(*i.e.*, k_{qT}) values for the quenching of fluorescence in the polymers are about half the value for naphthalene. In previous studies[22] Heskins and Guillet demonstrated that for these systems polymer diffusion may be neglected. Thus, if the singlet lifetimes of the chromophores were similar, the k_Q values would suggest that the efficiency of singlet quenching is not significantly different for isolated and adjacent naphthalene groups. However, the quenching of the PNMA excimer band alone shows a higher quenching efficiency and a marked curve upwards with increasing quencher concentration (Figure 8). This curvature suggests that intermolecular quenching competes effectively with excimer formation by singlet migration in the polymer at sufficiently high quencher concentration. The kinetic scheme is described by

$$\mathrm{N} \xrightarrow{h\nu} \mathrm{N}^* \tag{8}$$

$$\mathrm{N}^* \longrightarrow \mathrm{N} + h\nu_f \tag{9}$$

$$\longrightarrow \mathrm{N} \tag{10}$$

$$\longrightarrow {}^3\mathrm{N} \tag{11}$$

$$\xrightarrow{(\mathrm{N})} \mathrm{E}^* \text{ (excimer)} \tag{12}$$

$$\mathrm{E}^* \longrightarrow \mathrm{N}^* + \mathrm{N} \tag{13}$$

$$\longrightarrow \mathrm{N} + \mathrm{N} + h\nu_{\mathrm{ex}} \tag{14}$$

$$\longrightarrow \mathrm{N} + \mathrm{N} \tag{15}$$

In the presence of added quencher

$$\mathrm{N}^* + \mathrm{Q} \xrightarrow{k_{\mathrm{qN}}} \mathrm{N} + \mathrm{Q}^* \tag{16}$$

$$\mathrm{E}^* + \mathrm{Q} \xrightarrow{k_{\mathrm{qE}}} \mathrm{N} + \mathrm{N} + \mathrm{Q}^* \tag{17}$$

It can be shown that the ratio of the excimer fluorescence intensity in the absence and presence of the quencher at concentration [Q] is given by

$$\frac{I_{\mathrm{Ef}}{}^0}{I_{\mathrm{Ef}}} = \frac{\phi_{\mathrm{Ef}}{}^0}{\phi_{\mathrm{Ef}}} = 1 + \left[\left(\frac{k_{\mathrm{qE}}}{\tau_{\mathrm{N}}} + \frac{k_{\mathrm{qN}}}{\tau_{\mathrm{E}}}\right)[\mathrm{Q}] + k_{\mathrm{qE}}k_{\mathrm{qN}}[\mathrm{Q}]^2\right]\tau_{\mathrm{N}}\tau_{\mathrm{E}} \tag{18}$$

where τ_N and τ_E are lifetimes of the chromophore and excimer singlet states. The first term in [Q] in eq 18 accounts for the higher quenching efficiency in the linear portion of the plot in Figure 8. The curvature at higher values of [Q] shows the importance of the second term in $[Q]^2$.

Conclusions

Strong evidence has been observed for the process of triplet–triplet annihilation in PNMA in H_4furan–ether glasses at 77°K, leading to delayed fluorescence emission from the polymer. Intermolecular quenching of the emission from the polymer under these conditions shows very efficient triplet migration among the chromophores on the polymer chain by a mechanism similar to a diffusion process. The delayed fluorescence quenching is well described by the static Perrin model in the low-temperature glasses. Fluorescence spectra including excimer emission and quenching in room-temperature solutions show that intramolecular singlet migration does take place under these more mobile and flexible conditions. Solvent effects in the excimer emission do suggest that the coupled chromophores which form the excimer are non-nearest neighbors. Excimer emission may therefore be a useful probe of the conformation of aromatic polymers in solution.

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Studies of Diffusion in Polymers by Gas Chromatography

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ABSTRACT: The shapes of eluted peaks in gas chromatography on polymeric substrates are governed by several factors, one of the most important being slow diffusion in the polymer phase. By a suitable choice of conditions, the simple Van Deemter equation enables diffusion coefficients to be calculated from the variation in chromatographic peak width with carrier gas flow rate. The method is found to be applicable to some hydrocarbon penetrants in a polyethylene stationary phase.

In most previous gas chromatographic investigations of a polymeric stationary phase,[1-4] the primary experimental data were the chromatographic peak retention times for suitable volatile "probe" molecules. The shapes of the chromatographic peaks were of secondary interest. However, peak shape may have a significant effect on the validity of data derived from peak retention measurements, and in addition may be related to the thermodynamics and kinetics of the polymer-probe interaction. In this paper, the factors which govern peak shape in gas chromatography are outlined, and their relevance to diffusion measurements on polymeric substrates is investigated.

Ideally, an infinitely sharp input of vapor into a gas chromatograph should result in an infinitely sharp peak being eluted at the detector after a time interval dependent only on the interaction between the vapor and the stationary phase in the column. In practice, the vapor input is not infinitely sharp, and the eluted peak is broadened and skewed by a wide range of factors. These broadening factors may be divided into three main classes.

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Firstly, many instrumental factors outside the gas chromatographic column affect peak shape. For example, sample injection time, detector dead volume, and time lag for detector and recorder response all contribute to peak distortion, and should be minimized by careful instrument design and operation.

The thermodynamics of the interaction between vapor and stationary phase is a second, more fundamental factor which affects peak shape. Assuming for the present that equilibrium is reached instantaneously in the column, then no change in peak shape occurs if the concentration of vapor in the gas phase is linearly related to the concentration in the stationary phase. Normally this condition is achieved in gas chromatography by using very small concentrations of vapor. However, if the partition isotherms relating the vapor phase and stationary phase concentrations are not linear, then peak shapes change markedly on passage through the column. For isotherms concave toward the vapor pressure axis (*e.g.*, Langmuir adsorption isotherms) the resultant elution peaks show a sharp front profile and a diffuse rear tail, with the degree of peak skew increasing with increasing curvature of the isotherm. For isotherms convex toward the vapor pressure axis, the front of the peak is diffuse, and the rear sharp. Normally these effects on peak shape are avoided by a suitable choice of column conditions. However, the shape of chromatographic peaks has been used to calculate the shape of the corresponding isotherms for gas-solid chromatography[5] and a similar approach has been used to interpret adsorption peak shape on polymeric substrates.[6]

The third group of factors which affect chromatographic peak shape result from the finite time required to reach equilibrium as the eluting peak passes each point in the column. Van Deemter[7] first related some of these kinetic factors to column properties by an equation of the form

$$H = A + (B/u) + Cu \qquad (1)$$

where H, the plate height, may be defined as σ_x^2/x, where σ_x is the standard deviation of a peak at a point distance x from the start of the column, u is the linear carrier gas flow rate and A, B, and C are constants independent of flow rate.

In the second term, which described the diffusional spreading of the vapor as it is eluted in the gas phase, $B = 2\gamma D_g$, where D_g is the diffusion coefficient of the vapor in the gas phase and γ is a constant less than unity introduced to allow for the tortuous path followed by the gas flow through a packed column. In the simple Van Deemter approach

$$C = (8/\pi^2)(d_f^2/D_l)[k/(1 + k)^2] \qquad (2)$$

where d_f is the thickness of the stationary phase, D_l is the diffusion coefficient of the vapor in the stationary phase, and the partition ratio $k = (t_r - t_m)/t_m$, where t_r is the retention time from injection for the vapor, and t_m is the time for the carrier gas to pass through the column.

This simple version of the Van Deemter equation does not consider broadening effects due to the noninstantaneous equilibration of vapor across the column by molecular or hydrodynamic mass transfer.[8] Trans-column diffusion in the gas phase is assumed to be fast compared with diffusion through the stationary phase. Furthermore, the assumptions used to derive the C term are unrealistic for most practical gas chromatographic columns where the geometry of the column packing is very complex. Giddings[9] has developed a nonequilibrium treatment which enables calculation of peak dispersion in more complex cases by redefining the C term to take account of various dispersion factors. In the case of uniform film thickness, Giddings' result is the same as that for the Van Deemter C term but with the constant $8/\pi^2$ replaced by $2/3$. However, despite its shortcomings, the Van Deemter equation provides a convenient framework for considering the kinetic factors which affect chromatographic peak shape.

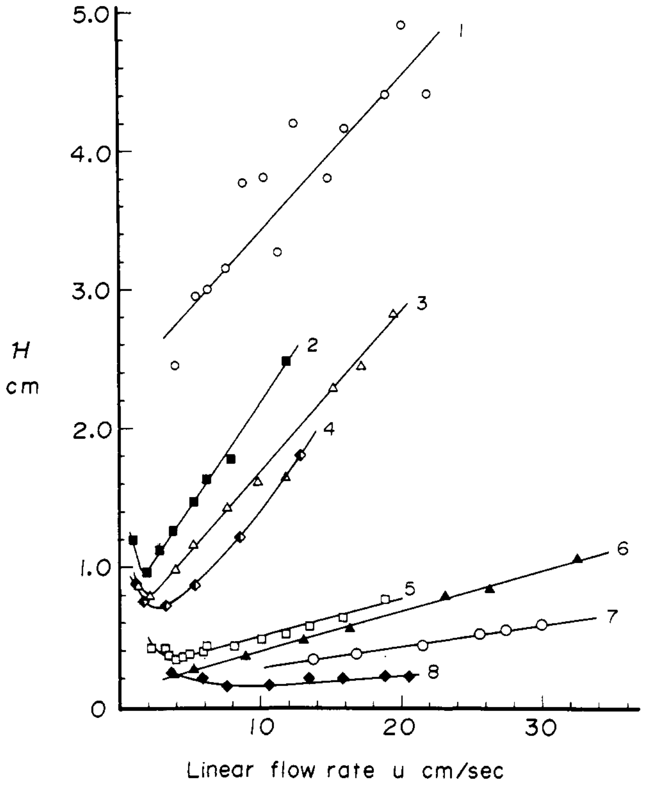

Figure 1. Van Deemter curves for various columns: (1) benzene-polyethylene, column A at 27°; (2) benzene-natural rubber, column D at 25°; (3) benzene-polyethylene, column B at 25°; (4) benzene-natural rubber, column C at 23°; (5' n-nonane-polyethylene, column B at 50°; (6) decane-natural rubber, column E at 40.2°; (7) dodecane-natural rubber, column E at 685°; (8) hexadecane-polyethylene, column A at 200°.

Of the many factors that lead to peak broadening, only the kinetics of diffusion of the volatile probe in the polymer is of interest here. If the broadening factors are independent, then the overall variance is the sum of the individual variances, $\Sigma_i\sigma_i^2$. As the actual peak spreading is measured by the standard deviations σ_i, the total broadening is less than the sum of the individual standard deviations

$$\sum_i (\sigma_i^2)^{1/2} \le \sum_i \sigma_i$$

Thus the total broadening is mainly due to the factor producing the largest individual broadening, and by a suitable choice of conditions the factor of interest, namely diffusion in the stationary phase, may be made to predominate. One important condition is that the amount of

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Table I
Gas Chromatographic Columns

Column	Length (cm)	O.d. (in.)	Packing Support	Wt of Packing in Column (g)	Polymer Coating	Wt of Coating in Column (g)
A	45	⅛	60–80 mesh Chromosorb W[a]	0.602	Low-density polyethylene[b]	0.021
B	120	¼	40–60 mesh glass beads	33.28	Low-density polyethylene[b]	0.170
C	60	¼	60–80 mesh glass beads[a]	15.93	Natural rubber[c]	0.033
D	500	¼	None		Natural rubber[c]	0.065
E	150	¼	60–80 mesh Corning glc 110[d]	35.17	Natural rubber[c]	0.039

[a] Me_2ClSi treated. [b] Eastman Tenite 800 E. [c] Courtesy of Professor B. M. E. van der Hoff, University of Waterloo. [d] Corning GLC 110 "textured surface" Me_2ClSi-treated glass beads.

vapor injected should be as small as possible; at infinite dilution the partition isotherms may approach linearity, and also the simple model for diffusion assumed in the derivation of the Van Deemter equation may be adequate.

Experimental Section

The experimental chromatograms were obtained using a Varian Aerograph Model 1720 gas chromatograph equipped with a thermal conductivity detector. Helium was used as the carrier gas. (Some of the preliminary results in Figure 1 were obtained using a Microtek flame detector gas chromatograph with nitrogen as carrier gas.) The polyethylene-coated columns were prepared as described previously.[10,11] Coating glass beads with natural rubber proved more difficult. When the beads were placed in a benzene solution of rubber, and the solvent evaporated by gently heating and stirring, either the rubber did not adhere to the bead surfaces or the resultant beads were so tacky that packing them in a column was impossible. Column C was prepared by packing a column with glass beads, running a solution of rubber in benzene through it, and removing the solvent with a gentle stream of nitrogen. The resultant distribution of rubber on the beads was not uniform. The open column was prepared using the solution plug method.[12] The standard solution evaporation method worked satisfactorily with textured surface glass beads (column E) (see Table I).

Injection of the diffusant "probes" onto the columns was performed using an automatic vapor injection system. This avoided variations in the output peak shapes due to nonuniform liquid injection sizes and evaporation rates. The vapor to be injected, together with some carrier gas, was held in a heated reservoir made from a 5-cm length of 2-cm diameter stainless steel bellows. The reservoir was connected to the injection port by a piece of fine stainless steel needle tubing. Compression of the reservoir for a short time using an electropneumatic system caused a small amount of vapor to be injected onto the column. The amount injected depended on the temperature of the reservoir, the duration and amount of compression applied to the reservoir, and on the bore size of the connecting needle tubing.

The carrier gas outlet flow rate was measured using a soap bubble flow meter, and corrected for water vapor pressure. This volume flow rate, $\dot{V}_0$, measured at flow meter temperature was converted to $\bar{u}$, the average linear flow rate at column temperature (corrected for gas compressibility) using the relationship[8]

$$\bar{u} = (j\dot{V}_0/\bar{a})(T_{\text{col}}/T_{\text{flow}}) \qquad (3)$$

where

$$j = \tfrac{3}{2}\{(p_i/p_o)^2 - 1\}/\{(p_i/p_o)^3 - 1\}$$

p_i/p_o was the ratio of column inlet pressure to column outlet pressure; T_{col}, T_{flow} were the temperatures of gas chromatographic column and flow meter, respectively; and $\bar{a}$ was the volume of gas phase per unit length of column.

Table II
Diffusion Coefficients from Gas Chromatographic Measurements on Low-Density Polyethylene

Probe	Temp (°C)	Van Deemter C Term (sec × 10³)[a]	k	k/(1 + k)²	D_l (cm sec⁻² × 10⁸)
n-Tetradecane	125	20 ± 7	20.4	0.045	~0.85
	140	13.0 ± 0.6	11.3	0.075	2.2
	150	10.3 ± 0.4	7.83	0.100	3.7
	160	12.5 ± 0.6	5.47	0.131	4.1
	170	8.6 ± 0.5	3.88	0.163	7.4
n-Decane	30	30.0 ± 1.8	34.3	0.028	0.35
	50	24.6 ± 0.7	13.2	0.066	1.03
	60	31.8 ± 0.7	10.0	0.083	1.00
	65	29.9 ± 1.5	8.0	0.099	1.28
	80	38.2 ± 1.0	5.3	0.133	1.34
Benzene	25	114 ± 6	1.50	0.240	0.82

[a] On column B, Table I.

The value of $\bar{a}$ for a given column may be determined by dividing the retention volume for a noninteracting substance such as nitrogen by the column length, l. For very short columns a correction for the detector dead volume may be necessary in calculating $\bar{a}$.

The output from the gas chromatographic detector was fed to a strip chart recorder. If t_r was the indicated retention time from injection to the peak maximum and d was the measured peak width at half height in the same units as t_r, then

$$H = (l/5.54)(d/t_r)^2 \qquad (4)$$

where H was an apparent plate height for the column and conditions and l was the column length. The experimental determination of d and t_r was performed in triplicate for each flow rate, and an average plate height was calculated. The linear portion of a graph of H *vs.* $\bar{u}$ was used to calculate C in the Van Deemter equation (eq 1), but with the numerical constant $8/\pi^2$ replaced by ⅔.

The value of the diffusion coefficient in the polymeric coating was calculated from C using the eq 2. The average thickness of the polymer layer $\bar{d}_f$ was found from the known volume of polymer on the column and the geometric surface area of the beads, which were assumed to be spherical. Thus a sample of N beads of radius r occupy a volume $V = N(4/3)\pi r^3$ and have a surface area of $N \times 4\pi r^2 = 3V/r \simeq 3V/\bar{r}$, where $\bar{r}$ is an average radius. If this sample of beads is coated with a weight w of polymer having a density ρ, then the average thickness of the polymer layer was taken to be

$$d_f = (w/\rho)/(3V/\bar{r}) \qquad (5)$$

The value of $\bar{r}$ was obtained from micrometer measurements of bead diameters, V was measured volumetrically, and w was determined by removal of the polymer from a weighted sample of the coated beads either by Soxhlet extraction using hot xylene for 36 hr or by stirring in hot chromic acid for 4 hr.

Table II indicates that in general, the precision of the C term, as indicated by the standard error in the slope of the Van Deem-

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ter plot is about 5%. The accuracy in determining H tends to become less for the faster flow rates where d and t_r are smaller and pressure drop along the column is greater. However, the largest errors in computing D_l result from uncertainties in the thickness of the polymer layer; a ±10% uncertainty in the area of the beads will lead to ±20% uncertainty in D_l, and further errors will result from nonuniform layer thickness and geometry. For a given column, the relative errors for different probes and temperatures should be very much less, as $\bar{d}_f$ remains constant.

Results and Discussion

The results of a series of experiments to measure the amount of peak spreading as a function of flow rate are shown in Figure 1. When sufficiently slow flow rates are employed, the plate heights can be seen to pass through a minimum, as predicted by the Van Deemter eq 1. At higher flow rates, H increases linearly with u, with a gradient C given by the simple Van Deemter expression where applicable. Not unexpectedly, the plate heights for these experiments on polymer stationary phases are generally much higher than the 0.5–2 mm values for H aimed for in analytical gas chromatography.[8] The increase in H with flow rate is also much steeper on polymer substrates. High plate heights may be rationalized by considering the nature of the polymer; the best example shown is for benzene injected onto a very short column (column A) consisting of chromosorb W coated with low-density polyethylene (Figure 1, curve 1). At room temperature polyethylene contains crystalline regions which are not penetrated by the probe molecule[10] and amorphous or rubbery regions. The rate of diffusion through this material is much slower than through the usual liquid stationary phases used in gas chromatography, and the smaller value for D_l results in a larger C term in the Van Deemter eq 2. A second factor results from the relatively short retention time for benzene on this column; the benzene retention time t_r was only about three times the air retention time t_m. Thus $k = (t_r - t_m)/t_m \simeq 2$ and the $k/(1 + k)^2$ term in eq 2 becomes $\simeq 0.22$ (close to its maximum value of 0.25 for $k = 1$). The short retention times and broad peaks also introduce experimental and theoretical difficulties in determining plate heights, which are reflected in the scatter of points for curve 1.

The large plate heights and C terms are not simply the result of poorly packed columns or experimental technique. This is clearly shown in curve 8 (Figure 1) for *n*-hexadecane at 200° on the same polyethylene–chromosorb column used for curve 1. In this case the plate heights are very much smaller than for benzene at room temperature, and are of the order expected for normal analytical columns. The value of k ($\simeq 2.3$) is still small so the improvement in column performance does not result from this factor. However at 200° the polyethylene stationary phase is well above its melting region, and the polymer chain mobility approaches that of a conventional liquid phase, so rates of diffusion through the molten polymer should be very much faster than through the semicrystalline polymer at room temperature (despite the effect of increasing diffusant size). The marked increase in efficiency when the same column is used at higher temperatures therefore reflects the decrease in diffusion coefficient D_l for the probe molecule through the polymer.

The column parameters for column A are a very poor choice for a study of peak spreading due to diffusion processes. This short column was initially used to try and minimize problems associated with correcting the Van Deemter equation for column pressure drop.[8] However the detector dead volume was found to be of the same order of magnitude as the column dead volume, introducing an instrumental source of peak spreading, while the pressure drop correction remained serious.

A much more satisfactory column (B, Table I) was prepared by coating glass beads with polyethylene. The column pressure drop was much less than for column A, and plate heights with benzene at room temperature were also smaller (Figure 1, curve 3). Van Deemter plots were also obtained on columns with natural rubber on ordinary glass beads (curve 4), on textured surface glass beads (curves 6 and 7) and with a layer of rubber on the inside of an open tube (curve 2).

The relationship between peak shape and rate of diffusion of the probe in the polymer is of fundamental interest. A quantitative interpretation of the shape of the experimental Van Deemter plots in terms of a diffusion coefficient D_l requires firstly that the only significant source of peak spreading be due to slow equilibration through the stationary phase. Thus instrumental dead volume and detector response time should be minimized, the isotherm relating vapor and stationary phase concentrations should be linear, and relatively thick stationary phase layers should be used. A second requirement for interpretation of the C term is that the geometry of the stationary phase should be well defined, so that a meaningful estimate of the thickness d_f of the polymeric phase may be obtained. This appears to rule out columns coated on chromosorb or other diatomaceous earth supports which have a very complex structure.[13] An obvious choice would be an open column such as column D; however Giddings[14] suggested that such a column will have a microscopically rough surface, and that a glass bead column with liquid phase attached to bead contact points by capillary forces provided a better-defined liquid phase distribution. With high molecular weight coatings, if the initial coating is relatively uniform, the high viscosities of polymer melts make significant capillary attraction towards the contact points very unlikely. If it is assumed that a polymer coating on glass beads exists as a film of mean square thickness $\bar{d}_f^2$, then D_l may be obtained from Giddings' form of the Van Deemter C term.

The most useful of the column configurations in Table I thus appears to be glass beads coated with polymer. As mentioned in the Experimental Section, the coating of spherical glass beads with natural rubber was not successful. However low-density polyethylene did appear to give a uniform coating on glass beads. Accordingly, further experiments were performed with column B for several probes and temperatures. The resultant peaks were broad, but relatively symmetrical. The slopes of lines relating plate height to corrected linear flow rate were used to obtain a C term. An average thickness was calculated from the amount of polymer and the geometric area of the bead surfaces, and D_l was thus obtained (Table II).

Comparison of these values with those obtained using conventional techniques[15] is complicated by the different areas of applicability of the methods. At any given temperature, the gas chromatographic method gives results with small concentrations of diffusants of rather lower volatility than is usual in sorption or permeation experiments. The gas chromatographic method requires a uniform polymer layer of known thickness; for practical reasons this requires a relatively small loading of polymer in the column, so that less volatile diffusants must be used to increase retention times. On the other hand, sorption or

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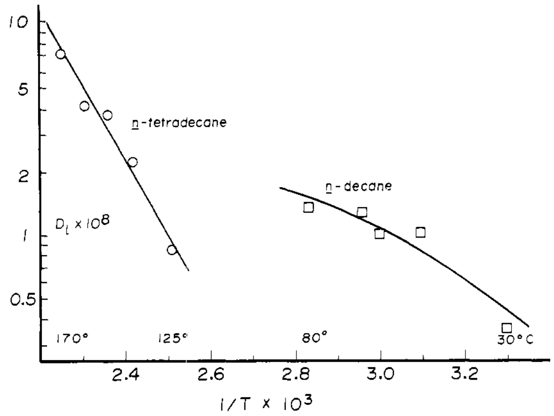

Figure 2. Arrhenius plots of diffusion coefficients for *n*-decane and *n*-tetradecane in polyethylene.

permeation experiments are normally performed with relatively high vapor pressures of diffusant. Thus for comparison, data at zero diffusant concentration were required for systems where the polymer, diffusant and temperature range were convenient for gas chromatography.

It proved possible to measure peak spreading as a function of carrier gas flow rate for benzene on column B (Table II). The resultant value of D_l of 0.82×10^{-8} cm^2 sec^{-1} calculated from the Van Deemter equation compares favorably with the values of 1.2×10^{-8} cm^2 sec^{-1} for the diffusion coefficient at zero benzene concentration in low density polyethylene obtained by McCall and Slichter(16) using both desorption and time lag measurements. (Even better agreement is obtained ($D_l = 1.0 \times 10^{-8}$) if the original Van Deemter equation is used in place of Giddings modified form but this may well be fortuitous.) Their values for the diffusion coefficient of *n*-decane at 25° are also in agreement with the data in Table II. Diffusion coefficients in polyethylene may be influenced by penetrant concentrations(16) and by polymer crystallinity(17) and morphology,(18) so the agreement with the gas chromatographic method is better than expected.

The diffusion coefficients for *n*-decane and *n*-tetradecane in polyethylene at different temperatures are presented as Arrhenius plots in Figure 2. The curvature of the data for *n*-decane is most probably due to the change in polyethylene crystallinity with temperature.(17) The data for *n*-tetradecane was obtained well above the melting point of the polymer, and gave a linear Arrhenius plot, with an activation energy for diffusion of 16.2 kcal/mol. Direct measurement of the activation energy for diffusion of this system would be difficult by the usual techniques. However, the temperature dependence of diffusion for *n*-tetradecane at zero penetrant concentration should correlate with the temperature dependence of viscosity of the pure polyethylene as rearrangements of similar hydrocarbon segments are involved in both processes. The above value of E_D for tetradecane falls within the 12-18 kcal/mol range of values given for apparent activation energy for viscous flow at low shear rates for a series of low-density polyethylenes at 150°.(19)

These results show that when polyethylene is coated evenly on spherical glass beads, reasonable values for penetrant diffusion coefficients may be calculated using the simple Van Deemter equation, from measurements of gas chromatographic peak width as a function of carrier gas flow rate. The success of this simple approach is perhaps surprising in view of the discrepancies often found with conventional gas chromatographic stationary phases of lower molecular weight.(14) Two reasons for this are possible. Firstly, rates of diffusion through polymers are in general much lower than through conventional stationary phases, so that the relative contribution to peak spreading is more important. Secondly, the polymers are very viscous and so form a more stable, even bead coating. The gas chromatographic measurement of diffusion rates appears to complement the usual sorption and permeation methods, as diffusion at low penetrant concentrations and through polymer melts may be readily studied. However, use of the simple Van Deemter equation to interpret the gas chromatographic data may only be valid for relatively nonpolar penetrants and polymers at temperatures well above the glass transition temperature of the polymer. Otherwise strong polymer-penetrant interactions may result in thermodynamic peak spreading and a diffusion coefficient which is dependent on both time and penetrant concentration. A more general and exact chromatographic method for the determination of diffusion coefficients must await experimental advances in determining the precise geometric distribution of polymer on the column, and theoretical methods for predicting the effect of this distribution on peak shape.

In addition to providing a novel method for the determination of diffusion data, the effects on peak shape of diffusion through the stationary phase must be considered when selecting experimental conditions for most gas chromatographic studies on polymers. Furthermore, the rate of diffusion is of fundamental importance for gas chromatography on polymers close to their glass transition temperatures.(20)

Acknowledgment. The authors acknowledge the generous financial support of the National Research Council of Canada and of the Dunlop Research Centre, Sheridan Park, Ontario.

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