MATHEMATICAL SIMULATION OF CONTINUOUS GAS CHROMATOGRAPHY IV. EQUILIBRIUM CHROMATOGRAPHY

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Summary

A generalized method is given to solve non-linear ordinary differential equations with non-linear boundary conditions. The problem of multiple boundary conditions is discussed. The method is applied to the equations describing continuous counter-current equilibrium chromatography.

The solutions approximate very well the solutions obtained from the exact non-equilibrium equations with high mass transfer coefficients, but the equilibrium calculations need much less time.

Both diffusion and non-equilibrium cause flattening of the concentration and velocity profiles. The effects caused by non-equilibrium can be approximately described by the equilibrium equations using an "effective" diffusion coefficient.

Introduction

In part III of this series [3] a solution method has been described for the differential equations given in part I and part II [1, 2]. In this part the solution method is generalized to treat problems with no linear boundary conditions, and the case of "equilibrium chromatography" is discussed in detail, with special regard to the choice of the boundary conditions.

The differential equations for equilibrium chromatography have been derived earlier [1]. In dimensionless form [2]:

$$\frac{d^2 y_i}{d\zeta^2} - C1 \left\{ [1 + v - C5\ \Phi'_i(y_i)] \frac{dy_i}{d\zeta} + y_i \frac{dy_i}{d\zeta} - C3 \cdot y_i^m \cdot w \right\} = 0$$

$$(i = 1, 2, \ldots, k) \qquad (1a)$$

$$\frac{dv}{d\zeta} - C3 \cdot w - C5 \sum_{j=1}^{k} \Phi'_j(y_j) \frac{dy_j}{d\zeta} = 0 \qquad (1b)$$

A set of boundary conditions has been given, as well [2], but it proved to be not a fortunate choice, so a new set will be given here.

General solution method for non-linear boundary conditions

The subsequent treatment is a generalization of the method given in part III [3]. To avoid unnecessary repetitions, some references are made to the earlier communication and this section may be hardly understandable without reading part III.

The method uses two—embedded—iterative cycles: an external one for the differential equations (Eq. (III/2) or rather Eqs (III/9 and III/7)) and an internal one for the boundary conditions.

The essence of the method is that there is a boundary with some *linear* boundary conditions:

$$\mathbb{C} \cdot \mathbf{y} = \mathbf{c} \tag{III/13}$$

where the degeneracy of $\mathbb{C}$ is r. After solving Eq. (III/9) and r times Eq. (III/7) to obtain the solutions $\mathbb{Z}_0, \mathbb{Z}_1, \ldots, \mathbb{Z}_r$ the next approximation to the true solution $\mathbb{Z}$ is sought as a linear combination

$$\mathbb{Z} = \mathbb{Z}_0 + \sum_{i=1}^{r} d_i \mathbb{Z}_i \tag{III/11}$$

The coefficients d_i are calculated from the "other side" and/or "mixed" boundary conditions.

If there is no linear boundary condition, one can create dummy ones. If $\mathbb{C}$ is a zero matrix and $\mathbf{c}$ is a zero vector of dimensions $m \cdot m$ and m respectively (m is the number of the necessary boundary conditions), Eq. (III/13) is fulfilled for any $\mathbf{y}$. In this case the degeneracy of $\mathbb{C}$ is m, so Eq. (III/7) has to be solved m times with initial conditions satisfying the "equation"

$$\mathbb{C} \cdot \boldsymbol{\eta}_i = 0 \qquad (i = 1, 2, \ldots, m)$$

Since this condition is fulfilled by any $\boldsymbol{\eta}$, the vectors $\boldsymbol{\eta}_i$ can be chosen freely.

In other words, an external iteration step is made as follows. Eq. (III/9) is solved with initial condition $\boldsymbol{\eta}_0 = 0$ to give $\mathbb{Z}_0$. Eq. (III/7) is solved m times with independent but otherwise arbitrary initial conditions to give the solutions $\mathbb{Z}_i$. An effective, orthogonal system is obtained if the vectors $\boldsymbol{\eta}_i$ are the columns of a unity matrix of dimensions $m \cdot m$.

The next approximation to the solution of the original differential equations—Eq. (III/2)—is sought as

$$\mathbf{Y}_{n+1} = \mathbf{y}_n + \mathbb{Z}_0 + \sum_{i=1}^{m} d_i \mathbb{Z}_i \tag{9}$$

where the coefficients d_i are obtained from the real boundary conditions treated as "mixed".

On substituting the boundary values of Y_{n+1} from Eq. (9) into the boundary conditions, a set of non-linear equations is obtained to calculate the coefficients d_i. These equations determine each d_i unambiguously, but there is no analytical method to solve them, so an internal iteration has to be applied based upon the linearization of the equations. This iteration can be made as given in part III.

Multiplicity of the boundary conditions

The differential equations need a definite number of independent boundary conditions to give a unique solution. The nature of the physical model makes it possible to state more independent boundary conditions than required. For example, the boundary conditions used in case of non-equilibrium chromatography are [2]

$$y_i(1)\,[1+v(0)]+\frac{C2}{C4}\,\Theta_i(0)-C3y_i^m=0 \tag{2a}$$

$$\Theta_i(1)=0 \tag{2b}$$

$$\frac{dy_i}{d\zeta}(1)=0 \tag{2c}$$

$$v(0)=0 \tag{2d}$$

From the mass balance for the carrier gas

$$I_v^o+I_v^m(1-\Sigma y_i^m)=v(1)q\,[1-\Sigma y_i(1)]$$

one obtains

$$v(1)-C3\,(1-\Sigma y_i^m)=[1+v(1)]\,\Sigma y_i(1) \tag{2e}$$

which is by no means deducible from the previous conditions (Eqs (2a–2d)). However, Eq. (2e) must be true if the equations truly describe the physical process. In fact, the solutions always did satisfy Eq. (2e), without using it anywhere during the computation.

The explanation of this seemingly surprising fact is, as shown by V. Kertész [4], that Eqs (2a–2e) are interconnected through—but only through—the differential equations given in Part II [2]:

$$\frac{d^2y_i}{d\zeta^2}-C1\left[(1+v)\frac{dy_i}{d\zeta}+y_i\frac{dv}{d\zeta}+C2(y_i-y_i^*)-C3\cdot y_i^m w\right]=0 \tag{3a}$$

$$\frac{dv}{d\zeta}+C2\sum_{j=1}^{k}(y_j-y_j^*)-C3\cdot w=0 \tag{3b}$$

$$\frac{d\Theta_i}{d\zeta}+C4(y_i-y_i^*)=0 \tag{3c}$$

Indeed, integration of Eqs (3b and 3c) gives

$$\int_0^1 \frac{dv_i}{d\zeta}\,d\zeta + C4 \int_0^1 \sum_{j=1}^k (y_i - y_i^*)\,d\zeta - C3 \int_0^1 w(\zeta)\,d\zeta = 0$$

and

$$\int_0^1 \frac{d\Theta_i}{d\zeta}\,d\zeta + C4 \int_0^1 (y_i - y_i^*)\,d\zeta = 0$$

Per definition

$$\int_0^1 w(\zeta)\,d\zeta = 1$$

$$\int_0^1 \frac{dv}{d\zeta}\,d\zeta = v(1) - v(0)$$

$$\int_0^1 \frac{d\Theta_i}{d\zeta}\,d\zeta = \Theta_i(1) - \Theta_i(0)$$

so using Eqs (2b and 2d) one obtains

$$-v(1) + C3 = \frac{C2}{C4} \sum_i \Theta_i(0) \tag{4}$$

Summing up Eq. (2a) for every i gives

$$\sum_{i=1}^k y_i(1)\,[1 + v(1)] + \frac{C2}{C4} \sum_{i=1}^k \Theta_i(0) - C3 \sum_{i=1}^k y_i^m = 0 \tag{5}$$

Substitution of Eq. (4) into Eq. (5) gives Eq. (2e).

This interconnection is an indirect proof that the set of Eqs (3a–3c) adequately describes the physical process. Any modification in the differential equations can abrogate the interconnection. On the other hand, it can be utilized to simplify the computation: one can select the simplest, most favourable boundary conditions. The omitted one(s) can be used to check the results.

Boundary conditions for equilibrium chromatography

Equilibrium chromatography is an idealization or rather a limiting case. It means that adsorption-desorption equilibrium is maintained throughout the column. Since the material entering the column is not in equilibrium, it is inevitable that some functions have a jump at the boundaries.

The quantities referring to the top and the bottom of the column are indicated by superscripts ^{t} and ^{o}, respectively; the upper sides of the boundaries are marked with a $^+$, the lower sides with a $^-$ sign (Fig. 1).

There is no jump in the gas concentration if diffusion is not negligible, but there can be a jump in the concentration gradient and in the gas flow rate. There can be a concentration jump in the condensed phase, as well, since there the diffusion is assumed to be negligible.

The differential equations are valid only inside the column, so the boundary conditions must not contain "outside" parameters marked with $^{t+}$ or $^{o-}$.

After these preliminary remarks, a new set of boundary conditions can be derived as follows.

The mass balance of the i-th component at the upper boundary can be written as

$$\frac{p}{RT}\, y_i^t (I_V^{t-} - I_V^{t+}) - \frac{Dpq}{RT}\left(\frac{dy_i^{t-}}{dz} - \frac{dy_i^{t+}}{dz}\right) + v_L(a_i^{t-} - a_i^{t+}) = 0$$

The first term is the difference of the convective flows to and from the boundary, the second one is the difference of the diffusive flows, the third term gives the material transported by the condensed phase. a_i^{t+} is usually zero since a pure sorbent is fed, dy_i^{t+}/dz must be zero since there is no interaction outside the column [5], so one can write

$$v_L a_i^{t-} = \frac{Dpq}{RT}\cdot\frac{dy_i^{t-}}{dz} + \frac{p}{RT}(I_V^{t+}\, y_i^t - I_V^{t-}\, y_i^t) \qquad (6a)$$
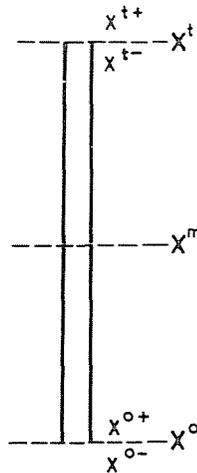

Fig. 1. Superscripts for the boundary values

The value of v_L is always negative since the condensed phase moves downwards.

Similarly, the mass balance for the lower boundary can be written

$$\frac{p}{RT} y_i^\circ (I_V^{\circ+} - I_V^{\circ-}) - \frac{Dpq}{RT} \left(\frac{dy_i^{\circ+}}{dz} - \frac{dy_i^{\circ-}}{dz} \right) + v_L(a_i^{\circ+} - a_i^{\circ-}) = 0$$

The quantity

$$I_V^{\circ-} y_i^\circ - q \frac{dy_i^{\circ-}}{dz}$$

must be zero, if pure carrier gas is fed [5], so the equation can be reduced to

$$v_L(a_i^{\circ+} - a_i^{\circ-}) = \frac{p}{RT} I_V^{\circ+} y^\circ - \frac{Dpq}{RT} \frac{dy_i^{\circ+}}{dz} \tag{6b}$$

A material balance can be stated for the total column, too. For the i-th component

$$\frac{p}{RT} I_V^{t+} y_i^t - v_L a_i^{\circ-} = I_V^m y_i^m \frac{p}{RT} \tag{6c}$$

where the first two terms give the material leaving the column with the carrier gas and with the condensed phase, respectively (the negative sign of v_L compensates that v_L is in itself negative). The term on the right hand side gives the feed in the middle.

A similar balance can be written for the carrier gas. It is fed in the middle and at the bottom and leaves the column at the top:

$$I_V^{\circ+} + I_V^m(1 - \Sigma y_i^m) = I_V^{t+}(1 - \Sigma y_i^t)$$

or

$$I_V^{t+} = \frac{I_V^{\circ+} + I_V^m(1 - \Sigma y_i^m)}{1 - \Sigma y_i^t} \tag{6d}$$

Eqs (6a–6d) include the "outside" parameters I_V^{t+} and $a_i^{\circ-} \cdot I_V^{t+}$ can be eliminated by substituting Eq. (6d) into Eqs (6a and 6c), while $a_i^{\circ-}$ is an inside parameter, as well, since

$$a_i^{\circ-} = a_i^{\circ+} = a_i^\circ \tag{6e}$$

This relation means that there is no finite sorption or description at $z=0$, in contrast with the upper boundary, where a finite amount must be adsorbed to ensure equilibrium concentration. The cause of this difference is that no diffusion in the condensed phase has been assumed, so the equilibration can be reached only by an abrupt change in concentration when the empty condensed phase enters the column, but there is no reason for concentration jump when the equilibrated condensed phase leaves it.

Eq. (6e) implies that there is no jump in the gas flow rate at $z = 0$, either, i.e.

$$I_V^{o+} = I_V^{o-} = I_V^o \tag{6f}$$

This latter relation can be considered as a new—linear—boundary condition.

Summing up, the following boundary conditions can be given:

$$v_L a_i^{t-} + \frac{p}{RT}(I_V^{t-} - I_V^o \omega) y_i^t - \frac{Dpq}{RT} \frac{dy_i^{t-}}{dz} = 0$$

$$I_V^o y_i^o - Dq \frac{dy_i^o}{dz} = 0$$

$$\omega \cdot \frac{p}{RT} I_V^o y_i^t - v_L a_i^o = I_V^m y_i^m$$

$$I_V^{o+} = I_V^o$$

In dimensionless form, substituting the equilibrium equations

$$a_i = \varphi_i(y_i)$$

or rather

$$\Theta_i = \Phi_i(y_i)$$

too:

$$C5\Phi_i[y_i(1)] + [1 + v(1) - \omega]y_i(1) - \frac{1}{C1}\frac{dy_i}{d\zeta}(1) = 0 \tag{7a}$$

$$y_i(0) - \frac{1}{C1}\frac{dy_i}{d\zeta}(1) = 0 \tag{7b}$$

$$\omega \cdot y_i(1) + C5\Phi_i[y_i(0)] = C3 \cdot y_i^m \tag{7c}$$

$$v(0) = 0 \tag{7d}$$

where

$$\omega = \frac{1 + C3(1 - \Sigma y_i^m)}{1 - \Sigma y_i(1)}$$

The definitions of the constants $C1, \ldots, C5$ and of the dimensionless quantities have been given in part II.

Equations (7a–7d) represent $3 \cdot k + 1$ conditions, though Eqs (1a–1b) require only $2 \cdot k + 1$ ones. It can be proved by the method presented in the previous section that conditions given by Eq. (7a) and Eq. (7c) are interconnected through Eqs (1a–1b) and so the more complicated Eq. (7a) can be omitted.

Solution of the equations for equilibrium chromatography

The differential equations are given by Eqs (1a–1b), the boundary conditions by Eqs (7b–7d). If the sorption isotherm is described by a Langmuir type equation, it can be written

$$\Theta_i = \Phi_i(y_i) = \Theta_i^\circ \frac{K \cdot y_i}{1 + K \cdot y_i} \tag{10}$$

where K is a sorption equilibrium constant. For small values of y_i Eq. (10) can be approximated by

$$\Theta_i = \alpha_i y_i \tag{10a}$$

where

$$\alpha_i = K \cdot \Theta_i^\circ$$

and the "normalized" capacity ratio [2] can be given as

$$\kappa_i = \alpha_i \cdot C5 \, .$$

In this latter case the boundary conditions are

$$v(0) = 0$$

$$y_i(0) - \frac{1}{C1} \cdot \frac{dy_i}{d\zeta}(0) = 0$$

$$\omega \cdot y_i(1) + \kappa_i y_i(0) = C3 \cdot y_i^m$$

or, for two partitioning components and using the notation

$$\mathbf{y} = \begin{bmatrix} y_1 \\ y_2 \\ y_3 \\ y_4 \\ y_5 \end{bmatrix} = \begin{bmatrix} v \\ y_1 \\ y_2 \\ dy_1/d\zeta \\ dy_2/d\zeta \end{bmatrix}$$

$$y_1(0) = 0 \tag{11a}$$

$$y_2(0) - \frac{1}{C1} y_4(0) = 0 \tag{11b}$$

$$y_3(0) - \frac{1}{C1} y_5(0) = 0 \tag{11c}$$

$$\omega \cdot y_2(1) + \kappa_1 y_2(0) = C3 \cdot y_i^m \qquad (11d)$$

$$\omega \cdot y_3(1) + \kappa_2 y_3(0) = C3 \cdot y_2^m \qquad (11e)$$

The first three equations are linear and refer to $\zeta = 0$, so the procedure given in part III. can be applied. The only difference is that the integration now must be made "normally", i.e. from $\zeta = 0$ to $\zeta = 1$.

The linear boundary conditions—Eqs (11a–11c)—can be written

$$\mathbf{B} \cdot \mathbf{y}(0) = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & -1/C1 & 0 \\ 0 & 0 & 1 & 0 & -1/C1 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix} \cdot \mathbf{y}(0) = \mathbf{0} \qquad (12)$$

The degeneracy of $\mathbf{B}$ is $r = 2$. A full orthogonal solution of Eq. (12) is

$$\boldsymbol{\eta}_1 = \begin{bmatrix} 0 \\ \gamma \\ 0 \\ -C1 \cdot \gamma \\ 0 \end{bmatrix} \qquad \boldsymbol{\eta}_2 = \begin{bmatrix} 0 \\ 0 \\ \gamma \\ 0 \\ -C1 \cdot \gamma \end{bmatrix} \qquad (13)$$

where

$$\gamma = \frac{1}{\sqrt{1 + C1^2}}$$

Integrating Eq. (III/9) [3] with initial conditions $\boldsymbol{\eta}_0 = \mathbf{0}$ and Eq. (III/7) with initial conditions $\boldsymbol{\eta}_1$ and $\boldsymbol{\eta}_2$ one obtains the solutions $\mathbf{Z}_0$, $\mathbf{Z}_1$ and $\mathbf{Z}_2$, respectively. The next approximation to y is given as

$$\mathbf{Y}_{n+1} = \mathbf{y}_n + \mathbf{Z}_0 + d_1 \mathbf{Z}_1 + d_2 \mathbf{Z}_2 \qquad (14)$$

and the following conditions must be fulfilled owing to Eqs (11d–11e):

$$\omega \cdot Y_{2,n+1}(1) + \kappa_1 \cdot Y_{2,n+1}(0) = C3 \cdot y_1^m$$

$$\omega \cdot Y_{3,n+1}(1) + \kappa_2 \cdot Y_{3,n+1}(0) = C3 \cdot y_2^m$$

On substituting Eq. (14) for $\mathbf{Y}_{n+1}$ and assuming ω to be constant, one obtains two linear equations to determine d_1 and d_2. From d_1 and d_2 $\mathbf{Y}_{n+1}$ is determined and a new value for ω is calculated. Substituting $\mathbf{Y}_{n+1}$ for $\mathbf{y}_n$ the

procedure can be continued until convergence is obtained. The convergence can be accelerated by the procedure given in part III.

To check the results, it is possible to integrate Eqs (1a–1b) backwards, from $\zeta = 1$ to $\zeta = 0$. In this case no linear condition is known at the starting point and only the generalized method given above can be applied. The initial conditions now are

$$\eta_0 = 0$$

$$\eta_1 = \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} \qquad \eta_2 = \begin{bmatrix} 0 \\ 1 \\ 0 \\ 0 \\ 0 \end{bmatrix} \qquad \eta_3 = \begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \\ 0 \end{bmatrix}$$

$$\eta_4 = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \\ 0 \end{bmatrix} \qquad \eta_5 = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 1 \end{bmatrix}$$

Eq. (III/7) has to be integrated five times, instead of twice as in the previous case. Five values of d_i have to be calculated from a more complicated set of non-linear equations obtained by substitution of

$$\mathbb{Y}_{n+1} = y_n + \mathbb{Z}_0 + \sum_{i=1}^{5} d_i \mathbb{Z}_i$$

into Eqs (11).

The final solutions obtained by the two methods are identical proving the reliability of both of them. The second method needs a greater amount of numerical integration, CPU time and memory space, but in some cases (with large values of C1) the convergence was more rapid and the whole system was more stable when using the general method.

It has to be noted that the general method can be used in case of linear boundary conditions, as well. The initial conditions given by Eqs (14) can also be used when integrating from $\zeta = 0$ to $\zeta = 1$. The final results are the same as in the previous two cases. The time and space requirements are similar to those of the case when integrating from $\zeta = 1$ to $\zeta = 0$. Care must be taken, however, that the arbitrary initial conditions do *not* satisfy the real boundary conditions,

since then the equations determining the coefficients d_i become overdetermined when approaching the real solution. After an eventual initial convergence the procedure becomes divergent and/or terminates by overflow or zerodivide.

Results and discussion

Equilibrium chromatography is a theoretical limiting case that can never be realized perfectly. It means infinitely great mass transfer coefficients β_i or, in terms of the dimensionless quantities, it is characterized by $C2 \rightarrow \infty$ and $C4 \rightarrow \infty$ while $C2/C4 = C5$ remains constant. This idealized case is very important, however, since with growing values of C2 and C4 the integration of the non-equilibrium equations requires more and more time and unsurmountable numerical problems arise when passing a certain limit. The integration of the equilibrium equations is much faster, and the results approximate very well those of the correct non-equilibrium equations for high values of C2 and C4.

Figure 2 presents the results of a series of calculations. C2 and C4 have been varied, while all the other parameters ($C1 = 150$, $C3 = 0.01$, $C5 = 1200$, $\kappa_1 = 0.8$, $\kappa_2 = 1.2$, $y_1^m = y_2^m = 0.5$) have been kept constant. It can be seen that for $C2 = 3600$ the curves are practically the same as for equilibrium chromatography, but one integration of the non-equilibrium equations takes much more time, the difference being at least one order of magnitude.
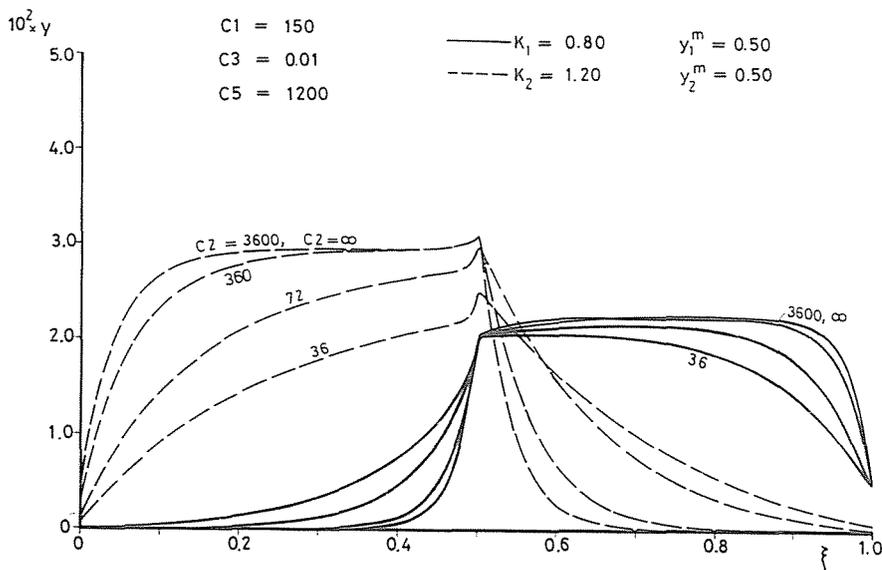

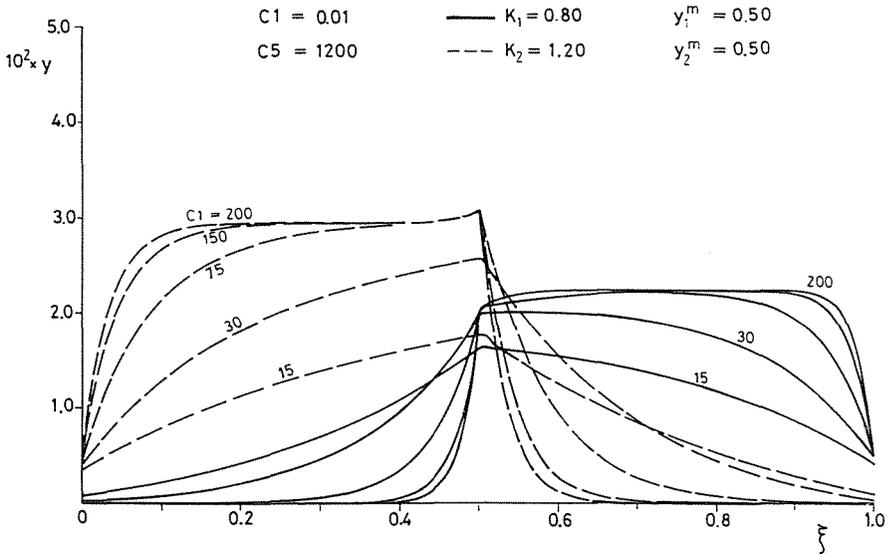*Fig. 2.* Effect of the mass transfer coefficient on the concentration profiles

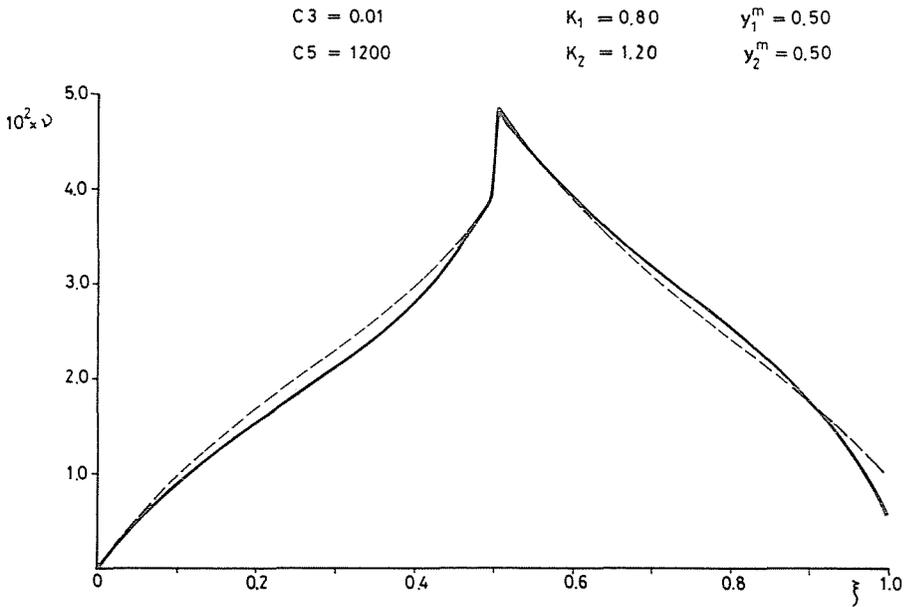*Fig. 3*. Effect of the Pe number on the concentration profiles

Fig. 4. Calculated velocity profiles.
Continuous line: non-equilibrium calculation with C1 = 150 and C2 = 36
Dotted line: equilibrium calculation with C1 = 25

Figure 3 shows the results of a series of equilibrium calculations. Here only the Peclet number, C1—i.e. the diffusion coefficient—has been varied. The effect of growing diffusion coefficients (decreasing values of C1) is qualitatively the same as that of the decreasing mass transfer coefficients. In fact, both diffusion and slow mass transfer cause dispersion in chromatography and, viewed in the large, the two processes cause the same effect: flattening of the profiles.

Strictly speaking, the profiles for equilibrium chromatography can never be identical with those of the non-equilibrium case, if not for other reason, then because of the different boundary conditions. In the non-equilibrium case $y'_i(1)$ $= 0$, while in equilibrium chromatography these values can never be zero.

The similarity is surprisingly good, however. Figure 4 presents two flow rate profiles: one for non-equilibrium chromatography with $C2 = 36$ and $C1$ $= 150$, and another for the equilibrium case ($C2 = \infty$) with $C1 = 25$. All the other parameters are the same: $C3 = 0.01$, $C5 = 1200$, $\kappa_1 = 0.8$, $\kappa_2 = 1.2$, $y_1^m = y_2^m$ $= 0.5$.

This similarity renders it possible, to use in many cases the simpler equilibrium equations instead of the correct ones. Non-equilibrium can be taken into account by an "effective" diffusion coefficient. It must not be forgotten, however, that the two dispersion effects are rather different. Molecular dispersion is decreasing with increasing flow rate, while non-equilibrium is characteristic at higher flow rates. (C.f. the van Deemter equation for elution chromatography.)

Acknowledgement

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