Journal of Chromatography, 589 (1992) 223–230
Elsevier Science Publishers B.V., Amsterdam

CHROM. 23 732

Prediction of the elution profiles of high-concentration bands in gas chromatography

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(Received July 10th, 1991)

ABSTRACT

The prediction of band profiles in non-linear gas chromatography requires the use of a mass balance equation for the carrier gas and for the components of the feed. An additional equation is required to account for the non-linearity of the pressure profile and the compressibility of the gas phase. Thus, the sorption effect, which is insignificant in liquid chromatography, becomes of major importance in gas chromatography. Originating from the difference between the partial molar volumes of the retained components in the mobile and the stationary phases, this effect combines with the isotherm effect to control the elution profile of high-concentration bands. The influence of the various parameters which determine the relative intensity of the sorption and the isotherm effects is discussed and illustrated.

INTRODUCTION

The profiles of elution bands in gas chromatography has been abundantly discussed, especially in the 1960s and 1970s [1–11]. The work done prior to 1977 has been reviewed by Conder and Young [12]. Because of the gas-phase compressibility, however, the problem of the accurate prediction of band profiles is much more complex in gas than in liquid chromatography. There is not even a closed-form solution available for the ideal model, in which the column efficiency is assumed to be infinite [13], whereas such a solution has been derived for liquid chromatography [13–15].

The sorption effect, which is negligible in liquid chromatography because the partial molar volumes of the solute in the stationary and mobile phases are nearly equal, is very significant in gas chromatography. It was identified very early [2], shortly after the discovery of gas chromatography itself [1]. Whether under steady-state conditions with a stream of pure carrier gas, or during the migration of a high-concentration band, the pressure profile along a column is monotonously decreasing. The pressure profile is in fact little changed by the passage of the band [12]. As the partial pressure of the component studied is high within the band, the local partial pressure of the carrier gas is lower within the band than in the part of the column where it is pure. However, the mass flow-rate of the carrier gas is constant, so the local velocity increases within the band [16]. This causes the high concentrations in the band to move faster than the lower concentrations. This is the classical mechanism of the formation of a discontinuity in the absence of axial dispersion (*i.e.*, when the ideal model is valid) [5]. In practice, a shock layer is formed instead [17,18].

Because of the gas-phase compressibility, a mass balance equation must be used for the carrier gas and for each component of the sample. Thus, the simplest problem, the calculation of the profile of a high concentration band for a pure component, involves two coupled partial differential equations [5,6,10]. This explains the need to resort to numerical solutions. The numerical analysis of the problem has been discussed previously by Rouchon *et al.* [10], using the method suggested by Godunov [11] for equation systems of the type found in chromatog-

0021-9673/92/$05.00

raphy. This method provides an extremely fast algorithm. Except for the influence of the column efficiency, early results demonstrated excellent agreement between the experimental band profiles and those calculated from the isotherm measured with an independent method [19]. A proper procedure to account for the influence of the column efficiency has been demonstrated [20]. It is entirely applicable to the calculations of band profiles in gas chromatography.

The aim of this work was to compare the elution band profiles obtained experimentally and those calculated from an independent determination of the equilibrium isotherm and the column efficiency, and to study the dependence of the intensity of the sorption effect on the column pressure drop and on the carrier gas flow-rate. This latter study is essentially based on the results of numerical calculations made using the equilibrium-diffusive model of chromatography validated by the agreement between experimental and calculated profiles.

THEORY

Basic assumptions

The model of chromatography used in this work is adapted to the practical problem with which we are dealing. We study the surface heterogeneity of powders of various materials, such as ceramics (*e.g.*, alumina), liquid chromatographic stationary phases, pigments and fillers. A porous-layer open-tubular column is prepared and we determine the adsorption isotherms of selected probe compounds [21–24]. The column efficiency is high and its pressure drop low [22]. In gas–solid chromatography, the initial curvature of the equilibrium isotherms is usually strong, so the range of partial pressures to be investigated is small [23], rarely exceeding a few millibars. This justifies the simplifying assumptions made to a general model of chromatography.

We assume that the carrier gas and the probe vapor have an ideal behavior. The correction for non-ideal behavior, using the first virial coefficients [12], is negligible [23]. We assume that the column is radially homogeneous and that the integrated Poiseuille law is valid, so we can treat the problem as unidimensional. The porous layer cannot be radially homogeneous, but the column is narrow and has only one gas channel, so radial heterogeneity of the layer thickness merely contributes to increase the height equivalent to a theoretical plate. It is important, however, that the layer thickness be homogeneous along the column length and that there is no local accumulation of particles creating a zone of low permeability. Because of the high carrier gas compressibility, this would invalidate the pressure profile model and the James and Martin coefficient would give a wrong correction for that effect [23].

We assume also that the carrier gas is not adsorbed by the stationary phase, which is true with helium on the materials investigated, and that the local pressure remains constant during the migration of a band, *i.e.*, the pressure profile is steady. This, again, is a more than reasonable assumption within the range of partial pressures investigated. The volume occupied by the sample is negligible compared with the column volume (the volume occupied by a typical 10-μg sample of diethyl ether is equivalent to that of 15 mm of the open-tubular column used). The perturbations to the flow profile resulting either from the sorption effect or from the change in viscosity due to the presence of a vapor which is much less viscous than the carrier gas are negligible because the probe vapor concentration exceeds 0.1% only over a very short part of the column, at its inlet [23]. Similarly, the effect of the heat of adsorption is negligible, because the amount of probe component adsorbed is very small and the heat generated locally by adsorption is small compared with the latent heat of the adsorbent.

The combination of these assumptions leads to a simplified equilibrium-diffusive model. This model is based on the use of two differential mass balance equations, one for the probe vapor and one for the carrier gas [10]. The adsorption isotherm and the column efficiency have to be determined by independent measurements. As shown previously by Rouchon *et al.* [19], good agreement should be expected between the experimental and calculated profiles.

Mass balance equations

Consider the flux, F_i (in moles per unit cross-sectional area) of the probe component into a differential section of the column of length, dz. Suppose that the adsorption–desorption kinetics are infinitely fast. As the column is an open tube, the column non-ideal band broadening is due essentially to axial diffusion in the mobile phase and to the parabolic flow profile in the tube [25]. The flux F_i of the probe into the incremental volume is then given by

$$F_i = Cu\mathrm{d}t - D \cdot \frac{\partial C}{\partial z} \cdot \mathrm{d}t \qquad (1)$$

where C is the local concentration at the point z, u is the linear mobile phase velocity at this point and D is the apparent dispersion coefficient of the solute, which is assumed to be constant, independent of the concentration. Assuming that the mobile phase is an ideal gas, and denoting by p the partial pressure of the component considered (P will be the local pressure, hence $X = p/P$ will be the mole fraction of the component), we may rewrite eqn. 1 as

$$F_i = \frac{1}{RT}\left(pu\mathrm{d}t - D \cdot \frac{\partial p}{\partial z} \cdot \mathrm{d}t\right) \qquad (2)$$

Because the mobile phase is an ideal gas, it expands during its migration along the column and neither the partial pressure of the component nor the carrier gas velocity remains constant. They must be incremented and the flux out of the column section, F_o, is given by:

$$F_o = \frac{1}{RT}\left[\left(p + \frac{\partial p}{\partial z} \cdot \mathrm{d}z\right)\left(u + \frac{\partial u}{\partial z} \cdot \mathrm{d}z\right)\mathrm{d}t - D \cdot \frac{\partial}{\partial z}\left(p + \frac{\partial p}{\partial z} \cdot \mathrm{d}z\right)\mathrm{d}t\right] \qquad (3)$$

Expanding eqn. 3 and neglecting the term in $(\mathrm{d}z)^2$ gives:

$$F_o = \frac{1}{RT}\left(pu + u \cdot \frac{\partial p}{\partial z} \cdot \mathrm{d}z + p \cdot \frac{\partial u}{\partial z} \cdot \mathrm{d}z - D \cdot \frac{\partial p}{\partial z} - D \cdot \frac{\partial^2 p}{\partial z^2} \cdot \mathrm{d}z\right)\mathrm{d}t \qquad (4)$$

Combining eqns. 2 and 4 gives the next flux entering the slice of column:

$$\Delta F = \frac{1}{RT}\left(-u \cdot \frac{\partial p}{\partial z} - p \cdot \frac{\partial u}{\partial z} + D \cdot \frac{\partial^2 p}{\partial z^2}\right)\mathrm{d}z\ \mathrm{d}t \qquad (5)$$

The net amount of material (in moles) entering the slice during the time $\mathrm{d}t$ is

$$\mathrm{d}n = \left(\frac{V_g}{RT} \cdot \frac{\partial p}{\partial t} + m_g \cdot \frac{\partial q}{\partial t}\right)\mathrm{d}z\ \mathrm{d}t \qquad (6)$$

where V_g is the volume available to the gas phase per unit column length, m_g is the mass of stationary phase contained in the unit length of column and q is the stationary phase concentration of the component in equilibrium with the partial pressure p. Hence the net flux per unit of column cross-sectional area is

$$\Delta F = \frac{1}{RT}\left(\frac{\partial p}{\partial t} + \frac{m_g RT}{V_g} \cdot \frac{\partial q}{\partial t}\right)\mathrm{d}z\ \mathrm{d}t \qquad (7)$$

Combining eqns. 5 and 7 gives

$$u \cdot \frac{\partial p}{\partial z} + p \cdot \frac{\partial u}{\partial z} + \frac{\partial p}{\partial t} + \frac{m_g RT}{V_g} \cdot \frac{\partial q}{\partial t} = D \cdot \frac{\partial^2 p}{\partial z^2} \qquad (8)$$

Eqn. 8 is the mass balance of the component in a gas chromatographic column. This equation can be rearranged into

$$\frac{\partial}{\partial z}(pu) + \frac{\partial}{\partial t}\left(p + \frac{m_g RT}{V_g} \cdot q\right) = D \cdot \frac{\partial^2 p}{\partial z^2} \qquad (9)$$

It is convenient to replace in eqn. 9 the partial pressure, p, of the component by XP, X being its mole fraction and P the local pressure of the mobile phase (see below). The product uP is proportional to the mobile phase mass flow-rate, $\dot{F}$. Hence the solute mass balance equation becomes

$$\frac{\partial}{\partial z}(\dot{F}X) + \frac{\partial}{\partial t}\left(PX + \frac{m_g RT}{V_g} \cdot q\right) = D \cdot \frac{\partial^2 PX}{\partial z^2} \qquad (10)$$

A similar mass balance equation must be written for the carrier gas, as its local density varies with the pressure along the column. As for the single-component problem the mole fraction of the carrier gas is the complement of the solute mole fraction, the mass balance for the carrier gas is written as

$$\frac{\partial}{\partial z}(\dot{F}) + \frac{\partial}{\partial t}\left(PX + \frac{m_g RT}{V_g} \cdot q\right) = 0 \qquad (11)$$

Eqns. 10 and 11 contain four functions, the mole fraction of the component, X, its concentration in the stationary phase, q, the total flow-rate, $\dot{F} = Pu$, and the local pressure of the mobile phase, P. Hence we need two more equations. Obviously, as we are using the equilibrium-diffusive model, the first equation will be the equilibrium isotherm relating the concentrations of the component in the two phases at equilibrium:

$$q = f(XP) = pX \qquad (12)$$

The second equation relates the local pressure to the column parameters and to the abscissa. It could be the differential Darcy or Poiseuille law:

$$u = -\frac{1}{\Phi\eta} \cdot \frac{\partial P}{\partial z} \tag{13}$$

where $1/\Phi$ is the column permeability and η the mobile phase viscosity. Difficulties arise in the determination of the mobile phase viscosity as a function of the local composition. As the permeability of an open-tubular column is high, the pressure profile under steady-state conditions is very flat. Local changes in the mobile phase viscosity and velocity cannot affect it greatly. Further, in gas–solid chromatography, the samples are usually small and the probe partial pressure is low. Integration of eqn. 13 when the column is swept with pure carrier gas, with no sample, under steady-state conditions, gives

$$P(z) = P_o \sqrt{\left(\frac{P_i}{P_o}\right)^2 - \frac{z}{L}\left[\left(\frac{P_i}{P_o}\right)^2 - 1\right]} \tag{14}$$

where $P(z)$ is the local pressure of the mobile phase, P_i and P_o the inlet and outlet pressures and L the column length. Eqn. 14 gives the pressure profile along the column. In the following, we shall assume as a first approximation that the local pressure does not change during the elution of a high concentration band. The pressure profile also remains constant and is given by eqn. 14. As we assume the validity of the integrated Darcy law, the local pressure does not deviate from that pressure given by eqn. 14. However, the local velocity is perturbed by the passing of the band (sorption effect).

The system of eqns. 10–12 and 14 constitutes the system of partial differential equations representing the equilibrium-diffusive model in gas chromatography in the case of a single component and of relatively fast kinetics of mass transfer. This model takes into account all the major effects encountered in non-linear gas chromatography, and especially the isotherm effect, the sorption effect and the effect of a finite column efficiency.

Discussion of the model

A simpler form of this model has been derived, discussed and used by several groups, especially by Aris and Amundson [5], Conder and Purnell [4] and Guiochon and co-workers [6–8]. The problem was studied within the framework of the ideal model. In this model, the column efficiency is assumed to be infinite, the axial dispersion is assumed to be negligible and the second-order term in the right-hand side of eqns. 10 and 11 disappears. Numerical solutions of this model were calculated with difficulty in the case of a linear isotherm by Guiochon and Jacob [6]. The accuracy of these solutions was poor. Rouchon *et al.* [10] derived much more accurate numerical solutions, using the Godunov algorithm [11], a first-order finite differences approach. Rouchon *et al.* [10] suggested that the effect of the finite column efficiency could be simulated by carefully choosing the space and time increments used in the integration. The errors that are produced by the first-order finite difference approximation propagate through the calculation and result in calculated band profiles which resemble the experimental band profiles eluted from columns with finite efficiency. The numerical diffusion caused by these errors can be used to simulate correctly the effect of the axial dispersion [20,26].

This procedure was implemented in the calculation method described by Guiochon *et al.* [20] and applied to the calculation of band profiles in liquid chromatography. In this case, two simplifying assumptions may be made. First, the flow velocity may be assumed to be constant along the whole column, as the mobile phase is not compressible. Second, for the same reason and also as the partial molar volumes of the solute in both the stationary and the mobile phases are very close, the mass balance equation for the mobile phase is unnecessary. The semi-ideal model [20] is a rapid procedure designed for the numerical calculation of solutions of eqn. 10 with no dispersion term (ideal model). However, by choosing the space and time increments carefully, one can actually obtain an accurate numerical solution of the second-order partial differential eqn. 10, with a finite dispersion coefficient. The dispersion coefficient, D, in eqn. 10 is related to the column height equivalent to a theoretical plate, H, by $D = Hu/2$ [3]. If the space and time increments, δz and δt, of the integration are chosen so that $\delta z = H$ and $\delta t = 2H(1 + k'_0)/u$ (k'_0 is the retention factor of the component at infinite dilution), the band profile obtained is an accurate solution of eqn. 10 [20,26].

Following the previous work of Guiochon and co-workers [20,27–29], it was simple to modify the algorithm used for liquid chromatography to calculate numerical solutions of the system of partial differential equations of gas chromatography (eqns. 10–14), taking into account the band broadening contribution due to axial dispersion, the isotherm and the sorption effects, and the column pressure drop. The finite difference equation are given by

$$(uPX)_i^{n+1} = (uPX)_i^n - \frac{\delta z}{\delta t}\left\{P^n X_i^n + \frac{m_g RT}{V_g} \cdot q(P^n X_i^n) - \left[P^n X_{i-1}^n + \frac{m_g RT}{V_g} \cdot q(P^n X_{i-1}^n)\right]\right\} \quad (15)$$

and

$$(uP)_i^{n+1} = (uP)_i^n - \frac{\delta z}{\delta t} \cdot \frac{m_g RT}{V_g}\left[q(P^n X_i^n) - q(P^n X_{i-1}^n)\right] \quad (16)$$

where the local pressure, P, is given by

$$P^n = P_o \sqrt{\left(\frac{P_i}{P_o}\right)^2 - \frac{n\delta z}{L}\left[\left(\frac{P_i}{P_o}\right)^2 - 1\right]} \quad (17)$$

The combination of eqns. 15–17 in a computer program, together with the proper choice of initial and boundary conditions and an isotherm equation, permit the rapid calculation of elution band profiles. In order to insure that the effect of axial diffusion is accurately simulated, one must set the ratio $\delta z/\delta t$ equal to $u_z/2$, where u_z is the average velocity $\bar{u}/(1 + k')$ corresponding to the most retained portion of the solute and δz is equal to the column HETP [20,26–28].

Initial and boundary conditions

The initial condition used in elution is an empty column. The concentration of the component is zero everywhere in the column which is filled with pure carrier gas:

$$p(z,t = 0) = 0 \quad (18)$$

The boundary condition is the concentration (or partial pressure profile) of the component at column inlet, on injection of the feed sample. This profile is digitized, *i.e.*, it is a series of rectangles of constant width, δt. It was desired to simulate the injection of a narrow rectangular plug of vapor, having the minimum physically realistic width possible. Two constraints must be considered. First, the height $p_{INJ,j}$ (where j is the time increment rank) of the rectangle injected cannot exceed the vapor pressure of the component, p^0. Second, the width of the plug, t_p, cannot be less than δt. If the area, A, required for the injected sample is greater than $p^0\delta t$, then t_p is determined by filling each successive time increment until all the area is used up. If A is less than $p^0\delta t$, then $t_0 = \delta t$ and the height of the injection profile is $A/\delta t$.

TABLE I

BOUNDARY CONDITIONS USED IN THE NUMERICAL INTEGRATION OF THE NON-EQUILIBRIUM MODEL

t_p, Width of the rectangular injection plug; p_i, partial pressure of the solute in the injection plug; P_i, inlet pressure of the carrier gas; P_o, outlet pressure of the carrier gas; δt, time increment in the numerical calculation; X_j^k, mole fraction of the component in the column, at time $j\delta t$, at the position $k\delta z$; u_j^k, carrier gas velocity at time $j\delta t$, at the position $k\delta z$; P^n, carrier gas pressure at position $n\delta z$.

Time interval	u_j^n	X_j^n
$j = 0$	$u_j^n = \frac{P_o u_o}{P^n}$	$X_0^n = 0$
$0 < j \leqslant \frac{t_p}{\delta t}$	$u_j^0 = \frac{P_o u_o}{P_i} \frac{p_i + P_i}{P_i}$	$X_j^0 = \frac{p_i}{P_i}$
$\frac{t_p}{\delta t} < j$	$u_j^0 = \frac{P_o u_o}{P_i}$	$X_j^0 = 0$

The boundary conditions are given in Table I.

RESULTS AND DISCUSSION

The accuracy of the algorithm of Rouchon *et al.* [10] was demonstrated by comparing calculated profiles and experimental profiles exhibiting an important sorption effect [19]. The ability of the modified form of this algorithm to take into account the column axial dispersion was tested as follows. Band profiles were calculated using column efficiencies ranging from 500 to 8000 theoretical plates. The plate number, N, for the simulated band profile was then calculated by

$$N = t_R^2/\sigma_t^2 \quad (19)$$

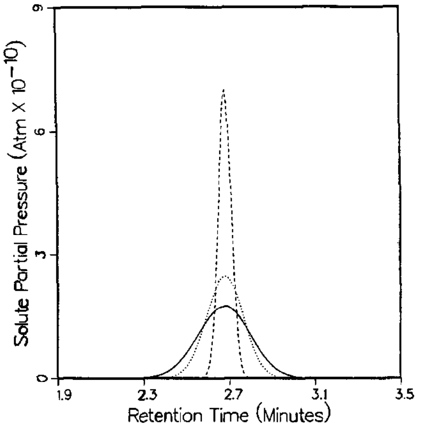

Fig. 1. Calculated elution profiles for different column efficiencies. Experimental conditions: linear isotherm with a slope of 0.02 mol/g · atm; column length, 1500 cm; column I.D., 0.53 mm; column temperature, 60°C; column pressure drop, 0.34 atm; outlet pressure, atmospheric; gas hold-up time, 22.7 s; mass of stationary phase, 44 mg; sample size, 50 pg; column efficiency, solid line 500 plates, dotted line 1000 plates, dashed line 8000 plates.

where t_R is the peak retention time (measured as the first normalized moment) and σ_t^2 is the peak variance (measured as the normalized, centered second moment, in time units). Peak areas corresponding to infinite dilution and a linear isotherm were used in the program. In each instance, the agreement between the plate number which was simulated and the plate number which was calculated from the band profile is excellent (within 1%). Three of these simulated band profiles are shown in Fig. 1.

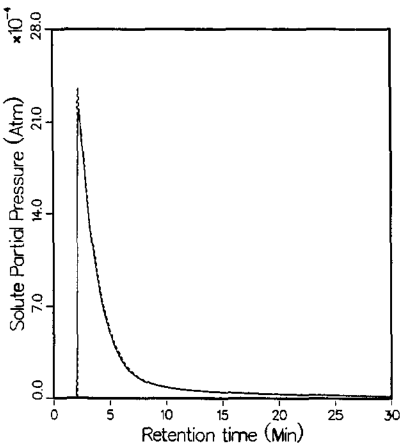

Fig. 2. Comparison between experimental (solid line) and calculated (dashed line) elution profiles. Experimental conditions as in Fig. 1, except non-linear isotherm of 1-chlorobutane on α-alumina at 40°C; sample size, 4.1 μg. Difference parameters between the experimental and the calculated profiles [23]: $t_{RMS} = 0.79\%$, $\Delta = 1.2 \times 10^{-4}$.

In Fig. 2, we compare an experimental profile recorded for a sample of 1-chlorobutane on an open-tubular column coated with a thin layer of particles of alumina for liquid chromatography (Universal Scientific, Atlanta, GA, USA) and the profile calculated with the procedure discussed above, using the adsorption isotherm obtained by ECP. The agreement between these two profiles is excellent. Their only difference is in the top of the band, which is sharper for the calculated profile. Similar agreements have been reported with data acquired on porous-layer open-tubular columns coated with α-alumina for ceramic [23] and on conventional columns packed with graphitized carbon black [19]. Because the isotherm was obtained with a pulse technique, the agreement reported with carbon black demonstrated that, in gas chromatography as in liquid chromatography, the relationship between the elution band profile and the thermodynamics of the phase equilibrium involved in the retention is well understood. In the present case, however, the isotherm is derived by the ECP method, from the experimental profile in Fig. 2. As the ECP method is based on the solution of the ideal model, the agreement between the two profiles merely shows that our calculation procedure is correct and accounts properly for the influence of the column efficiency and the gas compressibility.

There are two major differences between the propagation of high concentration bands in gas and in liquid chromatography. First, there is no sorption effect in liquid chromatography or, rather, it is negligible. Second, equilibrium isotherms in gas–solid chromatography tend to be concave upwards much more often than in liquid chromatography. As a consequence, the sorption and the isotherm effects have opposite directions and it is possible to find experimental conditions under which they compensate each other. We present here a study of the combination between the sorption and the isotherm effects.

Figs. 3–5 show series of calculated band profiles which are derived from a single isotherm, different for each figure. The average flow velocity is assumed to be constant, but the column inlet pressure (and

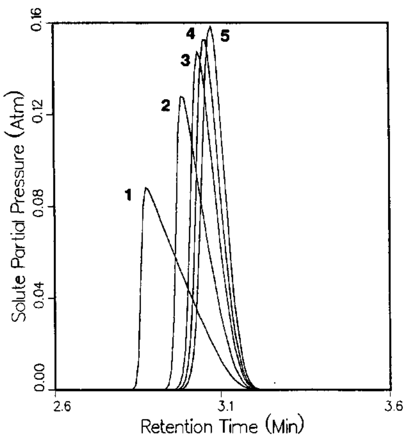

Fig. 3. Influence of the average pressure of the carrier gas on the overloaded elution profiles in gas chromatography. Profiles calculated for columns with different permeability operated at the same average velocity. Linear isotherm. Experimental conditions as in Fig. 1, except gas hold-up time, 23.6 s; sample size, 9.2 μg; column efficiency, 8000 plates. Inlet pressure: 1 = 1.5; 2 = 7.5; 3 = 15; 4 = 22.5; 5 = 37.5 atm.

hence also the average column pressure) is increased. This corresponds to a comparison between columns having decreasing permeabilities, but operated at the same average velocity.

In Fig. 3, a linear isotherm is used. The source of the band asymmetry is uniquely in the sorption effect. Because, under the influence of the sorption effect, the velocity associated with a concentration increases with increasing concentration, this effect tends to give a steep band front and a diffuse rear part of the profile, very much like what is observed with a Langmuir isotherm. The intensity of the sorption effect at constant sample size decreases with increasing average column pressure. We see that the band, which is strongly asymmetric for a low inlet pressure (*e.g.*, an open-tubular column), becomes nearly symmetrical for a low-permeability column, requiring a very high inlet pressure to achieve the same retention times.

The use of a convex upward isotherm, such as a Langmuir isotherm, would merely reinforce the sorption effect and the results (not shown) are not very illustrative. In Figs. 4 and 5, on the other hand, we have used a concave upward isotherm belonging to type III of the BET isotherm classification. We have taken for this isotherm the equation

$$q = \frac{ap}{1 - p/p^0} \tag{20}$$

which is similar to the Langmuir equation, but uses a negative constant in the denominator. This equation is empirical, but convenient for illustrative purposes.

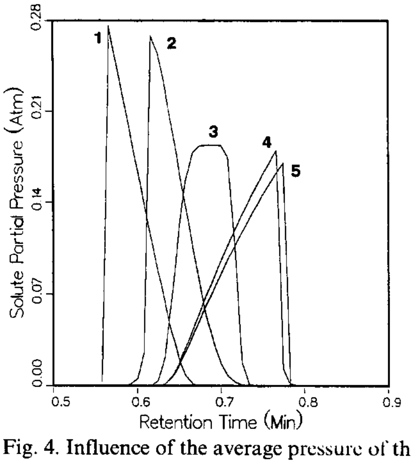

Fig. 4. Influence of the average pressure of the carrier gas on the overloaded elution profiles in gas chromatography. Profiles calculated for columns with different permeability operated at the same average velocity. Non-linear isotherm. Experimental conditions as in Fig. 1, except non-linear isotherm (eqn. 20, with a = 0.002 mol/g · atm, p^0 = 0.9 atm); gas hold-up time, 23.6 s; sample size, 9.2 μg; column efficiency, 8000 plates. Inlet pressure: 1 = 1.01; 2 = 2.0; 3 = 3.0; 4 = 7.5; 5 = 15.5 atm.

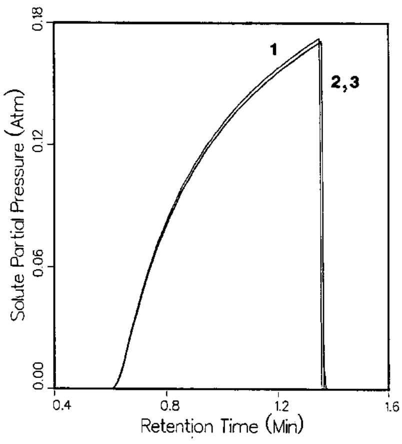

Fig. 5. Influence of the average pressure of the carrier gas on the overloaded elution profiles in gas chromatography. Profiles calculated for columns with different permeability operated at the same average velocity. Non-linear isotherm. Experimental conditions as in Fig. 4, except p^0 = 0.3 atm. Inlet pressure: 1 = 1.5; 2 = 3.0; 3 = 5.0 atm.

The amount adsorbed at equilibrium becomes infinite for $p = p^0$, which corresponds to capillary condensation near the vapor pressure. In Fig. 4, the experimental conditions correspond to a moderate curvature of the isotherm. At high values of the column inlet pressure (*i.e.*, for low-permeability columns), the isotherm effect dominates and the band has a diffuse front profile and a steep rear shock layer. In contrast, at low values of the column average pressure (*i.e.*, for high-permeability columns), the isotherm effect is more than compensated by a strong sorption effect which offsets its influence on the band profile. The band profile is Langmuirian at low values of the column average pressure. There is an intermediate value of the average column pressure where the influences of the two effects balance and a shock layer appears on either side of the band [7,8].

When the initial curvature of the isotherm is strong, the isotherm effect is already dominant at low values of the column average pressure and, thus, remains so when the average pressure increases. This phenomenon is illustrated in Fig. 5, where a change in the column permeability at constant flow velocity has almost no effect on the band profile.

These results demonstrate that the same model which permits accurate predictions of band profiles in liquid chromatography also gives excellent results in gas chromatography. The approximations made to a general equilibrium-diffusive model of chromatography are different because of the widely different physico-chemical properties of the mobile phase, but the model remains equally applicable. As a consequence, excellent results should be expected from its application to other forms of chromatography, and notably to supercritical fluid chromatography. The main question to investigate in this field is the degree of importance of the sorption effect. It is certainly less important than in gas chromatography, as suggested by the results shown in Figs. 3 and 4, but may not be entirely negligible as it is in liquid chromatography.

ACKNOWLEDGEMENTS

This work was supported in part by Grant DE-FG05-88ER13859 of the US Department of Energy, Office of Basic Energy Research, and by the cooperative agreement between the University of Tennessee and the Oak Ridge National Laboratory. We acknowledge the support of our computational effort by the University of Tennessee Computing Center.

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