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Gas Chromatography on Polymers at Temperatures Close to the Glass Transition

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ABSTRACT: The effect of very slow penetrant diffusion rates on chromatographic peak broadening was calculated in an attempt to explain the peak shapes and retention volumes on polymeric stationary phases at temperatures close to the glass transition. It was assumed that slow bulk diffusion was the predominant cause of peak broadening, and that polymer-penetrant equilibrium was approached exponentially with time. As illustration, peak shapes for *n*-tetradecane on a polystyrene stationary phase were calculated using chromatographic data determined well above T_g, together with data predicted by a free volume theory for the temperature dependence of diffusion rates close to T_g. This approach predicted the observed broadening and skewing of peaks as the temperature approached T_g from above, but further elaboration is necessary close to T_g.

It has been shown that a gas chromatographic technique may be used to determine the glass transition temperature of polymers.[2a,b] The method involves measuring the retention volumes as a function of temperature for a suitable low molecular weight "probe" on the polymeric stationary phase. The normally linear plot relating the logarithm of the retention volume to the reciprocal absolute temperature shows a discontinuity in the region of the transition temperature. The shape of the retention diagram has been qualitatively explained[2a] by assuming that below T_g the probe interacts only with the surface of the glassy polymer because the rate of diffusion of the probe through the polymer is too slow to permit significant bulk interaction. Conversely, well above T_g, surface effects are negligible and the retention volume is a measure of the thermodynamic interaction of the probe with the bulk polymer. Close to T_g, it has been proposed that a combination of these two retention mechanisms leads to nonequilibrium sorption of the probe molecule; as the temperature rises the increasing penetrability of the polymer outweighs the effects of increasing probe vapor pressure, so that retention volumes increase in this region. In this paper, the factors which affect the gas chromatographic retention of low molecular weight probes on polymers close to their glass transition temperatures will be considered in some more detail.

Experimental Section

Peak shapes above T_g were determined using *n*-tetradecane (Qualkits, PolyScience Corp.) with a 100-cm column of 0.25-o.d. copper tubing containing 27.9 g of 40–60 mesh glass beads coated with 0.16 g of polystyrene (Pressure Chemical, std mol wt 51,000). Average polymer thickness, estimated from the surface-to-volume ratio of the coating, was about 0.8×10^{-6} m. The column was used in a Varian Aerograph Model 1720 gas chromatograph with helium carrier gas and a thermal conductivity detector. Other details were as previously published.[3]

The calculations of peak shapes were made using a simple APL computer program. The hyperbolic Bessel functions in eq 13 were evaluated using either an appropriate asymptotic series[4] or an exponential approximation,[5] depending on the value of the argument.

Kinetic Aspects of Chromatographic Peak Shape

As the temperature of the polymer–probe system is reduced through the glass transition temperature, a considerable decrease in the rate of diffusion of probe through the polymer is expected. This kinetic phenomenon affects the rate at which equilibrium is attained between vapor and polymer at every position along the gas chromatographic (gc) column, which in turn governs the width of the eluted gc peak. To attempt to quantify this effect, a brief review of some aspects of chromatographic peak broadening is required. The following summary follows the approach and terminology of Littlewood.[5] The starting point is the "first-order conservation equation" of chromatography[6] which expresses the conservation of mass within a chromatographic peak as it is carried through a column.

$$\partial c/\partial x + a(\partial c/\partial V) + m(\partial q/\partial V) = 0 \qquad (1)$$

where V is the volume of gas passed through the column (cm^3), x is the distance from inlet end of column (cm), q is the vapor concentration in stationary phase (mol/g), c is the vapor concentration in gas phase (mol/cm^3), m is the mass of stationary phase per unit length of column (g/cm), and a is the volume of gas phase per unit length of column (cm^2). If the usual chromatographic condition of very small sample size is met, then the isotherm of interaction of the sample vapor between stationary and gas phase may be linear so that

$$q = \beta c \qquad (2)$$

where β is the partition coefficient. If, however, interaction between the two phases is not instantaneous, it is necessary to replace eq 2 by

$$q = \beta c f(t) \qquad (3)$$

where $f(t)$ is some function of time which approaches unity when time t is large. If equilibrium is reached exponentially

$$\mathrm{f}(t) = 1 + K' \exp(-Kt) \tag{4}$$

Substituting (4) in (3) and differentiating,

$$\mathrm{d}q/\mathrm{d}t = K(\beta c - q) \tag{5}$$

where K is equivalent to a first-order rate constant. If the vapor is injected as an infinitely sharp peak at the start of the column, the initial conditions are given by

$$\begin{aligned} q(0,x) &= 0 \\ C(V,0) &= \delta(V) \end{aligned} \tag{6}$$

where $\delta(V)$, the delta function is defined by

$$\delta(V) = 0 \quad \text{for } V \neq 0$$

$$\int_{-\infty}^{+\infty} \delta(V) = 1$$

Equations 1 and 5 may be solved for initial conditions (6) to give[5]

$$C(V,x) = \frac{K}{\dot{V}}\left(\frac{m\beta x}{V - ax}\right)^{1/2} I_1\left\{2\frac{K}{\dot{V}}[m\beta x(V - ax)]^{1/2}\right\} \times \\ \exp\left[-\frac{K}{\dot{V}}(m\beta x - ax + V)\right] + \\ \exp\left(-\frac{K}{\dot{V}}m\beta x\right)\delta(V - ax) \tag{7}$$

where $\dot{V}$ is the carrier gas volume flow rate and $I_1(z)$ is the first-order hyperbolic Bessel function of z.

This equation thus gives the concentration c of a vapor in the gas phase as a function of V and x when an initially sharp pulse of vapor is carried through a column, and the linear relationship between stationary and gas-phase concentrations of the vapor is approached exponentially. At the column exit, $x = l$, the column length (cm), and the column parameters a, l, m, and β in eq 7 may be replaced by measured retention volumes using the relationship[5]

$$V_R^0 = V_M^0 + ml\beta \tag{8}$$

where $V_M^0 = al$, the gas hold-up volume of the column.

For normal gas chromatographic conditions, this unwieldy equation may be simplified considerably. Thus the exponential decay of the initial input distribution, indicated by the second term in eq 7, is normally so fast that this term may be neglected. Furthermore the effective width of a chromatographic peak is normally only a small fraction of its retention. Under these conditions the Bessel function term in eq 7 reduces to an exponential, and the equation for $C(V)$ may be simplified to that for a Gaussian curve with a variance of

$$\sigma_{(V)}^2 = [2\dot{V}(V_R^0 - V_M^0)]/K \tag{9}$$

and a mean of V_R^0. Thus the retention volume of the vapor on the column remains unchanged by the slow rate of partition, but the initial sharp input peak has spread out to give a Gaussian distribution about the peak maximum at V_R^0. The variance of the peak may also be expressed in units of length along the column instead of in gas volumes. In length units, the variance is

$$\sigma_{(V)}^2 = 2kux/[(1 + k)^2K] \tag{10}$$

where $k = (V_R^0 - V_M^0)/V_M$ = partition ratio and $u = \dot{V}/a$ = linear carrier gas flow rate (cm/sec).

A variety of column conditions may affect the rate of equilibration of vapor between the stationary and gas phases. The effect of slow diffusion within the stationary phase is likely to be important with a polymeric stationary phase close to T_g. Slow diffusion into and out of a stationary phase is equivalent to a first order reaction at the surface[7] as required by eq 5. Van Deemter *et al.*[7] suggest that in this case

$$K = (\pi^2/4)(D/d_f^2) \tag{11}$$

where D is the diffusion coefficient of vapor in the stationary phase and d_f is an average thickness for the stationary phase. Substituting this in eq 10

$$\sigma_{(x)}^2 = (8/\pi^2)(d_f^2/D)[kx/(1 + k)^2]u \tag{12}$$

Thus when slow diffusion in the stationary phase is the only factor causing peak spreading, a plot of $\sigma_{(x)}^2/x$ (= H, the plate height) *vs.* the linear flow rate u should give a straight line with a slope inversely proportional to D. It has been shown[3] that by a careful choice of conditions, peak spreading is indeed governed by the simple Van Deemter relationship, and that polymer-penetrant diffusion coefficients measured in polyethylene by this method appear to be in reasonable agreement with literature values.

The Van Deemter equation predicts that a decrease in diffusion coefficient simply results in a broadening of the Gaussian peak, with no change in the peak maximum. Thus it fails to explain the effects on retention volumes found experimentally near the glass transition of polymers such as methyl methacrylate and vinyl chloride.[2b] However it should be noted that these polymers are more viscous than conventional gas chromatographic stationary phases, and also the retention volumes used in typical experiments are relatively short, so that the resultant gas chromatographic peaks are broad in comparison to their retention volumes. In effect, the conditions necessary for $C(V)$ to be represented by a Gaussian peak of width given by eq 9 are no longer met, and eq 7 must be employed.

It is convenient to rewrite eq 7 to give $C(V)$ at $x = l$ in terms of retention volume corrected for the column gas hold-up volume V_M^0. Thus if $V_R' = V_R^0 - V_M^0$ and $V' = V - V_M^0$, then eq 7 becomes

$$C(V) = ((K/\dot{V})(V_R'/V')^{1/2})(I_1[2(K/\dot{V})(V_R'V')^{1/2}) \times \\ (\exp[-(K/\dot{V})(V_R' + V')]) + (\exp[-(K/\dot{V})V_R'])(\delta(V')) \tag{13}$$

This equation gives the peak shape as a function of V', the eluted gas volume (measured from the air peak or otherwise corrected for column dead volume) for specified values of V_R', the corrected retention volume of the peak assuming instantaneous equilibrium between the phases. The kinetic factors are specified by $K/\dot{V}$ which is the ratio of the rate constant to the volume flow rate.

The effect of the equation parameters on the predicted shape of the gas chromatographic peak is illustrated in Figure 1. As K is decreased (or the flow rate is increased) the peaks become broader, but in addition become increasingly skewed. For very low values of $K/\dot{V}$ and of V', the spreading reaches the carrier gas front, which acts as a barrier to further spreading. In the limit the peak should appear simply as a tail extending from the carrier gas front. The peak maxima, where detectable, occur at lower retention volumes $V_{\max}'$ so that these apparent peak retention volumes are less than the true volume V_R' which would be obtained in the absence of kinetic effects. The magnitude of this effect is shown in Figure 2, where a linear relationship between the peak displacement and $\dot{V}/K$ is evident at lower values of $\dot{V}/K$. Thus the effect of slow

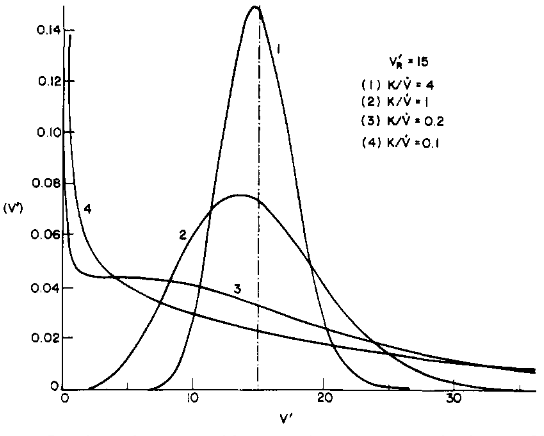

Figure 1. Predicted effect of kinetic factors on peak shape. V_R' is the corrected peak retention volume in the absence of kinetic effects, K is the rate constant, and $\dot{V}$ is the carrier gas volume flow rate.

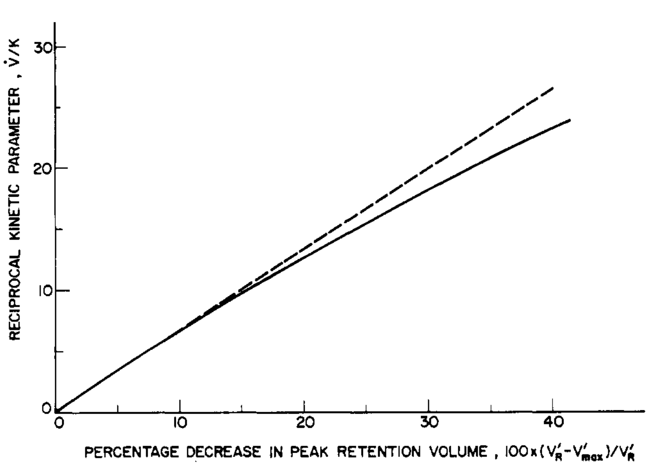

Figure 2. Predicted effect of reciprocal kinetic parameters on apparent peak retention volume. (V_R' was taken as 100, with $K/\dot{V}$ decreasing from 5 to 0.04.)

equilibration may be eliminated in accurate gas chromatography by measuring the variation in peak retention volume with flow rate $\dot{V}$ and extrapolating to zero flow rate where V_{max}' should equal V_R'. Extrapolation of retention data to zero flow rate has been used by Hammers and DeLigny[8] and by Newman and Prausnitz[9] to obtain accurate retention data on polymeric stationary phases.

These calculations predict that a decrease in $K/\dot{V}$ by a factor of 100 will result in a very slightly skewed peak becoming so broad that it is virtually undetectable. If bulk diffusion is the sole kinetic factor and $\dot{V}$ is constant, then from eq 11 a 100-fold decrease in diffusion coefficient D or a 10-fold increase in stationary-phase layer thickness d_f would produce this effect.

Effect of Temperature on Peak Shape and Retention Volume

The logarithm of retention volume of a vapor on a polymeric substrate log V_R' is normally inversely proportional to the absolute temperature. However, temperature will also exert a strong effect on the factors influencing peak shape. If all such factors other than bulk diffusion can be eliminated, the diffusion coefficient D is related to peak shape (*e.g.*, by eq 12). The width of the chromatographic peaks at different temperatures may then be used to determine the temperature dependence of D or *vice versa*. Using this method under appropriate experimental conditions, the temperature dependence of diffusion of tetradecane in polyethylene melt has been determined;[3] the measured value increased about 10-fold between 125 and 170°.

This relatively small temperature dependence of D exerts little effect on the shape and peak retention volumes of tetradecane on polyethylene far above its glass transition temperature. The situation is quite different for the same vapor on a polymer such as polystyrene in the same temperature range; rates of diffusion for large organic penetrants in a polystyrene melt would be expected to drop very sharply as the glass transition temperature is approached. The values for D in a polystyrene melt for this penetrant are apparently not available, but a reasonable approximation may be arrived at using Fujita's formula for diffusion coefficient at zero diffusant concentration.[10]

$$\ln (D/RT) = \ln A_d - (B_d/f) \qquad (14)$$

A_d and B_d are temperature and concentration dependent parameters. If the motion of the penetrant in steady state diffusion is analogous to that of polymer segments, B_d may be taken equal to unity. This appears reasonable for C_{12} to C_{16} n-alkanes in polystyrene. The fractional free volume, f, may be estimated[11] using the equation

$$f = f_g + (\alpha_1 - \alpha_2)(T - T_g) \qquad (15)$$

where $f = f_g$ for $T \leq T_g$, α_1 = coefficient of volume expansion in rubbery state, α = coefficient of volume expansion in glassy state, and T_g = glass transition temperature. Combining eq 14 and 15 and taking $B_d = 1$, the variation of D with temperature may be estimated using literature values for $\alpha_f = \alpha_1 - \alpha_2$, 6.9×10^{-4} ml and $f_g = 0.033$.[11]

The increase in diffusion coefficient predicted by this theory is very sharp; more than two orders of magnitude between T_g and $T_g + 20°$. As $K \propto D$ when the major cause of peak spreading is slow stationary phase diffusion (eq 11), $K/\dot{V}$ will also change by more than two orders of magnitude in this temperature range. This large variation in the kinetic parameter would be predicted to bring about the changes in peak shape shown in Figure 1. However, at the same time the change in temperature causes a change in the true retention volume V_R'. In order to illustrate the combined effect of these two factors, the variation in peak shape with temperature on approaching T_g from above was calculated for a specific set of column conditions. The starting point for the calculation was an experimentally determined peak shape and retention volume for n-tetradecane on a column containing polystyrene-coated glass beads at a temperature well above T_g,

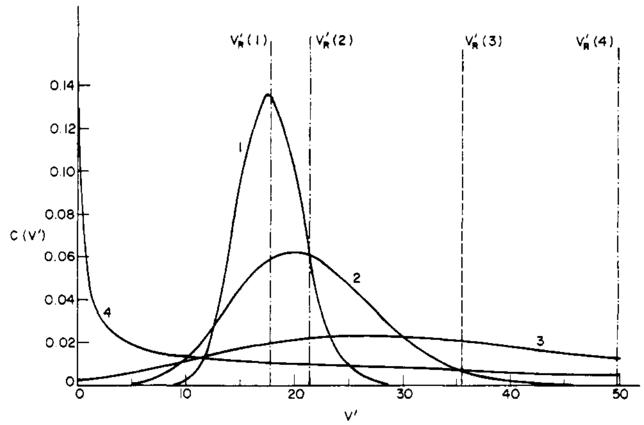

Figure 3. Calculated peak shapes illustrating the effect of rapidly decreasing diffusion rate as T_g approached from above on a column of poor performance. (For details, see text and Table I.)

Table I
Parameter Values Used to Calculate the Curves in Figure 3

Temp (°C)	V_R' (ml)	Log $(D/D_g)^a$	$K/\dot{V}$ (ml)
160	18	7.4	4.0
150	21	6.8	0.99
140	35	6.0	0.18
130	50	5.1	0.021

[a] D_g is the value of the diffusion coefficient D at T_g.

where the peak shape was close to symmetrical. The polymer layer on the column was relatively thick, in order to emphasize the effects of bulk diffusion on the peak shape. The peaks in Figure 3 were calculated from the data in Table I as follows.

(i) Peak $V_R'(1)$ corresponds in retention volume and peak shape to an experimental peak for *n*-tetradecane on a polystyrene-glass bead column (column 1) at 160°. $V_R'(1)$ is the measured peak retention value; $(K/\dot{V})_{160}$ is the value of the kinetic parameter which gave a peak of the appropriate breadth.

(ii) $V_R'(2)$, $V_R'(3)$, and $V_R'(4)$ are the peak retention volumes for *n*-tetradecane on polystyrene at 150, 140, and 130° predicted from the slope of the line relating ln V_R' and $1/T$ at temperatures above 160°. It is thus assumed that kinetic effects have negligible effect on the measured retention volumes above 160°.

(iii) The decrease in diffusion coefficient with temperature for tetradecane in polystyrene is assumed to be given by eq 14 and 15.

(iv) The values for $K/\dot{V}$ at 150, 140, and 130° were determined from the value at 160° using the relationship $(K/V)_T/(K/V)_{160^\circ} = D_T/D_{160^\circ}$, where T is the required temperature.

(v) The shapes of peaks having the appropriate V_R' and $(K/\dot{V})$ values were calculated from eq 13.

The results predict that at 140° the gc peak should be extremely broad and skewed forward. At 130° no peak should be detectable; most of the *n*-tetradecane is eluted with the carrier gas front, but a tailing to very long retention values is also to be expected. This was in fact observed on column 1; no peak maxima was detectable below about 135° due to the breadth of the peak, and the *n*-tetradecane appeared to be eluted along with the inert vapor (nitrogen) used to indicate the carrier gas front. A separate peak did not reemerge until the temperature had dropped below 95°, when retention of the *n*-tetradecane occurred by adsorption on the polystyrene surface. The experimental temperature at which recognizable peaks disappear is a function of detector response and injection size and hence somewhat arbitrary, but when these two factors are held constant, the predicted effects of slow diffusion do appear to be observed.

The absence of recognizable peaks at temperatures just above the glass transition temperature is not generally observed. It occurs in this case because the relatively thick polymer layer results in poor column performance; this in turn results in peak spreading which is large compared to the retention volume. (According to eq 11, the severity of peak spreading increases as the square of the layer thickness.) In general, peak retention data may be obtained in the nonequilibrium region above T_g,[2a,b] but in these cases the polymeric stationary phase has a higher surface-to-volume ratio, and the lower limit to peak spreading is no longer the carrier gas front, but the retention volume corresponding to surface retention. The surface retention volume is of course temperature dependent, which complicates the boundary conditions for eq 1. In addition, surface adsorption isotherms on polymers often appear to be nonlinear, so that eq 3 no longer holds. Exact solution of the equation for the shapes of curves under these conditions was not attempted; a more empirical approach may be necessary.

In summary, the shapes of gc peaks on a polymeric stationary phase were calculated, using simple assumptions about the rate of diffusion of organic penetrants through polymers and neglecting other causes of peak broadening. When peak spreading approached the same order of magnitude as peak retention time, the peaks became skewed forward, so that apparent retention volume was less than the true retention volume. Near T_g and with a thick polymer coating, kinetic effects may be so severe as to obscure the usual peak shape, and cause the penetrant to elute near the carrier gas front. The predictions explain at least semiquantitatively the departure from bulk retention behavior as T_g is approached from higher temperatures; further elaboration is necessary in the temperature region very close to T_g where departure from surface retention behavior governs peak shapes.

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