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THE CONTRIBUTION OF EDDY DIFFUSION AND OF THE MACROSCOPIC MOBILE PHASE VELOCITY PROFILE TO PLATE HEIGHT IN CHROMATOGRAPHY

A LITERATURE INVESTIGATION

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SUMMARY

From literature data, the coefficient for radial convective dispersion λ_R and the composite coefficient $(\kappa' + \kappa\varrho^2)$ for longitudinal dispersion by eddy diffusion and the macroscopic velocity profile are estimated as a function of the ratio ϱ of the diameters of the column and of the granules of the packing.

It does not appear to be possible to separate the effects of eddy diffusion and of the macroscopic velocity profile, on the basis of the experimental data available.

INTRODUCTION

The phenomenon of axial and radial dispersion of a solute when it is injected into a packed bed and transported by a moving fluid is both theoretically interesting and practically important, *e.g.*, in the fields of chromatography, chemical engineering and hydrology.

The main lines of the phenomenon appear to be understood now and a fair amount of experimental data has been obtained in the last few years by chromatographers as well as by chemical engineers.

Thus, the moment looks appropriate to present a critical discussion of the results obtained up till now, and to estimate the magnitude of the coefficients occurring in the dispersion equation.

THEORY

A big step forward in the field of interpretation of peak dispersion in chromatography was made in 1956 by VAN DEEMTER *et al.*[1] and by KLINKENBERG AND SJENITZER[2]. Their work led to the well-known VAN DEEMTER equation:

$$H = A + B/u + C_S u + C_M u \tag{1}$$

where:

H = plate height

A = contribution of eddy diffusion

B/u = contribution of diffusion

$C_S u$ = contribution of resistance to mass transfer in the stationary phase

$C_M u$ = contribution of resistance to mass transfer in the mobile phase

u = velocity of the mobile phase

After a couple of years it became apparent that eqn. 1 did not adequately represent the experimental data mainly forthcoming from the field of gas chromatography. Its main shortcomings are:

(1) The experimental values of the contribution of eddy diffusion are much smaller than expected from the physical model of this phenomenon;

(2) The experimental values of the $C_M u$ term are much larger than expected.

BERAN[3] showed, as early as 1957, that dispersion caused by eddy diffusion is independent of the mobile phase velocity only when the latter is large. He derived the equations for the limiting cases of very low and very large velocities and concluded that in the intermediate case "no simple procedure appears to be available and for want of anything better to do (the two limiting expressions for dispersion caused by eddy diffusion) may be added harmonically".

In doing so, he got, essentially, the same result as was obtained two years later by GIDDINGS[4] from a random-walk treatment.

The classical expression for the contribution of eddy diffusion to plate height and the result from GIDDINGS' "coupling theory" can be cast in the following forms:

$$\text{classical theory:} \quad H_{\text{e.d.}} = A = 2\lambda d_p = \frac{2\kappa' d_p^2 u}{\lambda_R d_p u} \tag{2}$$

$$\text{coupling theory:} \quad H_{\text{e.d.}} = \frac{2\lambda d_p}{1 + CD/d_p u} = \frac{2\kappa' d_p^2 u}{\lambda_R d_p u + \gamma D} \tag{3}$$

where:

$\lambda, \lambda_R, \kappa', C, \gamma$ = dimensionless coefficients, depending on the geometry of the column packing and the dynamics of flow

d_p = particle diameter

D = diffusion coefficient of the solute in the mobile phase.

The denominators in eqns. 2 and 3 represent effective diffusion coefficients for radial dispersion. This phenomenon reduces the longitudinal dispersion caused by the non-equivalence of the flow paths around the particles. It can be seen from eqns. 2 and 3 that in the classical theory radial dispersion by convection only is accounted for, whereas in the coupling theory both convection and diffusion are taken into account.

Under normal experimental conditions in gas chromatography it can be expected that $\lambda_R d_p u \ll \gamma D$ so that:

$$H_{\text{e.d.}} \approx \frac{2\kappa' d_p^2 u}{\gamma D} \tag{4}$$

So, both the above mentioned discrepancies between theory and experiment can be reconciled, at least partially, along these lines.

Peak dispersion by eddy diffusion can be regarded as being caused by a mobile phase velocity profile on the scale of the order of a particle diameter. HUYTEN *et al.*[5] in 1960 introduced an analogous term, due to a macroscopic velocity profile:

$$H_{\text{v.p.}} = \frac{2\kappa d_c^2 u}{D_R} \tag{5}$$

where·

κ = dimensionless coefficient, depending on the velocity profile

d_c = column diameter

D_R = effective radial diffusion coefficient.

The denominator was specified later[6] as follows:

$$D_R = \lambda_R d_p u + \gamma D \tag{6}$$

From the work of LITTLEWOOD[7] and HIGGINS AND SMITH[8] it follows that, if du/dr* changes sign at $r = r_0$ ($r_0 < d_c/2$) in wide columns, d_c should be replaced by $2\,r_0$. If this occurs, $H_{\text{v.p.}}$ will be proportional to d_c^2 up to a certain value of the column diameter and then become independent of d_c. Further, LITTLEWOOD showed that eqn. 5 also holds in the case of a one-dimensional velocity profile, as occurs in paper and thin-layer chromatography or electrophoresis. d_c is then equal to the breadth of the paper or thin-layer strip seen by the densitometer, *or* equal to the mean distance between maxima or minima in the velocity profile, whichever is the smaller.

Eqns. 3, 5 and 6 can be combined to:

$$H_{\text{e.d.+v.p.}} = 2u\,\frac{\kappa' d_p^2 + \kappa d_c^2}{\lambda_R d_p u + \gamma D} \tag{7}$$

To compare experimental data, obtained for different values of d_p, d_c and D it is advantageous to introduce the following dimensionless quantities:

the reduced plate height $h = H/d_p$

the reduced velocity $v = u d_p/D$

the reduced column diameter $\varrho = d_c/d_p$.

In terms of these variables, eqn. 7 reads as follows:

$$h_{\text{e.d.+v.p.}} = 2v\,\frac{\kappa' + \kappa \varrho^2}{\lambda_R v + \gamma} \tag{8}$$

It follows from eqn. 8 that h should be a universal function of ϱ and v, or nearly so as the values of the coefficients κ, κ', λ_R and γ may depend slightly on the geometry of the column packing and the dynamics of flow.

COMPARISON WITH EXPERIMENTAL DATA

Evidence for the coupling theory of longitudinal dispersion

There is now ample evidence for coupling in longitudinal dispersion but we shall show only one piece of evidence, from the literature on chemical engineering. In the absence of mass transfer between a mobile and stationary phase, and for simplicity neglecting the macroscopic velocity profile, the effective diffusion coefficient for

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* r = distance from the axis of the column.

longitudinal dispersion, accounting for both convective and diffusive dispersion, is (see eqns. 1, 2 and 3):

classical theory: $D_L = (A + B/u)u/2 = \lambda d_p u + \gamma D$ (9)

coupling theory: $D_L = (A + B/u)u/2 = \dfrac{\lambda d_p u}{1 + CD/d_p u} + \gamma D$ (10)

or:

classical theory: $\dfrac{D_L}{d_p u} = \lambda + \dfrac{\gamma D}{d_p u}$ (11)

coupling theory: $\dfrac{D_L}{d_p u} = \dfrac{\lambda}{1 + CD/d_p u} + \dfrac{\gamma D}{d_p u}$ (12)

It is customary in chemical engineering literature to present dispersion data as graphs of the logarithm of the longitudinal Peclet number, $Pe_L = d_p u/D_L$, vs. the logarithm of the Reynolds number, $Re = d_p u/\nu^*$. If eqn. 11 holds, such a graph should rise steadily to a value $-\log \lambda$, whereas the graph should have a maximum if eqn. 12 holds. Fig. 1, from the work of EDWARDS AND RICHARDSON[9], is clearly in favour of the coupling theory.
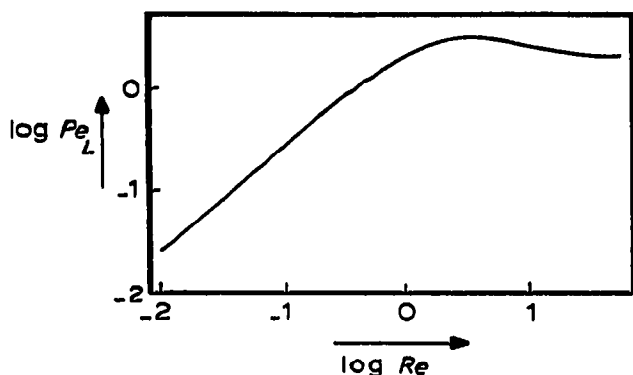

Fig. 1. Longitudinal Peclet number Pe_L as a function of Reynolds number Re Evidence for coupling in longitudinal dispersion.

The magnitude of λ_R and its dependence on ϱ

FAHIEN AND SMITH[10] have convincingly shown that λ_R depends on ϱ, due to a corresponding dependence of the void fraction on ϱ and to the influence of the column wall on the dynamics of flow. They propose, for gases, the equation:

$\lambda_R \text{ (gas)} = \dfrac{\varrho^2}{8\varrho^2 + 155}$ (13)

They investigated the range of ϱ values from $\varrho = 5.6$ to $\varrho = 26$. It follows from Fig. 2 that this equation also holds for the λ_R values at still smaller ϱ values, which can be deduced from an analysis of longitudinal dispersion data by means of eqn. 8. Further, packings of spheres and of irregularly shaped particles appear to yield comparable λ_R values.
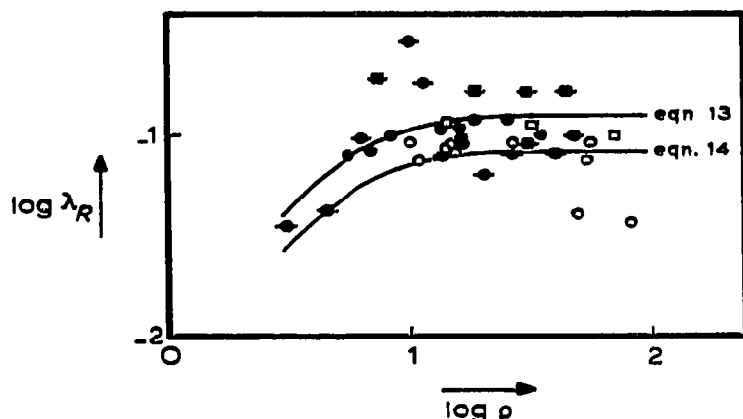
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* ν = kinematic viscosity.

Fig. 2. λ_R as a function of ϱ. ● gas, deduced from radial dispersion, spherical packing[10,11,17]; —●— gas, deduced from longitudinal dispersion, spherical packing[14,15], —■— gas, deduced from longitudinal dispersion, irregular packing[16], ○ liquid, deduced from radial dispersion, spherical packing[11,17,18,20]; □ liquid, deduced from radial dispersion, irregular packing[11,19], —○— liquid, deduced from longitudinal dispersion, spherical packing[12].

Fig. 2 shows also that λ_R values for liquids are substantially smaller than for gases. The values determined from radial dispersion are in good agreement with the values of GORDON et al.[12], calculated from longitudinal dispersion data. Again, the shape of the particles appears to have no influence on λ_R.

For the dependence of λ_R on ϱ we propose an equation of the same type as eqn. 13, viz.:

$$\frac{3}{2} \lambda_R \text{ (liquid)} = \frac{\varrho^2}{8\varrho^2 + 155} \tag{14}$$

The magnitude of γ

According to STERNBERG AND POULSON[20] γ is equal to 0.73 for massive spherical particles* and to 0.63 for irregularly shaped porous ones, and does not depend on ϱ or d_p. For irregularly shaped massive particles BLACKWELL[19] found a value of 0.65.

The magnitudes of $(\kappa' + \kappa\varrho^2)/\lambda_R$ and of $\kappa' + \kappa\varrho^2$ and their dependence on ϱ

The first mentioned quantity is equal to one half of the right hand side of eqn. 8 when v is so large that diffusion can be neglected, compared to convective dispersion**. In chemical engineering language, $(\kappa' + \kappa\varrho^2)/\lambda_R$ is equal to $1/Pe_L$ for the same condition. This quantity can easily be measured for *liquids*, due to the small value of D in liquids. Fig. 3 shows that the values of $1/Pe_L$ are constant for ϱ values larger than about 20 but decrease somewhat for smaller ϱ values. We propose the equation:

$$1/Pe_L \text{ (liquid)} = (\kappa' + \kappa\varrho^2)/\lambda_R = \frac{5\varrho}{2\varrho + 5} \tag{15}$$

for both spherical and irregularly shaped particles.
Combination of eqns. 14 and 15 yields:

$$\kappa' + \kappa\varrho^2 \text{ (liquid)} = \frac{10\varrho^3}{(6\varrho + 15)(8\varrho^2 + 155)} \tag{16}$$

* Exactly the same value was found by EDWARDS AND RICHARDSON[9]
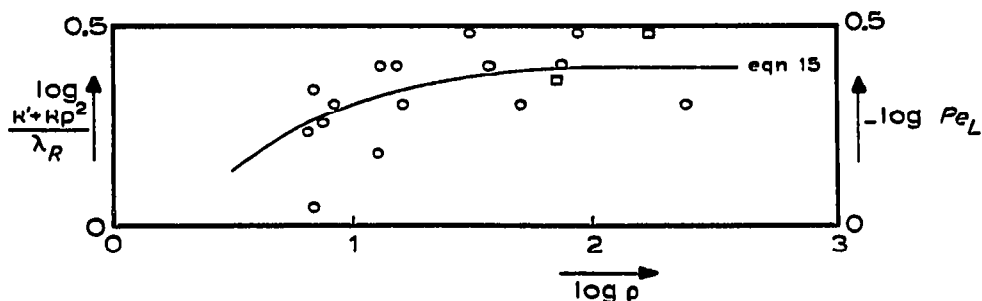** However, v should not be so large that turbulence sets in (at Re 10–100)

Fig. 3. $(\kappa' + \kappa\varrho^2)/\lambda_R$ as a function of ϱ for liquids. ◯ spherical packing[21-25], ☐ irregular packing[2,19]

Now we can investigate if h values in liquid chromatography can be described by the deduced values of λ_R, γ and $\kappa' + \kappa\varrho^2$. It must be admitted that for liquid eluents no general agreement exists upon the validity of eqn. 8. It describes perfectly the data of GORDON et al.[12] but predicts more curvature in plots of log h vs. log v than was found by KELLEY AND BILLMEYER[30] and by KNOX and his collaborators[15,27,28]. These data can be described better if v in eqn. 8 is replaced by $\frac{1}{3}v$. However, the resulting equation "does not seem very satisfactory from the theoretical point of view"[28]. Therefore, these data were also analysed by means of eqn. 8. The deduced values of λ_R and γ were substituted in this equation which was then applied to h data at large values of v. The resulting values of $\kappa' + \kappa\varrho^2$ are compared with values calculated from eqn. 16 in Fig. 4. The agreement is reasonable, even perfect for the data from ref. 28.
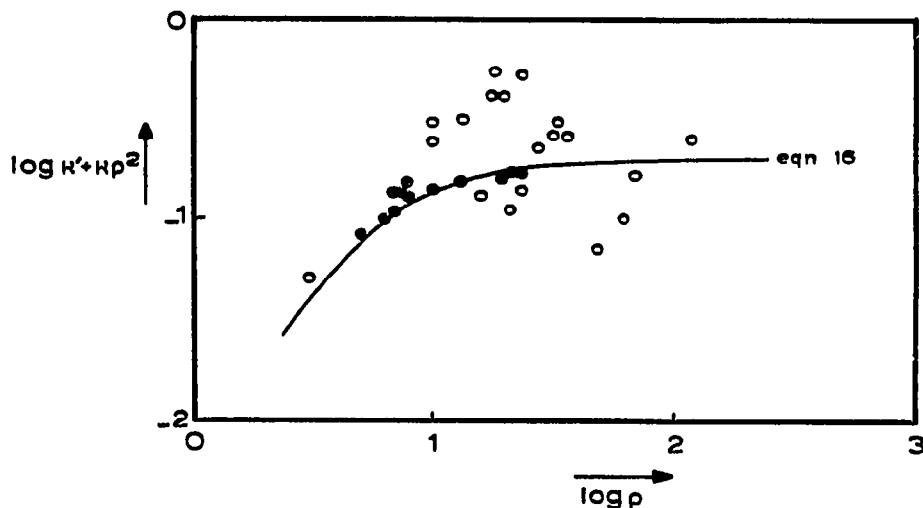

Fig. 4. $\kappa' + \kappa\varrho^2$ as a function of ϱ for liquids. ◯ data from refs 12, 15, 27, 36. ● data from ref 28.

For gases it is difficult to realise v values that are large enough to determine $(\kappa' + \kappa\varrho^2)/\lambda_R$. On the other hand it is easy to realise v values that are so small that the right hand side of eqn. 8 approaches $2v(\kappa' + \kappa\varrho^2)/\gamma$. For gases therefore, $\kappa' + \kappa\varrho^2$ is the more easily accessible quantity. Fig. 5 shows this quantity as a function of ϱ. It appears that the values of $\kappa' + \kappa\varrho^2$ for spherical particles are smaller than those for irregularly shaped ones. We propose the equations:
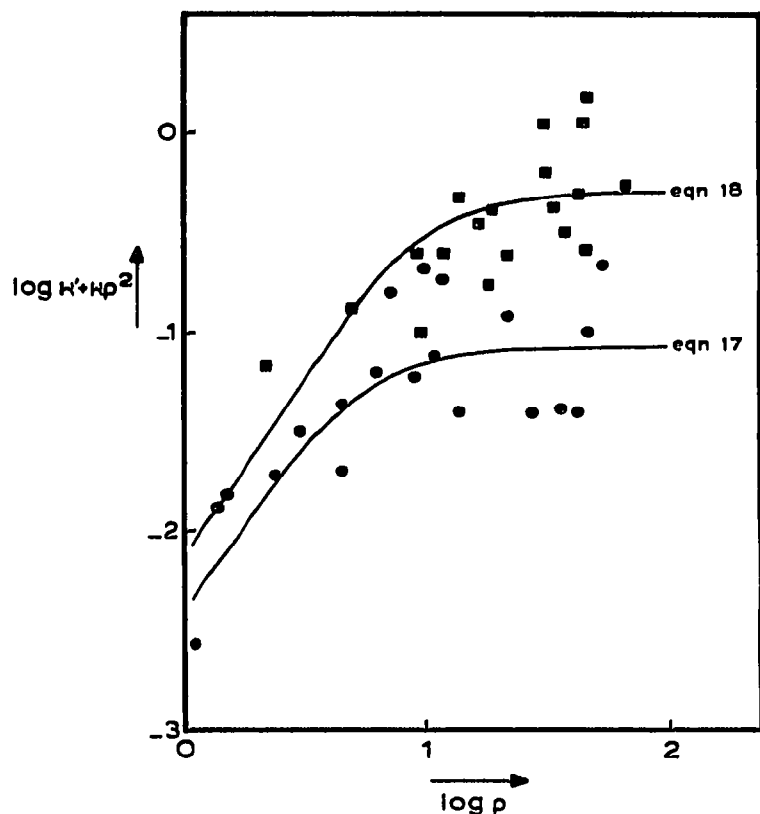
Fig. 5 $\kappa' + \kappa\varrho^2$ as a function of ϱ for gases. ● spherical packing[13-15,30,31,32,35], ■ irregular packing[7,15,16,30,29-34].

$$\text{spherical particles: } \kappa' + \kappa\varrho^2 \text{ (gas)} = \frac{\varrho^2}{12\varrho^2 + 230} \tag{17}$$

$$\text{irregular particles: } \kappa' + \kappa\varrho^2 \text{ (gas)} = \frac{\varrho^2}{2\varrho^2 + 125} \tag{18}$$

combination of eqns. 13, 17 and 18 yields:

$$\text{spherical particles: } 1/Pe_L \text{ (gas)} = (\kappa' + \kappa\varrho^2)/\lambda_R \simeq \frac{2}{3} \tag{19}$$

$$\text{irregular particles: } 1/Pe_L \text{ (gas)} = (\kappa' + \kappa\varrho^2)/\lambda_R = \frac{8\varrho^2 + 155}{2\varrho^2 + 125} \tag{20}$$

Fig. 6 shows that the experimentally found values of $1/Pe_L$ are in fair accord with eqns. 19 and 20.

The classical eddy diffusion coefficient λ

According to eqn. 2, λ is equal to κ'/λ_R. It follows from eqns. 15, 19 and 20 that it is impossible to make a reliable estimate of λ on the basis of the experimental data that have been obtained up to now: from the values of the right hand sides of these equations at $\varrho = 0$, λ values of 0, 0.7 and 1.2 would follow. Moreover, the validity of these equations at $\varrho \approx 0$ is questionable, as they are derived from data at $\varrho > 6$ for liquids and > 3 for gases.
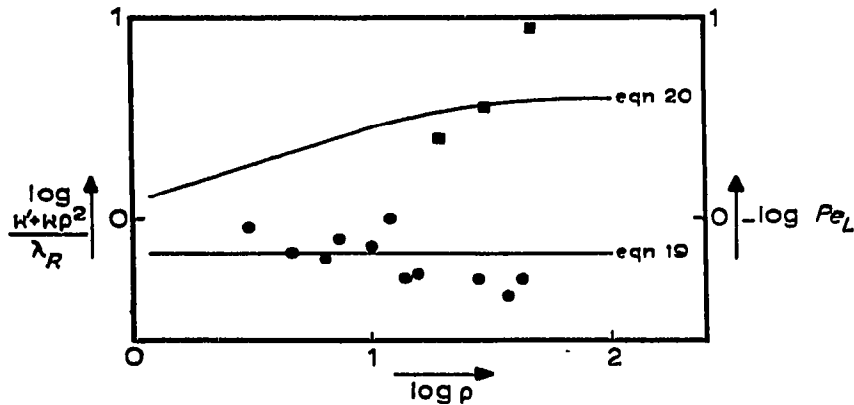
Fig. 6. $(\kappa' + \kappa\varrho^2)/\lambda_R$ as a function of ϱ for gases. ● spherical particles[13-15,35], ■ irregular particles[16].

Influence of the packing method

KNOX and his collaborators[15] have shown that a more efficient column packing is obtained when dry glass beads are packed into an empty column than when wet beads are packed into a column filled with a liquid. The ratio of h values, obtained for these two packing methods at identical values of v and ϱ, resp., is about 0.7 for liquid eluents.

However, this rather small effect is swamped by the variance between the data of different authors.

The influence of different methods of dry packing has been demonstrated by HIGGINS AND SMITH[8].

However, in view of the relatively small effect of the above mentioned extreme variation in packing method (wet vs. dry packing) we may assume that various methods of dry packing, chosen by different investigators as the most efficient one, do not yield significantly different results*.

CONCLUSION

The coefficients of eqn. 8 can be defined as follows in Table I.

TABLE I

Coefficients of eqn. 8	Liquid eluents		Gaseous eluents	
	Spherical packing	Irregular packing	Spherical packing	Irregular packing
λ_R	$2\varrho^3/3(8\varrho^3 + 155)$	$2\varrho^3/3(8\varrho^3 + 155)$	$\varrho^2/(8\varrho^3 + 155)$	$\varrho^2/(8\varrho^3 + 155)$
γ	0.73	0.64	0.73	0.64
$\kappa' + \kappa\varrho^3$	$10\varrho^3/(6\varrho + 15)(8\varrho^3 + 155)$	$10\varrho^3/(6\varrho + 15)(8\varrho^3 + 155)$	$\varrho^2/(12\varrho^2 + 230)$	$\varrho^2/(2\varrho^3 + 125)$
$(\kappa' + \kappa\varrho^2)/\lambda_R$	$5\varrho/(2\varrho + 5)$	$5\varrho/(2\varrho + 5)$	2/3	$(8\varrho^3+155)/(2\varrho^2+12$

* $i.e.$, the bias introduced by this factor merges into the variance between the data of different authors.

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