

COMPUTATIONAL ASPECTS OF TWO COMPONENT CHROMATOGRAPHY

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1. Summary

In analytical chemistry chromatography is a well-known method for separation of a mixture into its components. The separation is accomplished by the distribution of components of the mixture over two phases in close contact with each other. There exist many variations in the method of separation.

Since there is a large number of parameters in the process involved, we have the possibility to optimize the separation. Important parameters are temperature, pressure, flow velocity and packing of the column. The following assumptions have to be made to reach a reasonably (one dimensional) simple model:

1. Temperature and flow velocity are constant in time and place.
2. Longitudinal and radial diffusion are neglected.
3. Exchange of matter in adsorption is instantaneous.

An elegant use of wave theory was made by Rhee, Aris & Amundson⁴⁾. Their method is reviewed in sections 2.1 and 2.3. Combining a one-dimensional transport equation with a certain expression for the adsorption, they were able to derive a new coordinate system, similar to Jacobi's ellipsoidal coordinates¹⁾. With this system a convenient description of the separation process can be given. The dynamics of a single component in a chromatographic column under the assumptions as above were described by Smit, Smit & De Jager.⁵⁾ In this paper results are given for two component systems.

2. The model equations2.1 The Riemann problem

Consider a chromatographic column with constant cross section. Apart from the carrier gas there are two chemical components, A_1 , A_2 . The concentration in mobile and solid phases is denoted by c_i resp. n_i $i = 1, 2$; each in moles per unit volume of their own phase. The void fraction of the column is a constant ϵ ($0 < \epsilon < 1$). The total concentration f_i of component A_i satisfies

$$(2.1) \quad f_i = \epsilon c_i + (1-\epsilon)n_i.$$

Since the adsorption process is quite complex we cannot describe its dynamics in exact equations and, therefore we make simplifying assumptions. The concentrations n_i are generally considered to be nonlinear functions of mobile phase concentrations;

$$(2.2) \quad n_i = n_i(c_1, c_2) \quad i = 1, 2.$$

These relations are assumed to hold for all positions at any time and are called adsorption isotherms. We will discuss this in more detail in section 2.2.

Because of the constant cross section the above process can be described in one space variable. The incompressible mobile phase is supposed to have a constant velocity u . Consequently, the flux q_i of component A_i satisfies $q_i = u\epsilon c_i$. The mass conservation law for component A_i over a segment (z_1, z_2) of the column implies

$$(2.3) \quad \frac{d}{dt} \int_{z_1}^{z_2} f_i(z, t) dz + q_i(z_2, t) - q_i(z_1, t) = 0.$$

If f_i and q_i are continuously differentiable this yields in the limit $z_2 \rightarrow z_1$

$$\frac{\partial f_i}{\partial t} + \frac{\partial q_i}{\partial z} = 0.$$

Let Z be the characteristic length of the column. Substitution of the expression for the flux q_i and introduction of new dimensionless independent variables $x = z/Z$ and $\tau = u\epsilon t/Z$ leads to the transport equation

$$(2.4) \quad \frac{\partial c_i}{\partial x} + \frac{\partial f_i}{\partial \tau} = 0 \quad i = 1, 2.$$

Under the assumption that the 2×2 matrix $F = \left(\frac{\partial f_i}{\partial c_j} \right)$ has two distinct real eigenvalues for all values of the arguments (c_1, c_2) , the set of equations (2.4) is called a quasilinear hyperbolic system. In chemical terms this assumption corresponds to two solute components flowing with different velocities through the column, which means separation into pure components

after a sufficiently large time interval. In order to have a well posed problem we also need suitable initial- and boundary conditions,

$$(2.5) \quad \begin{aligned} c_i &= c_i^{\text{in}} & \text{at } \tau = 0 & \quad (\text{"initial"}) \\ c_i &= c_i^e & \text{at } x = 0 & \quad (\text{"entry"}) \end{aligned} \quad i = 1, 2.$$

The problem (2.4) with (2.5) can be solved with the theory of Riemann invariants. When there are more than two components, the existence of so-called generalized Riemann invariants is not guaranteed for these quasilinear hyperbolic systems. However, with certain restrictions on the initial- and boundary data a solution exists. Problems that can be solved in this way are also known as Riemann problems³⁾.

2.2 Adsorption isotherms

In section 2.1 a functional relation (2.2) was assumed between each n_i and c_1, c_2 . This relation is usually called the adsorption isotherm. A frequently used, nonlinear expression is the Langmuir isotherm. By assuming adsorption equilibrium at any place and time we have for each component separately that rate of adsorption equals rate of desorption. The adsorption rate of A_i is proportional to the product of concentration c_i and free adsorbing area of the stationary phase, where the total adsorbing area is scaled to 1. The rate of desorption is proportional to the fraction of area occupied by A_i . For two components we have accordingly

$$(2.6) \quad n_i = \frac{K_i c_i}{1 + K_1 c_1 + K_2 c_2}, \quad i = 1, 2.$$

or equivalently

$$(2.6a) \quad K_i c_i = \frac{n_i}{1 - (n_1 + n_2)}, \quad i = 1, 2.$$

Each mobile phase concentration is multiplied in (2.6) by a temperature dependent thermodynamic parameter K_i , which is a measure of adsorption affinity towards the stationary phase. Since the process is kept isotherm we may take the parameters as constants, with $K_1 < K_2$. It appears that only the Langmuir form (2.6) allows the construction of a coordinate system as

described in the following section. In this nice system of coordinates the variable D , defined in (2.7) plays a central role,

$$(2.7) \quad D = 1 + K_1 c_1 + K_2 c_2.$$

2.3 Constant states, simple waves and shockwaves

In this section we give a short description of the coordinate system introduced by Rhee, Aris and Amundson⁴⁾. They show that by assuming a Langmuir type of adsorption isotherm an alternative coordinate system can be derived, similar to the classical ellipsoidal coordinates¹⁾.

We need the following definitions²⁾:

DEFINITION 1. A constant state is a region in the x, τ -plane where the solution $c(x, \tau)$ is constant.

DEFINITION 2. A region in the x, τ -plane where the solution is in one-parameter form is called a simple wave, e.g. $(c_1(x, \tau), c_2(c_1(x, \tau)))$.

It is well known for continuous solutions that the region adjacent to a constant state must be a simple wave. Using the dependence of the solution on a single component in the simple wave regions, it is possible to rewrite $\partial f_i / \partial \tau$ as

$$\frac{\partial f_i}{\partial \tau} = \sum_{j=1}^2 \frac{\partial f_i}{\partial c_j} \frac{\partial c_j}{\partial \tau} = \left(\sum_{j=1}^2 \frac{\partial f_i}{\partial c_j} \frac{dc_j}{dc_i} \right) \cdot \frac{\partial c_i}{\partial \tau} = \frac{df_i}{dc_i} \cdot \frac{\partial c_i}{\partial \tau}.$$

Equation (2.4) now reads

$$(2.8) \quad \frac{\partial c_i}{\partial x} + \frac{df_i}{dc_i} \cdot \frac{\partial c_i}{\partial \tau} = 0, \quad i = 1, 2.$$

In a characteristic direction $\rho = \frac{d\tau}{dx}$ of this quasi linear hyperbolic system the total differentials df_i / dc_i are equal:

$$(2.9) \quad \rho = \frac{d\tau}{dx} = \frac{df_i}{dc_i} = \sum_{j=1}^2 \frac{\partial f_i}{\partial c_j} \cdot \frac{dc_j}{dc_i} = \left(\sum_{j=1}^2 \frac{\partial f_i}{\partial c_j} \cdot \frac{dc_j}{dD} \right) \frac{dD}{dc_i}$$

Using matrix $F (= \partial f_i / \partial c_j)$ and assuming that $dc_i / dD \neq 0$ we find

$$(2.10) \quad (F - \rho I) \frac{dc}{dD} = 0.$$

Consequently for non-trivial solutions ρ is an eigenvalue and $\frac{dc}{dD}$ is an eigenvector of F . The eigenvalues of F are labeled σ_1, σ_2 ($\sigma_1 \neq \sigma_2$ due to the hyperbolic character of the system). The two bundles of characteristics are indicated by C^1, C^2 . With each σ_k a quantity ω_k is associated in the following way:

$$(2.11) \quad \sigma_k = \epsilon + (1-\epsilon) \frac{\omega_k}{D}, \quad k = 1, 2.$$

The set (ω_1, ω_2) forms the alternative coordinate system. Their values are separated by the thermodynamic constants and can be calculated from these constants and concentration values¹⁾⁴⁾.

$$(2.12) \quad 0 < \omega_1 < K_1 < \omega_2 < K_2.$$

Hence the σ_k satisfy the inequality

$$(2.13) \quad \epsilon < \sigma_1 < \sigma_2.$$

Since the σ_k are reciprocal velocities of waves propagating in the column and ϵ is the reciprocal carrier velocity, both waves are travelling at a lower speed than the carrier. $\left(\frac{dz}{dt} = u = u\epsilon \frac{dx}{d\tau}, \text{ so } \frac{dx}{d\tau} = \frac{1}{\epsilon}\right)$.

Since it is not always possible to have diverging bundles of characteristics, we also have to discuss discontinuous solutions. A necessary condition for characteristics not to intersect is that

$$(2.14) \quad \frac{\partial \sigma_k}{\partial x} = \frac{d\sigma_k}{dD} \cdot \frac{\partial D}{\partial x} < 0.$$

As $d\sigma_k/dD = -2(1-\epsilon)\omega_k/D^2$ is negative, this condition is equivalent with the condition that D increases with x . In case of D decreasing with x the characteristics will intersect and there can be no continuous solution. With the mass conservation law (2.3) the well known jump relations can be found. Furthermore, the discontinuous solutions appear to meet all stability requirements for shocks³⁾ so they will be referred to as shock waves.

2.4 Computation of ω - values

For two components A_1, A_2 with given entry- and initial concentrations (2.5) the values of n_i are calculated according to the isotherm (2.6). The corresponding ω - values satisfy the relation

$$(2.15) \quad \frac{K_1 n_1}{K_1 - \omega} + \frac{K_2 n_2}{K_2 - \omega} = 1.$$

Solving this equation for ω amounts to solving a polynomial equation in ω of degree two. For the entry state there are two roots ω_1^e, ω_2^e and in the initial state $\omega_1^{in}, \omega_2^{in}$. The relation (2.15) implies the following important identity

$$(2.16) \quad D = \frac{K_1 K_2}{\omega_1 \omega_2},$$

where ω_1, ω_2 are the two roots of equation (2.15). Considering ω_1 and ω_2 as variables it appears that in the x, τ - plane they can only change one at a time and only ω_k changes its value (from ω_k^e on the left to ω_k^{in} on the right) on the wave given by σ_k (abbreviated: (k) - wave). It follows from (2.16) that D varies inversely proportional to ω_k on the (k)-wave. In case of a (k)-simple wave D must increase with x (2.14) ω_k must decrease with x , so $\omega_k^e > \omega_k^{in}$ is the condition for existence of a (k)-simple wave. When $\omega_k^e < \omega_k^{in}$ there must be a (k)-shock wave and $\omega_k^e = \omega_k^{in}$ implies there is no (k)-wave in the solution.

For two components we have the following picture in the x, τ - plane (see also figures in section 4). Going from the initial ($\tau=0$) to the entry state ($x=0$):

1. The initial constant state CS(0) with D - value $D_0 = K_1 K_2 / \omega_1^{in} \omega_2^{in}$.
2. The (1) - wave, shock or simple wave, where ω_1 changes to the entry value.
3. The intermediate constant state CS(1) with D - value $D_1 = K_1 K_2 / \omega_1^e \omega_2^{in}$, $\omega_1 = \omega_1^e, \omega_2 = \omega_2^{in}$.
4. The (2) - wave, shock or simple wave, where ω_2 changes to the entry value.
5. The entry constant state CS(2) with D - value $D_2 = K_1 K_2 / \omega_1^e \omega_2^e$.

The lower and upper σ_k - limit of a (k)-simple wave can be calculated with (2.11)

$$(2.17) \quad \begin{aligned} \sigma_k^{\min} &= \varepsilon + (1-\varepsilon)\omega_k^{\text{in}}/D_{k-1} \\ \sigma_k^{\max} &= \varepsilon + (1-\varepsilon)\omega_k^e/D_k . \end{aligned}$$

The reciprocal velocity of a (k)-shock wave is calculated from the jump conditions and the entropy condition³⁾⁴⁾.

$$(2.18) \quad \sigma_k^S = \varepsilon + (1-\varepsilon)\omega_k^{\text{in}}/D_k = \varepsilon + (1-\varepsilon)\omega_k^e/D_{k-1} .$$

In the following sections we will analyse some possible wave structures and interactions in the cases of one and two components.

3. One component chromatography

3.1 Shock wave solution

The case of one component adsorbing in a clean column is rather simple, there is just one shock wave with reciprocal velocity

$$(3.1) \quad \sigma^S = \varepsilon + (1-\varepsilon)\omega^e ,$$

where the ω^e - value is calculated from the entry concentration. The dependence on variables is given in table 1.

$$\begin{aligned} \frac{\partial \sigma^S}{\partial K} &= \frac{(1-\varepsilon)}{(1+K\varepsilon)^2} = (1-\varepsilon) \frac{(\omega^e)^2}{K^2} \\ \frac{\partial \sigma^S}{\partial c} &= -(1-\varepsilon) \left(\frac{K}{1+K\varepsilon} \right)^2 = -(1-\varepsilon) (\omega^e)^2 \end{aligned}$$

TABLE 1. Derivatives of reciprocal velocity with respect to thermodynamic parameter and entry concentration.

As seen from the formulas of table 1, changes are larger in magnitude for small ε and low concentration c . An increase in parameter K corresponds to

more adsorption and slowing down of the wave front. An increase in c results in an acceleration of the wave.

3.2 Simple wave solution

A single simple wave is associated with the removal of one adsorbed component from a column. It is characterized by its two bounding characteristics:

$$(3.2) \quad \sigma^{\min} = \varepsilon + (1-\varepsilon) \frac{(\omega^{\text{in}})^2}{K}, \quad \sigma^{\max} = \varepsilon + (1-\varepsilon)K,$$

where the ω -value is calculated from the initial concentration. The dependence upon K and c is displayed in table 2:

σ^{\max}	$1-\varepsilon$	0
σ^{\min}	$(1-\varepsilon) \frac{(\omega^{\text{in}})^2}{K^2} \left(\frac{2\omega^{\text{in}}}{K} - 1 \right)$	$-2(1-\varepsilon) \frac{(\omega^{\text{in}})^3}{K}$

TABLE 2. Derivatives with respect to thermodynamic parameter K (first column) and concentration c (second column).

Since the derivatives of the difference $\sigma^{\max} - \sigma^{\min}$ are positive, the simple wave spreads out for increasing values of K and c .

3.3 Transport of one component

Interaction between a shock and simple wave can also occur. The simplest case is given by the following initial and entry conditions:

$$(3.3) \quad \begin{aligned} c^{\text{in}}(t) &= c_0(U(t) - U(t-\delta)) \\ c^{\text{e}}(x) &= 0. \end{aligned}$$

Smit, Smit and de Jager⁵⁾ describe in detail the interaction between shock and simple wave for this model.

4. Two component chromatography

4.1 An initially clean column

Next we consider the adsorption of two components A_1, A_2 flowing into a clean column. In the model this results in two shock waves S^1 and S^2 . In constant state (2) both components enter the column, at S^2 component A_2 is completely adsorbed so constant state (1) contains only component A_1 and in constant state (0) the initial empty state of the column is still preserved. The values of ω_1^e, ω_2^e are calculated from entry concentrations. The reciprocal shock velocities are

$$(4.1) \quad \begin{aligned} \sigma_1^S &= \epsilon + (1-\epsilon) \frac{\omega_1^e}{D_0} = \epsilon + (1-\epsilon) \omega_1^e, \\ \sigma_2^S &= \epsilon + (1-\epsilon) \frac{\omega_2^e}{D_1} = \epsilon + (1-\epsilon) \frac{\omega_1^e \omega_2^e}{K_1}. \end{aligned}$$

The difference between the two shock waves directions is equal to

$$(4.2) \quad \Delta = \sigma_2^S - \sigma_1^S = (1-\epsilon) \frac{\omega_1^e}{K_1} (\omega_2^e - K_1).$$

Differentiating we find the following relations for Δ

$$\begin{aligned} \frac{\partial \Delta}{\partial K_1} &= -(1-\epsilon) \frac{\omega_1^2 (\omega_2 - K_1) (1 - n_1^e) + \omega_1 \omega_2^2 n_1^e}{K_1^2 (\omega_2 - \omega_1)} \\ \frac{\partial \Delta}{\partial K_2} &= (1-\epsilon) \frac{\omega_1 (1 - n_2^e) (K_2 \omega_2 (\omega_2 - \omega_1) + K_1 K_2 \omega_1) - K_1 \omega_1 \omega_2^2}{K_1 K_2^2 (\omega_2 - \omega_1)} \\ \frac{\partial \Delta}{\partial c_1} &= (1-\epsilon) \frac{\omega_1^2 \omega_2^2}{K_2} \frac{\omega_1 (\omega_2 - K_1) + K_1 K_2 - \omega_2^2}{K_1 (\omega_2 - \omega_1)} \\ \frac{\partial \Delta}{\partial c_2} &= (1-\epsilon) \frac{\omega_1^2 \omega_2^2}{K_1} \frac{\omega_1 (\omega_2 - K_1) + K_1^2 - \omega_2^2}{K_1 (\omega_2 - \omega_1)} \end{aligned}$$

TABLE 3. Derivatives of Δ in section 4.1, $\omega_1 = \omega_1^e, \omega_2 = \omega_2^e$.

From calculations in table 3 it can be shown that the derivatives with respect to K_1 and c_2 are negative definite and with respect to K_2 positive definite. The dependence upon c_1 is very complicated.

4.2 Two components initially adsorbed

The case of two simple waves C^1 and C^2 corresponds with two adsorbed components A_1, A_2 going into the mobile phase

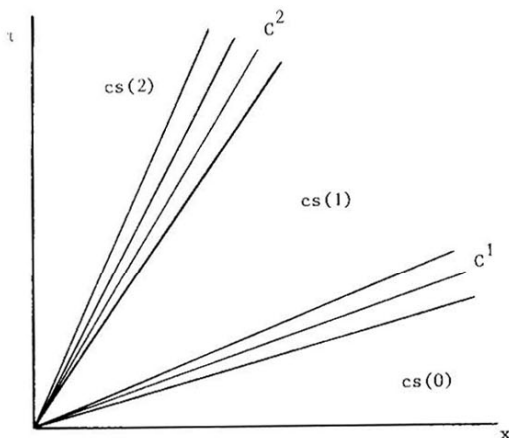


FIGURE 1. Desorption over two simple waves.

Again there are three constant states. The initial state of the column is in $cs(0)$. After the first simple wave component A_1 is completely removed, so in $cs(1)$ its concentration is zero. After the second simple wave A_2 disappears, consequently in $cs(2)$ all concentrations are zero. The bounding characteristics of constant state (1) are denoted by σ_2^{\min} and σ_1^{\max} . The difference between these reciprocal characteristic speeds is

$$(4.3) \quad \Delta = \sigma_2^{\min} - \sigma_1^{\max} = (1-\varepsilon) \frac{\omega_2^{\text{in}}}{K_2} (\omega_2^{\text{in}} - K_1),$$

where ω -values are calculated from initial concentrations. The dependence of Δ on concentrations and parameters is computed in table 4,

$$\begin{aligned} \frac{\partial \Delta}{\partial K_1} &= (1-\varepsilon) \left(\frac{2\omega_2 - K_1}{K_2} \cdot \frac{\omega_2^2}{K_1^2} \cdot \frac{\omega_1 - K_1(1 - n_1^{in})}{\omega_1 - \omega_2} - \frac{\omega_2}{K_2} \right) \\ \frac{\partial \Delta}{\partial K_2} &= (1-\varepsilon) \left(\frac{2\omega_2 - K_1}{K_2} \cdot \frac{\omega_2^2}{K_2^2} \cdot \frac{\omega_1 - K_2(1 - n_2^{in})}{\omega_1 - \omega_2} - \frac{\omega_2(\omega_2 - K_1)}{K_2^2} \right) \\ \frac{\partial \Delta}{\partial c_1} &= (1-\varepsilon) \cdot \frac{2\omega_2 - K_1}{K_2} \cdot \frac{\omega_1 \omega_2^2 (K_2 - \omega_2)}{K_2 (\omega_2 - \omega_1)} \\ \frac{\partial \Delta}{\partial c_2} &= (1-\varepsilon) \cdot \frac{2\omega_2 - K_1}{K_2} \cdot \frac{\omega_1 \omega_2^2 (K_1 - \omega_2)}{K_1 (\omega_2 - \omega_1)} \end{aligned}$$

TABLE 4. Derivatives of Δ in section 4.2, $\omega_1 = \omega_1^{in}$, $\omega_2 = \omega_2^{in}$.

The derivative with respect to c_1 is positive and for c_2 negative. This suggests that relatively low values of c_2 make the gap Δ between the two simple waves larger.

4.3 One component initially adsorbed, one component in solution

a) The case of permanent separation

Component A_2 enters the column, where A_1 has already been adsorbed. The adsorbed component dissolves in simple wave C^1 , the new one adsorbs over shock wave S^2 . For the two waves we have the following directions

$$(4.4) \quad \begin{aligned} \sigma_1^{\min} &= \varepsilon + (1-\varepsilon) \frac{(\omega_1^{in})^2}{K_1}, & \sigma_1^{\max} &= \varepsilon + (1-\varepsilon)K_1, \\ \sigma_2^S &= \varepsilon + (1-\varepsilon)\omega_2^e. \end{aligned}$$

The minimal difference in σ between the two waves is equal to

$$(4.5) \quad \Delta = \sigma_2^S - \sigma_1^{\max} = (1-\varepsilon)(\omega_2^e - K_1).$$

This relation is differentiated with respect to all variables in table 5.

$$\frac{\partial \Delta}{\partial K_1} = (1-\varepsilon) \left(\frac{\partial \omega_2^e}{\partial K_1} - 1 \right) = -(1-\varepsilon)$$

$$\frac{\partial \Delta}{\partial K_2} = (1-\varepsilon) \frac{\partial \omega_2^e}{\partial K_2} = (1-\varepsilon) \frac{(\omega_2^e)^2}{K_2^2}$$

$$\frac{\partial \Delta}{\partial c_1} = (1-\varepsilon) \frac{\partial \omega_2^e}{\partial c_1} = 0$$

$$\frac{\partial \Delta}{\partial c_2} = (1-\varepsilon) \frac{\partial \omega_2^e}{\partial c_2} = -(1-\varepsilon) (\omega_2^e)^2$$

TABLE 5. Derivatives of Δ in section 4.3a.

We find that c_1 does not influence Δ , since σ_1^{\max} is independent of c_1 . The derivatives with respect to K_1 and c_2 are negative, with respect to K_2 positive. Again, low concentration values of the second component (the one with the largest adsorption affinity) tend to make Δ larger.

b) The case of a mixed constant state

In the second case we have the same situation as in 4.3a, only the roles of A_1 and A_2 are interchanged. The reciprocal wave velocities are

$$(4.6) \quad \sigma_1^S = \varepsilon + (1-\varepsilon) \frac{\omega_1^e \omega_2^{\text{in}}}{K_2},$$

$$\sigma_2^{\min} = \varepsilon + (1-\varepsilon) \frac{\omega_1^e (\omega_2^{\text{in}})^2}{K_1 K_2}, \quad \sigma_2^{\max} = \varepsilon + (1-\varepsilon) \frac{\omega_1^e}{K_1} K_2.$$

In contrast to the first case the two components are now mixed in the constant state (1). The difference in σ between the shock wave and the nearest characteristic of the simple wave is equal to

$$(4.7) \quad \Delta = (1-\varepsilon) \frac{\omega_1^e \omega_2^{\text{in}}}{K_1 K_2} (\omega_2^{\text{in}} - K_1).$$

Differentiating Δ we find the following relations

$$\frac{\partial \Delta}{\partial K_1} = (1-\varepsilon) \frac{\omega_1 \omega_2}{K_1 K_2} \left(\frac{(\omega_1 - K_1)(\omega_2 - K_1)}{K_1^2} - 1 \right)$$

$$\frac{\partial \Delta}{\partial K_2} = (1-\varepsilon) \frac{\omega_1 \omega_2}{K_1 K_2} \left(\frac{(\omega_2 - K_2)(\omega_2 - K_1)}{K_2^2} + \frac{\omega_2^2}{K_2^2} \right)$$

$$\frac{\partial \Delta}{\partial c_1} = -(1-\varepsilon) \frac{\omega_1^2 \omega_2}{K_1 K_2} (\omega_2 - K_1)$$

$$\frac{\partial \Delta}{\partial c_2} = -(1-\varepsilon) \frac{\omega_1 \omega_2}{K_1 K_2} (\omega_2 (\omega_2 - K_1) + \omega_2^2)$$

TABLE 6. Derivatives of Δ in section 4.3b, $\omega_1 = \omega_1^e$, $\omega_2 = \omega_2^{in}$.

In the cases 4.1, 4.3a we find what might be expected for the thermodynamic constants, low values of K_1 and high values of K_2 make the gap Δ between two waves larger. In the other cases there is no such simple relation for K -dependence. With regard to concentrations the situation is completely different; the dependence on c_2 is always the same ($\frac{\partial \Delta}{\partial c_2} < 0$), while $\frac{\partial \Delta}{\partial c_1}$ is different in each case.

Two simple waves and two shock waves is from a practical point of view the most interesting case (figure 2). This subject will be treated in the next section.

4.4 The separation of two components

Taking piecewise constant boundary conditions on the τ -axis we assume a fluid containing two components A_1 , A_2 enters a chromatographic column at $x = 0$ during the time interval $(0, \delta)$. There will be adsorption over two shock waves S^1 and S^2 . After time δ clean fluid, entering the column at $x = 0$ removes the adsorbed components in reverse order. This happens in two simple waves C^1 and C^2 issuing from the point $(0, \delta)$. In the physical plane we have the following interactions

1. Shock S^2 meets simple wave C^1 at X_0 .
2. This interaction ends at X_1 .
3. Simple wave C^2 is adsorbed by shock S^2 in X_2 .
This interaction extends to infinity.
4. The same as (3) for simple wave C^1 and shock S^1 in X_3 .

These are six constant states with D-values

$$(4.8) \quad D_1 = \frac{K_1}{\omega_1^e}, \quad D_2 = \frac{K_1 K_2}{\omega_1^e \omega_2^e}, \quad D_3 = \frac{K_2}{\omega_2^e}, \quad D_0 = D_4 = D_5 = 1,$$

where ω -values are calculated from entry concentrations.

The separation is completed after X_1 . Component A_1 has been concentrated in the first wave, A_2 in the second. A new constant state with zero concentrations (= ideal separation) is created between the two waves. For a given time $t > \delta$ we investigate the location of B and C in figure 2. The shock S^2 is parametrized by ω_2 , which runs from ω_2^e (at X_2) up to K_2 (at infinity). After laborious calculations we find

$$X_B(\omega_2) = \frac{\delta K_1 K_2}{(1-\varepsilon) \omega_1^e \omega_2^e} \cdot \frac{(K_2 - \omega_1^e)(K_2 - \omega_2^e)}{(K_2 - \omega_2)^2 (K_2 - K_1)} = \frac{C}{(K_2 - \omega_2)^2}$$

(4.9)

$$X_C(\omega_2) = \frac{1}{\varepsilon + (1-\varepsilon)K_1} \cdot \left(\left\{ \varepsilon + (1-\varepsilon) \frac{\omega_2^2}{K_2} \right\} X_B - \frac{\delta K_1^2}{\omega_1^e \omega_2^e} \cdot \frac{(K_2 - \omega_2^e)(K_2 - \omega_1^e)}{(K_2 - K_1)^2} \right).$$

Consequently, the distance between B and C equals

$$(4.10) \quad (X_C - X_B)(\omega_2) = \frac{\delta K_1 n_2^e}{\varepsilon + (1-\varepsilon)K_1} \cdot \left(\frac{K_1 K_2}{K_2 - K_1} + \left\{ \frac{\omega_2}{K_2 - \omega_2} \right\}^2 \cdot \left(K_2 - K_1 \left\{ \frac{K_2}{\omega_2} \right\}^2 \right) \right).$$

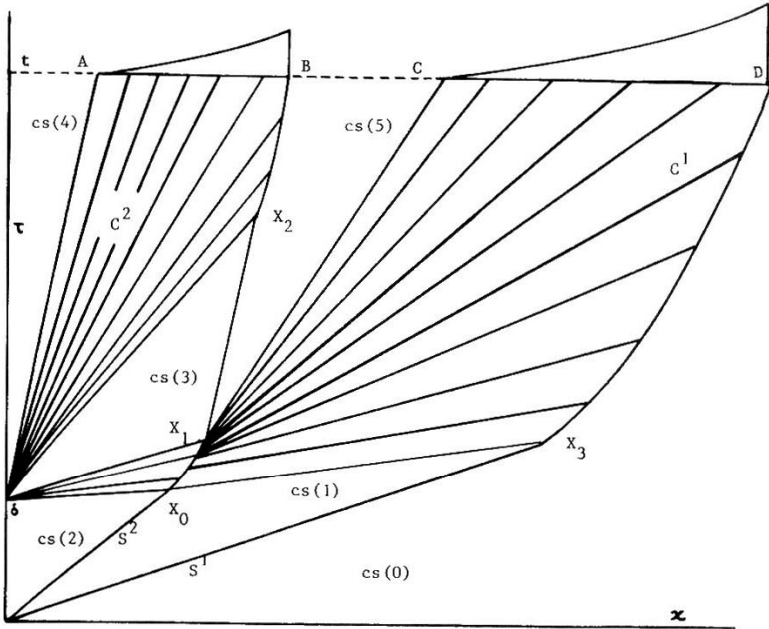


FIGURE 2. The separation of two components with concentration profiles at time $\tau = t$

The value of ω_2 in (4.10) is fixed by choosing a time t . Since the derivative of this last expression with respect to ω_2 is positive, it is clear that the distance between B and C increases in time. The parameter δ is a measure of the total amount of components fed into the column. A change in this parameter simply amounts to a scaling of all distances in the model. As a result of this we find for increasing δ a lower value of ω_2^e and consequently a smaller distance.

When K_1 is roughly equal to K_2 , a situation where good separation is hard to obtain, (4.10) indicates that the distance between B and C will be large for low values of c_2^e . The derivation of this result is not very interesting so it is omitted. The concentration profiles sketched in figure 2

for time $\tau = t$ are very simple convex functions of ω_1 and ω_2

$$(4.11) \quad \begin{aligned} c_1(\omega_1) &= \frac{1}{\omega_1} - \frac{1}{K_1} && \text{on CD,} && \omega_1^e \leq \omega_1 \leq K_1 \\ c_2(\omega_2) &= \frac{1}{\omega_2} - \frac{1}{K_2} && \text{on AB,} && \omega_2^e \leq \omega_2 \leq K_2 \end{aligned}$$

Although the theory is essentially based on an infinite column, it is interesting that "retention times" can be calculated when the arrival of a peak at a fixed location X (far away from the origin) is considered as an exit from the column. Since calculations for the first wave are much more difficult than for the second, in the following only the second wave is considered. This difference is a consequence of the fact that the simple wave C^1 emanating from the arc $X_0 X_1$ is not centered. For a given location X_B the arrival time of the second wave is

$$(4.12) \quad t(X_B) = (\epsilon + (1-\epsilon)K_2)X_B - 2(1-\epsilon)\sqrt{C} \sqrt{X_B} + \delta + (1-\epsilon)C/K_2$$

with C as in (4.9).

The peak width can also be obtained for the second wave. The arrival times of the shock S^2 in X_1 and X_2 are indicated by T_1 respectively T_2 . In the interval $[T_1, T_2]$ the peak width grows linearly in time

$$(4.13) \quad (X_B - X_A)(t) = \frac{\delta K_1 (K_2 - \omega_1^e) (K_2 - K_1)}{\omega_1^e (\epsilon + (1-\epsilon)\omega_2^e)} + (t-\delta) \frac{(1-\epsilon)(K_2 - \omega_2^e)}{(\epsilon + (1-\epsilon)\omega_2^e) (\epsilon + (1-\epsilon)K_2)}$$

When $t \geq T_2$ the peak width is a nonlinear function

$$(4.14) \quad (X_B - X_A)(t) = (1-\epsilon)(t-\delta) \frac{K_2^2 - \omega_2^2}{(K_2\epsilon + (1-\epsilon)\omega_2^2) (\epsilon + (1-\epsilon)K_2)}$$

where $\omega_2 = \omega_2(t)$ has to be replaced by the solution of equation (4.15) in the interval $[\omega_2^e, K_2]$

$$(4.15) \quad (C(1-\epsilon) - K_2(t-\delta))\omega_2^2 + 2K_2^2(t-\delta)\omega_2 + K_2C\epsilon - K_2^3(t-\delta) = 0$$

5. Concluding remarks

Apart from the restricting assumptions regarding diffusion, mentioned in section 1, one of the most crucial elements is the adsorption isotherm.

The simple Langmuir isotherm gives even in the case of two components formulas which are rather difficult to handle. Other types of nonlinear isotherms (Freundlich, anti Langmuir) however, cannot be treated with this theory. Accordingly, the best choice seems to be the Langmuir form, where the K-values have to be estimated from numerical data. It is expected that for large classes of related compounds reliable estimates of K-values can be obtained, with component interaction taken into account. Using these empirical values in the Langmuir form the theory yields information regarding the separation process, such as peak width, retention times and eventually other moments.

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