

USE OF THE STATISTICAL MOMENTS METHOD TO ESTIMATE THE INFLUENCE OF INTERNAL MASS TRANSFER ON THE FORM OF ADSORBER BREAKTHROUGH CURVES

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A model of an adsorption bed was treated under the assumption that the bed behaves as a linear system. Adsorption of a single gaseous component from an inert gas stream was considered. Only such kinetic processes were taken into account which take place inside the adsorbent particles. The kinetics of adsorption was described by the time course of saturation of an adsorbent particle during a stepwise change of the adsorbate concentration on its external surface. This method gives expressions for statistical moments of breakthrough curves in terms of statistical moments of kinetic curves, which are accessible from independent kinetic measurements. The obtained expressions involve the influence of internal adsorption kinetics on the form of breakthrough curves.

The method of statistical moments has been applied for many times in the theory of chromatography to describe the form of elution and frontal curves¹⁻⁴, as well as in the description of the dynamic behaviour of adsorbers^{5,6}. The resulting expressions for normal and central statistical moments show the dependence of the position and shape of the breakthrough curve on the regime, geometry of the adsorption bed and physical constants characterizing the adsorption equilibrium and kinetic processes in the system.

Kinetic processes in the adsorption bed can be divided into two groups: 1) Processes in the intergranular space and 2) those taking place inside the adsorbent grains. The first group includes kinetic processes related closely to the flow character of the carrier medium in the intergranular space, while the second group includes those which are generally denoted as internal transfer or internal adsorption kinetics, and bear principally no relation to hydrodynamics in the intergranular space.

This work is an attempt to characterize the influence of the internal adsorption kinetics on the form of breakthrough curves. To this purpose an idealized model of the adsorption bed is treated, where only the internal mass transfer is taken into account, and it is irrespective which mechanism of the internal mass transfer takes place. The overall kinetics is important, which can be determined experimentally with the aid of an independent kinetic measurement using a sample of the adsorption bed. The measurement is carried out so that the external surface of the adsorbent particles

is subjected to a stepwise change of the adsorbent concentration. The experimental time dependences of the relative saturation of the adsorbent are denoted as kinetic curves. It will be shown how their moments characteristics can be used to express statistical moments of breakthrough curves. Thus, simple criteria are obtained which with the aid of a small number of kinetic and dynamic experiments enable to find out the significance of the adsorption kinetics or hydrodynamics for the adsorption dynamics. In systems where the influence of the internal transfer prevails it is possible to estimate the moments of breakthrough curves on the basis of the derived relationships.

The case involving axial dispersion of the adsorbate in the intergranular space was treated analogously. The application of these results and their interpretation is, however, much more complicated.

Statistical Moments as Information about Adsorption Kinetics

For the dynamics of adsorption, it is important to measure the kinetics of adsorption under conditions where the sample of the adsorption bed is at time $\tau < 0$ exposed to an inert gas stream free of adsorbate, and at time $\tau = 0$ there is a stepwise increase of the adsorbate concentration on the surface of the adsorbent particles. The internal adsorption kinetics is measured in the region of high linear velocities of the carrier gas where the form of the kinetic curve is no more dependent on the rate of flow, hence it can be assumed that the transfer of the adsorbate from the vicinity of the particle to its surface is the rate controlling step. A common method of kinetic measurement is gravimetric determination of the increment of the adsorbate in adsorbent grains, whereby the so-called kinetic curve is obtained, defined by the following equation:

$$\gamma(\tau) = (g_\tau - g_0)/(g_\infty - g_0). \quad (1)$$

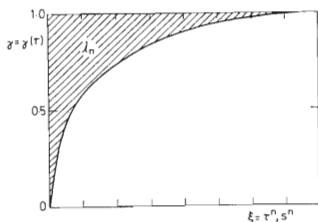


FIG. 1

Typical Course of Kinetic Curve in $\gamma - \tau^n$ Coordinates

The shaded area expresses the value of the moment λ_n .

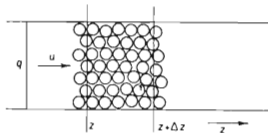


FIG. 2

Scheme of Adsorption Bed

The space coordinate is denoted as z , the linear velocity of the carrier medium as u .

Here $\gamma(\tau)$ denotes relative saturation of an adsorbent particle, g_τ , g_0 and g_∞ weight of the adsorbent at time $\tau = \tau$, $\tau = 0$ and $\tau \rightarrow \infty$, respectively. In solving problems of the adsorption kinetics, normal statistical moments of the kinetic curves⁸⁻¹¹ are used. The n -th normal moment, λ_n , of the kinetic curve is defined as

$$\lambda_n = \int_0^\infty \tau^n p(\tau) d\tau, \quad n = 0, 1, 2, \dots, \quad (2)$$

where $p(\tau) = d\gamma/d\tau$. The values of λ_n can be easily determined from experimental data since they are numerically equal to the area delimited by the axis of ordinates, line $\gamma = 1$ and curve $\bar{\gamma}(\xi)$ given parametrically as $\bar{\gamma} = \gamma(\tau)$ and $\xi = \tau^n$ (Fig. 1).

Expressions for the statistical moments, λ_n , can be also determined by the operational calculus with the assumption that the Laplace transform of the function $p(\tau)$ is known. We have¹²

$$\lambda_n = (-1)^n \lim_{s \rightarrow 0} d^n L[p(\tau)]/ds^n. \quad (3)$$

The operator L applied to the function $h(\tau)$ represents the Laplace transform of this function:

$$L[h(\tau)] \equiv \tilde{h}(s) = \int_0^\infty \exp(-s\tau) h(\tau) d\tau. \quad (4)$$

s is a complex variable.

MODEL OF ADSORPTION BED

We shall consider an adsorption bed of a cross section q filled with adsorbent particles of arbitrary size and shape which have generally a porous structure. The bed geometry is manifested in the magnitude of the external porosity, α , defined as the ratio of the intergranular to the total volume of the bed. We assume that local values of α do not differ appreciably from the mentioned average value.

An incompressible carrier medium moves through the bed in the direction of the z axis, which coincides with the column axis, with a linear velocity, u , given by

$$u = v/\alpha q, \quad (5)$$

where v is the volume rate of flow of the carrier medium. The adsorption isotherm of the given adsorbate-adsorbent system is assumed to be approximately linear:

$$a = Kc. \quad (6)$$

Here K is a constant, c concentration of the adsorbate in the intergranular space, and a concentration of the adsorbate in the adsorbent particles. The amount of the adsorbate is referred to the total volume of the adsorbent particles including their pores. The values of a and c are averaged over the total cross section of the column, q , and have the meaning of local concentrations depending on the coordinate z (Fig. 2).

To enable the formulation of solvable equations describing the system, it is assumed that the adsorbent particles are so small that an equal concentration is attained on the surface of all particles in a volume element $q dz$, and that the concentration of the adsorbate in the carrier gas is so low that its change during the process has no influence on the rate of flow. The influences of axial mixing and finite rate of mass transport to the surface of the adsorbent particles are assumed to be of no importance. The bed is isothermal and the pressure gradient in the column is negligible. Further the fulfillment of two general conditions is postulated: *A*) The bed behaves as a linear system, and *B*) all reactions proceed only in the adsorbent particles and are reversible. Then the mass balance equation takes the form

$$\partial C(z, t) / \partial t + u \partial C(z, t) / \partial z = -[(1 - \alpha) / \alpha] K \partial A(z, t) / \partial t. \quad (7)$$

Here $C = c/c_0$, c_0 denotes concentration of the adsorbate in the gas phase at the column inlet, $A(z, t) = a(z, t)/a_0$ instantaneous value of the saturation of the adsorbent in a given place in the column, a_0 equilibrium concentration of the adsorbate in the adsorbent corresponding to the concentration c_0 , and t time considered from the beginning of the experiment carried out under dynamic conditions. The time change of the value of $A(z, t)$ is expressed by the Duhamel integral¹³:

$$\frac{\partial A(z, t)}{\partial t} = \frac{\partial}{\partial t} \int_0^t \frac{\partial \gamma(t - \tau)}{\partial t} C(z, \tau) d\tau. \quad (8)$$

This equation is a result of the validity of the condition *A*. The initial and boundary conditions of the adsorption process in an initially unsaturated sorption bed are:

$$t = 0, \quad z > 0: \quad C(z, t) = A(z, t) = 0; \quad (9)$$

$$t < 0: \quad C(z, t) = 0; \quad t > 0: \quad C(z, t) = 1. \quad (10)$$

The condition *B* can be expressed as

$$0 < z < \infty: \quad \lim_{t \rightarrow \infty} C(z, t) = \lim_{t \rightarrow \infty} A(z, t) = \lim_{t \rightarrow \infty} \gamma(\tau) = 1. \quad (11)$$

Solution. With regard to the zero initial conditions, Eq. (7) can be rewritten with the use of the Laplace transform in the form

$$d\tilde{C}(z, s) / dz + (s/u) \tilde{C}(z, s) = -(s/u) K(1/\alpha - 1) \tilde{A}(z, s). \quad (12)$$

Similarly Eq. (8) gives

$$s\tilde{A}(z, s) = s\tilde{\gamma}(s) \cdot s\tilde{C}(z, s). \quad (13)$$

On eliminating $\tilde{A}(z, s)$ from Eqs (12) and (13) we obtain a first-order linear homogeneous equation:

$$d\tilde{C}(z, s)/dz + u^{-1}[1 + K(1/\alpha - 1) s\tilde{\gamma}(s)] s\tilde{C}(z, s) = 0. \quad (14)$$

The boundary condition (10) is transformed as

$$z = 0: \quad \tilde{C}(z, s) = 1/s. \quad (15)$$

By solving Eq. (14) with the condition (15) we obtain the resulting expression for the Laplace transform of the breakthrough curve:

$$\tilde{C}(z, s) = s^{-1} \exp[-s(\mu'_1)_v] \exp[-s(\mu'_1)_a s\tilde{\gamma}(s)], \quad (16)$$

where

$$(\mu'_1)_v = z/u, \quad (\mu'_1)_a = (z/u)(1/\alpha - 1)K. \quad (17), (18)$$

The first normal moment, μ'_1 and higher central moments⁵, μ_n ($n > 1$), are used as characteristics of the breakthrough curves. Normal and central moments of the breakthrough curve can be determined from a dynamic experiment. The operational calculus gives for the normal statistical moments an expression analogous to Eq. (3):

$$\mu'_n = (-1)^n \lim_{s \rightarrow 0} (d^n/ds^n) [s\tilde{C}(z, s)]. \quad (19)$$

The central moments can be derived from the normal ones¹². The first normal moment can be calculated from Eq. (16) with the use of the Laplace transform of the condition (11), which can be written in the form

$$0 < z < \infty: \quad \lim_{s \rightarrow 0} s\tilde{\gamma}(s) = \lim_{s \rightarrow 0} s\tilde{A}(z, s) = \lim_{s \rightarrow 0} s\tilde{C}(z, s) = 1. \quad (20)$$

Hence

$$\mu'_1 = (\mu'_1)_v + (\mu'_1)_a = (z/u) [1 + (1/\alpha - 1)K]. \quad (21)$$

The central moments can be calculated by displacing of the origin of the time scale into the point $t_0 = (\mu'_1)_v$. The corresponding normal moments in the new coordinate system are calculated by applying Eq. (19) to the function

$$\tilde{G}(z, s) = s^{-1} \exp[-s(\mu'_1)_a s\tilde{\gamma}(s)], \quad (22)$$

which is the Laplace transform of the function

$$G(z, t) = C(z, t - t_0). \quad (23)$$

From the moments thus obtained follow the expressions for central moments of the breakthrough curve by using Eqs (3), (20) and the corresponding known relations between central and normal moments:

$$\mu_2 = 2(\mu'_1)_a \lambda_1, \quad \mu_3 = 3(\mu'_1)_a \lambda_2, \quad \mu_4 = 4(\mu'_1)_a \lambda_3 + 12(\mu'_1)_a^2 \lambda_1^2. \quad (24)-(26)$$

These formulas show how the form of the breakthrough curve, represented by its central moments, depends on the quantity $(\mu'_1)_a$ equal to the mean residence time of an adsorbate particle in the stationary phase of the adsorption column, and on the quantities λ_n which characterize the internal adsorption kinetics and which can be experimentally determined from an independent kinetic measurement. By comparing measured values of the central moments of the breakthrough curves with values determined from a kinetic experiment it can be decided to what extent the internal kinetics is manifested in the dynamics of the process and what is the role of hydrodynamics in the resulting effect. If the influence of the internal kinetics prevails, Eqs (24)–(26) can be used to predict the form of the breakthrough curves.

To characterize the efficiency of the adsorption bed, a quantity called the number of theoretical plates of the column, N , is introduced in analogy to other separation processes. The value of N for a given column depends on the type of adsorbate and on working conditions. The number of plates, N , is determined by the first normal and second central moments of a given breakthrough curve¹⁴ independently of its higher moments:

$$N = (\mu'_1)^2 / \mu_2. \quad (27)$$

Since with respect to the dynamics of adsorption in the gas–solid system the capacity of the intergranular space is mostly negligible against the capacity of the stationary phase, we can set

$$\mu'_1 \approx (\mu'_1)_a. \quad (28)$$

Eq. (27) can then be rewritten with the use of (24) in the form

$$N \approx \mu'_1 / 2\lambda_1 \quad (29)$$

representing an estimate of the column efficiency with the aid of an independent kinetic experiment.

It can be concluded that the values of statistical moments of experimentally determined kinetic curves can include the influence of external diffusion provided that the external transfer takes place under given experimental conditions. This influence is manifested by an additive increment of the quantities λ_1 through λ_3 . However, for the prediction of breakthrough curves the kinetics involving external transfer

will obviously be of little value since it can be hardly imagined how to simulate similar hydrodynamic conditions during the kinetic measurement as exist in the adsorption bed.

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