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QUANTITATIVE ASPECTS OF HEATER DISPLACEMENT CHROMATOGRAPHY

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SUMMARY

This paper describes quantitative developments in heater displacement chromatography. The factors which control the quality of a heater displacement chromatographic separation are discussed, and relationships derived by which the conditions for optimum separation can be determined. An expression is also derived for the maximum sample capacity of a heater displacement column, enabling optimum use to be made of adsorbents, and an equation is generated which describes the concentration profile in the heater zone. This latter function is of importance in the evaluation of the rate of a reaction occurring on the heater displacement column.

The equations developed are tested using a series of model systems.

INTRODUCTION

In a recent paper¹ the technique of heater displacement chromatography was introduced and its ability to achieve preparative-scale separation with efficacy and simplicity was demonstrated. The advantages and disadvantages of displacement chromatography as a preparative method were enumerated, and it was shown how the replacement of the feed of displacer compound in conventional displacement chromatography by a moving heater effectively removed the disadvantages of the technique and transformed it into one of versatility and convenience. It was also shown that by using a catalyst as an adsorbent it was possible to carry out heterogeneously-catalysed reactions with simultaneous separation of products. The use of a displacement chromatographic environment for the conduct of reactions again showed valuable advantages such as the near-quantitative isolation of intermediate products in consecutive processes and the conversion of reactants to products past the thermodynamic equilibrium in cases of reversible reaction.

A heater displacement chromatograph is represented schematically in Fig. 1. It consists of an adsorbent column of length L contained in an oven at temperature T_0 and through which is passed a carrier gas flow F . The sample to be separated is introduced at the beginning of the column where it forms a band of length δL before it is displaced forward along the column by means of a heater moving at speed U_h .

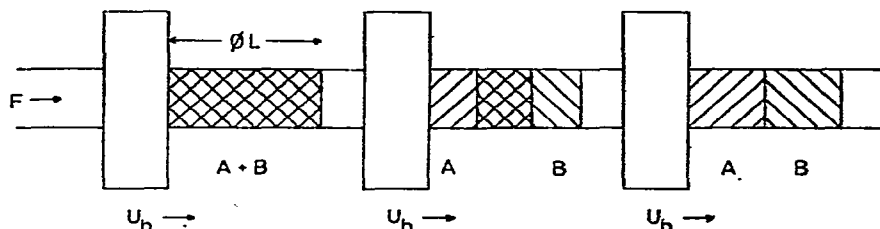


Fig. 1. Schematic representation of a heater displacement chromatograph showing three states of a band of a mixture of two components A and B as it is displaced along a column of length L , with a carrier gas flow-rate F at a heater speed U_h .

By the time it leaves the column the sample has been separated into its individual components ahead of the heater.

In this present paper we seek to place heater displacement chromatography on a quantitative basis. In order that the technique be reduced to one which can be used routinely, the various parameters controlling the separation, *i.e.* carrier gas flow-rate, heater speed, heater temperature and oven temperature, need to be related to the chromatographic (adsorption) properties of the compounds to be separated and the adsorbent used in the column and also the saturated vapour pressures of these compounds at the oven temperature employed. Accordingly in this paper there are three objectives: (a) to determine the limits of the separation parameters insofar as these are controlled by the properties of the adsorbent and adsorbates, so that these parameters can be chosen to allow an optimum heater displacement separation to be achieved; (b) to determine from the properties of the adsorbents and adsorbates, the maximum sample capacity of a heater displacement column to allow optimum use to be made of the adsorbents; and (c) to formulate an expression for the concentration of the adsorbate in the heater zone as a function of temperature, so that in later work the rate of reaction occurring on a catalytic heater displacement column may be predicted. The theoretical aspects of (a), (b) and (c) above are therefore set out and the results demonstrated by a series of experiments using a heater displacement chromatograph.

THEORETICAL

Conditions required for satisfactory displacement

In order to achieve a satisfactory displacement separation of particular adsorbates on a given adsorbent, it is necessary to set the primary heater displacement variables of heater speed and carrier gas flow to the appropriate optimum values. There are four factors which govern the bounds of these variables and these are listed below and illustrated diagrammatically in Fig. 2.

(i) If the ratio of the heater speed to the gas flow-rate (U_h/F) is excessive, the gas phase concentration of the adsorbate ahead of the heater exceeds the saturated vapour pressure of the latter and condensation occurs. This is illustrated by line i.

(ii) If the ratio (U_h/F) is insufficiently large then one or more of the adsorbate bands in the column may elute ahead of the heater. The onset of elution is represented by line ii. This results in possible loss of separation but certainly loss of sample capacity (A).

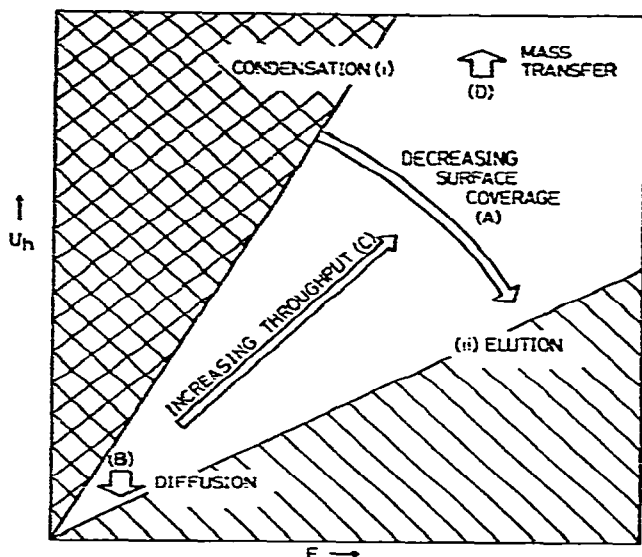


Fig. 2. Operating regime for heater displacement chromatography, with thermodynamic limits (lines i and ii) and kinetic limits (regions B and D) shown. Lines A and C indicate the effect of the heater speed to flow-rate ratio, and the overall speed of separation, on the throughput of material.

(iii) If the heater moves too slowly the regime arrowed B is entered where the separation is impaired by longitudinal diffusion on the column. A slow speed also means the throughput of material will be low (C).

(iv) If the heater moves too rapidly then resistance to mass transfer will impair the separation (D) and thermal gradients across the column may affect the displacement of the last band.

The slope of the condensation limit line (i) can readily be calculated as follows: consider a band of a single component A moving along a heater displacement column. The partial pressure P^A of the adsorbate leaving the column on which it was adsorbed with a concentration C_S^A is given by:

$$P^A = U_b \frac{\rho C_S^A RT}{Q} \quad (1)$$

where ρ = adsorbent packing density and Q = total volume flow leaving the column at temperature T . If P_0^A is the saturated vapour pressure of A, then the ratio F/U_b has to be set to a minimum value given by

$$(F/U_b)_{\min.} = \rho C_S^A RT / \left\{ \frac{P_0 - P^A}{P_0} \right\} \quad (2)$$

Eqn. 2 gives the slope of line i, a value which also corresponds to the minimum flow-rate for a multi-component separation where A is the component with the lowest vapour pressure at the separation temperature. The line ii represents a ratio

(U_b/F) below which the least strongly retained adsorbate is eluted ahead of the heater. The slope of this line can be conveniently calculated by setting the flow-rate to the velocity with which a small sample of the adsorbate is eluted as a symmetrical peak. If the measured retention time per unit column length for such a peak is V_R^A then the slope of the line is simply $(U_b/F)_{\text{min.}} = 1/V_R^A$. In practice, since the isotherm is curved, different concentrations move at different velocities, and it is therefore preferable to operate as close as is practicable to line i, to avoid partial elution of the bands with consequent distortion of band shape and loss of adsorbent capacity.

Sample capacity of a heater displacement column

In order to determine the maximum sample size for a column of given dimensions, use may be made of a modification of the approach introduced by Sillén². Consider a column in which two substances A and B are being separated by displacement. Suppose A is less strongly held to the surface than B and that they are initially placed on the column as a uniform mixture occupying a fraction \varnothing of the column. To achieve a separation of A and B in a unit column length, substance A must travel unit distance while substance B moves a distance $1 - \varnothing$. By considering a small interval of time during the development of the displacement chromatogram, it may readily be shown that the band velocity of substance A, U_A is given by: $U_A = C_G^A F / C_S^A \varnothing$. While A moves unit distance along the column substance B moves a distance $1 - \varnothing$ at a velocity $U_B = C_G^B F / C_S^B \varnothing$ and hence for a separation just to be achieved in unit column length, the initial band must occupy a fraction of the column not greater than

$$\varnothing_{\text{max.}} = 1 - C_S^A C_G^B / C_S^B C_G^A \quad (3)$$

which we can write

$$1 - X^{AB}$$

Hence the maximum capacity of a heater displacement column is readily computed from measurements of surface and gas phase concentrations of components from chromatographic measurements obtained at the separation temperature.

Concentration profile in the heater zone

Consider a single substance A being displaced by a moving heater. The isotherm governing the adsorption of the material by the adsorbent has to be of the Langmuir type, *i.e.* concave towards the pressure axis, but it need not necessarily fit the Langmuir equation. However, for the system which we have investigated experimentally the adsorption has followed the Langmuir equation satisfactorily over the relevant concentration ranges, so that we may write:

$$C_S^A = C_S^0 K C_G^A / (1 + K C_G^A) \quad (4)$$

where C_S^0 represents the maximum capacity of the surface and K is the adsorption constant. At a steady state we assume that while the adsorbate is displaced outside the heater zone, it is eluted within it. Moreover, at a steady state, each concentration

within the heater moves at the velocity of the heater. This is similar to the situation prevailing inside the heater of the chromatothermographic technique of Turkeltaub³. From the retention volume eqn. 4 which relates the retention volume of a particular finite adsorbate concentration to the slope of the adsorption isotherm at that concentration, we can write the velocity of a concentration C_G^A , $U(C_G^A)$, inside the heater zone as:

$$U(C_G^A) = F / \left\{ V_0 + \rho \frac{\partial C_S^A}{\partial C_G^A} \right\} \quad (5)$$

for a column of unit length, with a dead volume V_0 per unit length. Substituting the differentiated adsorption isotherm (eqn. 4) into eqn. 5, equating $U(C_G^A)$ with the heater speed U_h and rearranging, we obtain,

$$\frac{K}{\{1 + KC_G^A\}^2} = \frac{1}{PC_S^0} \left\{ \frac{F}{U_h} - V_0 \right\} = \alpha \quad (6)$$

If the adsorption constant K is expressed in terms of a heat of adsorption, ΔH^A ,

$$\ln K = \ln K^0 - \Delta H^A / RT$$

substitution into eqn. 6 and rearranging gives:

$$C_G^A = \{ \alpha K^0 e^{-\Delta H^A / RT} \}^{-1/2} - \{ K^0 e^{-\Delta H^A / RT} \}^{-1} \quad (7)$$

Substituting back into eqn. 4, eqn. 7 becomes:

$$C_S^A = C_S^0 \{ 1 - (\alpha / K^0 e^{-\Delta H^A / RT})^{1/2} \} \quad (8)$$

The shape of this function will be considered in more detail below, but its form is a monotonic decrease of C_S^A with increasing temperature. At a point $T = T_c$, C_S^A passes through zero, and thereafter the function has no physical significance. The fact that, according to this model, the value of C_S^A reaches zero at a finite point in the heater, means that there is no residue on the column after the passage of the heater, an important observation from the point of view of quantitative applications.

The results generated by the above theory may now be applied to experimental heater displacement chromatography.

EXPERIMENTAL

The small-scale heater displacement chromatograph used in these investigations has been described previously, together with operational details¹. The only modifications carried out for this work were to the heater and the automatic sampling valve.

A temperature-controlled heater was constructed to give the high temperature stability required for these experiments ($\pm 2^\circ\text{C}$). The heater consisted of a brass tube of length 5 cm, wound with approximately 5 m nichrome wire (0.46 mm diameter), which fitted snugly over the heater displacement column. A NiCr-NiAl thermo-

couple passed through the side of the brass tube halfway along its length and just touched the glass column. The thermocouple was connected to a Pye Ether "Mini" temperature controller (0–1000°C) which controlled the current to the heater, from a variable voltage transformer.

The automatic sampling system was improved by replacing the rotary sampling valve previously described, with a linear valve (type GSV-106-B-V) supplied by Negretti and Zambra (Aviation). This allowed the sampling system to operate reliably at temperatures up to 180°C, an improvement of 100°C on the rotary valve.

The adsorbents used in this work were Alcoa alumina (80–100 mesh) and Waters Assoc. GC Porasil type B (80–100 mesh), both supplied by Phase Separations (Queensferry, Great Britain). Hydrocarbons were supplied by Koch-Light Labs. (Colnbrook, Great Britain).

Isotherms for various adsorbates and stationary phases were extracted from elution chromatographic profiles using the method of Huber and Keulemans⁴ as modified by Conder⁵. This was carried out in a conventional gas chromatograph (Pye-Unicam 104) using 1.5 m × 0.4 cm I.D. glass columns.

Surface areas of adsorbents were measured using nitrogen as an adsorbate by the method of Nelsen and Eggertsen⁶.

RESULTS

Optimum conditions for displacement

The limits described in Fig. 2 were shown to control the quality of a heater displacement band of *n*-heptane on a Porasil B column (80 × 1.2 cm O.D.) using an oven temperature of 67°C and a heater temperature of 300°C. The heater speed was 3.33 cm min⁻¹ and the gas flow-rate was adjusted so that the operating point was just below and just above line i which corresponded to 35 ml min⁻¹ at the heater speed used. With a flow-rate of 44 ml min⁻¹ a satisfactory band shape was obtained (similar to that shown for *n*-hexane in Fig. 3) while with a flow-rate of 28 ml min⁻¹, distortion was apparent owing to condensation. This was manifested as a sharp rise in C_s at the centre of the displacement band to a value considerably in excess of C_s^0 . This distortion disappeared towards the end of the band as the increasing column temperature in the heater zone raised the saturated vapour pressure of the heptane.

By performing a similar run at a flow-rate of 61 ml min⁻¹ the effect of elution on the shape of the displacement band was observed. The band deteriorated into a severely tailing elution peak, the effect being observable even before line ii owing to curvature of the isotherm. This curvature resulted in the onset of elution of high adsorbate concentrations before lower concentrations with only the lowest concentrations being retained sufficiently to be displaced by the heater.

The effects of overall speed of separation (regimes B and D in Fig. 2) were investigated using a constant value for the heater speed–flow-rate ratio. It was found that, for the separation of hexane isomers on an alumina column, the chromatographic efficiency of the heater displacement system followed a Van Deemter type curve. Below a heater speed of about 1.5 cm min⁻¹ there was a fairly sharp decrease in efficiency due to longitudinal diffusion, while above this speed there was a slow decrease in efficiency due to mass-transfer effects.

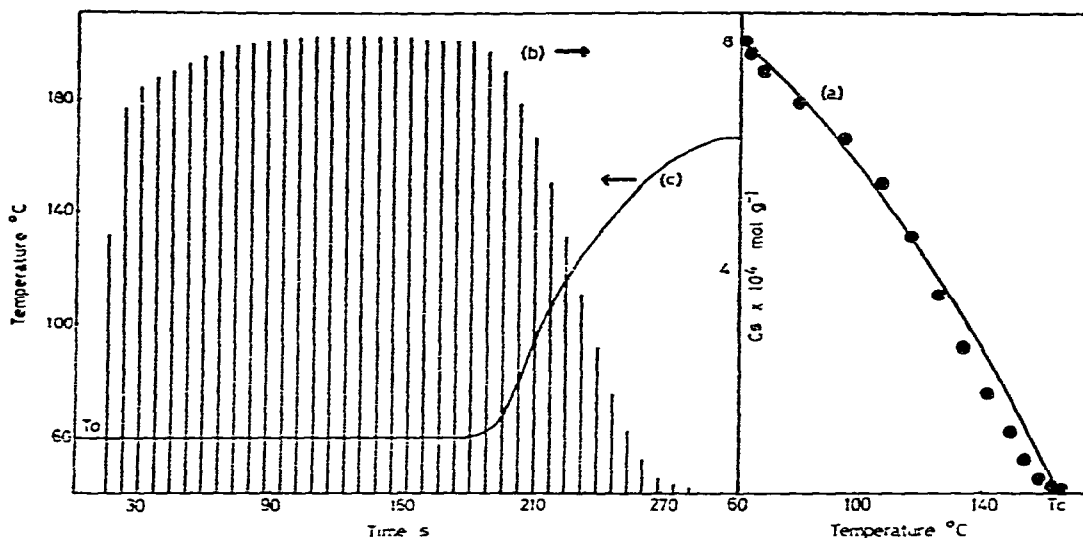


Fig. 3. (a) Theoretical band profile curve (continuous line) for *n*-hexane on alumina with experimental points, obtained from (b) heater displacement chromatogram and (c) heater temperature profile curve, superimposed. Theoretical cut-off temperature (T_c) = 161°C.

Sample capacity

In order to exploit eqn. 3 to determine a theoretical value for the sample capacity of a heater displacement column for a binary separation the value of X^{AB} has to be determined. This was carried out using two methods.

(i) The values of the surface and gas phase concentrations of the components to be separated were determined by a simple static method. Here an amount of the component mixture was injected into a flask sealed with a septum, containing a weighed amount of adsorbent. After shaking and allowing to equilibrate at the displacement temperature, the equilibrium concentration in the gas phase of each component was determined by withdrawing samples and analysing them using elution chromatography.

(ii) Values of the adsorption constant K were also determined by elution chromatography at several different temperatures and extrapolated to the displacement temperature. Although this technique suffered the disadvantage that concentrations were not measured under conditions of displacement, it was found to be a rapid and convenient method of evaluating X^{AB} .

The above methods were applied to determine the maximum sample capacity of a heater displacement column used for the separation of skeletal hexane isomers on Alcoa alumina and on Porasil B. The results are shown in Tables I and II and demonstrate the satisfactory correlation for calculated maximum loadings from methods (i) and (ii) above. They also show that the more difficult separations (e.g. that between *n*-hexane and 3-methylpentane) exhibit a correspondingly smaller maximum loading as would be expected. The results also show that an alumina column shows greater selectivity towards the hexane isomer separations than does Porasil B, leading to a greater maximum sample capacity in the former case. This increased selectivity coupled with the larger bulk density of alumina (0.91 g ml⁻¹ as

compared with 0.44 g ml^{-1} for Porasil B) means that approximately 3 times as much of the hexane isomers can be separated on an alumina column as on a Porasil B column of the same dimensions.

TABLE I

VALUES OF ϕ_{max} . FOR HEXANE ISOMERS AND HEXANE ON ALUMINA

<i>Isomers</i>	<i>Static method</i>	<i>Elution chromatography</i>	<i>Displacement chromatography</i>
<i>n</i> -Hexane and 2,2-dimethylbutane	0.47 ± 0.05	0.45 ± 0.05	0.47 ± 0.03
<i>n</i> -Hexane and 2,3-dimethylbutane	0.33 ± 0.02	0.33 ± 0.06	0.29 ± 0.02
<i>n</i> -Hexane and 2-methylpentane	0.24 ± 0.02	0.28 ± 0.06	0.27 ± 0.02
<i>n</i> -Hexane and 3-methylpentane	0.16 ± 0.03	0.19 ± 0.06	0.14 ± 0.02

TABLE II

VALUES OF ϕ_{max} . FOR HEXANE ISOMERS AND HEXANE ON PORASIL B

<i>Isomers</i>	<i>Static method</i>	<i>Elution chromatography</i>	<i>Displacement chromatography</i>
<i>n</i> -Hexane and 2,2-dimethylbutane	0.43 ± 0.02	0.31 ± 0.02	0.33 ± 0.02
<i>n</i> -Hexane and 2,3-dimethylbutane	0.34 ± 0.02	0.26 ± 0.02	0.30 ± 0.02
<i>n</i> -Hexane and 2-methylpentane	0.23 ± 0.02	0.19 ± 0.03	0.20 ± 0.02
<i>n</i> -Hexane and 3-methylpentane	0.15 ± 0.02	0.14 ± 0.03	0.17 ± 0.02

Thus while the properties of aluminas and silicas vary a great deal, and the above data only applied to the particular varieties used in this case, it is a relatively simple matter to determine optimum loadings on any adsorbent and use these to determine rationally the most selective adsorbent for any separation.

The loadings predicted in Table I were checked in practice by performing heater displacement separations in which the loading was set to values just above and just below the calculated maximum values. In each case, to provide a uniform initial band at the head of the column, the calculated amount of adsorbent was removed from the column, shaken in a closed flask with the mixture to be separated, and carefully repacked into the displacement column. The heater displacement separation was then carried out. The results are illustrated in Table I. The results of a typical separation obtained in this way on alumina for *n*-hexane and 2,2-dimethylbutane are shown in Fig. 4. It will be observed that exceeding the loading capacity of the column by a very little results in a significant deterioration in the quality of the separation, while consistent separation quality is maintained up to the maximum loading. This is in contrast to elution preparative methods, where the quality of the separation falls progressively as the loading is raised.

The results obtained above were achieved by removal, coating, and replacement of a band of adsorbent at the head of the column. This procedure was found inconvenient for the heater displacement separations, and the samples were normally introduced into the column, either by syringe injection, with the heater at the head of the column or by vapourizing the sample into the carrier gas stream in a small electrically heated saturator placed before the column inlet.

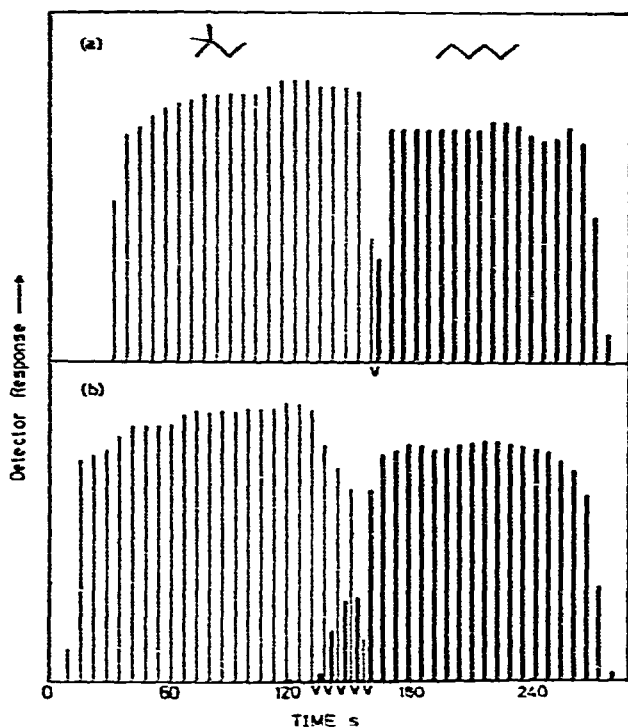


Fig. 4. Separation of 2,2-dimethylbutane and *n*-hexane on alumina at (a) just under the maximum loading ($\phi = 0.45$) and (b) just over the maximum loading ($\phi = 0.48$). Band overlap can be clearly seen in the latter. The peaks corresponding to a single sample analysis in the overlap regions are marked "V".

Because of the initial separation on the column of the components of the mixture during the development of the band and differences in their volatilities, both these methods result in a slight preliminary separation before the heater displacement run itself. Accordingly the capacity of a column under these conditions is somewhat higher than the predicted value, thus providing a margin of safety over the latter. The effect of initial separation during band formation was illustrated by the direct injection of a mixture of *n*-hexane and 2,2-dimethylbutane onto the alumina column. This gave a value for ϕ of 0.59 as opposed to 0.47 for introduction of the sample as a band, thereby giving an increase in effective column length of about 25%.

Experimental measurement of the concentration in the heater zone

The experimental validity of eqn. 8 was tested using *n*-hexane as the adsorbate on an alumina column. The parameters of eqn. 8 were measured in a series of preliminary experiments.

The heater temperature profile was measured by means of a thermocouple inserted centrally in the packing material of the column, and the heater allowed to descend over the junction, under conditions of gas flow, heater speed, etc. which prevailed in the intended displacement. The electromotive force (e.m.f.) of the

thermocouple was recorded during the descent of the heater and the temperature profile evaluated for several heater temperatures.

The heat of adsorption was determined from adsorption isotherms obtained from elution chromatography. Isothermic heats of adsorption were obtained at different coverages and the values at the coverages prevailing under heater displacement conditions obtained by extrapolation. Thus for *n*-hexane at a coverage of $4 \cdot 10^{-4}$ mol g⁻¹ the heat of adsorption was 33.8 kJ mol⁻¹.

The value of K^0 in eqn. 8 could, in principle, be found by extrapolation of the integrated Van 't Hoff isochore to infinite temperature, but the extrapolation is a long one, and precision is lost in this procedure. As an alternative eqn. 8 was used at $T = T_0$ by setting C_s^A to the measured surface concentration outside the heater, and K^0 evaluated accordingly. For *n*-hexane on alumina a value of $5.6 \cdot 10^{-1}$ ml mol⁻¹ was found.

Together with simple determinations of temperatures, gas flow-rate, etc., the above measurements permit the theoretical function of eqn. 8 to be plotted under any given conditions. Such a curve for the displacement of *n*-hexane on alumina at a nominal heater temperature of 200°C is shown in Fig. 3a. Superimposed on these are points determined from the experimental heater displacement profile (Fig. 3b). Relative location of the experimental points and the theoretical curve along the temperature axis was found to be difficult, since the exact positions of the temperature gradient curve (Fig. 3c) and the concentration profile were not precisely known. This problem was overcome by fitting an experimental point to the curve artificially. Approximate calculations on the positions of the experimental and theoretical curves showed that such fitting was entirely reasonable, and the fidelity with which the experimental points fitted the theoretical curve over a wide range of heater profiles indicates the validity of the model for band profile theory.

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LIST OF SYMBOLS

C_G^A, C_G^B	Gas phase concentrations of adsorbates A and B in mol ml ⁻¹
C_S^A, C_S^B	Surface concentrations of adsorbates A and B in mol g ⁻¹
C_S^0	Maximum capacity of stationary phase, mol g ⁻¹
F	Carrier gas flow-rate, ml min ⁻¹
K	Distribution coefficient in the Langmuir equation, ml mol ⁻¹
K^0	The value of K at infinite temperature
L	Column length, cm
P^A	Partial pressure of adsorbate A, atm
P_0^A	Saturated vapour pressure of adsorbate A at temperature T , atm
Q	Total flux of material leaving column, ml min ⁻¹
T	Temperature, °K

T_c	Temperature at which the theoretical band profile curve (eqn. 8) passes through zero
T_0	Oven temperature, °K
U_A, U_B	Band velocities of adsorbates A and B, cm min ⁻¹
U_h	Heater speed, cm min ⁻¹
V_R^A	Retention volume of adsorbate A per unit column length, cm ²
V_0	Column dead volume per unit length, cm ²
α	Constant defined by eqn. 6, ml mol ⁻¹
ΔH	Heat of adsorption, kJ mol ⁻¹
e	Column packing density, g cm ⁻¹
\emptyset	Fraction of column length occupied by adsorbate
$\emptyset_{\max.}$	Maximum value of \emptyset
X^{AB}	$C_S^A C_G^B / C_S^B C_G^A$

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