by analyzing the thermodynamic parameters of homopolymers and block copolymers under the conditions of LCCC.

For this study we have chosen samples of practical importance, which are in widespread use as non-ionic surfactants and emulsifiers: fatty alcohol ethoxylates (FAE) and

fatty acid ethoxylates (or fatty esters of polyethylene glycol, PEG).

These materials consist of a (polydisperse) hydrophilic polyoxyethylene chain (A) and a hydrophobic alkoxy or fatty ester group (B), which may be monodisperse, but is also polydisperse in most technical samples. While FAE have the general structure AB, there are typically three different polymer homologous series present in fatty acid polyglycol esters, namely polyethylene glycol, its mono- and diesters with the fatty acid used as starting material. These can be considered as polymers with zero, one or two adsorbing end groups or as homopolymers (A), two-(AB) and three-block (BAB) copolymers [9].

In this study we try to answer the following questions:

- What is the best way to adjust critical conditions ?
- What is the difference between the critical point and the entropy–enthalpy compensation point?
- How do the thermodynamic parameters of homopolymers A, diblocks AB and triblocks BAB depend on molar mass of A and B at the CAP for A?

For this purpose, chromatographic systems were studied in a typical temperature range (15–35 °C) at or close to the CAP for polyethylene glycols.

The influence of mobile phase composition and temperature on the retention of PEGs, FAEs, and PEG fatty esters is discussed in terms of interaction parameters, and the relation of the thermodynamic parameters $-\Delta G/RT$, $-\Delta H/RT$, and $\Delta S/R$ to the number of EO units is studied both theoretically and experimentally.

2. Theoretical consideration

2.1. Thermodynamics in liquid chromatography of polymers

The distribution coefficient $K = \exp(-G/RT)$ is related to the change of the Gibbs energy G of the polymer chain when it transfers from the interstitial volume V_i into the pore volume V_p

$$\Delta G = \Delta H - T\Delta S = -RT \ln K \quad (1)$$

wherein ΔG , ΔH , and ΔS are the changes in free energy, enthalpy and entropy, R is the gas constant, and T is the absolute temperature. V_i is the interstitial volume (the volume between the particles of the packing), V_p is the pore volume, and K is the distribution coefficient.

$$K = \frac{V_e - V_i}{V_p} = \frac{V_e - V_i}{V_0 - V_i} \quad (2)$$

According to a modified version of Eq. (1),

$$\ln K = \frac{\Delta G}{RT} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}, \quad (3)$$

in a plot of $\ln K$ versus $1/T$ (van't Hoff plot), one may calculate ΔH from the slope and ΔS from the intercept. It must be mentioned, that these volumes should be used instead of the void volume V_0 , which is the sum of V_i and V_p .

2.2. Thermodynamic parameters of homopolymers A, diblocks AB and triblocks BAB at the CAP for A

According to the theory of chromatography of polymers [3] the distribution coefficient K_A of an ideal polymer chain A in the vicinity of the critical interaction point is given by

$$K_A \approx 1 + \frac{c_A r_A^2}{d} \quad (4)$$

where r_A is the radius of gyration of the chain A (for an ideal chain $r_A \propto M_A^{0.5}$); d is the pore radius; and $c_A \approx 0$ is the interaction parameter.

At the critical point $c_A = 0$, and evidently $K_A = 1$, $\Delta G = 0$.

From Eq. (4) we can obtain the following expressions for ΔH and ΔS (which hold at the CAP):

$$-\frac{\Delta H}{RT} \frac{1}{T} \frac{\partial(\ln K)}{\partial(T^{-1})} \approx \alpha_A \frac{r_A^2}{d}; \quad \frac{\Delta S}{R} \approx \alpha_A \frac{r_A^2}{d} \quad (5)$$

where

$$\alpha_A = \left. \frac{1}{T} \frac{\partial c_A}{\partial(T^{-1})} \right|_{c_A=0}$$

The parameter α_A is determined by the temperature dependence of c_A ; it does not depend on molar mass of a polymer and on pore size. Since c_A is an effective complex parameter which depends on the set of interactions between a polymer chain element, adsorbent, and solvent molecules, the values of α_A may be very different in different systems. In the systems considered in the present study the parameter α_A is positive, but it may be negative as well [4]. As follows from Eq. (5), for a chain A at the CAP ΔH and ΔS are proportional to $M_A \propto r_A^2$ and inversely proportional to pore size d , while the values and signs of ΔH and ΔS depend on the value and the sign of α_A .

According to a theory of chromatography of diblock copolymers [7], the distribution coefficient K_{AB} of a diblock AB (with an adsorbing block B) in the vicinity of CAP for A can be expressed in a form:

$$K_{AB} \approx K_B + \frac{2c_A}{\pi d} [(r_A^2 + r_B^2) \arctg(r_A/r_B) - r_A r_B] \quad (6)$$

where K_B is the distribution coefficient of the adsorbing chain fragment B. According to [3], K_B has a form:

$$K_B \approx 1 - \frac{2}{\sqrt{\pi}} \frac{r_B}{d} + \frac{2}{c_B d} \exp(c_B^2 r_B^2) \quad (7)$$

In Eqs. (6) and (7) r_A and r_B are the radii of gyration of the blocks A and B, d is the pore size; and c_A and c_B are the effective interaction parameters for A and B.

At $c_A = 0$ Eq. (6) reduces to the well-known result [8]: $K_{AB} = K_B$.

By using Eqs. (6) and (7) we obtain the following equations for the thermodynamic functions of a diblock AB at the critical point for A:

$$-\frac{\Delta G}{RT} \approx \ln \left(\frac{2}{c_B d} \right) + c_B^2 r_B^2 \quad (8)$$

$$\begin{aligned} -\frac{\Delta H}{RT} &\approx \alpha_B \left(2c_B r_B^2 - \frac{1}{c_B} \right) \\ &+ \frac{\alpha_A c_B}{\pi \exp(c_B^2 r_B^2)} \left[(r_A^2 + r_B^2) \arctg \left(\frac{r_A}{r_B} \right) - r_A r_B \right] \\ &\approx \alpha_B \left(2c_B r_B^2 - \frac{1}{c_B} \right) \end{aligned} \quad (9)$$

$$\begin{aligned} -\frac{\Delta S}{T} &\approx \ln \left(\frac{2}{c_B d} \right) + \frac{\alpha_B}{c_B} - r_B^2 (2\alpha_B c_B - c_B^2) \\ &- \frac{\alpha_A c_B}{\pi \exp(c_B^2 r_B^2)} \left[(r_A^2 + r_B^2) \arctg \left(\frac{r_A}{r_B} \right) - r_A r_B \right] \\ &\approx \ln \left(\frac{2}{c_B d} \right) + \frac{\alpha_B}{c_B} - r_B^2 (2\alpha_B c_B - c_B^2) \end{aligned} \quad (10)$$

wherein

$$\alpha_A = \left. \frac{1}{T} \frac{\partial c_A}{\partial(T^{-1})} \right|_{c_A=0}, \quad \text{and} \quad \alpha_B = \left. \frac{1}{T} \frac{\partial c_B}{\partial(T^{-1})} \right|_{c_A=0}$$

As follows from the equations given above, the thermodynamic parameter $\ln K = -\Delta G/RT$ does not depend on the molar mass of the block A at the CAP (Eq. (8)).

The parameters $-\Delta H/RT$ and $\Delta S/R$ in principle may depend on M_A , these dependences should, however, be very weak (Eqs. (9) and (10)).

All thermodynamic parameters should be approximately linear functions of molar mass $M_B \propto r_B^2$ of the other block B. It is interesting that ΔH does not depend on the pore size d , and there is a weak logarithmic pore size dependence of ΔS .

A different situation will be found in the case of BAB triblocks or difunctionals [10]: the distribution coefficient K_{BAB} of symmetrical triblocks with blocks B at both ends equals [9,10]

$$K_{BAB} \approx 1 + 2(K_B - 1) + (K_B - 1)^2 \frac{d}{\sqrt{\pi} r_A} \quad (11)$$

In Eq. (11) K_B is the distribution coefficient of an adsorbing terminal block B (Eq. (7)).

As follows from Eq. (11), at the CAP for the block A $\ln K = -\Delta G/RT$ as well as $\Delta H/RT$ and $\Delta S/R$ of a triblock BAB will depend on the numbers of repeat units in blocks A and B.

2.3. Critical point and entropy–enthalpy compensation

Under the conditions of LCCC a homopolymer A with $c_A = 0$ elutes at the void volume: $V_e = V_0$ (at $K = 1$). This is the case at the point where $\Delta G = 0$ and consequently, entropic

and enthalpic contributions compensate each other exactly. Therefore, for a homopolymer the critical point is the same as the compensation point; at this point

$$\Delta H = T_c \Delta S \quad (12)$$

Many authors [11–18] use a plot of ΔH versus ΔS (“EEC plot”) in investigations of separation mechanisms. From the slope in such a plot they calculate the compensation temperatures. Identical values of the compensation temperature are considered as a proof for identical separation mechanisms. This assumption is, however, not justified [19].

Evidently, ascribing to the slope of ΔH versus ΔS the meaning of the critical temperature in the case of a homopolymer is meaningful if ΔH and ΔS changes (which are provided by varying molar mass in a homopolymer) are measured at the very critical point. If the conditions (mobile phase composition and temperature) are already close enough to the CAP (i.e. ΔG is negligible), the slope in the EEC plot can be used for fine adjustment of the critical temperature.

It follows from Eqs. (8) and (11) for a diblock AB and a triblock BAB, that at the CAP for A $\Delta G \neq 0$, therefore ΔH and ΔS changes in LCCC of block copolymers are not compensated: $\Delta H = T_c \Delta S + \Delta G$. Of course, at some special interactions c_A and c_B and at some special values of M_A and M_B a compensation may happen, but such compensation point has nothing to do with the CAP for A. So, it is evident that the critical point and the compensation point have different meanings in the case of block copolymers. However, since ΔG of a diblock AB does not depend on the parameters of A (Eq. (8)), the critical temperature T_c for a block A can still be estimated from the slope of the plot of ΔH versus ΔS , provided that the interaction condition is already close to the CAP, and that $\Delta G - \Delta S$ plot is obtained by variation of M_A at constant M_B .

3. Experimental

These investigations were performed using the density detection system DDS70 (CHROMTECH, Graz, Austria). Data acquisition and processing was performed using the software package CHROMA, which has been developed for the DDS70.

The columns and density cells were placed in a thermostated box, in which temperature was kept constant to $\pm 0.1^\circ\text{C}$ using a thermostat Lauda RM6 (Lauda-Koenigshofen, Germany).

In system A, the mobile phase was delivered by a JASCO 880 PU pump (Japan Spectroscopic Company, 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 refractive index (RI) detector (Bischoff, Leonberg, Germany) was connected to the DDS 70. Columns were connected to two column selection valves (Rheodyne 7060).

In system B, the mobile phase was delivered by an ISCO 2350 HPLC pump (from ISCO, Lincoln, NE, USA) at a flow rate of 0.5 ml/min.

Samples were injected using an autosampler Spark SPH 125 Fix (from Spark Holland, Emmen, The Netherlands) equipped with a 20 μl loop.

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. Evaporator temperature: 30°C . As has been shown previously [20,21], lower oligomers are not detected at higher temperatures.

The following columns were used in both systems:

- Prodigy ODS3, silica-based octadecyl phase; 250 mm \times 4.6 mm; particle diameter = 5 μm ; nominal pore size = 100 \AA , Phenomenex, Torrance, CA, USA.
- Zorbax 300 C18: silica-based octadecyl phase; 150 mm \times 4.6 mm, particle diameter = 3.5 μm , nominal pore size = 300 \AA .

The solvents (acetone, methanol and water, all HPLC grade) were purchased from Roth (Karlsruhe, Germany) and Merck (Darmstadt, Germany). Mobile phases were mixed by mass and vacuum degassed, their composition was controlled by density measurement using a DMA 60 density meter equipped with a measuring cell DMA 602 M (A. Paar, Graz, Austria).

FAE samples were purchased from FLUKA (Buchs, Switzerland), PEG monolaurate from Sigma-Aldrich. Fatty acid polyglycol esters were provided by “Blachownia” Institute of Heavy Organic Synthesis (ICSO), Kędzierzyn-Koźle, Poland.

Within the range used in this study, a constant value for V_i and a linear relation between V_p and T was assumed (if V_0 depends on T , this can only result from a dependence of V_p). Void volumes V_0 were taken from the solvent peak, the interstitial volumes V_i were determined by inverse SEC with PEG standards in acetone–water (65 wt.%), as described in a previous paper [22].

For each series of measurements a sufficiently large volume of mobile phase was prepared by weight, and the composition of the degassed mobile phase was controlled by density measurement.

Temperature was varied from day to day according to the Scheme 25–15–35–20–30 $^\circ\text{C}$ (with equilibration over night), and the solvent reservoir was closed carefully over night. In the course of the measurements the mobile phase composition was controlled several times by density measurement.

4. Results and discussion

4.1. Practical aspects

In this study we wanted to show the best strategy to adjust critical conditions in systems suitable for the analysis of

non-ionic surfactants. For this purpose we compared several reversed phase columns and selected those, which performed best in a certain mobile phase system. Columns with different length and pore diameter were chosen for the different mobile phases.

In methanol–water AB structures can be analyzed very well at the CAP (typically between 80 and 95 wt.% methanol) [23], but the retention of the corresponding diesters is too high in such a mobile phase: only C_{12} –EO $_n$ – C_{12} diesters elute within a reasonable time at the CAP for the EO unit, but these peaks are already very broad. Well-resolved peaks of diesters are only obtained at 95% methanol, which is clearly beyond the CAP. Among the tested columns, the wide-pore Zorbax 300 C18 was the column of choice for the methanol–water system.

In acetone–water there are two critical points on silica-based C18 columns [9,10]. At the first critical adsorption point (at 26–30 wt.% acetone) the retention of alkyl groups is very high: in such a mobile phase FAE (with 12 or more carbon atoms in the alkyl chain) do not elute at all. At the second CAP (at 90–92 wt.% acetone) retention is in the desired range for BAB with an alkyl chain length of 12–18 carbon atoms. Among the tested columns, the narrow-pore Prodigy ODS3 performed best: baseline-resolved peaks were obtained for the diesters with 1–10 EO units.

From the experimental point of view, one has to take into account, that possible errors in the distribution coefficients (which may influence slope and intercept of the lines in a van't Hoff plot) may have different origin: errors in elution volume, interstitial volume, and pore volume. The sources of such errors can be variations of flow rate, mobile phase composition, and temperature, moreover the peak maximum of homopolymer peaks (which elute at V_0 under critical conditions) cannot be easily determined from density and RI detection, as it overlaps with the solvent peak (this limitation does, of course, not hold for the ELSD). Temperature and flow rate variations can easily be controlled. The most serious source of error is, however, the variation of mobile phase composition by evaporation of one component of the mobile phase (methanol or acetone). This will result in a trend, if the temperature is increased (15–20–25–30–35 °C) or decreased stepwise. Hence, we have performed the measurements in a different order (25–15–35–20–30 °C). In our first measurements we observed deviations from linearity in the van't Hoff plots, which could clearly be assigned to evaporation. Using the experimental conditions described above we could eliminate this source of error.

4.2. Search for critical conditions

The first step in the application of LCCC is the search for critical conditions: this can be achieved by varying the composition of the mobile phase or the temperature (or both).

In order to obtain the critical mobile phase composition (at fixed temperature) or to find critical temperature (at fixed composition) one should find an intersection point in a plot of

elution volumes of homopolymers with different molar mass versus mobile phase composition or temperature.

For obtaining the critical temperature one can also use the van't Hoff plots for polymers with different molar masses: in these plots there should be an intersection point at $1/T_c$ [24]. Of course, this is basically the same as to use a plot of elution volumes versus temperature. This approach has the advantage, that the linear relation between $\ln K$ and $1/T$ allows the use of linear regression. On the other hand, it is subject to errors in the pore volume.

When studying separation of block copolymers by LCCC the more feasible way to adjust critical conditions for A is using diblocks AB rather than homopolymers A, for which the precise determination of the peak maximum is sometimes difficult. As the homopolymer A elutes at the void volume, the sample peak overlaps with the solvent peak, which originates from preferential solvation. Diblocks AB at the CAP for A elute at $V_e > V_0$, which makes the precise determination of elution volumes easier and the distribution coefficients more reliable.

4.3. Critical conditions for polyethylene glycols and behavior of thermodynamic parameters of PEGs at the CAP

Critical conditions for PEG were realized on the studied reversed phase columns in aqueous mobile phases containing methanol, or acetone as organic modifier. While in the methanol–water system one critical point is found (85.8 wt.% of methanol for Zorbax 300 C18 column), two critical points have been observed for acetone water [9,10]. For the Prodigy ODS3 column these critical points are localized at about 27 and 90 wt.% acetone, and for this study we have selected the mobile phase composition of 89.6% acetone.

In principle, critical conditions can also be adjusted by variation of temperature. On the Zorbax column in methanol/water at 85.8 wt.% of methanol we varied the temperature between 15.0 and 35.0 °C.

In order to be sure that the possible temperature dependence [25,26] of V_i and V_p (or V_0) does not influence the van't Hoff plots, we determined V_0 and V_p in the temperature range between 15.0 and 35.0 °C (V_i was considered to be constant). As can be seen in Fig. 1, void volumes and pore volumes show a very weak temperature dependence in this temperature range, which should, however, not be neglected.

Fig. 2 shows the van't Hoff plot obtained with PEG on the wide pore Zorbax 300 C18 column in 85.8 wt.% methanol in the temperature range between 15.0 and 35.0 °C.

As can be seen, horizontal straight lines are obtained, which almost perfectly coincide, and $\ln K$ is very close to zero for all molar masses in the studied temperature range.

A different situation is found on the Prodigy column at 89.6 wt.% acetone: in this mobile phase a pronounced temperature dependence is observed. The corresponding van't Hoff plot is shown in Fig. 3. From this plot, the critical temperature $T_c = 11.0$ °C is determined.

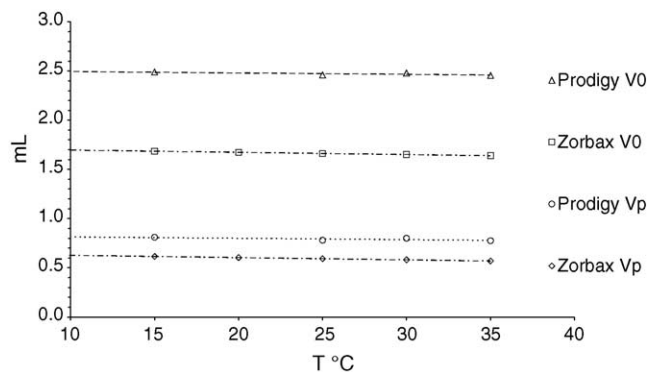


Fig. 1. Void volumes V_0 and pore volumes V_p of two C18 columns in different mobile phases: Zorbax in 85.8 wt.% methanol and Prodigy in 89.6 wt.% acetone.

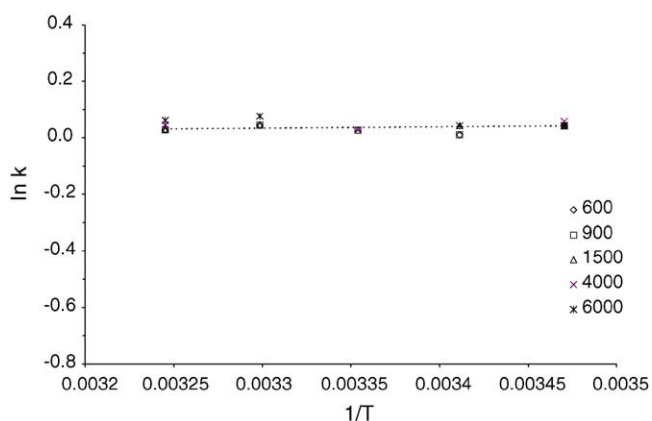


Fig. 2. van't Hoff plot of PEGs on the Zorbax column in 85.8% methanol (w/w).

A comparison of different mobile phases is shown in Fig. 4 (85.8% methanol, Zorbax) and Fig. 5 (89.6% acetone, Prodigy). The thermodynamic parameters $-\Delta G/RT$, $-\Delta H/RT$, and $\Delta S/R$ (at 25.0 °C) are plotted as a function of the number of EO units, n . In both cases, $\ln K = -\Delta G/RT$ is very close to zero up to high molar mass. As can be seen, both $-\Delta H/RT$, and $\Delta S/R$ are proportional to n , which agrees well with Eq. (5).

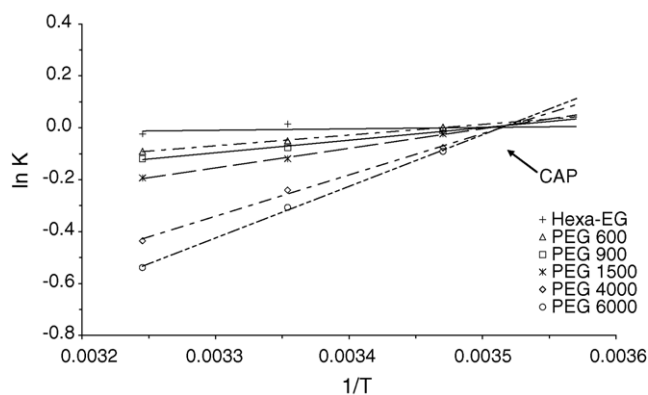


Fig. 3. van't Hoff plot of PEGs on the Prodigy column in 89.6% acetone (w/w).

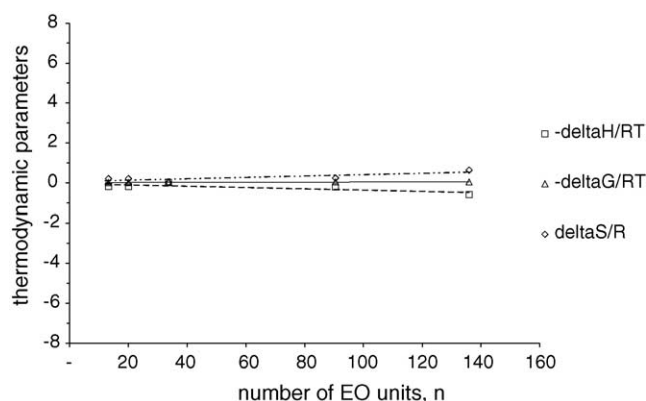


Fig. 4. Thermodynamic parameters $-\Delta G/RT$, $-\Delta H/RT$, and $\Delta S/R$ as a function of the number EO units in PEG, as obtained on the Zorbax column in 85.8% methanol.

There is, however, a big difference in the absolute values of $-\Delta H/RT$, and $\Delta S/R$ in different systems: while $-\Delta H/RT$ and $\Delta S/R$ are very close to zero up to rather high molecular PEG on the Zorbax column in 85.8% methanol, rather high values of $-\Delta H/RT$ and $\Delta S/R$ sum up to yield $-\Delta G/RT \approx 0$ on the Prodigy column in 89.6% acetone. Obviously this is due to the very different values of the parameter α_A for these systems.

Having critical conditions for PEG is necessary, but not sufficient. For a separation of amphiphilic molecules (such as fatty alcohol ethoxylates, etc.) according to the length of the hydrophobic chain two preconditions must be met: the interaction parameter of the EO unit must be as close to zero as possible, and the interaction parameter of the methylene group should be sufficiently large to yield a good resolution, and not too large in order to allow an analysis in a reasonable time.

This is fulfilled on the Zorbax column in 85.8 wt.% methanol at 25 °C, as can be seen in Fig. 6. An interaction parameter for the methylene group between 3 and 4 allows a separation of C_{12} to C_{18} FAE in a reasonable time. In this mobile phase, critical conditions can be adjusted very well

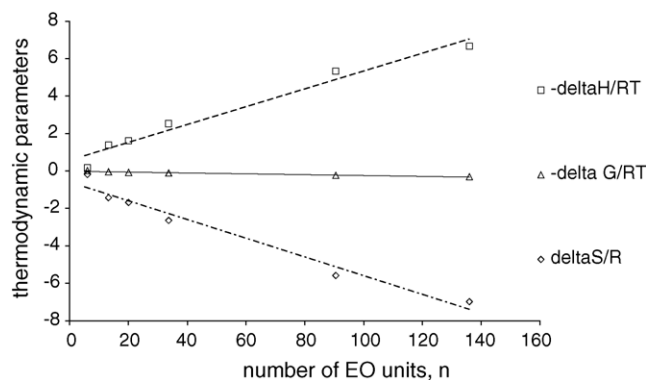


Fig. 5. Thermodynamic parameters $-\Delta G/RT$, $-\Delta H/RT$, and $\Delta S/R$ as a function of the number EO units in PEG, as obtained on the Prodigy column in 89.6% acetone.

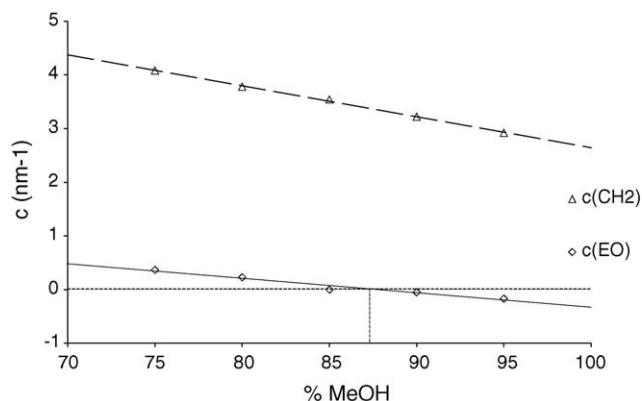


Fig. 6. Interaction parameters of the structural units EO and CH₂ on the Zorbax column in methanol–water mobile phases of different composition at 25 °C.

by variation of mobile phase composition, both interaction parameters show, however, almost no temperature dependence in the range between 15 and 35 °C, as can be seen in Fig. 7. On the Zorbax column in 85.8% methanol there is only a weak temperature dependence of c_A . Consequently the value of α_A is rather small, while this is not the case with the Prodigy column in 89.6% acetone.

In methanol–water it obviously does not make sense to adjust critical conditions by varying the temperature. In acetone–water, however, temperature variation can also be used.

4.4. Thermodynamic parameters of diblocks (monoalkyl ethers of PEG) and triblocks (diesters of PEG) at critical conditions for PEG

Fig. 8 shows the van't Hoff plot obtained for monodisperse oligoethylene glycol monododecyl ethers on the Zorbax column under critical conditions (85.8 wt.% methanol). Almost parallel straight lines are found, which have a positive slope.

In Fig. 9 the thermodynamic parameters $-\Delta G/RT$, $-\Delta H/RT$, and $\Delta S/R$ thus obtained are plotted as a function of the number of EO units, n . As can be seen, all three param-

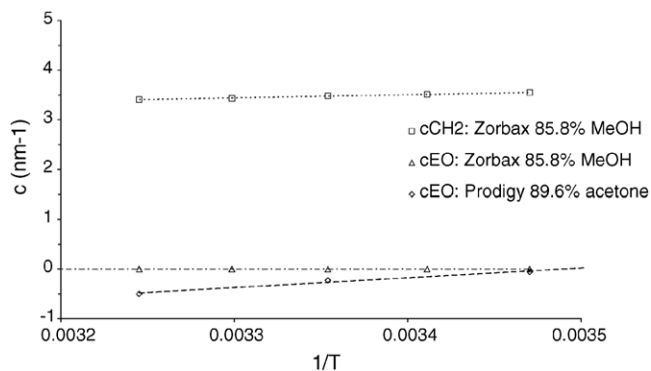


Fig. 7. Interaction parameters of the structural units EO and CH₂ on the Zorbax column in 85.8% methanol and on the Prodigy column in 89.6% acetone at different temperatures.

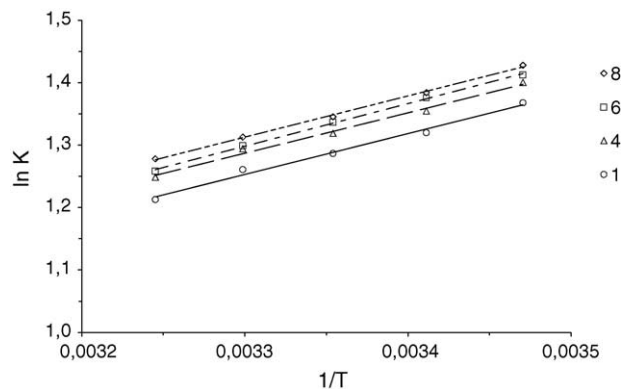


Fig. 8. van't Hoff plot of selected PEG oligomers (C12EO_n) on the Zorbax column in 85.8% methanol (w/w).

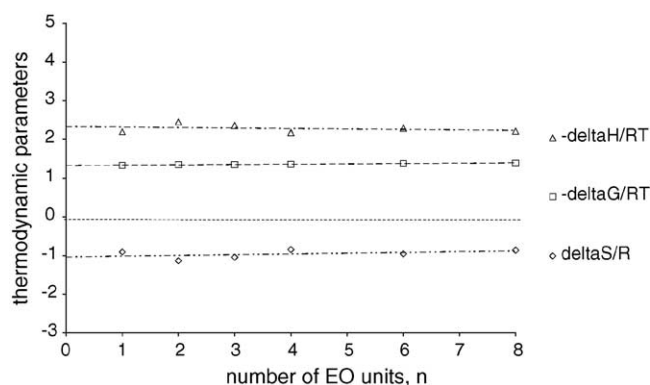


Fig. 9. Thermodynamic parameters $-\Delta G/RT$, $-\Delta H/RT$, and $\Delta S/R$ as a function of the number of EO units in C12EO_n (Zorbax column, 85.8% methanol, 25.0 °C).

eters are practically independent on n , as should be expected in accordance with Eqs. (8)–(10) under critical conditions for EO chain.

Fig. 10 shows the van't Hoff plot obtained with monodisperse hexaethylene glycol monoalkyl ethers on the Zorbax column under the same conditions. Straight lines are also found in this case, but with a different (positive) slope, which increases with the number of carbon atoms in the alkyl chain.

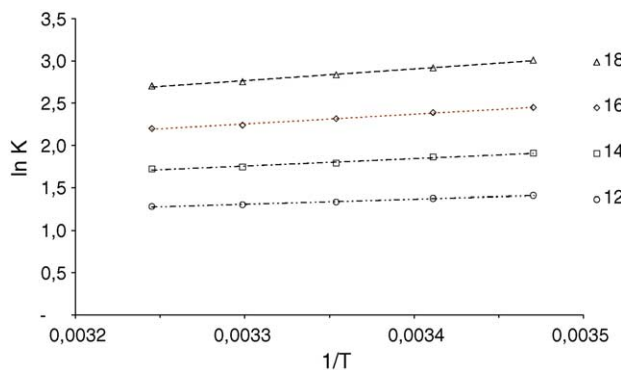


Fig. 10. van't Hoff plot of selected PEG oligomers (C_mEO₆) on the Zorbax column in 85.8% methanol (w/w).

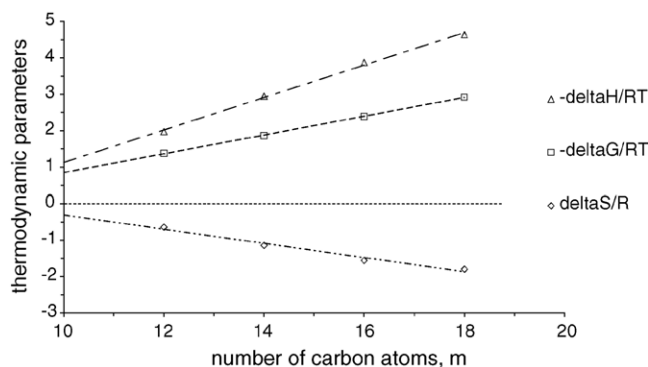


Fig. 11. Thermodynamic parameters $-\Delta G/RT$, $-\Delta H/RT$, and $\Delta S/R$ as a function of the number of CH_2 units in C_mEO_6 (Zorbax column, 85.8% methanol, 25.0 °C).

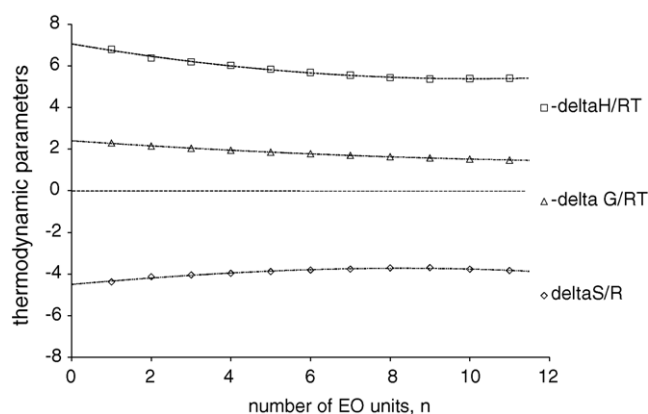


Fig. 12. Thermodynamic parameters $-\Delta G/RT$, $-\Delta H/RT$, and $\Delta S/R$ as a function of the number EO units in lauric acid diesters of PEG (Prodigy, 89.6% acetone, 25 °C).

In Fig. 11 the thermodynamic parameters $-\Delta G/RT$, $-\Delta H/RT$, and $\Delta S/R$ thus obtained are plotted as a function of the number of carbon atoms, m , in the alkyl chain.

As expected (Eq. (8)), $\ln K = -\Delta G/RT$ linearly increases with the number of carbon atoms, and so does $-\Delta H/RT$, while $\Delta S/R$ is negative and decreases with increasing m : both ΔH and ΔS are negative, which indicates, that the interaction with the stationary phase is enthalpically favorable and entropically unfavorable.

In Fig. 12 the thermodynamic parameters $-\Delta G/RT$, $-\Delta H/RT$, and $\Delta S/R$ for the C_{12} diesters on the Prodigy column in acetone–water are plotted as a function of the number of EO units.

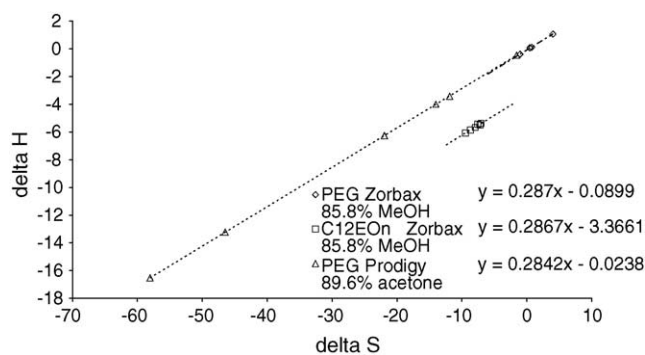


Fig. 13. EEC plot for the Zorbax column in 85.8% methanol and the Prodigy column in 89.6% acetone at 25.0 °C.

Obviously, $\ln K = -\Delta G/RT$ is positive and decreases with increasing n . This agrees well with the theory (Eq. (11)). $\Delta S/R$ is negative and increases within each series of diesters with the number n of EO units, while $-\Delta H/RT$ is positive and decreases with increasing n . The decrease of retention with increasing size of the polyoxyethylene chain at the CAP (Eq. (11)) results from the enthalpically favorable interaction of the hydrophobic end groups and the entropically unfavorable conformation of the polyoxyethylene coil, having two adsorbing terminal blocks in contact with the stationary phase.

4.5. Estimating critical temperature from the EEC plots

If the intersection point in the van't Hoff plot is not sharp enough, the plot of ΔH versus ΔS ("EEC plot") can be used for fine adjustment of critical conditions as explained in Section 2.3.

As can be seen in Fig. 13, the data points obtained with PEGs on the Prodigy column in 89.6% acetone fall on the same straight line, from which the critical temperature can be determined.

As can be seen in Table 1, the values of T_c obtained from the plots of Fig. 3 and from the EEC plot (Fig. 13) are in quite good agreement.

In the same plot the data obtained with PEG and oligoethylene glycol monododecyl ethers (C_{12}EO_n) on the Zorbax column in 85.8% methanol are shown. Although the range of ΔH and ΔS is rather narrow in this mobile phase (as the temperature dependence is very low), the critical temperatures obtained for both homologous series are in good agreement, as can be seen in Table 1.

Table 1

Critical temperatures of PEG and its monoalkylethers on the Zorbax column in 85.8% methanol and PEG on the Prodigy column in 89.6% acetone

Sample	Column	Mobile phase	Data shown in	Determined from	T_c (°C)
PEG	Zorbax	85.8% methanol	Fig. 13	EEC plot	13.9
C_{12}EO_n	Zorbax	85.8% methanol	Fig. 13	EEC plot	13.5
PEG	Prodigy	89.6% acetone	Fig. 13	EEC plot	11.1
PEG	Prodigy	89.6% acetone	Fig. 3	van't Hoff plot	11.0

5. Conclusions

On silica-based octadecyl stationary phases critical conditions are realized for the oxyethylene unit in methanol–water mobile phase containing 85.8 wt.% methanol (Zorbax 300 C18 column), and in acetone–water at about 90 wt.% acetone (Prodigy ODS3 column). In both systems, the adsorption interaction parameters depend strongly on the mobile phase composition.

In methanol–water the adsorption interaction parameters depend very slightly on temperature. In acetone–water the temperature dependence is much more pronounced.

Hence, the most feasible way of adjusting critical conditions is varying the composition of the mobile phase. Once the conditions are sufficiently close to the CAP, a fine adjustment of critical conditions is, however, possible by variation of temperature.

Straight lines are obtained in the van't Hoff plots in all studied systems; from these plots the enthalpy and energy changes were calculated.

We have obtained experimental evidence, that at the CAP for the EO unit, entropy and enthalpy changes of PEG exactly compensate each other, and $\ln K = -\Delta G/RT$ does not depend on the number n of EO units. The obtained changes in entropy and enthalpy of PEG at the CAP were found to be proportional to the number of EO units, which well agrees with the theory. In methanol–water, the changes in entropy and enthalpy are very small for PEG in a wide molar mass range. This is not the case in acetone–water: quite high values of $-\Delta H/RT$ and $\Delta S/R$ sum up to yield $\ln K = -\Delta G/RT \approx 0$ up to rather high molar masses.

Within each polymer homologous series of diblocks (fatty alcohol ethoxylates and fatty acid monoesters of PEG) there is no entropy–enthalpy compensation at the CAP for EO, $\ln K = -\Delta G/RT$ and $-\Delta H/RT$ are positive and increase linearly with the number m of carbon atoms in the hydrophobic part, while $\Delta S/R$ is negative and linearly decreases with increasing m .

At the same time, there are no considerable dependences of all thermodynamic parameters of these polymers on the number of EO units. These findings are also in a good agreement with a theoretical prediction.

In the case of BAB triblocks (PEG diesters), at the CAP for EO entropy and enthalpy contributions into the Gibbs energy change are also not compensated, and $\ln K = -\Delta G/RT$ decreases with the number n of EO units in the hydrophilic part, as it is predicted by the theory. The enthalpy change $-\Delta H/RT$ behaves with varying of n in a similar way, while $\Delta S/R$, decreases with increasing n .

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