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Analytical solution of the ideal, nonlinear model of reaction chromatography for a reaction A→B and a parabolic isotherm

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Abstract

The analytical solution of the ideal, nonlinear model of reaction chromatography for the simplest possible chemical reaction, A→B and with a parabolic isotherm for the reagent, is derived for two types of boundary conditions, the injection of a rectangular concentration pulse of finite width (elution) and that of an instantaneous concentration jump (Riemann problem or breakthrough curve). The areas of the profiles of the reagent and of the product of the reaction are calculated in both the ideal and the nonideal cases. The effects of the nonlinear behavior of the equilibrium isotherm and of axial dispersion on the reagent profile are discussed using analytical and numerical methods.

Keywords: Parabolic isotherm; Reaction chromatography, non-linear; Axial dispersion; Adsorption isotherms; Band profiles

1. Introduction

Since the early days of the applications of chromatography to chemical analysis, the simultaneous occurrence of chemical reactions affecting the analytes has plagued the analysts. Isomerization of carotenoid pigments on the neat silica used as packing materials by Kuhn and Lederer [1] is reported [2] to have slowed down their development of the first applications of chromatography after Tswett, who seemed to have been well aware of these problems and of ways to avoid them [2,3]. Later, nearly at the same time, Keller and Giddings [4] in thin-layer liquid chromatography, Kallen and Heilbronner [5] in gas chromatography (GC) made the first fundamental investigations of the elution band profiles of compounds that can undergo a first-order chemical reaction (decomposition or isomerization). The first group was concerned with the origin of ''multi-zoning'', i.e., of the observation of several spots on the chromatograms of some pure compounds. These authors considered a substance that exists under two different, interconvertible forms, A and B (e.g., keto-enol isomers), and for which the rate constant of the reaction A⇆B is small compared to the inverse of the time width of their chromatographic bands but significant compared to their migration velocity along the column. Their work addressed the fundamental concerns of

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analysts who needed to avoid artifacts [4]. This concern has nearly disappeared in high-performance liquid chromatography (HPLC) with the development of modern supports that are nearly inert. It remains actual in GC, which is carried out at far higher temperatures. The second group was more concerned with irreversible first-order reactions A→B, such as the dehydration of terpenic alcohols (compounds that are abundant in natural fragrances) that may take place in their extraction or purification by preparative gas chromatography. Because most, if not all, preparative applications of chromatography are now carried out in HPLC, this concern has also receded.

Both groups [4,5] derived equations for the band profiles in the cases studied, the first set based on the stochastic theory of chromatography [6], the second set on the plate theory [7]. Kramer [8] proposed a simple method of calculation of the profiles given by Keller and Giddings [4]. Later, the development of chiral separations in GC and the realization that reactions of enantiomerization in the stationary phase were not exceptional and could not always be eliminated by operating at sufficiently low temperatures lead several authors to investigate the influence of the corresponding first-order chemical reaction on the elution profiles of pure enantiomers or of the racemic mixture itself. Bürkle et al. [9] discussed the elution band profiles of two enantiomers on a chiral stationary phase under such experimental conditions that the reaction of inversion takes place at a finite rate. When this rate is slow, i.e., when the inverse of the rate constant is large compared with the retention time of the pair of enantiomers, the chromatogram is that of a conventional chiral separation: the extent of the inversion of the separated enantiomers during the analysis is negligible. When the reaction is fast and the inverse of the rate constant is small compared to the width of the peaks of the enantiomers (in time units), only one peak is observed. The racemic mixture cannot be separated because the inversion of the enantiomers is too fast. In the intermediate case, Bürkle et al. [9] showed that the two enantiomers are eluted as a doublet joined by a plateau or bridge corresponding to the elution of the reaction products formed during the analysis. On the basis of the plate theory, these authors calculated the band profiles of a racemic mixture eluted on a chiral stationary phase, assuming no reaction in the mobile (in their case, gas) phase but a finite rate of enantiomerization in the stationary phase. The profiles thus calculated are in excellent agreement with the experimental profiles obtained in several cases, all involving GC [9]. Such a phenomenon of enantiomerization has not yet been reported in liquid chromatography, to the extent of our knowledge.

It was realized early that, in principle, the combination of a chemical reaction and of the simultaneous separation of the reaction products allows the reaction to proceed to completion and eliminates the requirement of the concentration equilibrium demanded by thermodynamics. Accordingly, the combination of a reaction and a chromatographic separation could potentially achieve total conversion of the reagents into its products. This potential has lured many investigators into trying to develop processes of reaction chromatography, for which many schemes have been suggested [10,11]. Most, if not all so far, investigations of true reaction chromatography[1], i.e., of the process in which a reagent undergoes a chemical reaction inside a column that is able to separate this reagent from the reaction products, have been limited to linear chromatography [4–11,14–21]. The method is mostly used to measure directly the kinetics of interconversion reactions. Lee et al. [14] used the recorded band profiles to measure the kinetics of the unimolecular dissociation of dicyclopentadiene between 190 and 250 °C, Marriott and Lai [15] to study the intramolecular sterically hindered isomerization of several complex polynuclear aromatic hydrocarbons. Veciana and Crespo [16] used the equation derived by Keller and Giddings [4] to account for the elution profiles of two compounds that are interconvertible in the liquid phase. They showed the advantages of the dynamic HPLC method to measure rate constants, energy barriers and equilibrium constants for species interconvertible in the liquid phase, particularly when the activation energy is between 65

[1]Many references found under the keywords reaction and chromatography deal with either the use of chemical reactions carried out on-line with the separation, in order to allow or enhance the detection of certain analytes [12], or with the use of chromatography in the identification of the products of reactions or in the study of reaction mechanisms [13].

and 105 kJ mol^{-1}, a range within which the reaction is difficult to investigate by nuclear magnetic resonance (NMR). Another advantage of the method is the extremely small amount of sample required to perform accurate measurements [16]. The interconversion kinetics of numerous pairs of enantiomers has been studied systematically by Gasparrini et al. [17], by Oxelbark and Allenmark [18], by Hochmuth and Koenig [19], and by Trapp et al. [20], all using HPLC. Rathore and Horvath [21] used electrophoresis to measure the kinetics of interconversion of *cis*- and *trans*-conformers of peptidyl–proline dipeptides.

Many processes of great importance in the chemical industry involve both a reaction and the separation of the reagent and the reaction products. In most cases, these two steps are carried out successively. Their combination in a single step could often lead to considerable savings and, thus, could have major economical and environmental consequences. Accordingly, many papers have discussed the process known as reaction chromatography [10,11,22,23]. In the chemical industry, most processes are used at the production scale, the concentrations of the reagent and the reaction products are important, and the character of the process is usually nonlinear, some times strongly so. Thus, we must investigate the nonlinear reaction chromatography processes. Catalytic chromatographic processes in which the column is packed with a mixture of a catalyst and an adsorbent has been more particularly studied in the past [10,11].

The simplest case of reaction chromatography is the combination of a reaction of isomerization followed by the separation of the isomers formed [4–6,8–10,16]. The development of a reaction chromatography process requires the combination of a suitable catalyst, that promotes the reaction of isomerization or racemization, and an appropriate stationary phase, that separates reagent and product. Although investigations leading to the successful selection of these materials and to their appropriate combination are critical, this paper is not concerned with these issues. Instead, we merely investigate the modeling of reaction chromatography. We discuss here the solution of the system of equations of nonlinear reaction chromatography in the ideal and the nonideal cases, with the reaction model: A (reagent)→B (product), and assuming an isotherm behavior that deviates slightly from a linear one (parabolic isotherm) [24,25].

2. The ideal case

2.1. The mathematical model

In the ideal case, the mass balance equations for the reagent and the reaction product in reaction chromatography, in the case of the simple reaction A→B, are written:

$$u \cdot \frac{\partial C_1}{\partial x} + \frac{\partial C_1}{\partial t} + F \cdot \frac{\partial f_1}{\partial t} = -k_r f_1 \quad (1)$$

$$u \cdot \frac{\partial C_2}{\partial x} + \frac{\partial C_2}{\partial t} + F \cdot \frac{\partial f_2}{\partial t} = k_r f_1 \quad (2)$$

where C_1, C_2, f_1, and f_2 are the concentrations of the reagent (1) and the product (2) in the mobile (C) and in the stationary (f) phase, respectively, u is the mobile phase velocity, and F is the phase ratio [with $F=(1-\epsilon)/\epsilon$, and ϵ, is the total column porosity], and k_r is the rate constant of the reaction. The concentrations f_1 and f_2 in the solid phase are given by the isotherm equations for the reagent and the reaction product, respectively. These two compounds are assumed to compete for adsorption, and their isotherms are supposed to follow competitive Langmuir adsorption behavior. Hence:

$$f_1(C_1,C_2) = \frac{a_1 C_1}{1 + b_1 C_1 + b_2 C_2} \quad (3)$$

$$f_2(C_1,C_2) = \frac{a_2 C_2}{1 + b_1 C_1 + b_2 C_2} \quad (4)$$

where a_1, a_2, b_1 and b_2 are the numerical parameters of the isotherm [29]. We assume that the reagent concentration is moderate (i.e., that $b_1 C_1$ is small compared to 1). We assume also that the reaction is relatively slow at the scale of the retention time of the reagent [i.e., that $1/k_r >> t_R$, with $t_R = (1+Fa_1)\cdot t_0$ and $t_0 = L/u$ is the hold-up time]. Then, there are only moderate deviations of the two isotherms from linear behavior. Then, the Langmuir isotherm of the reagent can be replaced by a parabolic isotherm:

$$f_1(C_1,C_2) = a_1 C_1 - a_1' C_1^2 \quad (3a)$$

where $a_1' = a_1 b_1$. Because both $a_1' C_1 << a_1$ and C_2 are small, the second isotherm equation can be replaced by a linear isotherm:

$$f_2(C_1, C_2) = a_2 C_2 \tag{4a}$$

We will also assume a small deviation from linear behavior for the reagent, i.e., that $b_1 C_1$ is small. Using the approximation mentioned above in Eqs. (1) and (2), the concentrations of the reagent and the product can be calculated from:

$$\frac{\partial C_1}{\partial x} + \frac{1 + Fa_1 - 2Fa_1' C_1}{u} \cdot \frac{\partial C_1}{\partial t} = -\frac{\beta C_1}{u} \tag{5}$$

$$\frac{\partial C_2}{\partial x} + \frac{1 + Fa_2}{u} \cdot \frac{\partial C_2}{\partial t} = \frac{\beta C_1}{u} \tag{6}$$

where $\beta = Fa_1 k_r$.

Eqs. (5) and (6) are two partial differential equations that constitute the system of equations of the model, together with the isotherm equations (Eqs. (3a) and (4a)) and the initial and boundary conditions. The former will always be a column empty of both reagent and reaction product and containing only the mobile and the stationary phases in equilibrium. The latter will be the classical boundary conditions of either frontal analysis or elution chromatography.

2.2. Mathematical analysis of the model

Along the characteristic lines of the system of partial differential equations derived above, we can write the following equations:

$$\frac{dC_1}{dx} = -\beta \cdot \frac{C_1}{u} \tag{7}$$

$$\frac{dt}{dx} = \frac{1 + Fa_1 - 2Fa_1' C_1}{u} \tag{8}$$

Integration of Eq. (7) gives:

$$C_1 = C_1^*(\tau) e^{-\frac{\beta}{u} \cdot x} \tag{9}$$

where $C_1^*(\tau)$ is the boundary condition, i.e., the concentration profile of the reagent during injection of the feed into the column, at $x = 0$, and τ is the time given by the intersection of the characteristic line considered and the time axis. Integration of the characteristic Eq. (8) gives:

$$t = \tau + \frac{1 + Fa_1}{u} \cdot x - \frac{2Fa_1' C_1^*(\tau) \cdot \left(1 - e^{-\frac{\beta}{u} \cdot x}\right)}{\beta} \tag{10}$$

It is easy to prove that characteristic lines that started at different times have different slopes and that some of them will eventually intersect each other. The equation of the characteristic line originating from the point at $t = \tau + d\tau$ is given by:

$$t = (\tau + d\tau) + \frac{1 + Fa_1}{u} \cdot x - \frac{2Fa_1' C_1^*(\tau + d\tau) \cdot \left(1 - e^{-\frac{\beta}{u} \cdot x}\right)}{\beta} \tag{11}$$

Combining Eqs. (10) and (11) and letting $d\tau$ tend toward 0 gives:

$$0 = 1 - \frac{2Fa_1' \cdot \left(1 - e^{-\frac{\beta}{u} \cdot x}\right)}{\beta} \cdot \frac{dC_1^*(\tau)}{d\tau} \tag{12}$$

Since we always have $0 < 1 - e^{-\frac{\beta}{u} \cdot x} < 1$, the following condition is always satisfied:

$$\frac{dC_1^*(\tau)}{d\tau} > \frac{\beta}{2Fa_1'} \tag{13}$$

In the two cases studied, the step and the pulse injection, we have $dC_1^*(\tau)/d\tau = \infty$ at the front. Then condition (13) is always verified and the front of the injection band is always a discontinuity or concentration shock.

From the Rankine–Hugoniot condition [26], the velocity of the discontinuity is:

$$u_s = \frac{C_2 - C_1}{Q_2 - Q_1} = \frac{u}{1 + F\frac{[f]}{[C]}}$$

where $Q = (C + Ff)/u$. Combining Eq. (3a) and the above equation gives:

$$u_s = \frac{u}{1 + Fa_1 - Fa_1' C_1} \tag{14}$$

This equation satisfies the entropy condition [27]:

$$u_{z+} < u_s < u_{z-} \tag{15}$$

where $u_z = u/(1 + Fa_1 - 2Fa_1' C_1)$ is the characteristic

velocity. In this case, the discontinuity is stable, so it is a concentration shock, like in nonlinear, ideal chromatography [28].

2.3. Solution of the model for frontal analysis (step injection)

In frontal analysis, i.e., for a step injection, at time $t=0$, the concentration of the stream entering the column ($x=0$) is instantaneously raised from $C_1=0$ to $C_1=C_{1,0}$, so the boundary condition is $C_1(0,t)=C_{1,0}$ and, from $dC_1/dx=-(\beta C_1/u)$, we have for the concentration of the reagent:

$$C_1(x,t)=C_{1,0}e^{-\frac{\beta x}{u}}$$

Similarly, for the reaction product, we have: $dC_2/dx=\beta C_1/u$, and $C_2(0,t)=0$ as the boundary condition, thus the concentration of the reaction product is given by:

$$C_2(x,t)=C_{1,0}\cdot\left(1-e^{-\frac{\beta x}{u}}\right)$$

Introducing the relationship between C_1 and $C_{1,0}$ into Eq. (14) and integrating it gives:

$$t=(1+Fa_1)\cdot\frac{x}{u}-\frac{Fa_1'C_{1,0}\cdot\left(1-e^{-\frac{\beta x}{u}}\right)}{\beta} \qquad (16)$$

Compared with the result obtained under linear conditions, Eq. (16) contains an additional term that represents the effect of the nonlinear behavior of the isotherm. This term is a function of $\beta=Fa_1k_r$. The velocity of the shock in nonlinear chromatography depends on its amplitude, i.e., on the maximum concentration of the shock. This is why, in reaction chromatography, it depends on the rate constant (see Fig. 1).

2.4. Solution of the model for elution

In elution chromatography, the initial condition is the injection of a rectangular pulse of width t_p and of height $C_{1,0}$ a condition that is written as follows:

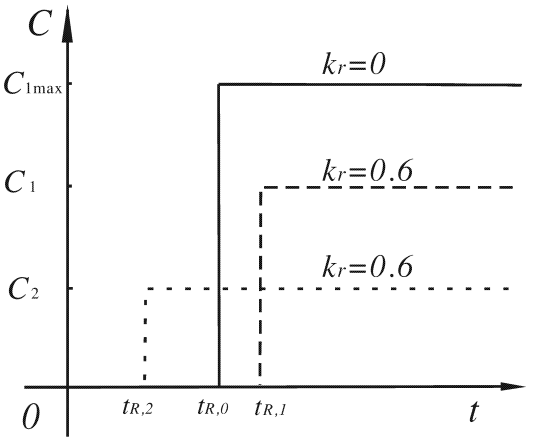

Fig. 1. Breakthrough curves of the reagent and the reaction product in reaction chromatography. The experimental conditions are linear for the reaction product and nonlinear for the reagent, but with a small deviation from linear behavior (parabolic isotherm). Numerical values of the parameters, $k_r=0.6$. Solid line, pure reagent breakthrough, in the absence of reaction, $C_{1,max}=0.4182$. Long-dashed line, reagent breakthrough when the reaction takes place, $C_1=0.3137$. Short-dashed line, reaction product breakthrough, $C_2=0.1046$.

$$C_1(0,t)=\begin{cases}C_{1,0} & 0<t<t_p\\ 0 & t>t_p\end{cases}$$

Obviously, the equation of the rear of the profile is:

$$t=t_p+(1+Fa_1)\cdot\frac{x}{u}-\frac{2Fa_1'C_1^*\cdot\left(1-e^{-\frac{\beta x}{u}}\right)}{\beta} \qquad (17a)$$

Since $C_1=C_1^*e^{-\beta x/u}$ this equation may be re-written as:

$$t=t_p+(1+Fa_1)\cdot\frac{x}{u}-\frac{2Fa_1'C_1\cdot\left(1-e^{-\frac{\beta x}{u}}\right)}{\beta e^{-\frac{\beta x}{u}}} \qquad (17b)$$

Next, we combine Eq. (17b) and the equation giving the shock velocity, u_s (Eq. (14)), with $u_s=dx/dt$. By eliminating C_1 between these equations we obtain the differential equation accounting for the shock migration:

$$\frac{\mathrm{d}t}{\mathrm{d}x} - \frac{\beta t \mathrm{e}^{-\frac{\beta x}{u}}}{2u\left(1-\mathrm{e}^{-\frac{\beta x}{u}}\right)} = \frac{1+Fa_1}{u} - \frac{\beta \mathrm{e}^{-\frac{\beta x}{u}} \cdot \left(t_\mathrm{p} + \frac{1+Fa_1}{u}\cdot x\right)}{2u \cdot \left(1-\mathrm{e}^{-\frac{\beta x}{u}}\right)} \quad (18)$$

This equation is an ordinary differential equation. It can be integrated into:

$$t = t_\mathrm{p} + \frac{1+Fa_1}{u}\cdot x + \text{constant}\sqrt{1-\mathrm{e}^{-\frac{\beta x}{u}}} \quad (19)$$

As long as the concentration plateau that is at the top of the boundary condition is not completely eroded, the shock velocity remains constant and the retention time of the shock that migrates at the front of this plateau is given by Eq. (16), hence its elution time is:

$$t_\mathrm{s} = (1+Fa_1)\cdot\frac{x}{u} - \frac{Fa_1' C_{1,0}\cdot\left(1-\mathrm{e}^{-\frac{\beta x}{u}}\right)}{\beta}$$

The point at the rear of the plateau is part of the rear, diffuse boundary. Its retention time is given by Eq. (17a) that may be rewritten as:

$$t_\mathrm{z} = t_\mathrm{p} + (1+Fa_1)\cdot\frac{x}{u} - \frac{2Fa_1' C_{1,0}\cdot\left(1-\mathrm{e}^{-\frac{\beta x}{u}}\right)}{\beta}$$

Because the velocity of the shock at the front of the concentration plateau, u_s, is lower than the velocity associated with the same concentration but on the rear, continuous part of the profile, u_z, the plateau shrinks. The plateau is completely breakthrough eroded when $t_\mathrm{s} = t_\mathrm{z}$. From this condition, we derive the coordinates, x_d and t_d, of the shock at this time. They are:

$$x_\mathrm{d} = -\frac{u}{\beta}\cdot\ln\left(1-\frac{\beta t_\mathrm{p}}{Fa_1' C_{1,0}}\right) \quad (20)$$

$$t_\mathrm{d} = -\frac{1+Fa_1}{\beta}\cdot\ln\left(1-\frac{\beta t_\mathrm{p}}{Fa_1' C_{1,0}}\right) - t_\mathrm{p} \quad (21)$$

Combining Eqs. (19)–(21) gives:

$$\text{constant} = -2\sqrt{\frac{Fa_1' C_{1,0} t_\mathrm{p}}{\beta}} \quad (22)$$

so:

$$t = t_\mathrm{p} + \frac{1+Fa_1}{u}\cdot x - 2\sqrt{\frac{Fa_1' C_{1,0} t_\mathrm{p}\cdot\left(1-\mathrm{e}^{-\frac{\beta x}{u}}\right)}{\beta}} \quad (23)$$

When $x = L$, Eq. (23) gives the retention time of the peak of reagent for a sample size such that the plateau just disappears when the band is eluted:

$$t_\mathrm{R} = t_\mathrm{p} + t_0\cdot(1+Fa_1) - 2\cdot\sqrt{\frac{Fa_1' C_{1,0} t_\mathrm{p}\cdot\left(1-\mathrm{e}^{-\beta t_0}\right)}{\beta}} \quad (24)$$

where $t_0 = L/u$ is the hold-up time of the column. When β tends toward 0, the result will be:

$$t_\mathrm{R} = t_\mathrm{p} + t_0(1+Fa_1) - 2\cdot\sqrt{Fa_1' C_{1,0} t_\mathrm{p} t_0}$$

or:

$$t_\mathrm{R} = t_\mathrm{p} + t_0\left[1 + Fa_1\cdot\left(1-2\cdot\sqrt{\frac{bC_{1,0}t_\mathrm{p}}{Fa_1 t_0}}\right)\right]$$

This is the same result as the one obtained for the retention time of the peak in nonlinear chromatography, in the absence of reaction and with a parabolic isotherm.

According to Eq. (24), the consequence of the reaction is that the retention time of the reagent peak increases with increasing reaction rate constant, which was expected since the concentration of the reagent decreases. From Eq. (17a), we have:

$$C_1(x,t) = \frac{\beta \mathrm{e}^{-\frac{\beta x}{u}}\cdot\left[t_\mathrm{p} + (1+Fa_1)\cdot\frac{x}{u} - t\right]}{2Fa_1'\cdot\left(1-\mathrm{e}^{-\frac{\beta x}{u}}\right)} \quad (25)$$

At the column outlet, the elution profile is given by:

$$C_1(L,t) = \frac{\beta \mathrm{e}^{-\beta t_0}\cdot\left[t_\mathrm{p} + (1+Fa_1)t_0 - t\right]}{2Fa_1'\cdot\left(1-\mathrm{e}^{-\beta t_0}\right)} \quad (26)$$

The peak width (in Fig. 2) is:

$$\Delta t = 2\cdot\sqrt{\frac{Fa_1' C_{1,0} t_\mathrm{p}\cdot\left(1-\mathrm{e}^{-\beta t_0}\right)}{\beta}} \quad (27)$$

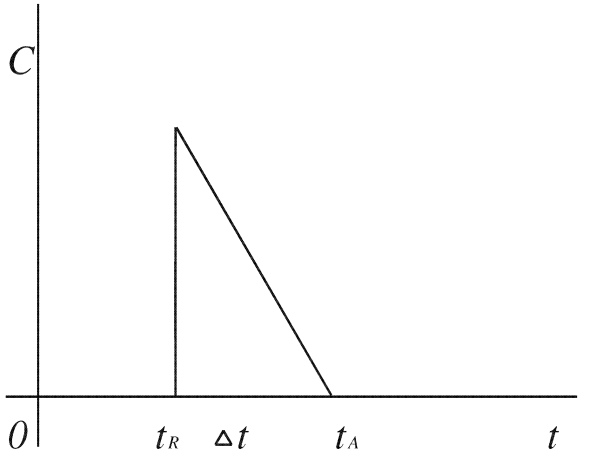

Fig. 2. Elution profile of a rectangular pulse of the reagent in reaction chromatography. The experimental conditions are non-linear, with a parabolic isotherm, the reaction rate, $k_r = 0.5$.

The maximum concentration of the peak or concentration at the retention time is given by:

$$C_{1,R} = \sqrt{\frac{\beta C_{1,0} t_p}{F a_1' \cdot (1 - e^{-\beta t_0})}} \cdot e^{-\beta t_0} \quad (28)$$

These results are illustrated in Fig. 2, which shows the elution band profile of the reagent. Note that Eq. (26) is that of a straight line because the isotherm equation used in this work is a parabolic isotherm.

The elution profiles of the reagent and of the reaction product can be obtained by numerical calculations. The result is presented in Fig. 3.

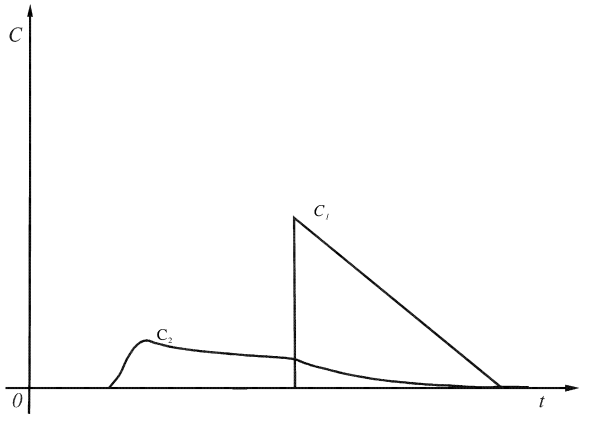

Fig. 3. Elution profiles of the reagent and the product of the reaction in reaction chromatography. Parabolic isotherm for the reagent and linear behavior for the product of the reaction., the reaction rate $k_r = 0.4$.

The influence of the nonlinear coefficient of the isotherm, b, on the band profile can be determined from the results of systematic computer calculations of these profiles. They are illustrated in Fig. 4.

2.5. Calculation of the band areas in the elution case

Integration of Eqs. (1) and (2) gives:

$$\int_0^\infty \left[\frac{\partial C_i}{\partial t} + F \cdot \frac{\partial f_i}{\partial t} + u \cdot \frac{\partial C_i}{\partial x} \pm k_r f_1 \right] \cdot dt = 0$$

$(i = 1, 2)$

Obviously:

$$\int_0^\infty \left(\frac{\partial C}{\partial t} + F \cdot \frac{\partial f}{\partial t} \right) \cdot dt = [C(x,\infty) - C(x,0)] + F \cdot [f(x,\infty) - f(x,0)] = 0 \quad (29)$$

Let $\int_0^\infty C_i dt = A_i$ be the area of the band of component i. For the reagent, we have:

$$u \cdot \frac{dA_1}{dx} = -\beta A_1$$

so:

$$A_1 = \alpha e^{-\beta \cdot \frac{x}{u}}$$

where α is a constant. When $x = 0$, the band area at

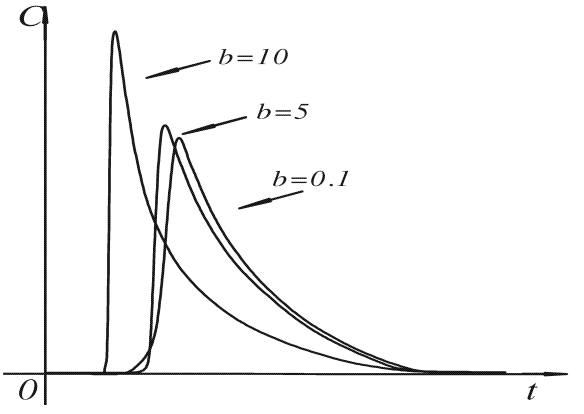

Fig. 4. Influence of the second isotherm coefficient on the band profiles. Nonlinear conditions, with a Langmuir isotherm $q = 29.2C/1 + 13.77C$.

injection is $A_1 = C_{10}t_p$, so we have $\alpha = C_{10}t_p$ and $A_1 = C_{10}t_p e^{-\beta\cdot\frac{x}{u}}$.

This result can also be obtained by calculating the area of the profile of the reagent in Fig. 2. In this figure, the:

$$A_1 = \frac{1}{2}\cdot C_{1R}(t_R - t_{10}) = C_{10}t_p e^{-\beta\cdot\frac{x}{u}} \tag{30}$$

From Eq. (7), we have:

$$u\cdot\frac{dA_2}{dx} = \beta A_1$$

where $A_2 = \int_0^\infty C_2 dt$. Combining this equation and the expression of A_1 given above, we have:

$$\frac{dA_2}{dx} = \frac{\beta}{n}\cdot C_{10}t_p e^{-\frac{\beta x}{u}} + \gamma$$

where γ is a constant. Since $A_2(0) = 0$, we have the value of the constant, $\gamma = C_{10}t_p = A_0$ where A_0 is the area of the injection profile, i.e., is the amount of reagent injected into the column. Therefore:

$$A_2(x) = A_0\cdot\left(1 - e^{-\beta\cdot\frac{x}{u}}\right) \tag{31}$$

It is obvious that the larger the value of β, i.e., the larger the adsorption coefficient and the reaction rate, the larger the amount of product formed.

From Eqs. (30) and (31), it is also obvious that we have: $A_1 + A_2 = C_{10}t_p$.

3. Non-ideal case

3.1. Mathematical model and profiles

In the non-ideal case, the equations for reaction chromatography are as follows:

$$\frac{\partial C_1}{\partial t} + F\cdot\frac{\partial q_1}{\partial t} + u\cdot\frac{\partial C_1}{\partial x} - D\cdot\frac{\partial^2 C_1}{\partial x^2} = 0 \tag{32}$$

$$\frac{\partial C_2}{\partial t} + F\cdot\frac{\partial q_2}{\partial t} + u\cdot\frac{\partial C_2}{\partial x} - D\cdot\frac{\partial^2 C_2}{\partial x^2} = 0 \tag{33}$$

with the following expressions for the time differentials of the stationary phase concentrations:

$$\frac{\partial q_1}{\partial t} = \frac{\partial f_1}{\partial t} + k_r f_1 \tag{34}$$

$$\frac{\partial q_2}{\partial t} = \frac{\partial f_2}{\partial t} - k_r f_2 \tag{35}$$

The isotherm equations are unchanged:

$$f_1(C_1, C_2) = \frac{a_1 C_1}{1 + b_1 C_1 + b_2 C_2} \tag{36}$$

$$f_2(C_1, C_2) = \frac{a_2 C_2}{1 + b_1 C_1 + b_2 C_2} \tag{37}$$

So the equations for nonideal, nonlinear reaction chromatography are:

$$u\cdot\frac{\partial C_1}{\partial x} + \frac{\partial C_1}{\partial t} + F\cdot\frac{\partial f_1}{\partial t} - D\cdot\frac{\partial^2 C_1}{\partial x^2} = -k_r f_1$$

$$u\cdot\frac{\partial C_2}{\partial x} + \frac{\partial C_2}{\partial t} + F\cdot\frac{\partial f_2}{\partial t} - D\cdot\frac{\partial^2 C_2}{\partial x^2} = k_r f_1$$

The profiles of the reagent and the reaction product can be obtained from the straightforward numerical analysis of this system and its numerical solution of the equation system. Some typical profiles are presented in Fig. 5.

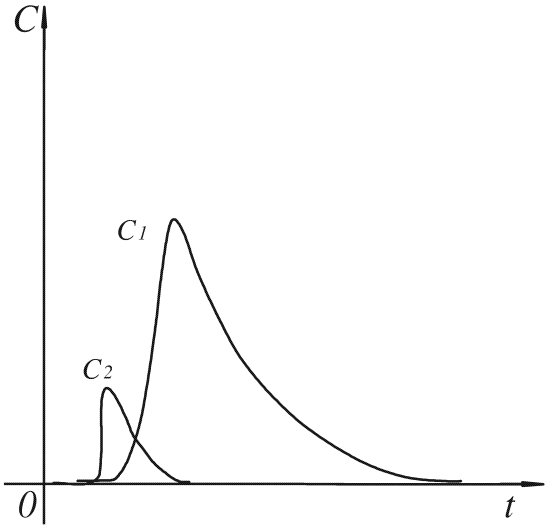

Fig. 5. Elution profiles of the reagent and the product in nonideal, nonlinear reaction chromatography. Langmuir isotherm for the reagent and the product of the reaction. The axial dispersion coefficient is $D = 0.001$.

3.2. Calculation of the band areas in the elution case

As we did in the previous section, we can derive the peak areas from Eqs. (32) and (34). We obtain the following equations:

$$D \cdot \frac{d^2 A_1}{dx^2} - u \cdot \frac{dA_1}{dx} - \beta A_1 = 0 \tag{38a}$$

$$D \cdot \frac{d^2 A_2}{dx^2} - u \cdot \frac{dA_2}{dx} + \beta A_1 = 0 \tag{38b}$$

From Eq. (38a), we derive that:

$$A_1 = \alpha_1 e^{k_1 x} + \alpha_2 e^{k_2 x} \tag{39}$$

where $k_{1,2} = (u \pm \sqrt{u^2 + 4D\beta})/2D$, $k_1 = k_+$ and $k_2 = k_-$.

Since A_1 is finite for $x = \infty$, we must have $\alpha_1 = 0$. Since when $x = 0$, we have $A_1 = C_{10} t_p$, hence $\alpha_2 = C_{10} t_p$ and we have:

$$A_1 = C_{10} t_p e^{\left(\frac{u}{2D} - \frac{u}{2D}\cdot\sqrt{1+\frac{4D}{u^2}\cdot\beta}\right)x} \tag{40}$$

When $4D\beta/u^2$ is small (i.e., when D is small and u is large), we have $\sqrt{1 + (4D/u)\cdot\beta} \approx 1 + (2D/u)\cdot\beta$ and:

$$A_1 \approx C_{10} t_p e^{-\beta \cdot \frac{x}{u}} \tag{41}$$

This result is the same as the one obtained in the ideal case, but this time it is only approximate. To a higher order of approximation, we have:

$$\sqrt{1 + \frac{4D}{u^2}\cdot\beta} = 1 + \frac{1}{2}\cdot\frac{4D}{u^2}\cdot\beta - \frac{1}{4}\cdot\left(\frac{4D}{u^2}\cdot\beta\right)^2 \tag{42}$$

and then:

$$A_1 = C_{10} t_p e^{-\frac{\beta x}{u}} e^{\frac{2D\beta^2 x}{u^3}} \tag{43}$$

The last factor in this equation expresses the effect of D on the area (i.e., the amount) of unreacted reagent. This means that the actual extent of reaction conversion or the apparent rate of reaction decreases due to the effect of axial dispersion. When $D \to 0$, the result of Eq. (43) is the same as in the ideal case.

From Eqs. (38a) and (38b), we have $D\cdot[d^2\cdot(A_1 + A_2)]/dx^2 - u[d\cdot(A_1 + A_2)]/dx = 0$. Like for Eqs. (38a) and (39), the solution is $A_1 + A_2 = \alpha_1 e^{k_1 x} + \alpha_2 e^{k_2 x}$, where $k_1 = 0$, $k_2 = D/u$.

Since $A_1 + A_2$ are both finite when $x = \infty$, we must have $\alpha_2 = 0$, hence we have:

$$A_1 + A_2 = \alpha_1$$

Since $x = 0$, $A_2 = 0$, $A_1 = C_{10} t_p$, so $\alpha_1 = C_{10} t_p$. Hence, in the nonideal case, we still have:

$$A_1 + A_2 = C_{10} t_p$$

so:

$$A_2 = C_{10} t_p - A_1$$

$$= C_{10} t_p \cdot \left[1 - e^{\left(\frac{u}{2D} - \frac{u}{2D}\cdot\sqrt{1+\frac{4D}{u^2}\cdot\beta}\right)\cdot x}\right]$$

When $D \to 0$, we have $A_2 = C_{10} t_p \left[1 - e^{-\frac{\beta x}{u}}\right]$, which is the same result as in the ideal case.

4. Conclusions

(1) The basic characteristic of the elution profiles obtained in reaction chromatography is that the equations of both the reagent and the reaction product profile contain the exponential factor, $e^{-\beta t_0}$, where β is a function of the reaction rate, k_r, and of the initial slope of the reagent isotherm, a_1.

(2) The effect of the reaction on the band profiles is different from that of axial dispersion. The effect of an increase in the reaction rate is merely to decrease the concentration of the reagent but it is not to diffuse the band. So, in the ideal, nonlinear case, a shock always appears on the profile, which is similar to the one obtained in nonlinear chromatography without reaction (except for the factor $e^{-\beta t_0}$).

(3) Due to the effect of the nonlinear behavior of the isotherm in nonlinear reaction chromatography, the actual extent of conversion of the reagent into product, hence the apparent reaction rate in the stationary phase decreases with increasing retention factor.

(4) Due to the effect of axial dispersion in chromatography, the band broadens and its concentration decreases. Accordingly, the degree of

conversion of the reagent and the apparent reaction rate decrease too.

(5) Reaction affects the separation of the bands of the reagent and the reaction product and their retention times. Due to the reaction, the concentration of the reagent decreases and its retention time increases in nonlinear reaction chromatography.

(6) Although these trends were determined for a parabolic isotherm, they remain qualitatively valid for all convex upward isotherms (e.g., Langmuir isotherm).

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