Liquid adsorption chromatography of polyethers
Theory and experiment

Bernd Trathnigg[a],*, Manfred Kollroser[a], Alexei Gorbunov[b], Alexander Skvortsov[c]

[a]*Institute of Organic Chemistry, Karl-Franzens University, Heinrichstrasse 28, 8010 Graz, Austria*
[b]*Institute for Highly Pure Biopreparations, Pudozhskaya 7, 197110 St. Petersburg, Russia*
[c]*Chemical-Pharmaceutical Institute, Prof. Popova 14, 197376 St. Petersburg, Russia*

Abstract

The chromatographic behavior of low-molecular-mass poly(ethylene glycol) (PEG), and of its mono- and dimethyl ethers (PEG-MME and PEG-DME, respectively) has been studied in the isocratic mode of reversed-phase liquid adsorption chromatography (RP-LAC) on C_{18}-modified silica (ODS2) column packings with pore diameters of 8 nm and 30 nm, using methanol–water of different compositions as mobile phase. For all three types of oligomers completely resolved chromatograms were obtained, in which all peaks could be identified. Precise and detailed data on the molar mass dependence of distribution coefficients resulted from these experiments. The experimental data were interpreted according to simple molecular statistical theory based on the model of a rigid-rod molecule, which is capable of being adsorbed inside the homogeneous layers near the pore walls. This approach allowed us to determine the free energies of transfer of the repeating unit (oxyethylene group) and of the two types of the end groups (methoxy and hydroxy groups) from a solution (in mixed eluents of different composition) into a bonded C_{18} phase. In addition, the effective thickness of the bonded layer was estimated as well as the critical point of adsorption for polyoxyethylene, which is of importance for separation of macromolecules by using the critical-condition mode of liquid chromatography.

Keywords: Adsorption liquid chromatography; Theromodynamic parameters; Retention mechanisms; Polyethers; Poly-(ethylene glycol)s

1. Introduction

Low-molecular-mass polyethers, such as poly-(ethylene glycol)s (PEGs) and their derivatives, are in widespread use as surfactants and wetting agents, as solubilizers in enhanced oil recovery and as important ingredients in the food and perfumery industries [1–3]. Polyethers are also extensively used in pharmaceutical and in biomedical technologies, playing the role of emulsifiers and of solubility

enhancers [4–8]. PEGs and their derivatives serve as stationary phases for gas chromatography and as reagents in the synthesis of semi-permeable materials [5].

Physical, chemical, and technological properties of polyethers depend substantially on molecular mass and upon the presence of specific end groups in polyether macromolecules, hence there is a strong need for reliable methods, which allow an accurate characterization of these important products.

While size-exclusion chromatography (SEC) is well established in the analysis of high polymers,

*Corresponding author.

liquid adsorption chromatography (LAC) using hydrocarbon-coated stationary phases seems now to be the most feasible method to analyse the molecular mass distribution (MMD) of low-molecular-mass polyether samples.

As has been demonstrated recently [9–11], this technique can yield chromatograms with completely resolved peaks for all individual oligomeric homologues in polyether samples of molecular masses up to several thousands.

It must be mentioned, that good results in separation of polyethers and of other similar compounds can only be achieved if the experimental conditions are selected very carefully: in particular, the combination of stationary and mobile phases as well as the operating temperature have to be chosen in a proper way to provide optimal chromatographic mode.

This optimization of chromatographic conditions would be made much easier by a deeper understanding of the chromatographic process in LAC of polymers and oligomers. Hence the objective of this paper was to establish an adequate theory, which describes the mechanisms involved in the adsorption liquid chromatography of oligomers.

For this purpose, we have analyzed PEGs and their mono- and dimethyl ethers (PEG-MME and PEG-DME, respectively), by LAC on three porous octadecyl bonded chromatographic packings of different pore diameters in methanol–water of different compositions as mobile phase. The data thus obtained were examined from the standpoint of a statistical molecular theory of chromatography, using a simple rodlike model for polyether molecules and a homogeneous adsorbing layer model for bonded C_{18} phase.

As a result of this comparison between theory and experiment, three important thermodynamic parameters could be obtained, namely the free energies of adsorption of repeating unit (the oxyethylene group) and the terminal methoxy and hydroxyl groups of polyether molecules.

2. Experimental

For these investigations, three different C_{18} columns were used, which were purchased from Phase Separations Ltd. (Deeside, Clywd, UK): (a) Spherisorb S5ODS2 (5 μm, 8 nm, 250×4.6 mm); (b) Spherisorb S3ODS2 (3 μm, 8 nm, 100×4.6 mm); and (c) Spherisorb S5XC18 (5 μm, 30 nm, 250×4.6 mm).

Methanol–water mixtures of different compositions were used as mobile phases, and were mixed by mass and degassed by vacuum. Both solvents were HPLC grade (ChromAR HPLC, Promochem, Wesel, Germany). The composition of mobile phase was controlled by density measurement using a density meter DMA 60 and a density measuring cell DMA 602M, both from A.Paar (Graz, Austria).

All chromatograms were run at a flow-rate of 0.5 ml/min, which was maintained by a JASCO 880 PU HPLC pump (Japan Spectrosopic Co., Tokyo, Japan). Samples were injected using an injection valve Rheodyne 7125 equipped with a 50-μl sample loop (Rheodyne, Cotati, CA, USA).

All measurements were performed with a density detection system DDS 70 (commercially available from Chromtech, Graz, Austria). The density detector was combined in series with a Bischoff 8110 refractive index (RI) detector (Bischoff, Leonberg, Germany).

Data acquisition and processing was performed on a MS-DOS computer using the software package CHROMA, which has been developed for the DDS 70.

The samples to be analyzed were purchased from Fluka (Buchs, Switzerland). Peaks were identified by spiking with monodisperse oligomers, such as tri- to hexa(ethylene glycol), tri- or tetra(ethylene glycol) mono- or dimethyl ether, which are commercially available. For higher oligomers, they were obtained by semipreparative LAC, as described previously [9], but on a 250×10 mm column packed with S5ODS2 at 2.0 ml/min, with subsequent analysis of the fractions by SEC on a set of 4 Phenogel columns (Phenomenex, Torrance, CA, USA), (2×500 Å+2× 100 Å, 5 μm, 30 cm each) in chloroform as mobile phase at a flow-rate of 1.0 ml/min.

The pore volume of the columns was determined from the SEC calibration in tetrahydrofuran using polystyrene standards from Polymer Labs. (Church Stretton, UK). These data were also used to determine the pore sizes by using the SEC-porosimetry method [12]. The average pore sizes obtained by

Table 1
Pore volume of columns and pore diameters of adsorbents used in these investigations, as obtained from porosimetry and data by the distributor

Column			Void volume V_0 (ml)	Pore volume V_p (ml)	Average pore diameter (nm)	
No.	Packing	Length (mm)			Specification	Porosimetry
a	S5ODS2	250	2.40	0.86	8	8.0
b	S3ODS2	100	1.04	0.354	8	6.8
c	S5XC18	250	3.39	2.50	30	26.5

porosimetry agreed quite well with the data provided by the distributor, as can be seen from Table 1.

3. Results and discussion

As has been shown previously [9], PEGs and their derivatives can be separated very well by isocratic reversed-phase LAC in methanol–water.

Fig. 1 shows a comparison of two typical chromatograms of PEG 600 and PEG-mono-methylether 550 (MME 550), which were obtained on a 250×4.6 mm column packed with S5XC18 (5 μm) in methanol–water (30:70, w/w) as mobile phase (for both chromatograms, only the RI trace is shown in this figure). As can be seen, the resolution is very good, and the elution volumes of corresponding oligomers (with the same number of EO units) are quite similar.

From several series of such chromatograms, which were obtained for different samples of PEG and their mono- and dimethyl ethers in different mobile phase compositions, we have plotted the elution volumes as a function of the number of EO units in each oligomer.

Fig. 2 shows the elution volumes of PEG, PEG-MME and PEG-DME series, as obtained on the S3ODS2 column (3 μm, 8 nm, 100 mm) in mixed methanol–water eluents with a different content of methanol.

The open symbols in Fig. 2a represent analogous data obtained in a previous study [9] for the same substances in the same mobile phases, but on the S5ODS2 column (5 μm, 8 nm, 250 mm).

It is clear, that the elution volumes V_e obtained on columns of different length or diameter must be different. In order to make a comparison of different columns possible, one may replace the elution vol-
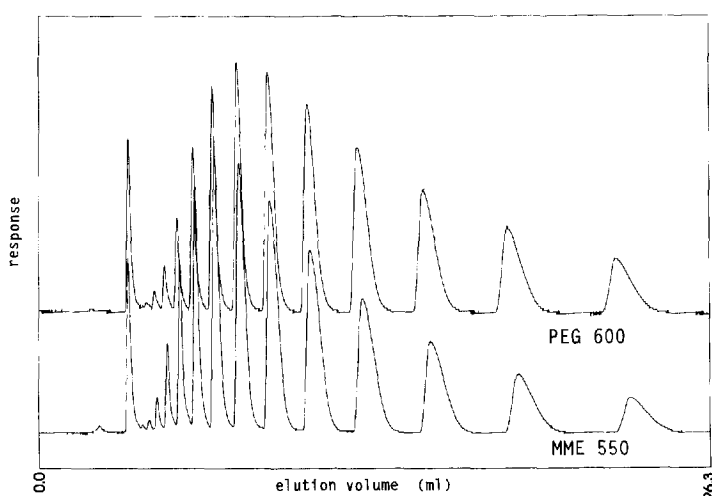

Fig. 1. Comparison of two chromatograms of PEG 600 and PEG-MME 550, as obtained on S5XC18 in methanol–water (30:70, w/w) with RI detection.
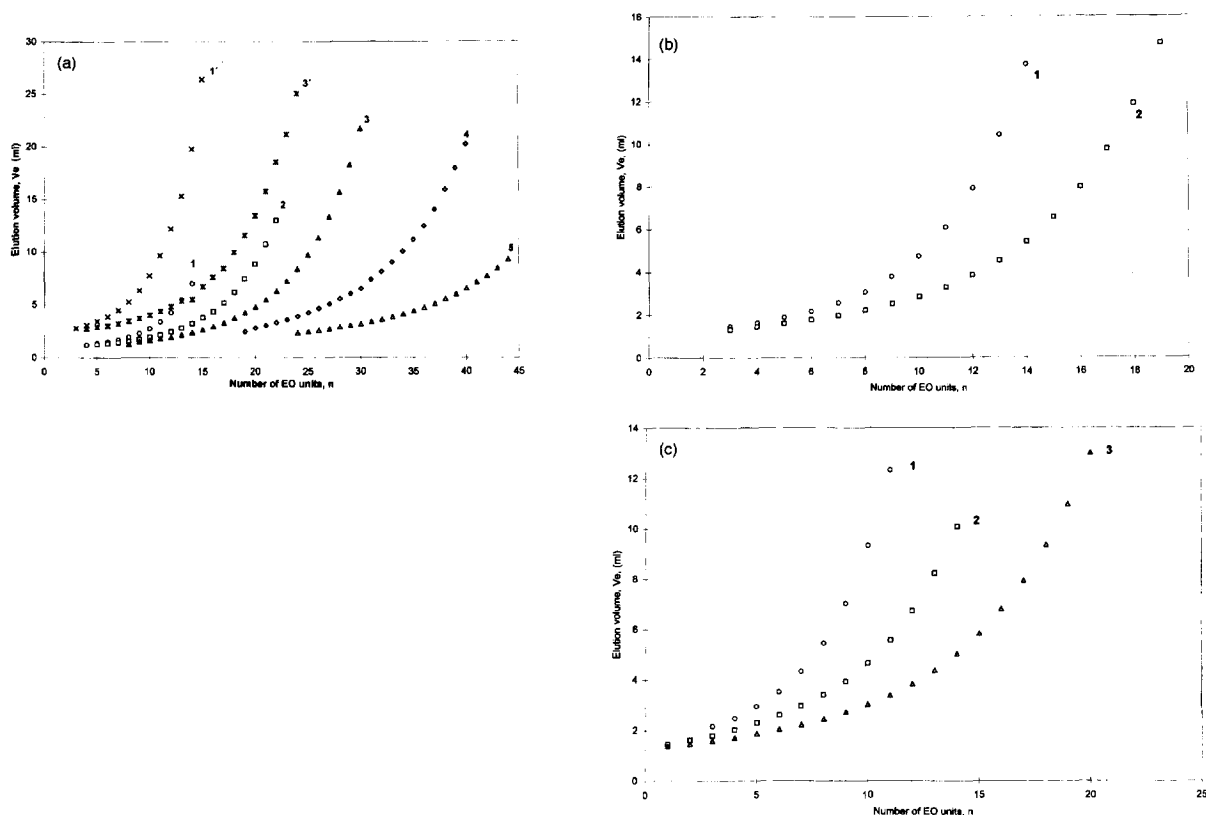
Fig. 2. (a) V_e vs. n plots for LAC of PEG molecules in methanol–water eluents. Percentage (w/w) of methanol in mixed eluent: 30 (1,1'), 35 (2), 40 (3,3'), 45 (4) and 50 (5). 1',3': S5ODS2, 250 mm; 1–5 (open symbols): S3ODS2, 100 mm. (b) V_e vs. n plots for PEG-MME molecules at 30 (1) and 35 (2)% (w/w) of MeOH in the mixed methanol–water eluent on S3ODS2 100 mm. (c) V_e vs. n plots for PEG-DME molecules at 30 (1), 35 (2) and 40 (3)% (w/w) of MeOH in the mixed methanol–water eluent on S3ODS2, 100 mm.

ume V_e by parameters, which do not depend on column dimensions [13], such as the capacity factor k':

$$k' = (V_e - V_0)/V_0 \qquad (1)$$

or better, the distribution coefficients K

$$K = (V_e - V_i)/V_p \qquad (2)$$

wherein V_i is the interstitial volume (the volume between the particles of the stationary phase, the so-called "outer volume" in SEC, which corresponds to the exclusion limit), V_p is the pore volume and V_0 is the so-called void volume (typically the elution volume of the solvent peak):

$$V_0 = V_i + V_p \qquad (3)$$

The values of the characteristic volumes V_0 and V_p

for the columns used in these investigations are given in Table 1.

In Fig. 3, the K values obtained with these two columns are plotted versus the degree of polymerization n of the polyether molecules: as can be seen, there is practically no difference between the normalized data obtained now on the 100 mm column packed with 3 μm particles (S3ODS2), and those measured previously [9] using the 250 mm column packed with 5 μm particles (S5ODS2).

This means, that for all practical purposes one can consider the chemical properties of the materials of these two ODS2 column packings as identical, which makes it possible to pool the new and previous data, provided the normalized chromatographic parameter (the distribution coefficient, K) is used in the course of all subsequent considerations.
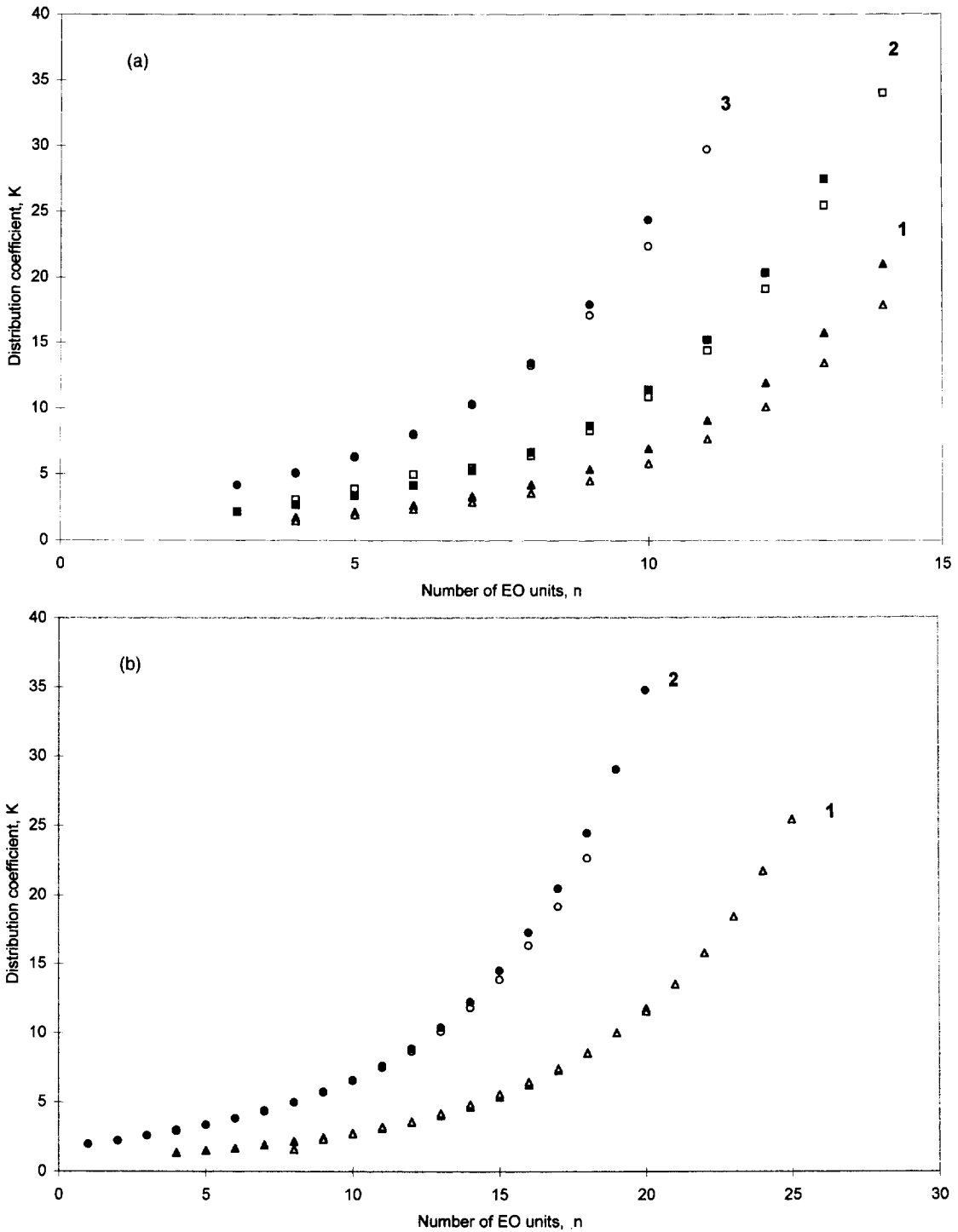
Fig. 3. (a) Distribution coefficient, K, vs. n for PEG (1), PEG-MME (2) and DME-PEG (3) at 30% (w/w) of MeOH in methanol–water eluent. Filled symbols: S3ODS2 (100 mm); open symbols: S5ODS2 (250 mm). (b) K vs. n plots for PEG (1) and DME-PEG (2) at 40% (w/w) of MeOH in methanol–water eluent. Filled symbols: S3ODS2 (100 mm), open symbols: S5ODS2 (250 mm).

3.1. Theoretical considerations

It is well known [13], that the distribution coefficient is an indicator of the ratio of concentrations of molecules inside pores and in a solution. Provided that concrete models for a macromolecule and for an adsorbent pore are specified, the K value can be calculated theoretically.

The theory of SEC of oligomers for the rigid-rod model of a molecule, and a slit-like model of a pore has been developed by Casassa in Ref. [14]. According to this theory, the distribution coefficient under SEC conditions K is given by

$$K = 1 - L/(2D) \qquad (4)$$

where L is the length of the molecule and D is a pore width.

In reversed-phase liquid adsorption chromatography (RP-LAC), the surface of a porous adsorbent is covered by-chemically bound-hydrocarbon chains, which typically consist of 4–18 carbon atoms. Such coatings may be modelled in the first approximation as adsorption active surface layers of the thickness δ, as is shown schematically in Fig. 4.

We shall suppose that in the course of their adsorption oligomeric molecules would sink completely in this adsorbing layer, and this would lead to the free energy gain, $-\Phi$ (all energy values in the following text are expressed in kT units).

Taking into account, that the terminal groups in macromolecules are always somewhat different from
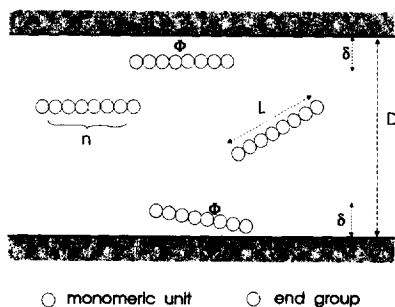

Fig. 4. The model of short polyether molecules inside an adsorbent pore: n = number of repeating EO-groups, L = contour length of a molecule, $\Phi = n\varphi + \varphi_1 + \varphi_2$ = free energy of adsorption interaction of a molecule, D = pore width, δ = thickness of adsorption active layer near a pore wall.

the repeating monomeric units, one can express Φ as a sum of three terms

$$\Phi = n\varphi + \varphi_1 + \varphi_2 \qquad (5)$$

where n is the number of repeating groups, φ is the repeating group adsorption interaction parameter, while φ_1 and φ_2 are those of the end groups.

As a simplest model of an oligomeric molecule we have chosen that of a rigid rod consisting of n repeating elements and two terminal units, all having the same size l_0, as is shown in Fig. 4. Hereby we assume equal sizes for the repeating chain units and for the terminal ones. Such a rigid-rod model can satisfactory describe the properties of short flexible chain macromolecules with contour lengths of order of tens Angströms.

The model under consideration has been developed in Ref. [15] in order to describe the features of LAC of oligomers. This model was also applied in Ref. [16] to study the hydrophobicity of porous materials by using LAC data obtained for homologous series of aliphatic alcohols.

According to Ref. [15], the following formula has been obtained for the distribution coefficient, K:

$$K = 1 - L/(2D) + \delta^2/(DL)[\exp(-\Phi) - 1] \qquad (6)$$

The first term in the right side of Eq. (6) is the same as in Eq. (4). The other term accounts for the free energy gain due to adsorption interactions of a molecule with layers bonded onto pore walls.

Thus, according to Eq. (6), the distribution coefficient of a rodlike macromolecule is expressed as a function of several parameters: of the contour length of a molecule, $L = (n+2) l_0$, of the pore width, D, and also of the set of adsorption free energy parameters for the repeating chain units and for terminal groups of all types.

PEG molecules have two terminal hydroxyl groups, while in PEG-MME molecules one terminal group is substituted by the methoxy group, and PEG-DME molecules have methoxy groups at both chain ends. As a first approximation we can assume, that the two terminal methoxy groups of the PEG dimethyl ethers have equal adsorption free energy parameter, φ_m, and similarly, that both of the hydroxyl groups of the PEG molecule have the same free energy parameter φ_h. We may thus write for the individual polymer homologous series:

PEG: $\quad \varphi_1 = \varphi_2 = \varphi_h \quad$ and $\quad \Phi_{PEG} = n\varphi + 2\varphi_h$

PEG – MME: $\quad \varphi_1 = \varphi_h, \varphi_2 = \varphi_m \quad$ and $\quad \Phi_{MME} = n\varphi + \varphi_h + \varphi_m$ $\qquad$ (7)

PEG – DME: $\quad \varphi_1 = \varphi_2 = \varphi_m \quad$ and $\quad \Phi_{DME} = n\varphi + 2\varphi_m$

3.2. Comparison of the experimental data with theory

Dependencies of K on n for PEG, PEG-MME and PEG-DME series, obtained with the use of a 100 mm column (S3ODS2) at 35% (w/w) of methanol in the mobile phase are shown in Fig. 5a.

As follows from Eq. (6), the distribution coefficient K of a given oligomer is determined by its contour length L, the (average) diameter D of the pores in the column packing, the thickness δ of the hydrocarbon layer and the free energy parameter φ, which is related to the number n of EO units in the molecule according to Eq. (7), one may express the $K(n)$ dependencies for each polymer homologous series.

Among the parameters in these equations, the value of pore width D is known or can be determined by porosimetry, and the contour length L of a molecule can be calculated using the value of $l_0 = 0.37$ nm for the EO repeating unit.

Hence there still remain several parameters, namely, φ, φ_h, φ_m and δ, which must be fitted to the experimental data in order to evaluate the ability of this theory to describe the $K(n)$ dependencies for the individual polymer homologous series. Doing so, we have found the following values for the parameters in Eqs. (6,7): $\varphi = -0.31$; $\varphi_h = 0.41$; $\varphi_m = -0.21$; $\delta = 2.8$ nm.

Using these values, the theoretically calculated curves were drawn in Fig. 5a together with the experimental data points. As can be seen, a proper fitting of four adjustable parameters yields a satisfactory theoretical description of the three experimental data sets, at least in the lower-molecular-mass region.

Once these initially unknown parameters have been determined from the comparison of the experimental data with the theory, it is possible to draw Φ vs. n plots for the systems under investigation.

According to the above theory the free energy change, $-\Phi$, has the following form:

$$-\Phi = \ln[1 + L^2/(2\delta^2) + (K-1)LD/\delta^2] \qquad (8)$$

The Φ vs. n plots for the data of Fig. 5a are presented in Fig. 5b. As was expected, the Φ vs. n plots for all three polyether series give straight lines with the same slope, which represents the free energy of adsorption of the repeating EO group, φ, but with different intercept, which is due to the influence of the end groups.

The distances between the neighbouring lines, which are determined by the difference in the adsorption free energy of methoxy and hydroxyl groups, also proved to be approximately the same. As can be seen in Fig. 5a,b, the agreement between theory and experiment is quite satisfactory in the low-molecular-mass range, corresponding to $n < 10$.

The chromatographic data obtained in Ref. [9] with the use of a 250 mm column (S5ODS2) at 30, and at 50% (w/w) of methanol are shown in Fig. 6 in the $-\Phi$ vs. n coordinates (only a part of the chromatographic data corresponding to small n values are presented in this figure).

Figs. 5 and 6 demonstrate the ability of the above theory to describe quantitatively the LAC behaviour of low-molecular-mass polyethers.

The same data treatment procedure was applied to all the experimental data on polyethers, both obtained now, and in Ref. [9]. The parameters obtained from these calculations (φ, φ_h, φ_m and δ) are presented in Table 2.

3.3. Influence of pore size

One more question concerned the influence of pore size on the chromatographic behaviour of polymers under conditions of adsorption chromatography. Hence we have compared the experimental data for the similar ODS adsorbents differing in their pore diameters. Fig. 7a shows $K(n)$ dependencies for PEG, PEG-MME and PEG-DME molecules at 30% (w/w) of MeOH in the methanol–water eluent, obtained on two adsorbents of different pore diameters (8 nm and 30 nm).

The same experimental data in the Φ vs. n coordinates are shown in Fig. 7b. As follows from Fig. 7a, all three types of oligomeric molecules have greater values of the distribution coefficient, K, when being chromatographed on the adsorbent with narrow pores. At the same time, in accordance with the Eq. (5), the free energy change due to the adsorption, Φ,
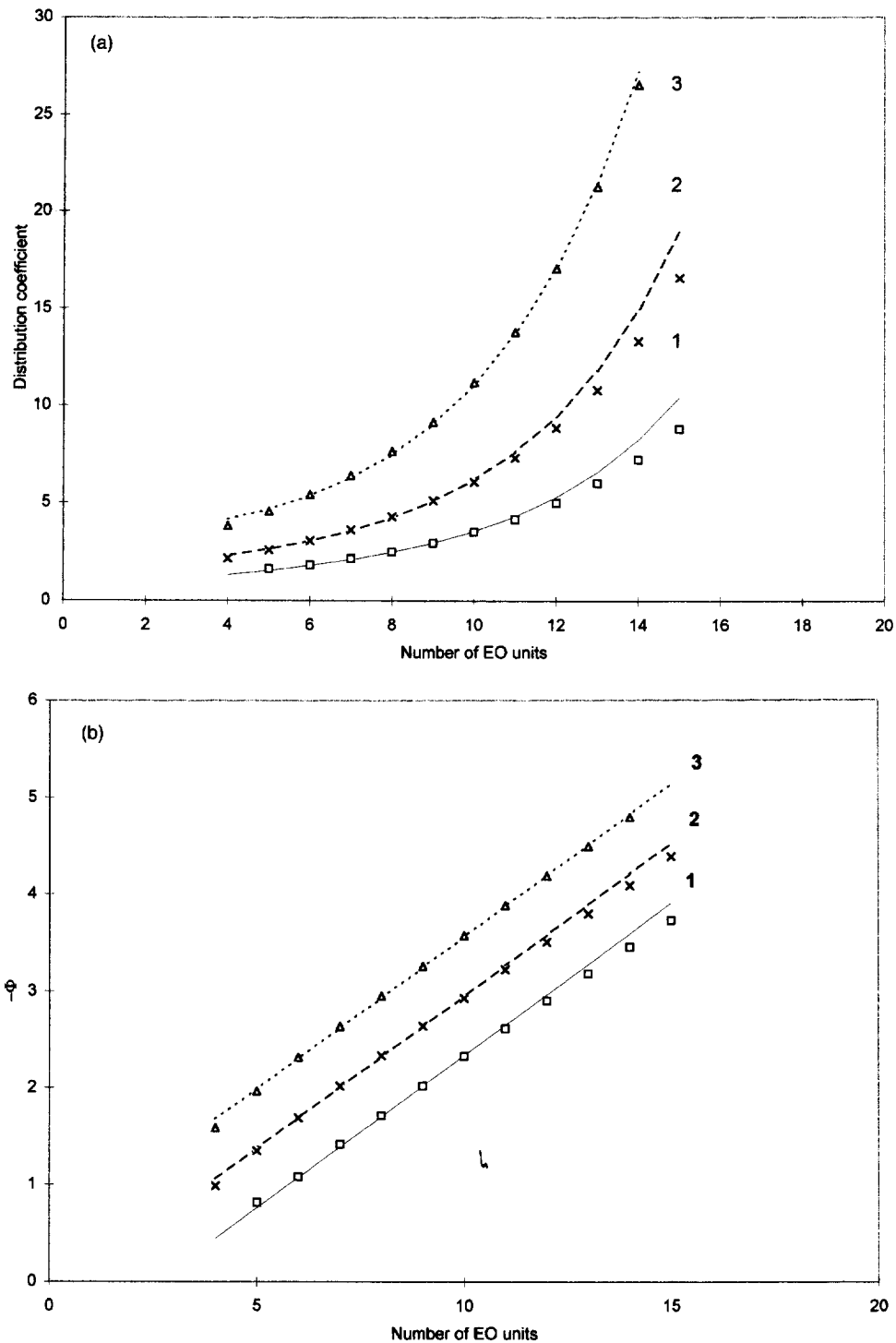
Fig. 5. (a) Distribution coefficient, K, vs. n for PEG (1), PEG-MME (2) and PEG-DME (3) at 35% (w/w) of MeOH in methanol–water eluent on S3ODS2 (100 mm). The lines represent the curves calculated by Eqs. (6,7). (b) Dependence of the free energy gain, $-\Phi$, due to adsorption of PEG (1), PEG-MME (2) and PEG-DME (3) molecules upon the degree of polymerisation, n, at 35% (w/w) of MeOH in methanol–water eluent on S3ODS2 (100 mm). The lines represent the curves calculated by Eq. (8).
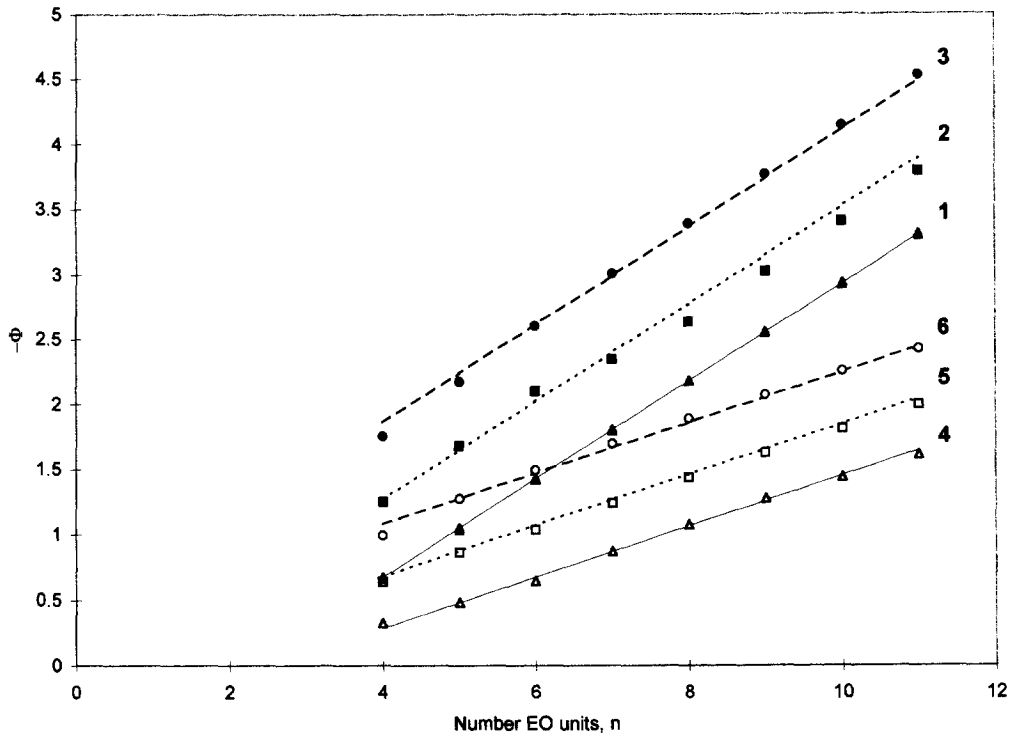
Fig. 6. $-\Phi$ vs. n plots for short macromolecules of polyethers at 30 (1–3) and 50 (4–6)% (w/w) of methanol in methanol–water eluent. PEG (1,4); PEG-MME (2,5); PEG-DME (3,6). Stationary phase: S5ODS2 Spherisorb, 250 mm column. The lines represent the curves calculated by Eq. (8).

does not depend on pore width. As a matter of fact, the data presented in Fig. 7b show, that there is really no dependence of the Φ parameter upon the pore diameter for all three oligomer series.

3.4. Effect of the mobile phase composition on the thermodynamic parameters of polyether molecules

The adsorption interaction parameter of a given

Table 2
Thermodynamic and structural parameters obtained from the data on adsorption chromatography of polyethers at various methanol content in mixed methanol–water eluent for three ODS packings of different pore diameter

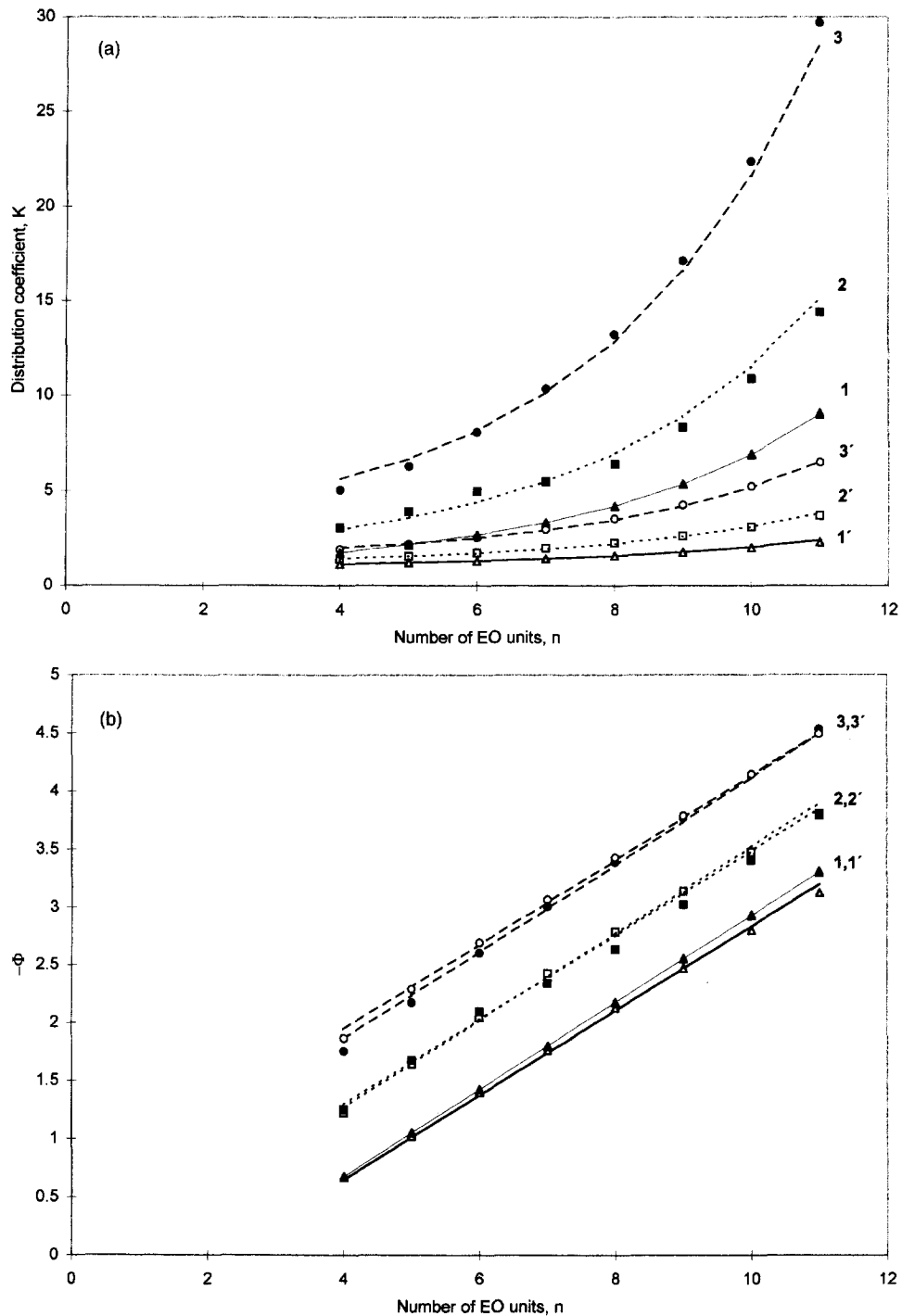| Column	MeOH (%, w/w)	EO Group free energy φ (kT units)	Hydroxy group free energy φ_h (kT units)	Methoxy group free energy φ_m (kT units)	Layer thickness δ (nm)
a	30	-0.38	0.41	-0.18	3.2
a	40	-0.27	0.33	-0.15	3.0
a	50	-0.19	0.24	-0.15	3.0
a	55	-0.17	0.24	-0.12	2.9
b	30	-0.41	0.48	-0.22	2.6
b	35	-0.31	0.41	-0.21	2.8
b	40	-0.27	0.32	-0.14	2.9
c	30	-0.36	0.40	-0.25	2.8

Fig. 7. (a) Distribution coefficient, K, vs. n for PEG (1,1'), PEG-MME (2,2') and PEG-DME (3,3') at 30% (w/w) of MeOH in methanol–water eluent. Stationary phases: S5ODS2, 8 nm pore diameter, 250 mm column (1–3) and S5XC18, 30 nm pore diameter, 250 mm column (1'–3'). The lines represent the curves calculated by Eqs. (6,7). (b) The same experimental systems as in (a), but data are plotted in $-\Phi$ vs. n coordinates. The lines represent the curves calculated by Eq. (7).

oligomer depends on the composition of the mobile phase is a trivial point. The question is, however, how the mobile phase composition will influence the individual interaction parameters of the repeating unit and of the end groups.

Fig. 8 presents the parameters of adsorption interaction of the repeating unit and of terminal groups, φ, φ_h and φ_m as a function of methanol

content in the methanol–water mixed eluent. As can be seen, the repeating group free energy, φ is always negative, which means, that the interactions of EO group with C_{18} bonded chains are thermodynamically more advantageous than those with solvent molecules. One can see that the $-\varphi$ parameter increases approximately linearly with decreasing methanol percentage.
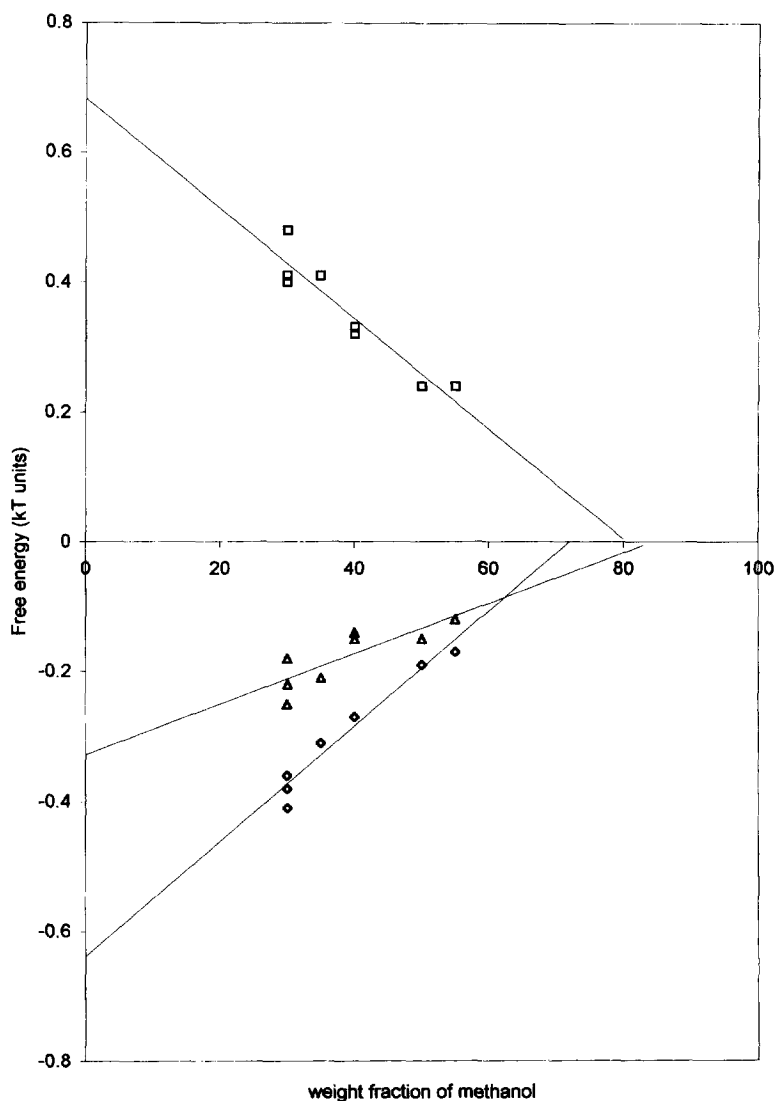
Fig. 8. Free energy of adsorption of EO group ($\diamondsuit$), hydroxyl group ($\square$) and methoxy group ($\triangle$) as a function of methanol percentage in methanol–water eluent.

A straight-line extrapolation of this tendency to pure water gives us the value of about 0.65 kT units for the free energy gain due to the EO group transfer from the pure water into the C_{18} bonded phase network. On the other hand, the φ parameter tends to zero at approximately 73% of methanol. This value may serve as an estimate of critical methanol–water eluent composition, at which the exponential dependence of K on n vanishes. As follows from the theory, this critical composition value is associated with the chemical properties of oligomer repeating groups, of mobile and of stationary phases and critical composition values neither depend on the kind of the end groups, nor on the pore width.

Actually, the critical composition for the columns used in these investigations is somewhat higher (approximately 80% of methanol). This deviation can be explained by the fact, that the values of φ scatter too much for a highly accurate determination of the critical composition from the slope of the regression line.

The methoxy-group free energy, φ_m, is also negative, depending upon mobile phase composition in a similar way. The $-\varphi_m$ value extrapolated to pure water is approximately one-half of the $-\varphi$ value. At approximately 85% of methanol φ_m parameters reach a zero-value level.

The hydroxyl group free energy, φ_h is positive at any composition of a mobile phase. We estimated a free energy loss value of about 0.7 kT for pure water conditions, and the value of approximately 80% of methanol, at which the φ_h parameter equals zero.

As follows from the Fig. 8, all three adsorption interaction parameters tend to zero at approximately the same interval of methanol percentage. Hence one can not expect a good critical-condition chromatographic separation of polyether molecules according to the number and sort of end-groups like hydroxy and methoxy in this adsorbent-mobile phase system. As has been shown previously [19,20], a good separation according to longer alkyl end groups (C_8 to C_{18}) under critical conditions for polyoxyethylene is achieved in methanol–water mobile phases.

The parameter characterizing the thickness of bonded layer was also estimated from the chromatographic data as having the value of about 3 nm (see Table 2). This is, of course, a little bit more than the

value of about 2 nm estimated from the geometry of the C_{18} chain, but the order of magnitude for this value seems us to be quite reasonable.

4. Conclusions

A rigid-rod model applied to macromolecules, such as polyethylene glycols was used in this theory. However, polyethers are known to be very flexible macromolecules. The Kuhn segment of the polyethylene oxide chain has a value of about 0.6 nm, and internal rotations around C–O bonds are only slightly restricted. Therefore the effective stiff element in these molecules consists of only two or three repeating EO groups. Nevertheless, the rigid-rod model proves capable of describing molecules consisting of up to ten monomer units, more or less pronounced deviations from the theory being observed for the longer macromolecules.

The other assumption was made about the full immersion of molecules into the C_{18} bonded layer. This assumption, of course, is valid at large energies of adsorption. However under the conditions of weak adsorption, at about the critical content of methanol in the mixed eluent, one can expect substantial deviation of experimental data from the theory. This effect is noticeable in Fig. 5.

In order to get a more correct description of chromatographic behavior under the conditions of weak adsorption, it is necessary to account for molecular conformations, which are partially immersed into the layer.

We would like to point out, that the data treatment scheme under consideration permits the determination of the φ parameter values with more accuracy than the values of φ_h, and φ_m and that our values obtained for these parameters are model-dependent. We think, however, that the main features of Fig. 8 are quite reasonable in a qualitative as well as quantitative sense.

In conclusion let us compare our data treatment scheme with the other method commonly used in liquid chromatography [13]. The parameter which is often exploited to describe the LAC data is known as capacity factor k', relating to the distribution coeffi-

cient, K, by the equation, which follows from Eqs. (1,2):

$$k' = (K - 1)V_p/V_0 \qquad (9)$$

The ln k' is usually treated as the free energy change resulting from the transition of a molecule from the eluent volume into the stationary phase [17,18]. It is obvious that the ln k' parameter has not the same meaning, as our Φ parameter. Besides Φ, the ln k' parameter includes an entropy term accounting for the various positions and orientations of a molecule within the adsorption-active layer, i.e., the C_{18} chains of the bonded phase layer. This additional entropy term depends on the degree of molecular freedom restriction within the C_{18} bonded phase layer.

Assuming that this entropy term does not depend on the chain length of the solute molecules and upon the mobile phase composition, one could expect the parallel lines in the ln k' vs. n plots for the oligomers differing only in their end groups. An example of such plots is given in Fig. 9 for PEG, PEG-MME

and PEG-DME at 50% of methanol. The same data in the Φ vs. n coordinates are presented in Fig. 5b and Fig. 6 (curves 4–6).

As can be seen, experimental data plotted in ln k' vs. n coordinates fit quite well to straight lines, but – unlike Fig. 6 (curves 4–6) – these lines are not parallel, which indicates, that the interpretation of ln k' parameter in terms of the free energy change per molecule is only a rough approximation.
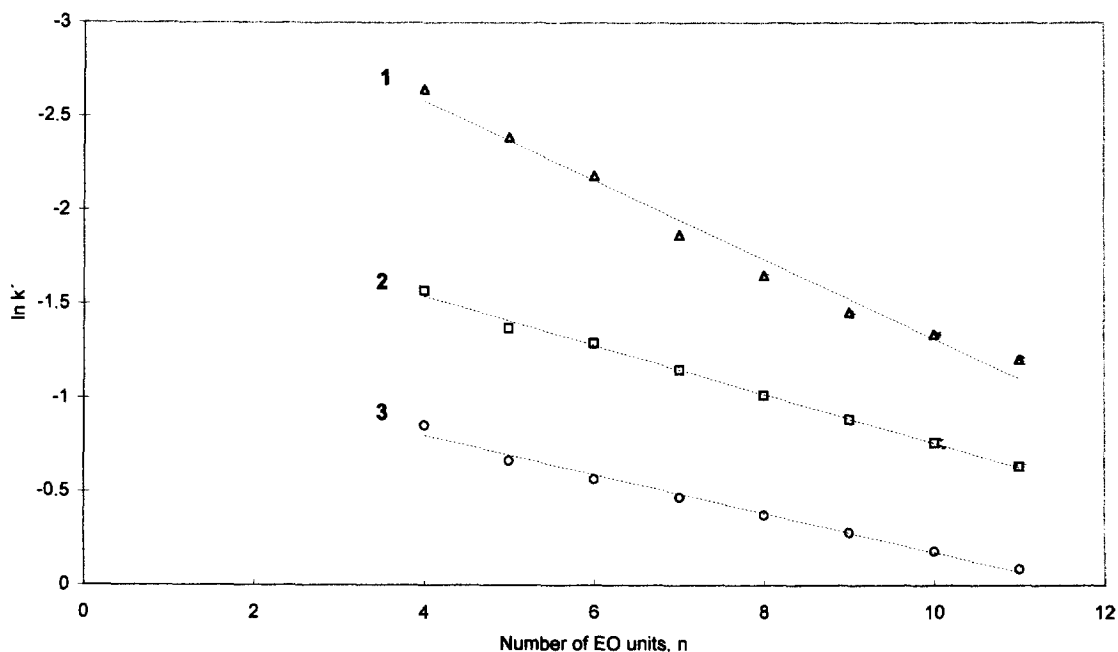
Acknowledgments

Fig. 9. The ln k' vs. n plots for PEG (1), PEG-MME (2) and PEG-DME (3) at 50 (w/w) of MeOH in methanol–water eluent on S5ODS2 (250 mm). The lines have been calculated by linear regression.

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