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MOMENT ANALYSIS OF MULTIPLE PHASE CHROMATOGRAPHY

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SUMMARY

A material-balance equation describing a linear non-equilibrium chromatographic system that involves finite mass transfer between many phases is derived. Mass-transfer terms are included in the equation, so that the reversible transfers among all the phases are permissible, provided that they remain first-order with respect to solute concentration. The solution for the equation is achieved by means of the Laplace-transform method, and statistical moments are calculated from the transformed solution. The moment expressions obtained include almost completely the preceding results which were limited to a special case of the present work.

INTRODUCTION

Many workers have dealt with the kinetic aspect of chromatographic processes in terms of non-equilibrium, *i.e.*, finite mass transfer between mobile and stationary phases. Among the earlier investigations, Lapidus and Amundson¹ first solved a material-balance equation for a linear non-ideal chromatographic system by treating a non-equilibrium process as a two-phase problem. Van Deemter *et al.*² utilizing the results of Lapidus and Amundson, obtained their equation relating the height equivalent to a theoretical plate (HETP) to the linear velocity of the mobile phase. The so-called *C* term in their equation has predicted well the contribution of mass-transfer resistance to the plate height so far as a single stationary phase is considered. However, there must be more than two phases in a real chromatographic process; in gas-liquid chromatography, for example, there are gas phase, gas-liquid interface, liquid phase, liquid-support interface and solid support phase. Moreover, if a solute undergoes chemical changes to produce a new substance in the stationary phase (*e.g.*, a charge-transfer complex), it can be regarded as a new phase³⁻⁶. Giddings applied the perturbation theory in solving multiple-phase chromatographic problems involving the consecutive or simultaneous sorption and desorption of the solute, and obtained analytical expressions for the longitudinal diffusion coefficient due to the non-equilibrium effect^{7,8}. Yamazaki⁹, using the Mellin-transform method, and Kočířík¹⁰, using the Laplace-transform method, have solved material-balance equations describing a linear non-ideal chromatographic system involving a first-order chemical reaction in the stationary phase, and have derived equations for the statistical mo-

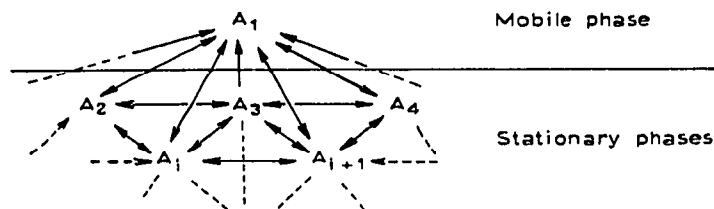


Fig. 1. Scheme of mass transfer.

ments. Their results are valid so far as the models considered by them are concerned. We shall now consider a multiple-phase chromatographic model combining the earlier mass-transfer models^{1,7-10} and involving both consecutive and simultaneous chemical reactions, and solve the material-balance equation describing such a model by means of a Laplace transform. The first four statistical moments can then be calculated from the transformed solution.

THEORY

The mass-transfer model to be considered is similar to that adopted by Giddings^{7,8} for deriving the non-equilibrium effect as shown in Fig. 1, which is based on the following assumptions:

- (1) that longitudinal diffusion and convection occur only in the mobile phase;
- (2) that lateral diffusion and mass transfer involving chemical reaction are together specified by the coefficient, k_{ij} , and
- (3) that the volume fraction of each phase does not change over whole column length.

If the mobile phase is specified by the subscript 1, the following simultaneous partial differential equations can be established.

$$\left. \begin{aligned} D \frac{\partial^2 C_1}{\partial z^2} - u \frac{\partial C_1}{\partial z} &= \frac{\partial C_1}{\partial t} + k_{11}C_1 + k_{12}C_2 + \cdots + k_{1n}C_n \\ 0 &= \frac{\partial C_2}{\partial t} + k_{21}C_1 + k_{22}C_2 + \cdots + k_{2n}C_n \\ 0 &= \frac{\partial C_3}{\partial t} + k_{31}C_1 + k_{32}C_2 + \cdots + k_{3n}C_n \\ &\dots\dots\dots \\ 0 &= \frac{\partial C_n}{\partial t} + k_{n1}C_1 + k_{n2}C_2 + \cdots + k_{nn}C_n \end{aligned} \right\} \quad (1)$$

where D is the longitudinal diffusion coefficient, u is the linear velocity of the mobile phase, C_i is the solute concentration in the i th phase, n is the total number of phases, and k_{ij} is the kinetic coefficient*.

* The meaning of this coefficient can be clarified by citing the example from Lapidus and Amundson's work¹, where a two-phase model was represented by the sets of equations

$$\left. \begin{aligned} D \frac{\partial^2 C_1}{\partial z^2} - u \frac{\partial C_1}{\partial z} &= \frac{\partial C_1}{\partial t} + \alpha/\epsilon (KC_1 - C_2) \\ 0 &= \frac{\partial C_2}{\partial t} - \alpha (KC_1 - C_2) \end{aligned} \right\}$$

where α , ϵ and K are the mass-transfer coefficient, the volume ratio of the mobile and stationary phases and the distribution coefficient, respectively. The kinetic coefficient, k_{ij} , in eqn. 1 is then related to α , ϵ and K by the expressions $k_{11} = \alpha K/\epsilon$, $k_{12} = -\alpha/\epsilon$, $k_{21} = -\alpha K$, and $k_{22} = \alpha$.

If there is no solute in the column at $t = 0$, and the solute is expressed in the form $f_i(t)$, the initial and boundary conditions can be written as follows (see also eqn. 8 in ref. 10)

$$\left. \begin{aligned} C_1(0,z) = 0, \quad C_1(t,0) = f_1(t), \quad C_1(t,\infty) = 0 \\ C_i(0,z) = 0, \quad C_i(t,0) = 0 \quad (i = 2, 3, \dots, n) \end{aligned} \right\} \quad (2)$$

Then, applying a Laplace transform to eqn. 1 with respect to t ,

$$\left. \begin{aligned} s \tilde{C}_1 + k_{11} \tilde{C}_1 + k_{12} \tilde{C}_2 + \dots + k_{1n} \tilde{C}_n &= D \, d^2 \tilde{C}_1 / dz^2 - u \, d \tilde{C}_1 / dz \\ s \tilde{C}_2 + k_{21} \tilde{C}_1 + \dots + k_{2n} \tilde{C}_n &= 0 \\ s \tilde{C}_3 + k_{31} \tilde{C}_1 + \dots + k_{3n} \tilde{C}_n &= 0 \\ \dots & \\ s \tilde{C}_n + k_{n1} \tilde{C}_1 + \dots + k_{nn} \tilde{C}_n &= 0 \end{aligned} \right\} \quad (3)$$

where s is the Laplace variable and

$$\tilde{C}_i(s,z) = \int_0^\infty e^{-st} C_i(t,z) \, dt \quad (4)$$

The application of matrix representation simplifies eqn. 3 to

$$(K + s E_n) \tilde{C} = (D \, d^2 \tilde{C}_1 / dz^2 - u \, d \tilde{C}_1 / dz, 0, 0, \dots, 0)^T \quad (5)$$

where T means the transposition of the vector, E_n denotes the n th order unit matrix, and

$$\tilde{C} = (\tilde{C}_1, \tilde{C}_2, \tilde{C}_3, \dots, \tilde{C}_n)^T \quad (6)$$

and

$$K = (k_{ij}) = \begin{bmatrix} k_{11} & k_{12} & k_{13} & \dots & k_{1n} \\ k_{21} & k_{22} & k_{23} & \dots & k_{2n} \\ k_{31} & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots \\ k_{n1} & k_{n2} & \dots & \dots & k_{nn} \end{bmatrix} \quad (7)$$

By eliminating $C_i(s,z)$ ($i = 2, 3, \dots, n$) from eqn. 5 through the application of Cramer's rule and then rearranging, we obtain

$$D \, d^2 \tilde{C}_1 / dz^2 - u \, d \tilde{C}_1 / dz - \tilde{g}(s) \tilde{C}_1 = 0 \quad (8)$$

where

$$\tilde{g}(s) = |K + s E_n| / |K_1 + s E_{n-1}| \quad (9)$$

In eqn. 9, E_{n-1} is the $(n-1)$ th order unit matrix and K_1 means the sub-matrix obtained by eliminating the first column and the first row of matrix K , and $| \cdot |$ indicates the determinant. The solution for eqn. 8 under the condition of Laplace transform of eqn. 2 is then given (see ref. 1) by

$$\bar{C}_1(s, z) = \bar{f}_1(s) \exp \left[\left[\left(\frac{u}{2D} \right) - \sqrt{\left(\frac{u}{2D} \right)^2 + \frac{1}{D} \bar{g}(s)} \right] z \right] \quad (10)$$

If the solute input form $f_1(t)$ can be regarded as Dirac's δ -function, the chromatographic elution curve, $\bar{f}_0(s)$, in the Laplace domain is represented by the equation

$$\bar{f}_0(s) = m \exp \left[\left[\left(\frac{u}{2D} \right) - \sqrt{\left(\frac{u}{2D} \right)^2 + \frac{1}{D} \bar{g}(s)} \right] L \right] \quad (11)$$

where m is the amount of solute in a unit of the δ -function and L is the column length.

To obtain the equations for the zero-th through to the third statistical moments* the well-known relationships (see ref. 11)

$$\left. \begin{aligned} M_0 &= \lim_{s \rightarrow 0} \bar{f}_0(s) \\ M_1' &= \lim_{s \rightarrow 0} (-\partial/\partial s) \ln \bar{f}_0(s) \\ M_2 &= \lim_{s \rightarrow 0} (\partial^2/\partial s^2) \ln \bar{f}_0(s) \\ M_3 &= \lim_{s \rightarrow 0} (-\partial^3/\partial s^3) \ln \bar{f}_0(s) \end{aligned} \right\} \quad (12)$$

are used, where \ln indicates the natural logarithm and M_0 , M_1' , M_2 and M_3 are the zero-th, the first ordinary, the second central and the third central moments, respectively, and the three last-named moments are also equal to the corresponding cumulants.

Substituting eqn. 11 into eqn. 12, the final forms of the first four moments are obtained as

$$\left. \begin{aligned} M_0 &= m \exp \left[\left[\frac{u}{2D} - \sqrt{\left(\frac{u}{2D} \right)^2 + \frac{1}{D} \bar{g}(0)} \right] L \right] \\ M_1' &= \frac{L}{2D} \left[\left(\frac{u}{2D} \right)^2 + \frac{1}{D} \bar{g}(0) \right]^{-0.5} \bar{g}'(0) \\ M_2 &= \frac{L}{4D^2} \left[\left(\frac{u}{2D} \right)^2 + \frac{1}{D} \bar{g}(0) \right]^{-1.5} [\bar{g}'(0)]^2 - \frac{L}{2D} \left[\left(\frac{u}{2D} \right)^2 + \frac{1}{D} \bar{g}(0) \right]^{-0.5} \bar{g}''(0) \\ M_3 &= \frac{3L}{8D^3} \left[\left(\frac{u}{2D} \right)^2 + \frac{1}{D} \bar{g}(0) \right]^{-2.5} [\bar{g}'(0)]^3 - \frac{3L}{4D^2} \left[\left(\frac{u}{2D} \right)^2 + \frac{1}{D} \bar{g}(0) \right]^{-0.5} \bar{g}'(0) \bar{g}''(0) + \frac{L}{2D} \left[\left(\frac{u}{2D} \right)^2 + \frac{1}{D} \bar{g}(0) \right]^{-0.5} \bar{g}'''(0) \end{aligned} \right\} \quad (13)$$

in which

$$\begin{aligned}
 \tilde{g}(0) &= \frac{|K|}{|K_1|} \\
 \tilde{g}'(0) &= \frac{\sum_i^n |K_i|}{|K_1|} - \frac{|K|}{|K_1|^2} \sum_i^{n-1} |K_{1i}| \\
 -\tilde{g}''(0) &= \frac{\sum_j^{n-1} \sum_i^n |K_{ij}|}{|K_1|} - 2 \frac{(\sum_i^n |K_i|)(\sum_i^{n-1} |K_{1i}|)}{|K_1|^2} + 2 \frac{|K| \sum_i^{n-1} |K_{1i}|}{|K_1|^3} - \\
 &\quad \frac{|K| (\sum_j^{n-2} \sum_i^{n-1} |K_{1ij}|)}{|K_1|^2} \\
 \tilde{g}'''(0) &= \frac{\sum_k^{n-2} \sum_j^{n-1} \sum_i^n |K_{ijk}|}{|K_1|} - 3 \frac{(\sum_j^{n-1} \sum_i^n |K_{ij}|)(\sum_i^{n-1} |K_{1i}|)}{|K_1|^2} + \\
 &\quad + 6 \frac{(\sum_i^n |K_i|)(\sum_i^{n-1} |K_{1i}|)}{|K_1|^3} - 3 \frac{(\sum_i^n |K_i|)(\sum_j^{n-2} \sum_i^{n-1} |K_{1ij}|)}{|K_1|^2} - \\
 &\quad 6 \frac{|K| (\sum_i^{n-1} |K_{1i}|)}{|K_1|^4} + 4 \frac{|K| \sum_j^{n-2} \sum_i^{n-1} |K_{1ij}|}{|K_1|^3} - \\
 &\quad \frac{|K| \sum_k^{n-3} \sum_j^{n-2} \sum_i^{n-1} |K_{ijk}|}{|K_1|^2}
 \end{aligned} \tag{14}$$

and $K_{ijk} \dots$ is a sub-matrix obtained by eliminating the i th, the j th and the k th columns and the rows of K^* .

APPLICATION OF THEORY

In this section, we shall develop the application of our results to a special system in which the total amount of a solute neither increases nor decreases during the chromatographic process, in other words, a system in which irreversible chemical reactions do not occur. However, if a reversible reaction does occur, it must remain

* As an example, and to avoid confusion of the notation, $\sum_{j,i} \sum_j |K_{ij} \dots|$, let K be (3×3) matrix, then

$$\sum_{j,i} \sum_j \begin{vmatrix} k_{11} & k_{12} & k_{13} \\ k_{21} & k_{22} & k_{23} \\ k_{31} & k_{32} & k_{33} \end{vmatrix} = \sum_j \left(\begin{vmatrix} k_{22} & k_{23} \\ k_{32} & k_{33} \end{vmatrix} + \begin{vmatrix} k_{11} & k_{13} \\ k_{31} & k_{33} \end{vmatrix} + \begin{vmatrix} k_{11} & k_{12} \\ k_{21} & k_{22} \end{vmatrix} \right) = [(k_{33} + k_{22}) + (k_{33} + k_{11}) + (k_{22} + k_{11})].$$

first-order with respect to solute concentration, although the over-all order may be different. For this system, a chromatographic peak area, M_0 , is the response due to the total amount of solute initially introduced into the column. Accordingly, $M_0 = m_i$, so that $\tilde{g}(0) = 0$; thus, $|K| = 0$, and the other moment equations can be reduced to

$$\left. \begin{aligned} M'_1 &= \frac{L}{u} \tilde{g}'(0) \\ M_2 &= \frac{2DL}{u^3} [\tilde{g}'(0)]^2 - \frac{L}{u} \tilde{g}''(0) \\ M_3 &= \frac{12D^2L}{u^5} [\tilde{g}'(0)]^3 - \frac{6DL}{u^3} \tilde{g}'(0) \tilde{g}''(0) + \frac{L}{u} \tilde{g}'''(0) \end{aligned} \right\} \quad (15)$$

where

$$\left. \begin{aligned} \tilde{g}'(0) &= \frac{\sum_i^n |K_i|}{|K_1|} \\ \tilde{g}''(0) &= \frac{\sum_j^{n-1} \sum_i^n |K_{ij}|}{|K_1|} - 2 \frac{(\sum_i^n |K_{1i}|) (\sum_i^{n-1} |K_{1i}|)}{|K_1|^2} \\ \tilde{g}'''(0) &= \frac{\sum_k^{n-2} \sum_j^{n-1} \sum_i^n |K_{ijk}|}{|K_1|} - 3 \frac{(\sum_j^{n-1} \sum_i^n |K_{ij}|) (\sum_i^n |K_{1i}|)}{|K_1|^2} + \\ &+ 6 \frac{(\sum_i^n |K_i|) (\sum_i^{n-1} |K_{1i}|)}{|K_1|^3} - 3 \frac{(\sum_i^n |K_i|) (\sum_j^{n-2} \sum_i^{n-1} |K_{1ij}|)}{|K_1|^2} \end{aligned} \right\} \quad (16)$$

Thus, $|K| = 0$ is characteristic to this chromatographic system, and, with appropriate substitution for k_{ij} , these equations reduce to the corresponding expressions in earlier work^{1,7-9}.

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