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Retention Time and the First Time Moment in Elution Chromatography. I. The Column Characteristic Ĝ

James E. Funk[a]; Peter R. Rony[b]
[a] COLLEGE OF ENGINEERING UNIVERSITY OP KENTUCKY LEXINGTON, KENTUCKY [b] CORPORATE RESEARCH LABORATORIES ESSO RESEARCH AND ENGINEERING COMPANY, LINDEN, NEW JERSEY

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Retention Time and the First Time Moment in Elution Chromatography. I. The Column Characteristic, $\hat{G}$

JAMES E. FUNK
COLLEGE OF ENGINEERING
UNIVERSITY OF KENTUCKY
LEXINGTON, KENTUCKY 40506

and

PETER R. RONY
CORPORATE RESEARCH LABORATORIES
ESSO RESEARCH AND ENGINEERING COMPANY
P. O. BOX 45
LINDEN, NEW JERSEY 07036

Summary

A useful chromatographic parameter—the *column characteristic*, $\hat{G}$—is defined and derived. It contains all of the dynamic information of interest for chromatography, yet it can be determined from a single-stage experiment. The column characteristic can be employed directly to derive the column transfer function and is related to the Murphree stage efficiency for the chromatographic column operated as a single equilibrium stage. The relationship of the column characteristic to the first normal statistical moment is derived. Application is made to a simple physical situation and results are obtained for both a distributed and a discrete description of the stationary liquid phase. The nature of the discrete approximation is discussed. This paper provides the foundation for two additional papers that explore in detail several aspects of nonequilibrium chromatography.

INTRODUCTION

The theory of chromatographic systems has been a popular subject for at least two decades. Giddings in his review of the evolution of zone-spreading concepts (*1*) has traced theoretical chromatography from its origin in Wilson's work (*2*) through the papers of Martin and Synge (*3*); Thomas (*4*); Van Deemter, Zuiderweg, and Klinkenberg (*5*); Giddings and Eyring (*6*); and Giddings (*7*). Theoretical work in the late 1960s has proved to be as diverse as that cited in Gidding's review. Such work includes papers on the use of infinite integrals (*8*), Mellin transforms (*9*), numerical solutions (*10*), and statistical moments (*11–16*) as well as papers on nonequilibrium theory (*17, 18*), gas chromatography at finite concentrations (*19*), multicomponent chromatography (*20*), and linear multistate chromatography (*21*).

One approximation that has been widely used to reduce the complexity of the conservation-of-mass equations of chromatography has been what Giddings calls the "long-term approximation," i.e., "the location and profile of a chromatographic zone is approximated by a limiting form which is exact only when the elution time is infinitely larger than the time of equilibration between phases" (*22*). Thus, most theoretical treatments of chromatography do not apply to the transient situation that exists before this approximation becomes valid.

Although the use of the long-term approximation has apparently been adequate for most applications of chromatography, it would be quite desirable to calculate the shape of the elution curve profile from the time of injection to the time at which the long-term approximation becomes valid. Since the peak shape and the location of the peak maximum are, at short times, quite sensitive to lateral broadening mechanisms such as diffusion or rate control in the stationary phase, the ability to simulate such curves may suggest experimental methods whereby the dynamic characteristics of a chromatographic column can readily be measured.

In this work, we will demonstrate procedures for calculating or simulating the elution curve profile in chromatographic systems. No long-term approximation will be made. In fact, the calculations will show at what time and for what types of column conditions this approximation becomes valid. Due to the length of the theoretical treatment, we have divided the material into three separate papers: I. The Column Characteristic, $\hat{G}$; II. Analytical Solutions (*35*); and III. General Conclusions (*34*).

In the first paper, the mathematical background for the three papers will be developed. The conservation-of-mass equation for a chromatographic system will be solved according to a procedure developed elsewhere (*21*). A useful transform quantity—the *column characteristic*, $\hat{G}$—will then be defined. Finally, the analytical expressions for $\hat{G}$ will be computed for several situations to illustrate the physical meaning of the characteristic and its application to real systems.

THEORETICAL

We will assume that the reader is familiar with the concept of a partition state (*23–25*). The derivation given below is, in many respects, similar to a previous one (*21*). Consider a chromatographic system in which component i distributes between two physical environments—the gas and liquid phases. The three-dimensional conservation-of-mass equation (at constant temperature and pressure) for component i in environment s is given by (*21*)

$$\frac{\partial c_{is}}{\partial t} - D'_{is}\nabla^2 c_{is} + v'_{is}\nabla c_{is} - R_{is} + \nabla_\perp \cdot \mathbf{N}_{\perp is} = 0 \qquad (1)$$

where c_{is} = molar concentration of partition state $\boxed{i:s}$

D'_{is} = local diffusion coefficient of $\boxed{i:s}$

$\mathbf{N}_{\perp is}$ = lateral molar flux of $\boxed{i:s}$

R_{is} = rate of production or loss of $\boxed{i:s}$

t = time

v'_{is} = local molar velocity of $\boxed{i:s}$

z = axial coordinate

∇ = gradient operator with respect to axial coordinate z

∇^2 = Laplacian operator with respect to axial coordinate z

We first integrate Eq. (1) over the total lateral cross-sectional area, $A_\perp$, sum over all of the partition states, and observe that the total lateral molar flux of component i has a value of zero (*21*),

$$\sum_{s=1}^{n} \iint_{A_{\perp is}} \nabla_\perp \cdot \mathbf{N}_{\perp is}\, dA_\perp \equiv 0 \qquad (2)$$

by Green's theorem (impermeable lateral boundaries) or by symmetry. Equation (1) therefore becomes

$$\sum_{s=1}^{n} \iint_{A_{\perp is}} \frac{\partial c_{is}}{\partial t}\, dA_{\perp} - \sum_{s=1}^{n} \iint_{A_{\perp is}} D'_{is}\nabla^2 c_{is}\, dA_{\perp} + \sum_{s=1}^{n} \iint_{A_{\perp is}} v'_{is}\nabla c_{is}\, dA_{\perp} - \sum_{s=1}^{n} \iint_{A_{\perp is}} R_{is}\, dA_{\perp} = 0 \quad (3)$$

Equation (3) is too difficult to solve for the general case, so we will now make a number of simplifications. Consider a chromatographic system in which (a) component i distributes between a gas $(s = 1)$, a liquid $(s = 2)$, and a complexing agent dissolved in the liquid $(s = 3)$;

$$\boxed{i{:}1} \rightleftarrows \boxed{i{:}2} \underset{k_{i3}''}{\overset{k_{i3}'}{\rightleftarrows}} \boxed{i{:}3} \quad (4)$$

(b) the liquid phase is stationary, $v_{i2} = v_{i3} = 0$; (c) the gas-phase velocity is constant, $v'_{i1} = v_1$; (d) there is a reversible chemical reaction between partition states $\boxed{i{:}2}$ and $\boxed{i{:}3}$,

$$R_{i2} = k''_{i3}c_{i3} - k'_{i3}c_{i2} \quad (5)$$

$$R_{i3} = k'_{i3}c_{i2} - k''_{i3}c_{i3} \quad (6)$$

$$\sum_{s=1}^{3} \iint_{A_{\perp is}} R_{is}\, dA_{\perp} = 0 \quad (7)$$

where k'_{i3} and k''_{i3} are pseudo-first-order rate constants that are independent of z and t; (e) the gas-phase concentration is independent of the lateral coordinates, $c_{i1} = c_{i1}(z,t)$; and (f) the axial dispersion terms are small,

$$\sum_{s=1}^{3} \iint_{A_{\perp is}} D'_{is}\nabla^2 c_{is}\, dA_{\perp} \approx 0 \quad (8)$$

With these assumptions, Eq. (3) first reduces to

$$\sum_{s=1}^{3} \iint_{A_{\perp s}} \frac{\partial c_{is}}{\partial t}\, dA_{\perp} + v_1 \iint_{A_{\perp 1}} \frac{\partial c_{i1}}{\partial z}\, dA_{\perp} = 0 \quad (9)$$

and then to

$$\frac{\partial c_{i1}}{\partial t} + \frac{\epsilon_2}{\epsilon_1}\left(\frac{\partial c_{i2}|_{Av}}{\partial t} + \frac{\partial c_{i3}|_{Av}}{\partial t}\right) + v_1 \frac{\partial c_{i1}}{\partial z} = 0 \tag{10}$$

where $c_{is}|_{Av}(z,t)$ represents the concentration c_{is} averaged over the later cross-sectional area, $A_{\perp 2}$, of the liquid phase,

$$c_{is}|_{Av}(z,t) \equiv \frac{\iint_{A_{\perp 2}} c_{is} dA_\perp}{\iint_{A_{\perp 2}} dA_\perp} \qquad (s = 2,3) \tag{11}$$

and

$$\epsilon_s \equiv \frac{\iint_{A_{\perp s}} dA_\perp}{A_\perp} \tag{12}$$

Equation (10) can be solved with the aid of Laplace transforms,

$$\hat{c}_{is}(y,z,p) \equiv \int_0^\infty e^{-pt} c_{is}(y,z,t)\, dt \tag{13}$$

to yield

$$p\hat{c}_{i1} + \frac{p\epsilon_2}{\epsilon_1}(\hat{c}_{i2}|_{Av} + \hat{c}_{i3}|_{Av}) + v_1 \frac{\partial \hat{c}_{i1}}{\partial z} = 0 \tag{14}$$

where y is the lateral coordinate. There will be a relationship (to be determined later) between $\hat{c}_{i1}$ and the transform of the average liquid-phase concentration, $(\hat{c}_{i2} + \hat{c}_{i3})|_{Av}$. This quantity is defined as the *column characteristic*, $\hat{G}$, and is given by the formula,

$$\hat{G} \equiv \frac{\hat{c}_{i2}|_{Av} + \hat{c}_{i3}|_{Av}}{\hat{c}_{i1}} \tag{15}$$

With the aid of Eq. (15), Eq. (14) can be simplified to

$$p\left(1 + \frac{\epsilon_2}{\epsilon_1}\hat{G}\right)\hat{c}_{i1} + v\,\frac{\partial \hat{c}_{i1}}{\partial z} = 0 \tag{16}$$

which has a solution of

$$\frac{\hat{c}_{i1}(z,p)}{\hat{c}_{i1}(0,p)} = \exp\left[-\frac{zp}{v_1}\left(1 + \frac{\epsilon_2}{\epsilon_1}\hat{G}\right)\right] \tag{17}$$

Equation (17) is the *column transfer function;* it relates the column outlet conditions to the column inlet conditions in terms of the transform variables and is identical to the system transform, $\bar{S}(p)$, discussed by Sternberg (*26*). We would like to note that the concept of a system transfer function is quite general and widely used in the field of control theory. The form of the transfer function depends upon the assumptions made in the description of the physical system. In the present analysis, these assumptions have been listed immediately after Eq. (3). Equation (17) becomes

$$\hat{c}_{i1}(z,p) = c_i^0 \exp\left[-\frac{zp}{v_1}\left(1 + \frac{\epsilon_2}{\epsilon_1}\hat{G}\right)\right] \tag{18}$$

for an impulse input,

$$c_{i1}(0,t) = c_i^0 \delta(t) \tag{19}$$

Since the term, $\exp(-zp/v_1)$, in Eq. (18) represents a simple transport delay, the solution to Eq. (18) will take the form

$$c_{i1}(z,t) = 0 \qquad \text{for} \qquad 0 < t < z/v_1 \tag{20}$$

$$c_{i1}\left(z,t - \frac{z}{v_1}\right) = \mathcal{L}^{-1}\left\{c_i^0 \exp\left[-\frac{z}{v_1}\frac{\epsilon_2}{\epsilon_1}p\hat{G}\right]\right\} \qquad \text{for} \qquad z/v_1 < t \tag{21}$$

where $t - (z/v_1)$ is the time variable for the inverse in Eq. (21).

FIRST NORMAL MOMENT

Of the various approaches to the theoretical description of chromatographic systems, the statistical moments technique has become increasingly popular (*11–16*). The partial differential equations describing the chromatographic system are first solved with the aid of Laplace transforms, as was done in a previous section. Successive normal statistical moments are then computed according to the formula (*27–29*),

$$\mu_n' = \frac{\int_0^\infty t^n c_{i1}(L,t)\,dt}{\int_0^\infty c_{i1}(L,t)\,dt} = (-1)^n \lim_{p\to 0} \frac{\dfrac{\partial^n \hat{c}_{i1}(L,p)}{\partial p^n}}{\hat{c}_{i1}(L,p)} \tag{22}$$

Such moments contain, in principle, all of the information associated with the elution profile of a chromatographic peak,

$$c_{i1}(L,t) = \mathcal{L}^{-1}\{\hat{c}_{i1}(L,p)\} \tag{23}$$

and possess the further advantage of not requiring the above inversion of $\hat{c}_{is}(L,p)$ back to the time domain.

According to Eq. (22), the first normal moment, μ_1', is given by the formula,

$$\mu_1' = -\lim_{p\to 0} \frac{\partial \ln \hat{c}_{i1}(L,p)}{\partial p} \tag{24}$$

If we apply this equation to the calculation of the first normal moment of the concentration profile whose transform is given by Eq. (25),

$$\ln \hat{c}_{i1}(L,p) = \ln \hat{c}_{i1}(0,p) - \frac{Lp}{v_1}\left(1 + \frac{\epsilon_2}{\epsilon_1}\hat{G}\right) \tag{25}$$

we obtain

$$\mu_1' = \underbrace{-\lim_{p\to 0} \frac{\partial \ln \hat{c}_{i1}(0,p)}{\partial p}}_{\text{contribution from input}} + \underbrace{\frac{L}{v_1}\left[1 + \frac{\epsilon_2}{\epsilon_1}\lim_{p\to 0}\left(\hat{G} + p\frac{\partial \hat{G}}{\partial p}\right)\right]}_{\text{contribution from chromatographic column}} \tag{26}$$

We have therefore separated out the contribution to μ_1' that is due to the shape of the input. For an impulse input, Eq. (26) simplifies to

$$\mu_1' = \frac{L}{v_1} + \frac{\epsilon_2}{\epsilon_1}\frac{L}{v_1}\lim_{p\to 0}\left(\hat{G} + p\frac{\partial \hat{G}}{\partial p}\right) \tag{27}$$

Application of the final-value theorem (*30*)

$$\lim_{p\to 0} \hat{G} = \lim_{u\to\infty} \int_0^u F(u)\,du \tag{28}$$

$$\lim_{p\to 0} p\frac{\partial \hat{G}}{\partial p} = -\lim_{u\to\infty} uF(u) \tag{29}$$

where the functions u and $F(u)$ are

$$u \equiv t - \frac{L}{v_1} \tag{30}$$

$$F(u) \equiv \mathcal{L}^{-1}\{\hat{G}\} \tag{31}$$

converts Eq. (27) to

$$\mu_1' = \frac{L}{v_1} + \frac{\epsilon_2 L}{\epsilon_1 v_1}\lim_{u\to\infty}\left[\int_0^u F(u)\,du - uF(u)\right] \tag{32}$$

COLUMN CHARACTERISTIC

The column characteristic is an important transform quantity in any diffusion- or rate-controlled chromatographic system. It can be computed according to the definition given by Eq. (15), provided that the differential equation and boundary conditions governing diffusion and reaction in the liquid phase are known. We will now compute the value of $\hat{G}$ for four different cases: (1) liquid-phase diffusion control (distributed), (2) liquid-phase diffusion control (discrete approximation), (3) liquid-phase rate control, and (4) impermeable liquid. Although we will develop equations for the capillary column shown in Fig. 1, the extension of the calculations to other types of chromatographic systems is straightforward.

Case 1. Liquid-Phase Diffusion Control (Distributed)

In the case where there is only diffusion control in the liquid phase ($k'_{i3} = k''_{i3} = 0$), the conservation-of-mass equation for partition state $\boxed{i:2}$ becomes

$$\frac{\partial c_{i2}}{\partial t} - D_{i2}\frac{\partial^2 c_{i2}}{\partial y^2} = 0 \tag{33}$$

where it has been assumed that the diffusion coefficient, D_{i2}, is constant. For the column shown in Fig: 1 and the boundary conditions,

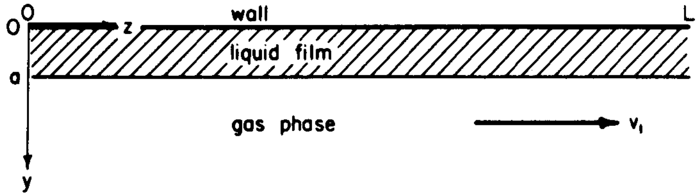

FIG. 1. Capillary chromatographic system.

$$c_{i2} = \kappa_{i2} c_{i1} \quad \text{at} \quad y = a \tag{34}$$

$$\frac{\partial c_{i2}}{\partial y} = 0 \quad \text{at} \quad y = 0 \tag{35}$$

where κ_{i2} is a gas-liquid partition coefficient,

$$\kappa_{i2} \equiv \frac{c_{i2}}{c_{i1}} \equiv \frac{\hat{c}_{i2}}{\hat{c}_{i1}} \tag{36}$$

Equation (33) can be solved with the aid of Laplace transforms to yield

$$\hat{c}_{i2} = \kappa_{i2}\hat{c}_{i1}\frac{\cosh qy}{\cosh qa} \tag{37}$$

$$q^2 \equiv \frac{p}{D_{i2}} \tag{38}$$

The average concentration of i in the liquid phase is

$$\hat{c}_{i2}|_{Av} = \frac{\int_0^a \hat{c}_{i2}\,dy}{\int_0^a dy} = \kappa_{i2}\hat{c}_{i1}\frac{\tanh qa}{qa} \tag{39}$$

Therefore,

$$\hat{G} = \kappa_{i2}\frac{\tanh qa}{qa} \tag{40}$$

With the aid of the series,

$$\frac{\tanh a\sqrt{\dfrac{p}{D_{i2}}}}{a\sqrt{\dfrac{p}{D_{i2}}}} = \frac{2D_{i2}}{a^2}\left[\frac{1}{p + \dfrac{\pi^2 D_{i2}}{4a^2}} + \frac{1}{p + 9\,\dfrac{\pi^2 D_{i2}}{4a^2}} + \cdots\right] \tag{41}$$

a first-term approximation to Eq. (40) can be obtained,

$$\hat{G} \approx \kappa_{i2}\frac{\dfrac{2D_{i2}}{a^2}}{p + \dfrac{\pi^2 D_{i2}}{4a^2}} \tag{42}$$

Case 2. Liquid-Phase Diffusion Control (Discrete Approximation)

As another way of eliminating the independent variable, y, we can represent the liquid film as a lumped system (Fig. 2). Equations (33) through (35) still apply and the average liquid-phase concentration, $c_{i2}|_{Av}$, is calculated by the following procedure, which is a variation of the method presented by Funk and Houghton (*31*).

We integrate Eq. (33) over the cross-sectional area to yield first

$$\frac{\partial}{\partial t}\left[\frac{1}{a}\int_0^a c_{i2}\,dy\right] = \frac{D_{i2}}{a}\frac{\partial c_{i2}}{dy}\bigg|_{y=a} \tag{43}$$

and then

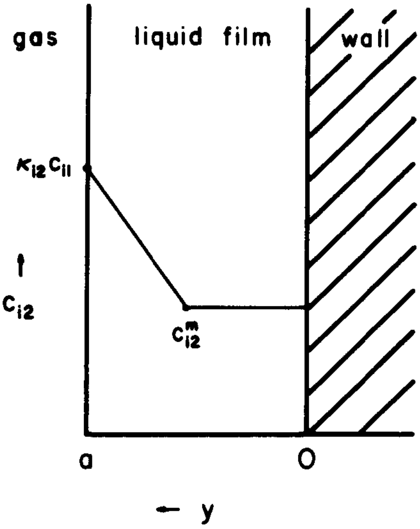

FIG. 2. Schematic diagram of the liquid film as a lumped system.

$$\frac{1}{a}\frac{\partial}{\partial t}\left[c_{i2}^m a + \frac{a}{4}\left(\kappa_{i2}c_{i1} - c_{i2}^m\right)\right] = \frac{D_{i2}}{a}\cdot\frac{\kappa_{i2}c_{i1} - c_{i2}^m}{a/2} \tag{44}$$

or

$$\frac{\partial}{\partial t}\left[\frac{3}{4}c_{i2}^m + \frac{1}{4}\kappa_{i2}c_{i1}\right] = \frac{2D_{i2}}{a^2}\left(\kappa_{i2}c_{i1} - c_{i2}^m\right) \tag{45}$$

Equation (45) is solved with the aid of Laplace transforms to give

$$\hat{c}_{i2}^m = \frac{\dfrac{8D_{i2}}{a^2} - p}{\dfrac{8D_{i2}}{a^2} + 3p}\,\kappa_{i2}\hat{c}_{i1} \tag{46}$$

The average liquid-phase concentration is calculated according to

$$\begin{aligned}\hat{c}_{i2}\big|_{Av} &= \frac{1}{a}\int_0^a \hat{c}_{i2}\,dy = \frac{3}{4}\hat{c}_{i2}^m + \frac{1}{4}\kappa_{i2}\hat{c}_{i1}\\ &= \frac{\dfrac{8}{3}\dfrac{D_{i2}}{a^2}}{p + \dfrac{8}{3}\dfrac{D_{i2}}{a^2}}\,\kappa_{i2}\hat{c}_{i1}\end{aligned} \tag{47}$$

The column characteristic is therefore

$$\hat{G} = \kappa_{i2} \frac{\frac{8}{3} \frac{D_{i2}}{a^2}}{p + \frac{8}{3} \frac{D_{i2}}{a^2}} \tag{48}$$

Equation (48) is similar in form to Eq. (42) and is, in fact, a one term approximation to Eq. (40).

Case 3. Liquid-Phase Rate Control

In the absence of diffusion control in the liquid phase, the conservation-of-mass equation can be written as

$$\frac{\partial c_{i3}}{\partial t} = k'_{i3} c_{i2} - k''_{i3} c_{i3} \tag{49}$$

which, via Laplace transforms, has a solution of

$$\hat{c}_{i3} = \frac{k'_{i3} \hat{c}_{i2}}{p + k''_{i3}} \tag{50}$$

Since neither $\hat{c}_{i2}$ nor $\hat{c}_{i3}$ is dependent upon the lateral coordinate, y, the integration in Eq. (11) need not be performed and $\hat{G}$ becomes simply

$$\hat{G} = \kappa_{i2} \left(1 + \frac{k'_{i3}}{p + k''_{i3}}\right) \tag{51}$$

Case 4. Impermeable Liquid

In this case, component i cannot readily permeate into the liquid and c_{i2} has a value of zero. Therefore

$$\hat{c}_{i2}|_{Av} = 0 \tag{52}$$

and

$$\hat{G} = 0 \tag{53}$$

PHYSICAL SIGNIFICANCE OF THE COLUMN CHARACTERISTIC

The column characteristic has a physical significance, which allows us to theoretically relate diffusion and rate control within a chromatographic column to diffusion and rate control within a single equilibrium stage (*32*). Equation (15) indicates that the inverse transform of $\hat{G}$,

$$F(t) = \mathcal{L}^{-1}\{\hat{G}\} \tag{31}$$

is the response of the average concentration of component i in the stationary phase to a unit impulse change in the concentration of i in the vapor phase. Accordingly, the time integral of this inverse transform, $\int_0^t F(t)\,dt$, is the response to a unit step change in the concentration of i in the vapor phase. That is,

$$c_{i2}|_{Av}(t) + c_{i3}|_{Av}(t) = c_i^0 \int_0^t F(t)\,dt \qquad \text{(step response)} \tag{54}$$

$$c_{i2}|_{Av}(t) + c_{i3}|_{Av}(t) = c_i^0 F(t) \qquad \text{(impulse response)} \tag{55}$$

It should be noted that Eqs. (54) and (55) no longer contain the axial distance, z, or the gas-phase velocity, v_1, yet they still contain the physical parameters that characterize diffusion or rate control within the liquid film. These equations suggest a single stage experiment to determine $\hat{G}$—the column packing is exposed to a step change in the concentration of i in the vapor phase and the uptake is measured as a function of time.

For the distributed liquid film description,

$$\hat{G} = \kappa_{i2} \frac{\tanh qa}{qa} \tag{40}$$

the inverse transform of the column characteristic is

$$\frac{F(t)}{\kappa_{i2}} = \frac{\mathcal{L}^{-1}\{\hat{G}\}}{\kappa_{i2}} = \frac{2D_{i2}}{a^2} \sum_{n=0}^{\infty} \exp\left[-\frac{D_{i2}(2n+1)^2\pi^2 t}{4a^2}\right] \tag{56}$$

and

$$\frac{\int_0^t F(t)\,dt}{\kappa_{i2}} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[-\frac{D_{i2}(2n+1)^2\pi^2 t}{4a^2}\right] \tag{57}$$

Equation (57) is shown in Fig. 3, along with the equivalent result for the discrete approximation. It is clear that there isn't much difference between the distributed and discrete solutions. The pertinent parameter to be extracted from the experimental data is a characteristic diffusion time, a^2/D_{i2}. *An effective value for this time can be obtained experimentally for any kind of packing*, not just the capillary chromatographic system described in this paper. One note

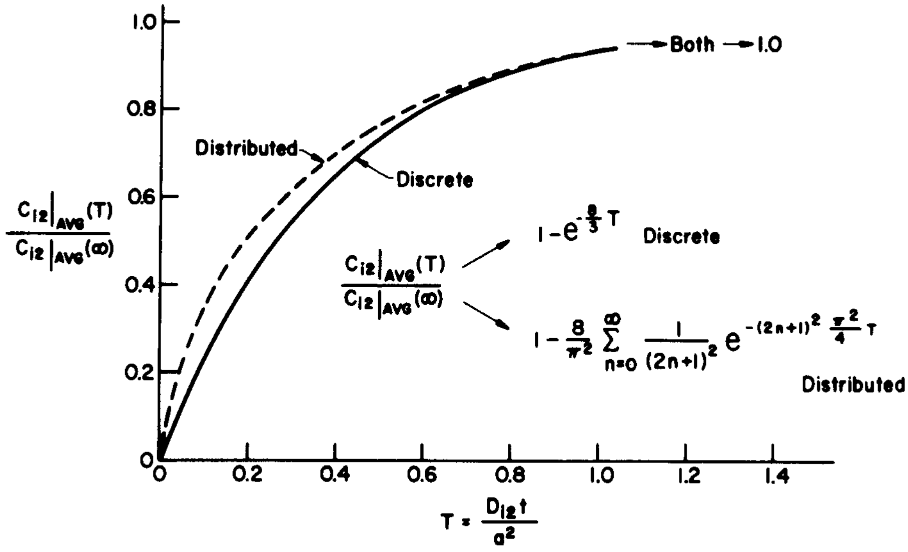

FIG. 3. Simulated uptake curves corresponding to Eqs. (57) and (61).

of caution should be mentioned, however. For the experimental value of a^2/D_{i2} from a single stage experiment to apply to a chromatographic column, the resistance to mass transfer in the gas phase must be small compared to that in the stationary liquid phase. Haller (*33*) has described the kind of single stage experiment described above and has even shown an experimental uptake curve similar to that in Fig. 3.

As we have shown elsewhere (*32*), the right-hand side of Eq. (57) is the formula for the Murphree stage efficiency, η_i (see Eq. 47 in Ref. *32*),

$$\kappa_{i2}\eta_i \equiv \int_0^t F(t)\,dt \tag{58}$$

and the right-hand side of Eq. (56) is the time derivative of the Murphree stage efficiency (see Eq. 51 in Ref. *32*),

$$\kappa_{i2}\frac{\partial \eta_i}{\partial t} \equiv F(t) \equiv \mathcal{L}^{-1}\{\hat{G}\} \tag{59}$$

Equation (59) is significant; it states that *the inverse of the column characteristic is equal to the product of* κ_{i2} *and the time derivative* *of the Murphree stage efficiency for the chromatographic column operated as a single equilibrium stage.* The quantity, $F(t)$, can therefore be determined by nonchromatographic experimental techniques. Once such a function is known, it is possible (in principle) to obtain its Laplace transform—the column characteristic—and thus to describe the behavior of elution peaks before the "long term approximation" becomes valid. For systems in which biological macromolecules are separated, there may be good reasons for performing these types of measurements (*33*, *34*).

OTHER EXAMPLES OF $F(t)$ AND $\int_0^t F(t)\,dt$

In the preceding section, we derived the inverse of the column characteristic $F(t)$, and the time integral of this inverse, $\int_0^t F(t)\,dt$, for Case 1. Summarized below are the corresponding results for Cases 2 through 4.

Case 2. Liquid-Phase Diffusion Control (Discrete Approximation)

$$\hat{G} = \kappa_{i2} \frac{\dfrac{8}{3}\dfrac{D_{i2}}{a^2}}{p + \dfrac{8}{3}\dfrac{D_{i2}}{a^2}} \tag{48}$$

$$F(t) = \frac{8}{3}\kappa_{i2}\frac{D_{i2}}{a^2}\exp\left[-\frac{8}{3}\frac{D_{i2}}{a^2}t\right] \tag{60}$$

$$\int_0^t F(t)\,dt = \kappa_{i2}\left(1 - \exp\left[-\frac{8}{3}\frac{D_{i2}}{a^2}t\right]\right) \tag{61}$$

Case 3. Liquid-Phase Rate Control

$$\hat{G} = \kappa_{i2}\left(1 + \frac{k'_{i3}}{p + k''_{i3}}\right) \tag{51}$$

$$F(t) = \kappa_{i2}\delta(t) + \kappa_{i2}k'_{i3}\exp\left(-k''_{i3}t\right) \tag{62}$$

$$\int_0^t F(t)\,dt = \kappa_{i2}\left[1 + \frac{k'_{i3}}{k''_{i3}} - \frac{k'_{i3}}{k''_{i3}}\exp\left(-k''_{i3}t\right)\right] \tag{63}$$

Case 4. Impermeable Liquid

$$\hat{G} = F(t) = \int_0^t F(t)\,dt = 0 \tag{64}$$

List of Symbols

a	thickness of liquid film (cm)
$A_\perp$	total lateral cross-sectional area (cm^2)
c	concentration (moles/cm^3)
$c\|_{Av}$	average concentration (moles/cm^3)
$\hat{c}$	Laplace transform of concentration
$\hat{c}\|_{Av}$	Laplace transform of average concentration
D	diffusion coefficient (cm^2/sec)
F	inverse of column characteristic
$\hat{G}$	column characteristic
k'_{i3}	forward pseudo-first-order rate constant (sec^{-1})
k''_{i3}	reverse pseudo-first-order rate constant (sec^{-1})
L	length of chromatographic column (cm)
$\mathbf{N}_\perp$	molar flux in lateral direction (moles/cm^2 sec)
p	Laplace transform variable
t	time (sec)
u	defined by Eq. (30) (sec)
v	velocity (cm/sec)
y	lateral Cartesian coordinate (cm)
z	axial Cartesian coordinate (cm)

Greek Letters

ϵ	volume fraction (cm^3/cm^3)
η	Murphree stage efficiency
κ	partition coefficient (moles/cm^3:moles/cm^3)
μ'_1	first normal statistical moment (sec)
μ'_n	nth normal statistical moment (sec^n)

Superscripts

0	initial value
m	value at lumping point
$'$	local value

Subscripts

i	component i
is	component i in environment s $\left(\text{i.e., partition state } \boxed{i:s}\right)$

n	number of partition states
n	power in Eq. (22)
s	environment s
$i1, i2, i3$	specific partition states
1, 2	specific phases

REFERENCES

1. J. C. Giddings, *Dynamics of Chromatography*, Dekker, New York, 1965, p. 14.
2. J. N. Wilson, *J. Amer. Chem. Soc.*, **62**, 1583 (1940).
3. A. J. P. Martin and R. L. M. Synge, *Biochem. J.*, **35**, 1358 (1941).
4. H. C. Thomas, *Ann. N. Y. Acad. Sci.*, **49**, 161 (1948).
5. J. J. van Deemter, F. J. Zuiderweg, and A. Klinkenberg, *Chem. Eng. Sci.*, **5**, 271 (1956).
6. J. C. Giddings and H. Eyring, *J. Phys. Chem.*, **59**, 416 (1955).
7. J. C. Giddings, *J. Chem. Phys.*, **31**, 1462 (1959).
8. P. Schneider and J. M. Smith, *A. I. Ch. E. Journal*, **14**, 762 (1968).
9. H. Yamazaki, *J. Chromatogr.*, **27**, 14 (1967).
10. H. Vink, *Ibid.*, **20**, 496 (1965).
11. P. Schneider and J. M. Smith, *A. I. Ch. E. Journal*, **14**, 886 (1968).
12. E. Kucera, *J. Chromatogr.*, **19**, 237 (1965).
13. M. Kocirik, *Ibid.*, **30**, 459 (1967).
14. O. Grubner, M. Ralek, and E. Kucera, *Collect. Czech. Chem. Commun.*, **31**, 2629 (1966).
15. O. Grubner, *Advan. Chromatogr.*, **6**, 173 (1968).
16. M. Kubin, *Collect. Czech. Chem. Commun.*, **30**, 1104 (1965).
17. J. C. Giddings and P. D. Schettler, *J. Phys. Chem.*, **73**, 2577 (1969).
18. P. D. Schettler and J. C. Giddings, *Ibid.*, **73**, 2582 (1969).
19. J. R. Conder and J. H. Purnell, *Trans. Faraday Soc.*, **65**, 824 (1969).
20. F. G. Helfferich, *Ind. Eng. Chem. Fundam.*, **6**, 362 (1967).
21. P. R. Rony, *Separ. Sci.*, **3**, 425 (1968).
22. J. C. Giddings, *Gas Chromatography 1964* (A. Goldup, ed.), Elsevier, Amsterdam, 1965, p. 3.
23. P. R. Rony, *Separ. Sci.*, **4**, 413 (1969).
24. P. R. Rony, *Ibid*, **4**, 447 (1969).
25. P. R. Rony, *A General Approach to Chemical Separations*, Monsanto, St. Louis, Mo., 1967.
26. J. C. Sternberg, *Advan. Chromatogr.*, **2**, 205 (1966).
27. V. A. Ditkin and P. I. Kuznetsov, *Spravochnik po operacionnomu ischisleniju*, Gostechizdat, Moscow, 1951, p. 140.
28. G. Doetsche, *Anleitung zum praktischen Gebrauch der Laplace Transformation*, Oldenbourg, Munich, 1956.
29. E. Th. Van der Laan, *Chem. Eng. Sci.*, **7**, 188 (1958).
30. H. S. Carslaw and J. C. Jaeger, *Operational Methods in Applied Mathematics*, Dover Publications, New York, 1963, p. 256.

31. J. E. Funk and G. Houghton, *J. Chromatogr.*, **6**, 193, 281 (1961).
32. P. R. Rony, *Separ. Sci.*, **3**, 519 (1968).
33. W. Haller, *J. Chromatogr.*, **32**, 676 (1968).
34. P. R. Rony and J. E. Funk, *Proceedings of the Sixth International Symposium on Advances in Chromatography* (A. Zlatkis, ed.), Department of Chemistry, University of Houston, Houston, Texas, 1970, p. 59; *J. Chromatogr. Sci.*, in press.
35. P. R. Rony and J. E. Funk, *Separ. Sci.*, **6**, 383 (1971).

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