

CHROM. 6761

NON-EQUILIBRIUM EFFECTS IN THE BRANCHED-CHAIN PEAK BROADENING PHENOMENON IN GAS CHROMATOGRAPHY ON PORAPAK P*

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(Received April 10th, 1973)

SUMMARY

Non-equilibrium coefficients (C_s and C_m) have been evaluated for iso-octane and *n*-octane on Porapak P at different temperatures in the range 130–180°. The reproducibility of the chromatographic parameters upon column conditioning has been investigated. An increase in the eddy diffusion contribution upon column conditioning is apparent. The stationary phase non-equilibrium coefficient for *n*-octane is affected due to a slight microstructural change in the polymer packing upon column conditioning, but that for iso-octane is unaltered under its existing large background effect. The temperature-sensitive and unusually high C_s coefficients for iso-octane reflect a high activation energy of 17.6 kcal/mole. The unusual branched-chain peak broadening phenomenon recently observed on certain organic porous polymer column packings has been rationalized as being due to the effect of restricted intraparticle diffusion and the relative affinities of the various adsorbates for the adsorbent.

INTRODUCTION

An eluted chromatographic peak of a compound is broadened owing to the non-ideality of the chromatographic process. In gas chromatography (GC), the mechanism of retention frequently has the result that the higher is the retention of a compound, the greater is the width of the chromatographic peak of the substance as measured on the chromatogram. An interesting opposite behaviour recently observed on certain organic porous polymer column packings¹⁻⁵ with compounds of the same chemical nature, but of different degrees of branching, can be defined as the branched-chain peak broadening phenomenon. In such cases, the standard deviation of the peak of the branched-chain compound is significantly greater than that of the linear compound, and this effect cannot be explained in terms of the capacity ratio change and insignificant differences in diffusivity values.

Non-equilibrium has a damaging effect as it causes zone dispersion⁶. It may originate due to the non-infinite rate of lateral diffusion of the solute in the mobile and the stationary phases, or it may result from the kinetics of adsorption. In some cases, surface diffusion can contribute significantly to the zone broadening. The role of

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non-equilibrium or mass-transfer resistance in peak broadening is reflected in the so-called non-equilibrium coefficients of mass-transfer resistance terms (C terms) in the expression for chromatographic plate height *versus* flow-rate. In GC, the stationary phase non-equilibrium effect is usually more significant than that of the gas phase. Hence, an insight into the problem of the branched-chain peak broadening phenomenon requires a knowledge of separate C_s and C_m coefficients.

THEORETICAL

The C_s coefficients for adsorbates on porous polymer column packings may originate from the sorptive-desorptive kinetics (C_k) and hindered surface diffusion, including intraparticle diffusion. Mobile phase mass-transfer coefficients in porous particles where the mobile phase is stagnant within pores of various geometries have been discussed recently by Hawkes⁷. A general equation describing these coefficients can be written in the form

$$C_m^* = \frac{q(1+k'-\varphi)^2 d^2}{(1-\varphi)(1+k')^2 \gamma_p D_m} \quad (1)$$

where q and d are the geometrical factor and the depth of the pore, respectively. The effective diffusivity (D_{eff}) of the sample into the micropore filled with stagnant mobile phase is $\gamma_p D_m$, where γ_p is the obstruction factor for diffusion in the porous mass and D_m is the diffusivity of the solute in the mobile phase. φ and k' are the interstitial porosity and the capacity ratio, respectively. For a particular adsorbent, q and d can be treated as constants provided that no gross change in the microstructure of the packing occurs in the working temperature range. In cases where D_{eff} is assumed to contribute largely to the above expression for C_m^* , the contribution of k' and φ to C_m^* can be neglected. Moreover, if the C_s coefficient originates mainly from the restricted diffusion into the stagnant mobile phase within the micropores of the polymer, one can write

$$C_s \approx C_m^* \approx K_1 / D_{\text{eff}} \quad (2)$$

where K_1 is a constant. If the diffusion in the porous mass is considered to be an activated process, D_{eff} can be expressed as

$$D_{\text{eff}} = A e^{-E/RT} \quad (3)$$

where A is a constant and E , R and T are the activation energy, gas constant and the absolute temperature, respectively. Eqns. 2 and 3 can be rearranged to the form

$$-(2.3026) \log(1/C_s) = (E/RT) - A_1 \quad (4)$$

where A_1 is a constant. Hence a plot of $-(2.3026) \log(1/C_s)$ versus $1/RT$ should be linear with a slope E .

EXPERIMENTAL

In order to determine the reproducibility of the chromatographic parameters during the evaluation of the C terms in the temperature range from 130 to 180°, the following procedure was adopted.

A freshly packed Porapak P column was equilibrated at 130° with nitrogen as the carrier gas until the background current was insignificant. Retention and standard deviation data were measured for iso-octane and *n*-octane peaks at different flow-rates, controlled by the inlet pressure, using nitrogen and hydrogen as the carrier gases, respectively. The measurements were made at 10° intervals and the reproducibility of the chromatographic parameters was studied at 140°. The measurements were then continued at 10° intervals up to the conditioning temperature of 210°. After the completion of the experiment the column was unpacked. Agglomeration of the polymer beads without any visible changes in their appearance was observed.

All measurements were made on Chrom 4 (Laboratory Equipment N.E., Prague, Czechoslovakia) equipped with a dual flame ionization detector and a katharometer. The columns were constructed from 3 mm I.D. stainless-steel tubing. A 90 cm long Porapak P (Waters Associates Inc., Framingham, Mass., U.S.A.; Batch No. 550, 100–120 mesh) column was packed tightly by the conventional technique. To check the equipment, a 100 cm long silicone oil F-60 (30% on 100–120 mesh Sterchamol) column was used. The sample was a model mixture of iso-octane and *n*-octane (analytical grade chemicals from Lachema N.E., Brno, Czechoslovakia). Iso-octane was chosen as a representative of the compounds showing the branched-chain peak broadening effect, while *n*-octane, showing normal peak broadening, was studied for comparison. In each case, 5–10 μ l of vapour mixture drawn from *ca.* 2 mm above the surface of the model liquid mixture at room temperature (*ca.* 23°) was injected with a micro-syringe (Zimmermann, Leipzig, G.D.R.). In most cases, three measurements were carried out at each \bar{u} (average linear velocity) level. The retention distance was measured from the injection point, and the standard deviation was determined from the peak width at the 0.607 peak height level from the base. The chart speed was adjusted to obtain a measured peak width of greater than 10 mm.

Methane has a significant retention on Porapak columns at low temperature. However, at 130° and above, an apparent but insignificant difference in the absolute retentions of nitrogen and methane (which falls within the error of measurements) was found on the Porapak P column. This measurement was carried out with a thermal conductivity detector using hydrogen as the carrier gas. As the minimum temperature of investigation was 130°, the linear flow-rate was determined from the absolute retention of the methane peak. All of the \bar{u} values were averages of five determinations.

Experiments were conducted under laminar flow conditions, confirmed from the linearity of the dependence of the measured \bar{u} values against $(P_i^2 - P_0^2) / \bar{P}$. The basic data were measured in the mass-transfer predominant flow-rate region.

The \bar{H} values were calculated from the equation

$$\bar{H} = L/4(Rd/2\sigma)^2$$

where Rd is the retention distance. The C_s coefficient was calculated from the following modified^b Giddings and Schettler's expression^o:

$$C_s = \Delta \left[\frac{\bar{H}}{f_1} (X) \right] / X \Delta (D_m' / \bar{P} f_1) \quad (5)$$

where the symbols have their usual meanings. The Δ terms designate the differences

between the respective items obtained by measurement for a given X , which represents $\bar{P}\bar{u}/D'_m$, at two different values of D'_m , the diffusivity of the solute in the carrier gas at 1 atm pressure. The C_m coefficients, $\omega dp^2/D'_m$ (ref. 6), were calculated from the equation

$$C_m = \left[\frac{H}{f_1}(X) - C_s X (D'_m / \bar{P}f_1) \right] / \bar{P}\bar{u}. \quad (6)$$

The D'_m values used in the evaluation of C terms were calculated by the Fuller-Schettler-Giddings method¹⁰.

RESULTS

Checks on the equipment

To check the equipment, the C coefficients for iso-octane and n -octane were determined on a 30% silicone oil F-60 column. The results are listed in Table I.

TABLE I

C_s AND C_m COEFFICIENTS OF ISO-OCTANE AND n -OCTANE MEASURED ON THE 30% SILICONE OIL F-60 COLUMN

Temp. (°C)	Iso-octane				n-Octane			
	k'	$C_s \times 10^3$ (sec)	$C_m \times 10^3$ (sec)		k'	$C_s \times 10^3$ (sec)	$C_m \times 10^3$ (sec)	
			N_2	H_2			N_2	H_2
100	7.95	7.2	7.5	2.3	16.39	4.8	5.8	1.8
110	6.30	6.7	7.9	2.6	12.42	4.2	6.9	2.1

To complete the data, C_m coefficients are listed in the table and are only approximate. They include eddy diffusion and longitudinal diffusion contributions. The latter contribution cannot be ignored, as the C_m coefficients were calculated from \bar{u} levels (9–10 cm/sec for nitrogen and 18–20 cm/sec for hydrogen), which were not entirely free from a longitudinal diffusion contribution. The tabulated C_s values, which are our present interest, have the normal magnitudes found in gas-liquid chromatography¹¹.

Reproducibility of the Porapak P column

The changes in the values of \bar{P} , relative retention, absolute retention and HETP for iso-octane and n -octane measured on Porapak P after conditioning the column above 140° are listed in Table II. Comparisons were made at a column temperature of 140° and at the \bar{u} levels listed in the table. Both the time and temperature of ageing the column with the carrier gases represent successive measurements made on the same column. The results show that, except for relative and absolute retentions, all of the parameters were affected gradually by both the time and temperature of conditioning at 150° and above; the deterioration in the column efficiency for n -octane was significantly large, and an increase in HETP by approximately 85% was observed

TABLE II
REPRODUCIBILITY OF THE CHROMATOGRAPHIC PARAMETERS OF THE PORAPAK P
COLUMN UPON COLUMN CONDITIONING

Temp. of ageing (°C)	Time of ageing (h)	Carrier gas	Comparison of results measured at 140°						
			\bar{u} (cm/sec)	\bar{P}/\bar{P}^*	r/r^*	\bar{H}/\bar{H}^*		Rd/Rd^*	
						Iso-octane	n-Octane	Iso-octane	n-Octane
140	20	N ₂	5.32	1.004	0.998	1.015	1.014		
150	5	N ₂	5.30	0.998	0.999	1.007	0.993		
150	10	N ₂	4.74	1.001	0.999	1.038	1.048		
150	10	H ₂	5.46	0.989	1.009	1.069	1.083		
160	10+10	N ₂ +H ₂	5.03	0.976	1.011	1.075	1.115		
			5.73	0.977	1.007	1.063	1.110		
180	10+10	N ₂ +H ₂	4.89	0.987	1.002	1.060	1.289		
			5.54	0.977	1.012	1.071	1.302	1.000	1.001
190	10	N ₂	4.89	0.992	1.002	1.089	1.422	0.977	0.978
			5.56	0.990	1.005	1.068	1.416		
200	8	N ₂	4.98	0.963	1.011	1.108	1.581		
			5.59	0.957	1.012	1.091	1.589	0.888	0.888
210	2	N ₂	5.80	0.957	1.018	1.097	1.801	0.875	0.884
210	6	N ₂	4.93	0.957	1.001	1.111	1.838	0.862	0.864
			5.38	0.955	1.014	1.099	1.855		

$$\frac{r}{r^*} = \frac{Rd_{n\text{-octane}}}{Rd_{\text{iso-octane}}} \bigg/ \frac{Rd^*_{n\text{-octane}}}{Rd^*_{\text{iso-octane}}}$$

The asterisk signifies results obtained from the newly packed column conditioned at 140° under a stream of nitrogen carrier gas for 10 h.

after conditioning at 210°. \bar{P} was virtually unaffected up to 190° and about a 5% decrease was observed above 190°. Although an increase in HETP for iso-octane up to the conditioning temperature of 190° was apparent, it was insignificant and fell within the experimental error. About a 10% increase in HETP for iso-octane was observed above 190°. No apparent effect of the nature of the carrier gas (nitrogen and hydrogen) on the chromatographic parameters was observed in the temperature

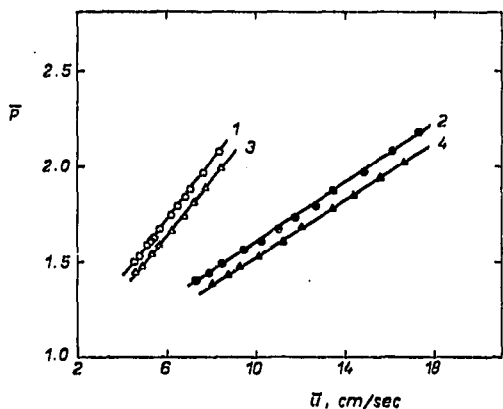


Fig. 1. Plots of \bar{P} versus \bar{u} on Porapak P column at 140°. 1 and 2, nitrogen and hydrogen as carrier gas, respectively, measured after conditioning the column at 140° for 10 h; 3 and 4, nitrogen and hydrogen as carrier gas, respectively, measured at the end of conditioning as shown in Table II.

range investigated. Although the relative retention was unaffected throughout the temperature range, the absolute retentions for both compounds were affected at 190° and there was a very large decrease in the latter above 190°. Except for the behaviour of *n*-octane, these results are in agreement with the temperature limit recommended for Porapak P by d'Aubigne and Guiochon¹².

Fig. 1 shows the effect of column conditioning on \bar{P} . The decrease in \bar{P} upon column conditioning may occur because of agglomeration of the polymer beads, which results in an increase in the effective average particle diameter.

The effect of column conditioning on the C coefficients and the specific surface area is shown in Table III. Although the unusually high C_s coefficient for iso-octane

TABLE III

EFFECT OF COLUMN CONDITIONING ON THE C COEFFICIENTS OF PORAPAK P MEASURED AT 140°

Column state*	S (m ² /g)	Iso-octane**				<i>n</i> -Octane**			
		k'	$C_s \times 10^3$ (sec)	$C_m \times 10^3$ (sec)		k'	$C_s \times 10^3$ (sec)	$C_m \times 10^3$ (sec)	
				N_2	H_2			N_2	H_2
A	111	14.72	158.7	22.1 (8.35)	9.0 (17.30)	28.20	7.9	7.0 (8.35)	2.3 (17.30)
B	114	12.44	151.9	40.7 (8.50)	13.7 (17.14)	24.60	11.9	15.3 (8.50)	4.7 (17.14)

* A, (90 cm × 3 mm) Porapak P column conditioned at 140° under nitrogen carrier gas for 10 h. B, the same column conditioned up to 210° in the sequence quoted in Table II.

** The values in parentheses are the \bar{u} levels for which the C_m coefficients were calculated.

was unaltered, a significant increase in the C_m value was observed.

Figs. 2 and 3 show the changes in \bar{H}/f_1 versus X for iso-octane and *n*-octane upon column conditioning. A parallel increase in \bar{H}/f_1 versus X for iso-octane indi-

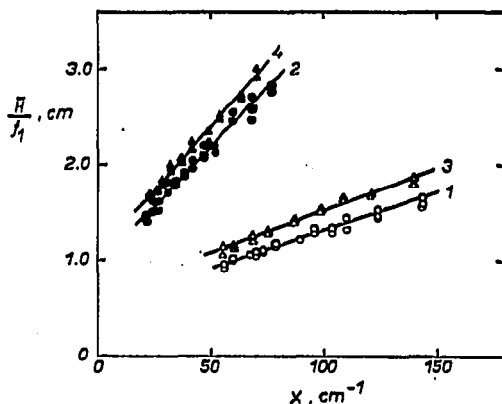


Fig. 2. Plots of \bar{H}/f_1 versus X for iso-octane on Porapak P at 140°. 1, 2, 3 and 4 as in Fig. 1.

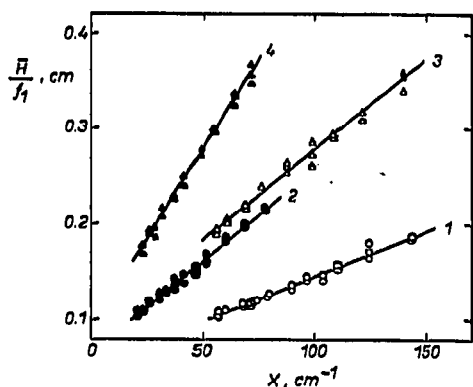


Fig. 3. Plots of \bar{H}/f_1 versus X for n -octane on Porapak P at 140° . 1, 2, 3 and 4 as in Fig. 1.

cates that the increase in the C_m value occurred because of an increase in the eddy diffusion contribution. Void spaces were observed in a glass column of Porapak P after conditioning at an elevated temperature for several weeks. The increased interstitial porosity originates from the shrinkage of the polymeric particles. Commercially available porous polymer beads for gas chromatography shrink after column conditioning², and the shrinkage of the individual polymer particles and hence their macroporous structures occurs as the residual solvent is distilled out¹³ upon column conditioning. It seems reasonable, that both the agglomeration and shrinkage of the polymer particles might be the cause of the increased eddy diffusion contribution observed upon column conditioning. The increase in the C_m coefficient for n -octane can be explained in a similar manner. A significant increase in the C_s coefficient for n -octane is reflected in the \bar{H}/f_1 versus X plots (Fig. 3), where the slopes of the lines have been increased. The C_s value for n -octane found after column conditioning can be expressed as

$$C_s = C_{s_0} + \Delta C_{s_0} \quad (7)$$

where C_{s_0} is the value obtained before conditioning and ΔC_{s_0} is the increase in C_{s_0} after conditioning. The ΔC_{s_0} value was not observed in the case of iso-octane, with its existing high value. A possible origin of ΔC_{s_0} will be discussed later.

A decrease in the absolute retention of about 14% (Table II) is reflected in the k' values listed in Table III. An unchanged absolute retention up to 180° indicates that no gross change occurred in the structure of the packing, but above 180° the changes may be due to several factors. Nevertheless, the changes in the absolute retentions can be attributed to the effect of increased interstitial porosity. An increase in only the V_m value (the change in the specific surface area of the packing upon column conditioning is insignificant) in the fundamental migration parameter

$$\mathcal{R} = \frac{V_m}{V_m + KV_S} = \frac{V_m}{V_R} \quad (8)$$

does not substantially affect the relatively large V_R value and hence an increase in \mathcal{R} results. Consequently, the absolute retention decreases.

The above results suggest that the increase in \bar{H} for iso-octane (Table II) is

mainly due to the increased eddy diffusion contribution upon column conditioning. A comparison of the C coefficients at 140° has been made only at the end of conditioning, as shown in the table. Hence, the change in the C_s coefficient for n -octane below the conditioning temperature of 210° is unknown. Nevertheless, a large eddy diffusion contribution to the increased \bar{H} values for n -octane upon column conditioning is apparent from the respective C_m coefficients (Table III).

It therefore follows from the above that a quantitative treatment of the measured data up to 180° for iso-octane, where our present interest lies, is reasonably reliable; with n -octane, the changes must be taken into account.

C coefficients of the Porapak P column

Figs. 4 and 5 are the \bar{H}/f_1 versus \bar{u} plots for iso-octane and n -octane, respectively, obtained from measurements on Porapak P with nitrogen and hydrogen as the carrier gases. All of the measured points in Fig. 4 lie on a single straight line, which suggests that the stationary phase mass transfer is the rate-controlling process. The separation of the nitrogen and hydrogen lines in the case of n -octane (Fig. 5) suggests that the gas phase non-equilibrium is not insignificant.

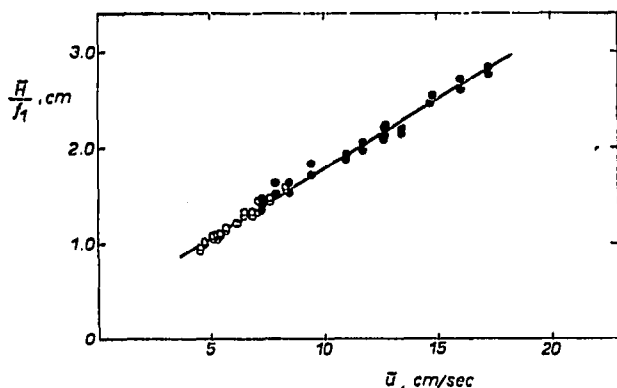


Fig. 4. Plots of \bar{H}/f_1 versus \bar{u} for iso-octane on Porapak P at 140° . O, Nitrogen; ●, hydrogen.

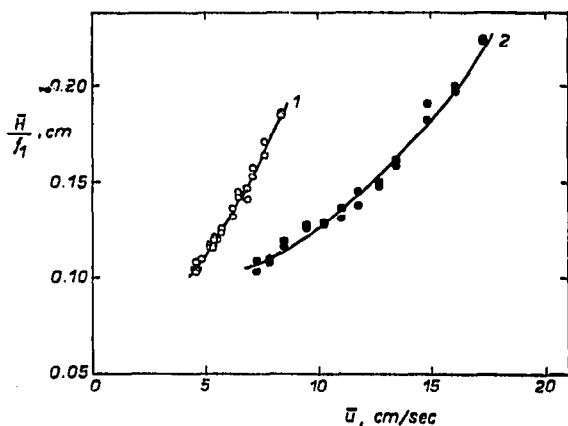


Fig. 5. Plots of \bar{H}/f_1 versus \bar{u} for n -octane on Porapak P at 140° . 1, Nitrogen; 2, hydrogen.

TABLE IV

C_s AND C_m COEFFICIENTS OF ISO-OCTANE AND n -OCTANE MEASURED ON THE PORAPAK P COLUMN AT DIFFERENT TEMPERATURES

Temp. (°C)	Iso-octane*				<i>n</i> -Octane*			
	k'	$C_s \times 10^3$ (sec)	$C_m \times 10^3$ (sec)		k'	$C_s \times 10^3$ (sec)	$C_m \times 10^3$ (sec)	
			N_2	H_2			N_2	H_2
130	21.27	239.6	51.6 (8.49)	17.6 (17.20)	43.07	8.1	8.6 (8.49)	2.9 (17.20)
140	14.72	158.7	22.1 (8.35)	9.0 (17.30)	28.20	7.9	7.0 (8.35)	2.3 (17.30)
150	10.20	99.6	21.3 (8.37)	8.2 (16.54)	18.91	7.7	8.0 (8.37)	2.7 (16.54)
160	7.52	57.1	20.1 (8.18)	7.1 (16.07)	13.34	5.7	8.8 (8.18)	2.9 (16.07)
180	4.10	24.3	10.9 (7.93)	3.6 (16.10)	6.73	5.3	8.1 (7.93)	2.7 (16.10)

* The values in parentheses are the \bar{n} levels for which the C_m coefficients were calculated.

The C_s and C_m coefficients for iso-octane and n -octane, together with their k' values measured on the Porapak P column at different temperatures in the range 130–180° are listed in Table IV. The unusually high C_s value for iso-octane decreased sharply as the temperature was raised from 130 to 180°, while the apparent decrease in the C_s values for n -octane, which have normal magnitudes, was relatively insignificant. The C_m coefficients, which are given in order to complete the data, are only approximate, as already mentioned in connection with the results concerning the silicone oil. The non-additivity of the gas and stationary phase mass transfer resistances^{8,14} is reflected in the relatively high C_m values for iso-octane. An anomalous drop in the C_m values as the column temperature is increased can be attributed to the effect of an increased eddy diffusion contribution caused by the column conditioning.

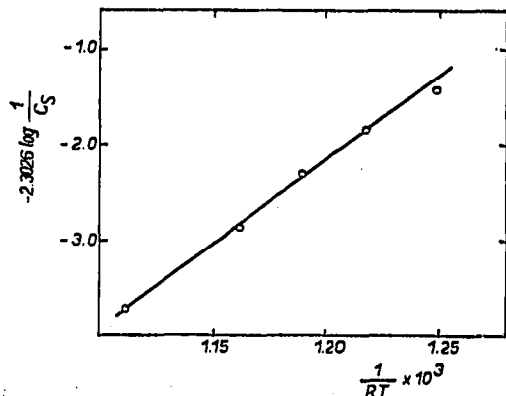


Fig. 6. Plot of $-2.3026 \log (1/C_s)$ versus $1/RT \times 10^3$ for iso-octane (Porapak P column).

Temperature dependence of the C_s coefficients and Arrhenius activation energy of iso-octane mass transfer

Eqn. 4 has been used to evaluate the activation energy graphically. An excellent fit of the measured C_s coefficients for iso-octane (Table IV) is shown in Fig. 6 and yields a high activation energy of 17.6 kcal/mole.

DISCUSSION

The branched-chain peak broadening phenomenon observed recently¹⁻⁵ on certain organic porous polymer column packings has three aspects, namely, the unusually large temperature-sensitive peak-broadening, dependent on the degree of branching, and the specificity of the phenomenon towards the adsorbate and the adsorbent. The peak broadening increases with the degree of branching, *i.e.*, as the effective cross-sectional diameter of the molecule increases.

The mechanism of GC separations on microporous polymers is believed to be either a partition process¹⁵ or an adsorption process¹⁶, or a combination of both^{2,17}. A solubilization process cannot account for the branched-chain broadening effect, although liquid phase diffusion has an activation energy. Diffusion of solutes in a liquid stationary phase is size (molecular weight) sensitive, but it is not a shape-sensitive process.

Porapak P, a non-polar type of Porapak, adsorbs molecules largely by means of the universal dispersion forces¹⁸. The expression and the numerical estimates for the rate of adsorptive-desorptive mass transfer (C_k) have been discussed by Giddings¹⁹. For uniform adsorption with porous adsorbents having surface areas of the order of 1 m²/g, C_k would probably range between 10⁻⁶ and 10⁻⁸. For solids with higher surface areas, the value will be even lower. Hence, the C_s coefficients listed in Table IV cannot originate from the sorptive-desorptive kinetics. Moreover, physical adsorption has no activation energy so that it cannot account for the sharp decrease in the C_s coefficients for iso-octane as the column temperature is increased. Silylation of Porapak has no effect on the anomalous peak broadening behaviour. Porapak PS displayed the same effects as Porapak P (ref. 3). The effects observed on Chromosorb 101 with ketones⁵ were unaffected when the adsorption sites were masked by using formic acid vapour in the carrier gas²⁰. Hence the phenomenon cannot be attributed to the effects of slow sorptive-desorptive kinetics of the energetically active sites. It seems reasonable that the phenomenon can be ascribed to slow interfacial mass transport in the micropores.

Early developments in adsorption and surface diffusion have been excellently reviewed by Dacey²¹. As is adsorption, surface diffusion is a common phenomenon. Adsorption is always accompanied by surface diffusion; in other words, an adsorbed molecule must diffuse some length along the surface before complete desorption occurs. Sub-monolayer surface diffusion is commonly described by an activated or "site-hopping" mechanism²², which postulates that an adsorbed molecule must be partially desorbed in order to migrate from a localized site to another site. Before complete desorption occurs, an adsorbed molecule can take as many as 6000 "hops" at room temperature²³. Because a migrating molecule is more likely to be re-adsorbed at a vacant site than at an occupied site, a net flux of "hopping" molecules in the direction of decreasing surface concentration results. With porous adsorbents, in

addition to hindered diffusion along the tortuous external surface, an adsorbate molecule, depending on its size, may suffer restricted intraparticle diffusion, provided that it has a strong affinity for the adsorbent. As a general rule, the C_s coefficient increases considerably when a solute has an affinity for a site while the ready access of the solute to the site is hindered⁶. Surface diffusion has an energy of activation^{22,24,25}. The diffusion of adsorbates on zeolites is known to have an activation energy similar to the enthalpy of adsorption^{24,25} or higher, which increases with the molecular weight of the gas²⁵. The temperature dependence of C_s coefficients for iso-octane measured on Porapak P reflects a high activation energy of 17.6 kcal/mole. Hence, both the unusually large C_s coefficient for iso-octane and its temperature sensitivity are due to the effect of restricted but activated diffusion into the micropores of the polymer. The normal behaviour of *n*-octane, which is a linear molecule, can be explained by its almost free access into the pores. The C_s coefficient of *n*-octane (Table IV) may originate partly from the restricted diffusion along the tortuous external surface and partly from the slightly hindered intraparticle diffusion. The apparent C_s value for alkanes and cycloalkanes showing normal peak broadening, as recognized from their retention distances and σ values³, can be explained in a similar manner.

It seems that the increase in the C_s coefficient, ΔC_{s_0} , for *n*-octane (Table III), obtained upon column conditioning, arises from the additional hindered diffusion. This hindered diffusion may originate from the small changes in the microstructure of the stationary bed, which are unlikely to affect the C_s coefficient for iso-octane with its already existing large background effect. The changes in the microstructure of the polymer occur as the residual solvent is distilled out upon column conditioning, which shifts the entire pore spectrum slightly to smaller pore diameters¹³. The effects of intraparticle diffusion in static gas adsorption measurements and under the dynamic conditions of gas and gel chromatography have been the subject of numerous studies. In particular it would be proper to mention a very recent work of MacDonald and Habgood²⁶, who separated the coefficients of mass-transfer resistance in the gas phase and in the micropores of certain zeolite catalysts, using the method of Giddings and Schettler⁹.

From the above discussion, the first aspect of the branched-chain peak broadening phenomenon, *viz.*, the unusual temperature-sensitive peak broadening dependent on the degree of branching, which reflects a serious stationary phase non-equilibrium, can be explained as the result of the restricted and activated intraparticle diffusion. The second aspect, *viz.*, the specificity of the phenomenon towards adsorbates, requires further discussion. Unlike Chromosorb 101, the effect observed on Porapak P was specific towards adsorbates³. Compounds that have only σ bonds displayed this effect. As Porapak P adsorbs molecules largely by the universal dispersion forces, it has an affinity for all types of molecules. However, compounds with lone pairs of electrons or with π -electron systems are expected to suffer electron repulsion on Porapak P, because a polyaromatic copolymer has aromatic nuclei with π -electron systems and hence the access of the above species of compounds into the pores is largely hindered. Porapak Q shows a repulsion effect with hydroxyl, ether or ketone oxygen functions, but interacts with hydroxyl hydrogen²⁷ (protonic hydrogen). The apparent effect of *tert.*-butyl sulphide³ can be realized from steric considerations. The two bulky *tert.*-butyl groups largely shield the electron repulsion suffered by the lone pair of electrons on the sulphur atom. In the case of *tert.*-butyl

alcohol, which is a highly branched alcohol, the affinity for the polymer and hence the access into the micropores depends on several factors. The electron-releasing effect of the *tert.*-butyl group decreases the charge separation between the O-H bond and hence restricts the specific interaction between the protonic hydrogen and the π -electron system in the polymer structure. On the other hand, it partially shields the electron repulsion suffered by the lone pair of electrons on the oxygen atom. *tert.*-Butyl alcohol did not show³ this effect on Porapak PS, which suggests that electron repulsion competes with other effects. Hence, for a polar molecule, an affinity for the polymer and hence the extent of penetration into the micropores depends on a net balance among dispersion forces, electron repulsion, and steric and polar effects. A quantitative estimation of the relative importance of these effects is not possible and hence, for a polar molecule, the degree of penetration into the micropores and the effect of this penetration on peak broadening can be understood only qualitatively. Thus, the specificity of the phenomenon observed on Porapak P can be understood from the relative affinity of the adsorbate for the adsorbent, which depends on the chemical nature of both materials.

The apparent C_s coefficients of compounds that have lone pairs of electrons or π -electron systems on Porapak P, recognized from their retention distances and σ values³, cannot be compared with the order of magnitude of the C_k term. They mainly originate from the restricted diffusion along the tortuous external surface. In cases where the molecule has partial access into the micropores, the contribution resulting from the extra partially hindered intraparticle diffusion should be added.

Chromosorb 102, which is a material related to Chromosorb 101, is known to have specific interaction sites²⁸, and the latter material is known to be more polar than the former. Hence both of these sorbents should display the effect with both polar and non-polar compounds. In fact, this has been observed¹ on Chromosorb 101. Moreover, it is expected that the extent of peak broadening should strictly depend on the effective cross-sectional diameter of the molecule, irrespective of its chemical identity. An increase in the peak width by about 50–55% for one isobutyl group in the structurally comparable ketone and acid⁵ on Chromosorb 101 supports this argument.

The third aspect of the phenomenon is its specificity towards the adsorbent. It has been observed that the effect is not displayed by all types of porous polymer. Although Porapak Q has a lower average pore diameter than Porapak P, it does not show the effect. Hence, it seems that there are gross differences in the pore geometry (*e.g.*, ink-bottle shaped, deep tapered pores, etc.) among the different types of porous polymers that are available commercially. Although aromatic hydrocarbons, olefins and other polar compounds did not show the effect on Porapak P, they had a considerably high retention³. Adsorption on the external surface alone cannot account for such a high retention, which seems to indicate that the pores are open at the surface while the effective restriction or constriction lies somewhere deep inside the pores, which is inaccessible to the above types of molecules because of the strong repulsion that occurs.

It has been observed from a scanning electron microscopic investigation of porous polymer sorbents²⁹ that different types of polymer sorbents do not have uniform structures and pore sizes. The sorbents also show a large variation in the depth of pores on the surface. Hence, the present studies indicate a new field of investigation of surface details, especially concerning the micropore geometry of porous polymer

sorbents. Control over these properties can significantly improve the efficiency and versatility of the above sorbents.

ACKNOWLEDGEMENT

The authors are grateful to Dr. D. Kouřilová for carrying out the specific surface area measurements on the two Porapak P samples.

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