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Liquid chromatography of macromolecules at the critical adsorption point: behaviour of a polymer chain inside pores

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The structure of macromolecules inside pores at the critical adsorption point (the point of exclusion–adsorption transition) is studied. The critical adsorption point is of importance in the liquid chromatography of polymers: chromatography under these special conditions represents an intermediate mode between size-exclusion and adsorption modes. The specific feature of this mode is the independence of elution volume on the molecular weight of the polymer (the distribution coefficient being unity for any molecular and pore sizes). The polymer segment concentration distributions for various distances of a macromolecule from the pore walls are calculated at the critical adsorption point. A simple picture of a polymer molecule inside a pore at the point of exclusion–adsorption transition is presented, based on the Debye–Bueche model. © 1997 Elsevier Science Ltd.

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INTRODUCTION

Liquid chromatographic (LC) methods presently dominate the separation and molecular characterization of macromolecules. LC separation processes yield the dependence of the concentration of eluted macromolecules on their retention volumes (V_R) as chromatograms. Retention volumes represent the most important data provided by analytical liquid chromatography. V_R is connected with the volume of interstitial mobile phase (V_0) and of the quasi-stationary phase within the pores (V_p) by the well-known equation:

$$V_R = V_0 + KV_p \quad (1)$$

The parameter K is called the distribution coefficient and represents the ratio of the concentrations of macromolecules inside the pores (i.e. in the quasi-stationary phase) and in the free volume of liquid (i.e. in the interstitial mobile phase).

Various LC techniques have been developed for the analysis of polymer molecules, but size-exclusion chromatography (SEC), also called gel permeation chromatography or gel filtration chromatography, is most commonly used. Under 'ideal' SEC conditions the role of the pore walls is limited exclusively to the steric restriction of the macromolecular conformation number and the separation of polymer species takes place exclusively according to their sizes. Consequently, the distribution coefficient K assumes values between 0 and 1. K decreases with increasing molar mass (M), i.e. with increasing molecular size of polymer chains.

In particular cases, liquid adsorption chromatography (LAC) can be applied to the selective separation of macromolecules. LAC uses differences in adsorption of separated macromolecules on the pore walls of the column packing. Under LAC conditions, $K > 1$ and as a rule increases fairly rapidly with increasing M of the polymer. Consequently, LAC in isocratic mode is typically limited to the separation of oligomers.

The theory of SEC is based on the work of Casassa[1–3] and the theory of LAC has been formulated by the present authors[4,5]. The behaviour of macromolecules in confining geometries was reviewed recently by Teraoka[6].

In the last few years, liquid chromatography of macromolecules at the critical adsorption point (LC CAP), also called liquid chromatography under critical conditions of adsorption, has attracted increased attention[7–22]. LC CAP represents an intermediate mode between SEC and LAC: at the critical adsorption point the equilibrium constant K (for a given structural unit) is unity irrespective of the size of both column packing pores and separated macromolecules. In other words, the point of exclusion–adsorption transition is reached and thus LC CAP belongs to the family of methods that are designated by the common name of liquid chromatography at the point of exclusion–adsorption transition (LC PEAT). At the critical adsorption point (CAP), macromolecules of any molar mass are eluted from the chromatographic column together with their initial solvent, i.e. within a retention volume equal to $V_0 + V_p$. One can say that at the transition point, macromolecules are 'chromatographically invisible'. The theoretical basis of LC CAP was laid by Skvortsov *et al.*[18] and further elaborated in subsequent papers[4,5]. Experimentally, LC CAP was

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successfully applied in the fields of oligomers[11,12], polymer mixtures and block copolymers[13–18], and selected graft copolymers[19].

It has also been found that the LC CAP principle can be used to discriminate polymers according to their tacticity[20]. On the other hand, several experimental problems accompany the use of the LC CAP method[21,22] and it is now evident that the appropriate experimental conditions must be identified and it must be ensured that they are highly stable in the course of separation.

Statistical properties of macromolecules inside pores at various energies of interaction with pore walls have been studied theoretically[23] and calculated numerically[24,25].

The aim of present study is to elucidate the physical background for the constant value $K = 1$ under CAP conditions. To do so, it is necessary to analyse in more detail the behaviour of macromolecules in pores at their critical adsorption point from the point of view of their structural characteristics. For simplicity we shall consider an ideal linear macromolecule of a homopolymer, neglecting its intramolecular interactions.

GENERAL CONSIDERATIONS

Presently it is accepted both theoretically[4,5] and also experimentally[8,11] that SEC and LAC represent particular cases of a general mechanism of chromatography of macromolecules. According to the theory[4,5], the chromatographic behaviour of polymer species is determined by the size of macromolecules, e.g. by their radius of gyration (R), pore diameter (D) and parameter of adsorptive interaction (ε) between column packing and polymer segments. ε is independent of the pore size D and of the molar mass of the polymer chains M. It depends on the chemical nature of both the column packing surface and the eluent, as well as on the chemical composition and the physical structure of the macromolecules and on temperature.

In general, LC CAP is performed in mixed mobile phases, the components of which are preferentially sorbed on the column packing surface and in the domain of macromolecular coils. Obviously the experimental conditions such as temperature and pressure that affect the extent of preferential sorption will also indirectly affect the extent of adsorptive interactions between polymer and column packing surface[22].

The ε value and consequently the retention of a given polymer can be affected by variations in mixed-eluent composition, pH, temperature and chemical composition of sorbent surface. The effect of some of these parameters on the relation between $\log M$ and V_R, i.e. on the SEC calibration curve, is demonstrated in *Figure 1*[20] for the system of isotactic poly(methyl methacrylate) (i-PMMA) plus tetrahydrofuran–trichloromethane mixed eluents plus bare silica gel. Tetrahydrofuran (THF) is a solvent for separated i-PMMA that suppresses adsorption of i-PMMA macromolecules on the bare silica gel surface. In contrast, trichloromethane ($CHCl_3$), which is also a solvent for i-PMMA, promotes polymer adsorption and the macromolecules are fully retained within the column in pure $CHCl_3$ eluent. The calibration curve *a* corresponds nearly to $\varepsilon = 0$ and to 'ideal' SEC. The presence of a small amount of $CHCl_3$ in the THF eluent slightly increases V_R of i-PMMA, mainly due to increased adsorption, because the coil dimensions remain approximately constant. However, the basic SEC elution order is preserved (curve *b*). When the amount of $CHCl_3$ in eluent increases further, the retention

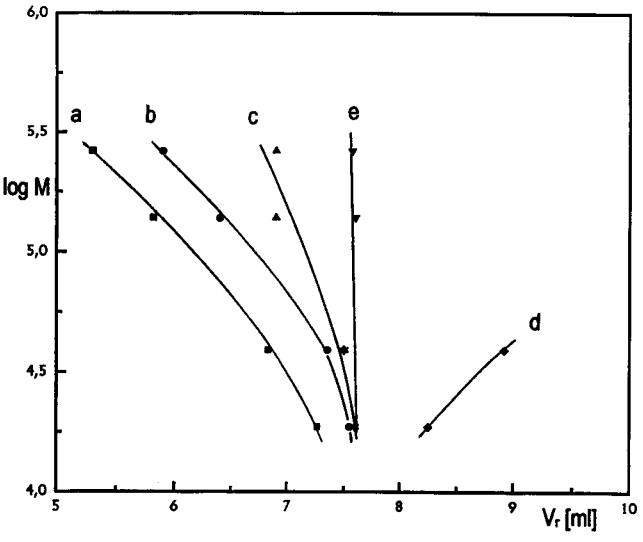

Figure 1 Experimental dependence of retention volume V_R on $\log M$ for narrow, highly isotactic poly(methyl methacrylate)s[19] on bare silica gels 12 + 30 + 100 nm pore diameter in tetrahydrofuran (THF) (a) and in THF–$CHCl_3$ mixtures: (b) 12.4 wt% THF, (c) 12.3 wt%, (d) 12 wt% (all at 30°C) and (e) 12.4 wt% at 35°C. PMMA was fully retained in the columns in pure $CHCl_3$

volume of i-PMMA rises substantially and the separation selectivity of smaller macromolecules is lost (curve *c*). Further increase in *n*-hexane concentration in the eluent brings about a change in separation mechanism from SEC to the LAC mode (curve *d*). The extent of adsorption of i-PMMA in the above system increases with increasing temperature. Thus it is possible to adjust the critical adsorption point by a slight temperature rise: we have arrived at the critical value of polymer adsorption, $\varepsilon = \varepsilon_{cr}$, i.e. at the situation where the retention volume does not depend on M, and $K = \text{const.} = 1$ (curve *e*).

The above situation results from the full compensation of adsorptive interactions between polymer segments and sorbent surface on the one hand, by entropy losses due to compression of polymer coils within the pores of the column packing on the other hand[4,5]. In other words, the conformational free energy of macromolecules within the pores of the packing exactly equals the free energy of macromolecules in the mobile phase in the interstitial volume of the column. When the courses of the calibration curves in the SEC and LAC modes are compared, one can see a pronounced difference not only in the sign but also in the extent of V_R changes with M. The retention volumes in SEC decrease much less rapidly with rising M than they increase with the same rise of M in the case of LAC. This leads to the question whether the superposition of the SEC curve *a* in *Figure 1* and the LAC curve *d* can produce the exclusion–adsorption transition conditions (curve *e*). We shall show that the PEAT conditions represent a new character rather than a simple superposition of SEC and LAC.

STATISTICAL SUM OF A MACROMOLECULE WITHIN AN ADSORBENT PORE

In the absence of any steric restrictions, the statistical sum of a macromolecule is proportional to the number of conformations that a given chain can assume. When a macromolecule is confined within a pore and if the walls of this pore present solely steric hindrances to the polymer

chain, the number of possible chain conformations decreases. Consequently, both the statistical sum and the distribution coefficient of the macromolecule also decrease. If adsorptive interactions exist between polymer segments and pore walls, then the statistical weight must be taken into account for each polymer conformation. The number of possible conformations of a macromolecule inside the pore is again lower than in the free interstitial solution. However, some of these inside conformations seem to be energetically more advantageous. Such conformations assume higher statistical weight. As a result, the statistical sum and the distribution coefficient of the macromolecule rise within the pores in comparison with the free solution.

Let us consider the conformation number Q_0 of a free, unrestricted macromolecule with one end fixed in a particular point of space. $Q(z_0)$ denotes the conformation number of a macromolecule situated in the pore at a distance z_0 from any pore wall. The value $K(z_0) = Q(z_0)/Q_0$ obviously represents the probability of finding this macromolecule at a given distance from the wall. By applying the above-mentioned model of the ideal macromolecule confined within a slit-like pore, the $K(z_0)$ values were calculated for several different values of ε[5].

It was found that the $K(z_0)$ values change with the distance between the end of the macromolecule and the pore wall. When $\varepsilon = 0$, i.e. in the absence of attractive interactions between sorbent surface and polymer segments ('ideal' SEC conditions), $K(z_0)$ decreases when the macromolecule approaches the pore wall. This effect is especially evident at distances smaller than the radius of gyration R of the macromolecule. The drop in $K(z_0)$ is caused by a decrease in the number of possible conformations of the macromolecule when approaching the pore wall. In contrast, $K(z_0)$ increases with decreasing distance between macromolecule and the pore wall in the case of LAC. Finally, $K(z_0)$ does not depend on the distance between pore wall and macromolecule at $\varepsilon = \varepsilon_{cr}$, i.e. at the critical adsorption point. In other words, the statistical sum of a macromolecule remains constant at any distance from the pore wall and coincides with the statistical sum of the chain in free solution. Formally, this situation can be treated as a constant number of chain conformations at any pore site. In fact, the conformation number of the macromolecule at the transition point is finite and it decreases when the chain approaches the pore wall. On the other hand, the adsorptive interactions augment the statistical weight of remaining conformations so that the overall statistical sum of the macromolecule remains constant. It is interesting to try to explain how this compensation is realized and what changes in the polymer structure accompany this compensation process.

STRUCTURE OF A MACROMOLECULE WITHIN A PORE AT THE CRITICAL ADSORPTION POINT

Let us consider an ideal macromolecule in the free volume. Let (x_0,y_0,z_0) and (x,y,z) be the coordinates of the ends of the macromolecule. The simplest structural characteristic of a polymer coil is the average concentration of segments $< n > = N/V$, where N is the number of segments and V is the average volume of the polymer coil. It is possible to define V as the volume of a sphere with a gyration radius equal to the average gyration radius of the polymer chain $R = (NI^2/6)^{1/2}$. Then the average concentration of segments is:

$$< n > = (3/4\ \pi)N(5/3\ R^2)^{-3/2} \propto N^{-1/2} \qquad (2)$$

It is known that the segment concentration in the polymer coil decreases with distance from the centre of mass, r_g, in accordance with the Gaussian function:

$$n(r_g) = n_{max} \exp(-3r_g^2/2R^2) \qquad (3)$$

where:

$$n_{max} = N(2\pi R^2/3)^{-3/2} \qquad (4)$$

It can be shown that $< n > \approx n_{max}/3$.

A more sensitive characteristic is the segment density around a given segment of the polymer chain, usually called local density. Local density, $\rho(r)$, is defined as the volume fraction occupied by the other segments within a sphere of radius r around the given segment. Local density may have a marked effect on the intramolecular segmental motion and determines the reaction and catalytic ability of macromolecules in solution. At small r, the local density $\rho(r)$ is high, and its value is independent of N. With increasing r, $\rho(r)$ decreases rapidly, and eventually at $r \approx R$ the local density approaches a much smaller value $\rho(R) \propto N^{-1/2}$.

In the following, we discuss not such an integral characteristic as local density but another density characteristic defined as segment concentration within a thin planar layer located at distance z from the one chain end. We place one end of the chain at an arbitrary distance z_0 from the adsorbent surface, and therefore $\rho(z_0,z)$ will now be a

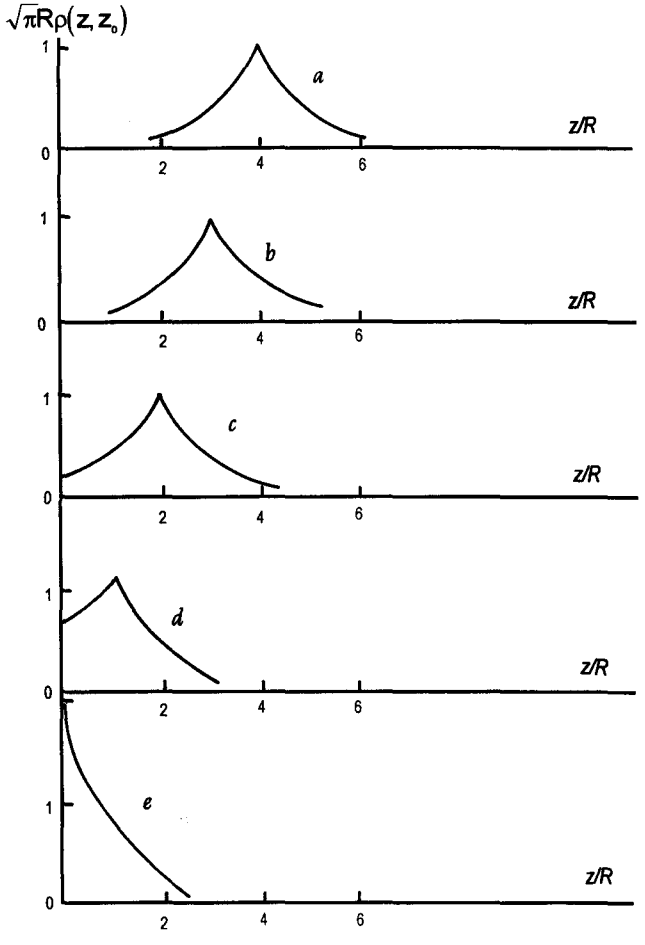

Figure 2 Distribution of chain concentration $\rho(z,z_0)$ around one of the ends of an ideal macromolecule inside a slit-like pore at the critical adsorption point. Distance of end of macromolecule from pore wall, z_0/R: (a) 4, (b) 3, (c) 2, (d) 1, (e) 0

function of two arguments: z and z_0. An exact formula for the $p(z_0,z)$ function was obtained[26] for an ideal chain at the critical conditions, and typical profiles are shown in *Figure 2*. For a chain in a free volume (when $z_0 >> R$), $\rho(z_0,z)$ is symmetrical function and can be described by the asymptotic equations:

$$\rho(z_0,z) \approx \begin{cases} \pi^{-1/2}R^{-1}\left\{\dfrac{\exp[(z_0+z)^2/(2R)^2]}{(z_0+z)^2/(2R)^2}+\dfrac{\exp[-(z_0-z)^2/(2R)^2]}{(z_0-z)^2}\right\} \\ \pi^{-1/2}R^{-1}\{1+(z_0-z)^2/(2R)^2-\pi^{1/2}|z_0-z|/(2R)\} \end{cases} \quad (5)$$

At $|z - z_0| < 2R$, one may write:

$$\rho(z,z_0)=\pi^{1/2}R^{-1}\left(1-\frac{\pi^{1/2}}{2R}|z-z_0|\right) \quad (6)$$

and at $|z - z_0| >> 2R$:

$$\rho(z,z_0)=\pi^{1/2}R^{-1}\left(\frac{2R}{z-z_0}\right)^2\exp\left[-\left(\frac{z-z_0}{2R}\right)^2\right] \quad (7)$$

Similarly to the case when the local density is calculated with respect to a spherical area, the density function $\rho(z_0,z)$ also decreases rapidly with the distance $|z - z_0|$.

As is known, the distribution of the end-to-end distances of an ideal polymer chain does not depend on the direction, and can be described by the Gaussian function. For example, considering coordinate z, we can write:

$$P_0(z,z_0)=(2\pi^{1/2}R)^{-1}\exp\left[-\left(\frac{z-z_0}{2R}\right)^2\right] \quad (8)$$

The spatial distribution of the polymer segment concentration is symmetrical as regards the distance from the locus (x_0,y_0,z_0), i.e. from the locus of one chain end. The segment concentration decreases monotonically with distance from the chain end.

As evident is from equations (5)–(8), the distribution functions $\rho(z,z_0)$ and $P_0(z,z_0)$ depend only on the difference in distance $(z - z_0)$ and are independent of the z_0 value itself, i.e. they are independent of the position of the chain end in the space.

If a macromolecule is situated inside a slit-like pore, then the above restrictions vanish in the directions parallel to the pore walls (i.e. the x and y coordinates). In other words, the Gaussian distribution of the end-to-end distances is preserved. Analogously, the chain concentration distributions ρ are preserved in these directions, i.e. $\rho(x,x_0)$ and $\rho(y,y_0)$.

In contrast, the distributions $P(z,z_0)$ and $\rho(z,z_0)$ in the direction normal to the pore wall become dependent not only on the difference $(z - z_0)$ but also on the distance z_0 of a particular chain end from the wall.

Figures 2 and 3 show the distributions $\rho(z,z_0)$ and $P(z,z_0)$ for several real distances z_0 of the chain end from the wall. At a long distance from the pore wall, i.e. in practically unrestricted space, the distribution of the distances between chain ends is Gaussian. At the same time, the distribution of the segment concentration around the particular chain end is symmetrical.

When the chain end approaches the pore wall, the distribution functions $\rho(z,z_0)$ and $P(z,z_0)$ decrease.

When one chain end touches the pore wall, the macromolecule at the CAP can be approximated by a chaotically coiled chain that is cut into two halves.

It has been shown[27] that the chain end distribution at the CAP can be described by a simple equation in the case of an ideal macromolecule situated inside a pore:

$$P(z,z_0)=(2\pi^{1/2}R)^{-1}\left\{\exp\left[-\left(\frac{z-z_0}{2R}\right)^2\right]+\exp\left[-\left(\frac{z+z_0}{2R}\right)^2\right]\right\} \quad (9)$$

$P(z,z_0)$ transforms into a common Gaussian distribution, centred around point z_0, if the distance of the macromolecule from the pore wall increases (i.e. $z_0 >> R$).

On the other hand, $P(z,z_0)$ assumes the form of a half-Gaussian function for a macromolecule one end of which just touches the pore wall. It seems that when one end of a

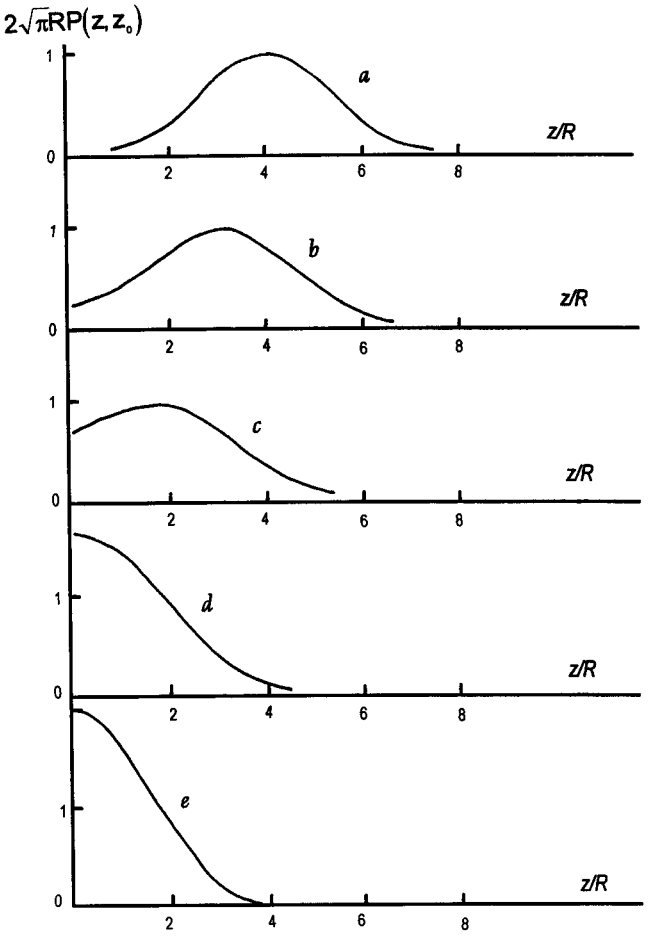

Figure 3 Functions describing the distribution of end-to-end distance $P(z,z_0)$ of an ideal macromolecule inside a slit-like pore at the critical adsorption point. Curves (a)–(e) as in *Figure 2*

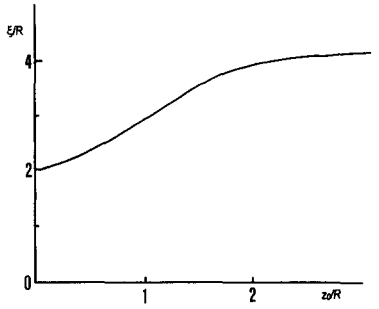

Figure 4 Dependence of elongation of an ideal macromolecule, ξ/R, on distance of its end from pore wall. The macromolecule is inside a slit-like pore at the critical adsorption point

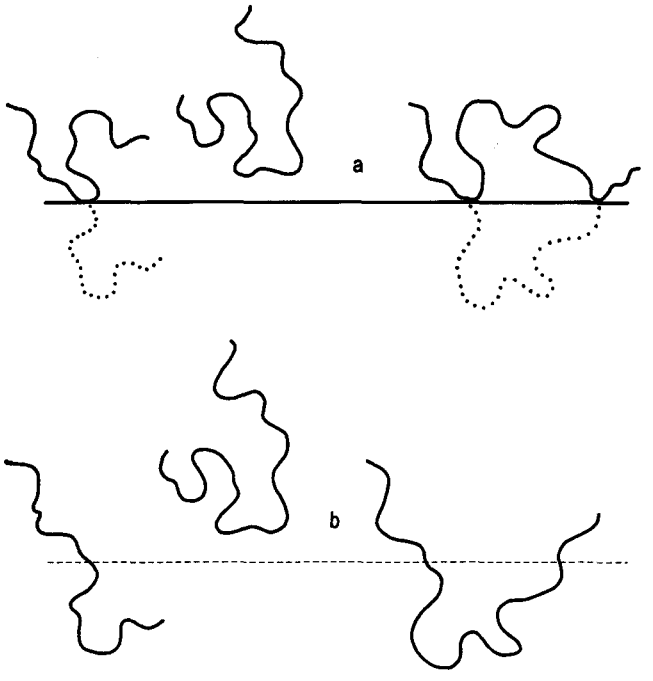

Figure 5 (a) Conformation of the macromolecule inside a pore at the critical adsorption point. The point indicates the conformation of the macromolecule that would be realized in the absence of pore walls. (b) Conformations of a macromolecule without external limitations. The point indicates the position of a fully permeable wall

macromolecule touches the pore wall the concentration distribution $\rho(z,z_0)$ is again expressed by equation (6) but multiplied by a factor of 2.

We take the following steps to describe the changes in the chain dimensions in the z-direction for a macromolecule at the pore wall at the critical adsorption point. We define the mean elongation of a macromolecule ξ as the distance at which the chain concentration decreases by 10% from its maximum value. As is evident from *Figure 3a*, the value of ξ reaches $\sim 4R$ for an ideal macromolecule, if its distance from the wall is large enough or if it is situated in the free solution. However, the macromolecule shrinks when its end approaches the pore wall at the critical adsorption point. This means that the elongation of the macromolecule decreases. *Figure 4* shows the dependence of ξ at the critical adsorption point on the distance of the chain end from the pore wall. The elongation ξ is related to the mean radius of gyration of a macromolecule at the CAP.

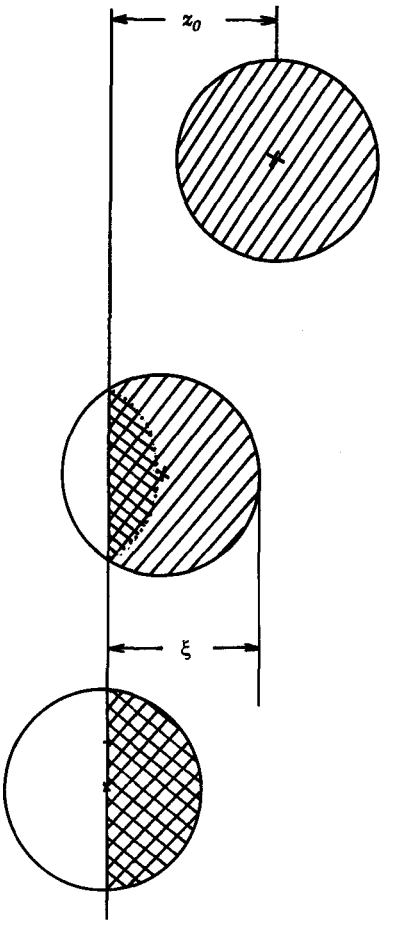

Figure 6 Representation of structure of a macromolecule inside adsorbent pores at the critical adsorption point. The cross indicates the position of the excluded end of the macromolecule

The analysis of equation (7) and *Figures 2 and 3* shows that the macromolecule assuming an arbitrary distance from the pore wall behaves peculiarly: as if it were able to penetrate the pore walls. At the same time, the small parts of the chain appearing 'behind' the wall form a mirror image. Therefore we can suppose that, formally, the pore wall at the critical adsorption point acts as a 'mirror' which 'reflects' the conformations of polymer chains that would be rejected due to steric hindrances (*Figure 5*).

At the same time, the statistical weight of each conformation should be considered equal to unity. The number of conformations of a macromolecule in arbitrary space of a pore equals the number of conformations of the same polymer chain in the free solution. In this way, the 'mirror reflection' of part of the conformations supports the constancy of the statistical sum of a macromolecule at any distance from the pore wall. Consequently, the distribution coefficient of an ideal macromolecule at the critical adsorption point is equals to unity, independent of both the pore diameter and the molar mass of the homopolymer.

The structure of a macromolecule in a pore at the critical adsorption point can be represented in a qualitative way when the Debye–Bueche model[28] is considered. Here, the macromolecule is represented as a sphere with a constant segment density (*Figure 6*). This model has been used in the past for the qualitative description of various characteristics of dilute polymer solutions. Under SEC conditions the Bueche model is equivalent to the model of hard spheres moving inside a pore and occasionally gently touching its

walls. For large pores, this model leads to conclusions that are consistent with the results obtained by applying the Casassa theory, although the latter works with a much more realistic model of an ideal macromolecule. In contrast to behaviour in SEC, macromolecules change their shape at the critical adsorption point. Their initially spherical shape is transformed to a form of more or less flattened droplets. The degree of deformation of the droplets depends on their distance from the pore walls and it increases when the macromolecules approach the wall. The maximum degree of flattening of the chain is reached when one of its ends appears in the immediate proximity of the pore wall, i.e. when it touches it. In this case, the macromolecule assumes the shape of a hemisphere.

The segment concentration inside the coils is uniformly distributed when the globular macromolecules are situated far from the wall. However, the segment concentration distribution becomes uneven if the macromolecules approach the pore walls. The segment concentration increases in the region of flattening of macromolecules (*Figure 6*).

This model describes only approximately the changes in macromolecular dimensions in the direction normal to the pore wall. On the other hand, this notion does reflect the complex character of the segment density changes in the interior of a macromolecule when it approaches the pore wall.

Here, we should stress again that the above analysis relates to an ideal macromolecule. We have neglected the volume interactions among chain segments. In a thermodynamically good solvent, however, the actual distribution of the end-to-end distances and the actual profile of segment concentrations differ from that given by equations (8) and (6) and represented in *Figure 2a* and *Figure 3a* for macromolecules in the unrestricted space. Naturally, some deviations from equation (8) and *Figure 3* are also to be expected for macromolecules exhibiting volume interactions of chains that are situated inside pores at the critical adsorption point, i.e. at the point of exclusion–adsorption transition. Further development of the theory will allow more precise analysis of the latter problems.

DISCUSSION

We have demonstrated that the structure of macromolecules is rather peculiar in the pores at the critical adsorption point, i.e. at the exclusion–adsorption transition: the structure of macromolecules does change with their distance from the pore walls. In this situation, macromolecules resemble coils, parts of which have been cut off. However, the statistical sum of polymer chain remains the same at any site within the pore and equals the statistical sum of the identical macromolecule within the free solution. Therefore the macromolecules of a homopolymer with any molar mass leave the l.c. column together with the zone of their initial low-molecular solvent. As result, the macromolecules can be separated only according to the type and number of functional end groups, irrespective of both their molar mass and molar mass distribution. In accordance with the theoretical predictions[29], oligomers have successfully been separated according to end-group number[11,12].

Molecular characterization of block copolymers represents another possible practical application of LC CAP. One kind of block can be considered as a 'heterogeneity' that can be separated according to its molar mass, while the blocks of the other kind can be made 'chromatographically invisible' by setting appropriate conditions to allow their elution at the critical adsorption point. From theoretical considerations, this procedure has been proposed by Skvortsov and Gorbunov[30] and confirmed experimentally[13–16]. A similar approach can also be adopted theoretically[30] for graft copolymers where the side chains can be made 'chromatographically invisible'. Recent experiments[20] confirmed the expectation, at least for short grafts. Similarly, theory predicts the possibility of applying LC CAP to the characterization of cyclic oligomers in the presence of chemically identical linear structures[31]. These predictions were confirmed by e.g. Gorshkov *et al.*[32].

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