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Behavior of Concentration Wave for Chromatography System with a Reaction

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Abstract

Based on fluid dynamics theory of the chromatographic process, combined with the effects of adsorption and reaction, the chromatography model with a reaction $A\rightarrow B$ was established by a system of two nonlinear hyperbolic partial differential equations (PDE). In some practical situations, the reaction chromatography model was simplified a semi-coupled system of two linear hyperbolic PDE's. In which, the reactant concentration wave model was the initial-boundary value problem of a self-closed hyperbolic PDE, while the resultant concentration wave model was the initial-boundary value problem of hyperbolic PDE coupling reactant concentration. The explicit expressions for the concentration wave of the reactants and resultants were constructed by characteristic curve method in general situations. By taking pulse width injection taken as an example, the solution of concentration wave for reactant and resultant were derived detailedly, and then the shape of the outflow curves were further analyzed in a variety of situations. It was significant for further analysis between input and output of chromatography, optimizing chromatographic separation, determining the physical and chemical characters.

Keywords

Reaction Chromatography Model, Concentration Wave, Outflow Curve, Hyperbolic Partial Differential Equations, Characteristic Curve Method

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1. Introduction

In recent years, with the appearance of diverse production chromatography (such as the reaction chromatography), the chromatography technology has been widely applied in chemistry, chemical engineering, biological engineering and pharmaceutical engineering, etc, while the demand of chromatography theory is increasing higher. The relationships among the chromatographic input-output and the system conditions play the very important role in chromatography model [1-3]. In fact, the mathematical model of chromatography system is an initial-boundary value problem of hyperbolic partial differential equations system [4-10], which is hard and challenging mathematics problem. The relative works of partial differential equations in the practical chromatography are still not much.

If the chromatographic process contains reactions, it is labeled as reaction chromatography. An important example is the catalyst for the column packing, accompanied the catalytic [2, 3] in the adsorption process, and the isomerization reaction is the common situation.

In this paper, a chromatography model with a reaction $A\rightarrow B$ was established, which is an initial-boundary value problem for the semi-coupled system of two linear hyperbolic partial differential equations. Then, using characteristic curve method, the explicit expressions of concentration wave of reactant and resultant were constructed in general situations. It was significant for further analysis between input and output of chromatography, optimizing chromatographic separation, determining the physical and chemical characters. Finally, the

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wide pulse was taken as an example, the solution of concentration wave for reactant and resultant were derived detailedly, and the equations of outflow curves were further worked out. The behavior and character of the outflow curves were discussed corresponding to every possible situation, providing the proper theory models for further chromatographic data analysis.

2. Reaction Chromatography Model

Set the concentrations of the reactant A and the resultant B in the mobile phase and in the stationary phase as c_1, c_2, f_1, f_2 respectively. Reaction rate was k_r, so the mass conservation equation between reactant and resultant in the catalytic chromatographic process was shown as below:

$$\begin{cases} \dfrac{\partial c_1}{\partial t} + F\dfrac{\partial f_1}{\partial t} + u\dfrac{\partial c_1}{\partial x} = -k_r F f_1 \\ \dfrac{\partial c_2}{\partial t} + F\dfrac{\partial f_2}{\partial t} + u\dfrac{\partial c_2}{\partial x} = k_r F f_1 \end{cases} \tag{1}$$

where, $-k_r f_1$ was the reactant reduction rate, and $k_r f_1$ was resultant increase rate, k_r was the coefficient of reaction rate. According to Langmuir type adsorption isotherms, f_1 (c_1, c_2) and f_2 (c_1, c_2) satisfied for:

$$\begin{cases} f_1(c_1, c_2) = \dfrac{G_1 c_1}{1 + b_1 c_1 + b_2 c_2} \\ f_2(c_1, c_2) = \dfrac{G_2 c_2}{1 + b_1 c_1 + b_2 c_2} \end{cases}, \tag{2}$$

where the constants b_1, b_2 were the adsorption coefficients for reactant A and the resultant B, respectively, and G_1 and G_2 were both constants. The concentration wave equations (1) were a system of two nonlinear hyperbolic partial differential equations, which was a hard mathematical problem. But in some practical situations, the problem can be simplified [2]. Assume c_1 was small, or the adsorption coefficient b_1 was small, so $b_1c_1 \ll 1$, while considering the assumed reaction rate k_r is relatively minor, therefore c_2 was also small, that was $c_2 \ll 1$, $b_2c_2 \ll 1$, and so the adsorption isotherm above can be approximated as a linear

$$f_1 \doteq G_1 c_1, \; f_2 \doteq G_2 c_2 \tag{3}$$

and denoted concretely:

$$\frac{1 + FG_1}{u} = \lambda_1, \; \frac{1 + FG_2}{u} = \lambda_2, \; \frac{k_r F G_1}{u} = \alpha. \tag{4}$$

They were positive constant, thus equations (1) can be simplified to the following semi-coupled system of two linear hyperbolic partial differential equations. In which, the reactant concentration wave model was the initial-boundary value problem of a self-closed hyperbolic partial differential equations, while the resultant concentration wave model was the initial boundary value problem of hyperbolic partial differential equations coupling reactant concentration.

$$\frac{\partial c_1}{\partial x} + \lambda_1 \frac{\partial c_1}{\partial t} = -\alpha c_1, \; \frac{\partial c_2}{\partial x} + \lambda_2 \frac{\partial c_2}{\partial t} = \alpha c_1. \tag{5}$$

In fact, in the quantitative analysis using high performance liquid chromatography (HPLC), the concentrations of most analytes, such as the reactant A and the resultant B here, were all very small [2, 3, 5], i.e. satisfied for $c_1 \ll 1$ and $c_2 \ll 1$. Therefore, *Langmuir* type adsorption isotherms (2) can be approximated as a linear case (3). This study mainly focused on the linear case, and deduced the behavior of concentration wave for chromatography system with a reaction $A \rightarrow B$.

Chromatographic process started from the boundary, and there were many types of the boundary conditions, such as the methods of delta-pulse, head-on, wide pulse, gradual change head-on, gradual change wide pulse, etc; whose corresponding boundary condition were not zero. The initial state of chromatography columns were typically empty, that the initial conditions corresponding to 0. However, in practical problems, there was some important chromatograph whose corresponding initial condition is not zero, such as simulated moving bed chromatography. Therefore, it is necessary to study the general initial-boundary value problem with both the initial and boundary values were not 0. That was, c_1, c_2 satisfied the following the general initial-boundary value problem.

$$\begin{cases} \dfrac{\partial c_1}{\partial x} + \lambda_1 \dfrac{\partial c_1}{\partial t} = -\alpha c_1 \\ c_1(x,0) = c_1^I(x), \quad 0 < x < +\infty \\ c_1(0,t) = c_1^B(t), \quad 0 < t < +\infty, \end{cases} \tag{6}$$

$$\begin{cases} \dfrac{\partial c_2}{\partial x} + \lambda_2 \dfrac{\partial c_2}{\partial t} = \alpha c_1 \\ c_2(x,0) = c_2^I(x), \quad 0 < x < +\infty \\ c_2(0,t) = c_2^B(t), \quad 0 < t < +\infty, \end{cases} \tag{7}$$

where, λ_1, λ_2, α were constants, $c_i^I(x), c_i^B(t), i=1,2$ were positive piecewise and continuous smooth functions, and meet the compatibility condition, $c_i^I(0) = c_i^B(0), i=1,2$ (If this compatibility condition was not satisfied, The results of this paper was still valid).

3. Explicit Solution of Concentration Wave

Firstly, solve the initial-boundary value problem (6) for c_1. According to characteristic curve method of initial-boundary value problem for hyperbolic partial differential equations, the characteristic curve t=t(x) of (x, t) plane satisfied the following equation:

$$\frac{dt(x)}{dx}=\lambda_1. \tag{8}$$

Along the characteristic curve t=t(x), we got:

$$\frac{dc_1(x,t(x))}{dx}=\frac{\partial c_1}{\partial x}+\lambda_1\frac{\partial c_1}{\partial t}=-\alpha c_1(x,t(x)). \tag{9}$$

Solve the ordinary differential equations about $c_1(x,t(x))\overset{def}{=}\tilde{c}(x)$, we got:

$$c_1(x,t(x))=ke^{-\alpha(x-\xi)}, \tag{10}$$

where, k, ξ were constants, corresponding to the beginning point of characteristic curve.

For $\forall(x,t)\in\{t\geq\lambda_1 x\}$, the characteristics curve and t axis intersected, $\exists\tau=t-\lambda_1 x$, $t(0)=\tau$, so $c_1(0,t(0))=c_1(0,\tau)=c_1^B(\tau)$

$$c_1(x,t)=c_1^B(\tau)e^{-\alpha x}=c_1^B(t-\lambda_1 x)e^{-\alpha x}.$$

For $\forall(x,t)\in\{t<\lambda_1 x\}$, characteristic curve and x axis intersected, $\exists\xi=t^{-1}(0)=x-\frac{\alpha t}{\lambda_1}$, so

$$c_1(\xi,t(\xi))=c_1(\xi,0)=c_1^I(\xi),$$

$$c_1(x,t(x))=c_1^I(\xi)e^{\alpha(\xi-x)}=c_1^I(x-\frac{t}{\lambda_1})e^{-\frac{\alpha t}{\lambda_1}}.$$

To sum up,

$$c_1(x,t)=\begin{cases}c_1^B(t-\lambda_1 x)e^{-\alpha x}, & t\geq\lambda_1 x\\ c_1^I(x-\frac{t}{\lambda_1})e^{-\frac{\alpha t}{\lambda_1}}, & t<\lambda_1 x\end{cases} \tag{11}$$

Then solved the initial-boundary value problem (7) for c_2, the characteristic curve t=t(x) of (x, t) plane satisfied the following equation.

$$\frac{dt(x)}{dx}=\lambda_2. \tag{12}$$

Along the characteristic curve, we got:

$$\frac{dc_2(x,t(x))}{dx}=\frac{\partial c_2}{\partial x}+\lambda_2\frac{\partial c_2}{\partial t}=\alpha c_1(x,t(x)). \tag{13}$$

For $\forall(x,t)\in\{t\geq\lambda_2 x\}$, $\exists\tau=t-\lambda_2 x$, $t(0)=\tau$, so $c_2(0,t(0))=c_2(0,\tau)=c_2^B(\tau)$, further we got:

$$c_2(x,t(x))=\alpha\int_0^x c_1(\zeta,t(\zeta))d\zeta+c_2^B(\tau).$$

For $\forall(x,t)\in\{t<\lambda_2 x\}$, characteristic curve and x axis intersected, $\exists\xi=t^{-1}(0)=x-\frac{t}{\lambda_2}$,

so $c_2(\xi,t(\xi))=c_2(\xi,0)=c_2^I(\xi)$, further we got:

$$c_2(x,t(x))=\alpha\int_\xi^x c_1(\zeta,t(\zeta))d\zeta+c_2^I(\xi).$$

To sum up,

$$\begin{cases}\alpha\int_{x-\frac{t}{\lambda_2}}^x c_1(\zeta,t+\lambda_2(\zeta-x))d\zeta+c_2^I(x-\frac{t}{\lambda_2}), & t<\lambda_2 x\\ \alpha\int_0^x c_1(\zeta,t+\lambda_2(\zeta-x))d\zeta+c_2^B(t-\lambda_2 x), & t\geq\lambda_2 x\end{cases} \tag{14}$$

Use the expression (11) of c_1 and the relation equation (14) of c_1 and c_2, the explicit solution expressions of c_2 were derived by dividing into the following three cases.

In the case of $\lambda_2=\lambda_1=\lambda$

(i) $\forall(x,t)\in\{t\geq\lambda x\}$, for $\zeta\in(0,x)$, we had $(\zeta,t+\lambda(\zeta-x))\in\{t\geq\lambda x\}$, according to (11) and (14), thus

$$\begin{aligned}c_2(x,t)&=c_2^B(t-\lambda x)+\alpha\int_0^x c_1^B(t-\lambda x)e^{-\alpha\zeta}d\zeta\\&=c_2^B(t-\lambda x)+c_1^B(t-\lambda x)(1-e^{-\alpha x}).\end{aligned}$$

(ii) $\forall(x,t)\in\{t<\lambda x\}$, for $\zeta\in(x-\frac{t}{\lambda},x)$, we had $(\zeta,t+\lambda(\zeta-x))\in\{t<\lambda x\}$, according to (11) and (14), thus

$$\begin{aligned}c_2(x,t)&=c_2^I(x-\frac{t}{\lambda})+\alpha\int_{x-\frac{t}{\lambda}}^x c_1^I(\zeta-\frac{t+\lambda(\zeta-x)}{\lambda})e^{-\frac{\alpha[t+\lambda(\zeta-x)]}{\lambda}}d\zeta\\&=c_2^I(x-\frac{t}{\lambda})+c_1^I(x-\frac{t}{\lambda})(1-e^{-\frac{\alpha t}{\lambda}}).\end{aligned}$$

To sum up,

$$c_2(x,t)=\begin{cases}c_2^I(x-\frac{t}{\lambda})+c_1^I(x-\frac{t}{\lambda})(1-e^{-\frac{\alpha t}{\lambda}}), & t<\lambda x\\ c_2^B(t-\lambda x)+c_1^B(t-\lambda x)(1-e^{-\alpha x}), & t\geq\lambda x.\end{cases} \tag{15}$$

In the case of $\lambda_2<\lambda_1$, see Fig. 1(a)

(i) $\forall (x,t)\in\{t<\lambda_2 x\}$, for $\zeta\in(x-\frac{t}{\lambda_2},x)$, we had $(\zeta, t+\lambda_2(\zeta-x))\in\{t<\lambda_2 x\} \subset\{t<\lambda_1 x\}$, according to (11) and (14), thus

$$c_2(x,t)=c_2^I(x-\frac{t}{\lambda_2})+\alpha\int_{x-\frac{t}{\lambda_2}}^{x} c_1^I(\zeta-\frac{t+\lambda_2(\zeta-x)}{\lambda_1})e^{-\frac{\alpha[t+\lambda_2(\zeta-x)]}{\lambda_1}}d\zeta$$

$$=c_2^I(x-\frac{t}{\lambda_2})+\frac{\alpha\lambda_1 e^{-\frac{\alpha(t-\lambda_2x)}{\lambda_1-\lambda_2}}}{\lambda_1\text{-}\lambda_2}\int_{x-\frac{t}{\lambda_2}}^{x-\frac{t}{\lambda_1}} c_1^I(y)e^{-\frac{\alpha\lambda_2 y}{\lambda_1-\lambda_2}}dy.$$

(ii) $\forall (x,t)\in\{\lambda_2 x\le t<\lambda_1 x\}$, the intersection of the characteristic curve of c_2 over (x, t) and the line $t=\lambda_1 x$ was $(\gamma,\eta)=(\frac{t-\lambda_2x}{\lambda_1-\lambda_2},\frac{\lambda_1(t-\lambda_2x)}{\lambda_1-\lambda_2})$, as shown in Fig. 1(a), for $\zeta\in(0,\gamma)$, we had $(\zeta,t+\lambda(\zeta-x))\in\{t\ge\lambda_1x\}\subset\{t\ge\lambda_2x\}$; and for $\zeta\in(\gamma,x)$ we had $(\zeta,t+\lambda(\zeta-x))\in\{\lambda_2x\le t<\lambda_1x\}$, according to (11) and (14), thus

$$c_2(x,t)=c_2^B(t-\lambda_2x)+\alpha\int_0^{\gamma} c_1^B(t-\lambda_2x-(\lambda_1-\lambda_2)\zeta)e^{-\alpha\zeta}d\zeta$$

$$+\alpha\int_{\gamma}^{x} c_1^I(\zeta-\frac{t+\lambda_2(\zeta-x)}{\lambda_1})e^{-\frac{\alpha[t+\lambda_2(\zeta-x)]}{\lambda_1}}d\zeta$$

$$=c_2^B(t-\lambda_2x)+\frac{\alpha e^{-\frac{\alpha(t-\lambda_2x)}{\lambda_1-\lambda_2}}}{\lambda_1\text{-}\lambda_2}\int_0^{t-\lambda_2x} c_1^B(y)e^{\frac{\alpha y}{\lambda_1-\lambda_2}}dy$$

$$+\frac{\alpha\lambda_1 e^{-\frac{\alpha(t-\lambda_2x)}{\lambda_1-\lambda_2}}}{\lambda_1\text{-}\lambda_2}\int_{x-\frac{t}{\lambda_2}}^{x-\frac{t}{\lambda_1}} c_1^I(y)e^{-\frac{\alpha\lambda_2 y}{\lambda_1-\lambda_2}}dy.$$

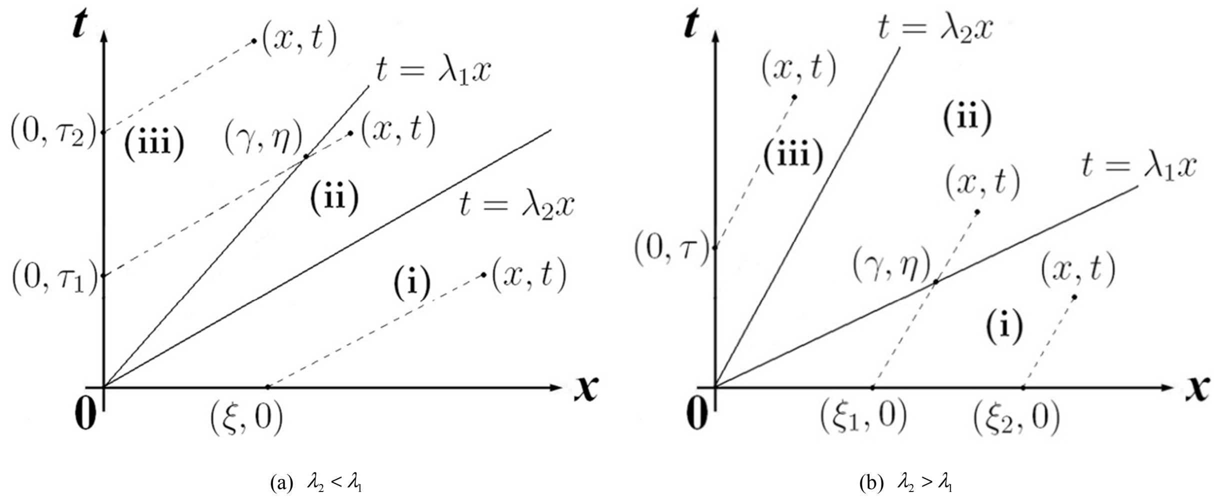
(iii) $\forall (x,t)\in\{t\ge\lambda_1 x\}$, for $\zeta\in(x-\frac{t}{\lambda},x)$, we have $(\zeta,t+\lambda_2(\zeta-x))\in\{t\ge\lambda_1x\} \subset\{t\ge\lambda_2x\}$, according to (11) and (14), thus

$$c_2(x,t)=c_2^B(t-\lambda_2x)+\alpha\int_0^{x} c_1^B(t-\lambda_2x-(\lambda_1-\lambda_2)\zeta)e^{-\alpha\zeta}d\zeta$$

$$=c_2^B(t-\lambda_2x)+\frac{\alpha e^{-\frac{\alpha(t-\lambda_2x)}{\lambda_1-\lambda_2}}}{\lambda_1\text{-}\lambda_2}\int_{t-\lambda_1x}^{t-\lambda_2x} c_1^B(y)e^{\frac{\alpha y}{\lambda_1-\lambda_2}}dy.$$

To sum up,

$$c_2(x,t)=\begin{cases} c_2^I(x-\frac{t}{\lambda_2})+\frac{\alpha\lambda_1 e^{-\frac{\alpha(t-\lambda_2x)}{\lambda_1-\lambda_2}}}{\lambda_1\text{-}\lambda_2}\int_{x-\frac{t}{\lambda_2}}^{x-\frac{t}{\lambda_1}} c_1^I(y)e^{-\frac{\alpha\lambda_2 y}{\lambda_1-\lambda_2}}dy,\ t<\lambda_2x \\ c_2^B(t-\lambda_2x)+\frac{\alpha e^{-\frac{\alpha(t-\lambda_2x)}{\lambda_1-\lambda_2}}}{\lambda_1\text{-}\lambda_2}\int_0^{t-\lambda_2x} c_1^B(y)e^{\frac{\alpha y}{\lambda_1-\lambda_2}}dy \\ +\frac{\alpha\lambda_1 e^{-\frac{\alpha(t-\lambda_2x)}{\lambda_1-\lambda_2}}}{\lambda_1\text{-}\lambda_2}\int_{x-\frac{t}{\lambda_2}}^{x-\frac{t}{\lambda_1}} c_1^I(y)e^{-\frac{\alpha\lambda_2 y}{\lambda_1-\lambda_2}}dy,\ \lambda_2x\le t<\lambda_1x \\ c_2^B(t-\lambda_2x)+\frac{\alpha e^{-\frac{\alpha(t-\lambda_2x)}{\lambda_1-\lambda_2}}}{\lambda_1\text{-}\lambda_2}\int_{t-\lambda_1x}^{t-\lambda_2x} c_1^B(y)e^{\frac{\alpha y}{\lambda_1-\lambda_2}}dy,\ t\ge\lambda_1x. \end{cases} \tag{16}$$



(a) $\lambda_2<\lambda_1$ (b) $\lambda_2>\lambda_1$

Fig. 1. Fragments range of c_2.

In the case of $\lambda_2 > \lambda_1$, see Fig. 1(b).

(i) $\forall(x,t)\in\{t<\lambda_1 x\}$, for $\zeta\in(x-\frac{t}{\lambda_2},x)$, we had $(\zeta,t+\lambda_2(\zeta-x))\in\{t<\lambda_1 x\}\subset\{t<\lambda_2 x\}$, according to (11) and (14), thus

$$c_2(x,t)=c_2^I(x-\frac{t}{\lambda_2})+\alpha\int_{x-\frac{t}{\lambda_2}}^{x}c_1^I(\zeta-\frac{t+\lambda_2(\zeta-x)}{\lambda_1})e^{-\frac{\alpha[t+\lambda_2(\zeta-x)]}{\lambda_1}}d\zeta$$

$$=c_2^I(x-\frac{t}{\lambda_2})+\frac{\alpha\lambda_1 e^{-\frac{\alpha(\lambda_2 x-t)}{\lambda_2-\lambda_1}}}{\lambda_2-\lambda_1}\int_{x-\frac{t}{\lambda_1}}^{x-\frac{t}{\lambda_2}}c_1^I(y)e^{\frac{\alpha\lambda_2 y}{\lambda_2-\lambda_1}}dy.$$

(ii) $\forall(x,t)\in\{\lambda_1 x\le t<\lambda_2 x\}$

The intersection of the characteristic curve of c_2 over (x, t) and the line $t=\lambda_1 x$ was $(\gamma,\eta)=(\frac{\lambda_2 x-t}{\lambda_2-\lambda_1},\frac{\lambda_1(\lambda_2 x-t)}{\lambda_2-\lambda_1})$, see Fig. 1(b), for $\zeta\in(x-\frac{t}{\lambda_2},\gamma)$, we had $(\zeta,t+\lambda(\zeta-x))\in\{t<\lambda_1 x\}\subset\{t<\lambda_2 x\}$, and for $\zeta\in(\gamma,x)$ we had $(\zeta,t+\lambda(\zeta-x))\in\{\lambda_1 x\le t<\lambda_2 x\}$, according to (11) and (14), thus

$$c_2(x,t)=c_2^I(x-\frac{t}{\lambda_2})+\alpha\int_{x-\frac{t}{\lambda_2}}^{\frac{\lambda_2 x-t}{\lambda_2-\lambda_1}}c_1^I(\zeta-\frac{t+\lambda_2(\zeta-x)}{\lambda_1})e^{-\frac{\alpha(t+\lambda_2(\zeta-x))}{\lambda_1}}d\zeta$$
$$+\alpha\int_{\frac{\lambda_2 x-t}{\lambda_2-\lambda_1}}^{x}c_1^B(t-\lambda_2 x+(\lambda_2-\lambda_1)\zeta)e^{-\alpha\zeta}d\zeta$$

$$=c_2^I(x-\frac{t}{\lambda_2})+\frac{\alpha\lambda_1 e^{-\frac{\alpha(\lambda_2 x-t)}{\lambda_2-\lambda_1}}}{\lambda_2-\lambda_1}\int_0^{x-\frac{t}{\lambda_2}}c_1^I(y)e^{\frac{\alpha\lambda_2 y}{\lambda_2-\lambda_1}}dy$$
$$+\frac{\alpha e^{-\frac{\alpha(\lambda_2 x-t)}{\lambda_2-\lambda_1}}}{\lambda_2-\lambda_1}\int_0^{t-\lambda_1 x}c_1^B(y)e^{-\frac{\alpha y}{\lambda_2-\lambda_1}}dy.$$

(iii) $\forall(x,t)\in\{t\ge\lambda_2 x\}$, for $\zeta\in(0,x)$, we had $(\zeta,t+\lambda_2(\zeta-x))\in\{t\ge\lambda_2 x\}\subset\{t\ge\lambda_1 x\}$, according to (11) and (14), thus

$$c_2(x,t)=c_2^B(t-\lambda_2 x)+\alpha\int_0^x c_1^B(t-\lambda_2 x+(\lambda_2-\lambda_1)\zeta)e^{-\alpha\zeta}d\zeta$$

$$=c_2^B(t-\lambda_2 x)+\frac{\alpha e^{-\frac{\alpha(\lambda_2 x-t)}{\lambda_2-\lambda_1}}}{\lambda_2-\lambda_1}\int_{t-\lambda_2 x}^{t-\lambda_1 x}c_1^B(y)e^{-\frac{\alpha y}{\lambda_2-\lambda_1}}dy.$$

To sum up,

$$c_2(x,t)=\begin{cases}c_2^I(x-\frac{t}{\lambda_2})+\frac{\alpha\lambda_1 e^{-\frac{\alpha(\lambda_2 x-t)}{\lambda_2-\lambda_1}}}{\lambda_2-\lambda_1}\int_{x-\frac{t}{\lambda_1}}^{x-\frac{t}{\lambda_2}}c_1^I(y)e^{\frac{\alpha\lambda_2 y}{\lambda_2-\lambda_1}}dy,\ t<\lambda_1 x\\ c_2^I(x-\frac{t}{\lambda_2})+\frac{\alpha\lambda_1 e^{-\frac{\alpha(\lambda_2 x-t)}{\lambda_2-\lambda_1}}}{\lambda_2-\lambda_1}\int_0^{x-\frac{t}{\lambda_2}}c_1^I(y)e^{\frac{\alpha\lambda_2 y}{\lambda_2-\lambda_1}}dy\\ +\frac{\alpha e^{-\frac{\alpha(\lambda_2 x-t)}{\lambda_2-\lambda_1}}}{\lambda_2-\lambda_1}\int_0^{t-\lambda_1 x}c_1^B(y)e^{-\frac{\alpha y}{\lambda_2-\lambda_1}}dy,\ \lambda_1 x\le t<\lambda_2 x\\ c_2^B(t-\lambda_2 x)+\frac{\alpha e^{-\frac{\alpha(\lambda_2 x-t)}{\lambda_2-\lambda_1}}}{\lambda_2-\lambda_1}\int_{t-\lambda_2 x}^{t-\lambda_1 x}c_1^B(y)e^{-\frac{\alpha y}{\lambda_2-\lambda_1}}dy,\ t\ge\lambda_2 x.\end{cases}\quad(17)$$

4. Wide Pulse Injection

Chromatographic process started from the boundary, and there were many types of the boundary conditions, such as the methods of delta-pulse, head-on, wide pulse, gradual change head-on, gradual change wide pulse, etc; whose corresponding boundary condition was not zero. Where, wide pulse was the most common way of chromatography injection method, its initial state of chromatography column was typically empty, so the initial condition was the follows,

$$c_1^I(x)\equiv 0,\ c_2^I(x)\equiv 0.\quad(18)$$

And the corresponding injection function was given as follows,

$$c_1^B(t)=\begin{cases}c_{10},\ 0<t\le t_p\\ 0,\ t_p<t,\end{cases}\quad c_2^B(x)\equiv 0.\quad(19)$$

where, t_p was the injection time, c_{10} was the injection rate, both of them are constant. So, in the case of wide pulse, c_1, c_2 satisfied the following the initial-boundary value problem (6), (7), (18) and (19). If the column length was L, outflow curve refers to the function of c_1 and c_2 when $x = L$. The character state of outflow curve was an important parameter of chromatographic process.

In this paper, pulse width was taken as an example, the solution of concentration wave for reactant and resultant were derived detailedly, and then according to the obtained explicit expressions of c_1 and c_2, the shape of the outflow curve were further analyzed in a variety of situations, providing theoretical models for the chromatographic quantitative analysis.

According to the equations (11), (15), (16) and (17), we had the explicit solution expressions of c_1 and c_2 as the follows,

$$c_1(x,t)=\begin{cases}0, & t<\lambda_1 x\\ c_1^B(t-\lambda_1 x)e^{-\alpha x}, & t\ge\lambda_1 x,\end{cases} \tag{20}$$

When $\lambda_2=\lambda_1=\lambda$

$$c_2(x,t)=\begin{cases}0, & t<\lambda x\\ c_1^B(t-\lambda x)(1-e^{-\alpha x}), & t\ge\lambda x,\end{cases} \tag{21}$$

When $\lambda_2<\lambda_1$

$$c_2(x,t)=\begin{cases}0, & t<\lambda_2 x\\ \dfrac{\alpha e^{-\frac{\alpha(t-\lambda_2 x)}{\lambda_1-\lambda_2}}}{\lambda_1-\lambda_2}\displaystyle\int_0^{t-\lambda_2 x} c_1^B(y)e^{\frac{\alpha y}{\lambda_1-\lambda_2}}dy, & \lambda_2 x\le t<\lambda_1 x\\ \dfrac{\alpha e^{-\frac{\alpha(t-\lambda_2 x)}{\lambda_1-\lambda_2}}}{\lambda_1-\lambda_2}\displaystyle\int_{t-\lambda_1 x}^{t-\lambda_2 x} c_1^B(y)e^{\frac{\alpha y}{\lambda_1-\lambda_2}}dy, & t\ge\lambda_1 x,\end{cases} \tag{22}$$

When $\lambda_2>\lambda_1$

$$c_2(x,t)=\begin{cases}0, & t<\lambda_1 x\\ \dfrac{\alpha e^{-\frac{\alpha(\lambda_2 x-t)}{\lambda_2-\lambda_1}}}{\lambda_2-\lambda_1}\displaystyle\int_0^{t-\lambda_1 x} c_1^B(y)e^{\frac{\alpha y}{\lambda_1-\lambda_2}}dy, & \lambda_1 x\le t<\lambda_2 x\\ \dfrac{\alpha e^{-\frac{\alpha(\lambda_2 x-t)}{\lambda_2-\lambda_1}}}{\lambda_2-\lambda_1}\displaystyle\int_{t-\lambda_2 x}^{t-\lambda_1 x} c_1^B(y)e^{\frac{\alpha y}{\lambda_1-\lambda_2}}dy, & t\ge\lambda_2 x.\end{cases} \tag{23}$$

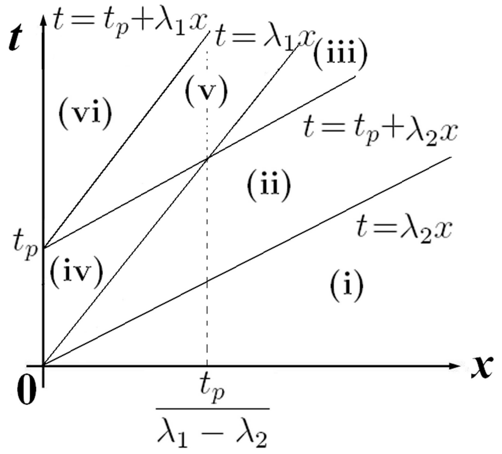
Put (16) into (17), we easily got,

$$c_1(x,t)=\begin{cases}0, & 0<t<\lambda_1 x\\ c_{10}e^{-\alpha x}, & \lambda_1 x\le t\le t_p+\lambda_1 x\\ 0, & t_p+\lambda_1 x<t\end{cases} \tag{24}$$

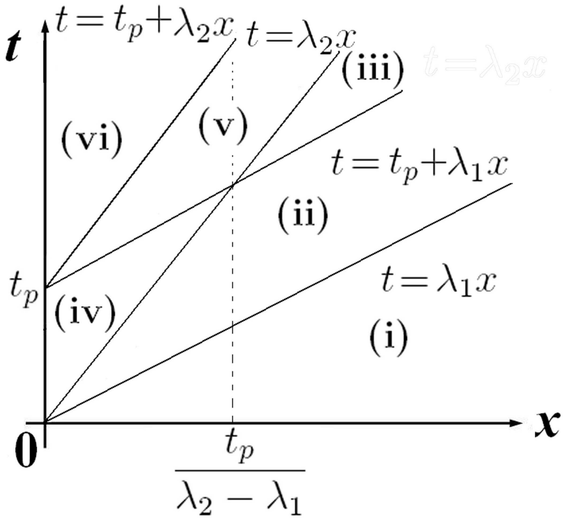
When $\lambda_2=\lambda_1=\lambda$, we got the same situations as the fragments range of c_1, similarly we got,

$$c_2(x,t)=\begin{cases}0, & 0<t<\lambda x\\ c_{10}(1-e^{-\alpha x}), & \lambda x\le t\le t_p+\lambda x\\ 0, & t_p+\lambda x<t.\end{cases} \tag{25}$$

When $\lambda_2<\lambda_1$, the fragments range of c_2 was showed in Fig.2(a).



(a) $\lambda_2<\lambda_1$



(b) $\lambda_2>\lambda_1$

Fig. 2. Fragments range of c_2, in case of pulse width injection.

(i) $\forall(x,t)\in\{0<t<\lambda_2 x\}\overset{def}{=}\Omega_1,\ c_2(x,t)=0$

(ii) $\forall(x,t)\in\{\lambda_2 x\le t<\lambda_1 x,\ t\le t_p+\lambda_2 x\}\overset{def}{=}\Omega_2$

$$c_2(x,t)=\frac{\alpha e^{-\frac{\alpha(t-\lambda_2 x)}{\lambda_1-\lambda_2}}}{\lambda_1-\lambda_2}\int_0^{t-\lambda_2 x} c_{10}e^{\frac{\alpha y}{\lambda_1-\lambda_2}}dy=c_{10}(1-e^{-\frac{\alpha(t-\lambda_2 x)}{\lambda_1-\lambda_2}}).$$

(iii) $\forall(x,t)\in\{\lambda_2 x\le t<\lambda_1 x,\ t\ge t_p+\lambda_2 x\}\overset{def}{=}\Omega_3$

$$c_2(x,t)=\frac{\alpha e^{-\frac{\alpha(t-\lambda_2 x)}{\lambda_1-\lambda_2}}}{\lambda_1-\lambda_2}\int_0^{t_p} c_{10}e^{\frac{\alpha y}{\lambda_1-\lambda_2}}dy=c_{10}e^{-\frac{\alpha(t-\lambda_2 x)}{\lambda_1-\lambda_2}}(e^{\frac{\alpha t_p}{\lambda_1-\lambda_2}}-1).$$

(iv) $\forall(x,t)\in\{\lambda_1 x\le t\le t_p+\lambda_2 x\}\overset{def}{=}\Omega_4$

$$c_2(x,t)=\frac{\alpha e^{-\frac{\alpha(t-\lambda_2 x)}{\lambda_1-\lambda_2}}}{\lambda_1\text{-}\lambda_2}\int_{t-\lambda_1 x}^{t-\lambda_2 x} c_{10}e^{\frac{\alpha y}{\lambda_1-\lambda_2}}dy=c_{10}(1-e^{-\alpha x}).$$

(v) $\forall(x,t)\in\{\lambda_1 x\le t,\ t_p+\lambda_2 x\le t\le t_p+\lambda_1 x\}\overset{def}{=}\Omega_5$

$$c_2(x,t)=\frac{\alpha e^{-\frac{\alpha(t-\lambda_2 x)}{\lambda_1-\lambda_2}}}{\lambda_1\text{-}\lambda_2}\int_{t-\lambda_1 x}^{t_p} c_{10}e^{\frac{\alpha y}{\lambda_1-\lambda_2}}dy=c_{10}(e^{\frac{\alpha(t_p+\lambda_2 x-t)}{\lambda_1-\lambda_2}}-e^{-\alpha x}).$$

(vi) $\forall(x,t)\in\{\ t>t_p+\lambda_1 x\}\overset{def}{=}\Omega_6,\ c_2(x,t)=0.$

So we got,

$$c_2(x,t)=\begin{cases}0, & (x,t)\in\Omega_1\\ c_{10}(1-e^{-\frac{\alpha(t-\lambda_2 x)}{\lambda_1-\lambda_2}}), & (x,t)\in\Omega_2\\ c_{10}e^{-\frac{\alpha(t-\lambda_2 x)}{\lambda_1-\lambda_2}}(e^{\frac{\alpha t_p}{\lambda_1-\lambda_2}}-1), & (x,t)\in\Omega_3\\ c_{10}(1-e^{-\alpha x}), & (x,t)\in\Omega_4\\ c_{10}(e^{\frac{\alpha(t_p+\lambda_2 x-t)}{\lambda_1-\lambda_2}}-e^{-\alpha x}), & (x,t)\in\Omega_5\\ 0, & (x,t)\in\Omega_6.\end{cases}\tag{26}$$

When $\lambda_2>\lambda_1$, the fragments range of c_2 was showed in Fig. 2 (b). Similar to the calculation method as used when $\lambda_2<\lambda_1$, we got:

$$c_2(x,t)=\begin{cases}0, & (x,t)\in\Omega_1'\\ c_{10}(e^{-\frac{\alpha(\lambda_2 x-t)}{\lambda_2-\lambda_1}}-e^{-\alpha x}), & (x,t)\in\Omega_2'\\ c_{10}e^{-\frac{\alpha(\lambda_2 x-t)}{\lambda_2-\lambda_1}}(1-e^{-\frac{\alpha t_p}{\lambda_2-\lambda_1}}), & (x,t)\in\Omega_3'\\ c_{10}(1-e^{-\alpha x}), & (x,t)\in\Omega_4'\\ c_{10}(1-e^{\frac{\alpha(t_p+\lambda_2 x-t)}{\lambda_1-\lambda_2}}), & (x,t)\in\Omega_5'\\ 0, & (x,t)\in\Omega_6',\end{cases}\tag{27}$$

where

$$\Omega_1'\overset{def}{=}\{0<t<\lambda_1 x\},$$
$$\Omega_2'\overset{def}{=}\{\lambda_1 x\le t<\lambda_2 x,\ t\le t_p+\lambda_1 x\}$$
$$\Omega_3'\overset{def}{=}\{\lambda_1 x\le t<\lambda_2 x,\ t\ge t_p+\lambda_1 x\}$$
$$\Omega_4'\overset{def}{=}\{\lambda_2 x\le t\le t_p+\lambda_1 x\}$$
$$\Omega_5'\overset{def}{=}\{t_p+\lambda_1 x\le t\le t_p+\lambda_2 x, t\ge\lambda_2 x\}$$
$$\Omega_6'\overset{def}{=}\{t>t_p+\lambda_2 x\}.$$

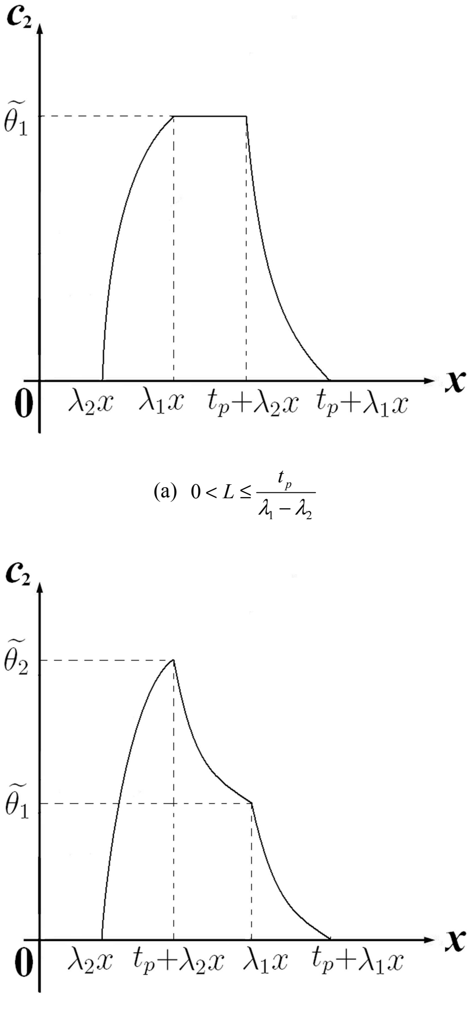
Next, we discussed the shape of the outflow curves. According to (24), the outflow curve of c1 was the follows,

$$c_1(L,t)=\begin{cases}0, & 0<t<\lambda_1 L\\ c_{10}e^{-\alpha L}, & \lambda_1 L\le t\le t_p+\lambda_1 L\\ 0, & t_p+\lambda_1 L<t,\end{cases}\tag{28}$$

the outflow curve of c_2, and we divided it into the following three conditions for analysis.

When $\lambda_1=\lambda_2=\lambda$, according to (25), the outflow curve of c_2 was the follows,

$$c_2(L,t)=\begin{cases}0, & 0<t<\lambda_2 L\\ c_{10}(1-e^{-\alpha L}), & \lambda_2 L\le t\le t_p+\lambda_2 L\\ 0, & t_p+\lambda_2 L<t.\end{cases}\tag{29}$$



(b) $L\ge\frac{t_p}{\lambda_1-\lambda_2}$

Fig. 3. Outflow curve of c_2 when $\lambda_2<\lambda_1$, in case of pulse width injection.

When $\lambda_2<\lambda_1$, the intersection of the line $t=\lambda_1 x$ and the line $t=t_p+\lambda_2 x$ was $(\frac{t_p}{\lambda_1-\lambda_2},\frac{\lambda_1 t_p}{\lambda_1-\lambda_2})$. If $0<L\le\frac{t_p}{\lambda_1-\lambda_2}$, then, c_2 can be divided into five regions: Ω_1, Ω_2, Ω_4, Ω_5, Ω_6, and according to (26), the outflow curve of c_2 was the follows,

$$c_2(L,t)=\begin{cases}0, & t\in\Omega_1(L)\\ c_{10}(1-e^{-\frac{\alpha(t-\lambda_2 L)}{\lambda_1-\lambda_2}}), & t\in\Omega_2(L)\\ c_{10}(1-e^{-\alpha L}), & t\in\Omega_4(L)\\ c_{10}(e^{\frac{\alpha(t_p+\lambda_2 L-t)}{\lambda_1-\lambda_2}}-e^{-\alpha L}), & t\in\Omega_5(L)\\ 0, & t\in\Omega_6(L).\end{cases} \tag{30}$$

It was also shown in Fig. 3(a). If $\frac{t_p}{\lambda_1-\lambda_2}\le L$, then, c_2 can be divided into five regions: Ω_1, Ω_2, Ω_3, Ω_5, Ω_6, and according to (26), the outflow curve of c_2 was the follows,

$$c_2(L,t)=\begin{cases}0, & t\in\Omega_1(L)\\ c_{10}(1-e^{-\frac{\alpha(t-\lambda_2 L)}{\lambda_1-\lambda_2}}), & t\in\Omega_2(L)\\ c_{10}e^{-\frac{\alpha(t-\lambda_2 L)}{\lambda_1-\lambda_2}}(e^{\frac{\alpha t_p}{\lambda_1-\lambda_2}}-1), & t\in\Omega_3(L)\\ c_{10}(e^{\frac{\alpha(t_p+\lambda_2 L-t)}{\lambda_1-\lambda_2}}-e^{-\alpha L}), & t\in\Omega_5(L)\\ 0, & t\in\Omega_6(L).\end{cases} \tag{31}$$

It was also shown in Fig. 3(b).

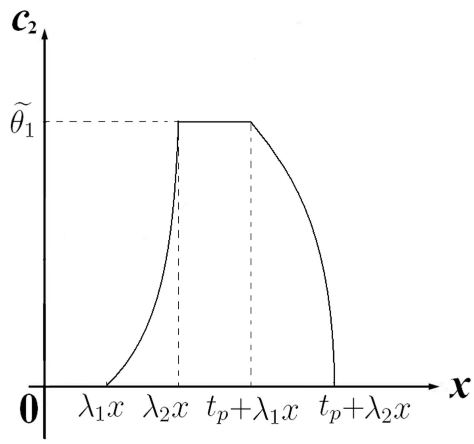
When $\lambda_2>\lambda_1$, the intersection of the line $t=\lambda_2 x$ and the line $t=t_p+\lambda_1 x$ was $(\frac{t_p}{\lambda_2-\lambda_1},\frac{\lambda_2 t_p}{\lambda_2-\lambda_1})$. If $0<L\le\frac{t_p}{\lambda_2-\lambda_1}$, then, c_2 can be divided into five regions: Ω_1, Ω_2, Ω_4, Ω_5, Ω_6, and according to (24), the outflow curve of c_2 was the follows,

$$c_2(L,t)=\begin{cases}0, & t\in\Omega_1'(L)\\ c_{10}(e^{-\frac{\alpha(\lambda_2 L-t)}{\lambda_2-\lambda_1}}-e^{-\alpha L}), & t\in\Omega_2'(L)\\ c_{10}(1\text{-}e^{-\alpha L}), & t\in\Omega_4'(L)\\ c_{10}(1-e^{-\frac{\alpha(t_p+\lambda_2 L-t)}{\lambda_2-\lambda_1}}), & t\in\Omega_5'(L)\\ 0, & t\in\Omega_6'(L),\end{cases} \tag{32}$$

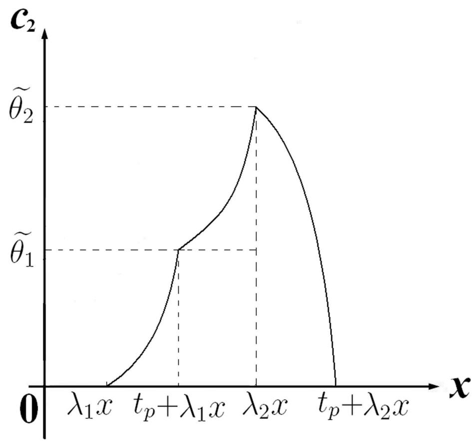
also was showed in Fig. 4(a). If $\frac{t_p}{\lambda_2-\lambda_1}\le L$, then, c_2 can be divided into five regions: Ω_1, Ω_2, Ω_3, Ω_5, Ω_6, and according to (27), the outflow curve of c_2 was the follows,

$$c_2(L,t)=\begin{cases}0, & t\in\Omega_1'(L)\\ c_{10}(e^{-\frac{\alpha(\lambda_2 L-t)}{\lambda_2-\lambda_1}}-e^{-\alpha L}), & t\in\Omega_2'(L)\\ c_{10}e^{-\frac{\alpha(\lambda_2 L-t)}{\lambda_2-\lambda_1}}(1\text{-}e^{-\frac{\alpha t_p}{\lambda_2-\lambda_1}}), & t\in\Omega_3'(L)\\ c_{10}(1-e^{-\frac{\alpha(t_p+\lambda_2 L-t)}{\lambda_2-\lambda_1}}), & t\in\Omega_5'(L)\\ 0, & t\in\Omega_6'(L),\end{cases} \tag{33}$$

It was also shown in Fig. 4 (b).



(a) $0<L\le\frac{t_p}{\lambda_2-\lambda_1}$



(b) $L\ge\frac{t_p}{\lambda_2-\lambda_1}$

Fig. 4. Outflow curve of c_2 when $\lambda_2>\lambda_1$, in case of pulse width injection.

5. Conclusion

The concentration wave equations of the chromatography process with a reaction $A\rightarrow B$ were a system of two nonlinear hyperbolic PDE's, which was a hard mathematical problem. But in some practical situations, the reaction chromatography model can be simplified to a semi-coupled system of two linear hyperbolic PDE's. In which, the reactant concentration wave model was the initial-boundary value problem of a self-closed hyperbolic PDE, while the resultant concentration wave model was the initial-boundary value problem of hyperbolic PDE coupling reactant concentration. The explicit expressions for the concentration wave of the reactants and resultants were constructed by characteristic curve method in general situations. The case of pulse width injection was taken as an example, the solution of concentration wave for reactant and resultant were derived detailedly, and then the shape of the outflow curves were further analyzed in a variety of situations, providing the proper theory models for further chromatographic data analysis.

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