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Theory of liquid chromatography of mono- and difunctional macromolecules
I. Studies in the critical interaction mode

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Abstract

The theory of liquid chromatography of mono- and difunctional polymers based on the model of ideal polymer chain in wide slit-like pores is presented. Analytical equations describing chromatographic behavior of functional macromolecules in both adsorption, exclusion and critical modes are derived and compared with experiments. The focus of this experimental study was on the verification of the theory in chromatography at critical conditions. Chromatographic behavior of low molar mass end-functionalized polyethylene glycols was found to be in a very good qualitative and in a reasonable quantitative agreement with the theory.

Keywords: Critical interaction mode; Polymers; Polyethylene glycols; Retention models

1. Introduction

Macromolecules with functional end-groups represent an important class of synthetic polymers [1–4]. Since the properties of functional polymers depend strongly on the number and type of functional groups, the determination of the functionality-type distribution (FTD) is a very important part of the analysis of these polymers.

Liquid chromatography is nowadays one of the most popular methods of the analysis of FTD [5,6]. One special chromatography mode, namely liquid chromatography at critical conditions (LCCC), has proven to be especially effective in the analysis of functional polymers [5–7]. In this mode, the retention volume of non-functional polymer becomes independent of molar mass [8], and this offers the opportunity to separate polydisperse polymers with respect to their functionality [9]. The critical interaction point (CIP) can be achieved by adjusting mobile phase composition, temperature or pH (when aqueous eluents are used), etc. Critical conditions for many polymer–adsorbent–solvent systems have been found experimentally [5,6], and many LCCC analyses of functional polymers have been reported [10–16].

Much work has been done on the theory of liquid chromatography of functional polymers [9,12,17–19]. In most of these papers, the lattice model of polymer chain was used. Analytical solutions have

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been obtained only for the case of very long chains and narrow-pore adsorbents; more realistic situation of shorter chains and wide pores was studied numerically. Using the continuum model, Gorbunov and Skvortsov [18] have obtained equations for mono- and symmetrical difunctional polymers and wide pores, but only two special cases have been studied: where the interaction of the repeating chain units with the adsorbent was either absent or critical. Thus, there is still no unified analytical theory for mono- and difunctional polymers and wide pores at arbitrary interactions for both types of chain units. Such a theory describing all important chromatographic modes will be presented in this paper.

In the theoretical consideration, the existing theory for non-functional polymers [20–22] will serve as a starting point, which gives reference equations and guidelines to the new theory for functional polymers. The experimental part of the paper will focus on the behavior of functional macromolecules at the critical interaction point (CIP).

The LCCC retention of selected poly(oxyethylene)s with different functional groups on different stationary phases will be studied and the observed chromatographic behavior compared with theoretical prediction.

2. Theory

We shall consider macromolecules without specific end-groups, and those having specific groups at one or both ends. Of course, any real polymer molecule has end fragments which are chemically different from the repeating units in the middle part of the chain, so, generally speaking, every real polymer may by considered as a difunctional one. Since we are interested in the interaction of molecules with the chromatographic stationary phase, we will consider a molecule as having a functional end-group, if the interaction of this end group with the porous adsorbent is different from that of the repeating unit.

We shall take into account an arbitrary interaction for the repeating units; the interaction of the functional groups will be assumed different from that of the repeating unit. We shall also assume that the radius of gyration of macromolecules is much smaller than pore size—this is often the case in separations of functional oligomers, and this is just the case in our experimental study.

The elution volume of a species in the liquid chromatography is given by

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

where V_i denotes the interstitial volume (i.e. the volume of the solvent outside the particles of the packing), V_p is the entire pore volume, and, consequently, $V_0 = V_i + V_p$ is the void volume of the column. K is the distribution coefficient relevant to the partition function of a polymer chain within an in-pore space [20].

The theory for the distribution coefficient in liquid chromatography of non-functional polymers capable of being adsorbed on pore walls has been developed by Gorbunov and Skvortsov in Refs. [20–22] for a model of an ideal polymer chain and a slit-like pore. The theory was based on the diffusion-type boundary problem with the boundary conditions accounting for polymer–surface interaction. Using the exact solution for the Green function of this boundary problem, the total partition function of a chain within the pore space was constructed, and the exact formula for the distribution coefficient was derived. According to Refs. [20–22], the distribution coefficient, K, is a function of three parameters: radius of gyration of polymer chain, R, pore width, $2d$, and parameter of adsorption interaction, c.

The adsorption interaction parameter c has been introduced by de Gennes in Ref. [23], and was used in many continuum model-based theories [20–22,24–26] describing the behavior of macromolecules at interfaces and in porous media. The parameter c has a meaning of the inverse correlation length of adsorption, which can serve as characteristics of the structure of a macromolecule near the surface of an adsorbent. Positive values of c correspond to the regime of adsorption, $c = 0$ corresponds to the critical conditions when the entropy losses of a macromolecule in a pore are precisely compensated by an energy gain due to the adsorption, and negative c values are characteristic of the situation, where adsorption interactions are small or absent. According to Refs. [27,28], the parameter of adsorption interaction, c, is directly related to the adsorption

energy parameter, ε, which was commonly used in the lattice model-based theories [29,30] of polymer adsorption.

In the vicinity of the critical point the adsorption interaction parameter c is proportional to the deviation of ε from the critical value, ε_{cr}, $c \sim (\varepsilon_{cr} - \varepsilon)$.

In the case where $R < d$, the formula for the distribution coefficient of non-functional macromolecules has the following form [20,26]:

$$K \approx 1 - \frac{2}{\sqrt{\pi}} \cdot g + \frac{g}{\Gamma}[1 - Y(\Gamma)] \quad (2)$$

where $g = \frac{R}{d}$, $\Gamma = -cR$, and the function $Y(\Gamma) = \exp(\Gamma^2) \cdot erfc(\Gamma)$ is related to the well-known complementary error function $erfc(\Gamma)$. Asymptotic forms of the function Y are also known [20,28].

Eq. (2) has been analyzed in Refs. [21,22,26], and simpler asymptotic equations describing various chromatographic modes have been obtained. In the particular case of no adsorption interaction, $\Gamma = -cR \gg 1$, which corresponds to size-exclusion chromatography, Eq. (2), of course, reduces to the well-known wide-pore approximation for the distribution coefficient of a macromolecule in size-exclusion chromatography [31,32]:

$$K_{SEC} \approx 1 - \frac{2}{\sqrt{\pi}} \cdot \frac{R}{d} \quad (3)$$

On the other hand, in the case of attraction of chain units to the pore walls, $-\Gamma \gg 1$ (this case corresponds to adsorption chromatography mode) Eq. (2) can be approximated by

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

In the point of critical interaction ($c = 0$), the general Eq. (2) takes the simple form:

$$K = 1 \quad (5)$$

In this case, all non-functional polymer molecules are eluted at the void volume ($V_e = V_i + V_p$), regardless of their length. Within the framework of an ideal-chain model, Eq. (5) is valid for macromolecules of any chain length and for pores of any size and form.

The unified theory of chromatography of non-functional polymers was verified experimentally in Refs. [33,34]. In particular, the behavior of non-functional macromolecules in adsorption chromatography has been studied in detail both theoretically and experimentally in Ref. [33]. In that study, Eq. (4) was used to give a meaning to the slope and intercept of the Martin plots (log k' vs. M).

Now we proceed with the similar unified theory for macromolecules with end-groups. This theory will be based again on the model of an ideal chain in a slit-like pore (Fig. 1). It will be developed in the same spirit and use the same basic solution of the diffusion boundary problem as the theory [20,26] for non-functional polymers. In order to construct the total partition functions for end-functional macromolecules, is necessary to take the chain conformations into account, with special emphasis on contacts of one and both end-groups with the pore walls (Fig. 1). Generally, the latter type of conformations may be realized by either ''loops'', starting and finishing at the same pore wall, or ''bridges'', connecting both walls. However in wide pores, only the loops are of importance (the bridges are impossible, if the pore width $2d$ exceeds the chain length, and very unfavorable entropically, if $d > R$).

Using the sub-partition functions for a chain with one and two ends at the pore walls, obtained from the exact Green function of the problem [20,26], we derived the following equations for the distribution

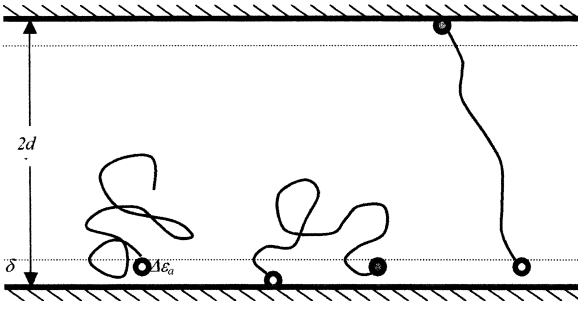

Fig. 1. Model for macromolecules with functional end groups interacting with the walls of the slit-like pore of width $2d$. The monofunctional molecule wins additional energy $-\Delta\varepsilon_a$ when its end-group a comes into the thin wall-adjacent layer of thickness δ. Difunctionals may have different end-groups (and hence different interaction parameters). Of importance are chain conformations with one and both ends at the pore walls—the latter ones can be either of loop- or of bridge-type.

coefficients of mono- and difunctional macromolecules:

$$K^{(a)} \approx K + q_a \cdot Y(\Gamma) \tag{6}$$

$$K^{(ab)} \approx K + (q_a + q_b) \cdot Y(\Gamma) + q_a \cdot q_b \cdot \frac{1 - \sqrt{\pi} \cdot \Gamma \cdot Y(\Gamma)}{\sqrt{\pi} \cdot g} \tag{7}$$

where K is the distribution coefficient of a non-functional polymer given by Eq. (2), and q_a is the effective interaction parameter for the end-group a, which is given by

$$q_a = \frac{\delta}{d}\left[\exp\left(-\frac{\Delta\varepsilon_a}{kT}\right) - 1\right] \tag{8}$$

In Eq. (8) a small length-dimensional parameter δ has a meaning of an effective radius of interaction (we assume δ being of order of a monomer unit size), while $\Delta\varepsilon_a$ accounts for the difference in the interaction free energy of a terminal chain fragment and the repeating unit. Positive values of q_a correspond to more attractive interaction for the end group a, negative q_a means more attraction for the repeating units, $q_a = 0$ if there is no difference in the interaction. The parameter q_b for the second end group has the same meaning and is defined in a similar way.

The second term of Eq. (6) as well as of Eq. (7) takes its origin in the chain conformations, having one end at the pore wall, while the last term of Eq. (7) comes from the loop structures (Fig. 1).

Eqs. (6) and (7) can be used for the detailed analysis of the chromatographic behavior of functional macromolecules at arbitrary interactions of repeating and terminal chain units with the pore walls. Additionally, a few simpler asymptotic expansions can be derived, which are useful for understanding the main features of behavior of functional macromolecules at different modes of chromatography.

Let us start with the case of weak interaction for the repeating units, $\Gamma \gg 1$, which corresponds to the size-exclusion chromatography mode of non-functional polymers. Some theoretical results for functional polymers in this mode have been obtained previously in Ref. [18].

Using the expansion for the function $Y(\Gamma) \approx \pi^{-1/2}\Gamma^{-1}$, one can recover the results of Ref. [18] and obtain a new equation for asymmetrical difunctionals. The results can be written in the form:

$$K^{(a)} \approx K_{\mathrm{SEC}} + \frac{(\delta/2)}{\sqrt{\pi}R} \cdot q_a \tag{9}$$

$$K^{(ab)} \approx K_{\mathrm{SEC}} + \frac{(\delta/2)}{\sqrt{\pi}R} \cdot (q_a + q_b) + \frac{(\delta/2)^2 d}{2\sqrt{\pi}R^3} \cdot q_a q_b \tag{10}$$

As follows from Eqs. (9) and (10), the molar-mass order of the retention for functional polymers is the same as in SEC of non-functional polymers. However, unlike the classical SEC, at which the distribution coefficient is always less than unity, the distribution coefficient of functional polymers can significantly exceed unity (taking values which are characteristic of adsorption chromatography), if the interaction of end groups with the stationary phase is strongly attractive. Such exclusion-adsorption type of chromatography has been recently realized by Trathnigg et al. [35,36] in studies of fatty alcohol ethoxylates (FAE). In these studies FAE molecules were considered as diblock-copolymers with a non-adsorbing polydisperse EO-block and a short adsorbing alkyl block. The observed chromatographic behavior was similar to that predicted by the present theory for monofunctional polymers. A baseline separation of lower oligomers in polydisperse FAE samples was achieved using an isocratic exclusion-adsorption mode of chromatography, thus yielding the full molar-mass and functionality-type distributions for several samples of commercial surfactants [36,37].

Now let us turn to the case of strong adsorption interaction of repeating units, $-\Gamma = cR \gg 1$. This case corresponds to the adsorption chromatography mode. At $-\Gamma \gg 1$, the function $Y(\Gamma)$ reduces to $2\exp(\Gamma^2)$, and we obtain the following approximate formula for the distribution coefficient $K^{(f)}$ of both mono- ($f=1$) and symmetrical difunctional ($f=2$) macromolecules in the adsorption chromatography mode:

$$K^{(f)} \approx K_{\mathrm{SEC}} + \frac{2}{cd}(1 + q_a \cdot cd)^f \exp(c^2R^2) \tag{11}$$

For asymmetrical difunctionals, one can easily obtain:

$$K^{(ab)} \approx K_{\mathrm{SEC}} + \frac{2}{cd}(1 + q_a \cdot cd)(1 + q_b \cdot cd)\exp(c^2R^2) \quad (12)$$

The special case of q_a, $q_b = 0$ corresponds to non-functional polymer. In this special case, Eqs. (11) and (12) will, of course, reduce to Eq. (4).

The effect of the end-groups was studied experimentally in Ref. [33], and it was obtained that the Martin plots for macromolecules with zero, one and two end-groups give parallel straight lines, shifted by about the same distance. These observations are in a very good agreement with the present theory, and Eqs. (11) and (12) can be used to determine the end-group interaction parameters from the shifts in Martin plots for non-functional and functional polymers.

Our present experimental study is focused on the chromatography at critical conditions, corresponding to the specific case of $c = 0$ ($\Gamma = 0$). In this case, the function $Y(\Gamma)$ turns to unity, and Eqs. (6) and (7) take especially simple forms. For monofunctional molecules (with one end group *a*), the distribution coefficient $K^{(a)}$ reduces to

$$K^{(a)} \approx 1 + q_a \quad (13)$$

while for the distribution coefficient $K^{(aa)}$ of symmetrical difunctionals with groups *a* at both ends, one can derive easily from Eq. (7):

$$K^{(aa)} \approx 1 + 2q_a + q_a^2 \cdot \frac{d}{\sqrt{\pi} \cdot R} \quad (14)$$

Eqs. (13) and (14) have been obtained previously in Ref. [18].

In the more general case of asymmetrical difunctionals having different end-groups *a* and *b*, the distribution coefficient equals:

$$K^{(ab)} \approx 1 + q_a + q_b + q_a \cdot q_b \cdot \frac{d}{\sqrt{\pi} \cdot R} \quad (15)$$

As follows from Eqs. (13)–(15), in a plot of the distribution coefficient versus $1/R$, the interaction parameters of the end groups can be obtained from the intercept. Obviously, the slope should be equal to zero in monofunctionals. If both end groups of difunctionals are identical, the shift in the intercept should be twice as large. For asymmetric difunctionals, the slope of the $K^{(ab)}(1/R)$ plot should be positive, if interaction with the stationary phase of both terminal chain units is more attractive or both more repulsive that of the repeating units, and negative, if the interaction parameters for the end groups have the opposite sign (one end-unit is more repulsive, the other one is more attractive).

3. Experimental

These investigations were carried out using the density detection system DDS70 (CHROMTECH, Graz, Austria), which has been developed in our group. 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 thermostated box, which was maintained at 25.0 °C for all measurements. 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 an 50-μl loop. In most measurements, a Bischoff 8110 RI detector (Bischoff, Leonberg, Germany) was connected to the DDS 70 (unless mentioned otherwise).

In order to eliminate errors due to preferential solvation, samples eluting in or very close to the solvent peak (PEG, PEG-MME) were also analyzed with an ELSD (SEDEX 45, SEDERE, Alfortville, France) coupled to the density detector. In ELSD, the evaporator temperature was 30 °C, and the pressure of the carrier gas (nitrogen) was set to 1.0 bar.

Columns were connected to two column selection valves (Rheodyne 7060; Rheodyne, Cotati, CA, USA).

The following columns were used in these investigations: Spherisorb ODS2 (Phase Separations Ltd., Deeside, Clywd, UK) silica-based octadecyl phase, 250×4.6 mm, particle diameter: 5 μm, pore diameter: 8 nm); Spherisorb S5X C_{18} (Phase Separations Ltd., Deeside, Clywd, UK), silica-based octadecyl phase, 250×4.6 mm, particle diameter: 5 μm, pore diameter: 30 nm).

All solvents were HPLC grade. Acetone was

purchased from Roth (Karlsruhe, Germany) and water from Riedel-de Haen (Seelze, Germany).

The polydisperse methacrylate samples used in these investigations were purchased from Fluka (Buchs, Switzerland), Aldrich (Milwaukee, WI, USA), and Polysciences (Warrington, PA, USA). Monodisperse samples and PEG 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 from 500 to 1 000 000 and ethyl benzene (all from Fluka, Buchs, Switzerland).

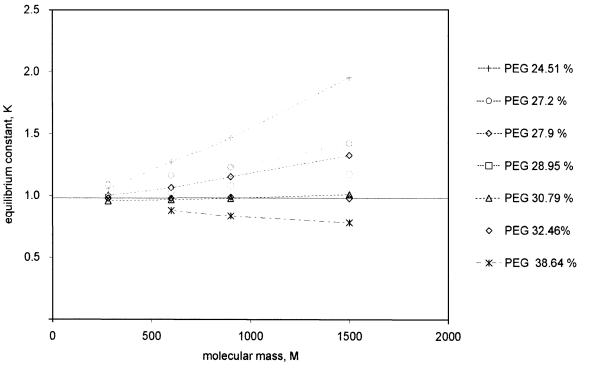

Fig. 3. Distribution coefficients of PEGs on ODS2 in acetone–water of different composition.

4. Results and discussion

The first step was the search for the critical interaction point (CIP) for PEG on the individual columns. In Fig. 2, the elution volumes of different PEGs on the Spherisorb ODS2 are plotted versus the composition of the mobile phase (acetone–water). All lines have an intersection point at 32.46%, which corresponds to the CIP of polyoxyethylene on this column.

Fig. 3 shows the experimental data obtained with ODS2 in the K versus M coordinates. A straight horizontal line is found for PEG at this mobile phase composition.

In order to check the validity of Eqs. (13)–(15), the radius of gyration of the polymer chain is required.

Based on the data given in the Polymer Handbook [38], the radius of gyration of PEGs and their derivatives was calculated using the following equation:

$$R = 0.079 \cdot M^{0.5} \tag{16}$$

Now we can determine the q-values for all types of end groups.

In Fig. 4, the distribution coefficients of PEG and its mono- and dimethyl ethers (PEG-MME and PEG-DME, respectively) on ODS2 are plotted versus $1/R$. As can be seen, straight horizontal lines are obtained (by linear regression) for PEG and PEG-MME, while

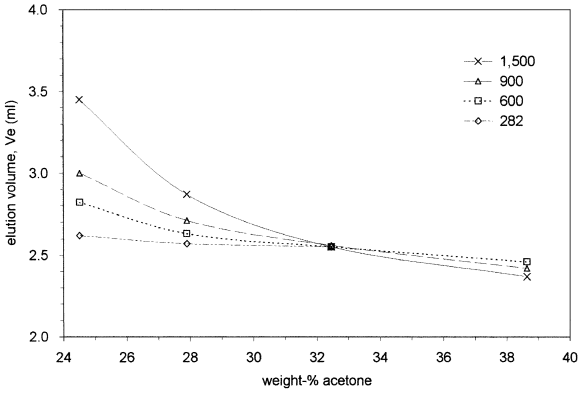

Fig. 2. Elution volumes of different PEGs on Spherisorb ODS2 in acetone–water of different composition.

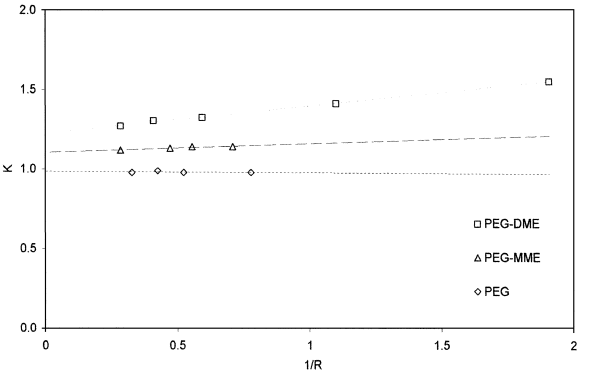

Fig. 4. Distribution coefficients of PEG, PEG-MME, and PEG-DME on ODS2 in acetone–water (32.46 wt.% acetone). Straight lines were determined by linear regression.

a straight line with a positive slope is observed for PEG-DME.

According to Eqs. (5), (13) and (14), the difference in K-values of PEG-ME and PEG is equal to the q_{ME} value for the ME end-group, and the difference between the K-values of PEG-DME and PEG should be twice as large, if both methyl groups are equivalent. As can be seen, this is indeed the case: the difference in the intercepts of PEG-DME and PEG-ME is equal to that of PEG-ME and PEG (0.120 and 0.121, respectively), hence it is obvious that PEG-DME macromolecules behave as symmetrical difunctionals.

If two more hydrophobic end groups are present (which are adsorbed more strongly), the intercept and also the slope should be larger than for PEG-DMEs. Presumably, the individual oligomers could be at least partially resolved.

In Fig. 5, a chromatogram of PEG 400 dimethacrylate is shown, which was obtained on ODS2 in 32.46% acetone. The individual oligomers could be identified by spiking with triethylene glycol dimethacrylate. The pattern is similar as in SEC, the mechanism of the separation has, however, nothing to do with size exclusion! According to the theory, the specific behavior of polymer loops under critical conditions is responsible for such chromatographic pattern in the critical mode.

In Fig. 6, the distribution coefficients of PEG, PEG-DME, and PEG-dimethacrylates (PEG-DMA) are plotted versus $1/R$. Obviously, the intercept as well as the slope of the regression line is much larger than for PEG-DME. As follows from Eq. (14), the

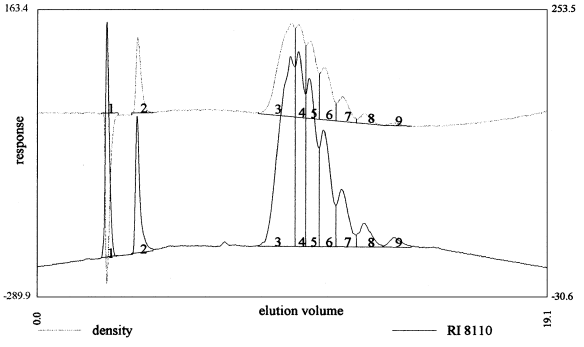

Fig. 5. LCCC of PEG-400-dimethacrylate, as obtained on ODS 2 in 32.46% acetone. Detection: density and RI.

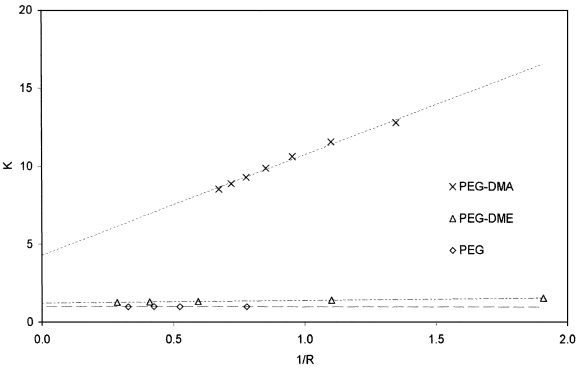

Fig. 6. Distribution coefficients of PEG, PEG-DME, and PEG-DMA on ODS2 in acetone–water (32.46 wt.% acetone). Straight lines were determined by linear regression.

pore size can be estimated from slope and intercept ($2q_a$):

$$d = (slope^{(aa)}/q_a^2) \cdot \sqrt{\pi} \quad (17)$$

In the case of DMA, slope and intercept are sufficiently large to yield a reliable result: for the Spherisorb ODS2 column we found a value of $D=$ 8.3 nm, which is very close to the nominal value of $D=8$ nm. This value is also in good agreement with that obtained by the SEC-porosimetry method ($D=$ 9.2) [39].

A similar behavior as on the (narrow pore) ODS2 column is found on the wide pore S5X C_{18} column, but in a different mobile phase composition: for this column, the CIP is found at 28.15% acetone.

In Fig. 7, the distribution coefficients of PEG and its mono- and dimethyl ethers (PEG-MME and PEG-DME, respectively), are plotted versus $1/R$. Again, the difference in the intercepts of the regression lines of PEG-MME and PEG (0.062) is very close to that between PEG-DME and PEG-MME (0.059).

The absolute values of the intercepts are, however, smaller than with the narrow pore ODS2 column. This can easily be explained from Eq. (8): as both columns are C_{18}-modified silica, $\Delta\varepsilon_a$ and δ should be quite similar, hence the difference in q_a will be due to the pore diameter, which should be about four times larger in this column (specification $D=30$ nm).

The plots of K versus $1/R$ for PEG, MePEG-MA and PEG-DMA are shown in Fig. 8. From the results

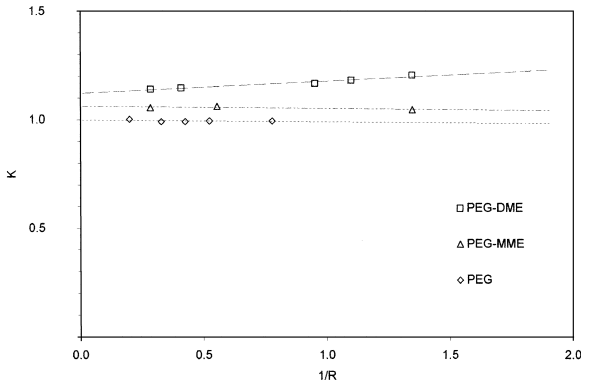

Fig. 7. Distribution coefficients of PEG, PEG-MME, and PEG-DME on S5X C_{18} in acetone–water (28.15 wt.% acetone). Straight lines were determined by linear regression.

obtained for the symmetric difunctionals (PEG-DME and PEG-DMA), q_{Me} and q_{MA} were calculated.

For PEG and PEG-DMA, the regression lines are shown in Fig. 8, the calculated line is drawn for the MePEG-MA series, which was obtained using Eq. (15) with the known q_{Me} and q_{MA} parameters (determined from the symmetrical difunctionals PEG-DME and PEG-DMA, as described above).

As can be seen, there is a very good agreement (both qualitative and quantitative) between theory and experiments.

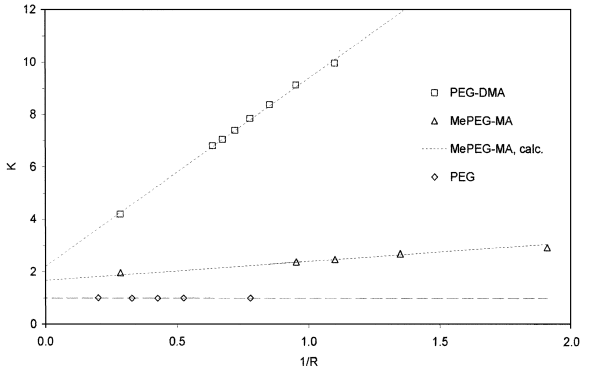

Fig. 8. Distribution coefficients of PEG, MePEG-MA, and PEG-DMA on S5X C_{18} in acetone–water (28.15 wt.% acetone). The straight lines for PEG and PEG-DMA were determined by linear regression, and for MePEG-MA calculated using Eq. 15 from the known q_{Me} and q_{MA} values.

5. Conclusions

A unified theory describes the chromatographic behavior of mono- and difunctional macromolecules at different interactions of the terminal and repeating chain units with porous stationary phase. Although based on a very simple model of an ideal polymer chain in a wide slit-like pore, this theory has proven to be in very good qualitative and in reasonable quantitative agreement with the experimentally observed behavior of functional poly(oxyethylene)s with different end-groups, on different stationary phases, and in different modes of liquid chromatography.

The theoretical predictions for liquid chromatography at the critical conditions could be verified experimentally. Critical conditions were realized experimentally for all the studied systems, and precise chromatographic data were obtained at the critical point for PEO chain. The experimental data have proven to be in excellent qualitative and quantitative agreement with the theory.

In particular, the theoretically predicted molar-mass dependencies of the distribution coefficient of difunctional polymers, similar to the dependencies in SEC, were really observed. The parameters of interaction of the end groups with the stationary phases were estimated from these data. Using these estimates and the theory, it was possible to predict quantitatively the chromatographic behavior of asymmetric difunctionals. The data obtained for stationary phases of different pore size were also in very reasonable agreement with the theory.

The extended experimental study of the retention behavior of functional polymers in different modes of liquid chromatography is in progress, and the results will be published separately.

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References

[1] D. Colombani, P. Chaumont, Acta Polym. 49 (1998) 225.
[2] D.J. Broer, J.A.M.M. van Haaren, P. van de Witte, C. Bastiaansen, Macromol. Symp. 154 (2000) 1.
[3] V. Coessens, T. Pintauer, K. Matyjaszewski, Prog. Polym. Sci. 26 (2001) 337.
[4] P. vanCaeter, E.J. Goethals, Trends Polym. Sci. 3 (1995) 227.
[5] S.G. Entelis, V.V. Evreinov, A.V. Gorshkov, Adv. Polym. Sci. 76 (1986) 129.
[6] H. Pasch, B. Trathnigg, HPLC of Polymers, Springer, Berlin, 1997.
[7] D. Berek, Macromol. Symp. 110 (1996) 33.
[8] M.B. Tennikov, P.P. Nefedov, M.A. Lazareva, S.Ya. Frenkel, Vysokomol. Soedin. A 19 (1977) 657.
[9] A.M. Skvortsov, A.A. Gorbunov, Vysokomol. Soedin. A 22 (1980) 2641.
[10] N.N. Filatova, A.V. Gorshkov, V.V. Yevreinov, S.G. Entelis, Vysokomol. Soed. A 30 (1988) 953.
[11] A.V. Gorshkov, S.S. Verenich, V.V. Evreinov, S.G. Entelis, Chromatographia 26 (1988) 338.
[12] A.V. Gorshkov, H. Much, H. Pasch, V.V. Evreinov, S.G. Entelis, J. Chromatogr. 523 (1990) 91.
[13] R.-P. Kruger, H. Much, G. Schulz, O. Wachsen, Macromol. Symp. 110 (1996) 155.
[14] H. Pasch, Macromol. Symp. 110 (1996) 107.
[15] J. Adrian, D. Braun, K. Rode, H. Pasch, Angew. Macromol. Chem. 267 (1999) 73.
[16] K. Baran, S. Laugier, H. Cramail, J. Chromatogr. B 753 (2001) 139.
[17] A.M. Skvortsov, E.B. Zhulina, A.A. Gorbunov, Vysokomol. Soed. A 22 (1980) 820.
[18] A.A. Gorbunov, A.M. Skvortsov, Vysokomol. Soed. A 26 (1984) 946.
[19] A.M. Skvortsov, A.A. Gorbunov, J. Chromatogr. 507 (1990) 487.
[20] A.A. Gorbunov, A.M. Skvortsov, Vysokomol. Soed. A 28 (1986) 2170.
[21] A.A. Gorbunov, A.M. Skvortsov, Vysokomol. Soed. A 28 (1986) 2453.
[22] A.M. Skvortsov, A.A. Gorbunov, J. Chromatogr. 358 (1986) 77.
[23] P.G. de Gennes, Rep. Prog. Phys. 32 (1969) 187.
[24] Y. Lepine, A. Caille, Can. J. Phys. 56 (1978) 403.
[25] E. Eisenriegler, K. Kremer, K. Binder, J. Chem. Phys. 77 (1982) 6296.
[26] A.A. Gorbunov, A.M. Skvortsov, Adv. Colloid Interface Sci. 62 (1995) 31.
[27] A.A. Gorbunov, A.M. Skvortsov, Vysokomol. Soed. A 31 (1989) 1244.
[28] A.A. Gorbunov, A.M. Skvortsov, J. van Male, G.J. Fleer, J. Chem. Phys. 114 (2001) 5366.
[29] R.J. Rubin, J. Chem. Phys. 43 (1965) 2392;
R.J. Rubin, J. Chem. Phys. 70 (1966) 237.
[30] E.A. DiMarzio, R.J. Rubin, J. Chem. Phys. 55 (1971) 4318.
[31] E.F. Casassa, J. Polym. Sci., Part B 5 (1967) 773.
[32] E.F. Casassa, Y. Tagami, Macromolecules 2 (1969) 14.
[33] A. Gorbunov, A. Skvortsov, B. Trathnigg, M. Kollroser, M. Parth, J. Chromatogr. A 798 (1998) 187.
[34] A.A. Gorbunov, L.Ya. Solovyova, A.M. Skvortsov, Polymer 39 (1998) 697.
[35] B. Trathnigg, A. Gorbunov, J. Chromatogr. A 910 (2001) 207.
[36] B. Trathnigg, J. Chromatogr. A 915 (2001) 155.
[37] B. Trathnigg, M. Kollroser, C. Rappel, J. Chromatogr. A 922 (2001) 193.
[38] J. Brandrup, E.H. Immergut (Eds.), Polymer Handbook, 2nd ed., Wiley, New York, 1975, p. IV-34.
[39] A.A. Gorbunov, L.Ya. Solovyova, V.A. Pasechnik, J. Chromatogr. 448 (1988) 307.