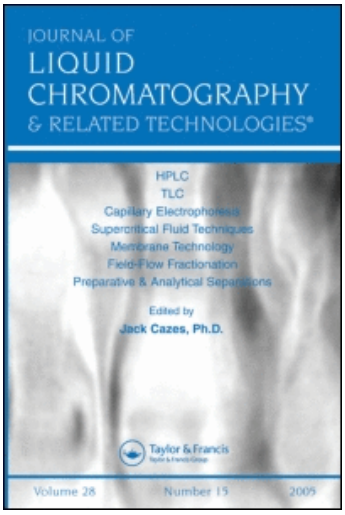

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LONG-CHAIN ALKYLSILANE-MODIFIED POROUS SILICA* BEADS AS GPC PACKINGS

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SUMMARY

A series of silica gels having various molecular weight exclusion limits has been modified by reaction with octadecyltrichlorosilane. Toluene being used as moving phase and hydroxyl-end blocked polydimethylsiloxane as solute, the chromatographic process on these modified silica packings is mainly controlled by size exclusion; an additional absorptive retention can still be observed with the low molecular species. Thus, calibration in this case should be performed using standard samples of the specific polymer to be determined.

INTRODUCTION

Porous silica gels, used as GPC packings, usually need to be modified with trimethylchlorosilane or hexamethyldisilazane[1-3] in order to suppress the adsorptive effect caused by surface silanol groups. It has been proven[4,5] that an appreciable number of unreacted silanol groups is still left on the surface of silica gels treated chemically with organochlorosilanes. The adsorptive

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effect due to remaining silanol groups can be very strong with short-chain bonded phases[6], since solute molecules penetrated through the phase to the surface easily. A variety of packing materials for reversed phase liquid chromatography, prepared by reaction of porous silica gels with long-chain alkylchlorosilanes, has commercially been available for a long time, but reports on the application of these modified silica gels for GPC have not yet been found. In the case of long-chain bonded phases, as noted by Kirkland[7], unreacted silanol groups are shielded by an "umbrella" of tightly packed organic groups, and the adsorptive effect may be reduced to a very low level. In this laboratory, a series of porous silica beads was modified with octadecyltrichlorosilane. Toluene being used as moving phase and hydroxyl-end blocked polydimethylsiloxane as solute, the gel chromatographic behaviour on the modified silica beads and the residual adsorptive effects were investigated.

EXPERIMENTAL

Materials

Octadecyltrichlorosilane was prepared by addition of silicon tetrachloride to octadecyl Grignard reagent; the product was distilled and collected at 210-214°C/6mmHg. Other chemicals were commercially available materials, AR and CP grade, and were not treated before use.

Cross-linked polystyrene gels, JD-type, were supplied by the Chem Dept., Jilin University. Silica packings, NDG-L, which had been treated by hexamethyldisilazane, were commercially available (2nd Chem. Reagent Plant, Tianjin). Silica packings Nos.1-6 were prepared by calcining spherical porous silica beads (Qingdao Sea Chem. Plant). Two procedures were employed for the silica modification:

Method I: by reaction with hexamethyldisilazane, according to the procedure described by Beijing Chem. Ind. Institute[8].

Method II: by reaction with octadecyltrichorosilane[4.7.9.]. A common procedure is as follows: A given amount of silica beads, whose surface had been fully hydrolyzed with HCl, was placed in a round-bottom flask, heated at 150-160°C for 2-4 hours and followed by cooling, in vacuum; then an excess of octadecyltrichlorosilane dissolved at 10-20% in dry toluene was drawn in. It was assumed that the amount of octadecyltrichlorosilane, Ws, required for monomolecular layer bonding can be estimated by the following relation:

$$W_s = \frac{Wg \times S \times 4 \times 10^{18} \times 388}{6.02 \times 10^{23}} \quad g$$

where Wg and S are the weight (g) and specific surface (M^2/g) of the silica beads to be treated, respectively. The mixture was refluxed with suitable stirring for 16-18 hours, while a small stream of dry nitrogen was passed through the solution. After cooling, the silica beads were separated from the solution by decantation, then washed by column-elution with dry toluene, acetone, a mixture consisting of 10% H_2O and 90% acetone, methanol successively until the final eluate was fully neutral. The silica particles were air dried and heated at 120°C for 4 hours. For silica packing No. 1, after treating as above, the reaction with octadecyltrichlorosilane was carried out once more in much the same way, except using dry xylene instead of toluene. In order to remove any residual silanol groups which could have been formed by octadecyltrichlorosilane hydrolysis, usually, the silica beads, treated as above, were further reacted with hexamethyldisilazane according to Method I.

Samples and Standards

Anionically polymerized polystyrene standards were supplied by the Chem. Dept. Jilin University.

Polydimethylsiloxane samples (blocked by hydroxyl-end) were obtained from this institute and fractionated at 15±0.1°C by addition of methanol to their dilute solutions (1g/dl). Benzene[10] or ethyl

acetate[11] was chosen as the good solvent. Each fraction was redissolved and reprecipated until a symmetrical peak of appropriate width was obtained by GPC. The intrinsic viscosities of the fractions were measured with a Ubbelodhe-type semi-microviscometer in toluene at 25°C and the molecular weights were calculated by the relation[12]:

$$[\eta]^{25°C}_{toluene} = 0.828 \times 10^{-4} \; M^{0.72} \quad dl/g \qquad (2)$$

and the results are listed in Table II.

Gel Chromatography Operation

A gel chromatograph (Tianjin Anal. Instrum. Plant, Model SN-01A) equipped with a differential refractometer was used. The elution volume was measured by counting with a syphon of 2.5ml. Provided that there are no special notes made in this paper, the chromatographic separations were performed with a column of 1m length x 8 mm i.d. at room temperature and flow rate range of 0.6-0.8ml/min. using toluene as moving phase.

Solute recovery check was made as follows: At the same sample size and instrumental sensitivity, a polydimethylsiloxane was chromatographed with modified silica gel columns and a polystyrene gel column respectively. Suppose the recovery of this polymer on polystyrene gel column is 100%; then the recoveries on modified silica gel columns may be expressed by S_1/S_2 ratio, where S_1 is the peak area values obtained with modified silica gels and S_2, with polystyrene gel.

RESULTS AND DISCUSSION

Chromatographic Properties of Modified Silica Gels

Molecular weight exclusion limit, ratio of pore volume to interstitial volume, and packed-column efficiency were measured; these results are listed in Table I. As shown in the last column of Table I, the particle size exerts an obvious effect on column

TABLE I. Properties of silica packings

No.of[a] Silica	Modification method	Particle size (mesh)	App. density (g/ml)	Mol.wt. exclusion limit (PS)	Ratio of pore[b] volume to interstitial volume (V_i/V_o)	Column[c] efficiency (theor.plate per meter)
1	untreated	120-180	0.434	1.8×10^4	1.07	
1-I	I	120-180	0.468	1.5×10^4	0.99	1570
1-II	II	120-180	0.537	1.2×10^4	0.82	1570
2	untreated	200-280	0.412	1.4×10^5	1.10	
2-I	I	200-280	0.428	1.4×10^5	1.10	4500
2-II	II	200-280	0.459	1.2×10^5	1.08	5000
3	untreated	160-200	0.448	4.4×10^5	1.07	
3-II	II	160-200	0.476	4.0×10^5	1.00	2950
4-II	II	160-200	0.447	8.0×10^5	1.03	2580
5-II	II	160-200	0.474	$>4\times10^6$		2650
6-II	II	160-200	0.528	$>4\times10^6$		2660

(a) The silica packings prepared by calcining in this laboratory were divided into six grades, denoted by Arabic numbers 1-6, according to their exclusion limit.
(b) Measured by GPC.
(c) Measured by using heptane as the solute and calculated:

$$N = 5.54 \times (V_R/2\Delta V_{\frac{1}{2}})^2$$

where $2\Delta V_{\frac{1}{2}}$ is the half-peak width.

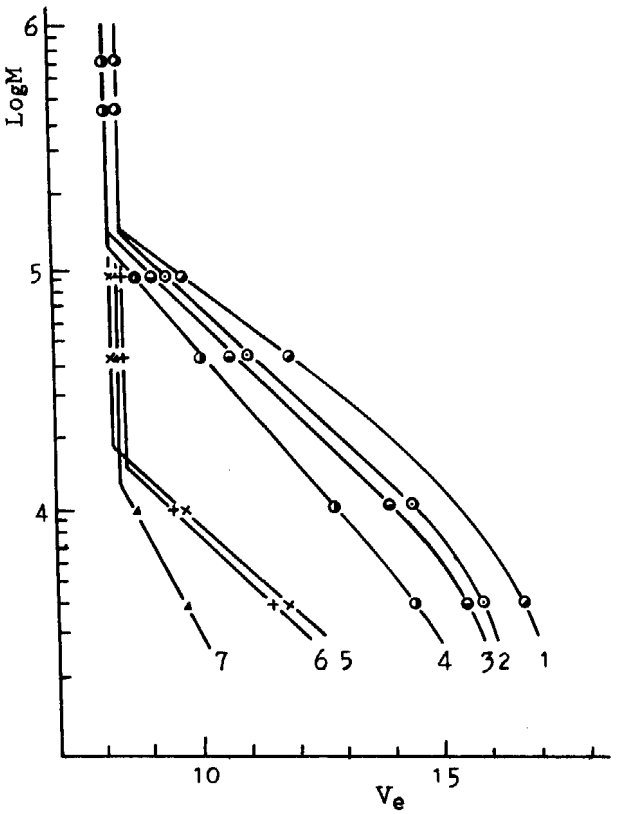

FIGURE 1. PS calibration curves before and after packing modification. Column of 1mm x 8mm i.d.; toluene as moving phase except curves 2,5.

1) Silica No.2
2) Silica No.2, in THF
3) Silica 2-I
4) Silica 2-II
5) Silica No.1 in THF
6) Silica 1-II
7) Silica 1-II

efficiency, but not much difference in efficiency can be found between the two packings, which were modified by Method I and Method II respectively (either Silica 1-I and Silica 1-II, or Silica 2-I and Silica 2-II).

It is important[13] that a monomolecular layer of organic groups should be chosen in silica modification, since the pore openings of gels, particularly those with small pore sizes, may be blocked by polymer layer, resulting in a drastic decrease in observed pore column. On this account, in our laboratory, the reaction of silica beads with octadecyltrichlorosilane containing three active functional groups have been well protected from moisture in the air. The value of V_i/V_o, as shown in the 6th column of Table I, have only a slight disparity from a comparison with Silica No. 2 and Silica 2-II, or Silica No. 3 and Silica 3-II. As regards Silica 1-II, however, the value of V_i/V_o is 22% less than before its modification; this might be attributed to the large specific surface of Silica No. 1, i.e. the great number of silanol groups available for reaction with the organosilane. Thus, this modified material has a high level of organic content which, of course, can occupy an appreciable amount of pore volume of the gels.

Effects of silica modification on the calibration curves are illustrated in Fig. 1.

Suppressing Adsorptive Effects

Adsorptive retention, which occurs simultaneously with the size exclusion process, is usually observed as excessive retention as well as tailing chromatographic peaks. When the adsorptive effect is strong, solute molecules may either be permanently retained in the column, or elute so slowly that the concentration of solute in eluate is below the minimum detectable limit. Accordingly, solute recoveries calculated from chromatograms are on the low side. In order to examine the residual adsorptive effect, hydroxyl-end-blocked polydimethylsiloxane (PDMS) samples of narrow or broad molecular weight distribution were chromatographed using various silica peaking which had been modified

by the two methods described above. For convenience, the same code numbers are employed for silica packing and the corresponding column packed with it.

The exclusion limit values are both approximately 1 x 10^5 for Silica 2-I and Silica 2-II, but retention behaviour of PDMS fractions on column 2-II is quite different from that on column 2-I. Fig. 2-b shows a chromatogram of a mixed sample on column 2-II where narrow distribution PDMS fraction V, PDMS fraction X and heptane are well separated from each other; the values of V_e at peak position are 10.15, 14.8 and 17.4 respectively, in agreement with the order of size separation. In the case of column 2-I, PDMS fraction X actually elutes later than heptane and peak tailing is very pronounced (Fig.2-c). A chromatogram of PDMS sample No. A (with broad distribution) lies before the total permeation volume, 17.4 (Fig.2-a-1), and the polymer sample recovery amounts to 100% on column 2-II, while a part of this PDMS sample eluting is beyond the normal volume range for GPC (Fig. 2-a-2) and the sample recovery detected is only about 80% on column 2-I.

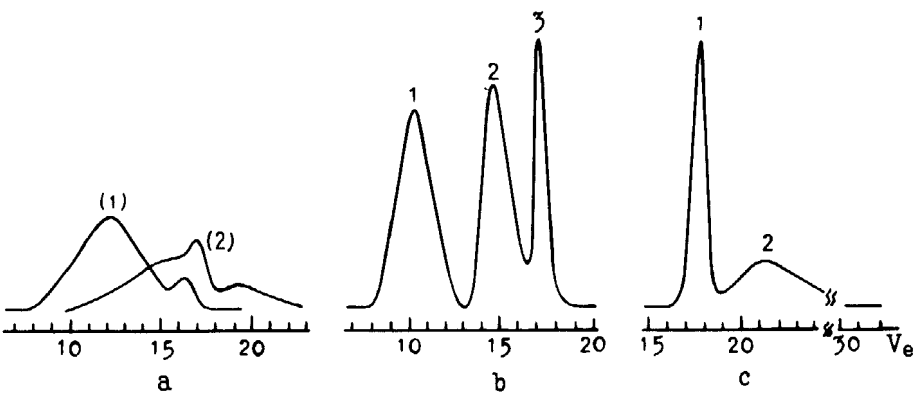

FIGURE 2. Elution curves on column 2-I or column 2-II.
a. PDMS sample No.A of broad distribution, $\bar{M}\eta$ 1.3x10^4
(1) column 2-II; (2) column 2-I b1) PDMS fraction V, $\bar{M}_\eta$6.07X10^4
2) PDMS fraction X, $\bar{M}_\eta$8.11x10^3, 3) heptane, column 2-II
c.1) heptane, 2) PDMS fraction; column 2-I

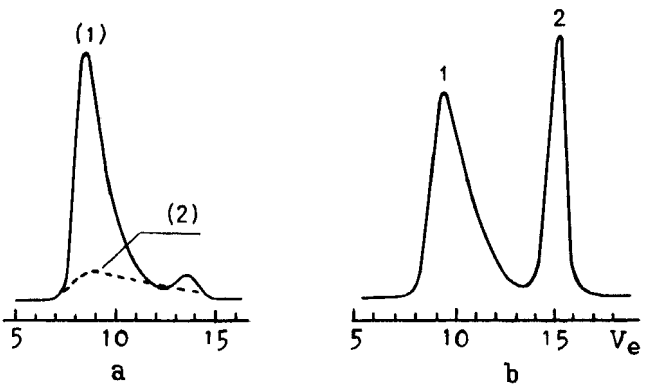

FIGURE 3. Elution curves on column 1-I or column 1-II.
a. PDMS sample No.A of broad distribution, $\bar{M}_\eta 1.3 \times 10^4$,
(1) column 1-II; (2) column 1-I b.1) PDMS fraction X, $\bar{M}_\eta 8.11 \times 10^3$
2) heptane; column 1-II

Silica I-II of exclusion limit $1.2.x10^4$ was treated twice with octadecyltrichlorosilane for removing reactive silanol groups. As usually expected in GPC, PDMS sample No. A or PDMS fraction X can elute within a fixed volume, (Fig.3-a-1, Fig.3-b) and the recovery also amounts to 100% on column 1-II. On column 1-I, however, the elution curve of PDMS sample No.A is scarcely to be recognized because of the strong adsorption by the packing materials (the dash line in Fig. 3-a).

While the exclusion limit value is as high as $1x10^6$ for Silica NDG-4L, an obvious adsorptive retention can still occur on this packing. As shown in Fig. 4-b. a skewed and tailing peak is observed for PDMS fraction VII on column NDG-4L and about a half of the polymer sample elutes beyond the elution volume of heptane. However, Fig.4-a shows a good separation based on molecular sizes on column 4-II, the values of V_e being 11.3, 15.5 and 17.75 for PDMS fraction II, PDMS fraction VII and heptane, respectively.

It is evident from the above that the adsorptive action by remaining silanol groups, as might be expected, can be effectively

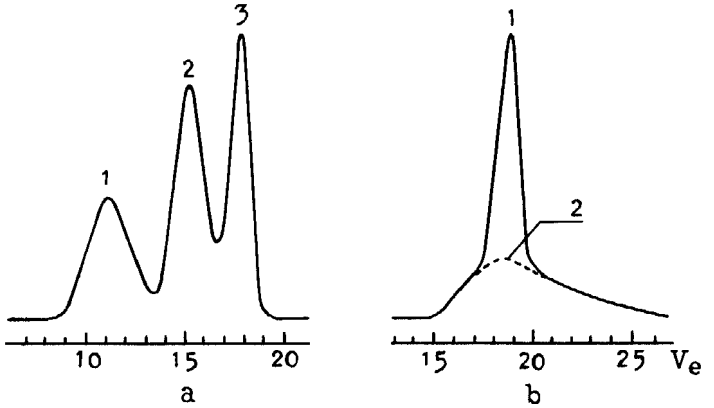

FIGURE 4. Elution curves on column 4-II or column NDG-4L. a. 1) PDMS fraction II, $\bar{M}_\eta 2.87 \times 10^5$, 2) PDMS fraction VII, $\bar{M}_\eta 3.26 \times 10^4$, 3) heptane; column 4-II. b.1) heptane 2) PDMS fraction VII; column NDG-4L.

suppressed by a long chain alkyl protective screen bonded onto the silica surface. In contrast to silica packings modified only with hexamethyldisilazane, on silica modified with octadecyltrichlorosilane the chromatographic process of hydroxyl-end-blocked polydimethylsiloxane in toluene is mainly controlled by size exclusion.

Examination of Universal Calibration Procedure

Gel chromatographic separation is based on molecular sizes. When there is no special interaction between solute and packing materials, hydrodynamic volume defined as $[\eta]M$ may be a universal parameter for calibration. It was proved with polystyrene gels by Dawkins[14] that polystyrene and polydimethylsiloxane followed the same M or $[\eta]M$ calibration in a good solvent such as chloroform. Andrianov et al.[15] also reported that the plots of $\log [\eta]M$-V_e were in agreement with each other for polystyrene and polydimethylsiloxane blocked by trimethylchlorosilane in a GPC system using toluene and porous glasses. For hydroxyl-end-blocked polydimethylsiloxane, its

TABLE II. Intrinsic Viscosities, molecular weights and elution volume values of polystyrene standards and PDMS fractions.

	PDMS fractions				PS		
No.	$[\eta]$(dl/g)	M	$[\eta]M$	V_e(peak)	M(peak)	$[\eta]M$	V_e(peak)
I	0.870	3.84×10^5	3.33×10^5	23.5	2.6×10^6	1.22×10^7	20.1
II	0.705	2.87×10^5	2.02×10^5	23.85	7.2×10^5	1.32×10^6	22.35
III	0.420	1.40×10^5	5.88×10^5	24.95	3.7×10^5	4.20×10^5	23.25
IV	0.385	1.25×10^5	4.83×10^4	25.15	9.1×10^4	3.70×10^4	25.8
V	0.230	6.07×10^4	1.40×10^4	26.8	4.3×10^4	1.01×10^4	27.6
VI	0.164	3.79×10^4	6.22×10^3	28.3	1.2×10^4	1.11×10^3	30.2
VII	0.147	3.26×10^4	4.79×10^3	28.6	1.0×10^4	8.12×10^2	30.65
VIII	0.104	2.10×10^4	2.09×10^3	29.95	9.0×10^3	6.77×10^2	31.1
IX	0.083	1.47×10^4	1.22×10^3	31.0	5.0×10^3	2.45×10^2	32.0
X	0.054	8.11×10^3	4.38×10^2	32.2	3.7×10^3	1.46×10^2	32.4

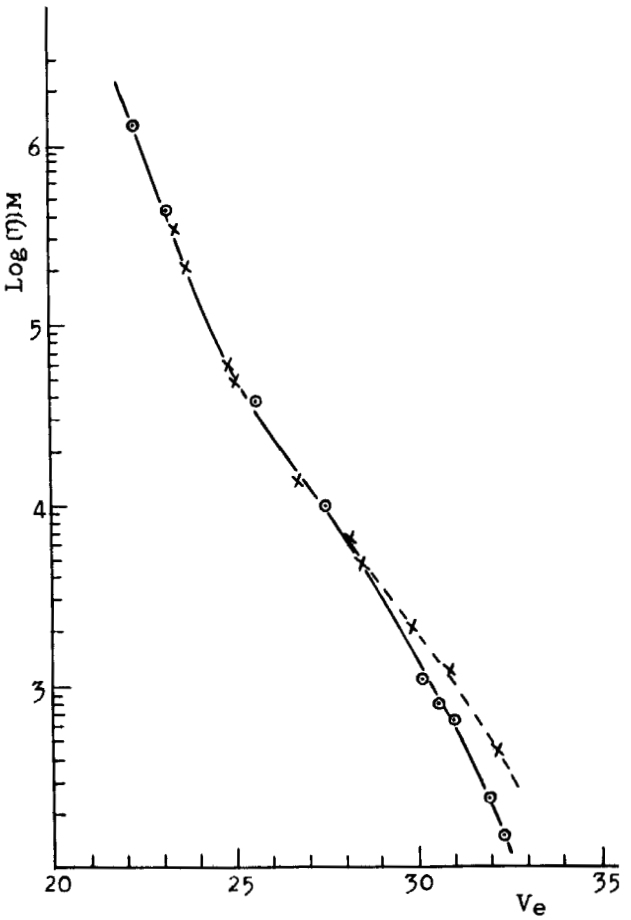

FIGURE 5. M calibration curves
two columns of 1m x 8mm i,d, in series, packed with Silica 5-II and Silica 2-II repsectively; toluene; 25°C.
⊙ PS, X PDMS fractions.

chromatographic behaviour on modified silica gels would follow the universal calibration prinicple if the adsorptive effect caused by remaining silanol groups were suppressed to a level comparable with experimental errors. Based on this thought, the values of $[\eta]$ M and elution volume from silica columns 2-II and 5-II in series are listed in Table II and plotted in Figure 5 for polystyrehe standards and PDMS fractions. The following relationship was employed to calculate the $[\eta]$M values for polystyrene[16]:

$$[\eta]^{25C}_{\text{toluene}} = 0.977 \times 10^{-4} M^{0.73} \quad \text{dl/g} \qquad (3)$$

Fig. 5 shows that the same M calibration curves may be obtained for polystyrene and PDMS fractions above a molecular weight of approximately 4×10^4. On the low side of the curves, however, PDMS fractions elute later than polystyrene of the same $[\eta]$M; the lower the molecular weights of the polymers, the greater is the difference in elution volume between them. In principle, this may be interpreted as additional adsorptive retention; then the calibration in such a case should be performed with standard samples of the specific polymer to be determined in order to avoid introducing an error into the molecular weight calculation.

Discussion Concerning "Adsorptive GPC"

The above residual adsorptive effect is further evidenced from a comparison of molecular weight calibration on modified silica gel columns and polystyrene gel columns. The log M-V_e plots are almost in coincidence for polystyrene and PDMS fractions in the system with toluene and polystyrene gel JD-103 of exclusion limit 1×10^5 (Fig. 6); however, a difference in molecular weight calibration between the two polymers, especially those of molecular weights below 4×10^4, can be found on silica column 2-II and column 1-II (Fig. 7). It is evident that the chromatographic behaviour displays "adsorptive-GPC" characteristics for hydroxyl-end-blocked polydimethylsiloxane on silica gels modified with octa-

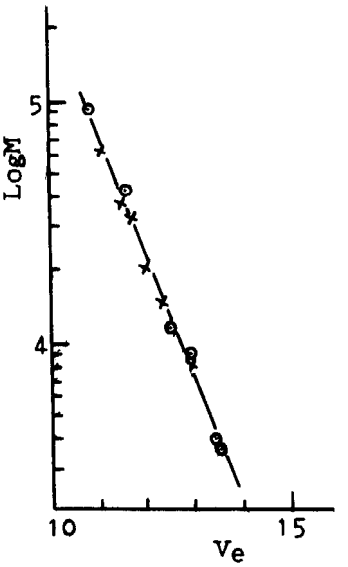

FIGURE 6. Molecular weight calibration on polystyrene gel JD-103. ⊙ PS, x PDMS fractions

decyltrichlorosilane. In this case, the excessive retention is due to the residual adsorption added to the size exclusion; the adsorptive strength decreases with increasing molecular sizes, since an increase in size exclusion is accompanied by a loss of the surface available for adsorption[17]. Finally, when the polymer molecular species are excluded from all of the pores, the adsorptive effect also immediately disappears.

As noticed by Gilpin[18] and Majors[4], if the porous structure leads to molecular exclusion, the surface available for chemical modification decreases. It may be assumed that there is actually no long-chain alkyl bonded phase on the internal surface of some pore openings from which octadecyltrichlorosilane molecules are all excluded. In general, the polymer molecular sizes are large so that they are also excluded,

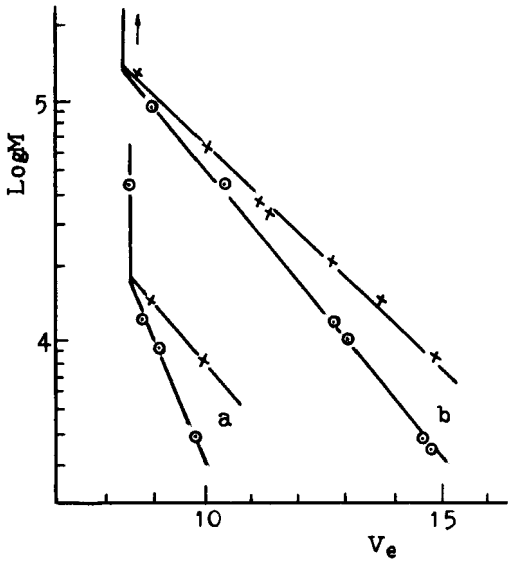

FIGURE 7. Molecular weight calibration on modified silica gels.
(a) column 1-II, ⊙ PS, x PDMS fractions
(b) column 2-II, ⊙ PS, x PDMS fractions.

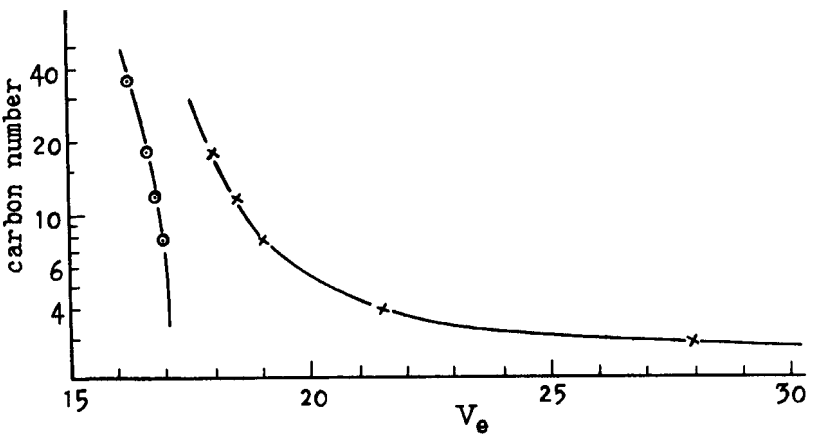

FIGURE 8. Retention behaviour of n-alkanes and n-alcohols.
column 2-II; toluene. ⊙ n-alkanes, x n-alcohols.

whereas the smaller molecules of polar solute may permeate into such micropores, resulting in strong retention and in the adsorptive effect becoming a controlling factor in chromatographic process. For this, an experimental example is given in Fig. 8, which qualitatively indicates that the differences between V_e values for n-alkanes and n-alcohols of the same carbon number increase rapidly as molecular weight decreases on column 2-II.

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