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## **Perturbation analysis of the influence of the isotherm coupling factor on the resolution between two compounds in chromatography**

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### SUMMARY

The influence of the coupling factor between the adsorption isotherms of the two components of a binary mixture on the elution profiles of their bands in liquid chromatography, on their retention times and on the resolution between these bands is discussed using a perturbation approach.

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### INTRODUCTION

The elution of the components of a complex mixture through a chromatographic column is easily described in linear chromatography. The migration of each band and its progressive broadening are independent of the migration and broadening of the other component bands. The chromatogram of the mixture is the superimposition of the chromatograms obtained with each of the individual components injected pure, successively, in the same amount as is in the sample mixture. A series of Gaussian bands is obtained, provided that there is a single retention mechanism involved and the kinetics of mass transfer between and across phases are fast enough. Obviously, some of these bands may interfere, but these interferences result merely in the addition of the detector signals corresponding to each band profile. The local concentrations of the two or more component whose bands interfere remain independent.

A different situation arises when the sample size is not negligible. Then, the chromatogram of the mixture is not the sum of the chromatograms of all the components of the mixture, and the chromatographic phenomenon becomes non-linear. This happens because the equilibrium isotherms of at least some of the components (the main ones) are not linear and because the equilibrium isotherms of most of these components depend on the concentrations of all or almost all the other components.

Several recent studies have been published on the behavior of the bands of a binary mixture at high concentrations involving the use of numerical solutions calculated with a computer<sup>1-6</sup>. When samples of large or very large sizes are injected,

the non-linear behavior of the equilibrium isotherm is the main source of band broadening and is, in fact, the factor which controls the band profile. The shock and shock layer theories<sup>7</sup> and the semi-ideal model<sup>8</sup> account very well for the band profiles obtained in elution and displacement chromatography, for the progressive separation of these bands and for their interference when separation is incomplete.

More fundamental approaches have been tried. The characteristic method has been extremely useful in providing an accurate description of the phenomena involved in the migration of the high-concentration bands and in explaining their profiles<sup>7,9,10</sup>. The shock theory is based on the results of this method<sup>11</sup>. The hodograph transform has been applied to the study of the elution band of a binary mixture and the results have been explained by the characteristic theory<sup>12</sup>.

A complementary approach, focusing on the phenomena that take place at the onset of non-linear behavior, would be interesting. Of special importance is an understanding of the various effects arising in analytical applications of chromatography when columns are overloaded, such as in trace analysis. The approach of Houghton<sup>13</sup>, who assumed a parabolic equilibrium isotherm and integrated a simplified mass balance equation, permits the investigation of the band profile at the beginning of column overload. Lin *et al.*<sup>14</sup> have successfully applied the perturbation theory to the same mass balance equation and predicted the progressive transition of the band profile from a symmetrical Gaussian curve to a tailing profile.

The aim of this work was to extend this type of investigation to the case of a binary mixture and to study how the bands of two closely eluted compounds begin to interfere when the sample size is increased. The work was carried out within the framework of the ideal model<sup>10-12</sup>.

#### MATHEMATICAL MODEL

We used the ideal model of chromatography, which assumes constant equilibrium between the two phases of the chromatographic system during the migration of a concentration signal. More specifically, we assume that the kinetics of mass transfers between phases are infinitely fast and that the axial dispersion proceeds at a negligible rate. Under these conditions the mass balances of the two components of a binary mixture can be written as

$$\frac{\partial C_1}{\partial t} + F \frac{\partial q_1}{\partial t} + u \frac{\partial C_1}{\partial x} = 0 \quad (1)$$

$$\frac{\partial C_2}{\partial t} + F \frac{\partial q_2}{\partial t} + u \frac{\partial C_2}{\partial x} = 0 \quad (2)$$

We assume that the injection profile is a rectangular pulse of maximum concentrations  $C_1^0$  and  $C_2^0$  and width  $t_p$ , and consequently that the initial condition is described by

$$C_1(x,0) = C_2(x,0) = q_1(x,0) = q_2(x,0) = 0 \quad x > 0 \quad (3)$$

and that the boundary condition is given by

$$C_1(0,t) = C_1^0 \quad C_2(0,t) = C_2^0 \quad 0 < t \leq t_p$$

and

$$C_1(0,t) = C_2(0,t) = 0 \quad t > t_p \quad (4)$$

$C_1$ ,  $C_2$ ,  $q_1$  and  $q_2$  are the concentrations of components 1 and 2 in the mobile and the stationary phases at time  $t$  and abscissa  $x$ , respectively;  $u$  is the mobile phase velocity and  $F$  the phase ratio, i.e.,  $V_s/V_m$ .

We have also assumed that the equilibrium isotherms of the two compounds studied are given by the classical binary Langmuir isotherm equations:

$$q_1 = \frac{a_1 C_1}{1 + b_1 C_1 + b_2 C_2} \quad (5)$$

$$q_2 = \frac{a_2 C_2}{1 + b_1 C_1 + b_2 C_2} \quad (6)$$

In eqns. 5 and 6,  $a_1$ ,  $a_2$ ,  $b_1$  and  $b_2$  are constants. They are the parameters of the Langmuir isotherm. The considerable advantage of this equation is that the coupling terms which are  $b_2 C_2$  for the first component and  $b_1 C_1$  for the second component, can be determined directly from experimental results regarding the single compound equilibrium isotherms of the pure components 1 and 2. No experiment involving mixtures of the two compounds is required, which is a great simplification.

#### PERTURBATION ANALYSIS

Since  $q_1$  and  $q_2$  are both functions of the two concentrations,  $C_1$  and  $C_2$ , we have the following relationships between their partial differentials:

$$\frac{\partial q_1}{\partial t} = \frac{\partial q_1}{\partial C_1} \cdot \frac{\partial C_1}{\partial t} + \frac{\partial q_1}{\partial C_2} \cdot \frac{\partial C_2}{\partial t} \quad (7)$$

and

$$\frac{\partial q_2}{\partial t} = \frac{\partial q_2}{\partial C_2} \cdot \frac{\partial C_2}{\partial t} + \frac{\partial q_2}{\partial C_1} \cdot \frac{\partial C_1}{\partial t} \quad (8)$$

The partial differentials of the concentrations in the stationary phase,  $q_1$  and  $q_2$  can be derived from eqns. 5 and 6:

$$\frac{\partial q_1}{\partial C_1} = \frac{a_1(1+b_2 C_2)}{(1+b_1 C_1+b_2 C_2)^2} \quad (9)$$

$$\frac{\partial q_2}{\partial C_2} = \frac{a_2(1+b_1 C_1)}{(1+b_1 C_1+b_2 C_2)^2} \quad (10)$$

$$\frac{\partial q_1}{\partial C_2} = \frac{-a_1 b_2 C_1}{(1 + b_1 C_1 + b_2 C_2)^2} \quad (11)$$

$$\frac{\partial q_2}{\partial C_1} = \frac{-a_2 b_1 C_2}{(1 + b_1 C_1 + b_2 C_2)^2} \quad (12)$$

As we are studying the changes in band profiles, retention times and resolution which take place at the onset of column overloading with a binary mixture, we may assume that the concentrations  $C_1$  and  $C_2$  are small and that the terms  $b_1 C_1$  and  $b_2 C_2$  are much smaller than unity. Then we may simplify eqns. 9–12 using the classical approximation  $1/(1+x) \approx 1-x$ :

$$\frac{\partial q_1}{\partial C_1} = a_1 - 2a_1 b_1 C_1 - a_1 b_2 C_2 \quad (13)$$

$$\frac{\partial q_2}{\partial C_2} = a_2 - 2a_2 b_2 C_2 - a_2 b_1 C_1 \quad (14)$$

$$\frac{\partial q_1}{\partial C_2} = -a_1 b_2 C_1 \quad (15)$$

$$\frac{\partial q_2}{\partial C_1} = -a_2 b_1 C_2 \quad (16)$$

Combination of eqns. 7, 8 and 13–16 with eqns. 1 and 2 gives the following equations, which are first-order approximations of the mass balance equations:

$$(1 + Fa_1 - 2Fa_1 b_1 C_1 - Fa_1 b_2 C_2) \frac{\partial C_1}{\partial t} - Fa_1 b_2 C_1 \frac{\partial C_2}{\partial t} + u \frac{\partial C_1}{\partial x} = 0 \quad (17)$$

and:

$$(1 + Fa_2 - 2Fa_2 b_2 C_2 - Fa_2 b_1 C_1) \frac{\partial C_2}{\partial t} - Fa_2 b_1 C_2 \frac{\partial C_1}{\partial t} + u \frac{\partial C_2}{\partial x} = 0 \quad (18)$$

The principle of the perturbation method consists in assuming that the solutions of the system of non-linear partial differential eqns. 1 and 2 are close to the solutions of the corresponding system of linear equations, *i.e.*, of the system of eqns. 1 and 2 in which the isotherms  $q_1$  and  $q_2$  are merely proportional to  $C_1$  and  $C_2$ , respectively. Then we can write

$$C_1 = C_1^d + C_1 \quad (19)$$

$$C_2 = C_2^d + C_2 \quad (20)$$

where  $C_1^d$  and  $C_2^d$  are the solutions of the system of eqns. 1 and 2, where the two isotherms are  $q_1 = a_1 C_1$  and  $q_2 = a_2 C_2$  instead and where  $C_1'$  and  $C_2'$ , which are both functions of  $C_1$  and  $C_2$ , are small.

$C_1^d$  and  $C_2^d$  are given by the following equations:

$$(1 + Fa_1) \frac{\partial C_1^d}{\partial t} + u \frac{\partial C_1^d}{\partial x} = 0 \quad (21)$$

$$(1 + Fa_2) \frac{\partial C_2^d}{\partial t} + u \frac{\partial C_2^d}{\partial x} = 0 \quad (22)$$

Replacing  $C_1$  and  $C_2$  in the left-hand side of eqns. 17 and 18 by their new expressions (eqns. 19 and 20), subtracting eqns. 21 and 22 from eqns. 17 and 18, respectively, and considering only the first-order terms, we obtain

$$(1 + Fa_1) \frac{\partial C_1'}{\partial t} + u \frac{\partial C_1'}{\partial x} = (2Fa_1 b_1 C_1^d + Fa_1 b_2 C_2^d) \frac{\partial C_1^d}{\partial t} + Fa_1 b_2 C_2^d \frac{\partial C_2^d}{\partial t} \quad (23)$$

$$(1 + Fa_2) \frac{\partial C_2'}{\partial t} + u \frac{\partial C_2'}{\partial x} = (2Fa_2 b_2 C_2^d + Fa_2 b_1 C_1^d) \frac{\partial C_2^d}{\partial t} + Fa_2 b_1 C_1^d \frac{\partial C_1^d}{\partial t} \quad (24)$$

Eqns. 23 and 24 are linear partial differential equations for the perturbation terms  $C_1'$  and  $C_2'$ . They are still coupled, however, through the terms in their right-hand sides.

#### LAPLACE TRANSFORMS AND MOMENT ANALYSIS

In spite of the simplification made, it is still impossible to solve eqns. 23 and 24. As they are linear, it is possible, however, to take their Laplace transform and to derive the first moment of the band of each compound of the binary mixture. This permits the calculation of the variation of the retention time with increasing sample size.

The Laplace transforms are

$$(1 + Fa_1) \overline{PC_1'} + u \frac{d\overline{C_1'}}{dx} = Fa_1 p (b_1 \overline{C_1^{d^2}} + b_2 \overline{C_1^d C_2^d}) \quad (25)$$

$$(1 + Fa_2) \overline{PC_2'} + u \frac{d\overline{C_2'}}{dx} = Fa_2 p (b_2 \overline{C_2^{d^2}} + b_1 \overline{C_1^d C_2^d}) \quad (26)$$

where

$$\bar{w} = \int_0^{\infty} e^{-pt} w(x,t) dt \quad (27)$$

Eqns. 25 and 26 are first-order non-homogeneous differential equations. Their solutions are

$$\overline{C}'_1 = \exp\left[\frac{-p(1 + Fa_1)x}{u}\right] \left\{ \int_0^x \frac{Fa_1}{u} (b_1 p \overline{C}_1^{d^2} + b_2 p \overline{C}_1^d \overline{C}_2^d) \exp\left[\frac{p(1 + Fa_1)x'}{u}\right] dx' \right\} \quad (28)$$

and

$$\overline{C}'_2 = \exp\left[\frac{-p(1 + Fa_2)x}{u}\right] \left\{ \int_0^x \frac{Fa_2}{u} (b_2 p \overline{C}_2^{d^2} + b_1 p \overline{C}_1^d \overline{C}_2^d) \exp\left[\frac{p(1 + Fa_2)x'}{u}\right] dx' \right\} \quad (29)$$

The two integration constants are 0, because  $C'_1(x=0) = C'_2(x=0) = 0$ . The first-order moments,  $\mu_{1,i}$ , of the two compounds,  $i = 1, 2$ , are related to the Laplace transform,  $\overline{C}_i$ , by the following equation:

$$\mu_{1,i} = - \lim_{p \rightarrow 0} \frac{1}{C_i} \cdot \frac{d\overline{C}_i}{dp} \quad (i = 1, 2) \quad (30)$$

Let

$$\mu_{1,i} = \mu_{1,i}^0 + \mu'_{1,i} \quad (31)$$

where  $\mu_{1,i}^0$  is the first moment, *i.e.*, the retention time, of compound  $i$  under linear conditions:

$$\mu_{1,i}^0 = - \lim_{p \rightarrow 0} \frac{1}{C_i^d} \cdot \frac{d\overline{C}_i^d}{dp} \quad (32)$$

In the ideal model, we have no band broadening. Thus the retention time under linear conditions is

$$\begin{aligned} \mu_{1,i}^0 &= t_p + \frac{L}{u_{zi}} \\ &= t_p + t_0 (1 + k_i^0) = t_p + t_{R,i}^0 \end{aligned} \quad (33)$$

since the limiting velocity associated with an infinitely small concentration is  $u/(1 + Fa_i) = u/(1 + k_i^0)$ . The second term of the right-hand side of eqn. 31,  $\mu'_{1,i}$ , is the first-order perturbation term, which we shall now calculate.

The two perturbation terms corresponding to the first-order moments at the end of the column ( $x = L$ ) are given by

$$\begin{aligned} \mu'_{1,1} &= - \lim_{p \rightarrow 0} \frac{1}{C_1} \cdot \frac{d\overline{C}'_1}{dp} \\ &= - \frac{1}{\int_0^\infty C_1 dt} \frac{Fa_1}{u} \left( b_1 \int_0^L \int_0^\infty C_1^{d^2} dt dx' + b_2 \int_0^L \int_0^\infty C_1^d C_2^d dt dx' \right) \end{aligned} \quad (34)$$

and

$$\begin{aligned} \mu'_{1,2} &= - \lim_{p \rightarrow 0} \frac{1}{C_2} \cdot \frac{d\overline{C_2'}}{dp} \\ &= - \frac{1}{\int_0^\infty C_2 dt} \cdot \frac{Fa_2}{u} \left( b_2 \int_0^L \int_0^\infty C_2^{d^2} dt dx' + b_1 \int_0^L \int_0^\infty C_1^d C_2^d dt dx' \right) \end{aligned} \quad (35)$$

As we assume the column to have an infinite efficiency (ideal model), the elution profile in linear chromatography is identical with the injection profile and we have

$$\int_0^\infty C_i dt = C_i^0 t_p \quad (36)$$

and:

$$\int_0^L \int_0^\infty C_i^{d^2} dt dx' = C_i^{0^2} t_p L \quad (37)$$

The elution profiles of both components are rectangles (see Fig. 1). The difference between the elution times of the rear of the first component profile and the front of the second component profile (*i.e.*,  $t_B - t_C$ , see Fig. 1) is

$$\Delta t = t_p + \frac{x'}{u_{z1}} - \frac{x'}{u_{z2}} = t_p - \frac{x'}{u} (k_2^{0'} - k_1^{0'}) \quad (38)$$

Complete separation is achieved when  $\Delta t$  becomes zero and the migration distance in the column is

$$x' = x_s = \frac{L t_p}{(k_2^{0'} - k_1^{0'}) t_0} \quad (39)$$

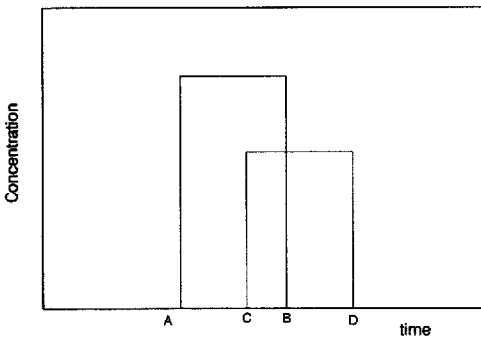


Fig. 1. Partially resolved band profiles in the case of a rectangular injection in ideal chromatography. Elution profiles at the position  $x'$  in the column. Retention times: A,  $t_A = x'/u_{z1}$ ; B,  $t_B = t_A + t_p$ ; C,  $t_C = x'/u_{z2}$ ; D,  $t_D = t_C + t_p$ .  $\Delta t = t_B - t_C$ .

The overlap integral gives

$$\int_0^{\infty} C_1^d C_2^d dt = C_1^0 C_2^0 \Delta t \quad (40)$$

when  $\Delta t > 0$  and  $x < x_s$  and

$$\int_0^{\infty} C_1^d C_2^d dt = 0 \quad (41)$$

when  $\Delta t \leq 0$ . Therefore, when the separation is incomplete, *i.e.*, for

$$L < x_s \quad \text{or} \quad t_p > (k_2^0 - k_1^0)t_0$$

we have

$$\int_0^L \int_0^{\infty} C_1^d C_2^d dx' dt = C_1^0 C_2^0 \int_0^L \left[ t_p - \frac{x'}{u} (k_2^0 - k_1^0) \right] dx' = C_1^0 C_2^0 L \left[ t_p - \frac{t_0(k_2^0 - k_1^0)}{2} \right] \quad (42)$$

Inserting eqns. 36–42 into eqns. 34 and 35 gives

$$\mu'_{1,i} = - (t_{R0,i} - t_0) \left\{ b_i C_i + b_j C_j \left[ 1 - \frac{t_0(k_2^0 - k_1^0)}{2t_p} \right] \right\} \quad (43)$$

On the other hand, when the column length exceeds the critical value  $x_s$ , we have

$$\int_0^L \int_0^{\infty} C_1^d C_2^d dx' dt = C_1^0 C_2^0 \int_0^{x_s} \left[ t_p - \frac{x'}{u} (k_2^0 - k_1^0) \right] dx' = \frac{C_1^0 C_2^0 t_p^2}{2t_0(k_2^0 - k_1^0)} \quad (44)$$

Inserting eqns. 36, 37 and 44 in eqns. 34 and 35 gives

$$\mu'_{1,i} = - (t_{R0,i} - t_0) \left[ b_i C_i + \frac{b_j C_j t_p}{2t_0(k_2^0 - k_1^0)} \right] \quad (45)$$

## RESOLUTION

If the sample size is very small, we have  $\mu_{1,i} = t_{Ri}$ , where  $t_{Ri}$  is the retention time observed for the band of a finite amount of component  $i$ , and we can write, as a first approximation,

$$t_{R2} - t_{R1} \approx \mu_{1,2} - \mu_{1,1} \approx (\mu_{1,2}^0 - \mu_{1,1}^0) + (\mu'_{1,2} - \mu'_{1,1}) \quad (46)$$

If, as a first approximation, we assume that the band width does not increase with increasing sample size at very low values<sup>15</sup>, the resolution between the two bands becomes



$$R = 2 \left( \frac{t_{R2} - t_{R1}}{\sigma_1 + \sigma_2} \right) = \frac{2}{\sigma_1 + \sigma_2} [(\mu_{1,2}^0 - \mu_{1,1}^0) + (\mu'_{1,2} - \mu'_{1,1})] = R^0 + \Delta R \quad (47)$$

where  $R^0$  is the resolution between these two bands under linear conditions. When the column length is smaller than  $x_s$ , the decrease in resolution,  $\Delta R$  is given by

$$\Delta R = 2 \left[ \frac{(\alpha - 1)(t_{R0,1} - t_0)}{\sigma_1 + \sigma_2} \right] \left[ b_1 C_1^0 \left( \frac{k_2^0 t_0}{2t_p} - 1 \right) - b_2 C_2^0 \left( \frac{k_1^0 t_0}{2t_p} + 1 \right) \right] \quad (48)$$

When the column length is larger than  $x_s$ , the two band profiles are resolved in linear ideal chromatography. This is not necessarily so in non-linear, ideal chromatography. The change in the resolution is now given by

$$\Delta R = 2 \left[ \frac{(t_{R0,1} - t_0)}{\sigma_1 + \sigma_2} \right] \left\{ b_1 C_1^0 \left[ 1 - \frac{\alpha t_p}{2t_0(k_2^0 - k_1^0)} \right] - b_2 C_2^0 \left[ \alpha - \frac{t_p}{2t_0(k_2^0 - k_1^0)} \right] \right\} \quad (49)$$

From eqns. 48 and 49, it is clear that  $\Delta R$  is related to the parameters  $b_1$  and  $b_2$  which are at the origin of the non-linear behavior of the equilibrium isotherms and of the coupling between these isotherms. Obviously, if  $b_1 = b_2 = 0$ , then the chromatographic behavior is linear and  $\Delta R = 0$ .

## RESULTS AND DISCUSSION

The essential results derived above are eqns. 43, 45, 48 and 49. They illustrate qualitatively the phenomena that take place when the sample size increases and non-linear behavior begins to affect the band profiles and their retention times. The most important effects are the following.

From eqns. 43 and 45, the variation of the first-order moment, *i.e.*, of the retention time of the band of each component of a binary mixture with increasing sample size, depends on the value of both coefficients  $b_1$  and  $b_2$  of the equilibrium isotherms of these two compounds. If  $b_1$  and  $b_2$  are both positive (such as with competitive Langmuir isotherms, as in eqns. 5 and 6),  $\mu'_{1,1}$  and  $\mu'_{1,2}$  are both negative. Both retention times decrease with increasing sample size. The sign and the magnitude of the variation of the resolution between the bands depend on the relative value of the coefficients  $b_i$  of the isotherms and on the relative concentration of the feed.

If the isotherms are accurately approximated by equation similar to eqns. 5 and 6, with negative values for both coefficients  $b_1$  and  $b_2$  (anti-Langmuir isotherms), the retention times of both components increase with increasing retention times and the resolution may increase or decrease, depending mainly on the relative composition of the feed.

When eqns. 5 and 6 are still valid, but with values of the two coefficients  $b_1$  and  $b_2$  which have opposite signs, the retention times of the components of a binary mixture can initially vary in either the same or the opposite direction, depending on the relative magnitude of the terms in eqns. 43 and 45. Situations where the retention time of one compound could remain constant are conceivable. Then the two terms in the right-hand side of either eqn. 43 or 45 are equal and opposite in sign.

The variation of the resolution between the two bands,  $\Delta R$ , is given by eqns. 48 and 49. The magnitude of the effect is determined by the importance of the two terms. If these two terms are close, the change in the resolution can be small. It would be better if the resolution could increase with increasing sample size. This takes place if  $b_1$  is positive and  $b_2$  is negative, as seen in eqns. 48 and 49. This can be only an exceptional case.

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