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THE PERFORMANCE OF PACKINGS IN HIGH-SPEED LIQUID CHROMATOGRAPHY

III. CHEMICALLY BONDED PELLICULAR MATERIALS

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SUMMARY

The reduced plate height, h, has been determined as a function of the reduced velocity, v, for Permaphases ETH and ODS** for several solutes at temperatures from 20° to 60° ($0 < k' < 10$). The data are interpreted in terms of the equation

$$h = B/v + Av^{0.33} + Cv$$

For Permaphase ETH A lies between 1.6 and 1.9 while C lies between 1.9×10^{-2} and 5.6×10^{-2}. These relatively high values of C for a pellicular material probably indicate slow mass transfer in the polymeric stationary phase. The relatively low value of A indicates that reasonably good packing has been achieved. For Permaphase ODS anomalous values are obtained, A increasing with degree of retention while C is near zero. This is an artefact arising from the increasing asymmetry of peaks as k' increases.

Heats of transfer have been determined with both materials. For Permaphase ETH ΔH for transfer from the stationary to mobile phase (hexane + 1% ethanol) lies between 1.8 and 3.7 kcal mol^{-1} but is not the only factor determining k'. For Permaphase ODS values of ΔH cover a wider range (0.9 to 5.9 kcal mol^{-1}) and closely follow the values of k'; thus retention on Permaphase ODS is largely determined by the heat of transfer from the stationary phase to the mobile phase (methanol–water, 40:60).

INTRODUCTION

Chemical bonding of the stationary phase to the surface of a chromatographic support offers many advantages[1–3], and several such materials have been produced for gas (GC) and liquid (LC) chromatography. Their major advantage in GC is greater

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** Permaphase is a trade-name of DuPont, Wilmington, Del., U.S.A.

thermal stability when compared to conventional non-bonded stationary phases, and their major advantage in LC is insolubility in solvents which would dissolve non-bonded stationary phases of similar chemical type. The first bonded stationary phases were those devised by Halász and Sebestian[1], in which the surface of a silica gel is esterified with a long-chain alcohol to give $\rightarrow$Si–O–C bonding of an organic group to the surface of the support. Unfortunately $\rightarrow$Si–O–C bonds are readily hydrolysed in acid or alkaline solution and the use of "Halász brushes" is accordingly somewhat restricted. Their performance has recently been favourably compared by Horgan and Little[4] with that of conventional stationary phases. In 1970 Kirkland and De Stefano[2,3] produced materials in which organic groups were attached to the surface of the porous silica layer of Zipax by $\rightarrow$Si–C bonds, which are much more stable to hydrolysis and reaction generally than $\rightarrow$Si–O–C bonds. In these materials (Permaphases), a lightly polymerized silicone layer is bonded to the surface of the silica to give a total loading of about 1 % by weight of stationary phase. This percentage has been shown to be the optimum in terms of both kinetic and thermodynamic performance[3], but their performance has been studied only to a limited extent[2,3,5]. The present study was undertaken in order to characterise the materials more thoroughly from the chromatographic point of view, and is a continuation of a program to evaluate the performance of packings presently available for high-speed LC[6-8] and in particular to determine their packing and mass transfer characteristics.

In previous papers[6-10] we have shown that the reduced plate height/reduced velocity plot for any packing material gives an excellent indication of its chromatographic performance, and that for most available packings the relationship between the two parameters is given to a good approximation by

$$h = B/v + Av^{0.33} + Cv \tag{1}$$

where h is the reduced plate height defined as H/d_p (H being the plate height and d_p the particle diameter), and v is the reduced velocity defined as ud_p/D_m (u being the linear velocity of the eluent, and D_m being the diffusion coefficient of the solute in the eluent). The first term in eqn. 1 represents the contribution to band dispersion from axial diffusion and is normally negligible in liquid chromatography. The second term is largely determined by the goodness of packing of the column; a well packed column has A around unity[6]. The best value of A so far obtained was 0.4 using 0.48-mm-diameter glass spheres[9]. The C term reflects the slowness of equilibration between the moving and motionless or stagnant parts of the column, and is often called the mass transfer parameter. Typically C ranges from zero to 7×10^{-2} for existing support materials[6-8]. C is expected to be high for completely porous supports such as silica gel and alumina, and low, say 1×10^{-2}, for pellicular materials. However, C will be higher than these values whenever the stationary phase is a polymer or viscous liquid in which diffusion is slow, or a fine pore material within which normal molecular diffusion is severely restricted. Fine pore silica gels may come into the latter category.

Resistance to mass transfer may occur in both the stationary phase proper and in the portion of the mobile phase which is held stagnant within the pores of the support material. Giddings[11] has shown that these two possible contributions to h have different dependences upon k', the column capacity ratio. Thus for stationary phase mass transfer the contribution to h (or H) passes through a maximum when k'

is unity, while for mass transfer in the stagnant part of the mobile phase the contribution rises gradually to a maximum as k' increases to infinity. In principle it should therefore be possible to determine whether the rate-determining part of the mass transfer occurs in the mobile or the stationary phase. In practice this is difficult because there is normally a contribution from each and the empirical dependence of h upon k' is often indecisive. The separation of the two contributions to h has not been achieved in LC although it is possible in GC by making use of the difference in diffusional properties of various carrier gases[12]. Nevertheless the experimental determination of the dependence of h and C upon k' is of great practical value since it may enable optimum separation conditions to be derived even if a theoretical explanation of the dependence escapes us.

In the present work we have determined the (h, v) curves for a number of solutes at several temperatures on Permaphases ETH and ODS. The dependence of C on temperature enables the activation energy of the diffusional process, which is rate determining, to be compared with the activation energy for diffusion in the mobile phase.

We have also determined the heats and estimated the entropies of transfer from the stationary to the mobile phases from the temperature dependence of k'. Peak symmetry has been measured in order to determine whether or not the isotherms for partition of solutes between the mobile and polymeric stationary phases are linear.

EXPERIMENTAL

The liquid chromatograph was constructed from components in the laboratory, and consisted of a pressure intensifier pump (Haskel Engineering Co.), a pressure gauge (Helicoid, American Chain and Cable Co.), a glass or stainless-steel column with a specially designed injection head housing a captive septum, and a fixed wavelength ultraviolet detector (DuPont Model 410 or Varian Model 4100). The Varian model was modified to give higher sensitivity by the insertion of a scintillator disk between the cell and the photoresistors (Type NE108 from Nuclear Enterprises, Edinburgh, Great Britain) and to give higher stability by thermostatting the detector cell and the photoresistors.

Columns were 2.1-mm-bore heavy-walled regular glass tubing (8 mm O.D.) or 2.1-mm precision bore stainless-steel tubes of $^1/_4$ in. diameter (Superior Tube Co., Norristown, Pa., U.S.A.). Glass columns were fitted with brass end pieces, and steel columns with end pieces constructed from Type 316 or EN58J stainless steel. The column temperature was controlled by a thermostatted water jacket.

Columns were packed by the rotate, bounce and tap method [6,13,14], using carefully graded Permaphase ETH and ODS packings. The Permaphase ETH was sieved and the 37- to 44-μm fraction (325–400 mesh size) used. Microscopic examination showed the particles to be of uniform size and shape. The Permaphase ODS after similar treatment gave poor and irreproducible performance, and indications that the frit retaining the packing was becoming blocked by small particles. Microscopic examination showed that even after sieving the material contained a high proportion of very small particles apparently adhering to larger particles. The material was therefore submitted to the following procedure, which yielded a clean, free flowing fraction of much improved chromatographic performance.

TABLE I

DIFFUSION COEFFICIENTS*, D_m, AND CAPACITY RATIOS**, k'

No.	Solute	% (w/w)	Solvent/ stationary phase	20°		30°		40°		50°		60°	
				$10^5 D_m$	k'	$10^5 D_m$	k'	$10^5 D_m$	k'	$10^5 D_m$	k'	$10^5 D_m$	k'
1	Toluene	0.02	n-Hexane–	3.8	0	4.3	0	4.9	0	5.6	0	6.3	0
2	Acetophenone	0.02	ethanol (99:1)/	3.6	0.12	4.1	0.10	4.7	0.09	5.3	0.08	6.0	0.07
3	2,6-Xylenol	0.02	Permaphase ETH	3.6	0.56	4.1	0.46	4.6	0.38	5.3	0.31	6.9	0.26
4	p-Cresol	0.1		3.8	1.4	4.4	1.3	5.0	1.2	5.6	1.1	6.3	1.0
5	Phenol	0.1		4.5	2.4	5.2	2.1	5.9	1.9	6.6	1.7	7.5	1.5
6	p-Hydroxybiphenyl	0.1		3.2	3.3	3.7	3.0	4.1	2.7	4.8	2.4	5.4	2.1
1	Acetone	1.5	Methanol–	0.67	0.11	0.91	0.10	1.24	0.10	1.62	0.10	2.21	0.10
2	Benzene	0.33	water (40:60)/	0.52	0.66	0.71	0.53	0.96	0.46	1.26	0.41	1.71	0.36
3	Bromobenzene	1.33	Permaphase ODS	0.58	2.5	0.79	1.85	1.06	1.50	1.39	1.22	1.9	0.96
4	Dibutyl phthalate	0.66		0.27	9.6	0.36	6.5	0.49	5.1	0.65	3.9	0.88	2.8
5	1,2,4-Trichlorobenzene	6.6		0.45	13.6	0.60	9.3	0.82	7.1	1.07	5.4	1.46	4.0

* Units of D_m are cm² sec⁻¹; values calculated by the Wilke and Chang equation[11,15].

** Values of k' determined experimentally.

Unsieved Permaphase ODS was washed three times with benzene and dried. The dried particles were suspended in a dense solvent (dried diiodomethane + tetrachloroethylene having a density of 2.1 g cm^{-3}) and placed in an ultrasonic vibrator for 1 h. The suspension was then shaken thoroughly and allowed to settle. When the uppermost of the settling particles had fallen half way to the bottom of the column of liquid 90% of the liquid plus any suspended particles was removed. This gravity fractionation process was repeated until microscopic examination showed the particles to be of satisfactory uniformity. The 37- to 44-μm fraction finally obtained was free flowing and packed well. No further problems with blocked frits were encountered.

Hexane containing 1% ethanol was used as eluent in the main study of Permaphase ETH, the hexane having been de-aromatized by passage through a column of activated silica gel. A 40:60 mixture by volume of methanol and water was used in the study of Permaphase ODS and in a limited study of Permaphase ETH. All solvents were degassed immediately before use by reflux.

Samples for analysis were dissolved as appropriate in hexane or methanol. Between 2 and 5 μl was injected into the top of the column packing for each elution using a 5-μl microsyringe (SGE Ltd., London, Great Britain; Melbourne, Australia).

Diffusion coefficients required in the calculation of reduced velocities were estimated from the Wilke and Chang equation[11,15], using viscosity data from the literature for hexane[16] and methanol–water mixtures[17] at the relevant temperatures. For the 40:60 methanol–water mixture the "molecular weight" of the solvent was taken as $M_1 = 23.6$, and the association constant as $\mu_1 = 2.32$. Table I lists the composition of the sample solutions used in the main studies, and the diffusion coefficients, D_m, and column capacity ratios, k', of their components at 20, 30, 40, 50 and 60°.

RESULTS AND DISCUSSION

Peak base widths, w, were measured in the normal way by drawing tangents to the points of inflection of the peaks to intersect the base. The empirical plate height, H, was then obtained from the formula

$$H = (w/t_R)^2(L/16) \tag{2}$$

where L is the column length (generally about 100 cm) and t_R the peak retention time. Peak asymmetry, A_s, was defined by eqn. 3

$$A_s = w_t/w_l \tag{3}$$

where w_t and w_l are the trailing and leading half widths, respectively; w_l, for example, is defined by dropping a perpendicular from the intersection of the two tangents (used to define w) to the baseline and is the distance between this intersection and the intersection of the leading tangent with the base line. The upper chromatogram of Fig. 1 shows symmetric and asymmetric peaks obtained at a low flow-rate with Permaphase ODS and illustrates how A_s is calculated. The lower chromatogram shows a typical high-speed separation on Permaphase ETH with which peaks were always symmetrical when using hexane as eluent. k' was determined from eqn. 4
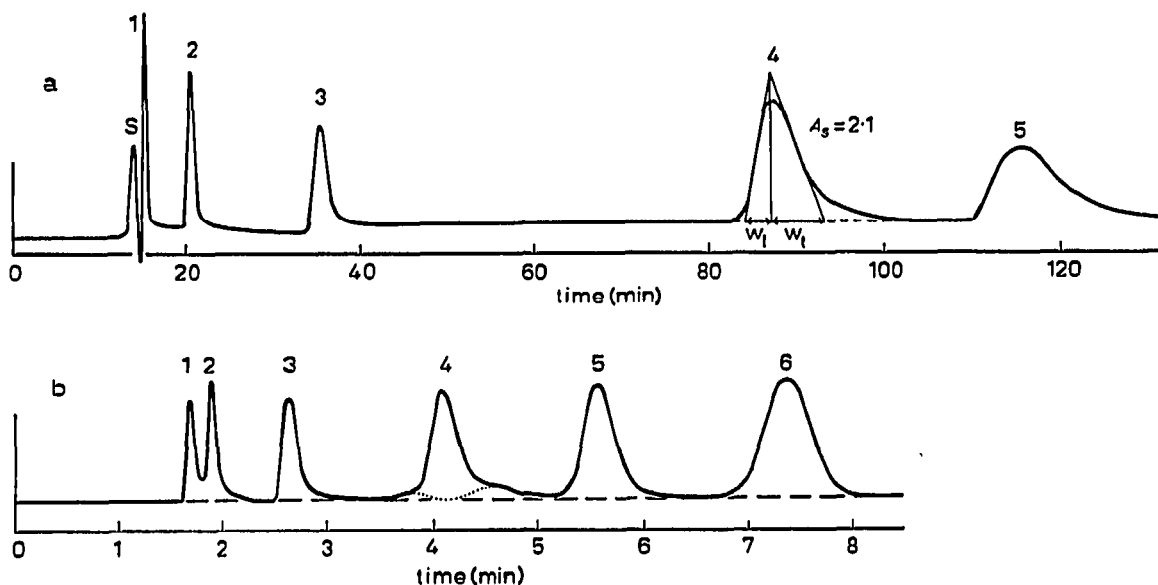
$$k' = (t_R - t_0)/t_0 \tag{4}$$

Fig. 1. Chromatograms obtained with Permaphases ODS and ETH. (a) Elution from Permaphase ODS at 40° and low flow-rate showing peak asymmetry; solutes identified in Table I; S shows the refractive index disturbance due to solvent. (b) Elution from Permaphase ETH at 20° and high flow-rate; solutes identified in Table I.

where t_0 is the retention time of an unretained solute. t_0 was determined by injecting relatively large quantities of undoubtedly unretained solutes such as pentane and water (for Permaphases ETH and ODS, respectively) and observing the differential peaks produced by the disturbance of the refractive index as these solutes pass through the detector cell. With Permaphase ETH it was found that toluene was essentially unretained; with Permaphase ODS acetone was very slightly retained (k' about 0.1). For all solutes k' was found to be independent of fluid velocity as found by Kirkland[3] for Permaphases containing around 1% of stationary phase.

In calculating the reduced plate height the particle diameter, d_p, was taken as 40.5 μm, the mean sieve opening of the fractions used. Column permeabilities, K^0, and column resistance parameters, φ, were obtained from eqn. 5

$$u_0 \equiv (L/t_0) = K^0 \frac{\Delta p}{\eta L} = \frac{\Delta p d_p^2}{\varphi \eta L} \tag{5}$$

where u_0 is the linear velocity of the eluent, Δp the pressure drop across the length of the column, and η the viscosity of the eluent. The values obtained for the Permaphases are compared to those previously obtained for Zipax[7] in Table II. The values are broadly similar: Permaphase ETH packed slightly more densely than Zipax of similar particle size, while Permaphase ODS packed about equally densely. With Permaphase ODS the permeability of the column decreased slightly with increase of temperature from 30 to 60° possibly due to swelling of the polymeric stationary phase.

TABLE II

COLUMN PERMEABILITIES, K^0, AND RESISTANCE PARAMETERS, φ

Packing material	Temperature (°C)	Particle diameter (μm)	$10^8 \times K^0$ (cm²)	φ	Reference
Zipax	20	49	3.45	690	7
		39	2.47	590	7
Permaphase ETH	20	40.5	2.30	715	This work
	60	40.5	2.34	700	This work
Permaphase ODS	30	40.5	2.90	565	This work
	60	40.5	2.50	655	This work

Fig. 2 shows plots of the reduced plate height against reduced velocity for the solutes listed in Table I eluted from Permaphase ETH at temperatures from 20 to 60°. The data of Fig. 2 show no dependence of h upon temperature at a specific reduced velocity for any solute, and only slight dependence of h upon k'. Thus the dependence of H upon temperature, previously reported by Schmit et al.[5], resulted from the decrease in diffusion coefficient with increased temperature, rather than from any intrinsic change in properties of the packing material. The data of Fig. 2 are summarised by the values of A and C (eqn. 1) listed in Table III, and by the curves of Fig. 3, which compare Permaphase ETH with other packings previously examined[6-8]. The values of A for Permaphase ETH are slightly higher than those for Zipax[7] and increase somewhat with degree of retention as found previously. There
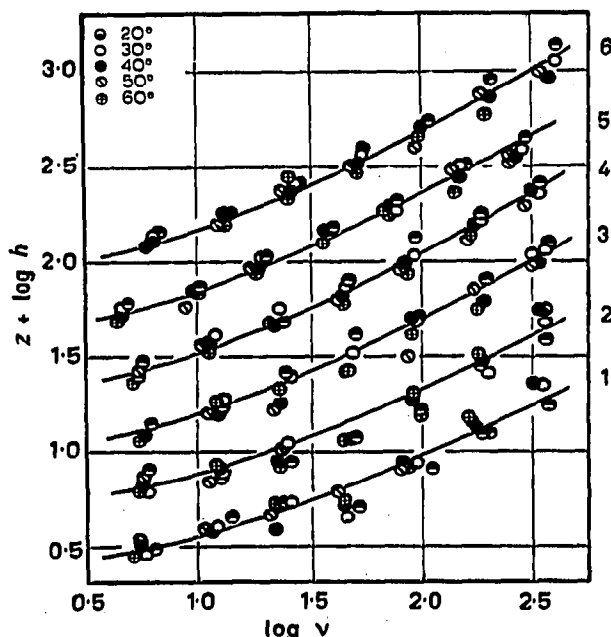

Fig. 2. Plots of reduced plate height, h, against reduced velocity, ν, for elution of solutes from Permaphase ETH at different temperatures. Values of z for different solutes (identified in Table I) are: (1) $z = 0.0$; (2) $z = 0.3$; (3) $z = 0.6$; (4) $z = 0.9$; (5) $z = 1.2$; (6) $z = 1.5$.

TABLE III

PARAMETERS A AND C OF EQUATION 1

| Material	Solute	k' range	A	C	Reference
Permaphase ETH	Toluene	0	1.6	1.9×10^{-2}	This work
	Acetophenone	0.07–0.12	1.7	2.8×10^{-2}	
	2,6-Xylenol	0.26–0.56	1.8	4.0×10^{-2}	
	p-Cresol	1.0 –1.4	1.7	5.4×10^{-2}	
	Phenol	1.5 –2.4	1.8	5.4×10^{-2}	
	p-Hydroxybiphenyl	2.1 –3.3	1.9	5.6×10^{-2}	
Permaphase ODS	Acetone	0.10–0.11	1.8	0	This work
	Benzene	0.36–0.53	2.4	0	
	Bromobenzene	0.96–1.85	3.2	0	
	Dibutyl phthalate	2.8 –5.1	4.0	0	
	1,2,4-Trichlorobenzene	4.0 –7.1	4.8	0	
Zipax, 29 μm		0	0.75	0	7, 8
		8	1.0	1.1×10^{-2}	
Corasil, 49 μm		0	1.2	0.3×10^{-2}	6, 8
		3.2	1.7	5×10^{-2}	
Porasil, 49 μm		0 –1	1.6	4.5×10^{-2}	6, 8
Corning porous glass, 49 μm		0.44	1.7	4.5×10^{-2}	6, 8
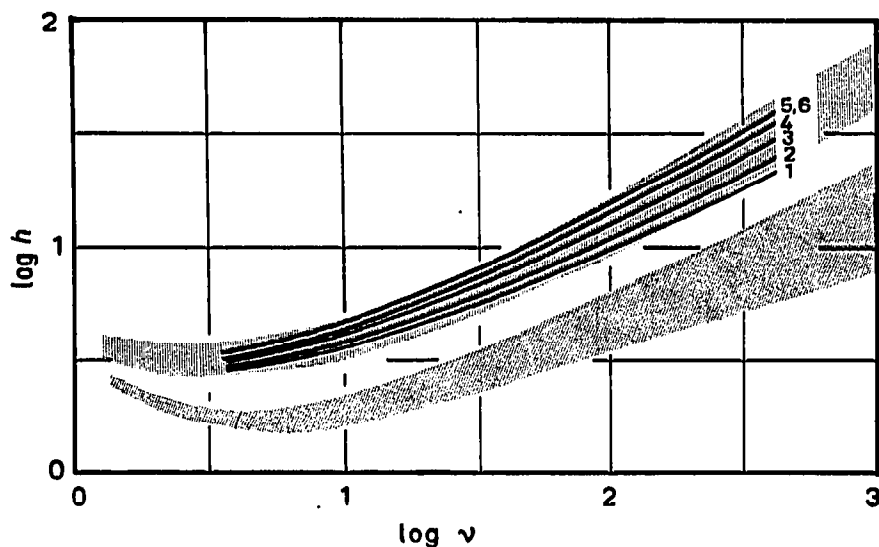
Fig. 3. Summary of reduced plate height data for Permaphase ETH; solutes identified in Table I. Shaded bands show range of data for Porasil and Corning controlled-pore glass (upper band), and for Zipax loaded with 1% β,β'-oxydipropionitrile (lower band).

is a corresponding increase in C which rises from 1.9×10^{-2} to 5.6×10^{-2}. The C-values are comparable to those obtained with Corasil[6] and are considerably higher than those obtained with Zipax[6,7], showing that there is considerable resistance to mass transfer in the surface layer of the Permaphase material. Since the surface layer of a Permaphase material immersed in a solvent must be thought of as a swollen poly-

mer, it is not possible to distinguish between stationary phase proper, and stagnant mobile phase (as it is for example in a wide-pore silica gel bearing a small proportion of a stationary liquid phase). Thus dependence of C upon k' cannot be used to determine whether slow mass transfer occurs in the mobile or the stationary phase. It is interesting to note, however, that even for the unretained solute toluene there appears to be a significant mass transfer term. The lack of dependence of C upon temperature indicates that the activation energy for the rate-determining process in equilibration is close to that for diffusion in the mobile phase.

Our plate height data for Permaphase ETH are compared with those of Kirkland[3] in Table IV. Our data, obtained with dry packed columns, are slightly lower than those obtained by Kirkland using a balanced slurry packing technique, and considerably lower than he obtained using dry packing.

TABLE IV

EFFECT OF PACKING METHOD ON H FOR PERMAPHASE ETH

Packing method	Temperature (°C)	Particle diameter (μm)	Carrier	Linear velocity (cm sec⁻¹)	Solute	H (mm)	k'	Reference
Dry	27	37–44	Hexane	1.33	Acetophenone	0.83	0.17	3
					Benzyl alcohol	1.56	1.65	3
Balanced slurry	27	37–44	Hexane	1.17	Acetophenone	0.47	0.17	3
					Benzyl alcohol	1.07	1.65	3
Dry (rotate, bounce, tap)	30	37–44	Hexane + 1 % ethanol	1.20	Acetophenone	0.36	0.11	This work
					p-Cresol	0.58	1.30	This work
					Phenol	0.58	2.1	This work

We conclude that in kinetic terms Permaphase ETH performs in a way similar to porous materials such as Porasil and Corning controlled-pore glass.

Fig. 4 shows data for the elution of five solutes from Permaphase ODS at temperatures from 20 to 60°. A and C values are listed in Table III and a comparison of the plate height data with those obtained from other supports is shown in Fig. 5. Fig. 6 shows the asymmetry index as a function of reduced velocity for the three more strongly retained solutes on Permaphase ODS at three temperatures. The peaks for slightly retained solutes were symmetrical within experimental error, apart from those for acetone, which showed some asymmetry at the highest velocities, probably due to incomplete mixing in end fittings.

The values of A and C for Permaphase ODS are anomalous, for C is always near zero while A increases from 1.8 to 4.8 as retention increases. These effects are artefacts which arise from the increasing peak asymmetry as the fluid velocity falls. When asymmetry of peaks increases with reduction in fluid velocity this is clear evidence that the partition isotherm for a solute is non-linear, for then the peak width is determined not only by kinetic but also by thermodynamic effects. A non-
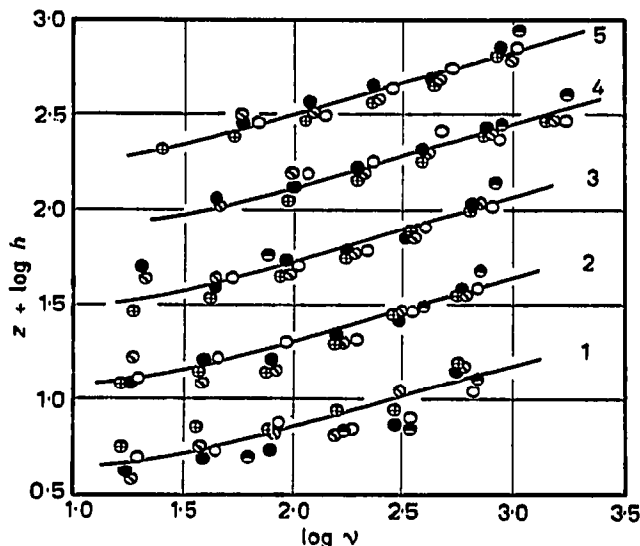
Fig. 4. Plots of reduced plate height, h, against reduced velocity, ν, for elution of solutes from Permaphase ODS at different temperatures. For symbol identification see insert in Fig. 2. Values of z for solutes (identified in Table I) are: (1) $z = 0.0$; (2) $z = 0.3$; (3) $z = 0.6$; (4) $z = 0.9$; (5) $z = 1.2$.
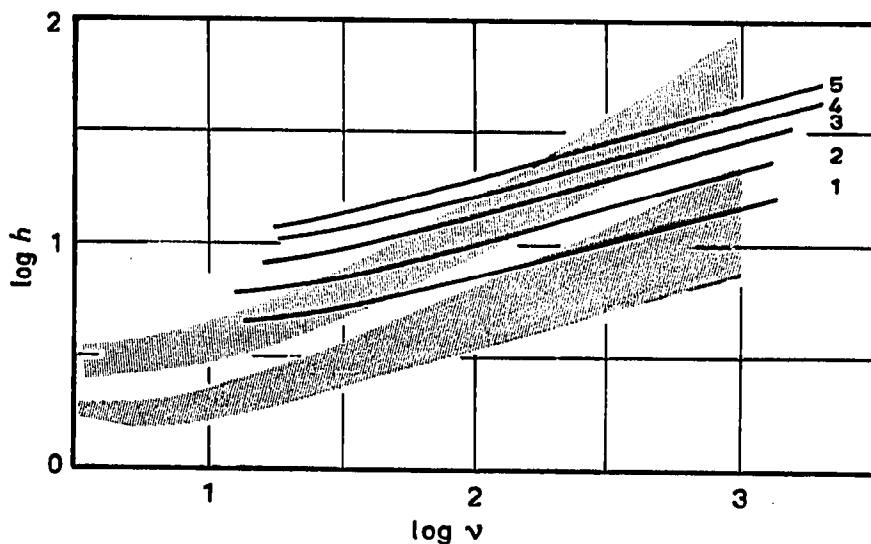

Fig. 5. Summary of reduced plate height data for Permaphase ODS. For details see caption to Fig. 3.

linear isotherm will inevitably produce a skew peak whose width will be independent of fluid velocity if kinetic effects are ignored. The kinetic contribution to peak width, which is symmetric, however, decreases with fluid velocity. The combined effect of the asymmetric and symmetric peak dispersion forces is therefore to produce a skew peak which is more asymmetric the lower the velocity. This is just the opposite to what is observed when peak skewness is caused by poor flow geometry through col-
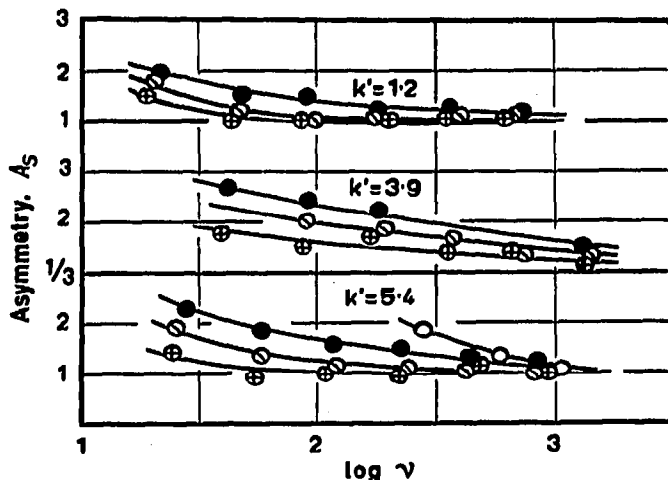
Fig. 6. Asymmetry of peaks eluted from Permaphase ODS at various temperatures for different solutes. For symbol identification see insert in Fig. 2. Values of k' are for 50°. Topmost group of curves: bromobenzene; centre group: dibutyl phthalate; lowest group: 1,2,4-trichlorobenzene.

umn connections, detector cells etc., or in general by effects with an invariant time constant.

The effect of a non-linear isotherm on the plate height velocity curve is therefore to raise the empirical plate height at low velocities. This has the subsidiary effect of producing high values of A and low values of C. The increased asymmetry with increased retention which we have observed can be explained as follows. According to thermodynamics the capacity ratio k' may be related to thermodynamic parameters by eqn. 6

$$\log k' = \log f + \Delta H_{s \to m}/RT - \Delta S^0{}_{s \to m}/R \tag{6}$$

where f is the ratio of the volumes of stationary to mobile phase, $\Delta H_{s \to m}$ is the heat of transfer from the stationary to mobile phase, and $\Delta S^0{}_{s \to m}$ is the standard entropy of transfer assuming that the standard state is unit molar concentration in either phase. When the partition isotherm is non-linear it is probable that $\Delta H_{s \to m}$ is a function of the concentration and that the range of $\Delta H_{s \to m}$ from the lowest concentration (zero) to the highest concentration of interest (the peak maximum concentration in this case) is likely to be roughly proportional to $\Delta H_{s \to m}$ itself. Thus we can write

$$\text{range of } \Delta H_{s \to m} \equiv \Delta(\Delta H_{s \to m}) = \alpha \Delta H_{s \to m} \tag{7}$$

where α is a constant. The skewness of a peak depends upon the range of k' embraced by the concentrations within the peak, and we can therefore write approximately

$$\log k_0'/k_m' = \Delta(\Delta H_{s \to m})/RT = \alpha \Delta H_{s \to m}/RT = \alpha \log (k'/f)$$

or

$$k_0'/k_m' = (k'/f)^\alpha \tag{8}$$

where k_m' is the value of k' at the peak maximum and k_0' is the value of k' for an

infinitely dilute sample. The fractional range of k' which determines peak skewness is thus proportional to a positive power of k' and so increases slowly with k', as is widely found in practice. An excellent test for the uniformity of an adsorbent or for the linearity of a partition isotherm is therefore the symmetry of a well retained solute peak.

It is noticeable that peak skewness is greatly reduced (Fig. 6) and indeed almost eliminated by running Permaphase ODS at 60°. Thus $\Delta(\Delta H_{s \rightarrow m})$ appears to decrease with temperature. The most likely explanation of this is that as the polymer layer becomes more swollen at higher temperatures (as suggested by the increased column resistance) the partition isotherm becomes more linear. This can be rationalized by supposing that the structure becomes more flexible as the temperature rises so that any configuration within the polymer which can act as a strongly retaining site at low temperatures becomes impermanent at high temperatures. The retaining power of different sites within the polymer layer thus becomes more uniform as the temperature is raised.

In Fig. 5 the comparison of Permaphase ODS with Porasil is favourable at high reduced velocities, since the main cause of peak spreading is kinetic, but is unfavourable at low reduced velocities and low temperatures, because non-linearity of the partition isotherm is now dominant. Changes in the extent of cross-linking of the polymer layer might improve its thermodynamic characteristics by allowing a greater degree of swelling at low temperatures.

A limited study of Permaphase ETH was carried out in the so-called "reversed-phase" mode, that is with an essentially aqueous eluent, methanol–water (40:60). Peaks were now asymmetrical as with Permaphase ODS, especially at low velocities, and the plate heights calculated from the base width were somewhat high. The asymmetry, increasing as the velocity decreases, again indicates that with the aqueous eluent the partition isotherm is no longer linear. There is, however, no evidence that mass transfer in the polymer layer is any slower with an aqueous eluent than with an organic eluent.

Van 't Hoff plots of log k' against $1/T$ shown in Fig. 7 enable heats of transition and entropies of transition to be determined in accordance with eqn. 6, if f is known. While this ratio cannot be determined exactly it can be estimated from published data. According to Kirkland[3] Permaphase materials contain about 1 % by weight of polymeric stationary phase. The glass core of the Zipax particle has a density of about 2.8 and the porous silica layer has a thickness of about 1 μm. The layer is about 50 % porous while the interparticle porosity of the packed column is about 40 %. On this basis f = volume of stationary phase/volume of mobile phase = 1/25 within a factor of about 1.5. Using f = 1/25 gives the values of $\Delta S^0_{s \rightarrow m}$ listed in Table V.

For elution from Permaphase ODS by methanol–water both $\Delta H_{s \rightarrow m}$ and $\Delta S^0_{s \rightarrow m}$ rise with k', but for Permaphase ETH neither quantities follow k'. With ODS, the values of $\Delta H_{s \rightarrow m}$ increase with retention but the effect is somewhat counteracted by the increasing entropy change. Large entropy changes are associated with strong retention, and this may be rationalized by supposing that strongly held molecules are also strongly orientated on the surface of the polymer structure. Although with Permaphase ETH neither $\Delta H_{s \rightarrow m}$ nor $\Delta S^0_{s \rightarrow m}$ follow k', it is noticeable that the highest values of $\Delta H_{s \rightarrow m}$ again go with the highest values of $\Delta S^0_{s \rightarrow m}$, only here the cancelling effect is such that no correlation exists with the trend in k'. The main reason for the
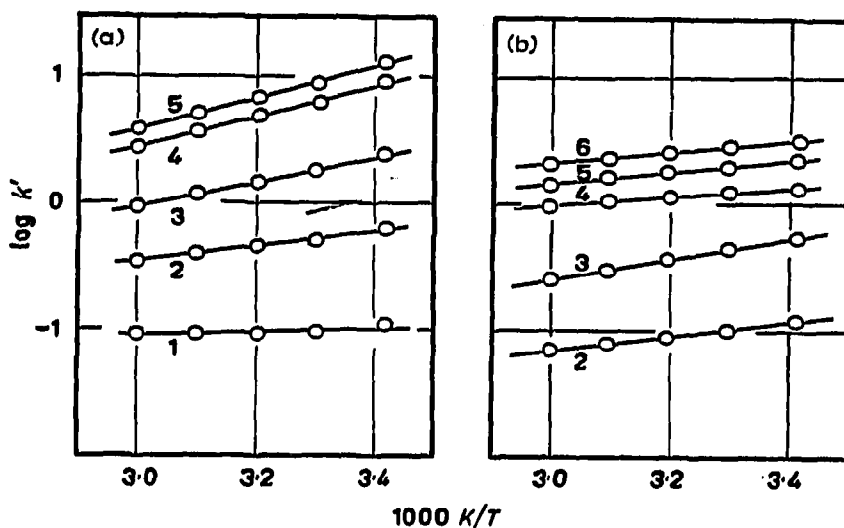
Fig. 7. Van 't Hoff plots of log k' against $1000/T$ for elution of solutes (identified in Table I) from Permaphases ODS (a) and ETH (b).

TABLE V

THERMODYNAMIC PARAMETERS FOR PARTITION BY PERMAPHASES ETH AND ODS

Substance	k' at 40°	$\Delta H_{s \to m}$ (kcal mol^{-1})	$\Delta S°_{s \to m}$ (cal K^{-1} mol^{-1})
Permaphase ETH; solvent, n-hexane $+$ 1 % ethanol; $f = 1/25$			
Acetophenone	0.09	2.57	6.5
2,6-Xylenol	0.38	3.68	7.3
p-Cresol	1.2	1.76	−1.2
Phenol	1.9	2.18	−0.7
p-Hydroxybiphenyl	2.7	2.15	−1.5
Permaphase ODS; solvent, methanol–water (40:60); $f = 1/25$			
Acetone	0.10	0.88	1.0
Benzene	0.46	2.93	4.4
Bromobenzene	1.5	4.57	7.3
Dibutyl phthalate	5.1	5.85	9.0
1,2,4-Trichlorobenzene	7.1	5.85	8.4

differences in thermodynamic behaviour of the two Permaphases is seen to be in the larger values of $\Delta H_{s \to m}$ for the ODS material and this probably arises from the large difference in polarities between ODS and aqueous methanol as compared to that between ETH and hexane.

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