

CHROM. 4566

MOBILE-PHASE DISPERSION IN LIQUID CHROMATOGRAPHY

R. S. DEELDER

Central Laboratory, Staatsmijnen/DSM, Geleen (The Netherlands)

(Received October 16th, 1969)

SUMMARY

Literature data on dispersion of inert components in liquid flow through chromatographic columns packed with glass beads are compatible with a plate-height equation based on a combination of radial and axial dispersion.

It also appears that the measurements can be described by means of a known empirical equation whose usefulness in liquid chromatography has not been verified so far.

Both equations contain constants which depend on the ratio of the column diameter to the particle diameter of the packing material.

INTRODUCTION

Peak-widening in chromatography is usually described by means of the plate height H ; with homogenous columns containing an incompressible mobile phase we have¹

$$H = \frac{\sigma^2}{z} \quad (1)$$

where σ^2 denotes the variance of the Gaussian concentration profile of the eluted component, and z the distance between the point of injection and the peak maximum. The plate height can be found by addition of a series of terms which are each the result of a given dispersion mechanism. In the case of chromatographic separation on a packed column, the dispersion processes in the interstitial mobile phase yield a contribution H_D to the total plate height. Assuming piston flow with axial dispersion² and a linear velocity v , we have³:

$$H_D = \frac{2D_L}{v} \quad (2a)$$

which, in dimensionless form, *i.e.* after dividing by d_p (diameter of the packing material), changes into

$$h_D = \frac{H_D}{d_p} = \frac{2D_L}{vd_p} \quad (2b)$$

The original theory of chromatography^{3,4} assumes that the axial dispersion coefficient D_L is the sum of the molecular diffusion coefficient D_m multiplied by an obstruction factor γ (ref. 5) and an eddy diffusion term $E\nu$; in dimensionless form this can be rewritten as follows:

$$\frac{D_L}{\nu d_p} = \gamma(ReSc)^{-1} + \frac{E}{d_p} \quad (3)$$

where $ReSc = \nu d_p / D_m$.

GIDDINGS^{1,6,7} has shown that it is incorrect to use a constant eddy diffusion coefficient E and suggested to replace it by a coupled eddy coefficient $\frac{1}{2} \sum (\frac{1}{2} \lambda_i d_p + D_m / \omega_i \nu d_p^2)^{-1}$, where λ_i and ω_i are constants. Applied to (2b), this gives

$$h_D = 2\gamma(ReSc)^{-1} + \sum_i (\frac{1}{2} \lambda_i + \frac{1}{\omega_i ReSc})^{-1} \quad (4)$$

The summation is necessary because GIDDINGS assumes that with a non-porous packing material at least four different mechanisms, each with its own λ_i and ω_i values, make additive contributions to this coupled eddy diffusion.

KNOX⁹ and HORNE *et al.*¹⁰ determined $h_D(ReSc)$ from the peak widening of an inert component in a column packed with glass beads. These authors did, however, not succeed in reconciling the experimental results with a relation similar in shape to (4) above.

HIBY¹¹, starting from some dispersion measurements in gases and liquids, derived the following empirical relation

$$\frac{D_L}{\nu d_p} = \gamma(ReSc)^{-1} + \lambda_1 \{1 + \lambda_2 (ReSc)^{-\frac{1}{2}}\}^{-1} \quad (5)$$

where λ_1 and λ_2 denote constants. Although this equation proves to hold good for gases¹², the accuracy of HIBY's measurements for liquids seems questionable¹³. HUBER AND HULSMAN¹⁴ used expression (5) for calculating plate heights in liquid chromatographic columns; supplementary experimental evidence for the correctness of (5) is lacking however.

FLOW PROFILE AND DISPERSION

Dispersion in the mobile phase is strongly influenced by the flow profile in the column. A known example is the parabolic velocity distribution in laminar flow through cylindrical tubes; the velocity profile gives rise to radial concentration gradients, which are partly smoothed out by molecular diffusion¹⁵.

Flow profiles occur also in flows through packed chromatographic columns; they can be ascribed for a large part to irregularities in the packing structure. Piston flow with axial dispersion characterized by a velocity ν and axial dispersion coefficient D_L is the simplest model for describing dispersion in flow through a packed column. LEVENSPIEL AND BISCHOFF² compared it with a general dispersion model with radial symmetry characterized by an axial velocity $\nu(r)$ and an axial and a radial

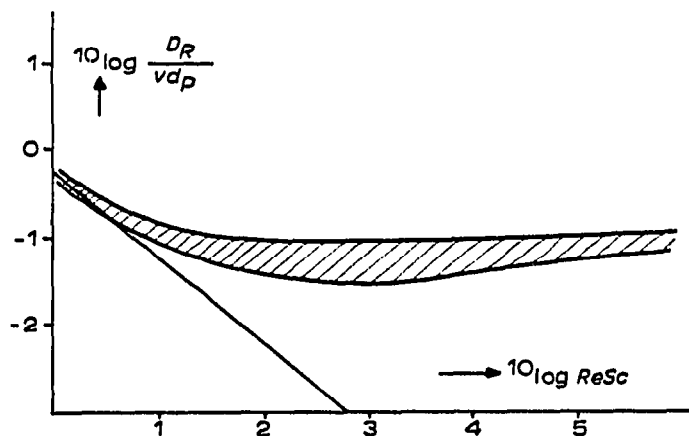


Fig. 1. D_R/vd_p versus $ReSc^{10, 11, 18, 19}$.

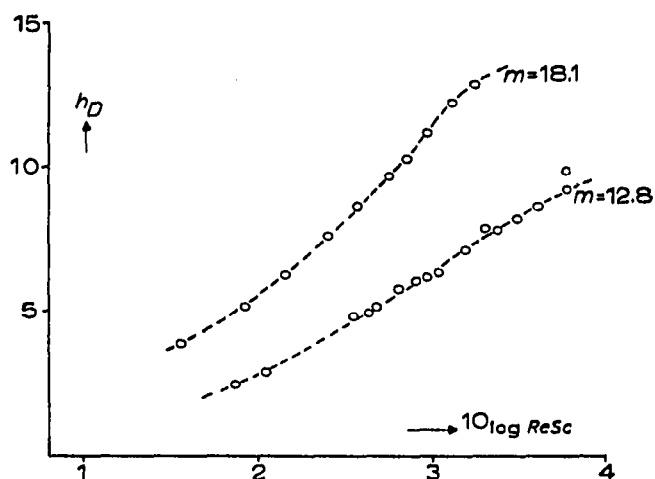


Fig. 2. Comparison of experiment with theory (eqn. 10). \circ , experimental values⁹; ----, curves according to eqn. 10. $m = 12.8$: $\lambda_L = 1.06$, $\lambda_R = 6.37 \cdot 10^{-4}$, $k = 6.6 \cdot 10^{-6}$; $m = 18.1$: $\lambda_L = 1.5$, $\lambda_R = 1.52 \cdot 10^{-3}$, $k = 1.16 \cdot 10^{-4}$.

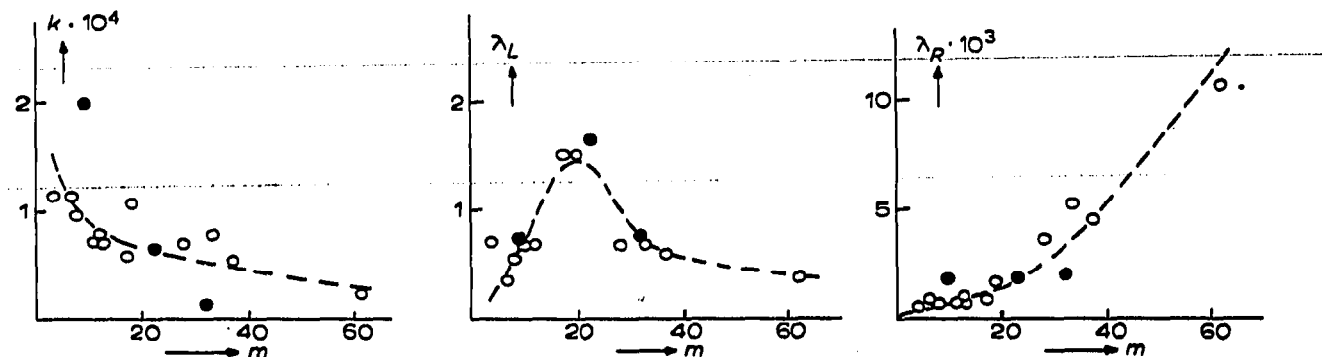


Fig. 3. λ_L , λ_R and k from eqn. (10) plotted versus m . \circ , values from ref. 9; \bullet , values from ref. 10.

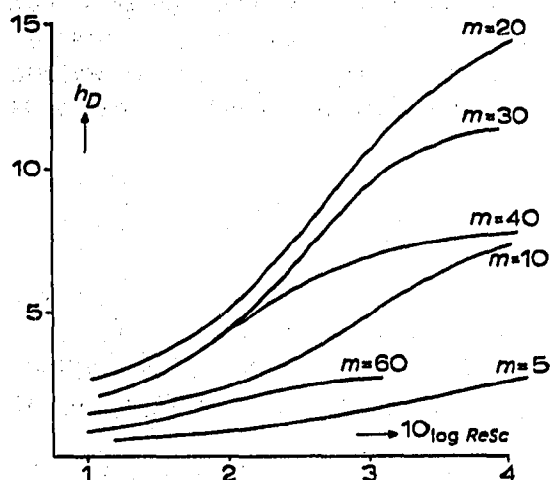


Fig. 4. Influence of m on the h_D ds function of $ReSc$ (calculated from eqn. 10 by means of the relation between m and the parameters λ_L , λ_R and h indicated in Fig. 3).

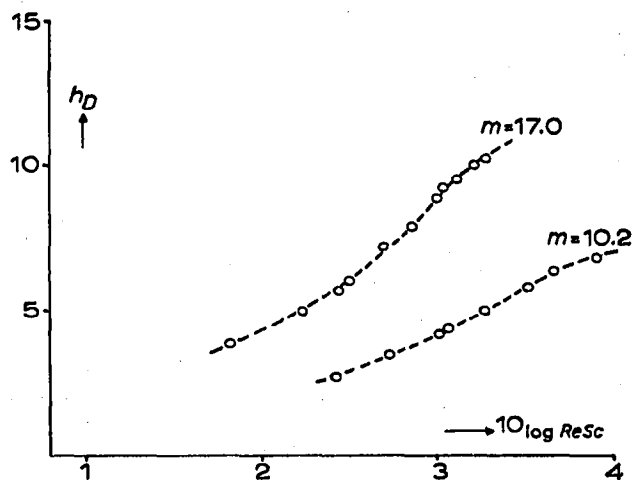


Fig. 5. Comparison of experiment with theory (eqn. 5). \circ , experimental values⁰; -----, curves according to eqn. 5. $m = 10.2$, $\lambda_1 = 10.14$, $\lambda_2 = 44.8$; $m = 17.0$, $\lambda_1 = 17.26$, $\lambda_2 = 31.6$.

dispersion coefficient $D_L(r)$ and $D_R(r)$ respectively; in this notation r denotes the radial coordinate.

The above authors demonstrated that

$$D_L = \bar{D}_L + \frac{h(\bar{v}R)^2}{\bar{D}_R} \quad (6)$$

Here, \bar{D}_L , \bar{D}_R and \bar{v} are the values of $D_L(r)$, $D_R(r)$ and $v(r)$ averaged over the column radius R , and h is determined by the flow profile in the column^{2,17}. Substitution of (6) in (2b) gives

$$h_D = \frac{2\bar{D}_L}{\bar{v}d_p} + \frac{hm^2\bar{v}d_p}{2\bar{D}_R} \quad (7)$$

Literature data summarized in Fig. 1 suggest that over the range where turbulence has as yet no noticeable effect (*i.e.* $Re < 1$, or with $Sc \sim 10^3$, $ReSc < 10^3$) liquids will obey the relation:

$$\frac{\bar{D}_R}{\bar{v}d_p} = \lambda_R + \gamma(ReSc)^{-1} \quad (8)$$

By analogy with (8), and under the same restriction, it may be assumed that

$$\frac{\bar{D}_L}{\bar{v}d_p} = \lambda_L + \gamma(ReSc)^{-1} \quad (9)$$

Substitution of (8) and (9) in (7) yields

$$h_D = 2\{\lambda_L + \gamma(ReSc)^{-1}\} + \frac{hm^2}{2}\{\lambda_R + \gamma(ReSc)^{-1}\}^{-1} \quad (10)$$

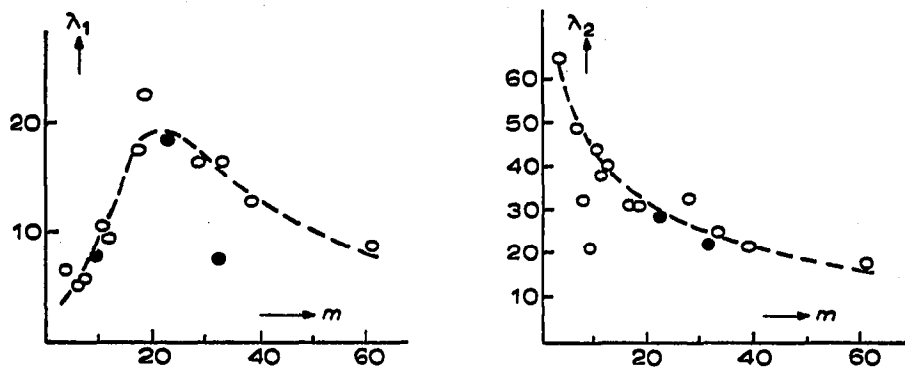


Fig. 6. λ_1 and λ_2 from eqn. 5 plotted versus m . O, values from ref. 9; ●, values from ref. 10.

DISCUSSION

Since \bar{D}_L and \bar{D}_R are functions of the flow profile in the column², it follows that, in addition to k (see above), λ_L and λ_R will also depend on it. This flow profile, however, is influenced again by the structure of the packing⁴, *i.e.*, by the method of packing, the ratio of the column diameter to the particle diameter, the particle size distribution and the shape of the packing material. The parameters λ_L , λ_R and k have been calculated by applying (10) to a series of curves of $h_D(ReSc)$ given in the literature^{9,10} in the range $10 < ReSc < 10^4$; it was assumed in the calculation that $\gamma = 0.7$.

The validity of (10) is shown in Fig. 2. In Fig. 3, the values found for λ_L , λ_R and k have been plotted versus m . The influence of m can be clearly recognized; the dotted lines in Fig. 3 serve to relate m to the parameter values calculated from measurements on identically packed columns by KNOX⁹, with, in principle, elimination of all variables other than m . It is evident that λ_R will increase with m : in a very regularly packed column with a high m value, the radial convection will be greater than in a column with an irregular packing arrangement and a low m value. The drop of k with increasing m is in conformity with expectation^{2,8}. A remarkable feature is that λ_L has its maximum at $m \sim 20$.

To illustrate the influence of m , Fig. 4 shows a collection of h_D-ReSc curves with variable m ; these have been calculated from (10) with the aid of the relation between λ_L , λ_R , k and m indicated in Fig. 3. The values of these parameters have practically all been calculated from measurements covering not more than two decades of $ReSc$ values (see Figs. 2 and 5); hence, the points on the curves have been extrapolated over approximately one decade.

The shift of the levelled part in the h_D curve towards lower $ReSc$ values with increasing m agrees with empirical evidence. We wish to point out that equation (10) does not express the decrease of h_D which, at $ReSc$ values exceeding $\sim 10^4$, sets in owing to the growing effect of turbulence.

It should also be noted here that (10) may in fact be looked upon as a special case of the general relation (4), if we assume that, for all dispersion mechanisms except one, $D_m/\omega_1 v dr \ll \frac{1}{2}\lambda_L$ over the $ReSc$ range considered here.

In Fig. 5 it can be seen that within the laminary flow region the empirical relation (5) is also in agreement with the experimental values.

The values calculated for λ_1 and λ_2 have been plotted *versus* m in Fig. 6; however, these quantities do not have any physical significance.

REFERENCES

- 1 J. C. GIDDINGS, *Dynamics in Chromatography*, Part I, Marcel Dekker, New York, 1965.
- 2 O. LEVENSPIEL AND K. B. BISCHOFF, *Advan. Chem. Eng.*, 4 (1963) 95.
- 3 J. J. VAN DEEMTER, F. J. ZUIDERWEG AND A. KLINKENBERG, *Chem. Eng. Sci.*, 5 (1956) 271.
- 4 A. I. M. KEULEMANS, *Gas Chromatography*, 2nd ed., Reinhold, New York, 1959.
- 5 J. H. KNOX AND L. MCLAREN, *Anal. Chem.*, 36 (1964) 1477.
- 6 J. C. GIDDINGS, *J. Chromatog.*, 5 (1961) 61.
- 7 J. C. GIDDINGS, *Anal. Chem.*, 38 (1966) 490.
- 8 S. T. SIE AND W. RIJNDERS, *Anal. Chim. Acta*, 38 (1967) 3.
- 9 J. H. KNOX, *Anal. Chem.*, 38 (1966) 253.
- 10 D. S. HORNE, J. H. KNOX AND L. MCLAREN, *Separation Sci.*, 1 (1966) 531.
- 11 J. W. HIBY, in P. A. ROTTENBURG (Editor), *The Interaction between fluids and particles*, The Institution of Chemical Engineers, London, 1962.
- 12 E. V. EVANS AND C. N. KENNEY, *Trans. Inst. Chem. Eng.*, 44 (1966) T 189.
- 13 D. J. GUNN, *Trans. Inst. Chem. Eng.*, 46 (1968) CE 153.
- 14 J. F. K. HUBER AND J. A. R. J. HULSMAN, *Anal. Chim. Acta*, 38 (1967) 305.
- 15 G. TAYLOR, *Proc. Roy. Soc. (London) A*, 219 (1953) 186.
- 16 A. LITTLEWOOD, in A. GOLDUP (Editor), *Proc. 5th Intern. Symp. Gas Chromatography, Brighton, 1964*, The Institute of Petroleum, London, 1965.
- 17 R. ARIS, *Proc. Roy. Soc. (London) A*, 235 (1956) 67.
- 18 M. E. HARTMAN, C. J. H. WEVERS AND H. KRAMERS, *Chem. Eng. Sci.*, 9 (1958) 80.
- 19 R. J. BLACKWELL, *Soc. Petrol. Eng. J.*, 2 (1962) 1.

J. Chromatog., 47 (1970) 307-312