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THE DERIVATION OF THERMODYNAMIC INFORMATION FROM ASYMMETRICAL CHROMATOGRAPHIC PEAKS WHEN MORE THAN ONE DISTRIBUTION MECHANISM CONTRIBUTES TO RETENTION

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SUMMARY

Asymmetry of elution peaks in gas–liquid chromatography is often caused by retention contributions from adsorption of solute at the liquid surface and/or on the solid support, the distribution isotherms for these mechanisms having greater curvature than the bulk partition isotherm. Analogous phenomena are observed in other forms of chromatography. A method is developed which allows determination of the slope of the distribution isotherm for any one retention mechanism in the presence of others, from measurements on asymmetrical peaks. The experimental production of the chromatogram and the method of treating the data are described.

INTRODUCTION

A problem often encountered in thermodynamic studies of bulk solution properties by gas–liquid chromatography (GLC) is the occurrence of asymmetrical peaks. Retention measurements on the peak maxima are unreliable in these cases[1]. Asymmetry is sometimes merely an artefact of the injection or detection system, in which case it can be reduced or eliminated by better design of apparatus. We are interested here, however, in asymmetry observed when solution in the bulk stationary phase is accompanied by other types of retention contribution, such as adsorption at the liquid–gas interface[2] and adsorption induced by the support. The phenomenon is a common one because of the inherent complexity of the GLC system. Observation of peak asymmetry implies that sample sizes are too large, so that the condition of effective infinite dilution is not achieved for one or more of the distribution mechanisms contributing to retention. For this reason, reported thermodynamic studies on bulk solutions at "infinite dilution" where asymmetry is observed are of doubtful value. Even the finding of symmetrical peaks guarantees only that infinite dilution has been attained and not that only one retention mechanism is operating.

Measurements on asymmetrical peaks can be used to evaluate the various retention contributions separately and quantitatively, so allowing detailed study[3] of

the retention mechanisms at work in the column and determination of thermodynamic parameters for any one mechanism. The method is based on finite concentration chromatographic theory. For generality, it is assumed that any number of retention mechanisms may be involved, of which one or all may be responsible for observed asymmetry. The approach is equally applicable to similar situations in other forms of chromatography where more than one mechanism contributes to retention.

The significance of peak profile

The major factors determining peak profile are threefold:

(a) The form of the distribution isotherm $q_i(c)$ for each contributing retention mechanism i; q_i is the concentration of solute in the stationary phase (liquid, interfacial or adsorbed) appropriate to mechanism i and c is the gas phase concentration.

(b) Flow rate changes across the two boundaries making up the peak, caused by flux of solute between stationary and mobile phases (sorption effect).

(c) Kinetic band-broadening processes such as diffusion and slow mass transfer (non-ideality).

Combination of these three factors frequently gives rise to asymmetrical peaks, one side being "self-sharpening" with a very steep slope and the other side being "diffuse" (Fig. 1, trace B). The direction and extent of asymmetry are measured by

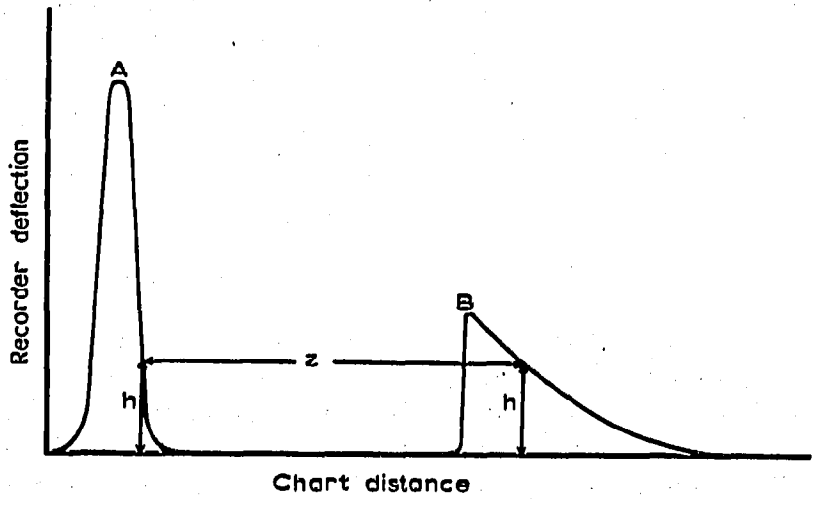

Fig. 1. An ECP peak as observed with detectors mounted (A) at inlet and (B) at outlet of the column. The diagram refers either to a positive peak for a distribution isotherm of Langmuir curvature, or to a negative peak for a distribution isotherm of anti-Langmuir curvature.

the skew ratio, η, defined as the slope of the rear (trailing) boundary of the peak divided by that of the front (leading) boundary at the points of inflexion[4]. η_+ and η_- refer to positive and negative peaks, *i.e.* peaks for which the solute concentration at the peak maximum is greater, or less, than the baseline concentration, respectively; to obtain a negative peak, the column must be pre-equilibrated with a gas stream containing a definite concentration of solute. Non-ideality tends to reduce the slope of both boundaries, so that η is determined primarily by effects (a) and (b). The sorption effect, (b), invariably skews the peak in the direction $\eta_+ < 1$, or $\eta_- > 1$.

Whether the effect is supported or opposed by that of (a) depends on the nature of the equilibrium distribution mechanisms contributing to retention. Thus, bulk solution is usually associated with a partition isotherm having curvature in the anti-Langmuir direction[5], resulting in $\eta_+ > 1$ and $\eta_- < 1$. In contrast, isotherms for distribution of solute between the gas phase and an adsorbed liquid surface phase[2,6] are generally of Langmuir curvature, giving $\eta_+ < 1$ and $\eta_- > 1$; while adsorption on, or induced by, a solid surface, such as that of the support, can be associated with isotherm curvature in either sense, but most commonly in the Langmuir sense which gives $\eta_+ < 1$ and $\eta_- > 1$.

The rate at which the distribution coefficient q_i/c changes with c is often one or two orders of magnitude greater for both types of surface sorption than for bulk solution. Thus at sample sizes of the order of 1 μmole, virtually symmetrical peaks may be observed when only bulk solution contributes to retention, whereas significant interfacial contributions can produce marked asymmetry at these sample sizes. Effective "infinite dilution" for one retention mechanism may be far from infinite dilution for another.

The profile of the diffuse boundary of an elution peak reflects in detail, as does the skew ratio in a more general way, the combined concentration dependences of each retention mechanism operating in the column, together with sorption and non-ideality effects. Thus, a given point on the diffuse boundary characterises passage through the column of a zone of constant concentration c, whose corrected retention volume is given (neglecting non-ideality and gas phase imperfection—the effects are discussed later) by the equation[7]

$$V_R^\circ(c) = JV_R(c) = V_G + (1 - Jy_o) \sum_i (\varphi_i \mathrm{d}q_i/\mathrm{d}c) \qquad (1)$$

where J is the usual James–Martin gas compressibility correction factor, V_G is the gas free space in the column (extra-column dead space is assumed to be negligible), y_o is the mole fraction of solute in the gas phase at the column outlet and corresponds to c, and φ_i is the total amount (volume or area as appropriate) of phase i present in the column. $\mathrm{d}q_i/\mathrm{d}c$ strictly refers to a mean column pressure, as defined elsewhere[7]. If the liquid phase loading of the column is varied, the relative magnitudes of the various φ_i, and hence the relative contributions of each retention mechanism to V_R°, also vary. There follows the possibility of determining $\mathrm{d}q_i/\mathrm{d}c$ for each retention mechanism by making measurements on the diffuse boundary of the peak at different liquid loadings.

A question arises, however, as to which points on the boundary should be used for the measurements, since both y_o and $\mathrm{d}q_i/\mathrm{d}c$ vary with solute concentration and this is reflected in variation of retention with height on the diffuse boundary of the peak. The simplest approach to this problem, which is also the one adopted here, is to choose the height on the boundary, for each column of different loading, in such a way that the concentration of solute in any given phase in the column is the same from column to column. The relevant values of $\mathrm{d}q_i/\mathrm{d}c$ for each retention mechanism are then independent of liquid loading and only the various φ_i are variables, so that analysis is greatly simplified.

We describe first the experimental aspects of the method and then show how $\mathrm{d}q_i/\mathrm{d}c$ for each mechanism can be evaluated from the chromatogram.

Production of the chromatogram

Use of the diffuse boundary of an asymmetrical positive elution peak for measurements at non-infinite dilution was introduced by CREMER AND HUBER[8] and by HUBER AND KEULEMANS[9] and has been named "Elution by Characteristic Point (ECP)" in the chromatographic classification scheme of CONDER AND PURNELL[10]. Suppose that an elution peak is passed through the column. Trace A in Fig. 1 represents the peak seen by a detector mounted at the column inlet. Passage along the column is accompanied by peak broadening and lowering of the overall peak height, to an extent depending mainly on the input band width and column efficiency. Trace B represents the peak observed at the outlet. It is assumed, for simplicity, that detectors mounted at inlet and outlet of the column have equal response factors. The retention volume (eqn. 1) of a zone of solute, whose gas phase concentration c is constant during transit through the column, is calculated from the experimental results by means of the equation[7]

$$V_R(c) = z(c)F(c)/s \qquad (2)$$

where $z(c)$ is the distance between a point of height h, corresponding to c, on the *diffuse* boundary (front or rear boundary, as the case may be) of the emergent peak, and a point of the same height on the corresponding boundary of the input peak (Fig. 1), s is the chart speed, and $F(c)$ is the total gas flow rate in a zone c, measured at outlet pressure. F varies with c because of the sorption effect and is given by the equation[7]

$$F(c) = \frac{F(0)[1 + k]}{1 + k(1 - Jy_0)} \qquad (3)$$

where k is the ratio of the number of moles of solute in the stationary phase to that in the mobile phase at equilibrium.

The velocity of the front boundary of the peak is affected by release of solute into the gas stream at the rear boundary, to an extent which varies as total peak height falls along the column. The proportional change in velocity at the rear boundary is $[ky/(1 + k)]$, y being the gas phase mole fraction of solute for the peak maximum at any given point in the column. This further manifestation of the sorption effect limits application of the ECP technique in its original form, either to cases in which the rear, rather than the front, boundary is diffuse, *i.e.* $\eta < 1$, or, if $\eta > 1$, to very low peak maximum concentrations at all points in the column. Thus, if the distribution isotherms are such that $\eta_+ < 1$, ECP can be used in its original form[8,9], which employs positive peaks. On the other hand, if $\eta_+ > 1$, either (i) the concentrations must be kept small enough for the time-averaged value of $[ky/(1 + k)]$ during transit to be small in comparison with unity, or (ii) the technique must be modified so as first to equilibrate the column with a gas stream of mixed carrier gas and solute vapour and then inject a plug of pure carrier, so producing a negative peak having $\eta_- < 1$. An alternative method (iii) is to avoid the restriction $\eta < 1$ altogether by operating the column in the "eluto-frontal" mode[11], *i.e.* using an input bandwidth sufficiently large to ensure that the band remains flat-topped and of constant height throughout transit. In this case the change in carrier velocity across the rear peak boundary is constant and can be calculated from eqn. (3), with c here relating to the eluto-frontal plateau.

Analysis of the chromatogram

The various retention mechanisms are assumed to be mutually independent. It is also assumed that the effect of non-ideality on peak profile can be neglected in comparison with isotherm non-linearity and the sorption effect. For simplicity, gas-phase interactions are neglected since achievement of the highest possible accuracy is in any case prevented by the last assumption and other factors, as discussed subsequently.

A series of columns, of equal length, l, but different liquid phase loading, is employed and a chromatogram such as that shown in Fig. 1 is obtained for each column. Let the columns and corresponding chromatograms be numbered $j = 0, 1, 2, \ldots$ The problem, as already defined, is to choose a set of heights, h_j, on the chromatograms such that the corresponding gas phase concentration, c, is the same in each column. Let $n_{ij}\delta l/l$ and $n_{Gj}\delta l/l$ denote the amounts of solute present in a stationary phase i (corresponding to retention mechanism i) and the gas phase, respectively, in length δl of column j at equilibrium with a gas phase concentration c. Then, taking column 0 as an arbitrary reference column

$$\frac{h_j}{h_0} = \frac{n_{Gj} + \sum_i n_{ij}}{n_{G0} + \sum_i n_{i0}} \tag{4}$$

Since the phases are in mutual equilibrium and c is the same in each column, the concentration q_i in any given phase is also the same in each column. If φ_{ij} denotes the total amount (volume or area, consistent with the units of q_i) of each phase in column j, and V_{Gj} the corresponding gas phase volume, then $n_{ij} = \varphi_{ij}q_i$ and $n_{Gj} = V_{Gj}c$, so that on substitution in eqn. (4),

$$\frac{h_j}{h_0} = \frac{V_{Gj} + \sum_i (\varphi_{ij}q_i/c)}{V_{G0} + \sum_i (\varphi_{i0}q_i/c)} \tag{5}$$

Provided c is not too large, eqn. (5) can be approximated by

$$\frac{h_j}{h_0} = \frac{V_{Gj} + \sum_i (\varphi_{ij}\mathrm{d}q_i/\mathrm{d}c)}{V_{G0} + \sum_i (\varphi_{i0}\mathrm{d}q_i/\mathrm{d}c)} \tag{6}$$

Since this equation involves only a ratio of parameters for two columns, the degree of approximation implied in passing from eqn. (5) to (6) is smaller than in the simpler assumption $q_i/c \approx \mathrm{d}q_i/\mathrm{d}c$. The latter assumption would, of course, violate the basic hypothesis of non-linearity of one or more of the relevant distribution isotherms. Combination of eqns. (6) and (1) now gives, since y_0 is small and, usually, $V_G \ll \Sigma$,

$$\frac{h_j}{h_0} = \frac{V_{Rj}^{\circ}}{V_{R0}^{\circ}} \tag{7}$$

According to eqn. (7), retention volumes measured on each chromatogram correspond to the same concentration c if the heights on each chromatogram are chosen so that this equation is obeyed. Choice of the set of h_j thus requires a process of successive approximations. A suitable first approximation is to choose the h_j in proportion to V_{Lj}, the total volume of liquid phase in a column j, *i.e.*

$$\frac{h_j}{h_0} = \frac{V_{Lj}}{V_{L0}} \tag{8}$$

With these h_j, a set of $V_{Rj}°$ is determined from the chromatograms. A more accurately proportionated set of h_j is then obtained by using eqn. (7), and re-measurement gives a better set of $V_{Rj}°$. The process is repeated until little or no change is observed in the set of $V_{Rj}°$, probably after about three cycles.

We have now obtained a series of retention volumes, $V_{Rj}°$, at a corresponding series of values of V_{Lj}, and all at the same solute concentration.

From each value of $V_{Rj}°$ the net retention volume, V_{Nj}, is calculated:

$$V_N = V_R° - V_G \tag{9}$$

Finally, $V_N/V_L(1 - Jy_o)$ is calculated for each j and plotted against $1/V_L$. Such a plot is shown in Fig. 2. Since eqn. (1) can be written in the form

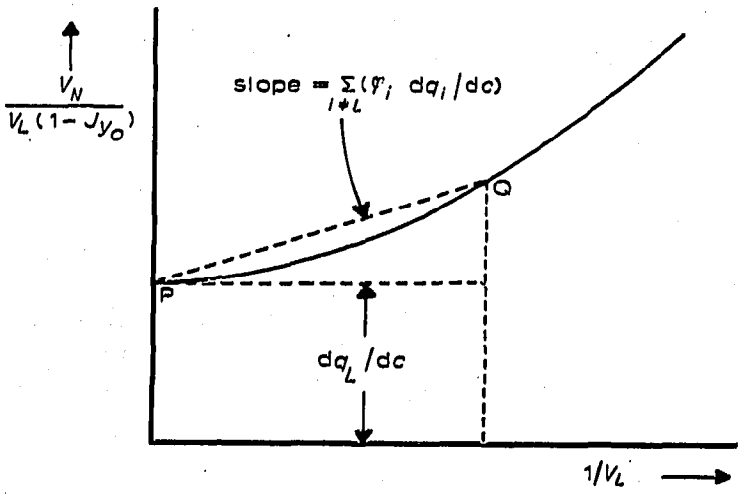

Fig. 2. Plot of $V_N/V_L(1 - Jy_o)$ against $1/V_L$.

$$\frac{V_N}{V_L(1 - Jy_o)} = \frac{dq_L}{dc} + \frac{1}{V_L} \sum_{i \neq L} \left(\varphi_i \frac{dq_i}{dc}\right) \tag{10}$$

where q_L is the concentration of solute in the liquid phase, the intercept on the ordinate axis is given by

$$\text{intercept} = dq_L/dc \tag{11}$$

Thus the intercept of the plot gives the gradient of the partition isotherm for bulk solution. This is usually the parameter of chief interest.

The gradients of the other, interfacial, distribution isotherms can also be determined, however, if sufficient additional information is available. In Fig. 2, the slope of the chord PQ is given by

$$\text{slope} = \sum_{i \neq L} (\varphi_i dq_i/dc) \tag{12}$$

If there is only one term in this sum, *e.g.* if either liquid surface adsorption or support adsorption provides the only retention contribution apart from bulk solution, then the relevant dq_i/dc can be evaluated provided the corresponding φ_i is known at the given value of V_L. This approach is of value for studying adsorption on the liquid surface in the absence of support adsorption, for example, with polar solvent/non-

polar solute systems. The required liquid surface areas can be measured independently, but it should be remembered that values so obtained may be only approximate when applied to the GLC situation. Areas measured by nitrogen adsorption should, of course, be adjusted to allow for the difference in areas covered by molecules of nitrogen and the solute used for the GLC measurements[6].

When more than one term in the sum in eqn. (12) contributes significantly to retention it may still be possible to derive useful information from the slope of the chord PQ. Let A denote area and subscripts I and S denote adsorption at the liquid–gas interface and induced by the support, respectively. Eqn. (12) can be written

$$\frac{\text{slope}}{A_I} = \frac{dq_I}{dc} + \frac{1}{A_I} \cdot \frac{dq_S}{dc} \qquad (13)$$

If A_I is known as a function of V_L, a plot of the left-hand side of this equation against $1/A_I$ yields both dq_I/dc and the product, $(A_S \cdot dq_S/dc)$. Further analysis to evaluate dq_S/dc separately is of little value and is in any case hindered by the difficulty of identifying and measuring A_S[3].

The procedure described is, of course, applicable not only to retention measurements at finite concentration on asymmetrical peaks, but also to measurements at infinite dilution on symmetrical peaks. In this case the experimental data refer to a single fixed concentration (infinite dilution) and so can be plotted immediately as V_N/V_L against $1/V_L$.

DISCUSSION

A method has been described for determining dq_i/dc for any one of several concurrent retention mechanisms, at both finite concentration and infinite dilution. The accuracy of the results depends mainly on three fractors.

First, because eqn. (1) provides the basis of the method, it is important that the influence of non-ideality on peak profile be much smaller than the combined influences of the relevant distribution isotherms and the sorption effect. The steepness and linearity of the self-sharpening side of the peak on emergence provide some test that this condition is achieved[12]. More quantitatively, one may quote the value of η. The further η is from unity the greater the influence of non-linearity, relative to non-ideality, on peak profile. The effect of significant non-ideality is always to make $|d^2q_i/dc^2|$ greater than it should be, irrespective of whether d^2q_i/dc^2 is positive or negative and whether positive or negative elution peaks are used. In practice, non-ideality is minimised by using moderately long columns and choosing gas flow rates in the region of minimum plate height[9,13].

Secondly, error introduced by the assumption stated in eqn. (6) increases with distance up the isotherm, *i.e.* with increasing concentration.

Thirdly, error arises from the fact that the chromatographic process always leads to rounding-off of the ends of a boundary, even of a self-sharpening boundary (see trace B, Fig. 1). In these regions boundary profile cannot be correlated with the form of the distribution isotherm. In ECP, the "rounding-off" effect on the diffuse boundary of the peak is most significant in the tail region, whereas that part of the boundary which appears near the peak maximum on emergence is well removed from

this position during the greater part of its transit through the column and so is less subject to the rounding process. The tail profile thus reflects the form of the distribution isotherm less accurately than does the profile of the rest of the boundary. The value of c below which such tailing becomes significant can be determined by plotting the calculated values of dq_L/dc against c and noting the value of c below which curvature becomes very marked with the curve approaching the ordinate axis asymptotically. This effect and the effect of the approximation in eqn. (6) thus combine to place rough upper and lower limits on the range of solute concentration which can be used.

In GLC it is often desired to evaluate the partition coefficient, $K = q_L/c$, for solution in the bulk phase at infinite dilution. With a sensitive detector, it may be found that sufficiently small samples give symmetrical peaks. In this case K can be determined directly from measurements of peak maximum retention volume at different liquid loadings by plotting V_N/V_L against $1/V_L$, as already indicated, without need to pre-adjust the data to constant solute concentration. On the other hand, if peaks are asymmetrical under the conditions of experiment, the full finite concentration procedure described can be adopted to give values of dq_L/dc at different values of c, chosen so as to avoid the tailing region of the peak. A plot of the results against c is likely to be sensibly linear and of fairly small slope, since the contribution of bulk solution to asymmetry is usually much smaller than that of interfacial sorption effects. Extrapolation to zero c is then easily carried out and gives K as the limiting value of dq_L/dc, equal to the limiting value of q_L/c. Results obtained by using the method will be described in a future publication[3].

An important feature of the method is that dq_i/dc for any one mechanism can be determined only if the corresponding φ_i is known as a function of liquid loading. V_L is, of course, easily evaluated, but knowledge of surface areas is sometimes less easy to obtain. For example, measurements on the frozen packing using nitrogen as adsorbent give false values of liquid surface area. An alternative, indirect technique of measuring areas has been described[6] which is more closely related to real chromatographic conditions and so gives more reliable results. A similar problem is encountered in determining the surface area appropriate to support-induced adsorption in the presence of the stationary phase: this area is not necessarily equal to the measured area of the naked support. Consequently, although the method can be used for measuring interfacial parameters, its main application is to the study of bulk solution properties when the presence of interfacial sorption mechanisms is regarded merely as a complicating feature of the system. In both contexts, the method should be useful for many common situations in gas–liquid and liquid–liquid chromatography.

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