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Review

Non-linear waves in chromatography

I. Waves, shocks, and shapes

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ABSTRACT

Cause and effect in non-linear chromatography are examined from the point of view of wave theory. This first of four instalments is restricted to single-component systems and examines monotonic concentration variations and chromatographic peaks and bands. It uses the wave equation, which states the velocity at which a given concentration advances, to establish the properties of "waves," that is, monotonic concentration variations. Depending on the sense of curvature of the isotherm, a wave may be self-sharpening or non-sharpening. A self-sharpening wave remains, or sharpens to become, a shock layer; a nonsharpening wave spreads indefinitely, eventually in proportion to traveled distance. The concentration profile of a shock layer depends on the shape of the isotherm and on the dispersive effect of non-idealities, of which resistance to mass transfer usually is the most important. Mass-transfer resistance in the moving phase causes "fronting;" mass-transfer resistance within the stationary sorbent causes "tailing." It is therefore in general not possible to model shock layers with only a single, lumped mass-transfer parameter. The concentration profile of a nonsharpening wave depends almost exclusively on the shape of the isotherm.

The knowledge of wave behavior is used to examine peak shapes in elution under overload conditions and bands in displacement. The peak shape in elution is almost entirely determined by the degree of overload and the shape of the isotherm. Wave theory confirms a rule previously stated by Knox that, in columns exceeding a certain length, samples containing the same amount of solute give peaks of essentially the same shape under conditions of predominant concentration overload, predominant volume overload, or any combination of the two. In displacement development, the final pattern can be established by determination of the lengths of the bands of the individual components according to Tiselius and separate calculation of the shock-layer profiles.

CONTENTS

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This first instalment of the series will examine the nature of non-linear waves and the implications for *single-component* non-linear chromatography, specifically, for the dependence of the shapes of waves, peaks, and bands on physical aspects such as isotherm shape and mass-transfer resistances. Multicomponent problems will be examined later in this series.

I.1. DEFINITIONS

For simplicity, the two phases between which a solute partitions will be called the *moving phase* and the *sorbent* (or sorbent phase). Thus, "sorbent" will refer to gel-type or porous sorbent beads, to the surfaces of impermeable adsorbent beads or column walls, or to a stationary liquid sorbent on or in a solid support which may be a particle or the column wall. "Moving phase" rather than "mobile phase" is used to make clear that the term refers exclusively to the fluid traveling through the column, not to a stationary liquid within or on a support.

In conformity with established usage, *linear chromatography* will be understood to refer to chromatography with no interaction between solute molecules of the same or different kinds (*i.e.*, linear sorption isotherms, no interactions through occupancy of moving-phase volume, axially uniform flow-rate). Linear chromatography thus does not exclude non-linear mass-transfer equations. Correspondingly, *non-linear chromatography* is taken to be chromatography with non-linear isotherms or other interactions between solute molecules.

The term *multicomponent chromatography* will be reserved for systems in which different solutes affect one another's behavior, specifically, systems in which the sorbent-phase concentration of a solute depends not only on the moving-phase concentration of that solute, but on those of all other solutes as well. Multicomponent systems thus are necessarily non-linear. This definition of multicomponent chromatography is practical because the response in systems with independent solutes is easily constructed by additive superposition of single-solute responses and so requires no theory beyond that for single solutes.

Ideal chromatography, in some earlier work also called equilibrium theory, will be understood to imply the following simplifying premises: (1) local equilibrium between moving and sorbent phases, (2) ideal plug flow, (3) mass transfer in axial direction by convection only, (4) axially uniform volumetric flow-rate of bulk moving phase, (5) isobaric behavior, (6) isothermal behavior, and (7) absence of chemical reactions that transform solutes and thereby alter their sorption behavior. Except where specifically mentioned, assumptions 4–7 will also be taken as valid when non-ideal systems are discussed.

Non-linear chromatography is most easily understood as a phenomenon of *waves*, a term borrowed from physics of compressible fluids [1,2], where quite similar differential equations apply. A wave is defined as a variation of dependent variables: in chromatography, of solute concentrations and possibly of temperature [3,4]. (Usually, a wave moves; however, standing waves can arise under certain conditions, *e.g.*, in countercurrent operation). A typical chromatographic wave is the advancing "front" of a solute that is being injected into a column initially free of solutes. In contrast to waves in acoustics and optics, those in chromatography thus are not oscillations, are not characterized by frequencies. It will prove expedient to reserve the term wave to a *monotonic* variation. A typical chromatographic peak then consists of two waves: its front and its rear (*i.e.*, the parts downstream and upstream of the apex, respectively); similarly, a flat-top peak under overload conditions or a band in displacement consists of a plateau between two waves (see Fig. 1.1). The behavior of peaks and bands is necessarily more complex than that of (monotonic) waves. Therefore, the properties of waves are discussed in detail before this knowledge is applied to peaks and bands.

1.2. VELOCITIES

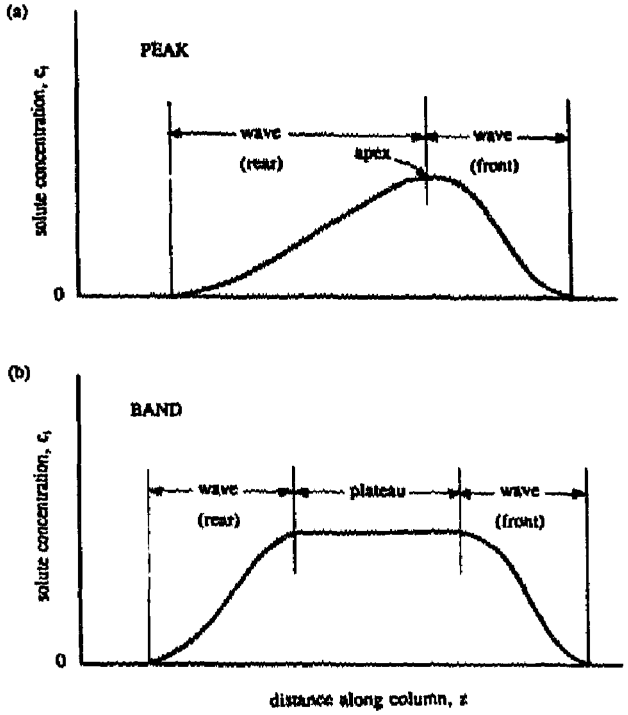

Fig. 1.1. Wave terminology for (a) chromatographic peak, (b) chromatographic band or flat-top peak.

Most of the conventional literature on chromatography and fixed-bed adsorption is in terms of retention times or volumes [5–7] or other throughput-related parameters [8,9] rather than velocities. The latter [4,10–13], although less directly related to observable effluent concentration histories, are used here because they allow waves to be studied regardless of their origin and position in a column, and so make it easier to visualize their properties and behavior: A velocity is a *local* phenomenon, independent of conditions elsewhere and thus of the column size, elapsed time, injection history, etc.

With this focus on waves, the central question in the analysis of any chromatographic phenomenon becomes, "how fast does any given solute *concentration* advance in the direction of flow?" This, rather than the velocity of solutes molecules, is the starting point. By definition, the velocity v_{c_i} of a moving-phase concentration c_i of solute i is

$$v_{c_i} \equiv (\partial z/\partial t)_{c_i} \qquad (1.1)$$

(z = linear distance in direction of flow, t = time). Granted the premises of ideal chromatography *except local equilibrium*, the equation for conservation of mass of solute in a differential cross-section of the column is

$$\underbrace{\frac{\rho}{\varepsilon}\left(\frac{\partial q_i}{\partial t}\right)_z + \left(\frac{\partial c_i}{\partial t}\right)_z}_{\text{accumulation}} + \underbrace{v^0\left(\frac{\partial c_i}{\partial z}\right)_t}_{\text{outflow - inflow}} = 0 \qquad (1.2)$$

and gives the concentration velocity [11]

$$v_{c_i} = \frac{v^0}{1 + (\rho/\varepsilon)(\partial q_i/\partial c_i)_z} \qquad (1.3)$$

(v^0 = velocity of moving-phase flow; q_i = sorbent loading, ρ = bulk density of sorbent, ε = fractional void volume of bed; ρ/ε is constant under normal conditions; for exact definitions see Symbols section). This "wave equation" is the most important equation in non-linear chromatography. Characteristic of non-linear chromatography is that the wave velocity, even under ideal conditions, varies with the solute concentration.

In *ideal* chromatography, the phases are in local equilibrium, so that q_i can be expressed as a unique function of c_i alone, regardless of distance and time. Accordingly, the partial differential in eqn. 1.3 can be replaced by the respective total differential, so that the wave equation becomes [4,11]

$$v_{c_i} = \frac{v^0}{1 + (\rho/\varepsilon)(\mathrm{d}q_i/\mathrm{d}c_i)} \qquad (1.4)$$

where $\mathrm{d}q_i/\mathrm{d}c_i$ is the slope of the equilibrium sorption isotherm of solute i (or of the tangent to the isotherm) at the respective concentration c_i (see Fig. I.2). This velocity, at which the concentration would travel if the phases were in equilibrium, will be called the "natural" wave velocity. *The steeper the isotherm, the lower is the natural wave velocity.*

In non-linear chromatography, the distinction between *particle velocities* and *wave velocities* is important [11,14]. In physics of fluids [1], a particle velocity is the (macroscopic and average) velocity of an identifiable *object*, say, a volume element of fluid; a wave velocity is the velocity of a given *value of a variable*. The two can be very different. For example, a hurricane with sustained winds of over a hundred miles an hour may advance at only, say, ten or twenty miles per hour and possibly in a quite different direction. The wind velocity (of volume elements of air) is a particle velocity, the velocity of the storm itself (the low-pressure system) is a wave velocity. The concentration velocities in eqns. 1.3 and 1.4 above are wave velocities. The particle velocity v_i of a solute i at a given concentration is readily derived with the argument that molecules of i advance, at the velocity of moving-phase flow, only while they are in that phase, and not at all while they are at rest on or in the stationary sorbent. The fraction of solute that is moving is $\varepsilon c_i/(\varepsilon c_i + \rho q_i)$ or, rearranged, $1/[1 + (\rho/\varepsilon)q_i/c_i)]$, and the particle velocity accordingly is [11,14]

$$v_i = \frac{v^0}{1 + (\rho/\varepsilon)q_i/c_i} \qquad (1.5)$$

While the natural wave velocity depends on the slope of the *tangent* to the isotherm at the respective concentration, the particle velocity depends on the

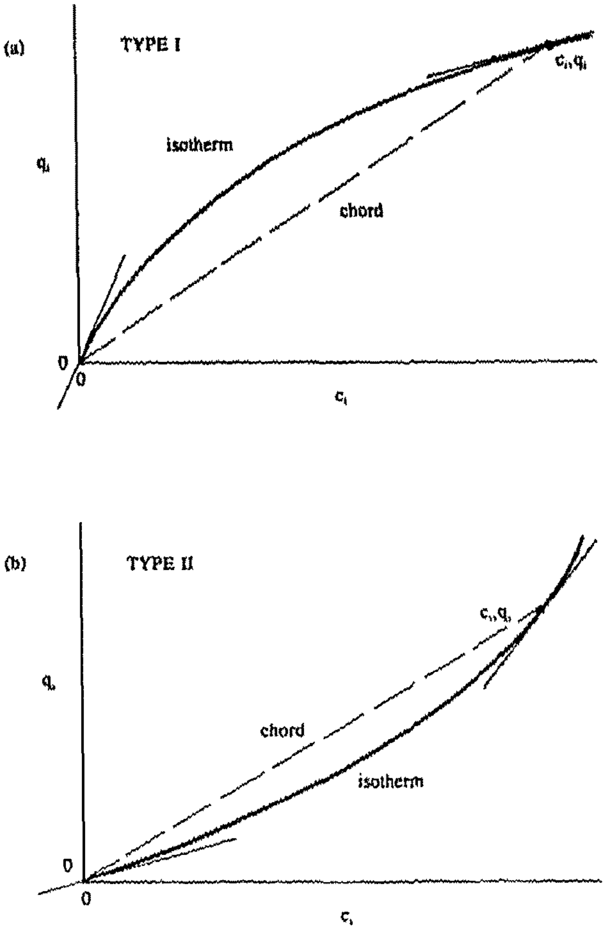

Fig. I.2. Isotherms with tangents $\mathrm{d}q_i/\mathrm{d}c_i$ at $c_i = 0$ and a point $c_i > 0$, and with chord of that point; (a) Type I; (b) Type II.

ratio q_i/c_i, that is, on the slope of the *chord* of the isotherm point corresponding to that concentration (see Fig. 1.2). Only in linear chromatography do waves (concentration variations) and particles (solute molecules) move at the same velocity.

To appreciate the difference between the two types of velocities, consider the advance of a pulse of incrementally higher moving-phase concentration of solute in a column whose sorbent, at the original, lower concentration, is already loaded to its maximum capacity. The sorbent cannot accommodate any more solute, so the pulse must advance at the velocity of moving-phase flow (the pulse velocity is a wave velocity); indeed, for zero isotherm slope, eqn. 1.4 gives $v_{c_i} = v^0$. Meanwhile, the solute molecules that, at any given moment, constitute the pulse spend part of their time at rest on or in the sorbent and so advance at a lower average velocity (particle velocity) given by eqn. 1.5; they are being overtaken by the pulse. A standard detector (measuring a spectral response, fluorescence, refractive index, conductivity, or any other property that is a measure of concentration) in the effluent registers the arrival of the *concentration pulse* that traveled at the *wave velocity*. In contrast, a radioactivity detector would register the arrival of a pulse of injected tagged molecules that traveled at the *particle velocity*. If the injected concentration pulse were to have contained radioactively tagged molecules, the concentration pulse and the radioactivity pulse would reach the column end at different times [14].

[The fact that a concentration perturbation (the concentration pulse) should outrun or lag behind the slug of molecules of which it consisted upon injection is not easy to accept. However, the underlying difference between wave velocities and particle velocities is one of the fundamental principles of physics and is absolutely essential for proper understanding of non-linear chromatography. A more easily visualized and somewhat analogous situation is that of a sonic boom, in which the wave (a pressure variation in this case) travels much faster than the molecules that generated the boom in the first place, as well as those being compressed by the boom at any given moment. Still another interesting example is that of a traffic jam, in which the congestion (a wave) is actually propagated *against* the direction of the flow of the cars (the particles). The reader who still has conceptual reservations may wish to study ref. 14 and section 3.III.B of ref. 11, where such matters are discussed in more detail.]

1.3. LINEAR WAVES

Waves in linear chromatography, thoroughly familiar to all practitioners, present a logical starting point for the application of the concepts and equations of wave theory.

In linear chromatography, the isotherm slope $\mathrm{d}q_i/\mathrm{d}c_i$ is constant, independent of the moving-phase concentration, so that according to the wave equation 1.4 all moving-phase concentrations of a given solute have the same natural velocity. In *ideal* linear chromatography, in which concentrations move with their natural velocities, any wave then travels "as is", that is, without sharpening or spreading (see Fig. 1.4a and b); the same is, of course, also true for a peak. In *real* linear chromatography, the dispersive effects of non-idealities make the wave spread. In chromatography, the relevant effects are: (i) deviation from local equilibrium because of finite rate of equilibration between the moving and sorbent phases, (ii) axial diffusion, and (iii) deviation from plug flow.

If local equilibrium were to be maintained, the rate coefficients of all steps required for equilibration of the moving phase with the sorbent would have to be infinitely large. With coefficients of finite values, transfer of solute from one phase to the other to establish equilibrium can occur only if non-equilibrium provides a "driving force". Accordingly, the concentration variation in or on the sorbent always lags slightly behind that in the moving phase as a wave moves through a position in the column. The sharper the wave, the faster is the concentration variation in the moving phase at a position in the column as the wave passes through, and so the harder it is for the concentration variation in or on the sorbent to keep pace with that in the moving phase. Accordingly, the stronger is the dispersive effect of non-equilibrium.

The flux of axial diffusion is proportional to the axial concentration gradient (Fick's law). Thus, here, too, the dispersive effect is stronger if the wave is sharper.

The irregular packing of a real column causes deviations from plug flow even if the flow is laminar. Stream lines branch and rejoin, and travel times

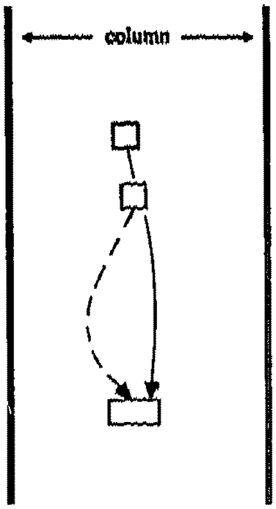

Fig. I.3. Branching and rejoining of stream lines with different residence times in an irregular packing. From ref. 15

along such branches are not equal. This amounts to mixing, at the confluence of two stream lines (or at the column exit), two moving-phase volume elements that were previously at different distances from the column entry (see Fig. I.3). The sharper a wave, the greater is the concentration difference between two such volume elements, and the stronger is the dispersive effect. The same is obviously true for eddy mixing in turbulent flow, where once again volume elements previously at different distances from the column entry are mixed.

In all three cases —finite equilibration rate, axial diffusion and non-plug flow— the dispersive effect thus is seen to diminish as the wave spreads. The familiar result is that the wave spreads in proportion to the *square root* of traveled distance (or elapsed time), as is common in diffusion processes. In non-linear wave theory, such linear waves are also called *indifferent* [11], in distinction from self-sharpening, nonsharpening, and composite non-linear waves (see farther below, and Table I.1, in which the sharpening or spreading behavior of linear and non-linear waves is summarized).

I.4. SELF-SHARPENING WAVES, SHOCKS, AND SHOCK LAYERS

We turn now to non-linear waves, that is, monotonic concentration variations in systems with non-linear isotherms.

Imagine a moving phase containing solute at constant concentration c_i^0 entering a column that was initially free of sorbate, and the adsorption isotherm being of *Type I* (negative curvature, see Fig. I.2a). The advancing "front" of solute *i* is a non-linear wave. At the leading edge of this sorption wave, where the concentrations of *i* are still low, the isotherm is steep and, according to the wave equation I.4, the natural wave velocity is low. At the tail end of the wave, at high concentrations of *i*, the opposite is true. Since the trailing portions tend to advance more rapidly than the leading ones, the wave tends to sharpen if initially diffuse (see Fig. I.4c) [16]. The wave is said to be *self-sharpening* [17] (in physics of fluids it is called a compressive wave).

In *ideal* chromatography, in which concentrations travel at their natural velocities, such a wave sharpens to become, or remains, a concentration discontinuity (see Table I.1). Unlike an ocean wave rolling onto a beach, such a wave cannot "break", *i.e.*, higher concentrations from its rear cannot

TABLE I.1

SHARPENING AND SPREADING BEHAVIOR OF WAVES

Wave	Ideal chromatography	Real chromatography
Indifferent wave (linear wave)	Travels without change in profile	Spreads in proportion to square root of traveled distance
Self-sharpening wave	Sharpens into discontinuity (shock) then travels as such	Sharpens (or spreads) into shock layer of finite width, then travels without change in profile
Nonsharpening wave	Width increases linearly with traveled distance	Width increases linearly with traveled distance

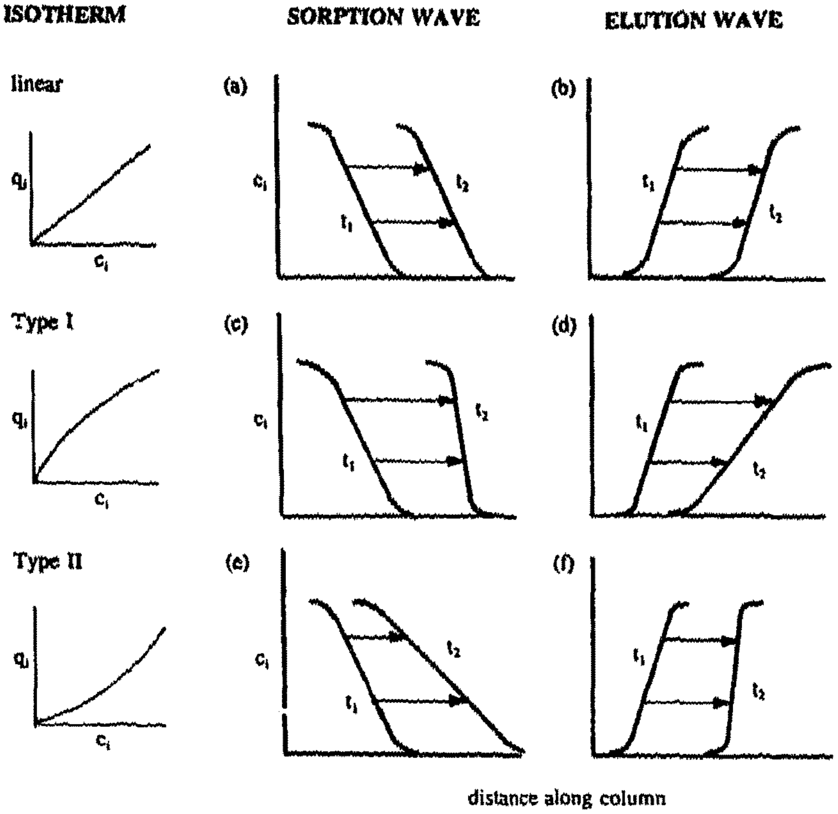

Fig. 1.4. Sharpening behavior of sorption and desorption waves of ideal chromatography resulting from shape of isotherm: concentration profiles at successive times t_1 and $t_2 > t_1$ of waves diffuse at t_1 (schematic).

overtake lower ones ahead because this would lead to the physically impossible coexistence of three different concentrations of the same solute at the same location. Instead, the wave keeps traveling as a discontinuity [16]. In terms of mathematics, the physically realized solution of the differential mass balance (eqn. I.2) is a so-called weak solution, with two branches separated by a discontinuity [18,19]. The velocity $v\Delta_{c_i}$ at which the discontinuity advances is readily derived from a mass balance across it [4,11]:

$$v\Delta_{c_i} = \frac{v^0}{1 + (\rho/\varepsilon)\Delta q_i/\Delta c_i} \qquad (I.6)$$

where Δ stands for the difference between the downstream and upstream sides of the wave. [Eqn. I.6 is equivalent to the Rankine–Hugoniot equation in physics of fluids.] The discontinuity is called a *shock*. An infinite number of weak solutions satisfy the differential mass balance (eqn. I.2) and the initial and input conditions since the position of the discontinuity remains unspecified, but eqn. I.6 uniquely identifies the appropriate one.

In our *real* world of compressible fluids or of chromatography, dispersive effects of non-idealities prevent a wave from sharpening into a discontinuity. As was shown for linear waves, the relevant dispersive effects of finite equilibration rate, axial diffusion, and deviation from plug flow all decrease in strength as the wave spreads (or increase as the wave sharpens). In contrast, the sharpening tendency of the wave resulting from the dependence of the natural velocity on concentration, given by the difference in isotherm slopes at its front and rear ends, is independent of the current sharpness of the wave. Therefore, at some finite width of the wave, the sharpening and spreading tendencies achieve a balance [9,17,20]. A shelf-sharpening wave sharpens if initially more diffuse, or spreads if initially sharper, until that balance is attained, and then continues its travel without further change in width or shape (see

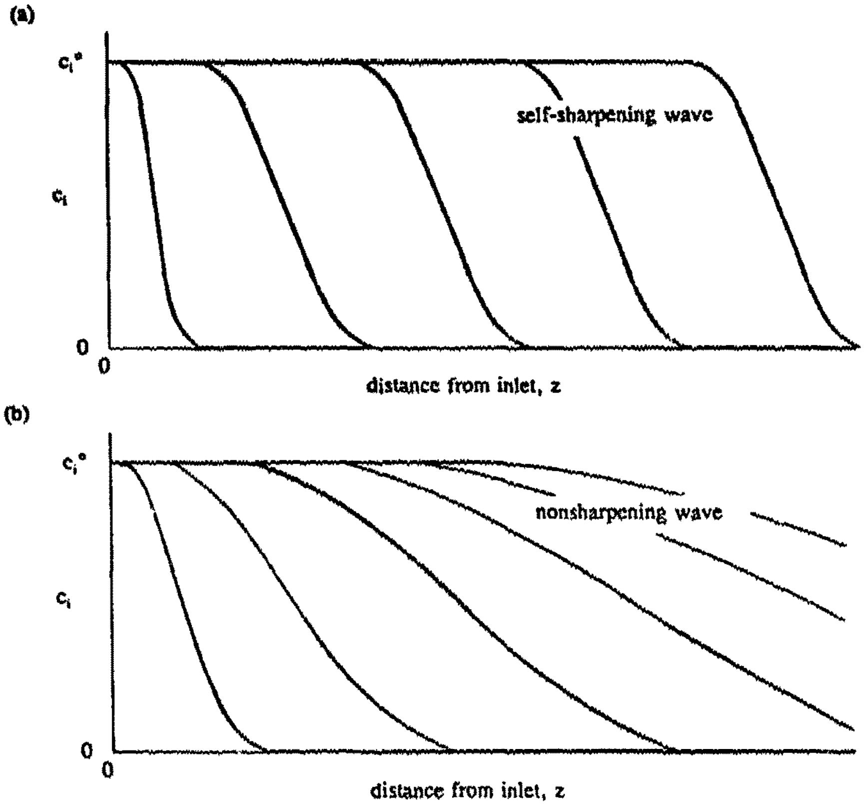

Fig. I.5. Concentration profiles in non-ideal chromatography at successive times for waves generated by step input: (a) self-sharpening wave; (b) nonsharpening wave.

Fig. I.5a and Table I.1). Such a wave with a steep, but continuous profile is often called a *shock layer* if attention is to be drawn to its not being a discontinuity. The shock velocity equation (eqn. I.6) remains valid for the shock layer [11].

A shock layer also results, for the same physical reasons, when a solute with an isotherm of Type II is eluted from the column by a solvent or carrier gas: In this case, the high solute concentrations are in the forward portion of the wave and are most strongly retarded because they have the steepest isotherm slopes (see Fig. I.2b), so that the wave sharpens if initially diffuse (see Fig. I.4f).

The terms shock and shock layer, adopted from physics of compressible fluids, are relatively new in chromatography and fixed-bed adsorption. However, the phenomena they describe have been familiar to chromatographers and adsorption engineers for almost half a century, if under different names. For a glossary of equivalent terms, see Table I.2.

I.5. NONSHARPENING WAVES

Consider the case in which the solute advancing in the initially sorbate-free column has an isotherm of *Type II* (positively curved, see Fig. I.2b). Here, the isotherm slope is less steep at the leading (low) concentrations than at the trailing (high) concentrations. According to the wave equation I.4, the forward portions now have higher natural velocities than those farther behind, so that the sorption wave tends to spread (see Fig. I.4e) [16]. Non-idealities only add to that tendency. Soon, the wave becomes so diffuse that the dispersive effects of the non-idealities no longer matter. From then on, the width of the wave increases *linearly* with traveled distance or elapsed time (see Fig. I.5b and Table I.1) [9]. Such a wave is said to be *nonsharpening* [17] (dispersive wave or rarefaction wave in physics of fluids).

A nonsharpening wave also results when a solute with Type I isotherm is eluted from the column by a

TABLE I.2

EQUIVALENT TERMS IN WAVE MATHEMATICS, FIXED-BED ENGINEERING AND NON-LINEAR CHROMATOGRAPHY

Terms used here are shown in bold. The equivalence of terms is not exact, in part because problems other than with uniform initial and constant influent conditions have rarely been considered except by wave mathematicians. Terms used with more restrictive meanings are shown in parentheses.

Wave mathematics	Fixed-bed engineering	Chromatography (pre-1970)
Wave	Mass-transfer zone[a] [21], transition [9,12], front or wavefront [13]	Boundary [16,17,22], (front) [23]
Compressive wave		**Self-sharpening** boundary [17]
Shock, **shock layer**	Constant mass-transfer zone[a] [15], abrupt transition [9], **constant pattern** [8,9,12,24]	Steady form of boundary [22]
Rarefaction wave, dispersive wave (simple wave)	Gradual transition [9]	**Nonsharpening** boundary [17]
Centered wave (self-similar wave)	**Proportionate pattern** [8,9,12]	
Linear wave, contact discontinuity (if sharp)		**Indifferent** boundary [11]

[a] Originally called exchange zone (for binary ion exchange).

solvent or carrier gas. Here, the isotherm slope and thus the retardation are greater for the trailing, low concentrations than for leading, high concentrations of the elution wave (see Figs. I.2b and I.4d).

Since the dispersive effects of non-idealities fade as the wave spreads, ideal theory is usually quite satisfactory for nonsharpening waves.

[As is often pointed out, in the mathematics of ideal chromatography a weak solution satisfying the differential and overall mass balances also exists for a nonsharpening wave that starts as a discontinuity, allowing it to travel as such. The intermediate concentrations then never come into existence, so that the wave equation I.4 remains inapplicable because no gradients $\mathrm{d}q_i/\mathrm{d}c_i$ can be defined. That this weak solution has no physical reality can be shown with a complex argument according to which the effect would be to decrease the entropy of the system, in violation of the second law of thermodynamics [18,25,26]. For practical purposes, however, it suffices to say that the slightest non-ideality of the real world causes the intermediate concentrations to become realized, so that the wave equation becomes applicable and produces proportionate spreading; this shows that, for a nonsharpening wave, the weak solution of ideal chromatography is not an asymptotic solution for vanishing non-idealities, and so is of no practical significance.]

I.6. CONSTANT AND PROPORTIONATE PATTERNS

A shock layer traveling without further sharpening or spreading is said to have attained a *constant pattern* [8,9,12,13,24]. A nonsharpening wave that spreads in proportion to traveled distance is said to have attained a *proportionate pattern* [8,9,12,13]. Exactly constant or proportionate patterns are possible only in ideal chromatography, and proportionate ones only for waves starting as discontinuities. Like equilibrium and steady state, in the real world the patterns are only approached asymptotically.

The time or distance of travel required for approach to a constant or proportionate pattern (to within a specified margin) in non-ideal chromatography depends on the shape of the isotherm [8,9]. For any wave that enters the column as a discontinuity (step change in solute concentration of enter-

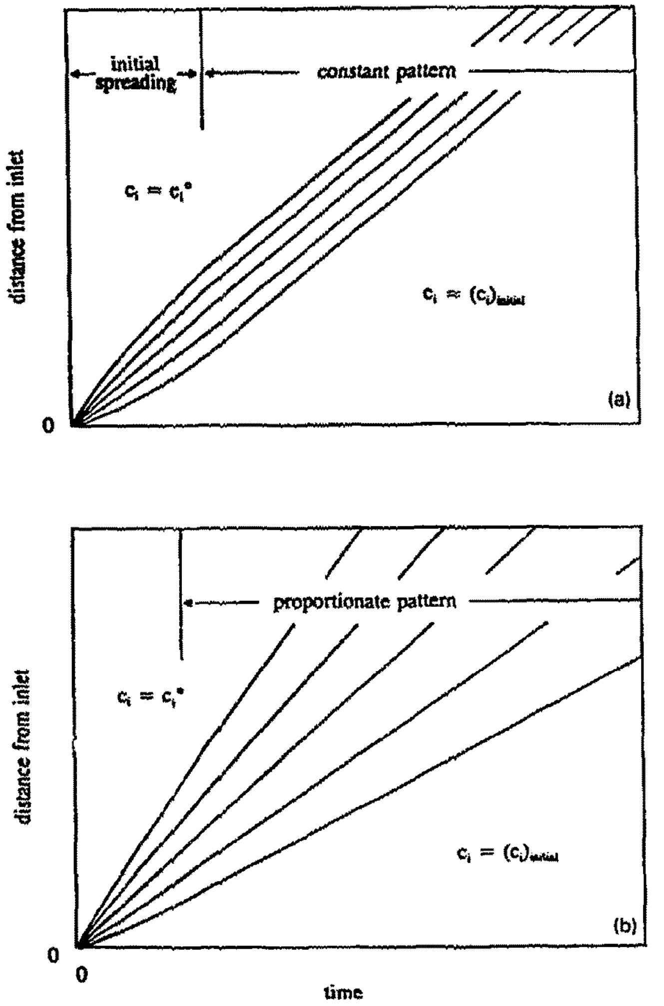

Fig. I.6. Concentration contours in distance–time diagrams in non-ideal chromatography, showing approach to final patterns of waves generated by step input: (a) constant pattern of self-sharpening wave; (b) proportionate pattern of nonsharpening wave. From ref. 15.

ing fluid), the dispersive effect of the non-idealities is overwhelming initially, making the wave spread at first in a square-root pattern regardless of its self-sharpening or nonsharpening nature (see Fig. I.6). If the isotherm is strongly curved, the final pattern is approached rapidly [*e.g.*, in passing through about 10 theoretical plates for a Langmuir isotherm $q_i/Q_i = Kc_i/(1 + Kc_i)$ with $K(c_i)_{max} =$ [illegible] In a self-sharpening wave, the sharpening tendency owing to the isotherm curvature then is so strong that the balance with the dispersive effects is closely approached when the wave has spread but a little; in a nonsharpening wave the spreading tendency then is so strong and spreading so fast that the dispersive effects of the non-idealities quickly become negligible compared with that of the isotherm curvature. On the other hand, if the isotherm is almost linear, the sharpening or spreading tendency resulting from the minute curvature is so weak that the dispersive effects of the non-idealities remain dominant for a long time; if so, the wave may leave the column before it has deviated much from square-root spreading. (For guidance concerning requirements for close approach to the final pattern, see Fig. 16-11 in Perry's Handbook [9]).

What matters in this context is the change in isotherm slope *within the isotherm segment over which the wave extends* or, in other words, the difference in isotherm slopes between the points corresponding to the concentrations upstream and downstream of the wave. Thus, for a given isotherm, the sharpening or spreading tendency is weaker, the smaller the concentration variation across the wave. In the extreme, very small waves or pulses are, as a rule, essentially indifferent and adequately described by linear theory, even if the isotherm spanning large variations is non-linear.

I.7. TERMINOLOGY

Use of a precise terminology can help to avoid confusion. Note the differences:

"*Sharp*" and "*diffuse*" describe current states of waves.

"*Self-sharpening*" and "*nonsharpening*" describe tendencies.

"*Sharpens*" or "*spreads*" describes what a wave currently does.

"*Shocks*" or "*shock layers*" are self-sharpening waves that have attained or closely approached their final patterns.

A self-sharpening wave may well be diffuse, for instance if it was recently generated by a gradual variation of the inlet concentration; likewise, a nonsharpening wave may still be sharp, not yet having had time to spread much from an initial, even sharper state. A self-sharpening wave may actually spread, namely, while it approaches its constant pattern after having started as a discontinuity, or if an increase in flow-rate makes it approach a new and less sharp constant pattern.

I.8. SHOCK-LAYER PROFILES

While non-idealities have little, if any, effect on a nonsharpening wave, they in combination with the isotherm curvature dictate the shape of the concentration profile in a shock layer. In *linear* chromatography, the lumping of all non-ideal effects into one parameter —a lumped dispersion coefficient, Peclet number, or height equivalent to a theoretical plate (HETP)— is customary [5,6,7,10,27]. However, *the classic doctrine of likeness and additivity of effects is not in general valid in non-linear chromatography*, as will be seen. (Even in linear chromatography it is valid only if linear driving force approximations are used for the equilibration rate: with more elaborate mass-transfer equations, distinct differences between non-ideal effects appear [28–30]).

Of the three principal non-idealities —finite equilibration rate, non-plug flow, and axial diffusion— the dispersive effect of the first increases with increasing flow-rate (faster wave), that of the second (branching and rejoining of stream lines) depends only weakly on flow-rate as long as the flow remains laminar, and that of the third increases with decreasing flow-rate (longer residence time gives more time for diffusion) [5–7,10,27]. Whereas the separation efficiency in analytical chromatography is best when the effects are comparable in magnitude [5–7,10,27], the desire for high throughput in preparative chromatography usually calls for flow-rates so high that local non-equilibrium caused by the finite equilibration rate is dominant and therefore must receive greatest attention.

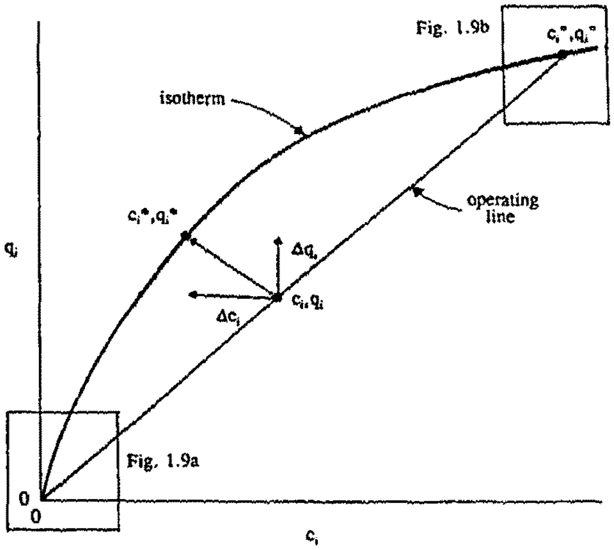

Fig. 1.7. q_i *vs.* c_i diagram with isotherm, operating line, and driving force with its contributions; boxes in lower left and upper right indicate areas enlarged in Fig. 1.9. From ref. 15.

I.8.1. Finite mass-transfer rate

To understand the effect of a finite mass-transfer rate on the profile of a shock, we must first establish how the sorbent loading q_i varies with the moving-phase concentration c_i within the constant-pattern shock layer. The concentrations are *not* in local equilibrium, as the shock would then be an ideal discontinuity. However, granted the effects of non-plug flow and axial diffusion are unimportant, the wave equation I.3 still holds since equilibrium was not postulated in its derivation. By definition, the wave in its constant pattern does not change its shape; this requires all concentrations to move at the same velocity. According to the wave equation, this is true only if the derivative $(\partial q_i/\partial c_i)_z$ has the same value at all concentrations. Therefore, the variation of q_i with c_i in a constant pattern must be *linear*! [9,17]. Fig. I.7 shows such a linear variation in the form of an "operating line" in a q_i *vs.* c_i diagram, together with the respective "equilibrium curve" (isotherm)[a], here of Type I. At any location within the constant-pattern shock layer, the bulk-phase concentrations correspond to a point (c_i, q_i) on the operating line, and the concentrations at the interface of sorbent and moving phase correspond to a point (c_i^*, q_i^*) on the isotherm (granted equilibrium at the interface).

I.8.1.1. Linear driving-force approximations

Many mathematical models for mass-transfer rates have been postulated, and depending on the type of sorbent one or the other may be more appropriate. The simplest model assumes equilibrium

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[a] The terms *equilibrium curve* and *operating curve* (or operating line, if linear) are from chemical engineering usage in mass-transfer operations such as distillation, liquid extraction, gas absorption, etc. The operating curve shows the actual, non-equilibrium condition of the column, and its distance from the equilibrium curve is a quantitative measure of the distance from equilibrium and thus of the driving force for interphase mass-transfer.

at the interface between the moving and stationary phases and postulates linear driving-force approximations for both phases, implying that the rate in each is proportional to the distance from equilibrium:

$$(\rho/a)(\partial q_i/\partial t)_z = k_f(c_i - c_i^*) = k_s\rho(q_i^* - q_i) \quad \text{(I.7)}$$

where a is the specific surface area, k_f and k_g are the coefficients of mass transfer between bulk moving phase and interface and between interface and sorption sites, respectively, asterisks refer to the interface between sorbent and moving phase (see also Fig. I.8; the transfer rates in two phases are equal because the interface, being two-dimensional, has no capacity.) The overall driving force corresponds to an arrow from (c_i, q_i) to (c_i^*, q_i^*) in Fig. I.7, with components $\Delta c_i \equiv c_i - c_i^*$ and $\Delta q_i \equiv q_i^* - q_i$. As the distance from equilibrium, the length of the arrow is a measure for the magnitude of the driving force.

The mass-transfer resistance in the moving phase may dominate. This is true if at all concentrations the product of mass-transfer coefficient and maximum possible driving force is much smaller in the moving phase than in the sorbent; that is:

$$\text{rate control in moving phase if } k_f c_i / k_s \rho f(c_i) \ll 1 \quad \text{(I.8)}$$

where $f(c_i)$ is the sorbent loading q_i in equilibrium with c_i. If so, $q_i^* \approx q_i$ (no significant concentration gradient in the sorbent), and the driving-force arrow in the q_i *vs.* c_i diagram (Fig. I.7) then is practically *horizontal*. Similarly:

$$\text{rate control in sorbent phase if } k_f c_i / k_s \rho f(c_i) \gg 1 \quad \text{(I.9)}$$

Here, $c_i^* \approx c_i$, and the driving-force arrow then is practically *vertical*. [Even if the mass-transfer coefficient is smaller in the sorbent, as is usually the case because of obstruction in the sorbent, a highly favorable partitioning of the solute into the sorbent, $f(c_i)/c_i \gg 1$, most likely at low c_i, may overcompensate this effect.]

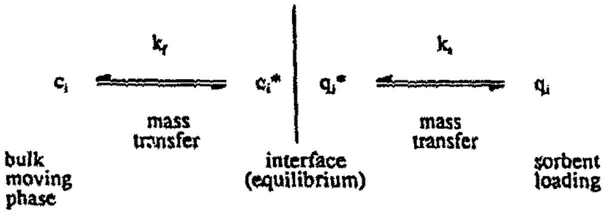

Fig. I.8. Model underlying driving-force approximations for mass transfer (sorbent loading q_i is averaged over bead and taken as bulk sorbent-phase concentration).

We consider first an adsorption shock with Type I, Langmuir-like isotherm of the solute. As can be seen in Fig. I.9, for ideal rate control in the moving phase the driving force (dashed arrows) is rather weak (short arrow) at low concentrations, and is still respectable even at quite high concentrations; reference to Fig. I.7 shows it to have its maximum (largest horizontal distance between operating line and isotherm) at concentrations well above the halfway point on the operating line. The opposite is seen to be true for rate control in the sorbent: Here, the driving force (solid arrows) is weak at high and still fairly strong at low concentrations, and has its maximum at well below the halfway point. The stronger the driving force, the faster are the concentration variations $(\partial q_i/\partial t)_z$ and $(\partial c_i/\partial t)_z$ in a sorbent layer (note that q_i varies linearly with c_i along the operating line). That is to say, the strength of the driving force translates directly into the steepness of the slope of the concentration history or profile at the respective concentration. Accordingly, for rate control in the moving phase, the profile or history of the sorption shock is less steep at the leading, low concentrations (weak driving force) than at the trailing, high concentrations (strong driving force); and for rate control in the sorbent the opposite is true. The profile and history are asymmetrical, depending on where the predominant mass-transfer resistance resides:

- *For rate control in the moving phase, the wave "fronts" and has a sharp tail; for rate control in the sorbent, the wave has a sharp front and "tails"* [9,22,31]

(see Fig. I.10; as used here, "fronting" of a wave implies a profile that is less steep in the forward than in the rear portion of the wave, and "tailing" implies the opposite). The effect is stronger, the stronger the isotherm is curved within the segment over which the wave extends, and is practically nonexistent if that segment is almost linear. Also, the profile is almost symmetrical if the two mass-transfer resistances are about equally important, that is, if $k_f c_i \approx k_s \rho f(c_i)$.

If the isotherm segment of interest is strongly curved, the driving-force ratio $\Delta c_i/\Delta q_i$ decreases sig-

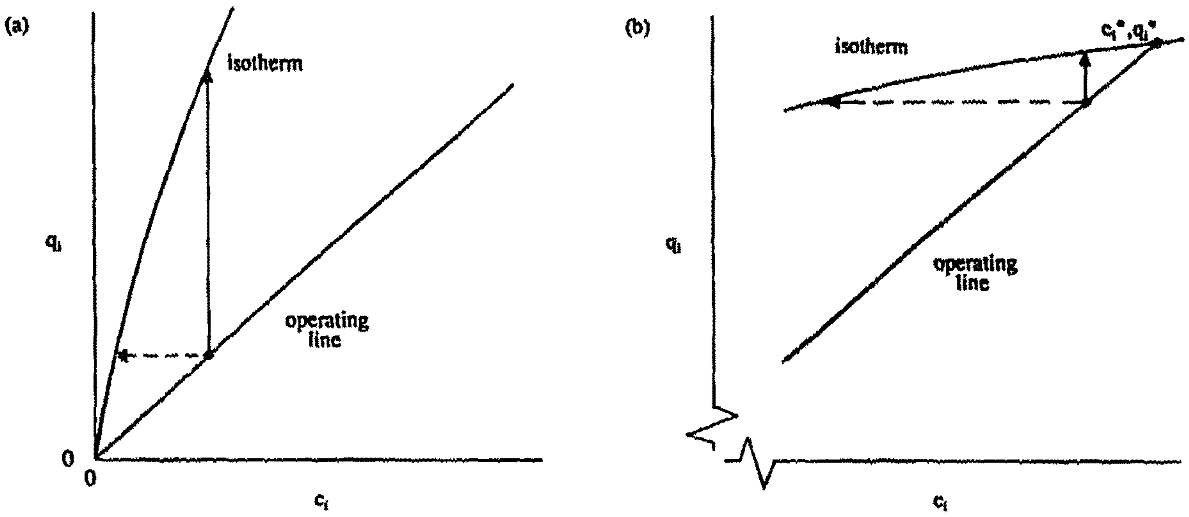

Fig. I.9. Driving forces for ideal moving-phase control (→) and ideal sorbent-phase control (→): (a) at low concentrations; (b) at high concentrations (enlarged portions of Fig. I.7). From ref. 15.

nificantly with decreasing concentration. As a result, the mass-transfer resistance in the moving phase is most serious at the very lowest concentrations and so causes some fronting even if it is negligible at higher concentrations [22]. This is very important in practice because fronting amounts to early breakthrough and so affects efficiency or purity.

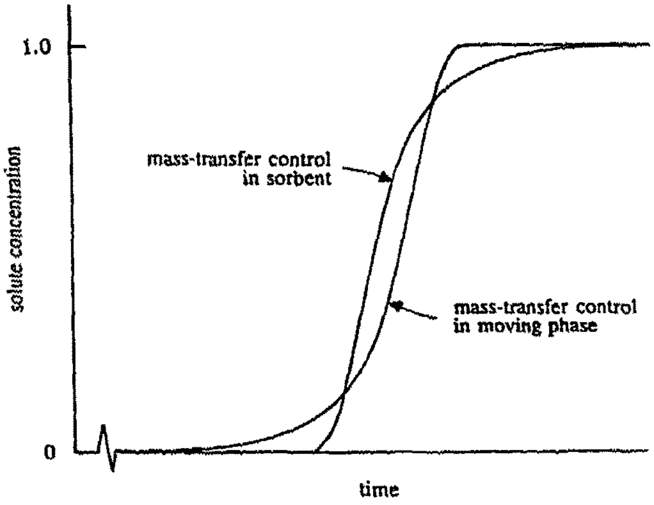

Fig. I.10. Concentration histories of shock layers for rate control by mass transfer in moving phase and in sorbent, exhibiting "fronting" and "tailing", respectively; calculated with linear driving-force approximations [17,21] for strongly curved Langmuir isotherm $q_i Q_i = Kc_i (1 + Kc_i)$ with $K(c_i)_{max} \approx 9$ (corresponds to binary ion exchange with separation factor $\alpha_{12} = 10$).

The discussion so far has assumed that the isotherm is reasonably Langmuir-like. Any deviation from such a shape also affects the shock-layer profile. As an illustration, Fig. I.11 shows a Type III isotherm with driving-force arrows corresponding to about equal importance of the resistances in the two phases. For this isotherm and under such mass-transfer conditions, the driving force is strong at low and weak at high concentrations, producing a wave with little fronting and fairly heavy tailing, an asymmetry in this case *not* attributable to a predominant mass-transfer resistance in the sorbent.

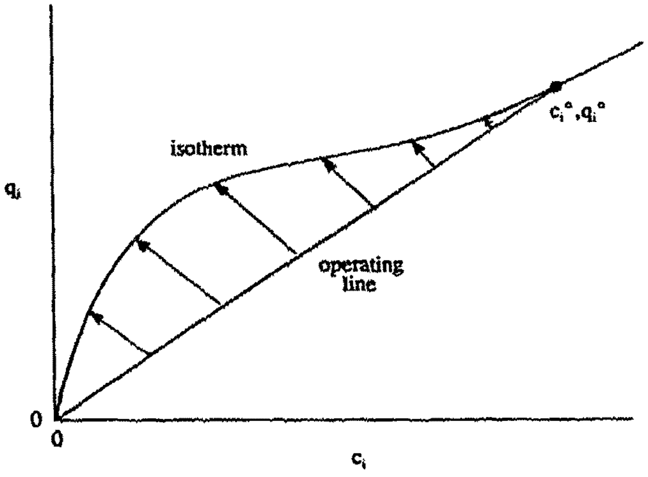

Fig. I.11. Type III isotherm, with operating line and driving-force arrows for shock layer.

In elution of a solute with Type II isotherm (Fig. I.2b), the driving-force arrows for sorbent-phase rate control tend to be long at the high (leading) and short at the low (trailing) concentrations, and for moving-phase rate control the opposite applies. Accordingly, the elution shock tends to tail in the former case and to front in the latter. The behavior thus is the same as for the Type I adsorption shock.

I.8.1.2. Other mass-transfer models

The linear driving-force relationships in eqn. I.7 are idealizations. For the moving phase the approximation is usually satisfactory; for the sorbent, much less so. In the first place, the structure of the sorbent phase may suggest a different mechanism, say, sorption by a stationary liquid in the pores of a support, followed by diffusion in that liquid and finally adsorption at the pore walls ("pore diffusion model") [32]. Even if the sorbent can be regarded as quasi-homogeneous, as is true for gel-type beads, the linear driving-force approximation is problematic: Strictly speaking, there is no "bulk-phase concentration" in the sorbent as the concentration at any time varies throughout the bead, so that the sorbent loading (amount of sorbate in bead, divided by sorbate-free bead mass) has to be used instead. Also, diffusion in such a bead obeys Fick's (see ref. 28) or Nernst–Planck's (see ref. 33) laws rather than a linear driving-force relationship. Moreover, because the rate under such conditions depends on the current shape of the concentration profile in the sorbent as well as on the loading, *no* equation in which the rate is a unique function of equilibrium, moving-phase concentration, and sorbent loading, regardless of its complexity, can fit actual behavior under all sets of possible initial and boundary conditions [33].

Chemical engineers have devised a great number of more realistic mass-transfer models, calculated the constant-pattern shock shapes they produce, and represented the results in various forms. The most complete collection, largely in form of dimensionless graphs, can be found in section 16 of Perry's Handbook [9]. The only justification for singling out the linear driving-force approximations here is because they are the simplest and easiest to visualize, and because the *qualitative* behavior of the other, more realistic models is the same, as a study of the information in the handbook section shows. In particular:

- *The more complex models give qualitatively the same fronting and tailing of shocks as do the linear driving-force approximations.*

This is not surprising since even in the more complex models the mass-transfer rate increases or decreases with the distance from equilibrium, though not in proportion to that distance as in the linear driving-force approximations.

I.8.2. Finite rate of attachment to sorbent ("reaction-rate control")

The equilibration rate may also be controlled by the rate of attachment to (or detachment from) active sites on the sorbent. This is sometimes called an adsorption "reaction", even if the solute undergoes no chemical transformation other than the attachment itself (*e.g.*, by hydrogen-bonding). Such behavior is fairly common in chromatography of large molecules, *e.g.*, peptides and proteins, on small or impenetrable sorbent particles. The most commonly used rate equation is that employed by Langmuir in the derivation of his famous isotherm [34]:

$$(\partial q_i/\partial t)_z = k_a c_i(Q_i - q_i) - k_d q_i \qquad \text{(I.10)}$$

[k_a = Langmuir adsorption rate coefficient, k_d = Langmuir desorption rate coefficient, Q_i = f(c_i) at $c_i \to \infty$ = ultimate sorption capacity]. Eqn. I.10 is mathematically equivalent to the rate equation in the Thomas model (see Appendix) and implies a Langmuir isotherm. Applied to constant-pattern shock layers it produces concentration profiles with *symmetrical* S-shapes (see Appendix for proof).

I.8.3. Other non-idealities

I.8.3.1. Axial diffusion

Axial diffusion contributes an additional term to the basic material balance. Eqn. I.2 becomes [10,11]:

$$\frac{\rho}{\varepsilon}\left(\frac{\partial q_i}{\partial t}\right)_z + \left(\frac{\partial c_i}{\partial t}\right)_z + v^0\left(\frac{\partial c_i}{\partial z}\right)_t - \underbrace{D\left(\frac{\partial^2 c_i}{\partial z^2}\right)_t}_{\text{diffusion term}} = 0 \qquad \text{(I.11)}$$

(D = diffusion coefficient, assumed concentration-independent) and results in a more complex wave equation. Under conditions of local equilibrium and with a reasonably Langmuir-like isotherm, this produces a tailing profile not unlike that resulting from rate control by sorbent-phase mass transfer. This is evident from the mathematical solutions [9,35] and can be made plausible as follows: Solute that has diffused forward into volume elements ahead of the main wave is effectively picked up by the sorbent which, preequilibrated at a still lower concentration, is loaded to a significantly lesser extent (steep isotherm); behind the main wave, solute that diffused forward and so depleted the solution is not as readily replaced by desorption from a sorbent whose equilibrium loading is not much lower at the lower solution concentration (flat isotherm).

I.8.3.2. Non-plug flow

The effect of non-plug flow (see Fig. I.3) is essentially the same as that of diffusion. Usually, both are accounted for by use of eqn. I.11 with D as a lumped dispersion coefficient. A more detailed model includes channeling and transverse diffusion [36].

I.8.4. Other non-linear effects

I.8.4.1. Axially non-uniform flow-rate

In gas and supercritical-fluid chromatography, the flow-rate may be axially non-uniform. If the pressure drop is significant, volume elements of the gas phase expand as they travel through the column, so the volumetric flow-rate is higher at the front end of a wave than at its tail. This effect is very slight (small pressure drop across any one wave) and is of little interest because it increases the distances between waves by the same factor as it broadens the waves themselves. A more important effect is that, at high solute concentrations, the mass and volumetric flow-rates are significantly higher where solute molecules are present and thus must be moved in addition to those of the carrier gas. This so-called *sorption effect* tends to sharpen the front of a solute peak or band and to spread its rear [37–41]. In liquid-phase chromatography, the effect is negligible because the change in total volume upon mass transfer between two condensed phases is insignificant.

I.8.4.2. Thermal effects and reactions

The effects caused by non-isothermal behavior and chemical transformation of the solute are different in kind from those discussed above: Rather than having a dispersive effect on wave profiles, they produce entirely different chromatographic patterns. Therefore, their discussion is deferred for the time being.

I.8.5. Analytical solutions

Constant-pattern profiles of shock layers are relatively easy to calculate by use of a frame of reference that travels with the wave. Within this frame there is no change with time, so only an ordinary rather than partial differential equation has to be solved [17]. Explicit analytical solutions or approximations have been given for some isotherms, including especially Langmuir's, in combination with linear driving-force equations in the moving phase [21] and in the sorbent [17] and for axial diffusion or dispersion [35] (see section 16 of Perry's Handbook [9] for details).

I.8.6. Summary of effects

The various non-idealities are seen to produce effects that differ in kind, as shown in Table I.3. Therefore, unless one single non-ideality completely dominates:

- *Shock layers cannot in general be modeled with a single dispersion parameter.*

The exception is that the effects of mass-transfer resistance in the sorbent, axial diffusion, and non-plug flow are similar (although not strictly additive) and so can be lumped. However, such single-parameter modeling fails to account for the mass-transfer resistance in the moving phase, which tends to produce significant fronting of any shock layers even if it is negligible elsewhere.

The profile or effluent history of a shock layer are seen to depend on the isotherm shape as well as on the effects of the non-idealities. Therefore, the isotherm cannot be determined from effluent histories of shock layers unless the effects of the non-idealities are known in detail, nor can the latter effects be established without exact knowledge of the isotherm shape. Because so many different non-ideal-

TABLE I.3

EFFECTS OF NON-IDEALITIES OF SHOCK-LAYER PROFILE

Dominant non-ideality	Effect on shock-layer profile
Mass-transfer resistance in moving phase	Fronting
Mass-transfer resistance in sorbent	Tailing
Rate controlled by attachment to sorbent ("reaction control")	Symmetrical spreading
Axial diffusion	Tailing
Non-plug flow	Tailing
Axially non-uniform flow-rate (in gas chromatography)	Slight sharpening (if saturation wave), slight spreading (if elution wave)

ities may affect the effluent history of a shock, the most reliable approach is to determine the isotherm first point-by-point by batch or column equilibration. Tentative conclusions about non-idealities can then be drawn from the shapes of shock profiles at different inlet concentrations and flow-rates.

I.9. PROFILES OF NONSHARPENING WAVES

Nonsharpening waves were seen to be affected by non-idealities only as long as they are still relatively sharp. Ideal chromatography is therefore a good approximation, provided the column is reasonably long and the isotherm curvature is significant. Accordingly, the profile of a nonsharpening wave that starts out as a discontinuity depends almost exclusively on the shape of the isotherm. An approximate profile can be calculated from the isotherm by application of the wave equation I.4 to a number of concentrations, with $\mathrm{d}q_i/\mathrm{d}c_i$ as the isotherm slopes at the respective concentrations. The wave velocity given by eqn. I.4 multiplied with the time t gives the distance which the concentration has advanced in the column. Similarly, for an approximate effluent history, the wave velocity divided by the column length gives the retention time of the concentration.

The procedure can be reversed in order to determine an isotherm from the effluent history of a nonsharpening wave [42] (an elution wave if the isotherm is of Type I). However, this procedure is not very accurate. One source of error is the difficulty of accounting correctly for the small but not negligible effect of non-idealities. Another is the fact that the technique yields isotherm *slopes* rather than points, so that the isotherm must be pieced together from the former, a procedure in which any error at a low concentration is propagated to all higher concentrations. Chromatographic techniques for isotherm determinations will be discussed in more detail in a later instalment.

I.10. COMPLEX ISOTHERMS AND COMPOSITE WAVES

Isotherms with inflection points may give rise to "composite waves" consisting of self-sharpening and nonsharpening portions. In the fully developed pattern resulting from a step input, shock portions have linear operating lines while nonsharpening portions have operating curves that coincide with the isotherm. Fig. I.12a shows a Type III isotherm and the operating curve for saturation of a column initially free of sorbate. For a given isotherm, the operating curve can be constructed with a rule based on the following argument. Concentrations (or shock portions) that have advanced farther must have higher velocities; according to the wave equations I.3 and I.6, the slope of the operating curve therefore must decrease monotonically from the point corresponding to the entering concentration (c_i^0, q_i^0) to that of the initial concentration ($c_i = q_i = 0$). As a result, the operating line of any shock portion is *tangential* to the isotherm [9,43,44]. One can envisage the operating curve as a rubber band stretched between the points of the initial and entering compositions and at most touching the isotherm but not intersecting it. For adsorption the operating curve is below the isotherm, for desorption it is above it. Among fixed-bed engineers this rule is known as the "Golden Rule" (named after Berkeley doctoral student F. M. Golden, quoted in section 16 of Perry's Handbook [9] but not separately published). The resulting saturation wave for the isotherm in Fig. 1.12a consists of a leading shock in which the concentration rises to c_i', followed by a nonsharpening portion in which it rises from c_i' to the influent value, c_i^0, and is shown in Fig. 1.12b. A convenient graphical procedure developed by Welge [45] for construction of wave profiles in two-phase flow in permeable media from fractional-flow curves and widely used in oil reservoir engineering can be adapted to the construction of concentration profiles of composite waves in chromatography from isotherms.

An inflection point on the isotherm does not necessarily produce a composite wave. For instance, the Type III isotherm in Fig. 1.11 has an inflection point at a concentration below that of the entering solution, yet application of the Golden Rule shows the wave to be a pure shock (no line from the origin is tangential to the isotherm at any concentration below that of the entering solution).

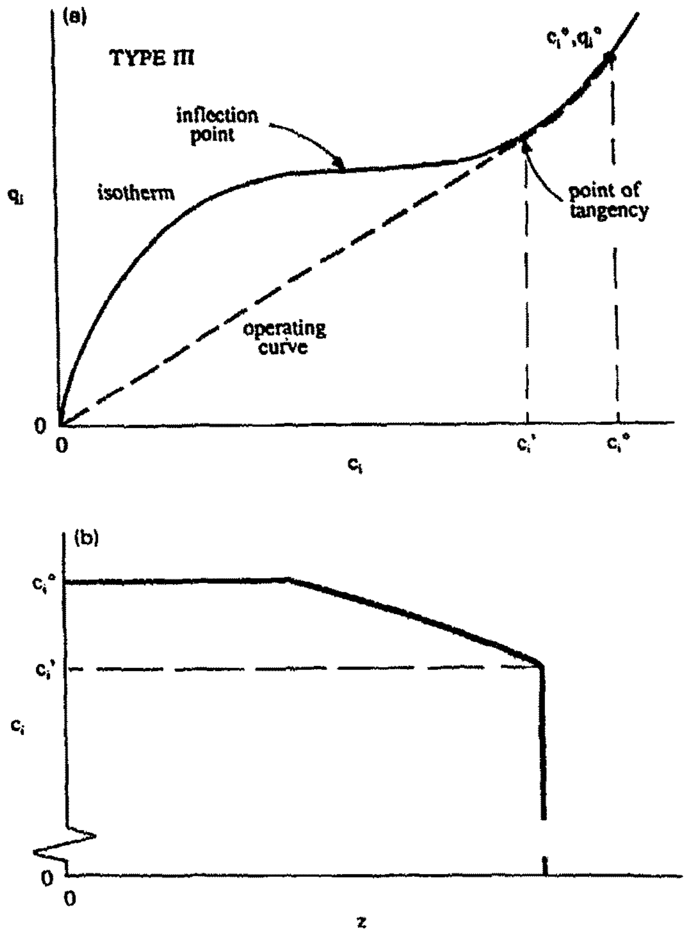

Fig. 1.12. Composite wave resulting from Type III isotherm: (a) isotherm and operating curve; (b) concentration profile of composite wave produced by step input (ideal chromatography).

1.11. STANDARD THEORIES AND MODELS

The non-linear models most commonly referred to can now be put in context.

1.11.1. Equilibrium-stage models

The concept of equilibrium stages, with an HETP accounting for the effects of non-idealities, has also been used for numerical stage-by-stage calculations in non-linear chromatography [46]. This is possible although the familiar correlations between HETP and wave spreading are not in general valid under non-linear conditions. Inasmuch as a succession of equilibrium stages physically amounts to back-mixing in the column, the calculations actually model the effects of axial diffusion and non-plug flow. That is, for symmetrically shaped isotherms, calculated *shock layers tail*. Because of the similarity with the effect of non-equilibrium owing to mass-transfer resistance in the sorbent, the results are reasonable approximations, *provided the mass-transfer resistance in the moving phase is negligible even at the lowest concentrations*. As was seen earlier, the latter resistance produces fronting rather than tailing of shock layers, and so invalidates the model.

1.11.2. "Semi-ideal" models

So-called semi-ideal models [47] postulate that all non-ideal effects can be accounted for in a single, lumped dispersion coefficient [47,48]. They use the material balance equation 1.11 with $q_i = f(c_i)$, that is, with q_i in equilibrium with c_i. Analytical solutions have been given for some special cases [48]. Because of the similarity of the effect of hydrodynamic dispersion with actual back-mixing in stages, semi-ideal models give essentially the same results as equilibrium-stage models. Specifically, they produce tailing shock-layer profiles if the isotherm shape resembles Langmuir's, and fail to show the shock-layer fronting that results from a significant mass-transfer resistance in the moving phase.

I.11.3. Thomas model ("reaction-kinetic model")

The model developed by Thomas [49,50] for binary ion exchange attributes local non-equilibrium to the finite rate of a second-order reversible exchange "reaction" and assumes ideal behavior in all other respects. The rate equation implies constancy of the separation factor (defined as q_ic_j/q_jc_i at equilibrium of exchanging ions i and j). The model has also been used for single-component adsorption [51,52]. In this modification, the rate is given by eqn. I.10 and implies a Langmuir isotherm (the mathematics of binary ion exchange with constant separation factor and single-component Langmuir adsorption are formally identical). Analytical solutions in terms of a tabulated function [53] have been derived for input in form of a step [49,50] or pulse [52] and for arbitrary input [51]. The solution for step input is valid for both nonsharpening and self-sharpening waves and, for the latter, covers the transient approach to the constant pattern.

I.11.4. Mass-transfer models

The simplest models that account explicitly for local non-equilibrium owing to finite mass-transfer rates use linear driving-force approximations, as discussed previously. In some of these procedures an HETP [22] or a "number of mass-transfer units" [8,9] is obtained from the mass-transfer coefficient and then used to calculate the shock-layer profile. For situations in which the resistances in both phases are significant, Glueckauf [22] sums up the dispersions caused by each; this tends to overstate spreading but gives a smooth transition from a fronting to a tailing profile as the dominant resistance shifts from the moving phase to the sorbent. In contrast, Vermeulen and co-workers [8,9,54] calculate an "overall" mass-transfer coefficient with the principle of additivity of resistances in series, apply an approximate correction factor for the error in that principle, and then use the resulting coefficient in the driving-force equation for the phase in which the resistance is more serious. This procedure gives an abrupt transition from extreme fronting to extreme tailing at the point where both resistances are equally important. A procedure that avoids this unrealistic result by construction of driving-force arrows in the q_i vs. c_i diagram to obtain concentration-history slopes at a set of concentrations in the shock layer and then piecing the effluent history together from short segments has been suggested by Klein [55].

More elaborate mass-transfer models for the sorbent phase use non-linear driving-force approximations, Fick's law of diffusion for the particles (assumed to be spherical), or diffusion in pores with adsorption onto the pore walls ("pore diffusion model"). For more detail, see Table I.4, section 16 of Perry's Handbook [9], and a recent review by Lee *et al.* [56].

I.11.5. General models

Analytical solutions for non-ideal chromatography are possible only in a few special cases. Since execution time is usually not a problem on today's computers, it makes sense to turn to the most general and flexible computer models where numerical calculation is required anyway. At present, the most general, publicly available and reasonably "user-friendly" program is VERSE-LC [63]. Written in FORTRAN, it is for single- and multicomponent adsorption with arbitrary isotherms and arbitrary input conditions and allows for finite rates of mass transfer in the moving phase, diffusion in pores, adsorption on pore walls, and reactions in both the moving and sorbent phases. The LC in the title indicates that it is intended for liquid chromatography only. The program is available from the Purdue Research Foundation.

I.12. ELUTION PEAKS

With knowledge of the behavior of non-linear waves, the shapes of peaks and bands under non-linear conditions ("overload") can now be predicted. For this purpose, the injected sample is viewed as a concentration plateau between two initially discontinuous waves which interact with one another on their travel through the column.

The asymmetry of a single-component peak or slug (flat-top peak) in elution under overload conditions depends on the shape of the isotherm. With a Type I isotherm, the peak or slug has a shock front and nonsharpening rear, and tails accordingly. With a Type II isotherm, the opposite is true, that is, the peak or slug fronts. Isotherms with inflection

TABLE I.4

COMMON MODELS OF NON-LINEAR, NON-IDEAL CHROMATOGRAPHY

Explanations: Axial dispersion = axial diffusion and dispersion from non-ideal flow; LDF = linear driving-force approximation; intraparticle diffusion = Fick's law or approximation; IEX constant α = ion exchange with constant separation factor (mathematically equivalent to Langmuir adsorption isotherm).

Features	Isotherm	Input	Solution method	Author(s)
Axial dispersion	IEX constant α	Step	Analytical	Acrivos [35]
	Parabolic	Pulse	Analytical approximation	Houghton [57]
	Arbitrary	Arbitrary	Finite difference	Smit *et al.* [58]
Axial dispersion and fluid-phase LDF	IEX constant α	Step	Numerical	Acrivos [35], Ruthven [12]
Lumped dispersion (semi-ideal model)	Parabolic	Pulse	Analytical	Haarhoff and Van der Linde [48]
	Langmuir, S-shaped	Pulse	Finite difference	Guiochon *et al.* [47]
	Langmuir	Pulse	Analytical approximation	Knox and Pyper [59]
Attachment to site (Thomas model)	IEX constant α	Step	Analytical	Thomas [49,50]
	IEX constant α and Langmuir	Arbitrary	Analytical	Goldstein [51]
	Langmuir	Pulse	Analytical	Wade *et al.* [52]
Moving-phase LDF	IEX constant α	Step	Analytical	Michaels [21]
Sorbent-phase LDF	IEX constant α	Step	Analytical	Glueckauf and Coates [17]
Both phases LDF	IEX constant α	Step	Analytical approximation	Glueckauf [22]
	IEX constant α, Langmuir	Step	Analytical approximation	Hiester *et al.* [54] Vermeulen *et al.* [8,9]
		Step	Semi-graphical	Klein [55]
Intraparticle diffusion	Langmuir	Step	Numerical Method of moments	Weber and Chakravorti [60] Radeke *et al.* [61]
Pore diffusion	IEX constant α, Langmuir	Step	Numerical	Hall *et al.* [62]
Moving-phase LDF, pore diffusion, dispersion and reactions	Arbitrary	Arbitrary	Orthogonal collocation	Berninger *et al.* [63] (VERSE-LC)
Non-uniform flow	Linear (pressure-dependent partition)	Arbitrary	Method of characteristics	Guiochon and Jacob [40]
Non-uniform flow and axial dispersion	BET	Step	Numerical	LeVan *et al.* [41]

points produce more complex asymmetries and shapes that also depend on how much the peak has already flattened.

The overload can be primarily a concentration overload (concentrated small sample) or a volume overload (dilute large sample) or some compromise between these two. Absolutely "pure" concentration or volume overloads are not possible: since the injected concentration cannot be infinite, the sample volume must be finite; and since the isotherm is curved over its entire range, strictly linear chromatography would require the dilution and thus the sample volume to be infinite. Fig. I.13 shows for comparison how the peak shape evolves from predominant concentration overload and predominant volume overload, granted a Type I isotherm and

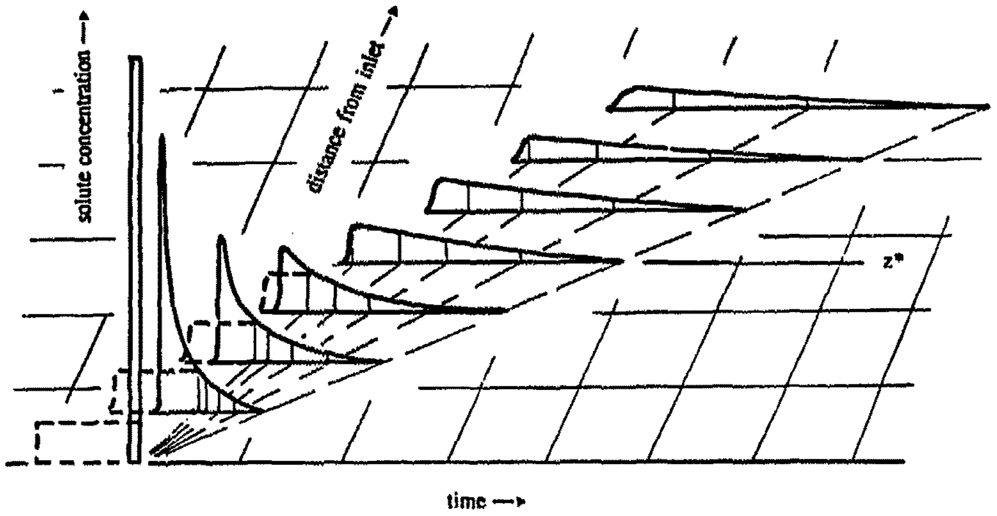

Fig. I.13. Concentration histories on distance-time field for elution of single solute under conditions of concentration overload (solid curves) and volume overload (dashed curves where different); histories are superimposed on one another for better comparison; z^* = survival distance of plateau in volume overload; also shown are concentration contours common to both overloads (thin dashed lines, originating from end of injection).

with the same amount of same solute injected into the same column.

Let us examine a peak or slug with Type I isotherm more closely. The nonsharpening rear travels practically in a proportionate pattern since the small, initial dispersive effect of non-idealities soon becomes negligible. For the shock front, $\Delta q_i \equiv (q_i)_{\max}$ and $(\Delta c_i) \equiv (c_i)_{\max}$, where the index max refers to the apex or, as long as it exists, to the plateau. Thus, according to eqn. I.6, the shock velocity at any time is

$$v_{\Delta c_i} = \frac{v^0}{1 + (\rho/\varepsilon)(q_i/c_i)_{\max}} \qquad (I.12)$$

For concentration overload, the shock travels rather rapidly at first, but slows down as the effect of isotherm curvature causes the peak to spread and its apex concentration to decrease (lower concentrations on the isotherm give steeper chord slopes q_i/c_i, resulting in stronger retardation; see Fig. I.1a). For volume overload, the shock is relatively slow to start with and travels at constant velocity until the plateau has eroded. In both cases, the nonsharpening rear of the peak or slug produces a fan of concentration contours in the distance–time plane; the difference is that for concentration overload the high-concentration contours are soon "eaten up" by the shock as the apex concentration diminishes, whereas for volume overload these contours, of concentrations higher than injected, do not exist in the first place. The contours of concentrations lower than those of volume-overload injection are practically the same in both cases (except for a slightly greater effect of non-idealities in the earliest stages of concentration overload because of the higher apex concentration), being traced by the same concentrations under identical conditions. Granted that overload is so heavy that the peak remains far from symmetrical, the profile of the nonsharpening rear of the peak depends almost exclusively on the shape of the isotherm; the exact profile of the self-sharpening front depends on both the isotherm and the non-idealities, but contributes little to the total peak width, fades as the peak attenuates, and so is not of much interest. A detailed knowledge of mass-transfer resistances etc. therefore is usually not needed:

- *Except for possible fronting caused by mass-transfer resistance in the moving phase, the peak shape and width depend almost exclusively on the shape of the isotherm.*

Since the contours of the concentrations lower than that of volume-overload injection are essentially the same in both cases, and since the area under the concentration history must also be the same

(same amount injected), the histories resulting from concentration overload and volume overload are practically the same once the pleateau of the slug in volume overload has disappeared (at distance z^* in Fig. I.12). In other words:

- *Beyond a certain column length, there is no significant difference between peak shapes from predominant concentration overload, predominant volume overload, or any combination of the two.*

An essentially equivalent rule, in terms of profiles and eluent volume rather than histories and column length, has been derived by Knox and Pyper [59] with some simplifying assumptions. However, it is necessary to specify that, for the effluent histories to be equal, the retention times must be measured from the *end* of injection, not from its start.

The rule of equal concentration histories for concentration overload and volume overload beyond some distance of travel holds even though the peak front is not an ideal discontinuity and, in fact, gradually loses sharpness as the apex concentration decreases [the self-sharpening tendency weakens as the isotherm slope at $(c_i)_{max}$ becomes more similar to that at $c_i = 0$]. This is because the width of the shock layer is essentially quasi-stationary, and so is the same in both cases at the same apex concentration, independent of prior events.

Other immediately apparent conclusions are that overload speeds up the apex, and that the extreme tail of the peak from any overload moves at the same velocity as does the peak of an infinitesimally small amount of solute.

If the isotherm is of Type II —resulting in a peak with diffuse front and sharp rear— any overload delays the apex, and the leading, lowest concentrations move at the velocity of a peak of infinitesimal size. The Knox rule of essentially equal effluent histories from concentration and volume overload also holds, but now with retention times counted from the *start* of injection. The behavior of isotherms with inflection points is more complex because the development may involve shock portions that are present only at higher concentrations and disappear with attenuation [47].

It is interesting to see that Knox and Pyper [59] employed the HETP concept of linear chromatography —additive HETP contributions that are independent of one another and of column length and produce square-root spreading—a concept they verified empirically by comparison with numerical results. A "kinetic" contribution is said to stem from non-idealities; an additional "thermodynamic" one, from the isotherm curvature. At first glance, this seems paradoxical because isotherm curvature sharpens rather than spreads the peak front and produces a proportionate rather than square-root spreading pattern of the peak rear, and the non-idealities help to turn the peak front into a shock layer and have no significant effect on the peak rear. However, closer inspection resolves the paradox. Firstly, provided the peak is *triangular*, as Knox and Pyper postulate, and the concentrations of its nonsharpening rear fan out in a proportionate pattern (straight-line contours), the base width must indeed increase in proportion to the square root of traveled distance because the constancy of peak area (amount of solute) requires the apex concentration to decrease —*i.e.*, the higher concentrations "get lost" (see Fig. I.14). Secondly, the non-idealities do contribute a little to peak spreading, approximately in proportion to the square root of traveled distance: while they have no effect to speak of on the nonsharpening flank of the peak, the shock flank loses sharpness as the sharpening effect of isotherm curvature fades with decreasing apex concentration.

Unfortunately, the concept of an HETP composed of additive, independent, and constant thermodynamic and kinetic contributions that make waves spread indefinitely in a square-root pattern is not in general applicable to non-linear chromatography. For instance, in displacement development, where the band of a solute travels between two shock layers, isotherm curvature sharpens rather than spreads the waves at *both* front and rear; moreover, after having traveled a finite distance, the entire sample slug attains a constant pattern that remains unchanged upon further travel.

I.13. BANDS IN DISPLACEMENT

In displacement development, massive overload is intentional. A large amount of mixture is injected and then displaced by an agent whose affinity for the sorbent is higher than that of any species of the mixture. Given competitive isotherms (*e.g.*, Langmuir-type), the mixture advances through the col-

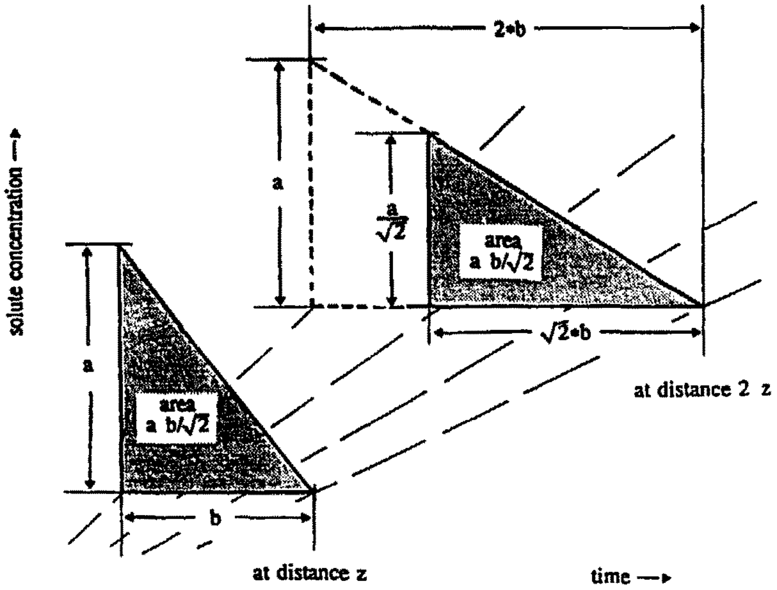

Fig. I.14. Spreading of triangular peak with proportionate pattern of diffuse flank; proportionate spreading of entire peak would double its area when distance of travel is doubled; reduction by linear factor $\sqrt{2}$ is required to keep area to original size (a = peak height at distance z; b = peak width at distance z).

umn in a piston-like fashion between two shocks. In the presence of one another, the particle velocities of the components of lower affinities for the sorbent are higher (lower values of q_i/c_i, see eqn. I.5). Accordingly, the components sort themselves out in the sequence of their affinities. The final, constant pattern has a shock between each two adjacent components in addition to the shocks at the front and the rear of the sample slug (see Fig. I.15).

The calculation of resolution distances in displacement development is a complex problem of multicomponent chromatography, to be discussed later in this series. However, the final pattern is relatively easy to predict with a knowledge of the single-component isotherms, as shown by Tiselius [64]. At each shock, the component present on one side is absent from the other, so that the shock wave equation I.6 reduces once again to eqn. I.12, here with q_i

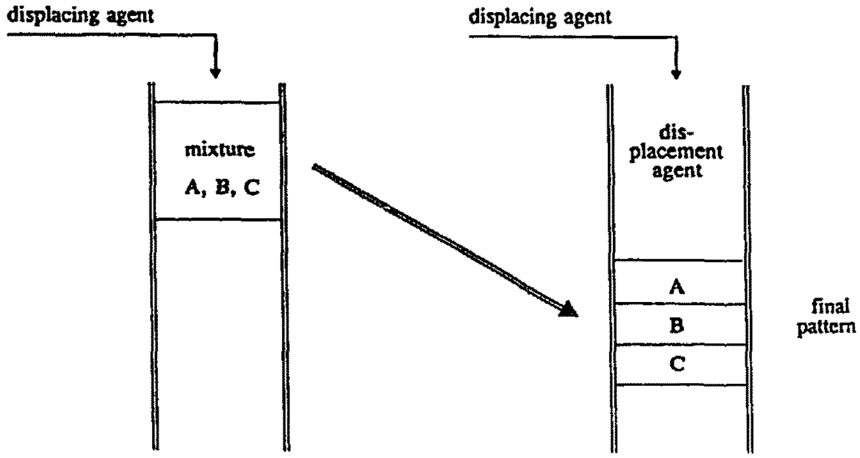

Fig. I.15. Principle of displacement development.

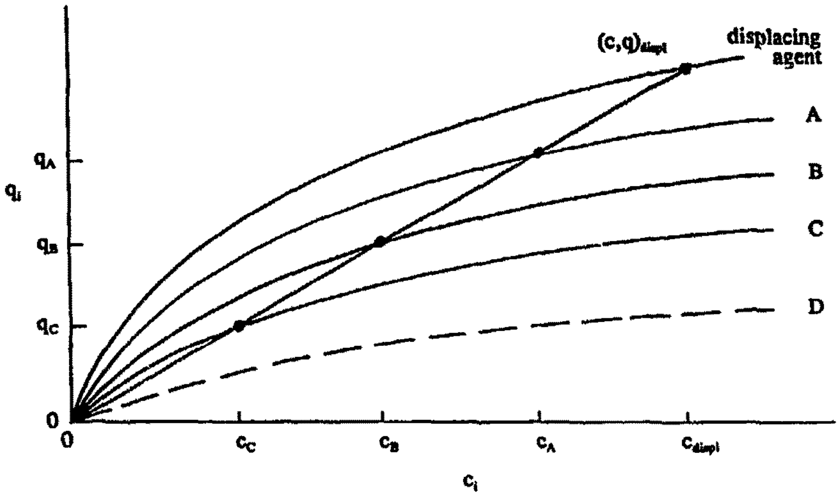

Fig. I.16. Tiselius method [64] for determining concentrations of solutes in their bands in final pattern of displacement development (Solute D runs ahead of displacement pattern).

and c_i as the concentrations in the respective adjacent bands. In the final constant pattern, material balance and constant amounts of all solutes of the mixture require all shocks move at the *same* velocity, so that q_i/c_i in eqn. I.12 must have the same value for all solutes, including the displacing agent. (It is interesting to see that, once the solutes have separated, the entire wave pattern and all solutes travel at one common particle velocity; see eqn. I.5.). The concentrations of the solutes in their bands can now be determined with a graphical procedure illustrated in Fig. I.16: The concentration c_{displ} of the displacing agent is known and identifies a point $(c,q)_{displ}$ on the isotherm of the latter, and the chord of that point intersects the isotherms of the other solutes at their concentrations c_i and q_i. The isotherms in this construction are the *single-component* isotherms, the mixture having been resolved into its components. If algebraic equations for the isotherms are available, all that is needed is to equate the partition coefficient q_i/c_i of the respective solute to that of the displacing agent at its concentration c_{displ} and solve for c_i. With all solute concentrations in both phases known, the band width of each solute of the mixture in the composition profile or history can be obtained from the injected amount of that solute by a material balance. This completes the quantitative prediction of the final pattern under ideal conditions. If more accuracy is required, the shock-layer profiles must be calculated. Since each shock in the final pattern is between two single-component bands, this can be done in much the same way as discussed previously.

If the concentration of the development agent is not high enough, not all isotherms may be intersected by the chord of $(c,q)_{displ}$. An example is the (dashed) isotherm of solute D in Fig. I.16. Any such solute breaks away from the displacement pattern, running ahead as an attenuating peak.

As can be seen from Fig. I.16, the concentrations in the individual bands of the final pattern are dictated by that of the displacing agent; often, they can be made much higher than those in the injected sample: *displacement development permits solutes to be concentrated while they are separated.* Also, large overload is beneficial: The higher the concentrations, the stronger are the self-sharpening tendencies of the shock layers (greater differences in isotherm slopes between front and rear ends of the shock layers); and the larger the amounts of solutes at given concentrations, the longer are the individual bands and, therefore, the smaller is the fractional overlap that results from the less than ideal sharpness of each shock layer. In short, overload, a detriment to be contended with in elution, is put to work for a good purpose in displacement.

I.14. SYMBOLS

a	specific surface area (area of interface sorbent/moving phase, per unit volume of column)	cm^{-1}
c_i	concentration of solute i in moving phase (per unit volume of moving phase)	$mmol\ cm^{-3}$
c_i^0	concentration c_i upstream of wave (or in entering fluid)	$mmol\ cm^{-3}$
c_i^*	concentration c_i at interface with sorbent (in equilibrium with q_i^*)	$mmol\ cm^{-3}$
D	axial diffusion or dispersion coefficient	$cm^2\ s^{-1}$
$f(c_i)$	sorbent loading q_i in equilibrium with c_i	$mmol\ g^{-1}$
k_a	Langmuir adsorption rate coefficient	$mmol^{-1}\ cm^3\ s^{-1}$
k_d	Langmuir desorption rate coefficient	s^{-1}
k_f	mass-transfer coefficient in moving phase	$cm\ s^{-1}$
k_s	mass-transfer coefficient in sorbent	$cm\ s^{-1}$
k_1,k_2	rate coefficients in Thomas law	s^{-1}
K	constant in Langmuir isotherm $q_i/Q_i = Kc_i/(1 + Kc_i)$	$mmol^{-1}\ cm^3$
q_i	sorbent loading with solute i: amount of i in sorbent (averaged over bead) per unit mass of sorbate-free sorbent	$mmol\ g^{-1}$
q_i^0	sorbent loading q_i upstream of wave (in equilibrium with c_i^0)	$mmol\ g^{-1}$
q_i^*	sorbent loading q_i at interface with moving phase (in equilibrium with c_i^*)	$mmol\ g^{-1}$
Q_i	ultimate sorbent loading: $f(c_i)$ for $c_i \rightarrow \infty$	$mmol\ g^{-1}$
t	time	s
v^0	linear velocity of moving-phase flow	$cm\ s^{-1}$
v_i	linear particle velocity of solute i	$cm\ s^{-1}$
v_{c_i}	linear wave velocity of concentration c_i	$cm\ s^{-1}$
$v_{\Delta c_i}$	linear wave velocity of shock Δc_i	$cm\ s^{-1}$
x_i	equivalent fraction of counterion i in moving phase	dimensionless
y_i	equivalent fraction of counterion i in ion exchanger	dimensionless
z	linear distance from column inlet (inlet end of packing)	cm
z^*	survival distance of flat top of peak from volume overload	cm
α_{ij}	separation factor of counterions i and j ($\equiv q_i c_j / q_j c_i$)	dimensionless
Δ	difference across shock, or difference in driving force approximation	operator
ε	fractional volume of moving phase in column	dimensionless
ρ	bulk density of sorbent: mass of sorbate-free sorbent per unit volume of column	$g\ cm^{-3}$

Special subscripts: effl = effluent; initial = state before passage of wave; max = apex of peak, or plateau of flat-top band, or maximum at respective wave; displ = displacing agent in displacement development.

Comments

For ease of perception it is obviously convenient to have the value of z at a point in the column correspond to the linear distance from the inlet (and z at the column end, to the column length). The corresponding velocities $\partial z/\partial t$ are the *linear* velocities [volume of moving phase per unit time and unit (average) cross-sectional area of column void]. Any other self-consistent set of variables equivalent to distance, time, and velocity could be chosen instead; *e.g.*, cumulative effluent volume instead of time, column volume upstream of a point instead of distance from column inlet, and the corresponding dimensionless equivalent of velocity.

Any other self-consistent set of concentrations and mass-transfer coefficients can be substituted for those used here. For mathematics, concentrations per unit volume of *column* are most convenient in that they obviate the factor ρ/ε in the wave equations [11]; also, the factor ρ then disappears from eqn. I.7 and condition I.8 and I.9.

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1.16 APPENDIX

That the Thomas model gives shock-layer profiles or histories with symmetrical S-shape is easiest to show with the original version of the model, for binary ion exchange converting the exchanger completely from the A to the B form [49,50]. In terms of counterion fractions x_i in the solution (moving phase) and y_i in the exchanger, the rate law is

$$(\partial y_A/\partial t)_z = k_1 x_A y_B - k_2 y_A x_B$$

For binary ion exchange:

$$x_B = 1 - x_A \text{ and } y_B = 1 - y_A$$

The concentrations are those in the bulk phases, so that pairs (x_A, y_A) correspond to points on the operating line, on which $y_A = x_A$ (diagonal in x–y diagram for complete conversion). With these substitutions the rate is

$$(\partial y_A/\partial t)_z = (k_1 - k_2)x_A(1 - x_A)$$

The rate is seen to be zero at $x_A = 0$ and $x_A = 1$, have its maximum at $x_A = 1/2$ (halfway point on operating line), and have the same value for any x_A as for the corresponding $1 - x_A$. This translates into a symmetrical S shape with equal fronting and tailing. (For the shock layer to form, the separation factor α_{AB} must be larger than unity; since $\alpha_{AB} = k_1/k_2$, this requires $k_1 > k_2$ and ensures a positive rate.)

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