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On the Stochastic Nature of the HETP

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Summary

The validity of several local plate height equations is studied using programmed pressure gas chromatography. The appropriate numerical methods of calculation as well as the experimental results obtained are given. Comparison between calculated data and the experimental results shows that the theory cannot meet the programmed flow-rate requirements in its present state. The discrepancy between the calculations and the experiments comes from the fundamental basis of the theory.

INTRODUCTION

The first theoretical papers discussing peak broadening in gas chromatography (*1*, *2*) used aleatory functions of time. The success of the HETP concept turned it into an aleatory function of space (or abscissa along the column) with "local" expressions involving a so-called "decompression" effect (*3*, *4*). The HETP is thus described, or even defined, as a local physical property of the column and flow velocity by the equation:

$$d(\sigma_X^2) = H\,dx$$

There was little notice of Kambara's paper (*5*) where an effort had been made to get a global effect with time as the variable.

Until now all the experimental studies carried out to test the various HETP equations have been performed in steady-state flow, and the number of parameters involved in the equations has made evaluation of the theory very unpractical (*3*). A "modern" plate height equation has 6 constants (cf. Ref. *7* and Eq. 1 below) which allow one to fit correctly the experimental data obtained over a broad range of flow velocity whether the equation itself is physically sound or not. The purpose of this paper is to widen the field of testing plate height equations by using pressure programmed chromatography in order to see whether the more obvious discrepancies can be detected, and if so, to find them.

NUMERICAL METHODS

The flow-velocity variations at any point of the column and thus the peak migration in pressure programming can be described by solving the following system of partial differential equations for the right initial and boundary conditions:

$$u = -\frac{K}{\eta\phi}\frac{\partial p}{\partial x} \tag{1}$$

$$\phi\frac{\partial p}{\partial t} + \frac{\partial(pu)}{\partial x} = 0 \tag{2}$$

where Eq. (1) is Darcy's law and Eq. (2) the mass balance equation. This system can always be solved numerically. It requires, however, a very long computation, and the use of a few hypotheses can dramatically reduce the computation time. The simplest one H1, supposes that the stationary flow prevails at any time, in any place, whatever the flow. We call C1 the calculations carried out "exactly," that is, solving the partial differential equations; and C2 those calculations made with hypothesis H1.

Evaluation of C1 and C2 shows that the relative discrepancy for the retention time t_R between C1 and C2 is 10% maximum (cf. Table 1); it drops to 5% only if programming rates that are not too high are used. A more drastic hypothesis H2 seems also to be valid: see Ref. (*6*).

Going from elution to dispersion is more difficult. The outlet velocities calculated by the same methods vary by more than 20% and the standard deviations by 5% between C1 and C2. A better parameter to use seems to be the resolution R ($R = \Delta t_R/(\psi_1 + \psi_2)$ where Δt_R is the difference between the retention times of the two peaks, and ψ_1 and ψ_2 their base widths) between two adjacent peaks with constant α ($\partial\alpha/\partial p = 0$). As shown in Table 1, R varies by only 2%.

Consequently, in what follows we shall use only R to characterize peak dispersion. We shall compare experimental data on R to values

TABLE 1

Per Cent Differences between Calculated Values Obtained Using Methods C_1 and C_2[a]

Initial programming pressure (abs atm)	4 stationary	2	1
Retention time t_R	0	5	12
Outlet velocity	0	8	25
Standard deviation σ	0	3	5
Resolution R	0	2	1.5

[a] The calculations have been performed so that the various programs should give similar retention times. This relates the initial inlet pressure to the program rate.

calculated with hypothesis H1. This hypothesis greatly reduces the computation time and also enables us to derive formulas from the equations of steady state.

EXPERIMENTAL

Apparatus

A packed capillary column extensively studied in a previous paper has been used (Ref. 7, Column 4c). Pressure programming was achieved using an Ionics Flow Programmer. The inlet pressure P_i follows an exponential law:

$$P_i = P_{i0}e^{at}$$

where P_{i0} is the initial inlet pressure and a the programming rate. P_{i0} and a can be chosen independently.

Experiments

Series of experiments have been performed using as Solute 3 methylhexane and n-heptane with capacity factors of $k_1' = 1.67$ and $k_2' = 2.17$, respectively (temp, 50°C). Special attention has been paid to vary both a and p_{i0} in such a way that various analyses be obtained with close retention times of the two compounds, using different programs. The results can be plotted in two ways, either the plot of R vs. p_{i0} or the plot of R vs. t_R.

Results

The relative standard deviation of experimental measurements at given boundary and initial conditions is less than 2%. The plot of R vs. t_R gives a single curve, all the points being on it whatever the program, with a deviation of 2% in the worst case (cf. Fig. 1).

Thus we can write:

$$R = \psi(t_R) \tag{3}$$

This result has been pointed out by Deininger (*9*).

Plotting R vs. p_{io} yields a lattice produced by horizontal straight lines at constant retention time and parallel, hyperbolic type curves at constant a programming rate (cf. Fig. 2). The horizontal lines express the fact that the resolution is a function of the retention time only.

CALCULATION

The following formulas were used for the HETP, and were combined with the partial differential Eqs. (1) and (2) to calculate the resolution of the two peaks at the column outlet.

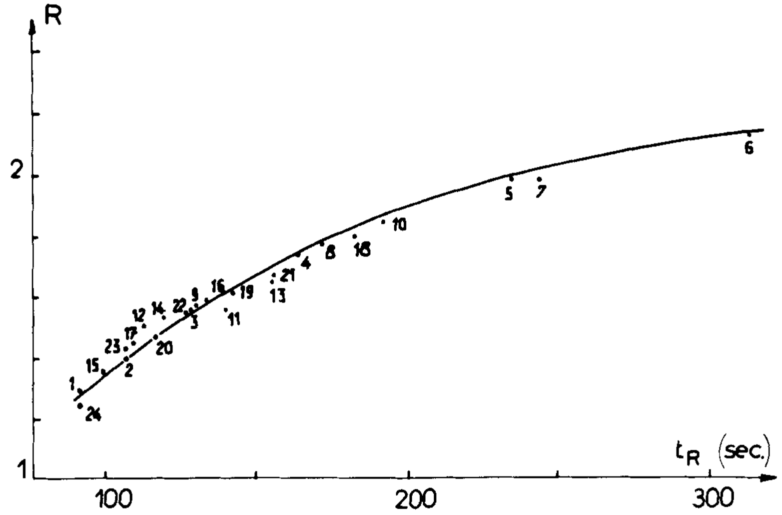

FIG. 1. Experimental plot of the resolution R vs. retention time t_R in seconds. The numbers refer to given initial and boundary conditions and are the same as in Fig. 2.

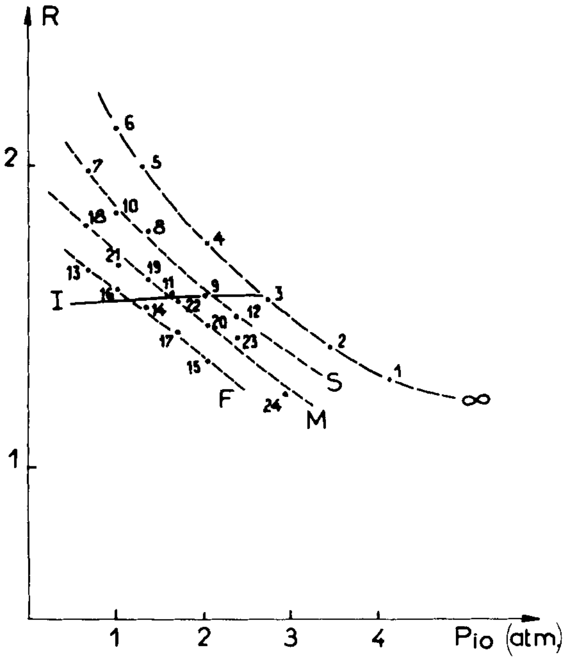

FIG. 2. Experimental plot of the resolution R vs. the initial inlet pressure P_{i0} (in atm). The dotted lines link the points obtained with the same programming rate (exponential law), stationary state: ∞, slow rate: S; medium rate: M; fast rate: F, point 11 excepted, which belongs to the experimental rate S. Full line I links points with almost identical retention times.

$$H = \left[\frac{a_1}{pu} + a_2 up + a_3 u + \frac{a_5 up}{a_7 up + a_6} + a_4\right] p^2$$
$$d\sigma_x^2 = H\, dx \tag{4}$$

where the a_i's are constant factors for a given column (a_5, a_6, and a_7 are not independent),

$$d\sigma_t^2 = H_1\, dt \tag{5}$$

$$d\sigma_x^2 = H_2 u\, dx\, p^2/p_0^2 \tag{6}$$

where H_1 and H_2 are two constant factors.

Equation (4) stems from Ref. *7* and was originated by Giddings (*3*, *8*). It had been fitted successfully with experimental data obtained

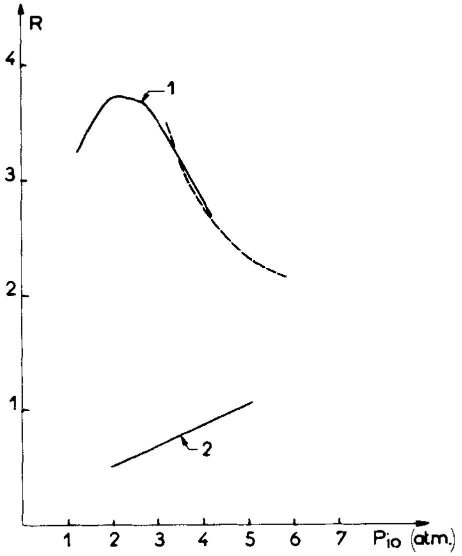

FIG. 3. Calculated plot of resolution R vs. initial inlet pressure (absolute atm). Curve 1 is calculated with Eq. (4), Curve 2 with Eq. (5). Both calculations were carried in the C_2 way. Dotted line represents the resolution in stationary state.

in steady-state flow with carrier gas velocities in the range 5–400 cm/sec (*7*).

Equation (5) is derived from Ref. *5* using the results in the Numerical Methods Section above. It is a relationship involving stochastic laws in time. Equation (6) gives the same result as Eq. (5) in stationary flow but appears as a stochastic law in space.

In steady-state flow, both Eqs. (5) and (6) give average H values expressed as $\bar{H} = A\bar{u}$ where $\bar{u}$ is the carrier gas average velocity.

Results

The results of the calculation are given in Fig. 3 where the resolution is plotted vs. p_{io} at constant t_R. Curve 1 is obtained when Eq. (4) is used. This curve has a parabolic shape, with a maximum which lies 25% over the boundary values, one of them corresponding to the stationary flow. The experiments discussed above give a constant R value, independent of t_R. This discrepancy is well over the experimental errors.

In the same conditions, Eq. 5 gives a straight line of positive slope (Curve 2, Fig. 3), the resolution increasing with decreasing program rate. Thus there is a minimum resolution which is 30% smaller than the maximum value obtained for stationary flow. This again is in disagreement with the experimental results.

Equation (6) gives results similar to those with Eq. (4). The variation in resolution is also about 30%.

Because in Eq. (4) the coefficients of the two terms proportional to the carrier gas velocity, u, are almost equal, we tried adding Eqs. (5) and (6). Setting $H_1 = H_2$, according to the experimental results in Ref. 7, leads to a curve which has still a maximum, but the variation is reduced to 10%. Setting $H_1 = 2H_2$ gives a plateau very comparable to the one derived from the experimental results.

Consequently, neither Eq. (4) nor Eq. (5) gives a satisfactory solution to the problem. Unfortunately, they are the only equations offered by the present state of the theory. It should be noted that Eqs. (5) and (6), although they yield the same average value of H in steady-state flow, give opposite results in pressure programming for the variation of the resolution with the starting inlet pressure at constant retention time, as the first one gives a minimum in the resolution, the second one a maximum.

CONCLUSION

The two plate height equations derived from theory and commonly used give unsatisfactory results. This seems to prove that neither a stochastic law in time nor in length is valid alone. A better fit of the experimental results can be obtained by adding the two effects, but no theoretical basis could be found to ground a stochastic law in length, and there is therefore no more basis to adding it to the stochastic law in time.

This at least proves that pressure programming can be a better field for testing HETP equations than the usual steady-state flow. Furthermore, it seems necessary to study the diffusion processes in chromatography again.

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