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Separation Science and Technology

Publication details, including instructions for authors and subscription information:
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A More Precise Criterion for the Formation of a Steady-State Sorption Front

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To cite this Article Safonov, M. S.(1971) 'A More Precise Criterion for the Formation of a Steady-State Sorption Front', Separation Science and Technology, 6: 1, 35 — 41

To link to this Article: DOI: 10.1080/00372367108055549

URL: http://dx.doi.org/10.1080/00372367108055549

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SEPARATION SCIENCE, 6(1), pp. 35–41, February, 1971

NOTE

A More Precise Criterion for the Formation of a Steady-State Sorption Front

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Summary

A more precise criterion for the formation of a steady-state sorption front is the convergence of the integrals which characterize the quantity of a sorbate in the leading edge of the front and the unused capacity of a sorbent behind the front. Existence of an asymptotic solution of the equation of sorption dynamics is not sufficient for convergence of these integrals, if the line passing through the points of the equilibrium isotherm, which correspond to the initial concentratons in the solution and in the sorbent, is tangent to the isotherm at one of these points.

AN INTEGRAL ESTIMATE OF SPREADING OF THE SORPTION FRONT

The concept of a "sorption front" implies that a moving transition zone exists in a column reactor between the initial unused and the saturated sorbent. Idealization of the process leads to an image of a step boundary where the concentration of a sorbate is changing discontinuously. The velocity of that step is defined by a well-known relationship, namely

$$u = \frac{\chi\nu(c_2 - c_1)}{(1 - \chi)(m_2 - m_1) + \chi(c_2 - c_1)} \tag{1}$$

A real front spreads because of the limited sorption rate and longi-

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tudinal mixing. This spreading occurs symmetrically about the imaginary point moving along the column with velocity u, i.e., the expression (1) determines the most natural mobile coordinate system, $\xi = z - ut$, for an observer analyzing the process.

There are two possible estimations of the spreading of the front. The usual "differential" one is the distance $\Delta\xi(\delta c)$ between the concentration points $c_1 + \delta c$ and $c_2 - \delta c$ when δc is sufficiently small. The disadvantage of this estimation arises in the indefiniteness of the choice of δc. As it follows from any solution of equations of sorption dynamics, the limit of $\Delta\xi(\delta c)$, as δc approaches zero,, does not exist. This is analogous to the properties of the ordinary diffusion equation.

A more natural estimate of the front spreading is the "integral" one, achieved by means of improper integrals, viz.,

$$I_1 = \int_{c(\xi=0)}^{c\to c_1} \{(1-\chi)(m-m_1) + \chi(c-c_1)\}\, d\xi \tag{2}$$

or

$$I_2 = \int_{m\to m_2}^{m(\xi=0)} \{(1-\chi)(m_2-m) + \chi(c_2-c)\}\, d\xi \tag{3}$$

These integrals show the quantity of a sorbate that has penetrated in front of the point $\xi = 0$, and the total unused capacity of the column behind that point. Similar integrals were used first in the theory of chromatography by De Vault (*1*) and Glueckauf (*2*). It follows from the law of conservation of matter that the integrals I_1 and I_2 should be equal. Front spreading is symmetrical relative to the point $\xi = 0$ only in the sense of equality of these integrals.

In accordance with these different estimations of front spreading, the approach to a steady-state front might be characterized with limiting transitions $\Delta\xi(t) \to \text{const}$ (when $t \to \infty$) or $I(t) \to \text{const}$ (as $t \to \infty$).

Previous investigators considered the existence of an asymptotic solution $\xi(c)$ to the sorption dynamics equation as a sole condition for the formation of a steady-state front. It has been shown in a general form (*3, 4*) that the asymptotic solution exists if, and only if, in the interval $c_1 < c < c_2$ the equilibrium isotherm lies above the line passing through the points (c_1, m_1) and (c_2, m_2) (Fig. 1).

However, as we shall show in the present note, in the case of some special kinds of the sorption isotherm the existence of such a solution is not yet sufficient for convergence of the integrals I_1 and I_2 as $t \to \infty$. Evidently, if a limit of I_1, when $t \to \infty$, does not exist, there is

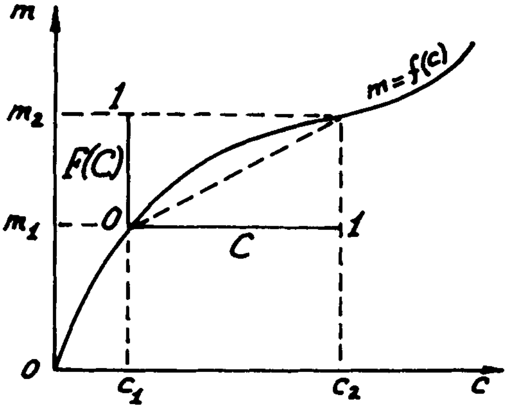

FIGURE 1.

no value in considering an established front of sorbtion in the column, as an infinite quantity of a sorbate penetrates ahead. Similarly, if I_2 diverges as $t \to \infty$, there is no value in discussion of an established front of total displacement of a preceding substance from the sorbent.

CONDITIONS OF CONVERGENCE OF THE INTEGRALS I_1 AND I_2 WHEN $t \to \infty$

For the sake of simplicity we shall consider the problem for a fixed bed of a sorbent and neglect longitudinal diffusion. Then the initial system of equations for mass transfer is

$$(1 - \chi)\frac{\delta m}{\delta t} + \chi\frac{\delta c}{\delta t} = -\chi\nu\frac{\delta c}{\delta z} \tag{4}$$

$$(1 - \chi)\frac{\delta m}{\delta t} = k\{f(c) - m\} \tag{5}$$

But results obtained might be generalized for a moving bed and longitudinal diffusion taken into account. The manner of expression of the "driving force" of mass transfer in Eq. (5) through concentrations in sorbent or in solution does not matter for the final conclusions.

The asymptotic steady-state solution $C(\xi)$ would satisfy the following ordinary differential equation, which the system (4)–(5) is reduced to,

$$h\frac{d^2C}{d\xi^2} + \{F'(C) - 1\}\frac{dC}{d\xi} = 0 \tag{6}$$

where

$$F'(C) \equiv f'(c)\,\frac{c_2 - c_1}{m_2 - m_1}$$

$$h \equiv \frac{\chi(\nu - u)(c_2 - c_1)}{k(m_2 - m_1)}$$

the generalized height of a transfer unit (attributed to the moving coordinate system), with boundary conditions

$$C \to 0,\ \frac{dC}{d\xi} \to 0 \text{ as } \xi \to +\infty \tag{7}$$

$$C \to 1,\ \frac{dC}{d\xi} \to 0 \text{ as } \xi \to -\infty \tag{8}$$

After integration we get

$$\int_{C\,(\xi=0)}^{C} \frac{dC}{F(C) - C} = -\frac{\xi}{h} \tag{9}$$

where the constant $C(\xi = 0)$ may be determined from equality of the integrals I_1 and I_2 (*3*). The solution (9) is feasible [satisfies conditions (7) and (8)] if $F(C) > C$, and the latter inequality just expresses the criterion of existence of an asymptotic solution (*3, 4*).

Existence of the limit of I_1, when $t \to \infty$, is conditioned by behavior of the asymptotic solution $C(\xi)$ as $C \to 0$; so it is sufficient to investigate convergence of the integral

$$\int_{\xi_i}^{\infty} C\,d\xi \tag{10}$$

where ξ_i is so large that the solution (9) could be substituted with a suitable asymptotic representation for $C \to 0$. By expanding $F(C)$ into a series near the point $C = 0$, we get

$$F(C) - C = \{F'(0) - 1\}C + \tfrac{1}{2}F''(0)C^2 + \cdots + \frac{1}{n!}F^{(n)}C^n + \cdots \tag{11}$$

As $F(C) > C$, we can imagine only two cases: (1) $F'(0) > 1$, (2) $F'(0) = 1$ (Fig. 2, Curve *a*); in the latter case we get $F''(0) > 0$ or, if $F''(0) = 0, \ldots, F^{(n-1)}(0) = 0$, then $F^{(n)}(0) > 0$. Neglecting in the expansion (11) all the terms with the exception of the first one, which is not equal to zero, we find the following representations for the solution (9) in the region of small C:

$$C = C_0 \exp\left\{-\frac{F'(0) - 1}{h}\,\xi\right\} \qquad \text{as } F'(0) > 1 \tag{12}$$

and

$$C = \frac{n!h}{F^{(n)}(0)}\,(\xi - \xi_0)^{-1/(n-1)} \qquad \text{where } n \geq 2, \text{ as } F'(0) = 1 \tag{13}$$

where C_0 and ξ_0 are constants. Evidently, integral (10) converges for integrand (12), whereas it diverges for integrand (13).

Similarly, expanding $F(C)$ into a series near the point $C = 1$ we should obtain that integral I_2 converges, when $t \to \infty$, for $F'(1) < 1$, but it diverges for $F'(1) = 1$ (Fig. 2, Curve *b*).

Therefore, a more precise criterion for the formation of a steady-state front is that the line passing through the points (c_1, m_1) and (c_2, m_2) must lie below the isotherm $m = f(c)$ in the interval $c_1 < c < c_2$ and must not be tangent to the isotherm at the points (c_1, m_1) and (c_2, m_2).

It should be noted that even if the differences $F'(0) - 1$ or $1 - F'(1)$ are not exactly equal to zero, when one of them is very small, the value of the integral I_1 or I_2 would be so large that we could not observe formation of steady-state front in any column of real length.

Isotherms with such points of tangency belong to the class of sigmoid isotherms that are characteristic, for example, of the ion-exchange of ions of different valencies. Development of the boundaries of chromatographic bands in the case of a sigmoid isotherm has been treated within limits of the "equilibrium" theory of chromatography (*5*). This theory has shown that progressive spreading must occur of that part of the front that corresponds to the segment of the isotherm

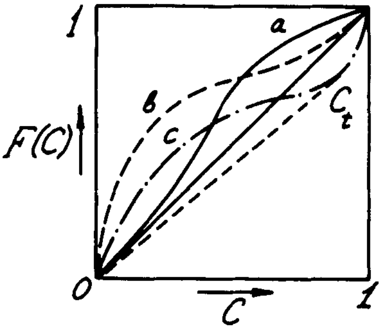

FIGURE 2.

from the point C_t, where the tangent from the point $C = 0$ touches the isotherm, to the point $C = 1$ (Fig. 2, Curve *c*), the remainder of the front being interpreted in the theory as a sharp boundary.

Experimental evidence of unlimited spreading of the sorption front with isotherm of the Type *b* was given in Refs. *6* and *7*. These authors have not succeeded in obtaining the steady-state front of displacement of (*a*) a mixture of K^+ and Rb^+ with $CaCl_2$ solution, or (*b*) a mixture of Rb^+ and Cs^+ with $BaCl_2$ solution from KU-1 resin in a countercurrent column; in both the cases the ion-exchange isotherm was of the type indicated.

LIST OF SYMBOLS

c	molar concentration in solution
$c_1 \equiv f^{-1}(m_1)$	the concentration in the solution that would be in equilibrium with the initial sorbent
c_2	the concentration in the solution that enters the column
$C \equiv \dfrac{c - c_1}{c_2 - c_1}$	dimensionless concentration
$f(c)$	function describing sorption equilibrium (sorption isotherm)
$F(C) \equiv \dfrac{f(c) - m_1}{m_2 - m_1}$	sorption isotherm in dimensionless concentrations
k	mass transfer coefficient
m	molar concentration in sorbent
m_1	the initial concentration in sorbent
$m_2 \equiv f(c_2)$	the concentration in the sorbent that would be in equilibrium with the entering solution
t	time
z	distance from the entrance
v	linear velocity of solution
ξ	distance in the moving coordinate system
χ	the part of volume occupied by solution

Acknowledgments

The author is grateful to Dr. A. Dyer, Department of Chemistry and Applied Chemistry, University of Salford, for his kind help in preparing this note. The author wishes also to thank the British Council for arranging a scholarship under the Anglo-Soviet Cultural Agreement, during which this work was carried out.

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Received by editor May 30, 1970