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Mass Transfer of Macromolecules in Steric Exclusion Chromatography. 1. Diffusional Transport in the Pores of Steric Exclusion Chromatography Materials

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ABSTRACT: The analysis of peak broadening as a function of flow rate in steric exclusion chromatography (SEC) of polymer samples gives information about transport processes of macromolecules in the pores of the stationary phase. Two different chromatographic materials—VITX glass and TSK polystyrene—were in studying the hindrance to diffusion and its dependence on porosity, pore size, and partition coefficient. For both stationary phase materials the hindrance to diffusion was considerably greater than expected, as shown by obstruction factor values around 0.2. Furthermore, the obstruction factor was found to be independent of the partition coefficient K in the range $0.35 < K < 1$. An increase of the obstruction factors calculated from peak broadening is found at lower values of K for the polystyrene column.

1. Introduction

It now seems generally accepted that the separation effect in gel permeation chromatography (GPC) is mainly based on steric exclusion of molecules from part of the internal pore volume. As in any other chromatographic process the separation can be described by equilibrium thermodynamics and—with the exception of some limiting cases—not by hydrodynamics. The coefficient K of the partition of molecules between the internal pore volume, V_i, and the interstitial volume, V_0, is given by the ratio of the configuration integral of the attainable positions in the pores and the integral in the same volume of free solution.[1,2] The separation effect of this type of chromatography—usually called GPC—is better described by the terminology "steric exclusion chromatography" (SEC).

Some effects however remain to be investigated concerning the behavior of molecules in SEC: (i) the possible influence of enthalpy effects (adsorption and nonideal behavior of flexible macromolecules), (ii) the diffusional transport of molecules in the internal pores, especially in the separation range, i.e., under the influence of steric hindrance, (iii) the possibility of convective transport of molecules in the internal pores and the resulting change in the separation mechanism, and (iv) the behavior of macromolecules in the interstitial volume if their radius is no longer small compared to the radius of the external pores.

In this series of papers theoretical considerations and experimental results concerning the last three topics are presented. The present paper is concerned with the diffusional transport of molecules in the internal pores. Steric exclusion from part of the internal volume might lead to a hindrance of the transport. Even if no exclusion takes place, the diffusion coefficient in porous materials is lowered compared with that in the free solution. While having no influence on the distribution coefficient, such effects deteriorate the mass transfer and, as a result, increase the peak broadening.

Diffusional transport in internal pores influences peak broadening in most versions of chromatography. Due to their low diffusion coefficient, macromolecules are especially suited for the investigation of diffusional mass transfer.

2. Theoretical and Experimental Background

The SEC of macromolecules normally operates in a range of velocities where longitudinal dispersion can be neglected and the broadening in the interstitial volume is independent of the flow rate ("eddy dispersion").

The broadening due to mass transfer in the stationary phase is proportional to the fow rate, $\dot{V}$. Therefore, in the

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case of the SEC of macromolecules, this part of the dispersion can be easily determined as the flow rate dependent part of the broadening.

The mass transport in the stationary phase is composed of diffusional transport and—if present—of the adsorption process. The adsorptive broadening can be important if the absorption has no measurable effect on the elution volume, V_e.

If one describes the separation process of steric exclusion under the influence of adsorption by

$$V_e = V_0 + KV_i + K_{ads}V_i \quad (1)$$

(where K_{ads} is dependent on K; compare ref 3–5), there results from the general equations of peak dispersion as given by Kubin[6,7] the following equation for the variance of peak broadening due to the permeation process, μ_{2perm}:

$$\mu_{2perm} = \tfrac{1}{30}(KV_i + 2K_{ads}V_i + K_{ads}^2V_i/K)\dot{V}d_p^2/D_s + 2K_{ads}V_i\dot{V}/k_d \quad (2)$$

d_p is the diameter of the particles of the packing, D_s the diffusion coefficient in the stationary phase, and k_d the kinetic constant of desorption.

The broadening due to diffusion and that due to adsorption are thus coupled processes. If $d_p^2/D_s \ll k_d^{-1}$, i.e., if the mean time of diffusion in the pores of a particle is small compared with the mean time of desorption, and if K_{ads} is not small compared with K, one gets from eq 2

$$\mu_{2perm} = 2K_{ads}V_i\dot{V}/k_d \quad (3)$$

Giddings[8] obtained the same results by using a simple random walk approach.

If K_{ads} and k_d^{-1} are sufficiently small, there results from eq 2 the well-known equation

$$\mu_{2perm} = \tfrac{1}{30}KV_i\dot{V}d_p^2/D_s \quad (4)$$

The separation of the effect of dispersion due to diffusional transport in the internal pores and the dispersion due to the kinetics of adsorption is a difficult task. Giddings, Bowman, and Myers[10] obtained the different contributions by using two solvents. Their neglect of coupled diffusion/adsorption terms in eq 2 and their assumption that K_{ads}/k_d is the same in both solvents seem questionable. In the present paper, the possible contribution of adsorptive broadening will first be neglected in the evaluation of the experimental results. As shall be demonstrated, for most cases studied the results obtained rule out the possibility of a significant broadening due to adsorption.

From the permeation dispersion, the diffusion coefficient D_s is calculated, which can be related to the diffusion coefficient in free solution, D, by the obstruction factor γ

$$D_s = \gamma D \quad (5)$$

As the real network of pores can only be described by simple approaches, a realistic theoretical description of the diffusional transport in pores provides difficulties.

The obstruction factor can be looked upon approximately as the product of a tortuosity factor τ and a constriction factor κ[11,12]

$$\gamma = \tau\kappa \quad (6)$$

The tortuosity factor describes the elongation of the mean path length of a molecule due to the tortuosity of the pores. Pismen[13] calculated for a network of cylindrical pores

$$\tau = 1 - \tfrac{2}{3}(1 + \epsilon)(1 - \epsilon)^{3/2} \quad (7)$$

where ϵ is the porosity of the material. τ lies between 1 (free solution) and $^1/_3$. The effective porosity (and with it τ) should decrease with increasing steric exclusion.

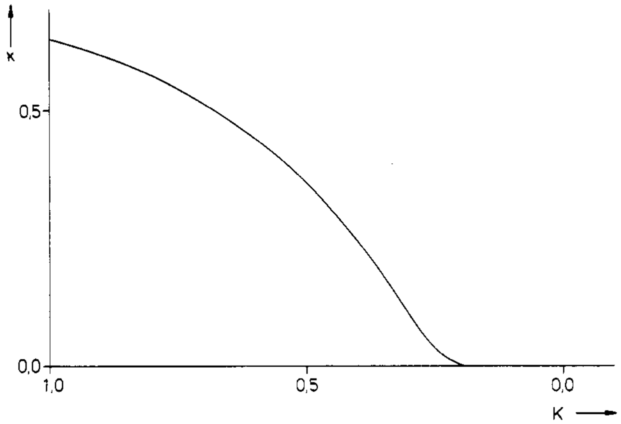

Figure 1. Distribution coefficient K and constriction factor κ calculated for rigid spherical molecules diffusing in series of pores of alternating radii r and $2r$.

For the obstruction of diffusion by constrictions Giddings[8] deduced

$$\kappa = (\langle A\rangle\langle 1/A\rangle)^{-1} \quad (8)$$

where $\langle A\rangle$ is the local pore cross section.

An example shall demonstrate the influence of steric exclusion on the constriction factor: A rigid sphere with radius a diffuses through a series of alternating cylinders of equal length with radius r and $2r$. The coefficient of distribution of a sphere between a cylindrical pore and free solution is calculated by the equation

$$K = (1 - a/r)^2 \quad (9)$$

With the help of this equation, values of K can be calculated for the pore system; κ is calculated from eq 8.

The calculated values (Figure 1) show that steric exclusion should have a substantial influence on κ.

Dead-end pores result in an additional decrease of D_s.[14] Normally, the number of effective dead-end pores will increase with increasing steric exclusion.

Finally the increased friction of the molecule in the pores causes a further decrease of γ; this obstruction effect, too, should increase with the ratio a/r.[15,16]

Experimental investigations on the diffusion in porous systems are rather rare. The relatively small obstruction which has been found in packings of nonporous materials (Knox and McLaren,[17] for example, determined for packings of spheres an obstruction factor of 0.6) has led to the assumption that for the stationary phase in chromatography an obstruction factor of about $^2/_3$ is adequate (e.g., ref 18).

Investigations with consolidated porous materials, however, gave smaller values of γ. Colton, Satterfield, and Lai[19] found at plates of deactivated porous glass for polymers obstruction factors of 0.2–0.4. Down to very small values of K the authors found no dependence of the obstruction on the steric exclusion, a result which is rather surprising if one considers the dependence of γ on K postulated above on theoretical grounds.

Giddings and co-workers[10] determined the permeation and from it γ of polymers on a packing of CPG glass particles with small pores. They found obstruction factors which were even lower than those obtained by Colton and co-workers. From their values of γ, which showed rather strong scattering, no dependence of γ on K can be seen.

According to the authors, the low obstruction factors found might be explained by special effects of small pores or by experimental flaws.

Table I
PS Standards with Molecular Weight Averages According to the Manufacturer

standard no.	batch no.	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
S1	26971	2 100	1 950	
S2	25169	4 000	3 100	
S3	25171	10 000	9 600	
S4	25168	20 800	20 000	
S5	25170	33 000	36 000	
S6	41995	111 000	111 000	
S7	41984	200 000	193 000	
S8	25166	498 000	404 000	
S9	25167	867 000	773 000	
S10	61970	2 610 000	1 990 000	
S11	F-870	9 500 000		1.03

As the permeation dispersion is inversely proportional to the obstruction factor, small factors have a considerable negative effect on the broadening in chromatography, which justifies further research on this subject.

In the experimental investigations described in the next section, the dependence of γ on K, the pore diameter, the porosity, and the structure of the packing shall be examined. The μ_2–$\dot{V}$ relation is determined and from its slope the permeation dispersion and D_s are calculated.

3. Experiments

3.1. Materials. Two SEC materials were investigated:

1. VITX Glass (Perkin-Elmer). This was a sieved and surface-modified 36–44-μm fraction of porous glass (CPG) with uniform pore diameter. The materials were obtained ready packed in columns of 50-cm length and 2.6-mm i.d. according to the distributor. A rough estimate of the pore diameters of the materials can be obtained from Telepchak,[20] although they probably refer to other lots of the materials. Hence the pore diameter of the materials as determined by Hg porosimetry is 84 Å for VITX-328, 171 Å for VITX-106, and 321 Å for VITX-5150.

2. Polystyrene Gel TSK GH6 (Toyo Soda). This material was packed in columns of 2-ft length and $^3/_8$-in. i.d. TSK GH8, which according to the producer has a twofold flow resistance, has a particle diameter of 8 μm;[21] hence for the material H6, 10 μm should be a good estimate.

The materials TSG G 3000H6, G 4000H6, G 5000H6, and G 6000H6 were used. Anionically polymerized polystyrene standards as supplied by Waters Associates and Toyo Soda (standard 11) were used (Table I). In the case of the VITX columns the solvent was $CHCl_3$; for the TSK columns it was THF.

3.2. Procedures. The experimental procedure shall first be described for the case of the VITX columns.

A total of 25 μL of each of the standards 2–9 with a concentration of 500 ppm was injected at four different flow rates ranging from 0.1–1.0 mL/min. For the determination of the calibration curve the standards toluene, S1 (500 ppm each), S10 (125 ppm), and partly S11 (63 ppm) were also used.

The flow rate showed long-term fluctuations, probably due to changing performance of the pumping valve. During one run, however, the flow rate can be regarded as constant.

At the highest flow rate its effective value was determined volumetrically. A 10-mL volumetric flask was sealed with foil in order to prevent evaporation. The foil was pierced with the outflow capillary and the flow rate calculated from the observed filling time.

The elution volume of the toluene standard was taken to be independent of the flow rate. The effective flow rate at slower velocities was calculated by using the elution time of toluene.

At the TSK columns, 50-μL aliquot solutions of the standards were injected, partly at five different velocities, ranging from 0.1–1.0 mL/min, and partly for the determination of the calibration curve, only at one velocity. The concentrations were 600 ppm for toluene and the standards S1–S9, 125 ppm for standards S10, and 31 ppm for standard S11.

The flow rate was again determined with the help of the elution volume of toluene, which was determined volumetrically at the highest flow rate. Due to the higher separation capability of the columns, toluene could be added to each standard solution and used as an internal standard.[22]

Table II
Slopes of the μ_2-$\dot{V}$ Relation

column	standard	KV_i, mL	slope × 10^3, mL min
VITX-328	S2	0.52	12.4
	S3[a]	0.25	15.9
VITX-1068	S2	1.15	22.3
	S3	0.93	24.9
	S4	0.72	29.0
VITX-5150	S2	1.08	29.4
	S3	0.97	46.8
	S4	0.86	44.5
	S5[a]	0.72	71.4
TSK 3000	S4	1.04	97.4
TSK 4000	S5	3.95	40.5
	S7	0.94	76.5
TSK 5000	S7	4.67	52.1
	S9	1.67	106.9
TSK 6000	S4	9.40	29.6
	S5	8.99	28.5
	S7	6.98	63.9
	S9	4.29	91.6

[a] For these measurements the broadening at the highest flow rate was not used for the regression.

4. Data Evaluation and Discussion

The variances μ_2 of the elution curves were calculated from the tangents at the points of inflection, and elution volumes were determined at the peak maximum.

While the elution volume of excluded polymers and of samples with higher values of K showed no significant variation with the flow rate, samples with small values of K showed a decrease of the elution volume (measured at the peak maximum) with increasing velocities; in this range, the μ_2–$\dot{V}$ relation flattened or even decreased with higher flow rate. These samples showed a strongly asymmetric elution curve.

Such behavior is in accordance with the theory of chromatographic broadening. From the equations given by Kubin,[6] there follows for the skewness of the elution curve by permeation the equation

$$\frac{\mu_{3\text{perm}}}{\mu_{2\text{perm}}{}^{3/2}} = \left(\frac{15}{98} \frac{\dot{V} d_p{}^2}{K V_i D_s} \right)^{3/2} \tag{10}$$

The skewness and the resulting shift of the peak maximum increase with decreasing values of KV_i (and D_s).

The variance, however, can only be calculated from tangents at the inflection points exactly in the case of Gaussian distributions; from skewed curves one gets values which are too small. This may also be the reason that other authors[23,24] found a decrease of the "variance" with increasing flow rate near the exclusion limit.

In this work the measurements in this region were not used for further calculations.

With the exception of this region of low values of K the broadening was, as expected, found to be a linear function of the flow rate. With increasing molecular mass the slope of the μ_2–$\dot{V}$ relation first increases (decrease of D_s) and then decreases (decrease of KV_i). Excluded standards, of course, showed the broadening $\mu_{2\text{mob}}$ only, which was independent of the flow rate (compare Figure 1 in part 2 of this series).

The slopes calculated from the μ_2–$\dot{V}$ relations of permeating standards are listed in Table II.

The interstitial volume V_0 was determined by excluded standards. The exact procedure of the calculation of V_0 of the TSK columns—where external effects complicated the determination of V_0—and on the estimation of V_0 in

Table III
Diffusional Obstruction as a Function of Porosity and Steric Exclusion

column	standard	ϵ	K	qd_p^2/γ, μm^2	γ
VITX-328	S2	0.476	0.591	319	0.17
	S3		0.284	488	0.11
VITX-1068	S2	0.761	0.839	261	0.20
	S3		0.679	205	0.26
	S4		0.526	221	0.24
VITX-5150	S2	0.642	0.900	365	0.15
	S3		0.808	369	0.15
	S4		0.717	284	0.19
	S5		0.600	385	0.14
TSK 3000	S4	0.459	0.118	754.5	0.004
TSK 4000	S5	0.598	0.356	56.6	0.060
	S7		0.085	173.4	0.019
TSK 5000	S7	0.625	0.397	23.9	0.140
	S9		0.142	57.9	0.058
TSK 6000	S4	0.634	0.787	25.1	0.133
	S5		0.753	17.3	0.193
	S7		0.585	19.5	0.171
	S9		0.359	19.3	0.173

the case of the TSK 6000 column—where no excluded standard was at hand—shall be described in the third paper of this series. The volume of $V_0 + V_i$ was derived from the elution volume of the toluene standard. From V_0, V_i, and the volume of the empty columns the internal porosity of the materials was calculated. In the case of the VITX columns, the volume of the empty column was determined by filling an emptied column with water and weighing; in the case of the TSK columns it was calculated by using the data given by the manufacturer.

The slope of the μ_2–V relation equals $qKV_id_p^2/\gamma D$ (where q is a form factor, which equals $^1/_{30}$ in the case of spheres) if the contribution of the kinetics of adsorption can be neglected.

KV_i can be determined experimentally, and the diffusion coefficients can be calculated from relations between D and the molecular mass given in the literature.

For the calculation of D of PS in THF the relation given by Mandema and Zeldenrust,[25] $D = 3.45 \times 10^{-4}M^{-0.564}$ cm^2/s, was used. D of PS in $CHCl_3$ was calculated from the equations $D = 1.61 \times 10^{-4}M^{-0.525}$ cm^2/s in the range $M < 36\,000$ and $D = 3.72 \times 10^{-4}M^{-0.553}$ cm^2/s in the range $M > 100\,000$.[19] The calculated values of qd_p^2/γ are presented in Table III together with K and ϵ.

In the range $K > 0.35$, qd_p^2/γ and with it the diffusional obstruction is found to be independent of K, which agrees with the observations of Colton and co-workers.[19] As has been shown in the theoretical part of this work, such an independence would not be expected if one approaches the flexible macromolecules as rigid spheres. Even the VITX glass possesses a broader range of pore diameters in spite of the very narrow distribution found by Hg porosimetry.[26] This should, as shown in Figure 1, lead to a strong dependence of γ from K, together with the tortuosity, the dead-end pores, and frictional effects. The independence of γ from K found might be a result of the flexibility of the macromolecules, although especially for the frictional hindrance such behavior is rather unexpected.

The influence of adsorption should decrease with decreasing pore surface (increasing pore diameter). The factor qd_p^2/γ, however, is found—in the case of the VITX material—to be a function of the porosity and not of the pore diameter, which leads to the conclusion that the broadening in these cases is not significantly influenced by adsorption.

Also the independence of qd_p^2/γ from the molecular mass in the case of the VITX columns and the column TSK G 6000H6 leads to the conclusion that adsorption plays no significant role in those systems.

For small values of K, however, a dependence of qd_p^2/γ on steric exclusion was found for the TSK columns, which might be the result of both adsorptive effects and a dependence of the hindrance of diffusion on exclusion in this region. Here, the experimental results only allow the tentative conclusion that in this range the dispersion due to transport in the internal pores is significantly greater than would be expected if one neglects the possibility of adsorption and the dependence of γ on K. The dependence of qd_p^2/γ found in this range is too great to be explained by an inexact measurement of KV_i or μ_2.

The fact that Colton and co-workers found no dependence of the obstruction factor on K at CPG glass down to very small values of K might result from a more uniform pore size distribution compared with that of the TSK material.

For the examination of the influence of the porosity and of K on the broadening it was sufficient to look at the term qd_p^2/γ. Now the values of q and of d_p shall be estimated to get the absolute values of γ.

The VITX material consists of broken pieces of glass, so for the configuration factor q and the radius only a rough approximation can be given. The 36–44-μm sieving fraction shall be approximated as spheres ($q = {}^1/_{30}$) of 40-μm diameter.

For the spherical TSK material a configuration factor of $^1/_{30}$ and a diameter of 10 μm should be rather good estimates; there are, however, no data concerning the size distribution of the particles.

The obstruction factors calculated (Table III) lie significantly beneath the value of 0.6 quoted above for nonconsolidated packings of spheres. For the case of the VITX particles, a decrease of γ with decreasing porosity is found, as would be expected from the theoretical considerations and as has been found by Colton, Satterfield, and Lai,[19] too. The values found in this work, however, are about 50% below the values found by these authors at about the same porosity. This fact might be the result of inaccurate estimates of q and d_p made for these materials.

The high obstruction of diffusion found for the TSK materials might be the result of the broad distribution of pore sizes of this macroporous gel.

The results presented show that the obstruction of diffusion has a significant influence on the permeation distribution and that especially at small values of K the permeation term is much greater than one would anticipate from simple theories of broadening, which assume γ to be constant. A detailed interpretation of the experimental results needs a deeper understanding of the diffusion, especially of partly excluded molecules, in porous media. On the other hand, the study of chromatographic broadening is a good tool for the experimental checking of theories of mass transfer in pores.

For the reduction of the permeation term by a proper design of the packing, not only the shape and diameter of the particles should be considered but emphasis should be given also to an open structure of the pores and to a maximum porosity.

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Mass Transfer of Macromolecules in Steric Exclusion Chromatography. 2. Convective Transport in Internal Pores (Hydrodynamic Chromatography)

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ABSTRACT: The transport of solute molecules through internal pores in steric exclusion chromatography is, under certain circumstances, not caused by diffusion but by convection ("hydrodynamic chromatography"). This results in a change of the separation mechanism and leads to an acceleration of the mass transfer. The retention behavior of macromolecules in hydrodynamic chromatography is examined. A drastic decrease of the peak broadening compared with diffusional transport in the pores is postulated. This effect is demonstrated to be operating at two porous glass packings having small particle diameters and large, regular pores.

1. Introduction

Under ordinary experimental conditions, the separation effect in steric exclusion chromatography (SEC) is based upon an equilibrium distribution between the interstitial volume and the stationary internal pore volume.[1,2] DiMarzio and Guttman[3-5] postulated an alternative separation mechanism based on the different residence times of molecules of distinct size in pores which are convectively permeated by the solvent. Verhoff and Sylvester[6] combined this idea with sieving effects at the pore entrance. As DiMarzio and Guttman have shown, this separation mechanism leads not only to different retention times but also to a decrease in peak broadening compared to the equilibrium distribution model.

As we show in this work, "hydrodynamic fractionation" is indeed operating in some specific SEC systems. First we give a critical evaluation of the theoretical concepts of this technique.

2. Theory

2.1. Mean Residence Time. Both DiMarzio and Guttman and Verhoff and Sylvester start with rather general assumptions which lead to complex calculations and, as Casassa[1] showed, different results. In this work, we start with the assumption that the flow rate in the internal pores of the separation material is small compared with the flow rate in the interstitial pores. The results of simple deductions based on this simplification will be compared with the results of the above-mentioned authors.

The chromatographic packing has large pores in its interstitial volume and small internal pores. If the internal pores are not large compared with the solute molecules, these may be sieved out from the solvent which flows into the internal pores. The sieving probability P shall be defined as the normed probability that a solute molecule whose center is situated at a stream line leading through an internal pore is actually entering the pore.

Solute molecules which have entered an internal pore flow through it with a mean linear velocity u_s', which, due to their higher probability of residence in regions of higher flow rate, is different from the mean velocity of the solvent in the pore, u_s.

The mean residence time t_e of a solute molecule is the sum of the time it travels in the interstitial volume, t_0, and the time t_i' it travels in the internal pores; t_i' is the fraction of the time t_i that a solvent molecule resides in internal pores.

A molecule which flows through internal pores has a shorter way to travel in the interstitial pores compared with an excluded molecule. If, however, the velocity in the interstitial pores is large compared with the velocity in the internal pores, this difference can be neglected.

Thus the following equation, which is independent of any particular model of pores, can be written:

$$t_e = t_0 + P(u_s/u_s')t_i \qquad (1)$$

Again using the above-mentioned approximation, one gets from eq 1 by multiplying with the volumetric flow rate

$$V_e = V_0 + P(u_s/u_s')V_i \qquad (2)$$

where V_e is the mean elution volume, V_0 the interstitial volume, and V_i the internal pore volume.

Detailed theoretical descriptions of the process of hydrodynamic fractionation are at this time not possible for two reasons: First, the structure of real porous networks

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