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## MECHANISM OF GEL PERMEATION CHROMATOGRAPHY: DISTRIBUTION COEFFICIENT

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### SUMMARY

In a study of the separation mechanism of gel permeation chromatography, we have represented the porous material by a structure built up from randomly distributed identical spheres and the macromolecules by random coils. The relationship derived between molecular weight and accessible pore volume is in excellent agreement with the experimental results.

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### INTRODUCTION

Gel permeation chromatography (GPC) is a type of liquid chromatography in which polymer molecules in solution are sorted according to their size in a column packed with a porous material. The mechanism underlying this separation has been dealt with in an extensive literature<sup>1–24</sup>, from which three major theoretical explanations have emerged: (a) restricted diffusion, (b) steric exclusion and (c) loss of conformational entropy of a macromolecule near a surface.

The restricted diffusion theory was originally proposed by Ackers<sup>6</sup>, and additional work has been carried out by Yau and co-workers<sup>7,18–20,22</sup>, who obtained experimental confirmation<sup>7</sup> of the dependence of the retention volume on the velocity of the mobile phase. However, when we applied our own criterion for the determination of a retention volume—the position of the first statistical moment<sup>25</sup> (see the chapter *Accuracy*, point (d), in the section Experimental)—to their experimental data, no effect of flow-rate on retention volume was observed. So, in our description of the separation mechanism, no attention has been paid to this theory. This leaves the two other theories to be considered. Since, in addition, it can be shown that the “steric exclusion” and “loss of conformational entropy” descriptions lead to similar results<sup>26</sup>, we have restricted our study to the steric exclusion theory.

A feature common to all chromatographic techniques is the distribution of a solute between a mobile and a stationary phase. In GPC, the mobile phase is a liquid stream flowing around the grains in the column; the stationary phase is the same liquid stagnant in the pores of the grains. In a simple theoretical description of GPC, we assume that throughout the column the partition equilibrium of the solute is im-

mediately established and we disregard the adsorption of solute molecules at the surface of the porous material. In order to describe the partition equilibrium of macromolecules, we require a detailed knowledge of the geometry of both the porous material and the macromolecules. We have devoted a separate section of this paper to the geometrical description of the porous material and another to a theoretical description of the macromolecules. Also, in order to verify the theoretical considerations, we have carried out a number of experiments.

At first, the only porous material used in GPC was cross-linked polystyrene gel<sup>27</sup>. This gel is not very suitable for an investigation into the separation mechanism of GPC, for two reasons. Firstly, its behaviour is affected by changes in the experimental conditions, such as pressure, temperature and solvent, and secondly, when techniques designed for the measurement of pore size and pore size distributions of dry porous material are used for swollen gels in solution, the information obtained can hardly be expected to be reliable enough for a verification of the steric exclusion theory. A rigid porous material that does not show any changes upon the various porosity measurements is Porasil. Since, in addition, its structure is also insensitive to varying experimental conditions, we have chosen this material as the porous column packing.

We were also very limited in the choice of macromolecules that we could use in our experiments. We needed macromolecular samples having an accurately determined average molecular weight and a narrow molecular weight distribution. As monodisperse macromolecular samples could not be obtained, we bought samples of polystyrene with a very narrow molecular weight distribution ( $M_w/M_n < 1.1$ ).

Because of the urgent need for accurate experimental data, we have paid special attention to and made improvements on the experimental arrangement.

## EXPERIMENTAL

### *Apparatus*

The experiments were carried out using a simple and rather conventional arrangement, a schematic diagram of which is shown in Fig. 1. The system comprises a storage vessel (a), combined de-gassing-constant level unit (b), sample introduction unit (c), column under investigation (d) and LKB Uvicord detector (e). The eluate is collected in a bottle (f) placed on a Mettler KT7 balance (h). The signal of the detector is fed to a Servogor RE 511 strip-chart recorder (j). A manually controlled marking unit (k) is used to provide the chromatogram with spikes, each of which indicates a certain weight of mobile phase eluted since the injection.

Tetrahydrofuran (THF), containing 0.025% of Ionol as antioxidant, was used as the mobile phase, which was driven through the column at 1.5 ml/min by applying a nitrogen pressure of about 0.3 kg/cm<sup>2</sup> above atmospheric pressure.

The columns used were made of aluminium tubes (1 m long, 8 mm I.D.) and were filled with Porasil C or D (Waters Associates Inc.) by using the dry filling technique developed previously in our laboratory<sup>28</sup>. Data on the columns and the Porasils are listed in Table I. Polystyrene standards with a narrow molecular weight distribution (Pressure Chemicals) dissolved in THF were used as samples for the chromatographic measurements. The specifications of these standards are listed in Table II. All experiments were carried out at room temperature ( $23 \pm 2^\circ$ ).

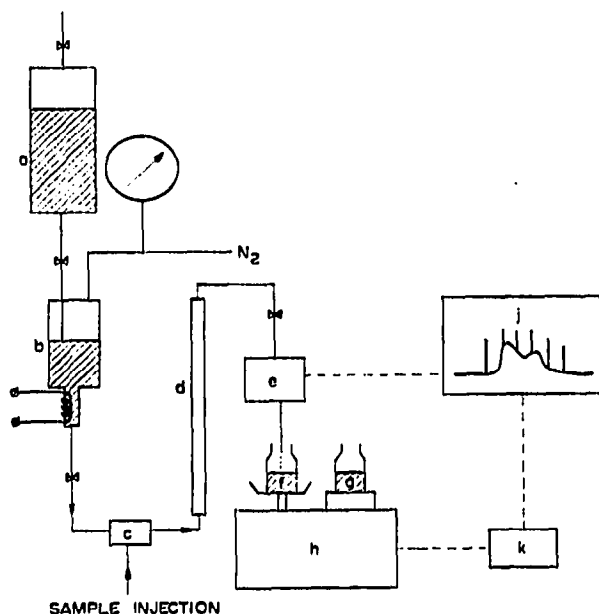


Fig. 1. Experimental arrangement for GPC experiments. For explanation, see text.

TABLE I  
SURVEY OF COLUMN AND PORASIL DATA

Parameter	Porasil C	Porasil D	Source
<b>Column</b>			
Length (cm)	100.0	100.0	} This work
I.D. (cm)	0.80	0.80	
Column contents (g Porasil)	24.13	22.32	
Total pore contents (g THF)	18.51	18.01	
Total liquid contents (g THF)	34.22	35.07	
Extra granular contents (g THF)	15.71	17.01	
<b>Porasils</b>			
Mesh size (A.S.T.M.)	100-150	100-150	} Manufacturer
Surface area (m <sup>2</sup> /g)	50	25	
Pore radius range (Å)	100-200	200-400	
Skeleton density (g/ml)	2.09	2.16	} This work
Skeleton volume (ml/g)	0.478	0.463	
Pore volume (ml/g)	0.864	0.912	
Void fraction, $\psi$	0.644	0.663	
Surface area (m <sup>2</sup> /g)	71	34.8	} N <sub>2</sub> adsorption KSLA***
$R_s^*$ (Å)	160	322.6	
$\bar{R}_p^{**}$ (Å)	165	345	} Data computed with RSM <sup>§</sup>
$\bar{R}_p^{**}$ (Å)	165	350	

\*  $R_s$  = radius of the sintered spheres calculated from surface area and  $\psi$ .

\*\*  $\bar{R}_p$  = mean pore radius.

\*\*\* KSLA = Koninklijke/Shell Laboratorium, Amsterdam.

§ RSM = random spheres model (see the section Geometry of porous material).

TABLE II  
MANUFACTURER'S DATA ON POLYSTYRENE

<i>M</i>	$M_w/M_n$		<i>Viscosity</i>	<i>Vapour-phase osmometer</i>	<i>Membrane osmometer</i>	<i>Kinematic</i>	<i>Rust method</i>	<i>Cryoscopy</i>	<i>Reported average</i>	<i>Light scattering</i>	<i>Fractionation</i>
	$M_w/M_n$	$M_n$									
900	<1.10		1220 ± 7%	927 ± 7% 1060 ± 7%		940 ± 10%		915 ± 5%	1050 ± 105		
2100	<1.10		2120 ± 3%	2210 ± 7% 2085 ± 7%			1585 ± 5%				
4000	<1.10		4170 ± 7% 3257 ± 7%	2930 ± 7%	5200 ± 10%			2900 ± 5%	3690 ± 365		
10,300	<1.06		10,500 ± 4%		10,900					10,000 ± 10%	
20,400	<1.06		20,400 ± 6%		20,200 ± 600					20,800 ± 800	
51,000	<1.06		51,000 ± 3%	50,100 ± 5%						50,500 ± 4%	
97,200	<1.06		98,200 ± 3%	97,600 ± 5%						96,200 ± 2%	
160,000	<1.06		160,000 ± 3%		154,000 ± 5%					160,000 ± 4%	
411,000	<1.06		411,000 ± 3%	392,000 ± 5%						394,000 ± 2%	
860,000	<1.15		842,000 ± 3%						1.121	862,000 ± 2%	886,898
1.8 · 10 <sup>6</sup>	<1.20		1.7 × 10 <sup>6</sup> ± 4%						1.19	1.7 · 10 <sup>6</sup> ± 4%	1.9 · 10 <sup>6</sup>

### Accuracy

As different theories of the mechanism of GPC yield calculated retention volumes that differ by only a few per cent, it is possible to test a theory only if the experimental accuracy is better than 1%. In order to achieve this high accuracy, we used the following means:

(a) The amount of liquid leaving the column was measured with the aid of a balance replacing the syphon-counting system normally used in GPC. Besides giving an accuracy of weighing higher than attained in volume measurements, this method also eliminates the variations in the measured volume due to fluctuations in the temperature of the collection vessel.

(b) Corrections were made for the evaporation losses that occurred during the chromatographic experiment, by simply placing a reference bottle, partly filled with THF, next to the balance (Fig. 1, g). From the decrease in weight of this bottle measured over a certain time interval, correction values can be calculated for the measured retention volumes, related to the duration of the experiments.

(c) Samples are introduced exactly when the zero of the balance scale passes the reference mark and spikes are given just around the centre of the chromatographic peaks. In this way, we have a perfect interpolation method for the estimation of the retention volume that is almost independent of flow variations.

(d) The median of the elution curve of a polymer sample (*i.e.*, the line perpendicular to the time axis that divides the peak area into two sections of equal surface area) is taken to be representative of the retention volume of the weight-average molecular weight ( $\bar{M}_w$ ). According to theoretical considerations<sup>25,29</sup>, it is much better to determine the first moment of each peak, but for peaks that are not very asymmetrical the median is very satisfactory as an approximation. Both a first moment and a median can be determined much more accurately than the peak top, especially with flat and broad elution curves. The increased accuracy achieved in this way is illustrated by the scatter of the results of a provisionally determined retention volume of cyclopentane\*. In an experiment replicated five times, values of 40.98, 41.02, 41.05, 41.03 and 41.03 g of mobile phase were measured.

### Verification of the basic equations

As a first approximation, we assumed that for dissolved polystyrene molecules the equilibrium between the liquid phases inside and outside the pores was established immediately; we also assume that the concentrations inside and outside the pores are the same. The retention volume can be written as<sup>30</sup>

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

The retention volume,  $V_R$ , is expressed as a function of the volume between the grains in the column,  $V_0$ , and the pore volume,  $V_p$ ;  $K$  is therefore the percentage of the pore volume that is accessible to the polymer molecules.

For a very large and a very small molecule (as compared with the pore radius),  $K$  is 0 and 1, respectively. This allows the prediction of the retention volumes of such solutes by non-chromatographic measurements, *viz.*, the pore volume found by titration with THF (see refs. 43 and 44), the total liquid hold-up of the column found by

\* Measured with a differential refraction detector.

TABLE III

COMPARISON OF CALCULATED AND MEASURED RETENTION VOLUMES FOR  $K = 0$  AND  $K = 1$ , INCLUDING EXTRA COLUMN CONTRIBUTIONS (1.24 g THF)

Solute	Retention volume, (g THF)			
	Porasil C		Porasil D	
	Calculated	Measured	Calculated	Measured
Polystyrene 860,000	16.95	17.00	18.30	17.95
Ethylbenzene	35.46	35.07	36.31	35.96

weighing both dry and completely wetted, and the hold-up of the detector and the sample introduction system. The last-mentioned value was measured by short-circuiting the column while the retention volume of ethylbenzene was being measured. A three-fold determination yielded values of 1.24, 1.22 and 1.25 g of THF. The mean value (1.24 g) was used in the calculations. The total liquid hold-up of the column plus the extra column contributions must equal the retention volume of the small molecules; the retention of the large molecules is found by subtracting the pore volume from this value.

Table III lists the retention volumes calculated from Table I together with the chromatographic measurements using polystyrene 860,000 and ethylbenzene as the solutes. The average absolute difference between the two methods is about 1%. Even these small discrepancies can be partly explained by the small difference in molecular dimensions between the titrant (THF) and the solute ethylbenzene (an ethylbenzene molecule is larger than a THF molecule).

#### *Conversion of retention volumes into percentage of pore volume*

In order to be able to compare the experimental results with the theory, it is necessary to calculate from the retention data the percentage of the pore volume that is effectively accessible to the polymer molecules.

As the validity of eqn. 1 was proved above, this equation can be used to convert  $V_R$  into  $K$ :

$$K = \frac{V_R - V_0}{V_p'} \quad (2)$$

where  $V_0$  represents the retention volume of the largest molecule, and  $V_p'$  is the pore volume found by titration, corrected by a certain percentage dependent on the size of the THF molecule with respect to the mean pore radius (see section Geometry of porous material). The Porasil C is also corrected ( $-2\%$ ) for the presence of a small amount of very large pores (radius about  $10^5$  Å), which was demonstrated by electron scanning microscopy (qualitatively) and mercury intrusion measurements (quantitatively).

#### *Experimental results*

According to the supplier, all of the polystyrene samples had a narrow molecular weight distribution ( $\bar{M}_w/\bar{M}_n < 1.1$ ). However, measurements by our own supercritical chromatography and calculations by a previously published method<sup>31</sup>

TABLE IV  
EXPERIMENTAL RESULTS AND THEORETICALLY CALCULATED DISTRIBUTION COEFFICIENTS

Molecular weight	$r_0$ ( $\text{\AA}$ )	$\bar{r}$ ( $\text{\AA}$ )	Porasil C			Porasil D		
			$R_v$ (g THF)	$K$	$\psi'/\psi$	$R_v$ (g THF)	$K$	$\psi'/\psi$
1,800,000	660	584.9	17.21	0.011	0.000	17.76	0.000	0.000
860,000	427.6	378.9	17.00	0.000	0.000	17.95	0.010	0.022
411,000	277	245.5	17.08	0.004	0.001	20.64	0.158	0.160
160,000	159.1	141.0	18.26	0.067	0.083	25.69	0.434	0.446
97,200	118.7	105.2	20.75	0.201	0.209	28.50	0.588	0.579
51,000	81.2	72.0	24.41	0.396	0.406	30.84	0.716	0.711
20,400	47.4	42.0	28.96	0.640	0.641	33.21	0.845	0.833
10,300	31.7	28.1	31.16	0.757	0.760	34.42	0.911	0.890
4000	18.2	16.1	33.26	0.870	0.864	35.27	0.958	0.937
2250	13.0	11.5	33.76	0.896	0.903	35.46	0.968	0.955
1250	9.2	8.1	34.06	0.912	0.932	35.58	0.975	0.969
Ethylbenzene	—	—	35.07	0.963	—	35.96	0.996	—

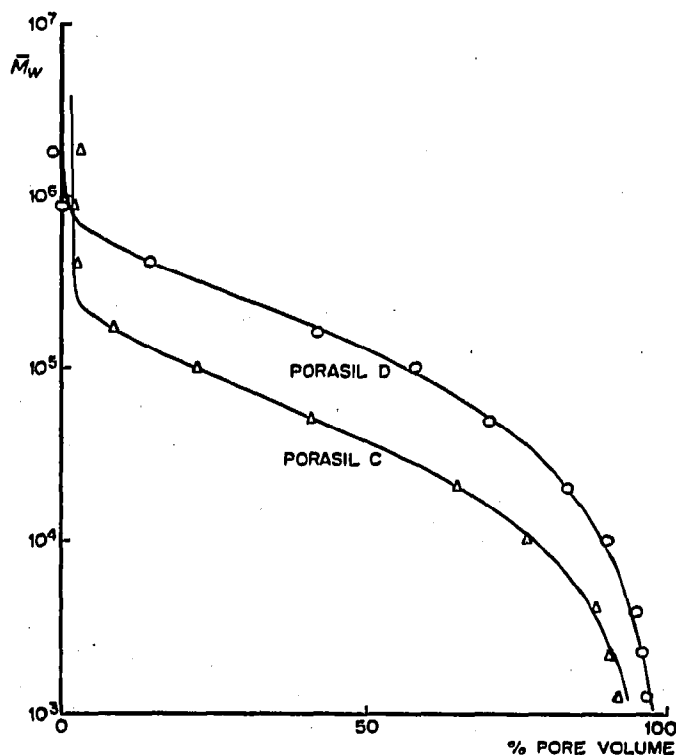


Fig. 2. Experimental GPC results (0% pore volume in this graph is taken to be equal to the void volume of the column determined by weighing and titration).

show that for some of the samples in the lower-molecular-weight range this is certainly not true. For the molecular weights, we used the values given by the manufacturer, except for samples 2100 and 900, which we corrected to 2250 and 1250 with the aid of supercritical chromatography. The measured retention volumes and  $K$  values are listed in Table IV, together with the  $K$  values calculated according to the theory. A graphical representation of these measurements is given in Fig. 2.

## GEOMETRY OF THE MACROMOLECULES

Assuming that the separation mechanism of GPC is completely governed by the geometry of the macromolecules and of the pores of the porous material, we have to define for both geometries a model that can be represented by mathematical equations, thus allowing theoretical distribution coefficients to be calculated. Starting from a known geometry of the porous material (see the next section), we can accurately define the accessible pore space in the porous material if we can give an indication of the effective diameter of a macromolecule near a surface<sup>32</sup>. We regard the polystyrene molecules used in our experiments as linear random coil chains. The configurational statistics of these model chains are well known<sup>33</sup>. A variety of average distances can be defined in a random coil chain, for example, the radius of gyration,  $r_g$ , the mean end-to-end distance,  $\bar{h}$ , and the mean maximal projection of the chain in a given direction,  $\bar{X}$ . We must decide which distance can be regarded as the effective diameter of a macromolecule near a solid wall. Each segment of the macromolecule that hits this wall experiences a repulsion that can be approximately described in terms of a Lennard-Jones potential between a segment and an atom or molecule of the wall material. Which segments are involved in this process depends on the speed of transformation of the chain molecule from one spatial configuration into another. The transformation of spatial configurations is governed by the speed of rotation of segments around the definite valence angles of the carbon atoms of the macromolecular chain. The ratio of this rotation speed and the diffusion speed of the centre of mass of the macromolecule will determine the effective diameter of the molecule near a surface. This can be reasoned as follows. A macromolecule approaches the solid surface of a porous material by diffusion. It is of crucial importance to know the number of configurations through which the molecule passes when it diffuses over a distance that is short as compared with the interaction distance between a segment and the solid surface. The latter distance is very small (only a few Ångströms); we therefore started from a value of 1 Ångstrom and estimated, on the basis of a rough calculation, whether the number of configurations involved is large or small.

For the determination of the diffusion we have the well known equation (ref. 34)

$$\bar{X}^2 = 2 D t \quad (3)$$

where  $\bar{X}^2$  is the mean square displacement ( $\text{cm}^2$ ),  $D$  the diffusion coefficient ( $\text{cm}^2/\text{sec}$ ) and  $t$  the time (sec). For macromolecules in most organic solvents,  $D$  is about  $10^{-7}$   $\text{cm}^2/\text{sec}$ ; this means that for an average displacement of about 1 Å ( $= 10^{-8}$  cm),  $t = \bar{X}^2/2 D = 10^{-16}/2 \cdot 10^{-7} = 5 \cdot 10^{-10}$  sec.

As the rotation times of segments in macromolecules are of the order of  $10^{-11}$  sec, we can expect that every segment has rotated between 10 and 100 times



during a 1 Å displacement of the centre of mass of the macromolecule. Hence the macromolecule passes through numerous consecutive spatial configurations while diffusing over a very short distance only. We assume that this situation exists when we are dealing with macromolecules in a good solvent, such as, in this work, polystyrene molecules in THF. We therefore further assume that, with a very fast succession of all possible spatial configurations, the effective radius,  $\bar{r}$ , of a linear macromolecule near a surface is equal to half of the mean maximal cross-section of the fluctuating random coil,  $\bar{Q}$  (ref. 33). All the quantitative relationships between all distinct average distances to be defined within a random coil molecule can be found by statistical calculations<sup>33</sup>. Therefore we have

$$\bar{r} = \frac{1}{2} \sqrt{\frac{\pi}{6}} \cdot \sqrt{Zb^2} \quad (4)$$

where  $Z$  is the number of segments in the macromolecule and  $b$  is the length of one segment. The widely used radius of gyration,  $r_g$  ( $= \sqrt{R^2}$  in Ref. 33), can also be expressed in the parameters  $Z$  and  $b$ :

$$r_g = \sqrt{\frac{1}{6}} \cdot \sqrt{Zb^2} \quad (5)$$

Combination of the two last-mentioned equations gives

$$\bar{r} = \frac{\sqrt{\pi}}{2} \cdot r_g = 0.886 r_g \quad (6)$$

We assume that in real chains, as in polystyrene, with hindered rotation and excluded volume effects, the ratio  $\bar{r}/r_g$  will remain equal to 0.886; the absolute values expressed by eqns. 4 and 5 will certainly be wrong.

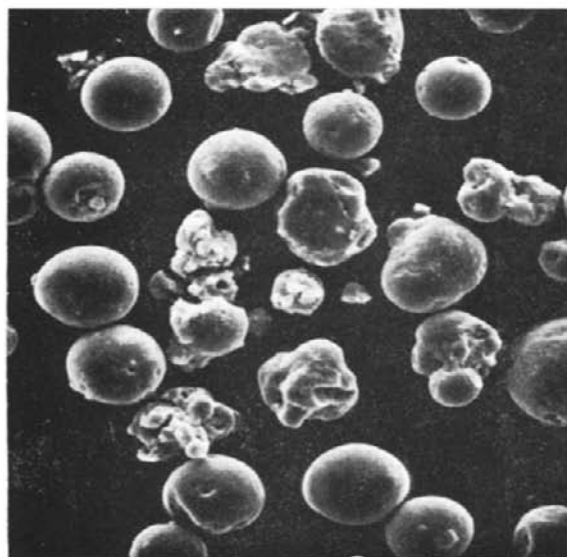
The radii of gyration of molecules of different molecular weight can be calculated from accurate light-scattering experiments of polystyrene in THF<sup>35</sup>. From the literature values<sup>35</sup>, we determined the value of  $x = 0.588$  in the approximate equation

$$r_g = a M^x \quad (7)$$

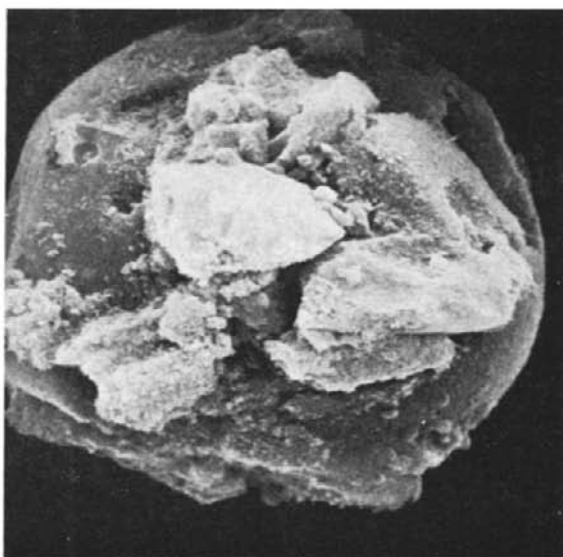
With the aid of eqn. 7 and using the data in ref. 35, we interpolated the radii of gyration of the polystyrene samples used in our experiments (see Table IV). If we multiply these radii of gyration,  $r_g$ , by the factor 0.886, we obtain the effective radii,  $\bar{r}$  (see Table IV).

## GEOMETRY OF POROUS MATERIAL

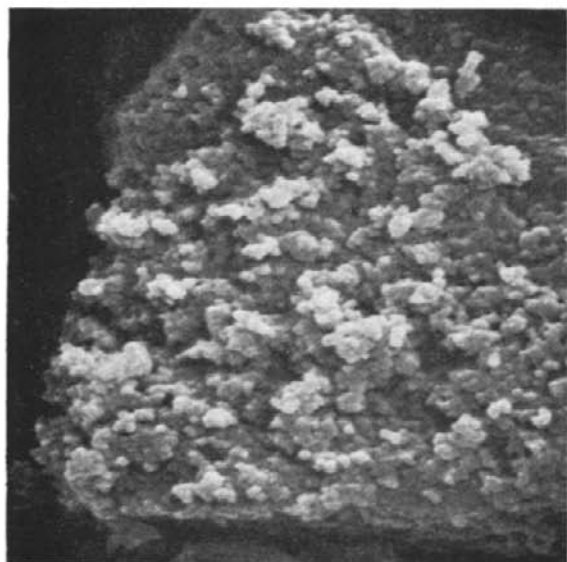
The structure of the silica gel beads of Porasil D used is revealed by scanning electron microscopy (Fig. 3). Although the structure of Porasil C cannot be detected by this technique, we assumed it to be similar. Scanning electron microscopy has a resolving power of about 150 Å, so it can therefore not be expected to reveal pores of a diameter of approximately 300 Å (as in Porasil C). From the photographs, it seems that the Porasil silica beads consist of a large number of randomly overlapping microspheres of solid silica, and the pore space is formed by the remaining space between the microspheres. This type of porous material we described in terms of the "random spheres model" (RSM). This model has been used by several workers to describe



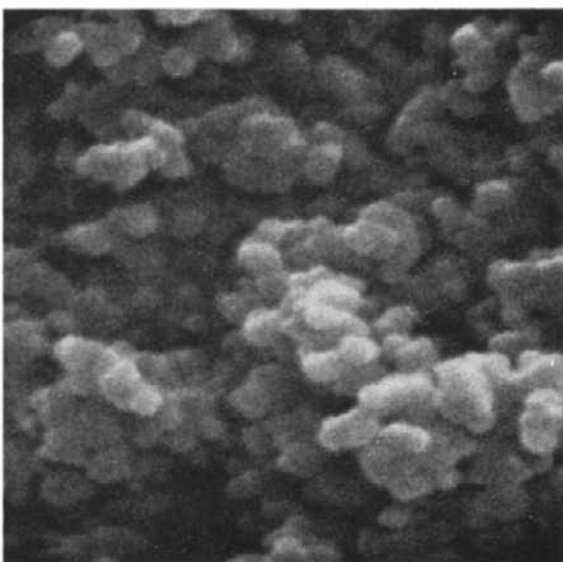
A | 100 μm



B | 10 μm



C | 1 μm



D | 1 μm

Fig. 3. Scanning electron microscopic photographs of Porasil D with different magnifications.

either the structure or the properties of a porous material, mainly a catalyst<sup>36-40</sup>. A cross-section through such a three-dimensional matrix of equal spheres is shown in Fig. 4. The dark area of intersecting spheres leaves an irregular white area, which

represents the voids of the porous material. According to the RSM, a relation between the void fraction,  $\psi$ , the radius of the solid spheres,  $R_s$ , and the total surface area,  $S$ , can be derived<sup>39</sup>:

$$R_s = -\frac{3\psi}{S} \ln \psi \quad (8)$$

Within the RSM, we can define a pore size distribution from which an average pore size,  $\bar{R}_p$ , can be calculated. The value of  $\bar{R}_p$  can be fairly closely approximated by the equation (ref. 40)

$$\bar{R}_p = (1.32 - \psi) \frac{2\psi}{S} \quad (9)$$

This equation provides us with an excellent possibility of testing the RSM as a description of the Porasils used in our chromatographic experiments. With the Brunauer–Emmett–Teller (BET) method<sup>41</sup>, we measured the surface area,  $S$ , of the porous material. The determination of the pore volume<sup>43,44</sup> and the skeleton density subsequently yield the value of  $\psi$ :

$$\psi = \frac{(\text{pore volume/gram})}{(\text{pore volume/gram}) + (1/\text{skeleton density})} \quad (10)$$

These values of  $S$  and  $\psi$  are substituted in eqn. 9 and give a value of the average pore size,  $\bar{R}_p$ . This  $\bar{R}_p$ , calculated with the aid of the RSM from  $\psi$  and  $S$ , can be compared with the results of the well known  $\bar{R}_p$  determination by mercury intrusion under high pressure. As can be seen from Table I, the agreement is excellent, so that we feel justified in using the RSM in further studies.

In the calculations, we used only one diameter of the silica microspheres, rather than starting from a size distribution because we found that the latter approach, keeping the average size equal to the fixed diameter, yields results that are much the same. The RSM also opens the possibility of quantitatively expressing the percentage of the pore volume that is accessible to molecules of a certain diameter, which, during a chromatographic process such as GPC, diffuse into the pores. For this purpose we start from an equation<sup>39</sup> expressing the relationship between the number of randomly placed uniform spheres per unit volume  $N$ , the volume of one of the spheres,

$\frac{4}{3}\pi R_s^3$ , and the void fraction,  $\psi$ :

$$\frac{4}{3}\pi N R_s^3 = -\ln \psi \quad (11)$$

The void fraction (or pore volume)  $\psi'(\bar{r})$  that is accessible to a molecule of radius  $\bar{r}$  diffusing into a random spheres system can be found by applying the same equation (see Fig. 4):

$$\frac{4}{3}\pi N(R_s + \bar{r})^3 = -\ln \psi'(\bar{r}) \quad (12)$$

When the void fraction,  $\psi$ , and the radius of the microspheres,  $R_s$ , of the porous silica gel are known, one can calculate the accessible pore volume as a function of the radius

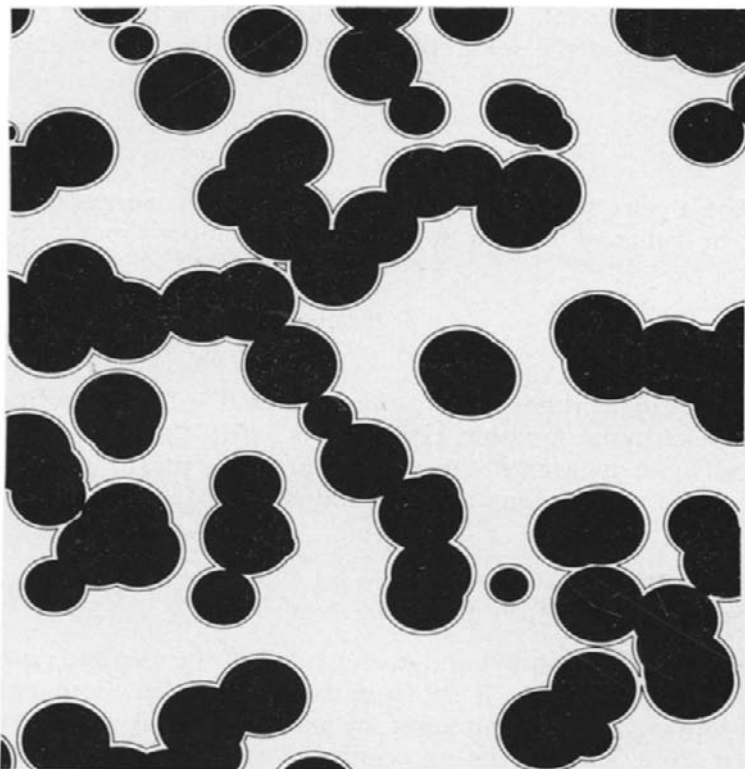


Fig. 4. Cross-section through randomly placed identical spheres. Void fraction = 0.643. The space between the lines and the solid black circles indicates the excluded volume.

of the entering molecules:

$$\ln \psi'(\bar{r}) = \left( \frac{R_s + \bar{r}}{R_c} \right)^3 \ln \psi \quad (13)$$

The percentage of the pore volume that can be entered by molecules of radius  $\bar{r}$  is subsequently found from the ratio  $\psi'(\bar{r})/\psi$  (see Table IV).

## DISCUSSION

As we assumed that the separation process of GPC is completely governed by the geometries of macromolecules and of the pores of the porous column packing, we used two statistical theories describing these geometries. The random coil description of macromolecules enables us to calculate the effective radius near a wall surface as a function of the average molecular weight with the aid of light-scattering data. The centre of a molecule of a certain effective radius diffusing into a porous material can never come closer to the solid surface than a distance equal to the molecular radius. This means that a certain proportion of the pore space cannot be entered by a molecule. With the aid of the RSM, we can calculate the percentage of the pore volume that is accessible to molecules as a function of their radius. Consequent-

ly, with a combination of eqns. 6, 7 and 13, we can calculate values of the theoretical distribution coefficients  $\psi'/\psi$  as a function of molecular weight. These values can be compared with the values of distribution coefficients,  $K$ , determined with eqn. 2 from our chromatographic experiments. As can be seen from Table IV, the agreement between the experimental and theoretically calculated distribution coefficients is excellent; it is in fact much better than the results reported so far in the literature<sup>42</sup>. This has been achieved by improving the accuracy of the experiments as well as of the theoretical description of the geometry of porous material and macromolecules. We feel that the conclusion is justified that the position of the median of a peak in GPC is determined solely by exclusion on the basis of geometry and that in our specific case no other effects need to be taken into account.

#### ACKNOWLEDGEMENTS

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