MATHEMATICAL SIMULATION OF CONTINUOUS GAS CHROMATOGRAPHY II

DIMENSIONLESS EQUATIONS

By

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Introduction

In a previous communication [1] a set of differential equations have been set up to describe the behaviour of a continuous chromatographic column:

$$D\frac{d^2y_i}{dz^2} = \frac{d(vy_i)}{dz} + \frac{RT}{pq}\cdot S_i - \frac{I_v^m y_i^m}{q} w \qquad (i = 1, 2, \ldots, k) \tag{1a}$$

$$\frac{dv}{dz} = \frac{I_v^m}{q} w - \frac{RT}{pq}\sum_{j=1}^{k} S_j \tag{1b}$$

$$\frac{da_i}{dz} = \frac{S_i}{v_L} \qquad (i = 1, 2, \ldots, k) \tag{1c}$$

Where:

z = axial co-ordinate;

D = diffusion coefficient;

p = pressure;

q = free cross sectional area;

y_i = mole fraction of component i in the gas phase;

a_i = amount (in moles) per unit length, of component i in the condensed phase;

v = linear gas velocity;

v_L = linear velocity of the condensed phase;

I_v^m = volume flow rate of the sample introduced in the middle;

y_i^m = mole fraction of component i in this sample;

w = weight function;

k = number of the eluted components (except the carrier);

S_i = sorption rate of component i per unit length.

In order to reduce the number of the parameters and to obtain more general results, a series of dimensionless parameters will now be introduced.

Non-equilibrium chromatography

The following boundary conditions prevail in this case [1]:

$$\left.\begin{aligned} v_L a_i^0 + \frac{p}{RT}(q v^t y_i^t - I_v^m y_i^m) &= 0 \\ a_i^t &= 0 \\ \frac{dy_i^t}{dz} &= 0 \end{aligned}\right\} (i = 1, 2, \ldots, k) \quad (2)$$

$$v^0 = \frac{I_v^0}{q}$$

The superscripts 0, m and t refer to the lower boundary, the central feeding zone and the upper boundary of the column, respectively.

Let us define the relative velocity difference

$$v = \frac{v - v^0}{v^0} \quad (3)$$

and the characteristic length

$$\zeta = \frac{z}{L} \quad (4)$$

where L is the total length of the column. A new weight function,

$$w^*(\zeta) = L \cdot w(L\zeta) \quad (5)$$

is then to be written instead of $w(z)$, since the equation

$$\int_0^1 w^*(\zeta)\, d\zeta = 1 \quad (6)$$

must remain valid, and

$$1 = \int_0^L w \cdot dz = \int_0^L \frac{w^*}{L} d(L\zeta) = \int_0^{L/L} w^* d\zeta$$

For sake of simplicity, the function $w^*(\zeta)$, Eq. (5) will henceforth be written as w.

The reference quantity a_0 for the adsorption a_i is the unimolecular adsorption, or some related, well-defined quantity, e.g. the adsorption at the so-called point B in case of a BET isotherm. So, the sorption can be

characterized by the dimensionless coverage

$$\theta_i = \frac{a_i}{a_0} \tag{7}$$

The overall sorption rates S_i — if the intrinsic rates are high enough — are controlled by diffusion and can be described by the mass transfer coefficient β_i:

$$S_i = \beta_i A(c_i - c_i^*) = \beta_i A \frac{p}{RT}(y_i - y_i^*).$$

c_i and c_i^* are the actual concentrations of the species i in the gas phase and that in equilibrium with θ_i, respectively, A is the surface of the sorbent per unit length (m^2/m). The terms β_i are theoretically different — they are essentially the ratios of diffusivities D_i to the film thickness — but once having accepted an average diffusivity D, the use of an average β is at hand. So we accept

$$S_i = \frac{\beta A p}{RT} \Delta y_i \tag{8}$$

where Δy_i stands for $(y_i - y_i^*)$.

By the aid of the quantities defined by Eqs (3) to (8) the set of Eqs (1) can be written in the form

$$\frac{d^2 y_i}{d\zeta^2} = \frac{LI_v^o}{qD}\left(\frac{dy_i}{d\zeta} + \frac{d(vy_i)}{d\zeta}\right) + \frac{\beta L^2 A}{qD}\Delta y_i - \frac{I_v^m L}{qD} \cdot y_i^m w$$

$$\frac{dv}{d\zeta} = -\frac{\beta AL}{I_v^o}\sum_{j=1}^{k}\Delta y_j + \frac{I_v^m}{I_v^o} w$$

$$\frac{d\theta_i}{d\zeta} = \frac{\beta LAp}{RTv_L a_0}\Delta y_i$$

and introducing the dimensionless groups

$$\begin{aligned} C1 &= \frac{v^0 L}{D} = \frac{LI_v^0}{qD} \\ C2 &= \frac{\beta LA}{I_v^0} \\ C3 &= \frac{I_v^m}{I_v^0} \\ C4 &= -\frac{\beta pLA}{RTv_L a_0} \end{aligned} \tag{9}$$

the set turns to

$$\frac{d^2y_i}{d\zeta^2} - C1\left[(1+v)\frac{dy_i}{d\zeta} + y_i \cdot \frac{dv}{d\zeta} + C2(y_i - y_i^*) - C3 \cdot y_i^m \cdot w\right] = 0 \quad (10a)$$

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

$$\frac{dv}{d\zeta} + C2 \sum_{j=1}^{k} (y_j - y_j^*) - C3 \cdot w = 0 \quad (10b)$$

$$\frac{d\theta_i}{d\zeta} + C4(y_i - y_i^*) = 0 \qquad (i = 1, 2, \ldots, k) \quad (10c)$$

C1 is the Peclet group Pe, and C3 is the ratio of flow rates of gases introduced in the middle and at the bottom. To interpret C2 and C4, let us notice that

$$\beta AL \frac{p}{RT} = \beta AL(c_0 - 0)$$

is the upper limit of mass transfer rate realizable on the column. C2 is the rate of this "mass transfer capacity" to the feed at the bottom, while C4 is the ratio of the "mass transfer capacity" to the "sorption capacity" $v_L a_0$. (This latter is the highest possible rate at which material can leave the column in adsorbed state.)

In case of gas-liquid chromatography, the mole fraction in the liquid phase x_i can be used instead of θ_i. Eqs (10a) and (10b) are not affected by this modification, but (10c) becomes

$$\frac{dx_i}{d\zeta} + C4' \frac{1 - \sum_{j=1}^{k} x_j}{1 + \dfrac{x_i}{1 - \sum_{j=1}^{k} x_j}} (y_i - y_i^*) = 0 \quad (i = 1, 2, \ldots, k) \quad (11c)$$

where

$$C4' = -\frac{\beta p AL}{RTv_L L_0} \quad (9'd)$$

and L_0 is the amount of solvent (in mol) per unit length.

The boundary conditions given by Eqs (2) can also be given in dimensionless form:

$$y_i(1) \cdot [1 + v(1)] - \frac{C2}{C4} \cdot \theta_i(0) - C3 \cdot y_i^m = 0 \qquad (12a)$$

$$\theta_i(1) = 0 \qquad (12b)$$

$$\frac{dy_i}{d\zeta}(1) = 0 \qquad (12c)$$

$$(i = 1, 2, \ldots, k).$$

$$v(0) = 0 \qquad (12d)$$

In case of gas-liquid chromatography the last two equations are the same, the first two turn to

$$y_i(1) \cdot [1 + v(1)] - \frac{C2}{C4'} \cdot \frac{x_i(0)}{1 - \sum_{j=1}^{k} x_j(0)} - C3 \cdot y_i^m = 0 \qquad (12'a)$$

and

$$x_i(1) = 0\,. \qquad (12'b)$$

Disregarding the weight function w — its form has little importance except for short columns — the system and its working parameters can be characterized by four dimensionless groups. This fact facilitates a general treatment. Naturally, to compute factual concentration profiles, one needs in addition the equilibrium data and input concentrations (y_i^m) of the components.

Equilibrium chromatography

For high sorption rates or high C2, an equilibrium between the gas and condensed phases can practically be achieved. It has been proved [1] that in this case both S_i and a_i can be eliminated from Eqs (1). a_i or rather θ_i can be calculated from y_i by equilibrium relationships. The set of equations then takes the form

$$D\frac{d^2y_i}{dz^2} = \frac{d(vy_i)}{dz} + \frac{RTv_L}{pq}\varphi_i'\frac{dy_i}{dz} - \frac{I_v^m y_i^m}{q}w \qquad (i = 1, 2, \ldots, k) \qquad (13a)$$

$$\frac{dv}{dz} = \frac{I_v^m}{q}w - \frac{RTv_L}{pq}\sum_{j=1}^{k}\varphi_j'\frac{dy_j}{dz} \qquad (13b)$$

The terms φ_i represent equilibrium relationships

$$a_i = \varphi_i(y_i) \qquad (14)$$

and

$$\varphi_i' = \frac{d\varphi_i}{dy_i}\,. \qquad (14')$$

Introducing the quantities defined by Eqs (3) to (8) and considering the definition

$$\Phi_i = \Phi_i(y_i) = \frac{\varphi_i}{a_0} \tag{15}$$

Eqs (14) may be written as

$$\frac{\mathrm{d}^2 y_i}{\mathrm{d}\zeta^2} = \frac{v_0 L}{D}\left[\frac{\mathrm{d}y_i}{\mathrm{d}\zeta} + \frac{\mathrm{d}(\nu y_i)}{\mathrm{d}\zeta} + \frac{RTv_L a_0}{I_v^0 p}\Phi_i' \frac{\mathrm{d}y_i}{\mathrm{d}\zeta} - \frac{I_v^m}{I_v^0} y_i^m \cdot w\right]$$

$$\frac{\mathrm{d}\nu}{\mathrm{d}\zeta} = \frac{I_v^m}{I_v^0} w - \frac{RTv_L a_0}{I_v^0 p} \cdot \sum_{j=1}^{k} \Phi_j' \frac{\mathrm{d}y_j}{\mathrm{d}\zeta}$$

or

$$\frac{\mathrm{d}^2 y_i}{\mathrm{d}\zeta^2} = \mathrm{C1}\left[(1 + \nu + \mathrm{C5} \cdot \Phi_i') \frac{\mathrm{d}y_i}{\mathrm{d}\zeta} + y_i \cdot \frac{\mathrm{d}\nu}{\mathrm{d}\zeta} - \mathrm{C3} \cdot y_i^m \cdot w\right] = 0 \tag{16a}$$

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

$$\frac{\mathrm{d}\nu}{\mathrm{d}\zeta} = \mathrm{C3} \cdot w + \mathrm{C5} \cdot \sum_{j=1}^{k} \Phi_j' \frac{\mathrm{d}y_j}{\mathrm{d}\zeta} = 0\,. \tag{16b}$$

C1 and C3 have already been defined, while

$$\mathrm{C5} = -\frac{RTv_L a_0}{pI_v^0} = \frac{\mathrm{C2}}{\mathrm{C4}} \tag{9e}$$

i.e. the ratio of the "sorption capacity" to the molar flow rate of the feeding at the bottom. To sum up, the column can now be characterized by three dimensionless groups.

In equilibrium chromatography the boundary conditions are rather different from Eqs (2) [1]:

$$-v_L \cdot \varphi_i(y_i^t) + \frac{Dpq}{RT} \cdot \frac{\mathrm{d}y_i^{t-}}{\mathrm{d}z} = 0 \qquad (i = 1, 2, \ldots, k) \tag{17a}$$

$$v_L \varphi_i(y_i^0) + \frac{pq}{RT}\left[v^{0+} y_i^0 - \left(v^{t-} + D\sum_j \frac{\mathrm{d}y_j^{t-}}{\mathrm{d}z}\right) y_i^t - D\frac{\mathrm{d}y_i^{0+}}{\mathrm{d}z}\right] + \frac{pI_v^m}{RT} y_i^m = 0$$

$$(i = 1, 2, \ldots, k) \tag{17b}$$

$$v^{0+} \cdot \left(1 - \sum_j y_j^0\right) = \frac{I_v^0}{q} - D\sum_j \frac{\mathrm{d}y_j^{0+}}{\mathrm{d}z} \tag{17c}$$

or in dimensionless form

$$\frac{dy_i}{d\zeta}(1-0) + C1 \cdot C5 \cdot \Phi_i[y_i(1)] = 0 \quad (i = 1, 2, \ldots, k) \tag{18a}$$

$$\frac{dy_i}{d\zeta}(+0) + C1 \cdot C5 \cdot \varphi_i[y_i(0)] + y_i(1) \cdot [C1 + C1 \cdot \nu(1-0) +$$

$$+ \sum_j \frac{dy_j}{d\zeta}(1-0)] - C1 \cdot [1 + \nu(+0)] \cdot y_i(0) - C1 \cdot C3 \cdot y_i^m = 0 \tag{18b}$$

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

$$\sum_j \frac{dy_j}{d\zeta}(+0) + C1 \cdot \nu(+0) - [1 + \nu(+0)] \sum_j y_j(0) = 0 \tag{18c}$$

There are discontinuities at the boundaries of the column, but they do not raise difficulties since only the column side limiting values occur in Eqs (18).

Linear isotherms

When θ_i or x_i are small enough, the sorption isotherms are nearly always linear, and can be characterized by a single partition coefficient or capacity ratio. Although our model is not limited to linear isotherms — in fact, we consider it to be the most important in non-linear cases — the general use of linear isotherms in chromatography justifies a somewhat detailed treatment of the topic. In addition, we can point out some relations between the parameters of classical and continuous chromatographies.

One of the fundamental quantities in classical chromatography is the capacity ratio (capacity factor, mass distribution ratio) k'. It means the fraction of a component in the stationary phase divided by the fraction in the mobile phase, supposing equilibrium. In case of a linear isotherm k' is constant and determines the migration velocity v_m:

$$v_m = \frac{v^0}{1 + k'} \tag{19}$$

v^0 is the velocity of the carrier gas supposed to be constant. But even at constant k', Eq. (19) is only true for infinitesimal concentration of the solute, since the gas velocity in the chromatographic wave is greater than v^0. It has also to be kept in mind that the term "linear isotherm" is never absolute, it refers only to a part of the isotherm — for small θ_i or x_i values.

Let us examine the relationship between k', v_L and v^0 in continuous chromatography, when the concentration of the solute is infinitesimal. Be v_r the migration velocity of the solute referred to the moving condensed phase. It is evident that the linear gas velocity, *referred to the moving condensed phase*, is

$$v_r^0 = v^0 - v_L \,.$$

Since v^0 and v_L are always of opposed sign,

$$| v_r^0 | > | v^0 |$$

in every case.

Equation (19) is valid only for the moving condensed phase, i.e.

$$v_r = \frac{v^0 - v_L}{k' + 1} \tag{20}$$

In the special case where the solute does not migrate *referred to the column wall*,

$$v_r + v_L = 0$$

and, considering Eq. (20),

$$k^* = - \frac{v^0}{v_L} \tag{21}$$

is the characteristic capacity ratio of the column. For $k' = k^*$, the solute "does not migrate".

In fact, this "non-migration" causes an accumulation of the solute in the feeding zone, the gas velocity increases and an upward migration will be observed. It is therefore more correct to say that downward migration is not to be expected when $k' \leq k^*$.

The definition of k^* permits to introduce a "dimensionless" or "relative" or rather normalized capacity ratio

$$\varkappa = \frac{k'}{k^*} \tag{22}$$

For $\varkappa \leq 1$, no downward migration is possible if not due to dispersion effects.

Equation (15) can be written for linear isotherms

$$\theta_i = \alpha_i y_i \tag{23}$$

where α_i is constant. The definition of the capacity ratio by the aid of Eq. (23),

$$k_i' = \frac{a_i}{\frac{pq}{RT} y_i} = \frac{a_0 RT}{pq} \alpha_i ,$$

combined with Eqs (21) and (22) gives

$$\alpha_i = - \frac{pqv^0}{RTa_0 v_L} \varkappa_i = \frac{C4}{C2} \varkappa_i$$

or

$$\alpha_i = \frac{\varkappa_i}{C5} . \tag{24}$$

Substituting Eq. (24) into the sets of equations (16) and (18), the dimensionless group C5 is eliminated. So in case of linear isotherms *and* equlibrium chromatography the column can be characterized by not more than two dimensionless groups (C1 and C3). For a total description of the system — for computing concentration profiles — the $\varkappa_i$ values and inlet concentrations (y_i^m) of the solutes have to be known additionally.

In case of non-linear isotherms, $\varkappa$ can be defined analogously from Eq. (24):

$$\varkappa_i = \frac{C5 \cdot \Phi_i(y_i)}{y_i} . \tag{25}$$

$\varkappa_i$ is now a function of y_i, but, by this transformation of the sorption isotherm, C5 can be eliminated from Eqs (16) and (18) also in non-linear cases.

Results

Computer programs have been written to solve the sets of equations given above. A number of runs have been made, others are in progress. Both the programs and the results will be reported in separate papers. Only a few selected cases are exposed now, merely for sake of illustration (Figs 1—5). Only one solute has been examined in these runs. The column parameters were always the same: C1 = 150, C2 = 37, C3 = 0.05, C4 = 0.03, and a pure solute was introduced in the middle ($y^m = 1$).

Typically, the concentrations in the middle are much higher than at the ends. This is true both for the condensed and the gas phases, confirmed

by experimental results. For $\varkappa < 1.0$, the solute moves only upwards (Fig. 1). Increasing $\varkappa$ above unity, the direction of migration does not change but very slowly. For $\varkappa = 1.028$ the solute still moves practically upwards (Fig. 2), and even for $\varkappa = 1.37$ the distribution is nearly symmetrical (Fig. 3).

The length of the feeding zone does not modify the distribution but in the zone itself and in its immediate vicinity. In Fig. 2 the feeding zone is

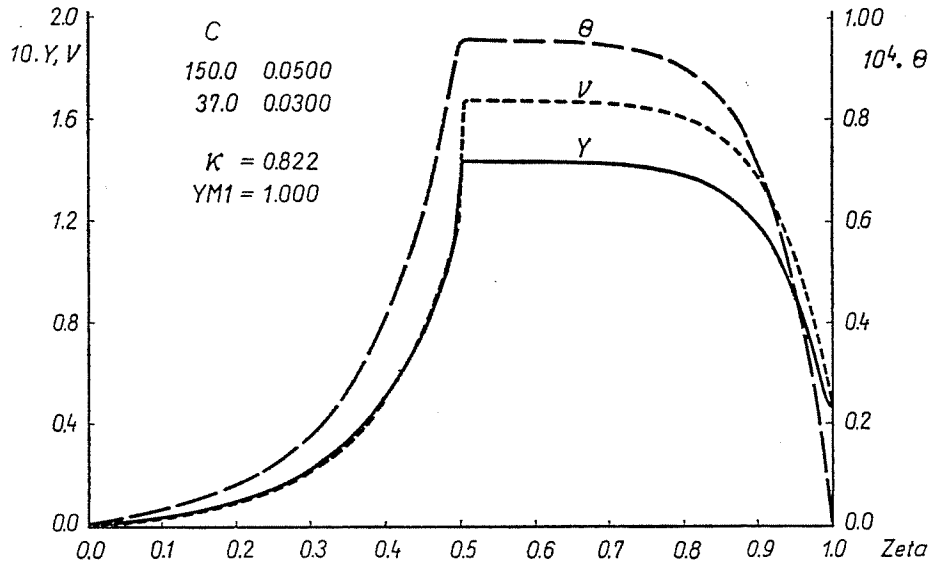

Fig. 1. Computed concentration and velocity profiles. Length of the feeding zone 0.01, $\varkappa = 0.822$

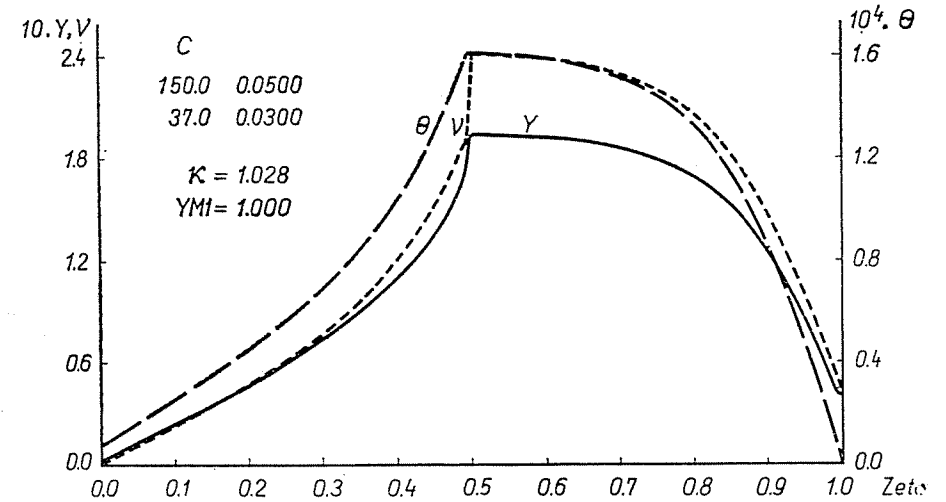

Fig. 2. Computed concentration and velocity profiles.
Length of the feeding zone 0.01, $\varkappa = 1.028$

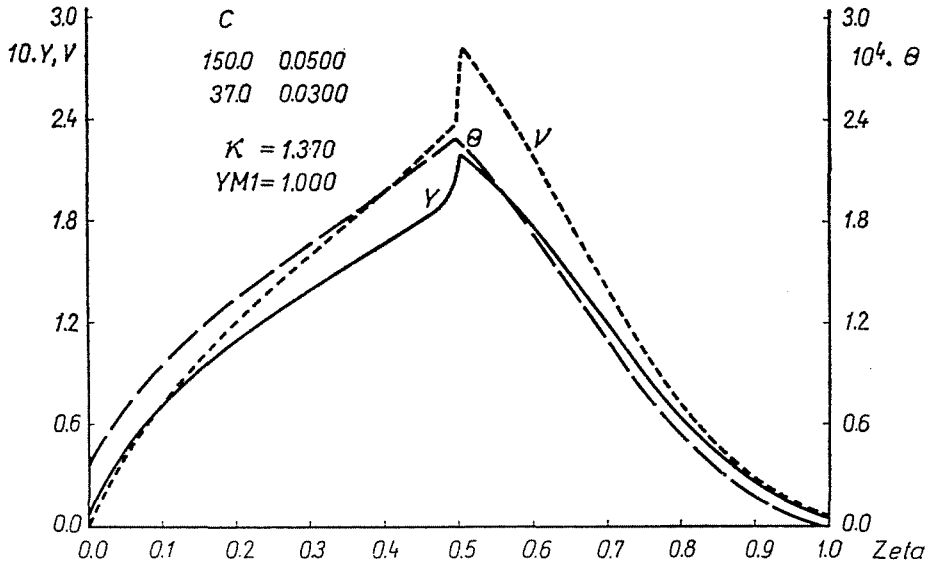

Fig. 3. Computed concentration and velocity profiles.
Length of the feeding zone 0.01, $\varkappa = 1.37$

1% of the column, while in Fig. 4 it is 5%. In practice even 1% is a rather high value, so it can be stated that this parameter is negligible.

The parameters in Figs 1 and 5 are the same, but in the second case the sample is fed near the bottom of the column. It is clearly observable that, in spite of the low value of $\varkappa$, a significant portion of the solute moves downwards. In the short lower part of the column the chromatographic separation cannot fully develop: it is offset by dispersion effects.

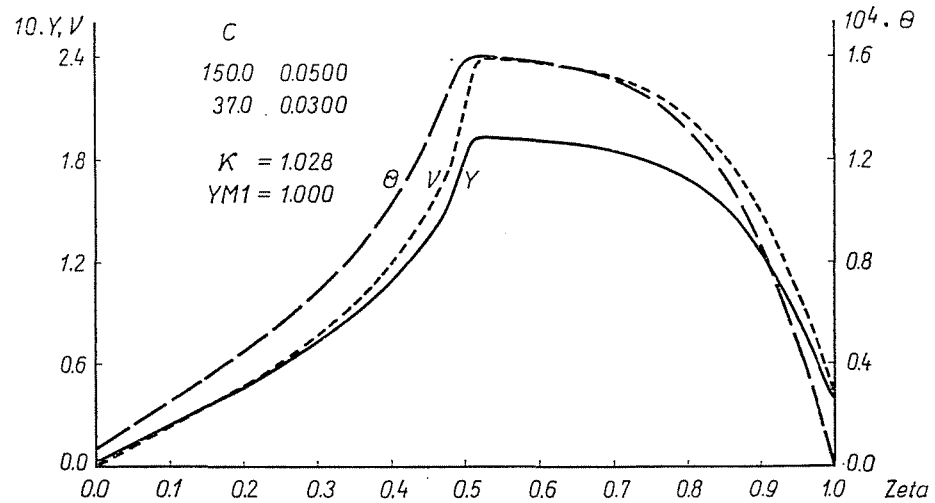

Fig. 4. Computed concentration and velocity profiles.
Length of the feeding zone 0.05, $\varkappa = 1.028$

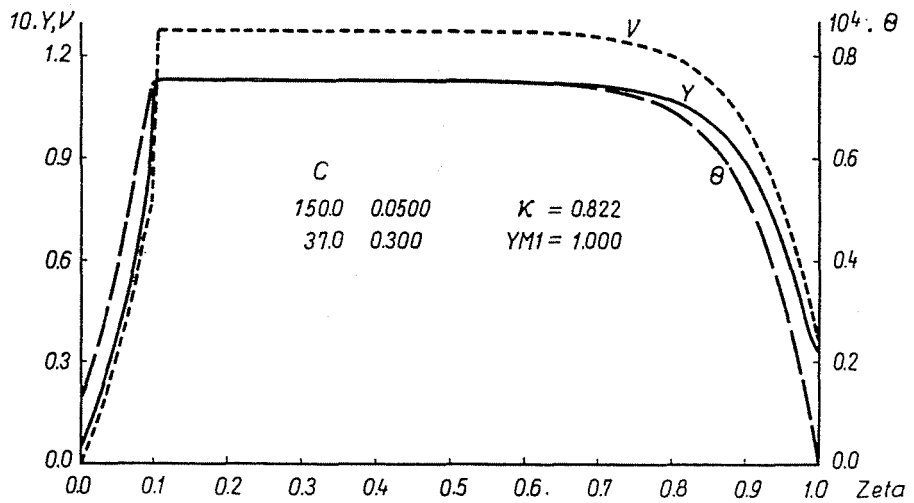

Fig. 5. Computed concentration and velocity profiles. Length of the feeding zone 0.01, $\varkappa = 0.822$. Asymmetrical feeding

Summary

The differential equations and boundary conditions describing a continuous chromatographic column are given in dimensionless form. In non-equilibrium chromatography four independent dimensionless groups are necessary to characterize the column and its working parameters. If the sorption processes are fast enough (equilibrium chromatography), three dimensionless groups are sufficient.

The solutes can be given by their sorption isotherms and inlet concentrations. In equilibrium chromatography the number of the dimensionless groups can still be reduced by an appropriate transformation of the sorption isotherms: then two groups are sufficient to describe the column.

Reference

1. PARLAGH, GY.—SZÉKELY, GY.—RÁCZ, GY.: Periodica Polytechnica Chem. Eng. **20,** 205 1976

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