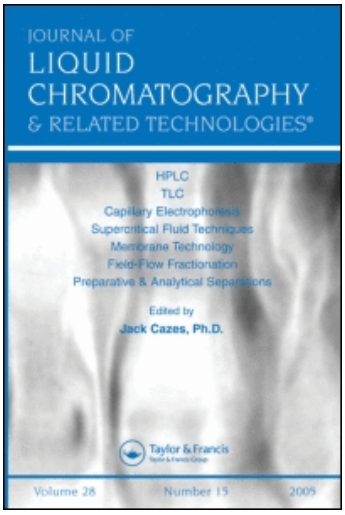

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Size Exclusion of Associating Systems. II. A Model Describing the Hindered Release of Solute from the Stationary Phase

Karel Procházka[a]; Bohumil Bedná[b]; Zdenek Tuzar[c]; Milan Kočiík[d]
[a] Department of Physical Chemistry, Charles University, Prague 2, Czechoslovakia [b] Department of Polymers, Prague Institute of Chemical Technology, [c] Institute of Macromolecular Chemistry Czechoslovakia Academy of Science, [d] Heyrovsky Institute of Physical Chemistry and Electrochemistry, Prague, Czechoslovakia

To cite this Article Procházka, Karel , Bedná, Bohumil , Tuzar, Zdenek and Kočiík, Milan(1989) 'Size Exclusion of Associating Systems. II. A Model Describing the Hindered Release of Solute from the Stationary Phase', Journal of Liquid Chromatography & Related Technologies, 12: 6, 1023 — 1041
To link to this Article: DOI: 10.1080/01483918908051777
URL: http://dx.doi.org/10.1080/01483918908051777

JOURNAL OF LIQUID CHROMATOGRAPHY, 12(6), 1023-1041 (1989)

SIZE EXCLUSION OF ASSOCIATING SYSTEMS. II. A MODEL DESCRIBING THE HINDERED RELEASE OF SOLUTE FROM THE STATIONARY PHASE

KAREL PROCHÁZKA[1], BOHUMIL BEDNÁŘ[2], ZDENEK TUZAR[3] AND MILAN KOČIŘÍK[4]

[1]*Charles University*
Department of Physical Chemistry
Albertov 2030
128 40 Prague 2, Czechoslovakia
[2]*Prague Institute of Chemical Technology*
Department of Polymers
[3]*Institute of Macromolecular Chemistry*
Czechoslovakia Academy of Science
[4]*Heyrovsky Institute of Physical Chemistry*
and Electrochemistry
Prague, Czechoslovakia

ABSTRACT

During a separation process of reversibly associating species (e.g. tensides, block copolymers etc.) in size exclusion chromatography (SEC), some amount of solute can be temporarily trapped in the gel phase. A model covering this effect, namely hindered release of a solute form the gel phase, has been developed. Results of numerical calculations have been compared with experimental data of micellizing block copolymers and the effect of trapping of the solute in the gel pores has been demonstrated.

INTRODUCTION

Size exclusion chromatography (SEC) is a very useful method for the investigation of reversibly associating macromolecules.

Chromatograms obtained with such systems result from two competing processes: Separation of the solute in a column and continuously disturbing and reestablishing association $\rightleftharpoons$ dissociation equilibrium. Thus the chromatograms, the shapes of which depend on the relative rates of these two processes, can, in principle, provide an information on the dynamics of association and dissociation of macromolecules. To draw a quantitative information from SEC experimental data, theoretical model must be developed first describing adequately the behavior of associating systems during a SEC experiment.

Works, enabling the determination of the rate characteristics in a large range of the association numbers and for different rates of association and dissociation, are lacking. The reason for it can be seen in the fact that the nonlinear partial differential equations,which must be necessarily used for the modelling of SEC experiment, are not easy to solve numerically. Papers published so far are mostly limited to cases of the infinitely fast establishing unimer $\rightleftharpoons$ micelle equilibrium (Gilbert (1), Coll (2)) or of a very small association numbers (3). It seems that it is impossible to describe a SEC chromatogram for a general case of an associating system by an analytical function.

In our previous paper (4) we have introduced a simplified model of a reversibly associating systems, consisting of a mixture of unimer (molecularly dissolved molecules) and monodisperse associates (micelles) having association number up to 16 (axial dispersion in the mobile phase has been neglected). It has been assumed in our mathematical model (as it is the common practice in the SEC theories of this kind (1-4)) that the establish ment of the separation equilibrium of unimer between mobile and stationary phases is very fast (practically instantaneous). This assumption has been substantiated by some experimental data(5,6) concerning micellization of block copolymers in selective solvents. On the other hand, an effect of the detainment of an associating solute (block copolymers or nonionic surfactants) has been reported (6-8) and interpreted as an adsorption (7,8) or as

a trapping of the secondarily formed micelles in the gel pores (6), respectively.

The aim of this paper is an extension of our previous simplified model of the SEC of an associating system, covering also the hindered release of solute from the gel phase. We also introduce a few experiments supporting the idea of solute trapping in the gel pores.

THEORETICAL

Our model of an associating system in SEC is based on three assumptions, the first two of them coinciding with those in our previous paper (4).

1. There are two kinds of particles present in a dilute solution of a block copolymer in a selective solvent (in mobile phase), which are in reversible equilibrium: Molecularly dissolved copolymer (unimer), U, and monodisperse spherical associates (micelles), M, the latter consisting of a core formed by insoluble blocks and a shell formed by soluble blocks. Association can be described by a quasichemical equilibrium

$$nU \underset{k_d}{\overset{k_{as}}{\rightleftharpoons}} M \qquad (1)$$

where n is association number (number of copolymer molecules forming one micelle), k_{as} and k_d are rate constants of association and dissociation, respectively.

2. Chromatographic column is homogeneously packed with uniform spherical particles of porous gel representing a stationary phase. Mobile phase (selective solvent) moves through the interstitial volume between the gel particles (fraction of this volume is further denoted as α) by a velocity v, in the flow direction ,x.

3. Unimer can penetrate by a finite velocity (it was infinitely fast process assumed in our previous paper (4)) into pores of the stationary phase. The volume fraction of the pores in the stationary phase is further denoted as β. Gel pores are sufficiently small in comparison with the micellar dimensions so that micelles cannot penetrate into the stationary phase. Nevertheless, as the pores have a certain size distribution, some of them are able to accomodate micelles with the same or lower association number than those in the mobile phase. We assume that the micelles in the pores can be built by a step mechanism, i.e., by a consecutive attachment of unimer molecules. During that process, the entanglement of the core-forming blocks take place. Once a micelle in a given pore is formed, the rest free volume in the pore for the movement of polymer chains is small and thus the disentanglement and dissociation of micelle is slowed down. The release of the polymer is hindered even after the polymer concentration in mobile phase in the neighbourhood of a gel particle drops due to the convective flow.

A detailed mathematical description of the process outlined in the paragraph above, disentanglement kinetics in particular, would be extremely difficult. Instead, simple linear relations describing mass transfer between mobile and stationary phases are used in this paper for the modelling of the temporal changes of polymer concentration in the stationary phase.

The time derivative of the copolymer concentration in the stationary phase ($\partial c_p^{(s)}/\partial t$) can be expressed as

$$\partial c_U^{(s)}/\partial t = \begin{cases} k_s(c_U^{(m)} - c_U^{(s)}) \text{ ; for } c_U^{(m)} > c_U^{(s)} \\ (\delta_1 k_{f1} + \delta_2 k_{f2})(c_U^{(m)} - c_U^{(s)}) \text{ ; for } c_U^{(m)} < c_U^{(s)} \end{cases} \quad (2)$$

where $c_U^{(m)}$ is the mass concentration (in g per unite volume) of unimer in the mobile phase, $c_U^{(s)}$ the total copolymer concentration

in the stationary phase, k_s denotes the rate constant of the penetration of unimer into the pores of stationary phase, and k_{f1} and k_{f2} are the rate constants of the release of unimer and trapped micelles from the stationary phase, respectively. Coefficients δ_1 and δ_2 characterize the volume fraction of larger pores where the trapped micelle can be built. The rate of the release of copolymer from the stationary phase can be expressed using an effective constant k_{ef}

$$k_{ef} = \delta_1 k_{f1} + \delta_2 k_{f2} \tag{3}$$

Substitution of eq.(3) into eq.(2) leads to

$$\partial c_U^{(s)}/\partial t = \begin{cases} k_s(c_U^{(m)} - c_U^{(s)}) \ ; \text{ for } c_U^{(m)} > c_U^{(s)} \\ k_{ef}(c_U^{(m)} - c_U^{(s)}) \ ; \text{ for } c_U^{(m)} < c_U^{(s)} \end{cases} \tag{4}$$

For the sake of simplification of the mathematical calculation (analogically to our previous model in (4)), it is useful to introduce reduced variables

$$\tau = tv/L \qquad X = x/L \tag{5}$$

$$S = c_U^{(m)}/c_{oU} \qquad F = (k_d/k_{as})c_M^{(m)}/c_{oU}^n \tag{6}$$

$$G = (k_{ef}/k_s)c_U^{(s)}/c_{oU} \tag{7}$$

where L is the length of the column in the direction of x axis, v is the velocity of passage of mobile phase in the direction of x axis and t is time. Symbols $c_U^{(m)}$ and $c_M^{(m)}$ describe the mass concentrations of unimer and micelles, respectively, in the mobile phase, $c_U^{(s)}$ is copolymer concentration in the stationary phase (regardless of the state of copolymer in pores) and c_{oU} is the maximum unimer concentration in the input puls. Constants k_{as} and k_d are rate constants of micelle formation and dissociation, respectively.

Based on the mass balance in the infinitely thin layer of the column, the following differential equations have been derived

$$\partial S/\partial \tau + \partial S/\partial X = w_{as}(F-S^n) - \gamma(\partial G/\partial \tau) \quad (8)$$

$$\partial F/\partial \tau + \partial F/\partial X = w_d(S^n-F) \quad (9)$$

$$\partial G/\partial \tau = w_s S - w_{ef} G \quad (10)$$

where

$$w_{as} = (k_{as} c_{oU}^{n-1} L)/v \ , \quad w_d = (k_d L)/v \quad (11)$$

$$w_s = k_s L/v \ , \qquad w_{ef} = k_{ef} L/v \quad (12)$$

$$\gamma = (1 - \alpha)\beta/\alpha$$

α is the volume fraction of mobile phase in a column and β is the volume fraction of pores in the stationary phase, k_s is the rate constant of the penetration of unimer into gel pores and k_{ef} is the effective rate constant of the slowed down release of copolymer from the pores into mobile phase.

Initial and boundary conditions for reduced concentrations of unimer ,S, and micelles ,F, in mobile phase are the same as in our previous paper (4)

$$S(\tau, X) = 0, \qquad \text{for } \tau \geq 0, \ X = 0 \quad (13)$$

$$S(\tau, X) = f(X) \quad \text{for } \tau = 0, \ X > 0, \quad (14)$$

$$F(\tau, X) = (w_{as}/w_d)\left[S(\tau, X)\right]^n, \ \text{for } \geq 0, \ X \quad 0. \quad (15)$$

Initial condition for the reduced variable $G(\tau, X)$ defines an empty stationary phase at the beginning of SEC experiment:

$$G(\tau, X) = 0, \quad \text{for } \tau = 0, \ X > 0 \quad (16)$$

This condition makes the present model different from the previous one (4) in which an instantaneous establishment of the separation equilibrium of unimers between mobile and stationary phases and thus an equal concentration of copolymer in the gel pores and in the mobile phase from the very beginning of SEC experiment were assumed. The function f(X) specifies a slightly rounded (as if modified by free diffusion), originally rectangular peak, which is located in the immediate vicinity of the top of the column. For the reduced concentration S the maximum value of f(X) equals one. This shape and the position of the original peak fits satisfactorily the physical reality and prevents also serious mathematical complications which are encountered when working with the rectangular peak, namely oscilations in numerical calculations of nonlinear parabolic partial differential equations. Numerical calculations of the differential equations, using the Wendroff scheme, have been described in (4).

RESULTS AND DISCUSSION

Calculated Chromatograms

In this paper we have concentrated mainly on the effect of the rate of establishment of the separation equilibrium of unimer between mobile and stationary phases on the shape of SEC elution curves. We present only results elucidating a) the effect of w_s and w_{ef} values on the separation mechanism in a column(separation efficiency, peak broadening) and b) the effect of trapping of micelles in gel pores. The least mechanism can be operative in the SEC of micellar systems with the association number at least eight and the rate of micellization and dissociation as well as the rate of establishment of separation equilibrium of unimer between mobile and stationary phases significantly higher than the flow rate of a mobile phase.

First, an influence of the increasing values of w_s and w_{ef} (for the case: $w_s = w_{ef}$) on the shape of elution curves has been studied. The finite values of the rates of solute penetration into gel phase (w_s) and its release into the mobile phase (w_{ef}) diminish the separation efficiency of the column as compared with the case of an instantaneous establishment of the separation equilibrium of unimer between phases. If the processes of unimer penetration and release into and from the stationary phases, respectively, are not reasonably fast in comparison with the flow rate of mobile phase, the unimer cannot penetrate into gel pores in a sufficient amount, its actual concentration in stationary phase decreases, and only a smaller part of solute molecules can undergo a separation process.

The reasoning outlined above is demonstrated for the case of independent components (Fig.1). Fig.1 shows clearly a decrease of the separation efficiency with decreasing values of w_s and w_{ef}. All theoretical curves are compared for the same value of τ as in paper (4). In the region of intermediate values of w_s and w_{ef}, a new interesting effect appears: A significant fraction of the slow component which is temporarily retained in the stationary phase, causes an asymmetrical broadening of the slow peak (Fig.1b). For low values of w_s and w_{ef} (Fig.1c), the separation of components is practically eliminated and the slow peak becomes sharper again (with the exception of the long tail of negligible concentration).

The total amount of the slow component increases with the decreasing values of w_s and w_{ef}, which is a consequence of the initial condition given by eq.(16), defining an empty stationary phase for $\tau = 0$. At the beginning of a SEC experiment, a certain amount of slow component (depending on the rate of penetration of the slow component into stationary phase and its release) enter into the gel pores and its concentration in the mobile phase drops.

All these three factors, i.e., (a) the deterioration of the separation efficiency, (b) the asymmetry of the slow peak and

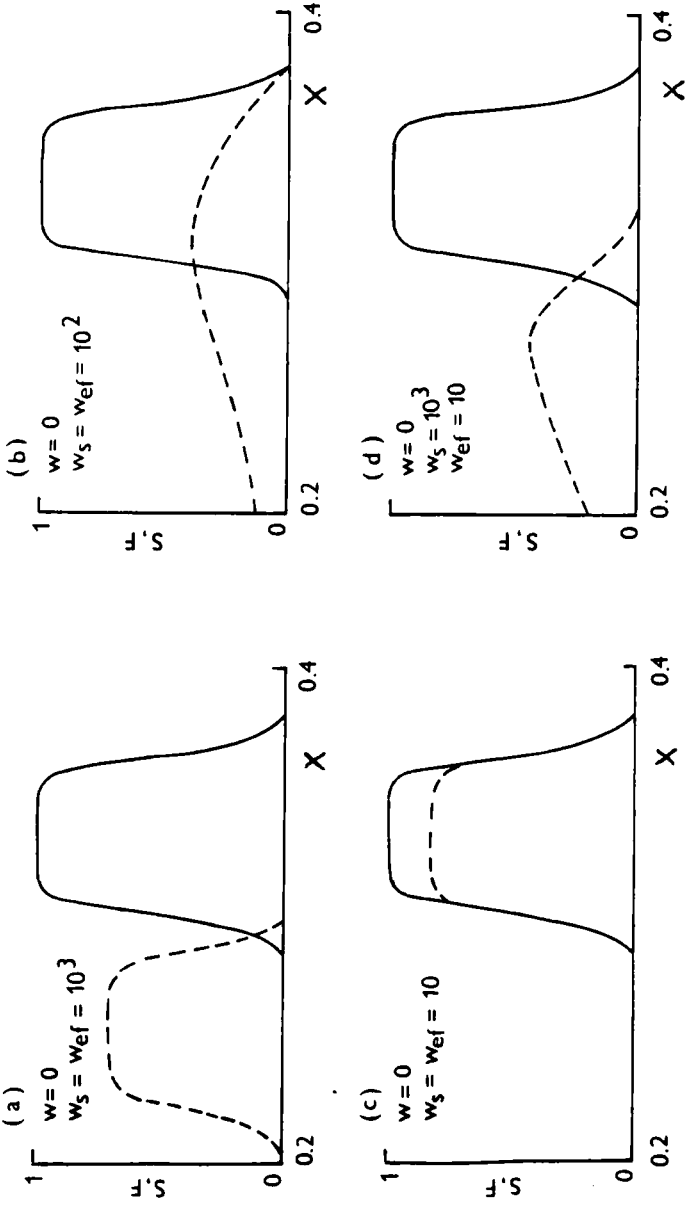

Figure 1. Concentration profiles of two independent components, the fast (F, full line) and the slow (S, dashed line). X is the reduced column length, w_s and w_{ef} are the rates of solute penetration into gel phase and its release into the mobile phase, respectively, and $w=(w_s=w_d)$ is the relative rate of association/dissociation process.

(c) the increasing amount of the slow component in the mobile phase with decreasing rates of unimer penetration into and its release from the gel pores have to be kept in mind, when theoretical chromatograms of the associating systems will be discussed.

Fig.1d shows the theoretical peaks for fast penetration of the slow component into pores of the stationary phase and its temporary trapping in the pores (much slower release, $w_s = 10^3$, $w_{ef} = 10$). In this case the separation efficiency is not dramatically reduced. Nevertheless, the slow peak is rather broad with a well pronounced tail and the total amount of slow component in the mobile phase drops down significantly.

In Fig.2, the influence of changing values of w_s and w_{ef} on theoretical chromatograms for fast associating systems (n = 16, $w_{as} = w_d = 10^3$) is shown. For high values of w_s and w_{ef} ($w_s = w_{ef} \geq 10^4$, Fig.2a), the calculated curves exhibit the typical features of Gilbert's type chromatograms. As concerned the moderately high values of w_s and w_{ef} (the range of 10^2 to 4×10^2), the asymmetry of the slow peak increases and a significant decrease of the amount of the fast component (micelles) can be seen (Fig.2b). For such systems, the rising deficit of the slow component (unimer) in the mobile phase, caused by its continuous transition into gel pores, is readily compensated for by the fast dissociation of micelles. For a slow establishment of the separation equilibrium of unimer between the mobile and stationary phases, (Fig.2c), the separation efficiency, as well as the total amount of polymer retained in the stationary phase, decreases and an effect of self-sharpening of both peaks is evident. Simultaneously, the amount of slow component (unimer) in the mobile phase approaches that of the fast component (micelles).

The true trapping of secondarily formed micelles in the gel pores, described in the theoretical part, can be simulated numerically for $w_s > w_{ef}$. Fig.3 gives the comparison of results for a fast penetration of unimer into and out of gel pores with those for a temporary trapping if secondarily built micelles in the gel pores. The theoretical concentration profiles of both components

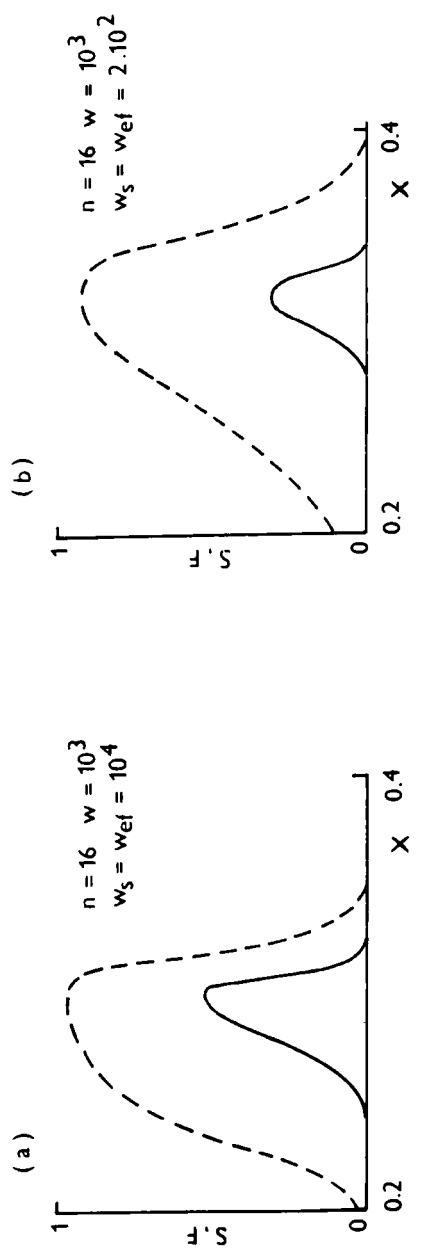

Figure 2. Concentration profiles of unimer (S) and n-mer (F), for fast association equilibrium. n is the association number.

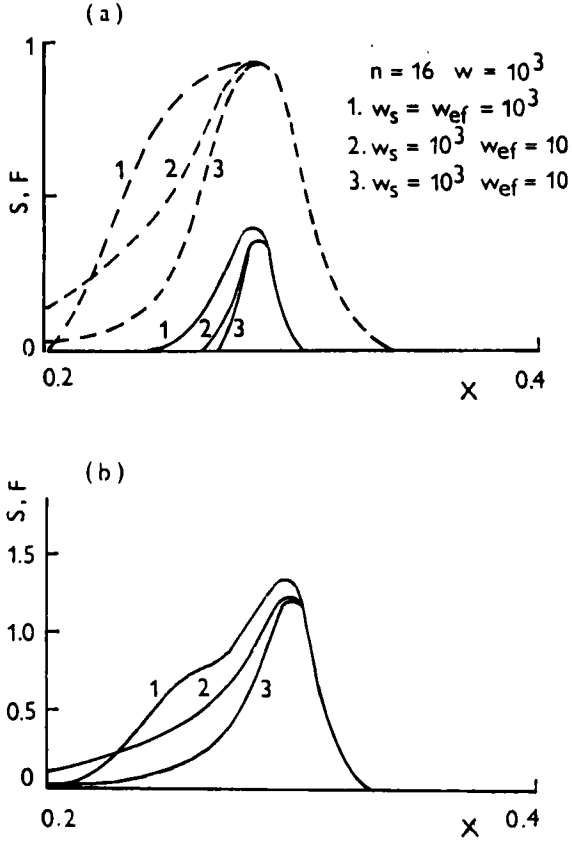

Figure 3. Concentration profiles of unimer (S) and n-mer (F) components (a) and resulting concentration profiles(b) for fast association equilibrium and different relative rates of w_s and w_{ef}.

for $w_s < w_{ef}$ and the resulting chromatograms are shown in Figs.3a and 3b, respectively. The results based on the model which includes temporary trapping of a solute in the stationary phase are important from the practical point of view: The peak of unimer is extremely broad, the position of the maximum concentration of micelles coincides with that of unimer (the separation efficiency does not deteriorate significantly) and the mass fraction of

micelles decreases dramatically during the passage of the components through the column.

Two important conclusions concerning a rapidly micellizing real copolymer system in a SEC column, where secondarily built micelles may be temporarily trapped in gel pores, can be drawn from our theoretical calculations:

a) a chromatogram with two maxima can never be obtained,

b) for micellar systems, where under disturbed condition (out of column) the micellization equilibrium is not considerably shifted in favour of micelles, a decrease of the mass fraction of micelles in the mobile phase during the passage through a SEC column, may cause the total disappearence of micelles from the solution which is leaving the column.

Comparison with Experiment

Experiments in this paper have been performed with a three-block copolymer G-1650 (Shell) polystyrene-block-poly(hydrogenated butadiene)-block-polystyrene (M_w = 74×10^3, 28 wt.% polystyrene). In all selective solvents employed, unimer ⇌ micelle equilibrium is shifted towards micelles with cores formed by aliphatic blocks and protective shells formed by polystyrene blocks. Basic parameters of micelles in the respective solvents are in Tab.1.

The SEC experiments have been performed with a Waters 150 C apparatus, RI detector and four μ-Bondagel E-linear columns. All analyses were carried out at $30^{\circ}C$, using a flow rate 1.0 ml/min and injection volume 100 μl.

The model introduced in this paper predicts - at least semi-quantitatively - the SEC behavior of numerous real block copolymer micellar systems. Similarities between theoretical and experimental chromatograms discussed below, concern mainly the loss of the mass fraction of micelles during the passage of solute through the column, and the broadening of a unimer peak and its shifting towards lower values of the elution volume.

TABLE 1
Micellar Molar Masses, $M^{(m)}$, and Association Numbers, n, of G-1650 in some Selective Solvents at 25°C.

Solvent	$M^{(m)} \times 10^{-6}$	n	Ref.
1,4-dioxane /20 vol.% n-heptane	4.20	57	(9)
1,4-dioxane /30 vol.% n-heptane	3.77	51	(9)
THF/24 vol.% ethanol	5.85	79	(10)

Fig.4 shows elution curves of the copolymer G-1650 injected in a solvent mixture (1,4-dioxane/20 vol.% n-heptane), identical with the mobile phase, where the unimer ⇌ micelle equilibrium is strongly shifted towards micelles (9). The chromatogram has a form of a relatively narrow, slightly asymmetric peak of the fast component, followed by a long tail exceeding permeation limit of the column used. Results obtained by a light-scattering detector proved that the fast peak corresponds to high-molar-mass particles, i.e. micelles (11). The long tail reflects a slow release of the copolymer from the stationary phase. The mass balance at the end of the experiment indicates that a part of the solute was trapped in the column. A substantial part of the solute was eluted by a zone of a good solvent, THF (curve 2). To wash out the rest of the solute, another injection of THF was needed (curve 3). The shape of the curve 2 can be qualitatively explained by the following reasoning: THF enters the gel pores occupied by trapped micelles, causing a swelling of their cores, this process leading to their dissociation and a release of the unimer into the mobile phase. As a consequence the copolymer concentration in front of the THF zone increases. When the unimer concentration exceedes that of cmc, micelles are formed. These micelles pass through the column faster than the unimer. As soon as their concentration drops below cmc, they

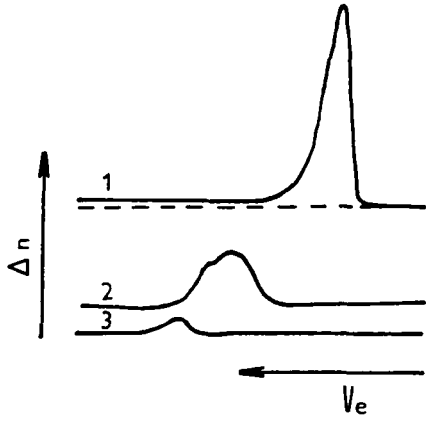

Figure 4. Chromatograms of Kraton G-1650 at 25°C. Mobile phase: 1,4-dioxane/20 vol.% n-heptane. 1: injected solution ($c=2.5\times10^{-3}$ g/cm^3) in 1,4-dioxane/ /40 vol.% n-heptane; 2 and 3: THF.

dissociate again. Being able to enter more gel pores than unimer, THF delays behind the just released unimer, swelling and releasing another portion of the still trapped micelles. As a consequence of the described complex processes the asymmetric concentration profile as in Fig.4, curve 2, may result. Orientation data obtained with the light-scattering detector indicate that the higher V_e part of the elution curve contains heavier particles than the lower one. This surprising result will be discussed in more detail in the following paper (11).

The elution curve (Fig.5, curve 1) resembling a superposition of the curves 1 and 2 in Fig.4 has been obtained by the injection of a solution of G-1650 in a good solvent, THF, into the selective mobile phase, 1,4-dioxane/20 vol.% n-heptane. Polymer molecules in form of unimer, moving faster than the THF zone, reach finally the selective mobile phase, forming a unimer ⇌ micelle equilibrium. The situation is analogous to that described in the previous case (Fig.4), with only one difference:

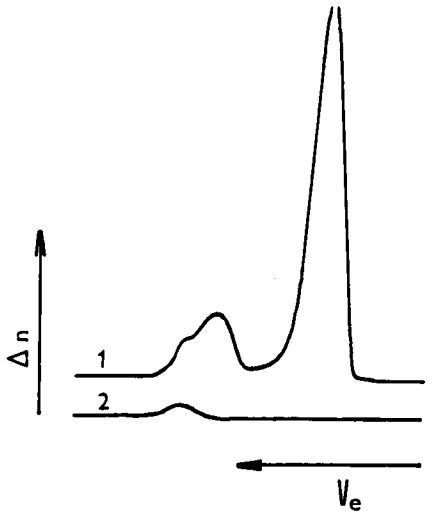

Figure 5. Chromatograms of Kraton G-1650 at 25°C. Mobile phase: 1,4-dioxane/20 vol.% n-heptane. 1: injected solution ($c=3.9\times10^{-3}$ g/cm^3) in THF; 2: THF.

The copolymer, trapped in the stationary phase is washed out by the delayed THF, the process leading to the formation of the asymmetric peak (Fig.5, curve 1). The rest of trapped solute can be washed out by an injection of THF (Fig.5, curve 2).

The elution curve in Fig.6 resembles in many respects the theoretical curves in Fig.3b. Although in the mixed solvent 1,4--dioxane/30 vol.% n-heptane the unimer ⇌ micelle equilibrium is still shifted towards micelles (as concluded from static measurements), the difference between the resulting chromatogram and that in Fig.4, curve 1, is apparent. The chromatogram in Fig.6 shows a drop in the mass fraction of micelles and a broadening of the unimer peak which reaches a region of the elution volumes for low-molar-mass species. An easier release of trapped solute can be explained by a much faster dissociation process, probably due to a more swelled and thus not so tightly knotted micellar cores.

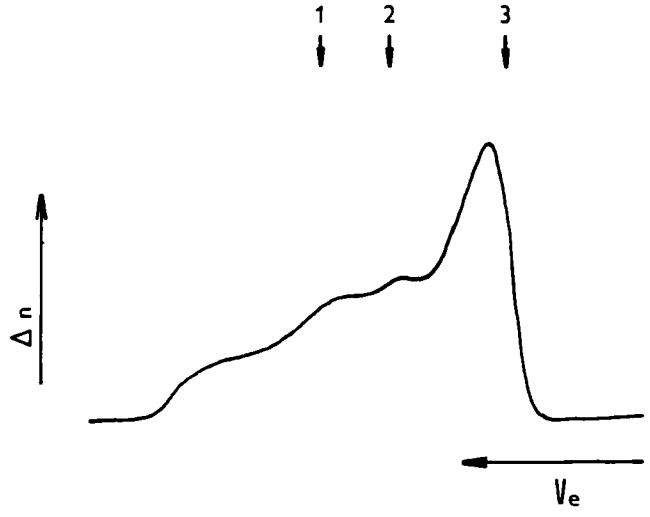

Figure 6. Chromatograms of Kraton G-1650 at 25°C. Mobile phase: 1,4-dioxane /30 vol.% n-heptane. Injected solution ($c=2.5\times10^{-3}$ g/cm^3) in the same solvent mixture. Elution volume of polystyrene standards with M_w: 1- 5×10^7, 2- 10^5, 3- 3×10^5.

To demonstrate that the phenomenon of the hindered release of a solute from the column is based not on a true adsorption but on a trapping of micelles in the gel pores,the following experiment has been performed: The injected sample was G-1650 in a solvent mixture selectively good for polystyrene, THF/24 vol.% ethanol. Resulting chromatogram in Fig.7 is similar to that in Fig.4 , curve 1. Evaluation of the mass fraction of the eluted unimer, based on our theoretical model leads to the value 0.29, which is much higher than that in the injected solution (i.e., below 0.08 (10)). We have proved that the rest of the solute could be completely washed out not only by THF but also by a zone of a good solvent mixture of THF containing less than 15 vol.% of ethanol, i.e. by a solvent differing only slightly from a mobile phase. This experiment rules out the conception of a

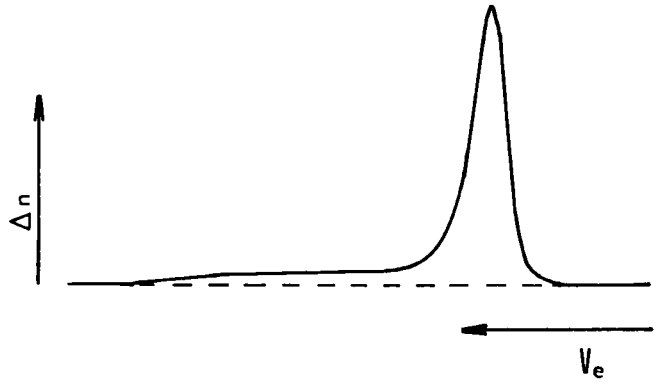

Figure 7. Chromatogram of Kraton G-1650 at 25°C. Mobile phase: THF/24 vol.% ethanol. Injected solution ($c=0.9\times10^{-3}$) in the same solvent mixture.

relatively strong true adsorption of the copolymer on the surface of the gel particles.

It can be concluded that during a separation process of a micellinzing block copolymer in SEC experiment a trapping of the secondarily built micelles in gel pores takes place. This phenomenon may affect an interpretation of SEC data concerning both unimer/micelles ratio and dynamics of the unimer ⇌ micelle equilibrium. On the other hand, it must be emphasized that due to the polydispersity in size of the gel pores, not only unimer, but also micelles can enter and exit the gel pores, making thus the resulting process - at least in comparison with our model - more complex.

REFERENCES

(1) Gilbert, G. A., Discuss.Faraday Soc. 20, 68 (1955).

(2) Coll, H., Sep. Sci. 6, 207 (1971).

(3) Ackers, G. K., Thompson, T. E., Proc. Natl. Acad. Sci. 53, 342 (1965).

(4) Procházka, K., Bednář, B., Tuzar, Z., Kočiřík, M., J. Liquid Chrom., In press.

(5) Procházka, K., Glockner, G., Hoff, M., Tuzar, Z., Makromol. Chem. 185, 1187 (1984).

(6) Špaček, P., J. Appl. Polym. Sci. 30, 143 (1985).

(7) Booth, C., Naylor, T. D., Rajab, N. S., Stubbersfield, R. B., J. Chem. Soc., Faraday Trans. 74, 1 (1978).

(8) Teo, H. H., Styring, M. G., Yeates, S. G., Price, C., Booth, C., J. Colloid Interface Sci. 114, 416 (1986).

(9) Koňák, C., Tuzar, Z., Štěpánek, P., Sedláček, B., Kratochvíl, P., Progress Colloid Polym. Sci. 71, 15 (1985).

(10) Bednář, B., Devátý, J., Koupalová, J., Králíček, J., Tuzar, Z., Polymer 25, 1178 (1984).

(11) to be published