CHROMSYMP. 2006

Nature of the eddy dispersion in packed beds

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ABSTRACT

Relationships describing the dependence of the height equivalent to a theoretical plate (HETP) on the linear velocity u contain a term that is traditionally called the eddy dispersion term. In some theories, this term is independent of velocity, in others it results in a curved relationship with velocity. Both have been observed experimentally. In this paper, we advocate a theory which is capable of explaining both. This theory is based on the mass-transfer between sections of the mobile phase that move at different velocities. The equation obtained is formally identical to the equation derived by Giddings. However, the meaning of the coefficients in both theories is different. In our approach, the coefficients are related to structural parameters of the packed bed and can be assessed quantitatively. This is helpful in the interpretation of eddy dispersion terms obtained in column packing experiments.

The mathematical approach used here allows the calculation of all moments of the peak and therefore a prediction of the peak-shape. Although a relationship exists between structural parameters of the packed bed and the experimental observations of peak width and peak symmetry, this relationship can only be expressed in the form of the product of velocity difference with a characteristic distance. This term cannot be deconvoluted further. Thus, large velocity differences over small distances result in the same peak-width and -shape as small velocity differences over large distances.

INTRODUCTION

Klinkenberg and Sjenitzer [1] and Van Deemter *et al.* [2] first introduced an equation for the relationship between band-spreading and linear velocity, which contains a term which was called eddy dispersion. In their theory, this term is independent of velocity. Subsequent treatments adopted this term and related it to the non-uniformity of the packed bed. Giddings [3] postulated, that some of the terms related to flow-path non-uniformities couple with mass-transfer terms originating in the same type of non-uniformities. These coupled terms result in a curved relationship with velocity. Kennedy and Knox [4] approximated the Giddings equation with a term containing the third root of the velocity.

It has been argued [5], that the origin of the coupling postulated by Giddings lies in the relaxation of radial concentration gradients by the combined effect of diffusion and eddy dispersion. This is precisely the model which is used in the quantitative theoretical treatment which follows.

BACKGROUND

The propagation of a solute in a liquid flowing through a capillary was first

considered in the famous works of Aris [6] and Taylor [7]. They found that the band width depends on the diffusion coefficient of the solute, the flow profile and the flow-rate. The result is the diffusion equation (1), which describes the change of the average concentration, C, of a species as a function of the longitudinal coordinate x and the time t. Averaging was done over the cross-section of the capillary.

$$\frac{\partial}{\partial t}C + v\frac{\partial}{\partial x}C = D\frac{\partial^2}{\partial x^2}C \qquad\qquad (1)$$

Here, v is the average linear velocity of the liquid and D is an analogue of the diffusion coefficient. This coefficient is often called the effective diffusion coefficient and sometimes the dispersion coefficient.

In laminar flow regimes the expression for this coefficient is as follows

$$D = D_{\text{mol}} + c\frac{r_c^2 v^2}{D_{\text{mol}}} \qquad\qquad (2)$$

Here, D_{mol} is the molecular diffusion coefficient, r_c is the radius of the capillary and c is a constant which depends on the flow profile. For laminar flow in a circular capillary the value of the constant c is $1/48$. This effective diffusion coefficient is closely related to h, the reduced plate height, which is the parameter commonly used in chromatography.

$$h = \frac{D}{rv}$$

It is important to note, that the deduction of the eqns. 1 and 2 assumes that the time of peak propagation is sufficiently large. The result of this "long" peak propagation is that the shape of the peak becomes completely symmetrical. Such peaks are called Gaussian peaks.

Golay [8] has generalized the deduction of Aris and Taylor to the case in which the surface layer of the capillary has retentive properties. In this case, sample molecules spend some time in the boundary layer thus causing a delay of the peak in the capillary and some additional band spreading. In general, the form of the equation which describes the evolution of the concentration profile remains the same as in the case of no retention. In other words, chromatography in long capillaries always yields symmetrical peaks. The work of Golay is a cornerstone of the theory of chromatography, which has been refined since by a large number of researchers [9,10].

The phenomena observed in a capillary are also encountered in a packed bed. However additional complications arise from the structural properties of the packed bed. These structural properties give rise to additional terms in the relationship of band-broadening and flow velocity. They can also be the cause of peak asymmetry. In the theory developed below, both effects are explained on the basis of the propagation of the sample band under equilibrium conditions in a packed bed with non-uniformities on the micro-scale. In this context the prefix "micro" means that the scale is in the range of a few particle diameters.

It is proper to point out, that the results of this work are applicable not only to packed beds, but also to any other porous media, since no assumption is made on the particular inner geometry of the medium. Nevertheless, for the sake of consistency we will refer to the medium as a packed bed.

STATEMENT OF THE MODEL

Let us suppose, for simplicity, that our packed bed consists of two component phases in which the migration velocity of the peak is different. Segments with different interstitial porosities or particles with different particle porosities or surface chemistry could cause this effect. The parameters of these phases are denoted by the indices 1 and 2. Each of them will be considered as a continuum. Let v_β and D_β be respectively the average linear velocity and coefficient of effective diffusion of a solute in the segments with the index β (β can take the values 1 or 2). Also suppose, that these phases are evenly mixed. A clear and simple example of such a mixture might be a structure, where flat layers of these phases alternate and the column axis is parallel to these layers. Let δ_β be the thickness of these layers.

It is important to remember, that v_β and D_β are not just flow velocities and molecular diffusion coefficients, but are rather the peak propagation velocities and effective dispersion coefficients (which are, generally speaking, a function of the velocities v_β). The tensor nature of the diffusion coefficients is apparent from the difference between the components of these tensors in the direction of the respective velocities and the components in the directions orthogonal to the velocities. Denote C_α the concentration of the sample in each phase and λ the mass transfer coefficient between these phases. The system of equations describing the band propagation in such a medium may be written as follows

$$\frac{\partial}{\partial t}C_1 + v_1\frac{\partial}{\partial x}C_1 = D_1\frac{\partial^2}{\partial x^2}C_1 + \kappa_1(C_2 - C_1) \tag{3}$$

$$\frac{\partial}{\partial t}C_2 + v_2\frac{\partial}{\partial x}C_2 = D_2\frac{\partial^2}{\partial x^2}C_2 + \kappa_2(C_1 - C_2) \tag{4}$$

If the volume fractions of the phases are α_1 and α_2 then

$$\alpha_1 + \alpha_2 = 1 \tag{5}$$

$$\kappa_1 = \frac{\lambda}{\alpha_1} \qquad \kappa_2 = \frac{\lambda}{\alpha_2} \tag{6}$$

Eqns. 3 and 4 are one-dimensional and have the same nature as eqn. 1. The coefficients D_1 and D_2 are just the longitudinal components of the corresponding effective diffusion tensors. Cross-sectional mixing is taken into account by adding the mass-transfer terms to the system of equations. The mass-transfer coefficient λ can be derived from the effective diffusion coefficients in the direction across the column (which generally speaking are different for the two components because they are functions of the velocities v_1 and v_2).

MASS-TRANSFER COEFFICIENT

Let C^* be the concentration of the sample at the interface between these two phases. The mass flux of the sample from the first phase to the second is

$$F = D_{\mathrm{rad}_1} \frac{S}{\delta_1}(C_1 - C^*) \tag{7}$$

Here, D_{rad_1} is the effective diffusion coefficient in the first phase in the radial direction and S is the interface area per unit of column volume.
    On the other hand

$$F = D_{\mathrm{rad}_2} \frac{S}{\partial_2}(C^* - C_2) \tag{8}$$

and

$$F = \lambda(C_1 - C_2) \tag{9}$$

Eliminating F and C^* from the eqns. 7, 8 and 9 one obtains the expression for the mass-transfer coefficient λ

$$\lambda = \frac{S D_{\mathrm{rad}_1} D_{\mathrm{rad}_2}}{\delta_2 \delta_1 \left(\dfrac{D_{\mathrm{rad}_2}}{\delta_2} + \dfrac{D_{\mathrm{rad}_1}}{\delta_1} \right)} \tag{10}$$

To estimate the mass-transfer coefficient λ one must first derive the effective coefficients of the radial diffusion. In a packed bed, this type of diffusion is a sum of essentially two terms. One is related to molecular diffusion and the second is caused by the branching of the flow-paths on the micro-scale. From the dimensional analysis the expression is of the following form

$$D_{\mathrm{rad}} = \frac{1}{1 + k''}(B D_{\mathrm{mol}} + 2 A r w)$$

In this expression the interstitial velocity of the flow w is usually used instead of the peak propagation velocity v. The ratio of these velocities is $w/v = 1 + k''$. k'' is called the zone capacity factor [9]. k'' is equal to zero for samples which do not penetrate the particles and are not retained on the surface of the particles.
    The dimensionless constant B contains the obstruction factors for molecular diffusion in the packed bed and in the particle combined with a factor for the ratio of the pore volume to the interstitial volume.
    The dimensionless quantity A may also be a function of the dimensionless velocity $r w/D_{\mathrm{mol}}$ (at least the dimensional analysis creates no obstacle for such a dependence). In the literature [11,12] a constant value has been accepted for this term.

For further estimations we simplify the expression 10 via the following two hypotheses:

$$D_{\mathrm{rad}_1} = D_{\mathrm{rad}_2} \qquad S = \frac{a}{(\delta_2 + \delta_1)}$$

The second expression might be obtained for specific structures, when the phases are stretched along the column and evenly distributed over the cross section. A chess board structure (in the cross section of the column) might be a good example here. The constant a is a dimensionless constant, which is proportional to the number of interphase surfaces passing through the unit area of the cross section of the column. In this case one can get the following expression for λ

$$\lambda = \frac{a}{(\delta_2 + \delta_1)^2} D_{\mathrm{rad}} = \frac{a(BD_{\mathrm{mol}} + 2Arw)}{(\delta_2 + \delta_1)^2 (1 + k'')} \qquad (10a)$$

EQUATION FOR THE AVERAGE CONCENTRATION

In practice, the only measurable quantity is the average concentration C.

$$C \equiv C_1\alpha_1 + C_2\alpha_2$$

Hence, it is suitable to transform the eqns. 3 and 4 into the form where C is one of the dependent variables. As a coupled variable, the difference $\varDelta$ between concentrations C_1 and C_2 might be chosen

$$\varDelta \equiv C_2 - C_1$$

At equilibrium, this number becomes much smaller than the average concentration C and in the limit approaches zero. In this way, the value of $\varDelta$ is the indicator of the closeness to the state of equilibrium.

It is easy to see that

$$C_1 = C - \varDelta\alpha_2 \qquad C_2 = C + \varDelta\alpha_1 \qquad (11)$$

To derive the equation for C one can multiply the eqns. 3 and 4 by α_1 and α_2, respectively, add the results, and substitute then C_1 and C_2 by the expressions 11.

$$\frac{\partial}{\partial t}C + v\frac{\partial}{\partial x}C = D\frac{\partial^2}{\partial x^2}C - (v_2 - v_1)\frac{\partial}{\partial x}\varDelta + (D_2 - D_1)\frac{\partial^2}{\partial x^2}\varDelta \qquad (12)$$

Here, v is the average velocity

$$v = v_1\alpha_1 + v_2\alpha_2$$

and D is the average effective longitudinal diffusion coefficient

$$D = D_1\alpha_1 + D_2\alpha_2$$

Subtracting eqns. 4 and 3 and substituting the expressions 11 and 12 one can get the equation for Δ

$$\frac{\partial}{\partial t}\Delta + (v_2\alpha_1 + v_1\alpha_2)\frac{\partial}{\partial x}\Delta - (D_2\alpha_1 + D_1\alpha_2)\frac{\partial^2}{\partial x^2}\Delta + \Delta(\kappa_2 + \kappa_1) =$$

$$= -(v_2 - v_1)\frac{\partial}{\partial x}C + (D_2 - D_1)\frac{\partial^2}{\partial x^2}C \qquad (13)$$

EQUATIONS FOR THE MOMENTS

Further analysis of the system of eqns. 12 and 13, is facilitated by rewriting this system in the frame moving along the axis x with the velocity v. If v is the peak migration velocity, then all the moments of C in this coordinate system will automatically be central.

The corresponding equations are as follows

$$\frac{\partial}{\partial t}C - D\frac{\partial^2}{\partial x^2}C = -(v_2 - v_1)\frac{\partial}{\partial x}\Delta + (D_2 - D_1)\frac{\partial^2}{\partial x^2}\Delta \qquad (14)$$

$$\frac{\partial}{\partial t}\Delta + (v_2 - v_1)(\alpha_1 - \alpha_2)\frac{\partial}{\partial x}\Delta - (D_2\alpha_1 + D_1\alpha_2)\frac{\partial^2}{\partial x^2}\Delta + \Delta(\kappa_2 + \kappa_1) =$$

$$= -(v_2 - v_1)\frac{\partial}{\partial x}C + (D_2 - D_1)\frac{\partial^2}{\partial x^2}C \qquad (15)$$

By definition, the nth moment of functions $C(t,x)$ and $\Delta(t,x)$ are

$$M_n(t) = \int_{-\infty}^{+\infty} x^n C(t,x)dx \qquad N_n(t) = \int_{-\infty}^{+\infty} x^n \Delta(t,x)dx$$

Let at the initial time $C(0,x) = \delta(x)$ and $\Delta(0,x) = 0$.

Multiplying the eqns. 14 and 15 by x^n and integrating them (by parts, where it is necessary) one can get

$$\frac{d}{dt}M_n = Dn(n-1)M_{n-2} + (v_2 - v_1)nN_{n-1} + (D_2 - D_1)n(n-1)N_{n-2}$$

$$\frac{d}{dt}N_n = (v_2 - v_1)(\alpha_1 - \alpha_2)nN_{n-1} + (D_2\alpha_1 + D_1\alpha_2)n(n-1)N_{n-2} \qquad (16)$$

$$- N_n(\kappa_2 + \kappa_1) + (v_2 - v_1)nM_{n-1} + (D_2 - D_1)n(n-1)M_{n-2}$$

It was taken into account that $N_{-2} = N_{-1} = M_{-2} = M_{-1} = 0$ and the limits of the expressions like $x^n C(t,x)$ and $x^n(t,x)$ are equal to zero in the limit $x \to \infty$.

We can now proceed to calculate step by step the moments of the peak. The second moment is a measure of the peak-width, and the third moment is a measure of the asymmetry of the peak.

The procedure for the solution of this system of equations is merely a recursion. Asymptotically for $t \to \infty$ one can get the solution for the first four moments of the average concentration (the most important from a practical standpoint). How fast these values are reached (or in other words how quickly the equilibrium state is reached) depends only on the constant $\lambda/\alpha_1\alpha_2$. The larger this constant is, the faster this system reaches the state of equilibrium.

The zeroth moment has the meaning of the total sample mass in the system. For normalization it is set to $M_0 = 1$.

The first moment M_1 is the coordinate of the center of gravity of the peak. It is easy to show that $M_1 = 0$. This means that the velocity of the band (in the moving coordinate system) is zero. Hence, v is indeed the peak migration velocity.

The second moment

$$M_2 = 2\left[D + \frac{\alpha_1\alpha_2}{\lambda}(v_2 - v_1)^2 \right] t$$

may be interpreted as the action of some effective diffusion, equal to

$$D_{eff} = D + \frac{\alpha_1\alpha_2(v_2 - v_1)^2}{\lambda}$$

As soon as the velocity difference is not zero, the new effective diffusion D_{eff} differs from D. The consequences of such a difference are discussed later.

The last moment to be considered here is M_3. This moment serves as a measure of the asymmetry of the peak.

$$M_3 = 6\left[(\alpha_1 - \alpha_2)\left(\frac{\alpha_1\alpha_2}{\lambda}\right)^2 (v_2 - v_1)^3 + \frac{\alpha_1\alpha_2}{\lambda}(D_2 - D_1)(v_2 - v_1) \right] t$$

It is clear now, that the magnitude and the sign of the third moment (and consequently the degree of tailing or fronting of the peak) is not automatically zero. The skewness α is a dimensionless measure of asymmetry and is defined as $M_3/M_2^{3/2}$. The skewness is approaching zero with $1/\sqrt{t}$. Hence, after a sufficiently long time the peak always becomes symmetrical. The significance of the asymmetry effect is determined solely by the relation between the second and the third moments, which in turn is a function of time.

NUMERICAL ESTIMATIONS

For comparison with other equations commonly used in chromatography, the model presented here should be translated into the nomenclature of chromatography.

As it was mentioned in the introduction, $h = D_{\mathrm{eff}}/rv$. Substituting the expressions for the effective diffusion coefficient and the mass-transfer coefficient λ one obtains

$$h = \frac{D}{rv} + \frac{4\alpha_1\alpha_2\omega^2\delta^2 wr}{a(BD_{\mathrm{mol}} + 2Arw)} \tag{17}$$

Here the following abbreviations have been used:

$$\delta^2 = \frac{(\delta_2 + \delta_1)^2}{4r^2} \qquad \omega^2 = \frac{\alpha_1\alpha_2(v_2 - v_1)^2}{v^2}$$

δ is the characteristic size of the non-uniformity (in non-dimensional form) and ω is a measure of the velocity variation. With the Peclet number $Pe = 2wr/D_{\mathrm{mol}}$ the eqn. 17 can be expressed in non-dimensional form

$$h = \frac{B^*}{Pe} + C^*Pe + \frac{EPe}{\left(\dfrac{B}{A} + Pe\right)} \tag{18}$$

The first and second terms in eqn. 18 are nothing but the effect of molecular diffusion and mass-transfer in the two phases considered. The form of this equation is identical to the coupling equation derived by Giddings [3]. The coefficient E is defined as

$$E = \frac{2\omega^2\delta^2}{aA}$$

This coefficient contains all assumed non-uniformities, *i.e.* the velocity ratio in the two phases, the characteristic size of the phases, their volume fractions and their characteristic contact area.

When Pe is large compared to the ratio B/A in the denominator of the last term of eqn. 18 then this term becomes constant. Therefore it is interesting to estimate the order of the ratio B/A. If one accepts the value of 0.75 as a typical obstruction factor for molecular diffusion, then $B \approx 0.75$ for a bed prepared from non-porous particles and $B \approx 1.5$ for a bed packed with fully porous particles. In the literature [9], the factor A is given as $A = 0.278(1 - \varepsilon)^{1/2}$, where ε is the interstitial porosity. For a typical column $\varepsilon \approx 0.4$ and consequently $A \approx 0.215$. The ratio B/A then becomes about 3.5 for non-porous particles and 7 for porous particles.

Typical coefficients B^* *and* C^* for a column packed with a well-designed fully porous chromatographic adsorbent are $B^* \approx 3$ and $C^* \approx 1/12$. Therefore the point at which the terms in Pe and $1/Pe$ of eqn. 18 are equal is at $Pe \approx 6$. Consequently the curvature of these two terms intermingles with the curvature of the term derived in this paper and the minimum of the $h(Pe)$ relationship becomes a function of the term E.

There are two equations commonly used in the chromatographic literature to describe the observed relationship between dispersion and velocity. The older one was first derived by van Deemter *et al.* [2] and is given here in dimensionless form:

$$h(Pe) = A^* + \frac{B^*}{Pe} + C^*Pe$$

The second one was first given by Knox and Parcher [13]:

$$h(Pe) = A^* Pe^{\frac{1}{3}} + \frac{B^*}{Pe} + C^* Pe$$

In both equations the A^* term is an empirical descriptor of the quality of the packed bed (eddy diffusion). As above, the B^* term describes molecular diffusion in the direction of flow and the C^* term incorporates all mass-transfer phenomena. It can be shown, that the model 18 yields curves which are indistinguishable from both equations and thus serves as an explanation of the empirical terms with A^*, and our constant E corresponds to the constant A^*.

        This constant can be obtained experimentally and can be used to estimate the magnitude of the velocity fluctuations ω over the size of the non-uniformities δ.

$$\omega \delta \leqslant \sqrt{\frac{1}{2} EaA} \tag{19}$$

This relationship is obviously indeterminate, *i.e.* within the context of the model it is impossible to tell whether a particular value of E determined by experiment is caused by large velocity fluctuations over a small distance or by small velocity fluctuations over a large distance. It can only be said that at the averaging scale δ the average fluctuation ω of the velocity does not exceed a value given by the square-root in eqn. 19. This "uncertainty principle" should be considered in attempts to understand the internal structure of a packed bed based on experimental data of dispersion as a function of velocity.

SYMBOLS

C	average concentration of the solute
w	average linear velocity of the liquid
v	peak migration velocity
D_{mol}	molecular diffusion coefficient
r_c	radius of the capillary
h	reduced plate height
v_β	average linear velocity of a solute in the continua with the index β (β can take the values 1 or 2)
D_β	coefficient of effective diffusion of a solute in the continua with the index β
δ_β	characteristic size of the continua with the index β
α_β	volume fraction of the continua with the index β
λ	mass transfer coefficient between these phases
D_{rad}	effective diffusion coefficient in the radial direction
S	interface area per unit of column volume
k''	zone capacity factor
Δ	difference between concentrations C_1 and C_2
D	average coefficient of the effective longitudinal diffusion
M_n	nth central moment of a function $C(t,x)$

N_n nth central moment of a function $D(t,x)$
D_{eff} effective diffusion coefficient
δ non-dimensional characteristic size of the non-uniformity
ω non-dimensional measure of the velocity variation
Pe Peclet number

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