Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Propagation of Signals of Finite Concentration in Gas Chromatography. III. Influence of the Pressure Gradient

Patrick Valentin[a]; Georges Guiochon[b]
[a] CENTRE DE RECHERCHES ELF, SOLAIZE, FRANCE [b] LABORATOIRE DE CHIMIE ANALYTIQUE PHYSIQUE ECOLE POLYTECHNIQUE, PARIS 5ÈME, FRANCE

To cite this Article Valentin, Patrick and Guiochon, Georges(1975) 'Propagation of Signals of Finite Concentration in Gas Chromatography. III. Influence of the Pressure Gradient', Separation Science and Technology, 10: 3, 289 — 305
To link to this Article: DOI: 10.1080/00372367508058020
URL: http://dx.doi.org/10.1080/00372367508058020

SEPARATION SCIENCE, 10(3), pp. 289–305, 1975

Propagation of Signals of Finite Concentration in Gas Chromatography. III. Influence of the Pressure Gradient

PATRICK VALENTIN

CENTRE DE RECHERCHES ELF
69 SOLAIZE, FRANCE

GEORGES GUIOCHON

LABORATOIRE DE CHIMIE ANALYTIQUE PHYSIQUE
ECOLE POLYTECHNIQUE
PARIS 5ÈME, FRANCE

Abstract

Resolution of the equations of the quasi-ideal chromatography model at finite concentration is possible in the case of a finite pressure gradient in the column provided the elution does not change the pressure profile and the pressure variation inside the solute band is neglected. A study of the solution shows that there still exists three models of peak migration, as in the zero pressure gradient case, but that the pressure gradient enhances the isotherm effect. It is not possible, however, to account for the effect of pressure gradient by using an average pressure because there is a convolution between the effect of the pressure gradient and a nonlinear isotherm. Analysis of the double-shock propagation mode and the determination of the limiting transition conditions permit accurate measurement of the curvature of the isotherm at infinite dilution. The experimental results (variation of retention time with peak height for *n*-pentane in squalane) are in excellent agreement with the predictions of the theoretical model.

INTRODUCTION

In two previous papers we have discussed a quasi-ideal chromatography model for large concentration bands (*1*) and studied some of its most important properties in the case of constant pressure throughout the column (*2*). The model neglects the kinetics and diffusion effects on band spreading, which are second-order, and focuses attention on the first-order effects arising from the very existence of a finite concentration of solute in the gas phase (*1*). The consequence of this simplification is to make possible the appearance and propagation of stable concentration discontinuities.

The conditions of stability of these discontinuities are determined using a stability diagram (*2*) which allows a qualitative description of the progressive variation of band shape during its elution while a quantitative, but numerical, description can be obtained from a computer using the equations of the model (*3*). We want to discuss here the application of these results to the case where the pressure drop through the column is not negligible. We shall successively show how the stability diagram and the transition range can be defined and used in this case, what is the influence of the pressure gradient on the elution, and how these results can be applied to account for the variation of retention times with sample size.

Since in this case the effect of the pressure gradient along the column is accounted for, it is possible to carry out the experiment under realistic conditions. The results of these experiments will therefore be compared to those of the theoretical calculations.

THEORETICAL

System of Equations and Resolution

The model discussed previously (*1*) assumes that the mobile and stationary phases are constantly in equilibrium and that the local pressure and temperature do not change during the elution of a large concentration band. This is a rather crude assumption, but consideration of the time dependance of pressure would give an untractable set of equations except for the case of linear isotherms which has already been considered (*12*). As we are now considering the interaction of nonlinear isotherms and the pressure drop, we shall neglect the time variation of pressure which can appear, in fact, as a correction to the following treatment. The pressure profile will thus be the same as in steady-state conditions for a flow of pure carrier gas (*4*):

$$p^2 = P^2 - \frac{z}{L}(P^2 - 1) \tag{1}$$

All pressures are given in relative units, with the outlet pressure taken as the pressure unit. Furthermore, the carrier gas is assumed to be ideal. These assumptions yield the first set of equations describing the model which includes the isotherm equation (Eq. 3, Table 1). The other equations are derived from the mass balance for the solute and the carrier gas (Eqs.

TABLE 1

Mathematical Translation of the Quasi-Ideal Model of Gas Chromatography at Finite Concentration

General assumptions:

$$p^2 = P^2 - \frac{z}{L}(P^2 - 1) \tag{1}$$

$$Y = \frac{pX}{P_A{}^0} = X_A{}^L \gamma_A \tag{2}$$

$$\gamma_A = \gamma_A(X_A{}^L) \tag{3}$$

$$T = T_c = \text{constant} \tag{4}$$

Mass-balance equations:

F, *X* continuous		*F*, *X* discontinuous	
$p[1 + k'(1 - X)]\frac{\partial X}{\partial t} = -F\frac{\partial X}{\partial z}$	(5)	$\nu_{12} = \frac{u_1}{1 + \frac{k_2 - k_1}{X_2 - X_1}(1 - X_2)}$	(8)
$pk'\frac{\partial X}{\partial t} = -\frac{\partial F}{\partial z}$	(6)	$\nu_{12} = \frac{u_2}{1 + \frac{k_2 - k_1}{X_2 - X_1}(1 - X_1)}$	(9)
$k' = k_0{}'\frac{\gamma_A{}^\infty}{\gamma_A}\frac{1}{1 + X_A{}^L\frac{d\ln\gamma_A}{dX_A{}^L}}\frac{1}{(1 - X_A{}^L)^2}$	(7a)	$k_1 = k_0{}'\frac{P_A{}^0\gamma_A{}^\infty}{p}\frac{X_{A,1}{}^L}{1 - X_{A,1}{}^L}$	(10)
$k' = k_0{}'\gamma_A{}^\infty\frac{1}{\frac{dY}{dX_A{}^L}}\frac{1}{(1 - X_A{}^L)^2}$	(7b)	$k_2 = k_0{}'\frac{P_A{}^0\gamma_A{}^\infty}{p}\frac{X_{A,2}{}^L}{1 - X_{A,2}{}^L}$	(11)

Boundary conditions:

$$u(0, t) \equiv u_i \tag{12}$$

$$t = 0 \qquad X(z, 0) \equiv 0 \tag{13}$$

$$0 < t \leq \tau \qquad X(0, t) = X_i(t) \tag{14}$$

$$t > \tau \qquad X(0, t) = 0 \tag{15}$$

5 and 6, Table 1) and from similar equations in the case of a concentration discontinuity. The retardation factors express the retention of the solute by partition with the stationary phase.

In the chromatographic conditions ($P > 1$), Eq. (1) is a one to one correspondence between p and z. We may thus study the propagation of chromatographic signals in the space (t,p) instead of in the space (z,t), the advantage being the elimination of the square-root relationship. Let

$$\theta = \frac{2L}{P^2 - 1} \tag{16}$$

Since $(\partial X/\partial t)_z = (\partial X/\partial t)_p$ and $(\partial X/\partial z)_t = -(\partial X/\partial p)_t/\theta p$, we can easily transform the equations of Table 1. Only Eqs. (1), (5), and (6) are changed:

$$z = \frac{\theta}{2}(P^2 - p^2) \qquad \text{Eq. (1)} \rightarrow \text{Eq. (17)}$$

$$\theta p^2[1 + k'(1 - X)]\frac{\partial X}{\partial t} = F\frac{\partial X}{\partial p} \qquad \text{Eq. (5)} \rightarrow \text{Eq. (18)}$$

$$\theta p^2 k'\frac{\partial X}{\partial t} = \frac{\partial F}{\partial p} \qquad \text{Eq. (6)} \rightarrow \text{Eq. (19)}$$

In this system the variable appears in the coefficients of the partial derivatives, the opposite of what happens in the simplified system obtained by the assumption of a constant pressure throughout the column (*2*). Thus it is not possible to make direct use of the method of characteristics (*4*). To do this, we shall assume that the pressure is constant along the band. Before going on with the calculation, we shall discuss the validity of this assumption. The maximum pressure difference between the points at the front and rear ends of the peak is observed when the front is at the column outlet. This pressure difference is then

$$\Delta p = \frac{P^2 - 1}{2}\frac{\Delta t}{t_R}p_0 \tag{20}$$

In conventional preparative chromatography, P is usually between 2 and 3, the outlet pressure p_0 being the atmospheric pressure, and the ratio $\Delta t/t_R$ is between 0.1 and 0.2. In these conditions, Δp will vary from 0.1 to 0.5 atm. This is small compared to $P - 1$ but it is not negligible, although it should be noted that Δp is much smaller for most of the column, since the nearer the peak is to the column outlet, the wider the peak and the steeper the pressure gradient. Because the effect of the pressure gradient is the integral of all local effects, we shall neglect Δp as a first approximation.

Consequently, the value of k' is assumed to be independent of the pressure along the peak width but not along the column.

If we eliminate $\partial X/\partial t$ between Eqs. (18) and (19), we obtain

$$\frac{1}{F}\frac{\partial F}{\partial p} = \frac{k'}{1 + k'(1 - X)}\frac{\partial X}{\partial p} \tag{21}$$

which can be integrated at constant time:

$$F = F_i(t)\exp\left(\int_0^X \frac{k'\,dX}{1 + k'(1 - X)}\right) \tag{22}$$

$F_i(t)$ is determined by the boundary conditions and is kept constant (Eq. 12). It is then possible to define the apparent transport velocity associated with the mole fraction X in the space (t,p):

$$v^* = \left(\frac{\partial p}{\partial t}\right)_X = \frac{(\partial X/\partial t)_p}{(\partial X/\partial p)_t} \tag{23}$$

v^* cannot be measured directly since it is defined in the space (t,p), but it can be derived from experimental measurements when the pressure profile is known. Then from Eqs. (18) and (22) we can calculate

$$v^*(X, P) = -\frac{F_i}{\theta P^2}\,\frac{\exp\left[\int_0^X \frac{k'\,dX}{1 + k'(1 - X)}\right]}{1 + k'(1 - X)} \tag{24}$$

This relationship permits calculation of the variation of the peak profile during elution along the column by an iteration process. This equation is very similar to the one obtained in the simplified case of constant pressure throughout the column (*5*). This result shows that the study of the propagation of a finite concentration signal in a column with finite pressure drop will be similar to the study made with the assumption of constant pressure.

If there is no discontinuity, the residence time of a mole fraction X will be given by

$$t_X = \int_P^1 \frac{dP}{v^*} \tag{25}$$

or

$$t_X = \frac{\theta}{F_i}\int_1^P \frac{1 + k'(1 - X)}{\exp\left[\int_0^X \frac{k'\,dX}{1 + k'(1 - X)}\right]} \tag{26}$$

This relationship is valid only if there is no interaction, even temporarily, with a discontinuity, i.e., if no discontinuity occurs during the elution of the corresponding side of the peak, the shape of which is then determined by the equations of the continuous case. If a discontinuity occurs, Eq. (26) is no longer valid, even when the discontinuity has collapsed.

It will be noted that if X becomes very small, the limit of Eq. (26) is

$$t_0 = \frac{L}{j_3{}^2 u_i}(1 + k_0') \tag{27}$$

where

$$j_m{}^n = \frac{m}{n}\frac{P^n - 1}{P^m - 1} \tag{28}$$

which is the conventional retention time in analytical chromatography, a result which is obtained with a very similar model in which equilibrium is assumed all along the column between the two phases at any time, and the pressure profile remains unchanged.

Equations (24) and (26) account for the propagation of the continuous profile. We shall now study the propagation of concentration discontinuities.

Propagation of Discontinuities. Stability Diagram. Transition Range

In the (t,p) space, Eqs. (8) and (9) become

$$v_{12}{}^* = -\frac{1}{\theta p}\frac{F_1}{1 + \dfrac{k_2 - k_1}{X_2 - X_1}(1 - X_2)} \tag{29}$$

$$v_{12}{}^* = -\frac{1}{\theta p}\frac{F_2}{1 + \dfrac{k_2 - k_1}{X_2 - X_1}(1 - X_1)} \tag{30}$$

where F_1 and F_2 are given by Eq. (22) with the consequence that

$$\frac{v_{12}{}^*}{v_1{}^*} = \frac{1 + k_1'(1 - X_1)}{1 + \dfrac{k_2 - k_1}{X_2 - X_1}(1 - X_2)}p \tag{31}$$

which is identical to the equation obtained under constant pressure conditions except for the appearance of the factor p (*2*) and the dependance of k on p.

Thus there exists at any point of the column a local stability diagram identical to the one obtained at constant column pressure, and having the same properties as those described previously (*2*). But since k_1 and k_2 (Eqs. 10 and 11), k_1' and k_2' (Eq. 7), $X_m = P^0/p$, and the ratios v_{12}^*/v_1^* and v_{12}^*/v_2^* all depend on the local pressure, the conditions of stability of concentration discontinuities will change progressively along the column. The study of the propagation of the shocks, as well as of their appearance and destruction, will be much more complicated and in practice will make necessary the numerical solution of the equations. The transition points, for example, defined as the points where $dv/dX = 0$ in the constant column pressure assumption (*2*), depend on the pressure at all boundaries of the stability diagram, except the bisector. It is possible, however, to give a general definition of the transition range and to study its boundaries.

The mean transition range along the column is the set of experimental conditions (p, P_A^0) for which the equation

$$\left(\frac{\partial t_X}{\partial X}\right)_p = 0 \qquad (32)$$

(where t_X is defined by Eq. 26) is satisfied for values of X which are physically acceptable. This means that if preparative scale experiments are carried out under experimental conditions (p, T) which belong to the transition range, a rectangular injection, or part of it, will be eluted between two discontinuities, with a minimum change in shape and therefore with minimum spreading.

Differentiation of Eq. (26) yields

$$\frac{\partial t_X}{\partial X} = \frac{\theta}{F_i} \int_1^P \frac{(1 - X)\dfrac{dk'}{dX} - 2k'}{\exp\left[\displaystyle\int_0^X \frac{k'\, dX}{1 + k'(1 - X)}\right]} p^2\, dp = 0 \qquad (33)$$

This equation permits calculation of the experimental conditions (p, T) which belong to the transition range. We first observe that the limit of Eq. (33) when p becomes unity, which corresponds to a zero pressure gradient, is the same equation which gives the transition points in this case ($2k' - (1 - X)dk'/dX = 0$, Ref. *2*; Eq. 26). This shows that the two definitions are self-consistent.

The limit transition conditions are those for which the origin of the stability diagram is a transition point in the constant column pressure case. In the general case they will be such that Eq. (33) has $X = 0$ as a root. This equation can then be written as

$$\int_1^P \left(\frac{dk'}{dX_{(X=0)}} - 2k'_{(X=0)} \right) p^2 \, dp = 0 \tag{34}$$

Using Eq. (7b) (Table 1), Eq. (34) becomes

$$\int_1^P \left[\frac{p}{P^0 Y_0'} \left(2 - \frac{Y_0''}{Y_0'} \right) - 2 \right] p^2 \, dp = 0 \tag{35}$$

where Y_0' and Y_0'' stand for dY/dX^L $(X^L = 0)$ and $d^2Y/(dX^L)^2$ $(X^L = 0)$, respectively.

Integration of Eq. (35) yields

$$j_3{}^4 \frac{1}{P^0 Y_0'} \left(2 - \frac{Y_0''}{Y_0'} \right) - 2 = 0 \tag{36}$$

with $j_3{}^4$ given by Eq. (28). Equation (36) relates the experimental conditions (p, T) under which the peak corresponding to a very small sample will migrate without spreading due to thermodynamic effects. It also relates an experimental phenomenon to the curvature of the isotherm at the origin. Furthermore, Eq. (36) allows an easy determination of one of the boundaries of the transition range, and therefore an idea of its position.

Finally, when looking at the origin of the various terms in Eq. (36) [the pressure gradient ($j_3{}^4$), the isotherm effect $[(2 - Y_0''/Y_0')/P^0 Y_0']$, and the sorption effect (-2)], it is seen that in the special case where $X = 0$ at the limit transition point, one can write

(effect of pressure gradient) × (isotherm effect) = (sorption effect)

Although the validity of this relationship is limited to very low molar fractions and to certain values of T and p, it illustrates the general trend of the influence of the pressure gradient to enhance the isotherm effect.

Influence of Pressure Gradient on Band Migration

This influence is complicated. The calculation of $\partial^2 t_X/\partial P \partial X$, which gives the influence of the pressure gradient on the residence time of mole fraction X, is tedious and of limited interest because it also incorporates the direct, mechanical effect of pressure on residence times which is taken into account under analytical conditions by the James and Martin term. It shows, however, that this second partial differential is usually negative.

In other words, the pressure gradient will usually increase the isotherm effect, and thus the peak will lean backwards.

If for a zero pressure gradient the propagation is controlled by the isotherm effect and the band has a shock at the rear side, an increase in the pressure drop will enhance the phenomenon, which will appear sooner and remain stable against the influence of diffusion and kinetics for lower partial pressures. Conversely, if the sorption effect controls the elution of the band at zero pressure gradient, a shock appearing at the front side of the peak, the effect of a pressure gradient will be to make the shock appear at larger concentrations only and to degrade into a continuous profile earlier.

When the isotherm is not linear, the origin of this effect is obvious: k' increases with increasing pressure at a constant mole fraction. The larger the column pressure drop, the larger the weight of this nonlinearity of the partition process and the larger the isotherm effect appears to be.

If k' is constant (linear isotherm), Eq. (26) can be integrated to

$$t_X = \frac{4\eta L^2}{3k} \frac{(P^3 - 1)}{(P^2 - 1)^2} \frac{[1 + k'(1 - X)]^2}{1 + k'} \tag{37}$$

which shows that t_X decreases with increasing X and $\partial t_X/\partial X$ decreases with increasing P. The trend of a large concentration band to become asymmetrical with a very steep front profile will also decrease with increasing P, making it look as if some isotherm effect were present.

CONCLUSION

It is possible to take into account the pressure gradient in the study of the propagation of signals of finite concentration through a chromatographic column and to obtain relatively simple equations if we assume that the pressure gradient is independent of time and that the pressure difference between both ends of the band is negligible.

The results obtained show that it is unjustified to assume, as has been done previously, that the pressure drop has no effect or practically no effect on peak broadening and deformation. Quite the opposite, for Eq. (26) shows that the influence of the pressure gradient is important and cannot be accounted for by the use of an average pressure of any kind. In fact, there is a coupling between the isotherm effect and the pressure gradient much as a convolution. This alone casts considerable doubt on the general validity of most methods of determining isotherms by using gas chromatography (*6*).

It would be possible to solve a more realistic model which does not assume that the pressure drop between the front and rear side of the peak is negligible, but the calculations become so much more complicated that only numerical calculations are possible and would take a great deal of time. The improvement does not seem worthwhile, except for columns with very low permeability, which should be avoided in preparative scale gas chromatography anyway because they have quite a lower productivity than those with a large permeability (7). It should be noted that in such a case the concept of the sorption effect should be slightly changed. This is the effect on the kinetic momentum of the carrier gas of the mass transfer between the two phases. This momentum depends on the local flow velocity and pressure. When the column permeability is infinite, the effect on pressure is zero and the sorption effects result simply from the change in velocity of the gas phase. When the pressure drop becomes important, both the local pressure and the velocity change.

Only the pressure would change in a closed vessel. It seems that in most practical conditions in which gas chromatography is carried out, the column permeability is large enough so that only the gas velocity varies and the pressure can be taken as a parameter.

Experiments have been carried out primarily to study the newest and most unexpected results of these theoretical developments: the limit transition point, the variations of the retention time with sample size in the range commonly used in analysis and immediately above, and the relationship between these variations and the curvature of the isotherm at the origin.

EXPERIMENTAL

The chromatograph was built in our laboratory, using a thermal conductivity detector (Carlo Erba, Milan, Italy), and a temperature-controlled oil bath (Haake, Germany). The temperature fluctuations were about 0.02 °C in 1 day and the gradient along the column was less than 0.05 °C. The inlet pressure was controlled by reference to atmospheric pressure. The fluctuations were about 0.5 mbar in 1 day. The flow rate was measured using a soap bubble flow meter with optical detection of the bubbles providing a time resolution of 0.02 sec. After correction for the variations of atmospheric pressure, ambiant temperature, and water partial pressure, the accuracy of the flow measurements was about 0.5 % at the 95 % confidence level.

The sample was introduced either as a liquid with a Hamilton 701 microsyringe or as a gas with a Carlo Erba sampling valve. The signal was recorded on a conventional paper recorder but the retention time was measured directly on a chronometer which is started at the injection time and stopped at peak maximum by a mechanical device mounted on the recorder. This device introduces a small time lag, so the accuracy of time measurements, determined by comparison to a more precise system (*8*), is 1% at the 95% confidence level. The reproducibility is about 0.1% (relative standard deviation).

In the experiments reported here, the 1-m long, 1/8 in. i.d. column was packed with Chromosorb P, 80–100 mesh, coated by 20% w/w Squalane (Supelco). The solute was *n*-pentane (Fluka, technical grade, 99% pure). The temperature was set at various values between 30 and 48 °C, and the pressure was between 295 and 577 Torr.

RESULTS AND DISCUSSION

When the sample size is increased from very low values, the retention time of the peak maximum varies and the peak height increases, the maximum concentration at first being proportional to the sample size but then increasing more slowly as the peak width increases. The experimental conditions (T, p) were kept constant for each curve. Figures 1 and 2 show the variation of the retention time of peak maximum vs the corresponding concentration, given in mole fraction, and determined from a previous calibration of the detector. In Fig. 1 the temperature is the same for all curves, but the inlet pressure is different; the retention times have been related to the one obtained for zero sample size by extrapolation of the measurements. In Fig. 2 the pressure is the same for all curves, the temperature is different, and the absolute retention times are given.

Figure 1 shows that at constant temperature (P^0 constant) the retention time has a marked minimum for a rather large mole fraction at small values of the pressure gradient and that, when this gradient increases, the minimum is less and less apparent, occurs at lower and lower mole fractions, and eventually disappears above some value of the pressure gradient. Conversely, Fig. 2 shows that for a constant pressure gradient there is no minimum in retention time at low temperatures; a minimum appears at some critical temperature, above which it becomes more and more important, and occurs at larger and larger mole fractions. This behavior shows that the sorption effect dominates the elution at high temperatures and low pressure gradients. At low temperatures and large pressure gradients, the isotherm effect is the major one.

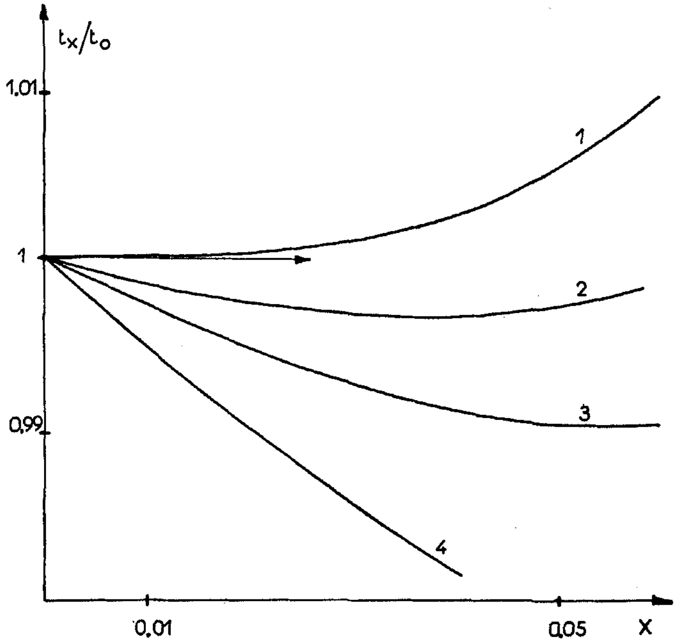

FIG. 1. Variation of the retention time of the peak maximum vs the corresponding mole fraction. Maximum mole fractions are changed by using different sample sizes. t_0 is the retention time observed under the same experimental conditions with a zero sample. Temperature: 42°C. Column inlet pressure: (*1*) 577 Torr; (*2*) 500 Torr; (*3*) 432 Torr; and (*4*) 295 Torr. Outlet pressure: atmospheric.

This behavior seems to have been overlooked in the literature up to now, probably because the variations in retention time observed are relatively small (less than a few percent in most cases).

The existence of a minimum in the retention time can be explained by our model. The experiments have been carried out in the transition range. At low pressure gradients all the local stability diagrams along the column are similar and the peak shape is not very different from the one obtained with a zero pressure gradient (*2*). Figure 4 of Ref. *2* shows the variation in shape during elution of a rectangular band at constant sample size with variable column length. Here the column length is constant while the sample size increases. As for small sample sizes, the sorption effect dominates, a front shock will appear, and the peak maximum is at the

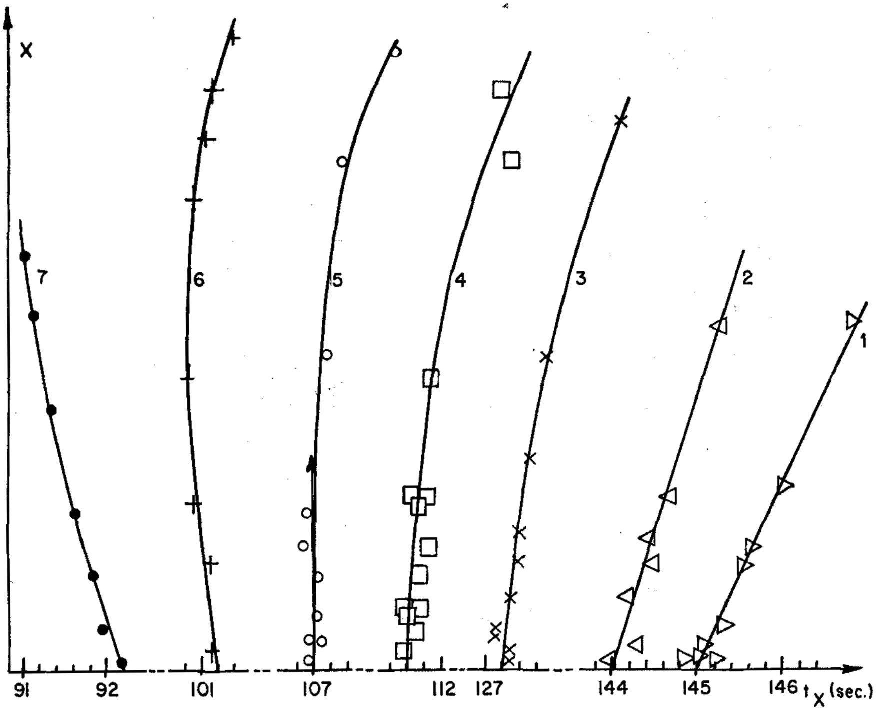

FIG. 2. Same as Fig. 1. Inlet pressure: 577 Torr. Outlet pressure: atmospheric. Temperature: (*1*) 30°C; (2) 36°C; (*3*) 38°C; (*4*) 40°C; (*5*) 42°C; (*6*) 44°C; and (*7*) 48°C.

front of the peak; when the sample size increases, the front shock moves faster and faster and the retention time decreases as long as we are in the case described by Fig. 4 (Ref. *2*). The situation changes when the existence of a rear shock becomes possible. Then the peak height increases suddenly and, as the top of the rear shock is the peak maximum, the retention time begins to increase. This is illustrated by Fig. 3 which gives the shape of larger and larger rectangular injections and of the corresponding elution profiles. As the diffusion and mass-transfer kinetics relax the profiles, the actual variation of t_X vs X is smoothed as shown in Figs. 1 and 2.

Figure 1 shows also that at constant peak height the retention time increases with increasing pressure gradient. This illustrates how the pressure gradient enhances the isotherm effect. Dividing Eq. (26) by Eq. (27)

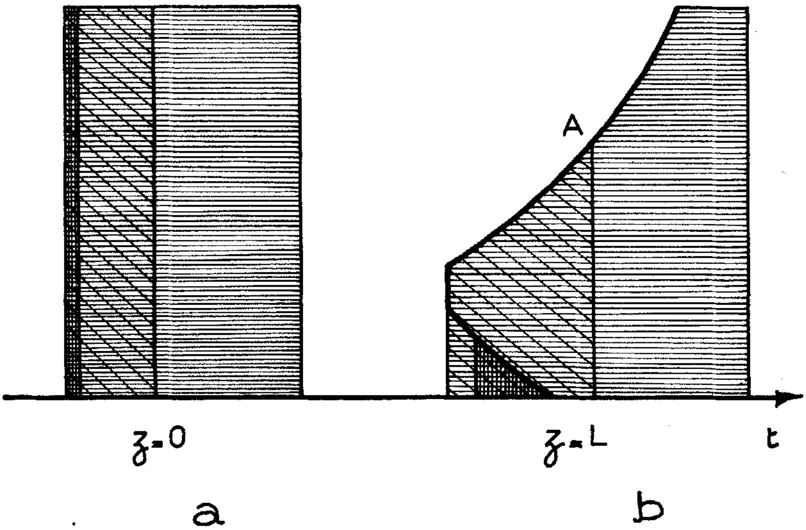

FIG. 3. Variation of the retention time of peak maximum with the sample size. (*a*) Injection profiles. (*b*) Variation of peak profile and of the position of peak maximum (Curve A).

gives

$$\frac{t_X}{t_0} = \int_1^P \frac{1 + k'(1 - X)}{\exp\left[\int_0^X \frac{k'\,dX}{1 + k'(1 - X)}\right]} \frac{1}{1 + k_0'} \frac{3p^2\,dp}{P^3 - 1} \tag{38}$$

As the mole fractions used here are small ($X < 0.05$), we can assume the exponential term to be unity. At constant X the variation of t_X/t_0 is the same as that of:

$$\tau = \frac{1}{P^3 - 1} \int_1^{P^3} k'\,d(P^3) \tag{39}$$

k' is a function of pressure which increases with increasing P, hence P^3 [the definition of k' is $k' = (\partial n_A{}^L/\partial n_A{}^G)_p$ (*1*)]. Thus k' is constant as long as the solution follows Henry's law, then it increases. Therefore the model predicts correctly that t_X/t_0 will increase with P at constant mole fractions.

These results also demonstrate that linear chromatography is an ideal model, which is not in agreement with experiment. Integration of Eq. (33), using the same method as the one resulting in Eq. (36), gives

$$\frac{t_X - t_0}{t_0} = \frac{k_0'}{1 + k_0'}\left[\left(2 - \frac{Y_0''}{Y_0'}\right)\frac{j_3^{\,4}}{P^0 Y_0'} - 2\right]X + \cdots \tag{40}$$

Equation (40) shows that even for small sample sizes the retention time does vary with the sample size, the relative variation in retention time being proportional to the concentration at the peak maximum. This effect should be taken into account in accurate measurements (*8*). When the retention is large ($k_0' \simeq 1 + k_0'$) and the vapor pressure of the solute is also large, so that the isotherm effect is negligible, Eq. (40) becomes

$$\Delta t_R/t_R = -2X \tag{41}$$

which has been suggested previously by Littlewood (*9*).

Finally, it is possible, using Eq. (36), to measure the curvature of the isotherm at infinite dilution. Figures 1 and 2 show that the limiting transition point (t_R minimum for $X = 0$) is obtained at $T = 42\,°\mathrm{C}$ and $P_i - P_0 = 577$ Torr. These conditions are those for which Eq. (36) is valid, which gives

$$Y_0'' = 2\gamma^\infty\left(1 - \frac{P^0\gamma^\infty}{j_3^{\,4}}\right) \tag{42}$$

since $Y_0 = \gamma^\infty$. For *n*-pentane at 42°C, $P^0 = 1.22$ atm. For an inlet pressure of 577 Torr, $P = 1.76$ and $j_3^{\,4} = 1.45$. The variation of the activity coefficient of *n*-pentane in squalane has been determined by Ashworth and Everett (*10*) using static measurements. Their results are thus completely independent of chromatography. Their measurements can be represented by using the Wilson equation (*6*). After optimization of the parameters of the Wilson equation, the following results are obtained at infinite dilution:

$$\gamma^\infty = 0.62$$

$$Y_0'' = 2\left(\frac{d\gamma}{dX^L}\right)_{X^L=0} = 0.58$$

Introducing this value of γ^∞ and the other data of Eq. (42) gives

$$Y_0'' = 0.59$$

The agreement between the results of static measurements and gas chromatography is thus excellent, as is often the case for solutions of hydrocarbons where adsorption at the various interfaces can be neglected.

Gas chromatography offers not only a simple method of measurements of the activity coefficient at infinite dilution, but also a method of measurement of the curvature of the isotherm. The method of the limiting transition point is almost as simple to use as the chromatographic method of determination of the activity coefficient at infinite dilution. The advantage over other nonchromatographic methods is the very short time necessary for the experimental work, which is also very simple. In addition, precision and accuracy are not limited by the size of the sample or the concentration used. The advantage over other chromatographic methods is that a calibration of the detector is not necessary since only measurements of retention times are made. Although these measurements are carried out using samples of various sizes, a normal analytical instrument can be used, provided the column is isothermal, which is rare with commercial equipment (*11*), and the assumptions usually made in analytical chromatography remain valid; i.e., the column temperature and the pressure profile are not modified during the elution, and the peak is symmetrical in the most interesting range, so that diffusion and mass-transfer kinetics do not change the retention time and the method described above is valid even when the contribution of these phenomena to band spreading is not negligible. Finally, the method takes into account the pressure gradient so there is no objection to the use of a column with low permeability (as are most efficient columns), and the calculations are very simple.

The main drawback of the method is that it works well only if the column outlet pressure is of the same order of magnitude as the vapor pressure of the compound studied, so when isotherms are to be studied at temperatures very different from the boiling point, the outlet pressure should be adjusted to a value different from atmospheric pressure.

Nevertheless, gas chromatography provides us with a very useful method to determine the characteristics of the isotherm at infinite dilution: γ^{∞} and $d\gamma^{\infty}/dX^{L}$. As the Wilson equation depends on two parameters *only*, that should be enough, in principle, to know all the characteristics of the binary solution. The accuracy of this method is presently under study.

Acknowledgments

The technical assistance of Guy Preau for the construction of the equipment and Marcel Sultan for the measurements is gratefully acknowledged.

REFERENCES

1. P. Valentin and G. Guiochon, *Separ. Sci.*, *10*, 245 (1975).
2. P. Valentin and G. Guiochon, *Ibid.*, *10*, 271 (1975).
3. L. Jacob, P. Valentin, and G. Guiochon, *Chromatographia*, *4*, 6 (1971).
4. L. Jacob and G. Guiochon, *Chromatogr. Rev.*, *14*, 77 (1971).
5. J. R. Conder and J. H. Purnel, *Trans. Faraday Soc.*, *64*, 3100 (1968).
6. P. Valentin and G. Guiochon, *J. Chromatogr. Sci.*, In Press.
7. P. Hagenbach, P. Valentin, B. Roz, and G. Guiochon, in *Gas Chromatography 1972* (S. G. Perry ed.), Institute of Petroleum, London, 1973, p. 157.
8. M. Goedert and G. Guiochon, *Anal. Chem.*, *45*, 1188 (1973).
9. A. B. Littlewood, *Ibid.*, *38*, 2, (1966).
10. A. J. Ashworth and D. H. Everett, *Trans. Faraday Soc.*, *56*, 1609 (1960).
11. M. Goedert and G. Guiochon, *Anal. Chem.*, *45*, 1180 (1973).
12. P. C. Haarhoff and H. J. Van Der Linde, Ibid., *38*, 573 (1966).

Received by editor March 11, 1974