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Analysis of Multicomponent Separation by Displacement Development

The separation of multicomponent mixtures by displacement development is fully analyzed by applying the theory of multicomponent chromatography. With Langmuir isotherms it is possible not only to elucidate all the characteristic features of the process but also to derive analytic expressions for the critical value of the developer concentration and the plateau concentration as well as the width of each pure component band attained at the ultimate stage. A specific example demonstrates that the actual solution at the ultimate stage is identical to that predicted *a priori* by using these expressions. The bed length required for complete separation is determined by examining the wave interactions involved. This procedure is clearly illustrated.

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SCOPE

Displacement development is well known in the field of chromatography. The characteristic feature is that, when a mixture of adsorbable species is displaced through a column of adsorbent by adding a solution of a species with higher adsorptivity than any of the species present, the species are gradually separated and form pure component bands. These bands maintain sharp boundaries at both ends and propagate side by side in sequence with the same speed.

The technique was first introduced by Tiselius (1943), who noticed that the plateau concentrations of pure component bands depend only upon the concentration of the development agent (to be called a "developer" in the following) and are independent of the concentrations in the original mixture. Glueckauf and Coates (1947) demonstrated experimentally that for a packing of good quality the boundaries of pure component

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bands were very steep with fringes of thickness less than 3 or 4 grain diameters; i.e., less than 4×10^{-3} cm in their experiments.

Earlier studies on the theoretical aspects (Glueckhauf, 1946 and 1949; Claesson, 1949; Sillén, 1950) were concerned with the development of a single-solute or a two-solute chromatogram. Among those, Glueckauf (1946, 1949) made major contributions by presenting a method of solution for a system subject to Langmuir isotherms. Realizing that the level of developer concentration would have a significant effect on the pattern of solution, the author discussed various cases distinguished essentially by the developer concentration. The analysis, however, was not complete and had some inadequacies perhaps because his treatment did not bring out the connection with the mathematical theory of quasilinear partial differential equations.

The process has been applied to commercial separation of rare earths on a cation exchanger (Spedding and Powell, 1956; Silvernail and Geotzinger, 1968). For separations of binary and ternary mixtures Powell et al. (1968) and James et al. (1968) established the theoretical basis by extending Sillén's approach (1950). More recently, Helfferich and James (1970) presented a general theory that could be applied to a system of any number of components by using the so-called h-transformation (Helfferich and Klein, 1970). Due to the assumption of stoichiometric exchange of adsorbable species, their treatment turned out to be unaffected by the level of developer concentration and ultimately gave rise to pure component bands of equal concentrations which were the same as the developer concentration. It was implied that the process would be successful no matter how low the developer concentration might be.

The purpose of this study is to extend Glueckauf's approach to a system involved with many solutes by applying the existing theory of multicomponent chromatography subject to Langmuir isotherms. Although the essential content of the theory is reviewed briefly here, an earlier paper (Rhee, Aris and Amundson, 1970) may be referred to for detail. The major concern is the effect of the level of developer concentration on the quality of separation. For various ranges of developer concentration solutions are illustrated to make it self-evident that there exists a critical value of the developer concentration below which some or all of the rear boundaries of pure component bands become diffuse and do not propagate with the same speed. This observation is first elucidated in some detail for the separation of a two solute mixture and then extended to the case of a multisolute mixture. Equations of practical significance are derived. Numerical examples are worked out to illustrate how the solutes are actually separated and form pure component bands through wave interactions. Discussions also include the determination of the bed length required for complete separation and the validity of the equations derived here.

CONCLUSIONS AND SIGNIFICANCE

Multicomponent mixtures can be effectively separated by using the technique of displacement development. When adsorption equilibrium follows the Langmuir isotherm, the process can be completely analyzed by applying the existing theory of multicomponent chromatography. In particular, there exists a critical value for the developer concentration below which the process becomes unsatisfactory because the developer exercises no influence over all the species or over the less adsorbable species depending on the level of the developer concentration. In such a case those species are simply eluted by the solvent. The critical value is dependent only on the adsorption characteristics of the developer and the least adsorbable solute and independent of the concentrations of the original mixture to be separated.

The plateau concentration of each pure component band is determined by a simple expression in terms of the developer concentration and the adsorption characteristics of the pure component and the developer. This observation suggests that displacement development may be used to identify an unknown mixture as well as to determine the isotherm parameters. Although dependent upon the concentrations of the original mixture, the width of each pure component band can be predicted without going through the detailed analysis of the process.

For the bed length required for complete separation, it is necessary to analyze all the wave interactions involved. With the developer concentration higher than its critical value the analysis is fairly straightforward since the solution contains only one or no simple wave.

It is confirmed by the analyses of numerical examples that the solution at the ultimate stage may be directly determined by using the simple expressions derived in the present study without analyzing the wave interactions. The bed length required for complete separation is much shorter than that for the case of conventional elution by pure solvent. This is attained at the cost of the relatively high developer concentration and thus we expect the latter value would be approached as the developer concentration decreases.

THEORY OF MULTICOMPONENT CHROMATOGRAPHY

Basic Formulation

Consider an isothermal adsorbent bed of constant void fraction ϵ through which a fluid stream containing m different adsorbable solutes, $\{A_i\}$, passes with a constant interstitial velocity u. The system is assumed to be one dimensional in the direction of flow with uniform cross-sectional area. The effect of diffusion is negligible and local equilibrium is established everywhere at any time.

Let c_i and n_i denote the molar concentrations of the solute species A_i in the fluid and solid phases, respectively. If the axial position z is taken in the direction of flow, the material balances for every solute at time t yield a hyperbolic system of m quasilinear partial differential equations of first order, all coupled to one another through nonlinear adsorption isotherms:

$$\frac{\partial c_i}{\partial x} + \frac{\partial c_i}{\partial \tau} + \nu \frac{\partial n_i}{\partial \tau} = 0 \qquad (1)$$

$$n_i = f_i\,(c_1, c_2, \ldots, c_m)$$

for $i = 1, 2, \ldots, m$, where the independent variables are nondimensionalized by using a characteristic length Z of the system as

$$x = z/Z \text{ and } \tau = ut/Z \qquad (2)$$

and

$$\nu = (1 - \epsilon)/\epsilon \qquad (3)$$

Suppose the initial and feed conditions are specified by two different constant states of concentrations with a jump discontinuity at the origin; i.e.,

$$\begin{cases} \text{at} \quad \tau = 0, \quad c_i = c_i^0 \text{ (= constant)} \\ \text{at} \quad x = 0, \quad c_i = c_i^f \text{ (= constant)} \end{cases} \qquad (4)$$

for $i = 1, 2, \ldots, m$ and $c_i^0 \neq c_i^f$ for some i. This mathematical problem is referred to as a Riemann problem for which the existence of a solution has been proved (Lax, 1957).

In fact, the solution in the (x,τ)-plane consists of $(m + 1)$ constant states connected by m waves. The waves, either shocks or centered simple waves, all emanate from the origin as depicted in Figure 1. Across each wave, there exists a one-parameter representation of states and so there are m parameters to characterize the m waves and $(m - 1)$ intermediate constant states. Note that the two outermost constant states are identical to the feed state and the initial state, respectively.

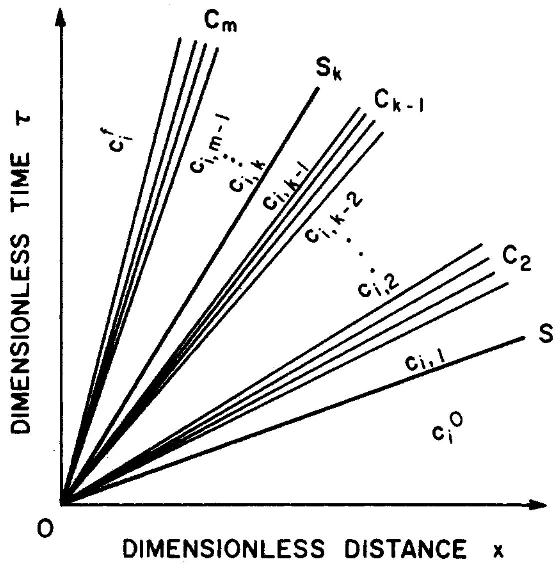

Figure 1. Schematic portrait of a solution in the (x,τ)-plane, showing regions of constant state connected either by centered simple waves or by shocks. —— Characteristic C, —— Shock Path S

Solution subject to a Langmuir Isotherm

We shall now assume that the equilibrium relation is given by the Langmuir isotherm:

$$n_i = \frac{\gamma_i c_i}{1 + \sum_{j=1}^{m} K_j c_j}, \quad i = 1, 2, \ldots, m \tag{5}$$

in which both γ_i and K_i are positive constants. Here γ_i is defined as $\gamma_i = N_i K_i$, where N_i denotes the saturation value of n_i. In the original paper (Rhee, Aris and Amundson, 1970) N_i was assumed independent of the supercript i. We shall further assume that the solute species are numbered in the order of adsorptivity from the smallest to the largest so that

$$\gamma_1 < \gamma_2 < \gamma_3 \cdots \gamma_{m-1} < \gamma_m \tag{6}$$

With the Langmuir isotherm the above mentioned m parameters, which we shall call the characteristic parameters and designate as $\{\omega_k\}$, are determined by solving the m^{th} order algebraic equation

$$\sum_{i=1}^{m} \frac{K_i n_i}{\gamma_i - \omega} = 1 \tag{7}$$

It is not difficult to see that Eq. 7 has m real, distinct, positive roots $\{\omega_k\}$ which may be arranged as

$$0 \le \omega_1 \le \gamma_1 \le \omega_2 \le \gamma_2 \le \omega_3 \ldots \omega_{m-1} \le \gamma_{m-1} \le \omega_m \le \gamma_m \tag{8}$$

Equation 7 represents a transformation of the concentration space $\{c_i\}$ or $\{n_i\}$ into the ω-space $\{\omega_k\}$ and it is one-to-one with the inverse given by

$$K_i c_i = \left(\frac{\gamma_i}{\omega_i} - 1\right) \prod_{j=1,i}^{m} \frac{\dfrac{\gamma_i}{\omega_j} - 1}{\dfrac{\gamma_i}{\gamma_j} - 1}, \quad i = 1, 2, \ldots, m \tag{9}$$

Let us number the waves and the intermediate constant states counterclockwise so that the uppermost wave is the m-wave and on the left-hand side of the k-wave there appears the k-constant state, designated by $\{c_{i,k}\}$, for $k = 1, 2, \ldots, m - 1$. It can be shown that, across the k-wave, only the parameter ω_k varies while the others ω_j, $j \neq k$, remain unchanged. Consequently, with the sets $\{\omega_k^f\}$ and $\{\omega_k^0\}$ known from the feed state and the initial state, respectively, the k-constant state can be represented by the following set of characteristic parameters:

$$[\omega_1^f, \omega_2^f, \ldots, \omega_k^f, \omega_{k+1}^0, \ldots, \omega_{m-1}^0, \omega_m^0] \tag{10}$$

Once the set is identified, the concentrations $\{c_{i,k}\}$ may be evaluated by using Eq. 9.

If $\omega_k^f > \omega_k^0$, the k-wave is a centered simple wave in the region of which the state changes continuously. The k-simple wave may be represented by a family of straight characteristics C_k, all emanating from the origin of the (x,τ)-plane and along each of these characteristics the state remains unchanged. The characteristic of the k^{th} kind, C_k, has a slope given by

$$\frac{d\tau}{dx_k} = \sigma_k = 1 + \nu\omega_k \prod_{j=1}^{m} \frac{\omega_j}{\gamma_j} \tag{11}$$

(It can be shown that $D = 1 + \Sigma_{j=1}^{m} K_j c_j = \Pi_{j=1}^{m} \gamma_j/\omega_j$, which may be used to derive Eq. 11 as well as Eqs. 13 and 14.) Here the simple wave region is bounded by the k- and $(k - 1)$-constant state on the left- and right-hand sides, respectively, and hence Eq. 11 may be rewritten in the form

$$\sigma_k = 1 + \nu\frac{\omega_k^2}{\gamma_k} \prod_{j=1}^{k-1} \frac{\omega_j^f}{\gamma_j} \prod_{j=k+1}^{m} \frac{\omega_j^0}{\gamma_j} \tag{12}$$

The two factors with the product sign are constant while ω_k varies over the range $\omega_k^0 \le \omega_k \le \omega_k^f$. It is then straightforward to generate the family of C_k, each of which carries a fixed value of ω_k and thus a fixed state of concentrations. This state can be determined by using the particular value ω_k in Eq. 9 together with ω_j^f for $j = 1, 2, \ldots, k - 1$ and ω_j^0 for $j = k + 1, \ldots, m$.

It becomes evident now that the characteristics C_k must fan clockwise as we proceed in the x-direction; otherwise we encounter a physically impossible situation. We also notice that σ_k is a monotomic function of ω_k. Consequently, in the k-simple wave region the parameter ω_k monotomically decreases in the x-direction. This implies that the concentrations change monotomically.

If $\omega_k^f < \omega_k^0$, the k-wave is a shock and thus the state changes discontinuously. With constant states on both sides the k-shock propagates along a straight line in the (x,τ)-plane, whose direction is given by

$$\frac{d\tau}{dx_k} = s_k = 1 + \nu\omega_k^l \prod_{i=1}^{m} \frac{\omega_j^r}{\gamma_j} \tag{13}$$

$$= 1 + \nu\omega_k^r \prod_{j=1}^{m} \frac{\omega_j^l}{\gamma_j} \tag{14}$$

where the superscripts l and r denote the left- and right-hand sides of the shock, respectively. For the present case, therefore, the k-shock path S_k is readily located by drawing a straight line from the origin with a slope given by

$$s_k = 1 + \nu\omega_k^f \prod_{j=1}^{k-1} \frac{\omega_j^f}{\gamma_j} \prod_{j=k}^{m} \frac{\omega_j^0}{\gamma_j} \tag{15}$$

In case $\omega_k^f = \omega_k^0$, the k-wave simply does not exist and hence we have $\{c_{i,k}\} = \{c_{i,k-1}\}$.

The procedure discussed above may be summarized as follows for a given set of conditions $\{c_i^f\}$ and $\{c_i^0\}$: (1) Solve Eq. 7 to obtain the sets $\{\omega_k^f\}$ and $\{\omega_k^0\}$; (2) Identify the characteristic parameters $\{\omega_k\}$ for each of the $(m - 1)$ and intermediate constant states as exhibited in Eq. 10; (3) Determine the concentration state $\{c_{i,k}\}$, $k = 1, 2, \ldots, m - 1$ by using Eqs. 9 and 10; (4) If $\omega_k^f > \omega_k^0$, construct the k-simple wave by employing Eqs. 9 and 12; (5) If $\omega_k^f < \omega_k^0$, use Eq. 15 to locate the k-shock path S_k. Once the solution is completed in the (x,τ)-plane, the distribution of solutes can be directly read at any moment.

Special Cases

In the practice of chromatography one or more solute species may be absent from the initial bed or from the feed mixture. If a particular solute A_j is absent, it follows from Eq. 7 that one of the characteristic parameters $\{\omega_k\}$ must be equal to γ_j and then from Eq. 8 that

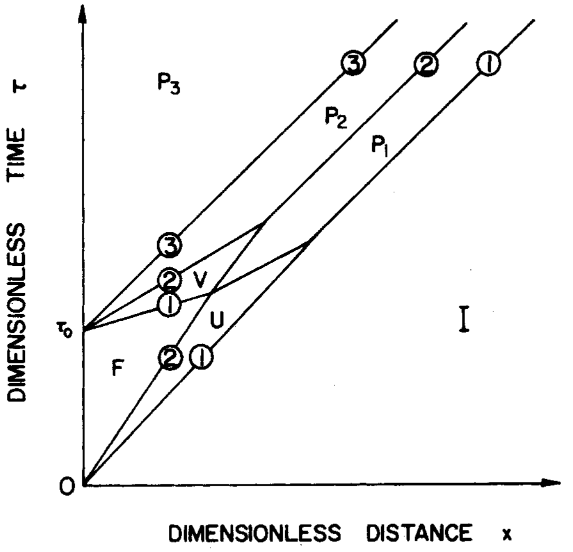

Figure 2. Schematic portrait of the solution in the (x,τ)-plane when displacement development is applied to a feed mixture (F) containing two solutes. —ⓚ— k-Shock Path S_k

$$\omega_j = \gamma_j \quad \text{or} \quad \omega_{j+1} = \gamma_j \tag{16}$$

The only exception is that, if A_m is absent, we necessarily obtain

$$\omega_m = \gamma_m \tag{17}$$

For the clean bed as well as for the pure solvent Eq. 7 yields

$$\omega_k = \gamma_k, \quad k = 1, 2, \ldots, m \tag{18}$$

In later sections these properties will be central to the analyses of the system.

We recall that, among m parameters $\{\omega_k\}$, ω_j is the only variable in a j-wave which is a centered simple wave if ω_j decreases in the x-direction or a shock if ω_j increases in the x-direction. These rules together with Eqs. 16 and 17 lead us to the following conclusions. (1) Solute A_j can be exhausted only across a j-shock or a $(j + 1)$-simple wave through which ω_j increases to γ_j or ω_{j+1} decreases to γ_j, respectively. (2) Solute A_j can emerge only across a j-simple wave or a $(j + 1)$-shock through which ω_j decreases from γ_j or ω_{j+1} increases from γ_j, respectively. (3) Solute A_m can be exhausted only across an m-shock and emerge only through an m-simple wave.

Inequality Conditions

For a particular state of concentrations $\{c_i\}$ or $\{\omega_k\}$, there exist m different characteristic directions. These directions are given by Eq. 11 for $k = 1, 2, \ldots, m$ in which, we note, the factor with the product sign is independent of k. It then follows from Eq. 8 that

$$1 < \sigma_1 < \sigma_2 < \sigma_3 \ldots \sigma_{m-1} < \sigma_m \tag{19}$$

Given the state on one side, say $\{c_i^l\}$, and one concentration on the other side, there are m different states for $\{c_i^r\}$ that can be connected to the state $\{c_i^l\}$ by a discontinuity. The propagation directions of these discontinuities are given by Eq. 13 or 14 for $k = 1, 2, \ldots, m$. Therefore, for shocks with the state on one side in common it can be shown from Eqs. 8 and 14 that

$$1 < \mathrm{s}_1 < \mathrm{s}_2 < \mathrm{s}_3 \ldots \mathrm{s}_{\mathrm{m}-1} < \mathrm{s}_{\mathrm{m}} \tag{20}$$

From the previous discussion, it is clear that we have $\omega_k^l < \omega_k^r$ for a k-shock. When applied to Eqs. 11, 13, and 14, this condition gives the inequality

$$\sigma_k^l < s_k < \sigma_k^r \tag{21}$$

for $k = 1, 2, \ldots, m$. Also, one can show by using Eq. 8 that

$$\sigma_{k-1}^r < s_k < \sigma_{k+1}^l \tag{22}$$

The inequalities in Eqs. 21 and 22 are what we call the "shock condition" (or "entropy condition" in a broader sense) (Lax, 1971). If the shock condition is satisfied across a discontinuity, it is called a shock. In this sense, the discontinuities encountered here are all shocks.

Wave Interactions

Since the transformation of $\{c_i\}$ to $\{\omega_k\}$ defined by Eq. 7 is independent of both x and τ, the solution scheme is equally applicable to any point in the (x,τ)-plane if an initial discontinuity is imposed at the point. If there are two or more points with discontinuity along the x-axis and/or the τ-axis, then the solution as a whole may be established by constructing the wave solutions separately from each point of discontinuity. After a finite period of time, however, any two wave solutions centered at two different, but adjacent, points of discontinuity will meet each other so that an overlapped region appears in which the solution is influenced by two different sets of data at the same time. Such a phenomenon is called an interaction between waves.

By examining Eqs. 19 through 22 and taking into account the variations of the parameters $\{\omega_k\}$, one can identify the interacting wave pairs as well as the patterns of interaction.

Interacting Wave Pairs. (1) Two shocks of the same kind. (2) A shock and a simple wave of the same kind. (3) A k-wave traveling behind an l-wave if $k < l$.

Patterns of Interaction. (1) Interaction between shocks is instantaneous whereas interaction involved with a simple wave is gradual. (2) Two shocks of the same kind are superposed by interaction. (3) A shock absorbs a simple wave of the same kind while interacting and becomes weak in strength. (4) Two waves of different kinds transmit across each other while interacting.

Analyses of various interactions have been fully discussed in the original paper (Rhee, Aris and Amundson, 1970).

TWO SOLUTE SEPARATION BY DISPLACEMENT DEVELOPMENT

Before treating the general problem, it would be heuristic to analyze in some detail the process applied to a two solute mixture and elucidate various features that are of importance. Hence the bed (I), initially clean, is first saturated with a mixture (F) containing two solutes A_1 and A_2 for a finite period of time τ_0 and afterwards the feed is switched to a stream (P_3) containing A_3 only. The species A_3 which is the developer here is more strongly adsorbed than the species A_1 or A_2; i.e., $\gamma_1 < \gamma_2 < \gamma_3$. In this section we shall use the notation $Q[\omega_1,\omega_2,\omega_3]$ to represent the characteristic parameters $\{\omega_k\}$ corresponding to the state Q.

Solution Scheme

Since there are two points of discontinuity, one at the origin and the other at point $(0,\tau_0)$, two wave solutions appear in the (x, τ)-plane and these are involved with interactions as shown in Figure 2. We shall construct the solution step by step.

For the state of the initial bed (I), Eq. 7 readily gives $I[\gamma_1,\gamma_2,\gamma_3]$ whereas for the state F we obtain one root γ_3 and a quadratic equation which gives two more roots such that $0 < \omega_1^f \leq \gamma_1 \leq \omega_2^f \leq \gamma_2$ and thus we have $F[\omega_1^f,\omega_2^f,\gamma_3]$. It is then evident that two shocks would develop from the origin with the 3-wave missing because $\omega_3 = \gamma_3$ for both I and F. As we proceed in the x-direction, ω_2 increases from ω_2^f to γ_2 across the 2-shock and so species A_2 is exhausted whereas across the 1-shock ω_1 increases from ω_1^f to γ_1 with A_1 being exhausted. The new intermediate constant state U is represented as $U[\omega_1^f,\gamma_2,\gamma_3]$. With the ω-values known for F, U and I one can easily determine the propagation directions of two shocks by using Eq. 13 or 14:

$$s_2 = 1 + \nu\omega_1^f\omega_2^f/\gamma_1$$

$$s_1 = 1 + \nu\omega_1^f$$

TABLE 1. CONSTANT STATES AND THE CHARACTERISTIC PARAMETERS $\{\omega_k\}$

Constant State	Solute Present	Parameters $\{\omega_k\}$			Connecting Wave
		ω_1	ω_2	ω_3	
I	None	γ_1	γ_2	γ_3	1-Shock
P_1	A_1	ω_1^*	γ_2	γ_3	
P_2	A_2	ω_1^*	$\overset{\downarrow}{\gamma_1}$	γ_3	2-Shock
P_3	A_3	ω_1^*	γ_1	$\overset{\downarrow}{\gamma_2}$	3-Shock

* Arrow indicates the variation when the shock is crossed counterclockwise.

For the state P_3 where both A_1 and A_2 are absent Eq. 7 yields two roots, γ_1 and γ_2, and another root ω^* determined by the developer concentration c_3^* as

$$\frac{K_3 n_3^*}{\gamma_3 - \omega^*} = 1$$

or

$$\omega^* = \frac{\gamma_3}{1 + K_3 c_3^*} \tag{23}$$

Obviously, the value of ω^* varies from zero to γ_3 depending on the value of c_3^* so that the ordering of the parameters $\{\omega_k\}$ is not fixed. If for instance $\omega^* < \gamma_1 < \gamma_2$, then we have $P_3[\omega^*,\gamma_1,\gamma_2]$. Compare this with Eq. 16. The wave solution from point $(0,\tau_0)$ consists of a 3-shock, a 2-shock and a 1-shock if $\omega^* < \omega_1^f$ for a 1-simple wave if $\omega^* > \omega_1^f$.

The ω-values for the intermediate constant states P_2 and V are readily identified as $P_2[\omega^*,\gamma_1,\gamma_3]$ and $V[\omega^*,\omega_2^f,\gamma_3]$. This implies that the state P_2 contains A_2 only and thus represents the pure component band for A_2. Across the 3-shock ω_3 increases from γ_2 to γ_3 so that A_3 is exhausted while A_2 emerges. This is consistent with previous conclusions. The three waves can be established by using Eq. 11 or 13:

$$s_3 = 1 + \nu\omega^*$$

$$s_2 = 1 + \nu\omega_2^f\omega^*/\gamma_2$$

$$s_1 = 1 + \nu\omega_1^f\omega_2^f/\gamma_2 \quad \text{if} \quad \omega^* < \omega_1^f$$

$$\sigma_1 = 1 + \nu\omega_1\omega_2^f/\gamma_2 \quad \text{for} \quad \omega^* \geq \omega_1 \geq \omega_1^f \quad \text{if} \quad \omega^* > \omega_1^f$$

All the interactions can be analyzed without difficulty once the ω-values are identified for the states involved. [See the reference (Rhee, Aris and Amundson, 1970) for details.] The state P_1 will turn out to have the ω-values as $P_1\{\omega^*,\gamma_2,\gamma_3\}$ and thus a pure component band for A_1 is formed.

Critical Value of the Developer Concentration, $c_{3,cr}^*$

If the development is to be satisfactory, the process should eventually reach a stationary state at which the constant state P_i contains A_i only for $i = 1, 2, 3$, respectively, and the four constant states P_3,P_2,P_1, and I will be separated by three shocks as shown in Figure 2. Now it is clear that two of the ω-values for each P_i are known to be γ_j, $j \neq i$ while for the state I we have $I[\gamma_1,\gamma_2,\gamma_3]$.

Let us start from the state $I[\gamma_1,\gamma_2,\gamma_3]$ and cross the 1-shock counterclockwise. The only variable here is the parameter ω_1 which is to decrease from γ_1 to a lower value ω_1^*. For the state P_1, therefore, we should have $P_1[\omega_1^*,\gamma_2,\gamma_3]$. Next when we cross the 2-shock in the same direction, the parameter ω_2 is the only variable and decreases from γ_2 to γ_1 to give $P_2[\omega_1^*,\gamma_1,\gamma_3]$. Finally, across the 3-shock only the parameter ω_3 is allowed to vary and actually decreases from γ_3 to γ_2 to yield $P_3[\omega_1^*,\gamma_1,\gamma_2]$. The above argument is summarized in Table 1.

It is then obvious that ω_1^* should be equal to ω^* given by Eq. 23 and hence $\omega^* < \gamma_1$ or

$$c_3^* > \frac{1}{K_3}\left(\frac{\gamma_3}{\gamma_1} - 1\right) \equiv c_{3,cr}^* \tag{24}$$

Consequently, for a successful operation the developer concentration c_3^* should be higher than the critical value $c_{3,cr}^*$ defined by Eq. 24. This limit was recognized by Glueckauf (1946) in his analysis of an equivalent problem. It may be emphasized that $c_{3,cr}^*$ depends only on the adsorption characteristics of the developer A_3 and the least adsorbable species A_1 and independent of that of A_2 as well as the state of the feed mixture to be separated.

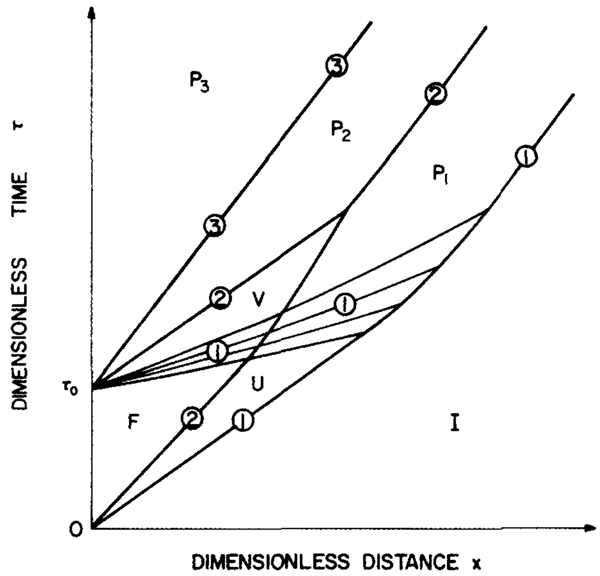

Figure 3. Schematic portrait of the solution when $\omega_1^f < \omega^* < \gamma_1$. —ⓚ— k-characateristic C_k, —ⓚ— k-shock path S_k

The value ω_1^* is common to states P_1, P_2 and P_3 in Table 1 and so

$$\omega^* = \omega_1^* = \frac{\gamma_3}{1 + K_3 c_3^*} = \frac{\gamma_2}{1 + K_2 c_2^*} = \frac{\gamma_1}{1 + K_1 c_1^*} \tag{25}$$

in which c_1^* and c_2^* denote the non-vanishing concentrations at P_1 and P_2, respectively. Therefore, c_i^* is readily determined as

$$c_i^* = \frac{1}{K_i}\left(\frac{\gamma_i}{\gamma_3} - 1\right) + \frac{\gamma_i K_3}{\gamma_3 K_i} c_3^* \quad i = 1, 2 \tag{26}$$

We note that c_i^* is independent of the state (F) of the original mixture. This fact was observed experimentally by Tiselius (1943) as early as 1943 and also theoretically by Glueckhauf (1946) and Claesson (1949).

Using Eq. 13 or 14 with the help of Table 1, one can find the propagation directions of shocks all of which turn out to be the same as

$$s = s_1 = s_2 = s_3 = 1 + \nu\omega^* = 1 + \frac{\nu\gamma_j}{1 + K_j c_j^*} \tag{27}$$

This equation is compatible with Eq. 25. It then follows that all three shock paths are parallel and so the widths of pure component bands, P_1 and P_2, remain unchanged. This is just what we would expect from the conservation of mass. Incidentally, one may begin with Eq. 27 from the physical point of view not only to derive Eq. 26 but also to deduce the condition given by Eq. 24. Indeed this approach was adopted in earlier work (Glueckauf, 1946; Claesson, 1949). Glueckauf (1946), although he obtained Eq. 27, apparently overlooked this simple relation and presented a complicated procedure to determine an approximate value of c_2^*.

Illustrations

Here we shall analyze various cases classified in terms of the developer concentration c_3^*; first the satisfactory situations and then unsatisfactory cases.

Case A: $c_3^* > c_{3,cr}^*$. We have $\omega^* < \gamma_1$ and so the process will reach ultimately the state shown in the upper part of Figure 2 with the parameter values given in Table 1. We expect, however, that different situations may be encountered in the intermediate stage depending on the comparison between ω^* and ω_1^f.

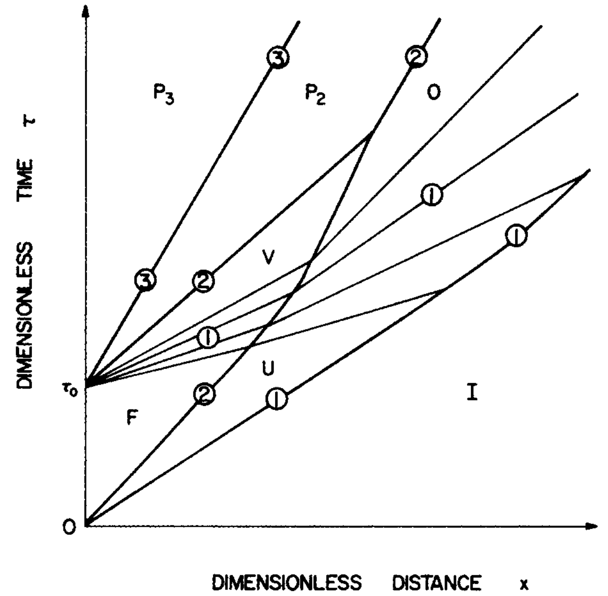

Figure 4. Schematic portrait of the solution when $\gamma_1 < \omega^* < \gamma_2$. —ⓚ— k-characteristic C_k, —ⓚ— k-shock path S_k

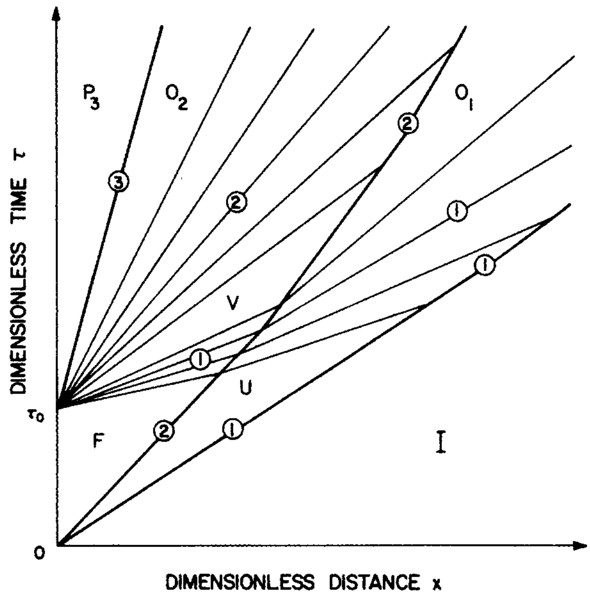

Figure 5. Schematic portrait of the solution when $\gamma_2 < \omega^* < \gamma_3$. —ⓚ— k-characteristic C_k, —ⓚ— k-shock path S_k

(1) Suppose now that the developer concentration c_3^* is sufficiently high so that $\omega^* < \omega_1^f < \gamma_1$. Then the connection between $P_3[\omega^*,\gamma_1,\gamma_2]$ and $F[\omega_1^f,\omega_2^f,\omega_3^f]$ are made by three shocks because all three parameters $\{\omega_k\}$ increase in the x-direction. The portrait in the (x,τ)-plane is exactly the same as depicted in Figure 2. A numerical example will be presented later showing the same situation for $m = 4$.

(2) If $\omega_1^f < \omega^* < \gamma_1$, the overall situation remains the same except for the fact that the 1-wave from point $(0,\tau_0)$ is a centered simple wave as shown in Figure 3. This 1-simple wave transmits through the 2-shock from the origin while interacting. With $U[\omega_1^f,\gamma_2,\gamma_3]$ and $V[\omega^*,\gamma_1,\gamma_3]$ it is clear that we have $P_1[\omega^*,\gamma_2,\gamma_3]$ because only ω_k varies across the k-wave. This implies that the state P_1 contains A_1 only. The transmitted 1-simple wave will interact with the 1-shock from the origin to be adsorbed completely because $\omega^* < \gamma_1$. Therefore, pure component bands are formed in a satisfactory fashion. It is expected, however, that the length of bed required may become larger than that in the previous case.

Case B: $c_3^* < c_{3,cr}^*$. This is the situation when we have $\omega^* > \gamma_1$ and thus the process is expected to become unsatisfactory in the sense that pure component bands are not partitioned by sharp boundaries. We shall discuss two different cases to be encountered depending on the ω^*-value.

(1) Suppose c_3^* is slightly less than $c_{3,cr}^*$ so that we have $\gamma_1 < \omega^* < \gamma_2$ or $P_3[\gamma_1,\omega^*,\gamma_2]$. The 3-wave from point $(0,\tau_0)$ is again a shock across which ω_3 increases from γ_2 to γ_3 in the x-direction to give $P_2[\gamma_1,\omega^*,\gamma_3]$. The 2-wave now is a shock if $\omega^* < \omega_2^f$ or a simple wave if $\omega^* > \omega_2^f$. In either case we have $V[\gamma_1,\omega_2^f,\gamma_3]$. The 1-wave from point $(0,\tau_0)$ is necessarily a simple wave because ω_1 decreases from γ_1^f in the x-direction.

With $U[\omega_1^f,\gamma_2,\gamma_3]$ and $V[\gamma_1,\omega_2^f,\gamma_3]$ the interaction between the 1-simple wave and the 2-shock (from the origin) will generate a new constant state $O[\gamma_1,\gamma_2,\gamma_3]$ which represents a state of no solute as shown in Figure 4. Since both the state O and I have $\omega_1 = \gamma_1$, the interaction between the transmitted 1-simple wave and the 1-shock from the origin will go on indefinitely. An immediate consequence is that the pure component band for A_1 does not stay adjacent to that for A_2 and continuously diffuses in the rear with decrease in the height of the front. This is exactly what we would expect to obtain when a chromatogram of A_1 is eluted by pure solvent. The interaction between the 2-waves will eventually give rise to a 2-shock, across which the state changes from $P_2[\gamma_1,\omega^*,\gamma_3]$ to $O[\gamma_1,\gamma_2,\gamma_3]$.

In conclusion, the process becomes only partially successful in the sense that the pure component band for A_2 maintains sharp boundaries whereas that for A_1 not only departs from the A_2-band but also the rear boundary is diffuse. Here the presence of the developer A_3 has no influence over the behavior of solute A_1. However, one may find this situation advantageous if A_1 is an impurity to be removed completely from A_2 or if it is desired to recover A_1 in high purity.

(2) If c_3^* is very small, we may have a case when $\gamma_2 < \omega^* < \gamma_3$ or $P_3[\gamma_1,\gamma_2,\omega^*]$. The 3-wave from point $(0,\tau_0)$ is again a shock but across the shock now the parameter ω_3 increases from ω^* to γ_3 to give a state of no solute $O_2[\gamma_1,\gamma_2,\gamma_3]$ as shown in Figure 5. It is then obvious that the situation on the right-hand side of the region of state O_2 is exactly the same as what we would expect in the conventional elution of a two solute chromatogram by pure solvent. The analysis has been illustrated elsewhere (Glueckauf, 1949; Rhee, 1968; Rhee, Aris and Amundson, 1970). Clearly, the developer A_3 has no influence over the behavior of solutes A_1 and A_2 so that the two solutes are simply eluted by pure solvent.

Since both ω_2 and ω_1 decrease from the state P_3 to the state $F(\gamma_2 > \omega_2^f$ and $\gamma_1 > \omega_1^f)$, the 2- and 1-waves from point $(0,\tau_o)$ are simple waves. The intermediate constant state is $V[\gamma_1,\omega_2^f,\gamma_3]$. The 1-simple wave then transmits through the 2-shock from the origin while interacting with each other. With $U[\omega_1^f,\gamma_2,\gamma_3]$ and $V[\gamma_1,\omega_2^f,\gamma_3]$ the interaction will give a new constant state $O_1[\gamma_1,\gamma_2,\gamma_3]$ as depicted in Figure 5. Consequently, the two solutes are separated into pure component bands with the state O_1 in between. Both bands tend to broaden in width and to be lessened in height through the indefinite interactions between the simple wave and the shock of the same kind. Therefore, the process becomes unsatisfactory.

To summarize this section, we conclude that displacement development would be successful only if $c_3^* > c_{3,cr}^*$. Otherwise, the developer has no influence over both solutes A_1 and A_2 or over the least adsorbable species A_1 which are then simply eluted by pure solvent. Glueckauf (1949) discussed an equivalent problem by using the characteristic curves in the (c_1,c_2)- and (c_2,c_3)-planes. This treatment, though not necessary, is very useful in understanding the physical situation that is expected with various levels of developer concentration.

GENERALIZATION

Although it should be obvious from the previous section, we will extend the discussion to the multi-solute system. Let us now consider the application of displacement development to a mixture

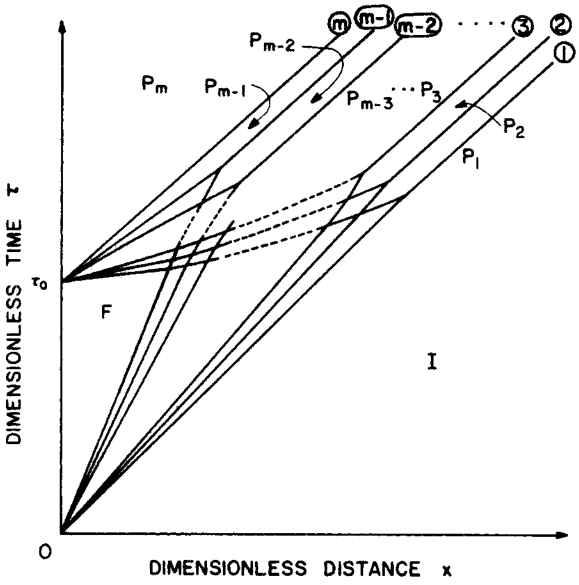

Figure . 6. Schematic portrait of the solution in the (x,τ)-plane when displacement development becomes satisfactory for a feed mixture (F) containing ($m - 1$) different solutes. The lines represent the shock paths and the capital letters denote the constant states.

containing $(m - 1)$ different solute species. The developer A_m is more strongly adsorbable than any solutes in the original mixture; i.e., $\gamma_m > \gamma_{m-1}$. An initially clean bed (I) is first saturated with the original mixture (F) for a finite period of time (τ_o) and next fed with a stream containing A_m only (P_m). Here again we shall employ the symbol $Q[\omega_1,\omega_2, \ldots, \omega_k, \ldots, \omega_m]$ to represent the characteristic parameters $\{\omega_k\}$ corresponding to the state Q.

For the initial state of the bed (I), Eq. 7 gives

$$I[\gamma_1,\gamma_2, \ldots ,\gamma_k, \ldots ,\gamma_m]$$

while we would obtain, for the state F,

$$F[\omega_1^f,\omega_2^f, \ldots ,\omega_k^f, \ldots ,\omega_{m-1}^f,\gamma_m]$$

where $w_1^f \leq \gamma_1 \leq \omega_2^f \leq \omega_3^f \ldots \omega_{m-1}^f \leq \gamma_{m-1} < \gamma_m$. Consequently, $(m - 1)$ waves will develop from the origin with the m-wave missing as shown in Figure 6. These are all shocks since in the x-direction ω_k increases from ω_k^f to γ_k across the k-wave for $k = 1, 2, \ldots, m - 1$.

For the state P_m Eq. 7 directly yields $(m - 1)$ roots $\gamma_1,\gamma_2, \ldots, \gamma_{m-1}$ because solutes $A_1,A_2, \ldots ,A_{m-1}$ are absent. Another root ω^* is determined by the developer concentration c_m^* as

$$\omega^* = \frac{\gamma_m}{1 + K_m c_m^*} \tag{28}$$

Since the value of ω^* may vary from zero to γ_m, the ordering of the parameters $\{\omega_k\}$ is not fixed. If $\gamma_{j-1} < \omega^* < \gamma_j$, ω^* becomes the j^{th} root of Eq. 7 so that

$$P_m[\gamma_1, \gamma_2, \ldots, \gamma_{j-1}, \omega^*, \gamma_{j+1}, \ldots, \gamma_{m-1}, \gamma_m]$$

Thus, the wave solution from point $(0,\tau_0)$ consists of $(m-j)$ shocks on the left-hand side and $(j - 1)$ simple waves on the right-hand side. The j-wave will be a shock if $\omega^* < \omega_j^f$ or a simple wave if $\omega^* > \omega_j^f$.

The two wave sets will be involved in a series of interactions which can be fully analyzed. After all the interactions are over, we expect to have m shocks in order for the process to be successful. These shocks should propagate along parallel paths as depicted in Figure 6.

Critical Value of Developer Concentration, $c^*_{m,cr}$

If we start from the state I the cross the 1-shock counterclockwise, ω_1 is the only variable among $\{\omega_k\}$. It certainly decreases from γ_1 to a finite value ω_1^*; i.e., $0 < \omega_1^* < \gamma_1$. Since ω_1 varies only across the 1-wave, such a value ω_1^* remains unchanged while we cross successively the 2-shock through the m-shock. In other words the value ω_1^* is the smallest root of Eq. 7 for every constant state P_j, $j = 1,2, \ldots, m$.

TABLE 2. NUMERICAL VALUES FOR THE PARAMETERS AND CONDITIONS

i	1	2	3	4
γ_i (mol/L)	5	10	15	20
K_i (L/mol)	5	10	15	20
c_i^0 (mol/L)	0	0	0	0
c_i^f (mol/L)	0.05	0.05	0.05	0

Recalling the fact that Eq. 7 for the state P_m has $(m - 1)$ roots given by $\gamma_1,\gamma_2, \ldots, \gamma_{m-1}$ and another root ω^* determined by Eq. 28, one can conclude that

$$\omega^* = \omega_1^* = \frac{\gamma_m}{1 + K_m c_m^*} < \gamma_1$$

or

$$c_m^* > \frac{1}{K_m}\left(\frac{\gamma_m}{\gamma_1} - 1\right) \equiv c^*_{m,cr} \tag{29}$$

Note that the critical value of the developer concentration is given in terms of the adsorption characteristics of only itself and the least adsorbable solute species in the system. It is independent of the properties of intermediate species as well as of the state of the original mixture. If Eq. 29 is satisfied, all the waves at the ultimate stage are shocks which form boundaries of $(m - 1)$ pure component bands propagating side by side without interval, and hence the process becomes satisfactory.

Plateau Concentration and Band Width

Since at the ultimate stage ω^* is the smallest root of Eq. 7 for every pure component band P_j, $j = 1,2, \ldots$, m while the other $(m - 1)$ roots are given by γ_k, $k \neq j$, one can immediately write the equations

$$\omega^* = \frac{\gamma_1}{1 + K_1 c_1^*} = \frac{\gamma_2}{1 + K_2 c_2^*} = \cdots$$
$$= \frac{\gamma_j}{1 + K_j c_j^*} = \cdots = \frac{\gamma_m}{1 + K_m c_m^*} \tag{30}$$

where c_j^* denotes the concentration of A_j in its pure component band. Equation 30 is then readily solved to give an expression for c_j^* in terms of c_m^*:

$$c_j^* = \frac{1}{K_j}\left(\frac{\gamma_j}{\gamma_m} - 1\right) + \frac{\gamma_j K_m}{\gamma_m K_j} c_m^* \tag{31}$$

for $j = 1,2, \ldots, m - 1$. On the basis of Eq. 31 one may apply displacement development not only to identify an unknown mixture as suggested by Claesson (1949) but also to determine the isotherm parameters γ_j and K_j.

Also it can be shown from Eq. 13 or 14 that

$$s = s_1 = s_2 \cdots = s_m = 1 + \nu\omega^* = 1 + \frac{\nu\gamma_j}{1 + K_j c_j^*} \tag{32}$$

and thus all the shock paths are parallel in the (x,τ)-plane. On the other hand, if we let Δx_j denote the horizontal width of the A_j-band, a simple material balance yields

$$\left[c_j^* + \frac{\nu\gamma_j c_j^*}{1 + K_j c_j^*}\right] \Delta x_j = \tau_0 c_j^f$$

or

$$\Delta x_j = \tau_0 c_j^f / s c_j^* \tag{33}$$

The vertical width $\Delta\tau_j$ is then

$$\Delta\tau_j = \tau_0 c_j^f / c_j^* \tag{34}$$

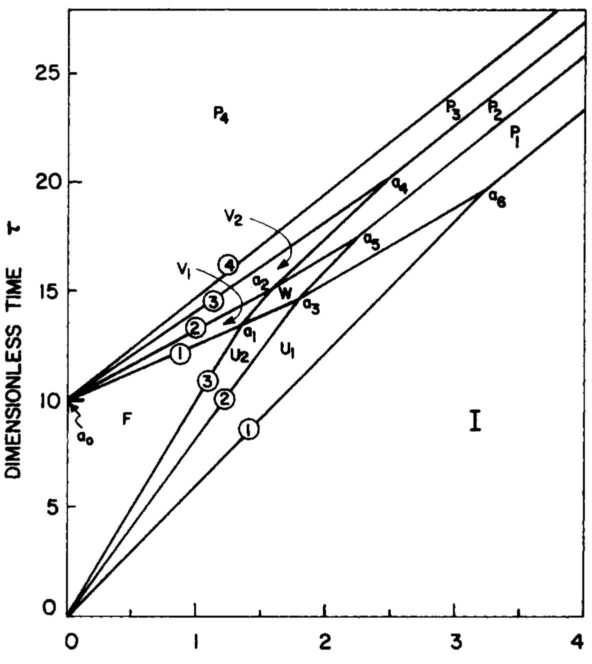

Figure 7. Portrait of the solution in the (x,τ)-plane when $c_4^* = 0.35$ mol/L. Capital letters represent the constant states while a_i's denote the intersections of shock paths. —ⓚ— k-shock path S_k

and this is the width of the pure component band we would expect to observe in the breakthrough curve. Since the path of the m-shock is known a priori, Eq. 33 or 34 enables us to locate all the shock paths at the ultimate stage without going into the analysis of interactions.

For the bed length required for complete separation, however, we have to analyze all the interactions involved. All the waves being shocks, the analysis should be straightforward although it may become tedious as the number of components involved increases. If $\omega^* > \omega_1^f$, the 1-wave from point $(0,\tau_0)$ is a simple wave and so the successive interactions between this 1-simple wave and each of the shocks from the origin will have to be analyzed. This case will be illustrated for m = 4 in the next section.

NUMERICAL EXAMPLES FOR $m = 4$

Here we shall consider a specific system with numerical values for all the parameters and discuss the analysis in some detail to illustrate the application of the theory. Let us set

$$\epsilon = 0.4 \quad \text{or} \quad \nu = 1.5$$

and

$$\tau_0 = 10$$

with other parameters and conditions specified as given in Table 2. Here it is assumed for convenience that $N_i = 1$ mol/L for all the species and so $\gamma_i = K_i$, $i = 1, 2, 3, 4$. The critical value of developer concentration is

$$c_{4,cr}^* = \frac{1}{20}\left(\frac{20}{5} - 1\right) = 0.15 \text{ mol/L}$$

which is fairly high when compared to the feed concentrations.

In the following we shall use the symbol $Q[\omega_1,\omega_2,\omega_3,\omega_4]$ to represent the characteristic parameters $\{\omega_k\}$ corresponding to the state Q. For the initial state of the bed we readily have $I[5,10,15,20]$ whereas for the feed state (F) Eq. 7 becomes a cubic equation for ω which may be solved to give the first three ω-values; i.e., $\omega_1^f = 3.387$, $\omega_2^f = 7.050$ and $\omega_3^f = 12.563$. The largest root ω_4^f is equal to $\gamma_4 = 20$, so that we have $F[3.384, 7.050, 12.563, 20]$.

Obviously, three shocks will develop from the origin as shown in the neighborhood of the origin in Figure 7. The two intermediate constant states are characterized as $U_2[3.389, 7.050, 15, 20]$ and $U_1[3.387, 10, 15, 20]$. The slopes of the shock paths are determined by Eq. 13:

$$s_3 = 1 + (1.5)(12.563)\left(\frac{3.387}{5}\right)\left(\frac{7.050}{10}\right)\left(\frac{15}{15}\right)\left(\frac{20}{20}\right) = 10.0$$

$$s_2 = 1 + (1.5)(7.050)\left(\frac{3.387}{5}\right)\left(\frac{10}{10}\right)\left(\frac{15}{15}\right)\left(\frac{20}{20}\right) = 8.164$$

$$s_1 = 1 + (1.5)(3.387) = 6.081$$

The discussion above is independent of the level of developer concentration c_4^*.

A Case When $c_4^* > c_{4,cr}^*$ and $\omega^* < \omega_1^f$

First we shall be concerned with a case when the developer concentration is much higher than its critical value. Let us take $c_4^* = 0.35$ mol/L. Then we have $\omega^* = 20/[1 + (20)(0.35)] = 2.5 < \omega_1^f$ and so $P_4[2.5,5,10,15]$. The concentration plateaus at the ultimate stage are determined by using Eq. 31:

$$c_3^* = \frac{1}{15}\left(\frac{15}{20} - 1\right) + \frac{(20)(15)}{(15)(20)}(0.35) = 0.3333 \text{ mol/L}$$

$$c_2^* = 0.30 \text{ mol/L and } c_1^* = 0.20 \text{ mol/L}$$

The boundaries will propagate along parallel lines in the (x, τ)-plane, having slope

$$s = 1 + \frac{(1.5)(20)}{1 + (20)(0.35)} = 4.75$$

and hence the band widths are given by Eqs. 33 and 34 as follows:

$$\Delta x_3 = (10)(0.05)/(0.333)(4.75) = 0.316, \quad \Delta\tau_3 = 1.5$$

$$\Delta x_2 = (10)(0.05)/(0.3)(4.75) = 0.351, \quad \Delta\tau_2 = 1.667$$

$$\Delta x_1 = (10)(0.05)/(0.2)(4.75) = 0.526, \quad \Delta\tau_1 = 2.5$$

The path of the 4-shock from point $a_0(0,10)$ can be located by using the slope s and then the paths of the other three shocks by using the band widths Δx_j or $\Delta\tau_j$ with the same slope. This procedure will complete the solution attained at the ultimate stage. In this manner we can obtain all the information needed for practical purposes except for the length of the bed required. In order to determine the bed length we will have to go through the analysis of interactions which will be discussed here in detail for the purpose of illustration.

With $P_4[2.5,5,10,15]$ in the upstream side and $F[3.387,7.050,12.568,20]$ in the downstream side we expect four shocks to develop from point $a_0(0,10)$ as depicted in Figure 7. The intermediate constant states will have ω-values as $P_3[2.5,5,10,20]$, $V_2[2.5,5,12.563,20]$ and $V_1[2.5,7.050,12.563,20]$. Note that the state P_3 contains A_3 only. The shock paths are determined more conveniently by using Eq. 14:

$$s_4 = 1 + (1.5)(20)\left(\frac{2.5}{5}\right)\left(\frac{5}{10}\right)\left(\frac{10}{15}\right)\left(\frac{15}{20}\right) = 4.75$$

$$s_3 = 1 + (1.5)(12.563)\left(\frac{2.5}{5}\right)\left(\frac{5}{10}\right)\left(\frac{10}{15}\right)\left(\frac{20}{20}\right) = 4.141$$

$$s_2 = 1 + (1.5)(7.05)\left(\frac{2.5}{5}\right)\left(\frac{5}{10}\right)\left(\frac{12.563}{15}\right)\left(\frac{20}{20}\right) = 3.214$$

$$s_1 = 1 + (1.5)(3.387)\left(\frac{2.5}{5}\right)\left(\frac{7.050}{10}\right)\left(\frac{12.563}{15}\right)\left(\frac{20}{20}\right) = 2.50$$

After interactions between shocks of different kinds, new constant states W, P_2 and P_1 will appear as shown in Figure 7. The ω-values for each of these new states may be easily identified by looking at the ω-values for the known constant states: i.e., U_1, U_2, V_1, V_2, P_3 and I. Thus we have $W[2.5,7.050,15,20]$, $P_2[2.5,5,15,20]$

TABLE 3. SLOPES OF VARIOUS SHOCK PATHS

State on Left-Hand Side	State on Right-Hand Side	Index of Shock, k	Slope of Shock Path, s_k
V_1	W	3	7.643
V_2	P_2	3	5.711
P_3	P_2	3	4.75
P_2	W	2	3.644
W	P_1	2	6.288
P_2	P_1	2	4.75
W	U_2	1	2.791
P_1	U_1	1	3.540
P_1	I	1	4.75

and $P_1[2.5,10,15,20]$. The states P_1 and P_2, rrespectively contain A_1 and A_2 only. Therefore, when interactions are over, pure component bands for A_1, A_2 and A_3 are formed with sharp boundaries at both ends.

The slopes of shock paths after each interaction can be calculated by using the ω-values on both sides in Eq. 13 or 14. Once these slopes are known, the points of interaction are determined by computation or by a graphical method. The slopes are tablulated in Table 3 and the points of interaction are given in Table 4.

With these data we can complete the solution in the (x,τ)-plane as shown in Figure 7. At the ultimate stage all the shock paths become parallel and the band widths are found the same as the values obtained *a priori*. Since the ultimate stage is attained at point a_6, we may conclude that the bed length required is 3.255. It is noticed, however, that the state U_1 also contains A_1 only and complete separation actually obtains at point a_4. Therefore, one may proceed with a bed of length 2.464 as well. If so, the state U_1 will make the breakthrough first and then the state P_1 follows. The ratio of the bed volume required to the sample volume introduced here is $x/\epsilon\tau_0 = 2.464/(0.4)(10) = 0.616$. Such a low value for this ratio is attained at the expense of higher developer concentration. If the same volume of sample mixture is to be separated by using pure solvent ($c_4^* = 0$), the ratio will turn out to be 1.538. This implies that when $c_4^* = 0.35$ mol/L one can reduce the bed volume required by 60%.

Although the constant states are represented so far in terms of ω-values, the actual concentrations can be readily determined by using Eq. 9. Only non-vanishing concentrations for various constant states are listed below the units in mol/L.

$$U_1\colon\ c_1 = 0.0952$$

$$U_2\colon\ c_1 = 0.0554,\ c_2 = 0.0817$$

$$V_1\colon\ c_1 = 0.1050,\ c_2 = 0.0768,\ c_3 = 0.0729$$

$$V_2\colon\ c_2 = 0.1836,\ c_3 = 0.1293$$

$$W\colon\ c_1 = 0.1163,\ c_2 = 0.1255$$

$$P_1\colon\ c_1 = 0.20$$

$$P_2\colon\ c_2 = 0.30$$

$$P_3\colon\ c_3 = 0.3333$$

The concentrations for the states P_i are the same as the values obtained earlier by using Eq. 31.

With these data and Figure 7 it is now possible to construct the concentration profiles at various stages of development. These are presented in Figure 8 from which one may gain better understanding of how the separation is realized. At $\tau = 10$ (Part (a)), the feed mixture has just been put on the bed and the next figure (at $\tau = 12$) shows the development of the pure component band for A_3. At $\tau = 14$ (Part (c)) the state W appears after an interaction and A_1 is almost separated from A_3. Part (d) clearly shows that A_1 is completely separated from A_3 and A_2 is being separated from both A_1 and A_3. In the next two parts we see the separation of A_1 from A_2 and that of A_2 from A_3. Afterwards the pure component bands for A_1, A_2 and A_3 do not change in shape and simply propagate side by side with the same speed.

TABLE 4. LOCATION OF THE POINT OF INTERACTION

Symbol Used in Fig. 7	Coordinate x	τ	Pattern of Interaction
a_1	1.333	13.333	Transmission
a_2	1.549	14.978	Transmission
a_3	1.789	14.605	Transmission
a_4	2.464	20.203	Superposition
a_5	2.261	17.573	Superposition
a_6	3.255	19.794	Superposition

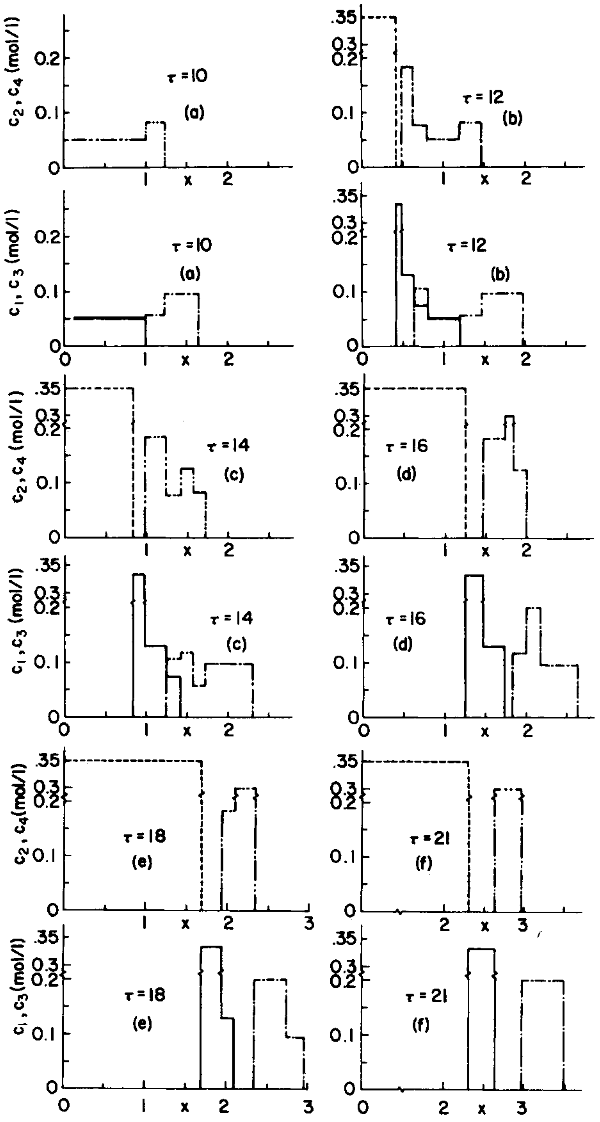

Figure 8. Concentration profiles at successive times when c_4^*= 0.35 mol/L (cf. Fig. 7). —·— Solute A_1, —·— Solute A_2, —— Solute A_3, —— Solute A_4

A Case When $c_4^* > c_{4,cr}^*$ and $\omega_1^f < \omega^* < \gamma_1$

Let us consider a case when the developer concentration is slightly higher than its critical value so that $\omega^* > \omega_1^f$. With $\omega_1^f = 3.387$ we have $\omega^* = \omega_1^f$ when $c_4^* = 0.245$ mol/L and so we shall take $c_4^* = 0.2$ mol/L. Then $\omega^* = 20/(1 + 20 \times 0.2) = 4.0$ and $P_4[4,5,10,15]$. At the ultimate stage the pure component bands will be formed in a satisfactory manner with the concentration plateaus given by

$$c_3^* = 0.1833 \text{ mol/L}$$

$$c_2^* = 0.150 \text{ mol/L}$$

$$c_1^* = 0.050 \text{ mol/L}$$

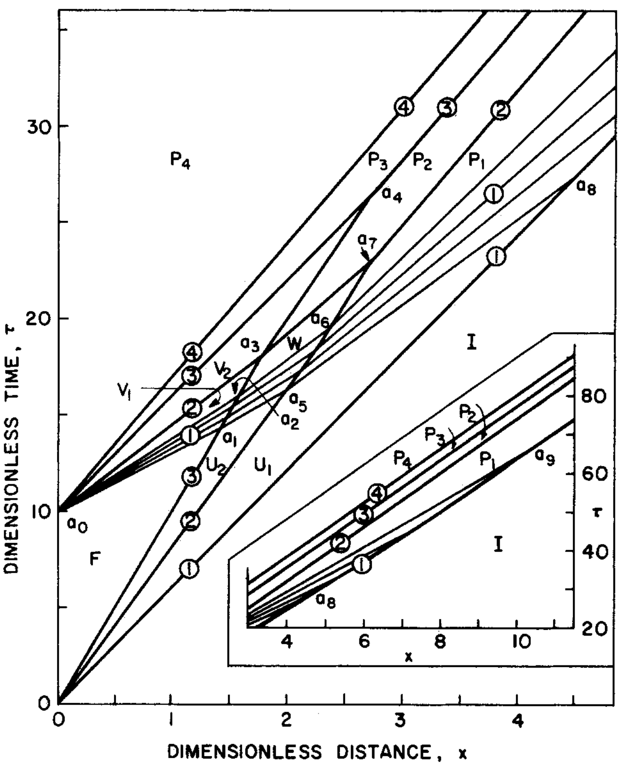

Figure 9. Portrait of the solution in the (x,τ)-plane when c_4^* = 0.20 mol/L. Capital letters represent the constant states while a_i's denote the interactions of lines. —ⓚ— k-characteristic C_k, —ⓚ— k-shock path S_k

The boundaries will propagate in the same direction in the (x, τ)-plane which is

$$s = 1 + \frac{(1.5)(20)}{1 + (20)(0.2)} = 7.0$$

The band widths are determined as

$$\Delta x_3 = 0.3897 \quad \text{or} \quad \Delta\tau_3 = 2.7278$$

$$\Delta x_2 = 0.4762 \quad \text{or} \quad \Delta\tau_2 = 3.3333$$

$$\Delta x_1 = 1.4286 \quad \text{or} \quad \Delta\tau_1 = 10.0$$

It may not be necessary to repeat the interaction analysis in detail. The major difference from the previous case is the 1-simple wave developing from point $a_0(0,10)$ and its successive interactions with the three shocks from the origin. These interactions can be fully analyzed by applying the approach presented in the original paper (Rhee, Aris and Amundson, 1970).

The solution is first constructed in the (x,τ)-plane as shown in Figure 9. Although the shocks undergo interactions with the 1-simple wave, their paths become parallel at the ultimate stage and the band widths from Figure 9 match the values determined in the above very well. The ultimate stage obtains at point $a_9(10.576,67.134)$ due to the slow interaction between the 1-simple wave and the 1-shock. However, the complete separation of solutes is actually accomplished at point $a_4(2.796,26.846)$. If a bed of length 2.796 is used, the pure component band for A_1 in the breakthrough curve will consist of the plateau U_1, a gradual change from U_1 to P_1, and the plateau P_1 whereas for A_2 and A_3 we obtain uniform bands. The ratio of the bed volume required to the sample volume is 0.699 which is about 13.5% higher than that in the previous case. Yet, it is fairly low in comparison to the value 1.538 for the case with $c_4^* = 0$.

The concentrations for each constant state as well as along the 1-characteristics can be determined in the same way as in the previous case. Combining these values with the portrait in Figure 9, one may obtain the concentration profiles at various times. These are presented in Figure 10. The first part (τ = 13) shows how the influence of developer propagates through the bed while the next two figures at τ = 15 and τ = 17 reveal how A_1 is separated from A_3. At τ = 21, A_2 is being separated from both A_1 and A_3. In part (f) we see the complete separation although the A_1-band still undergoes an interaction in itself. If the bed is long enough, the ultimate stage will be eventually obtained as shown in the past (τ = 70).

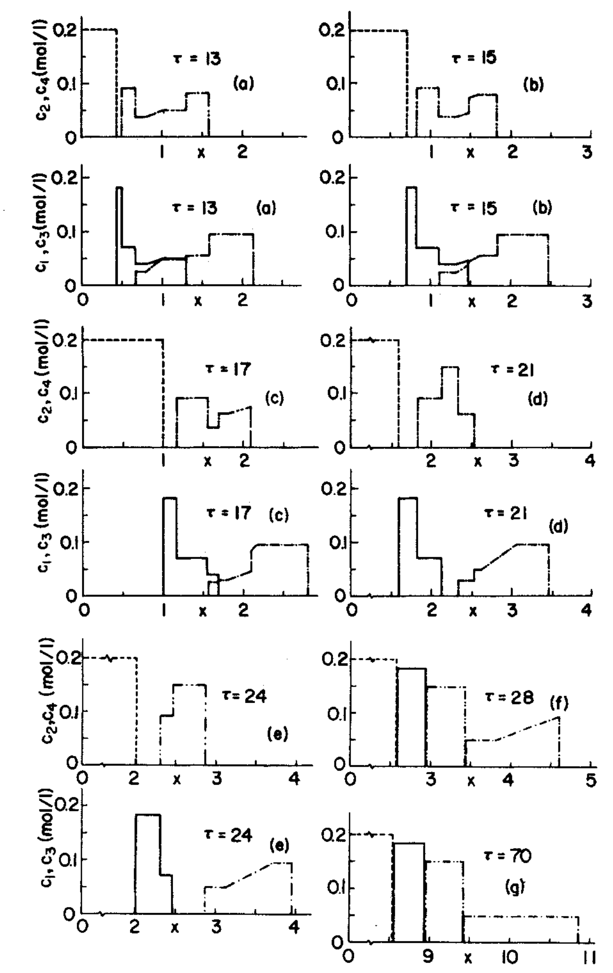

Figure 10. Concentration profiles at successive times when c_4^* = 0.20 mol/L (cf. Fig. 9). —•— Solute A_1, —••— Solute A_2, —— Solute A_3, - - - Solute A_4

Cases when $c_4^* < c_{4,cr}^*$

Here the process is expected to become unsatisfactory. We would like to briefly comment on three different cases.

If c_4^* = 0.1 mol/L, when ω^* = 6.667 and we have a case with $\gamma_1 < \omega^* < \gamma_2 < \gamma_3$. This implies that we would obtain pure component bands for A_3 and A_2 propagating side by side with sharp boundaries but the A_1-band will have a diffuse rear boundary and departs from the A_2-band. In other words, solute A_1 is not aware of the presence of the developer and is simply being eluted by the solvent (cf. Figure 4).

If c_4^* = 0.04 mol/L, we obtain ω^* = 11.111 and so $\gamma_1 < \gamma_2 < \omega^* < \gamma_3$. One would then expect that at the ultimate stage both the A_1- and A_2-bands have diffuse rear boundaries while the A_3-band has sharp boundaries at both ends and remains adjacent to the A_4 front. The A_2-band departs from the A_3-band and so does the A_1-band from the A_2-band. Here the developer exercises no influence over the behavior of solutes A_2 and A_1. As far as these two solutes are concerned, the process is equivalent to the conventional elution using pure solvent.

Suppose the developer concentration is very low, say c_4^* = 0.01 mol/L. Now we have ω^* = 16.667 which is even larger than γ_3. It then follows that the feed state (F) remains indifferent to the developer. In other words, a region of pure state (no solutes) develops just ahead of the A_4-front from the very beginning so that the feed mixture is not developed by the displacement agent A_4 but by the solvent (cf., Figure 5). Consequently, the solution in the (x,τ)-plane would be very much the same as what we see in Figure 16 of the original paper (Rhee, Aris and Amundson, 1970) except for the additional path for the 4-shock (slope = 26) emanating from point $(0,\tau_0)$ to remain on the left-hand side of the 3-simple wave. Although a complete separation can be attained, all the pure component bands will have diffuse rear boundaries and propagate independently from one another. When the process is analyzed, we obtain 1.538 for the ratio of the bed volume required to the sample volume which is still relatively low due to the large differences in K_i-values.

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NOTATION

A_i = i^{th} solute species
C_k = characteristic of the k^{th} kind in the (x,τ)-plane
c_i = molar concentration of species A_i in fluid phase (mol L^{-3})
f_i = equilibrium relationship for species A_i
K_i = Langmuir isotherm parameter (L^3 mol^{-1})
N_i = limiting concentration of adsorbed solute A_i (mol L^{-3})
n_i = molar concentration of adsorbed solute A_i (mol L^{-3})
S_k = k-shock path in the (x,τ)-plane
s_k = propagation direction of k-shock in the (x,τ)-plane, dimensionless
t = actual time (t)
x = z/Z, dimensionless position variable
Z = characteristic length of the system (L)
z = distance in flow direction (L)

Greek letters

γ_i = N_iK_i, Langmuir isotherm parameter, dimensionless
ϵ = fractional void space of fixed bed, dimensionless
ν = $(1-\epsilon)/\epsilon$, volume ratio of solid phase to fluid phase, dimensionless
σ_k = characteristic direction of the k^{th} kind in the (x,τ)-plane, dimensionless
τ = ut/Z, dimensionless time variable
ω_k = characteristic parameter of the k^{th} kind, dimensionless

Brackets

$\{c_i\}$ = collection of m elements of c_i associated with the subscript i

Superscripts

f = feed state
l = state on the left-hand side of a shock
O = initial state
r = state on the right-hand side of a shock
$*$ = developer state or state of a pure component band

Subscripts

$,cr$ = critical value of developer concentration
i,j = index of solute species in multicomponent system
j,k,l = index of characteristic parameters, characteristics, shock paths, simple waves, or shocks
$,k$ = k-constant state
m = number of species appearing in the system or equivalently the most adsorbable species
1,2,3 = index of solute species or index of characteristic parameters, characteristic directions or shock propagation directions

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