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MODELING AND NUMERICAL SIMULATION OF TWO SPECIES SEPARATION USING NON-LINEAR HPLC CHROMATOGRAPHY

*** Ali Taghvaie Nakhjiri and Amir Heydarinasab**

Department of Chemical Engineering, Science and Research Branch, Islamic Azad University, Tehran, Iran.

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ABSTRACT

High performance liquid chromatography (HPLC) can be regarded as one of the most usual and widespread separation techniques in different sciences. In this paper, the role of important parameters like chromatography column and the mobile phase on the separation efficiency has been investigated. The modelling and simulation of the separation process of two species was done using finite element method (FEM). Two simulations were done in this work. The first simulation was about the separation of two species with similar concentration and the second simulation was about the separation process of two species with different concentration. The modelling and simulation results showed that the concentration of species has direct relationship with the time of separation and the width and shape of each area are considerably influenced by the migration and movement of analyte in the non-linear domain of absorption isotherm.

1. INTRODUCTION

Chromatography defines as a group of methods which are usually used for separating mixtures of various compounds into their individual components. The fundamental arrangement of a chromatographic system consists of two phases. One phase is stationary and the other phase is mobile. A compound, known as Solute, is introduced into the system, and necessarily has a selection. If it is absorbed to the mobile phase (have the attractions of van der Waal to the mobile phase) it will move through the system with the mobile phase. It will lag behind, if it is absorbed to the stationary phase. It's quite comprehensible that some solute components with some degree of attraction for both phases move through the system with some intermediate travel rate (ITR) [1, 2]. The first report about the use of a chromatographic system was announced by Mikhail Tswett, a chemist from Estonia in 1903 [3]. High performance liquid chromatography (HPLC) is a technology which is used to separate a combination of compounds in analytical chemistry and biochemistry with the aim of perceiving, identifying, quantifying or purifying the individual compounds of the mixture. Before the invention of HPLC, chemists and biochemists had column chromatography at their disposal, and column chromatography was time consuming [4].

In HPLC technique, an injector introduces a sample as a region in a mobile phase of liquid. The mobile phase including the sample zone is pumped through a column including an immobile phase of solid [5]. The mobile and immobile phases are chosen so that the components of sample are distributed to varying degrees between the two phases. Those components adsorb to the stagnant phase move only slowly with the flow of the mobile phase, and those compounds that are weakly adsorbed move faster. As the sample region migrates through the column, the components are separated into discrete zones that are identified in a detector, located after the outlet of the column [6].

The HPLC parameters, similar to the other operational instrument, are important and are dependent on sample. The solvent mixture, including a strong solvent and a include water, methanol and acetonitrile [7]. In this paper, as a novel work, the numerical simulation of the separation process of two species was done by

Corresponding author:* **Ali Taghvaie Nakhjiri, Email: taghvaiali@yahoo.com
Department of Chemical Engineering, Science and Research Branch, Islamic Azad University, Tehran, Iran.

a finite element method. Once the separation of two species was simulated when two species had similar concentration and in the second time the simulation was done in the state of different concentration. Chromatography general rate model is the most detailed and comprehensive model of all the transport models and has been applied to explain both linear and nonlinear chromatographic systems [8-11]. The development of this model (general rate model) was done by berninger et al [10].They evaluated the probability of reactions in mobile and immobile phases.

The modern form of chromatography technique was appeared in 50s decade. An important change in the concept of chromatography was because of martin and synge research [12].There are Several chromatographic models in the scientific literature for demonstrating the behavior of chromatographic operations. Important models involve chromatographic general rate model, lumped kinetic model and the equilibrium-dispersive model [13, 14]. The equilibrium dispersive model (EDM) is formed based on fundamental assumptions that are presented as following [13-15]:

1. A continuous equilibrium is assumed between immobile and mobile phases in different positions of the column.
2. Radial concentration gradients aren't existed in the column.
3. It is assumed that compressibility of mobile phase is negligible.
4. There is no interaction between the carrier (solvent) and solid phase.

2. MATERIAL AND METHODS

2.1. Model Development

This model investigates two species separation under nonlinear chromatography conditions, where the concentration of analyte is high, and the geometry is 1-D. The governing equation for analyte transport through a chromatographic column, with constant porosity, is defined as follows [8]:

$$\left(\varepsilon + \rho_b k_{p,i}\right)\frac{\partial c_i}{\partial t} + u.\nabla c_i = \nabla.\left[D_{D,i} + \varepsilon\tau_{F,i}D_{F,i}\right] \quad (1)$$

In this equation, ε is the porosity, ρ_b is bulk density of the column solid phase, c_i is the concentration of component i, $k_{P,i}$ is the adsorption isotherm and u is the volume average velocity of the fluid phase (m/s).The second term in the right hand side renders the combination of the solutes, consisting of mechanical mixing (dispersion) and molecular diffusion.

The two last terms on the right-hand side are regarded as reaction rate term and a fluid source term. If you neglect the chromatographic zone dispersion during the migration, the mass transport equation can be described as follows:

$$\frac{S\left(\rho(1-\varepsilon)\right)}{\varepsilon}\frac{\partial n_i}{\partial t} + \frac{\partial c_i}{\partial t} = -\frac{\vartheta}{\varepsilon A}\frac{\partial c_i}{\partial x} \quad (2)$$

Where ρ is the density of the solid particles, S is the specific surface area of the particles in the column, ε is the porosity of the column, A renders the inner area of the column tube, n_i is regarded as the analyte concentration in the stationary phase of component i, ci equals the concentration of analyte in the mobile phase of component i and v is mobile phase flow. The ideal model for chromatography having been applied in Equation 1, assumes that the equilibrium for the analyte between the stationary and mobile phases is rapid, that is [16]:

$$\frac{\partial c_{p,i}}{\partial t} = \frac{\partial c_{p,i}}{\partial c_i}\frac{\partial c_i}{\partial t} = k_{p,i} \quad (3)$$

In this equation, $C_{p,i}$ is defined as the concentration of component having been adsorbed to the solid (moles per dry unit). Therefore, the mass transport equation for the model of ideal chromatography is defined as [8]:

$$\left(\frac{1 + S\left(\rho(1-\varepsilon)\right)}{\varepsilon}\frac{\partial n}{\partial c}\right) + \frac{\partial c_i}{\partial t} = -\frac{\vartheta}{\varepsilon A}\frac{\partial c_i}{\partial x} \quad (4)$$

The dispersion or band broadening of the analyte zone which is achieved during the migration through the column is a conclusion of a great number of processes that the analyte experiences (for example, heterogeneous flow and diffusion in pores and the mobile phase).Therefore, It is feasible to explain the

dispersion as a diffusion process with an effective diffusion constant, D_{eff}. Thus, D_{eff} is a measure of the efficiency of chromatographic system for a particular analyte.

This constant is related to the concept of the height equivalent of a theoretical plate, *H*, which is applied in chromatographic practice. It can be illustrated that [9]:

$$D_{eff} = \frac{Hv_{z,i}}{2} \tag{5}$$

It can be expressed in this equation that v_{zi} is the velocity of migration of the analyte zone through the column. A mass balance which includes the zone-dispersion term renders the following equation [10]:

$$\left(1 + \varphi \frac{dn}{dc}\right)\frac{\partial c_i}{\partial t} = -\vartheta \frac{\partial c_i}{\partial x} + D_{eff}\frac{\partial^2 c_i}{\partial x^2} \tag{6}$$

Here $v_1 = v/(\varepsilon A)$ presents the linear velocity of movable phase in the column, $\varphi = S\rho(1-\varepsilon)/\varepsilon$ renders the phase ratio of the column, and D_{eff} is the effective diffusion constant. It is assumed that Langmuir adsorption isotherm is used for both components as follow [10]:

$$\frac{dn_i}{dc_i} = \frac{n_{0i}K_i}{(1+K_i c_i)^2} \tag{7}$$

Where K_i is the adsorption constant of component i, and n_{0i} is regarded as the monolayer capacity of the stationary phase for component i. By applying an effective zone-dispersion term, the *1-D* equation is presented as follow [10]:

$$\left(\varepsilon + \rho_b k_{p,i}\right)\frac{\partial c_i}{\partial t} + u\frac{\partial c_i}{\partial x} = \frac{\partial}{\partial x}\left(D_{eff,i}\frac{\partial c_i}{\partial x}\right) \tag{8}$$

This article investigates the migration of a chromatographic zone migrating within the column. The physical data for the column correspond to a 12 cm-by-4 mm internal diameter column having been filled with 5 μm porous particles are illustrated in Table 1. The initial concentrations for the two components are presented by the normal distribution as follow [11]:

$$C_{0i}(x) = C_{0i}e^{-a(x-0.01)^2} \tag{9}$$

Where *a* is equal with $1 \times 10^{-5}\ m^{-2}$, and the starting point at $t = 0$ is at $x = 0.01\ m$.

Table 1 Physical properties used in modeling and simulation

Name	Value	Unit
υ_1	2.22	mm/s
$D_{eff,1}$	1×10^{-8}	m^2/s
ε	0.6	
S	100	m^2/g
$D_{eff,2}$	3×10^{-8}	m^2/s
K_1	0.04	m^3/mol
K_2	0.05	m^3/mol
n_{01}	1×10^{-6}	mol/m^2
n_{02}	5×10^{-7}	mol/m^2
φ	1.533×10^{8}	m^{-1}

3. RESULT AND DISCUSSION

In this paper, at first, solving the model for the initial injector concentrations $c_{01} = c_{02} = 0.1\ mol/m^3$ is done that is correspondent with the linear regime for the adsorption isotherm. In a second stage, increase of the injector concentrations to $c_{01} = 1\ mol/m^3$ and $c_{02} = 10\ mol/m^3$ is occurred to study the accuracy of the modeling and simulation.

Figure 1 illustrates the zones of the two components at different times (0s, 80s and 160s) as they migrate within the column. In this study, the concentration of analyte at $t = 0$ is low for both components ($c_{0i} = 0.1\ mol/m^3$). The procedure of solution is in the linear domain of the adsorption isotherm. This issue indicates that the zones are normally distributed and completely symmetrical.

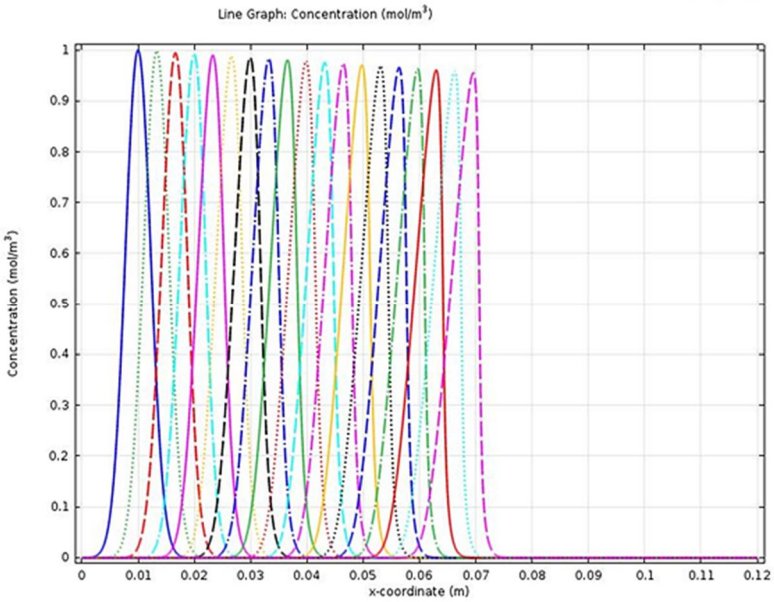

Figure1 the concentrations of components 1 (solid) and 2 (dashed) in the mobile phase during the migration through the column at times 0, 80, and 160 s for initial injector concentrations $c_{01} = c_{02} = 0.1$ mol/m^3

By increasing the initial concentrations, c_{01}= 1 mol/m^3 and c_{02} = 10 mol/m^3, the solution moves toward the nonlinear domain of the adsorption isotherm, changing the behavior radically (see Figure 2. A comparison of the zone for component 2 between two simulations apparently indicates that both the zone width and form is strongly affected by migrating into the nonlinear domain of adsorption isotherm.

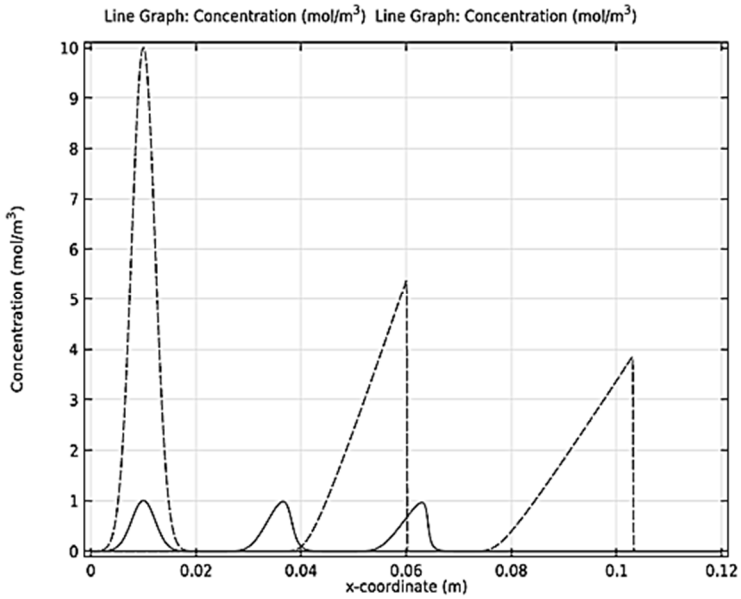

Figure 2 The concentrations of components 1 (solid) and 2 (dashed) in the mobile phase during migration through the column at times 0 s, 80 s, and 160 s for initial injector concentrations c_{01} = 1 mol/m^3 and c_{02} = 10 mol/m^3

4. CONCLUSION

It was found out from the results of modeling and simulation that the concentration of species is one of the most important parameters of species separation in chromatography technique that has direct relationship with the time of separation. The width and shape of each area are considerably influenced by the migration and movement of analyte in the non-linear domain of absorption isotherm. In the future work we are into investigate the impacts of the other important parameters such as diffusivity and the porosity of the column on increasing or decreasing the efficiency of two species separation chromatography in chromatography technique. It can be seen from the figures that by elapsing the time the concentrations of both components in the mobile phase during the migration through the column for similar initial injector concentrations of $c_{01}=c_{02} = 0.1$ *mol/m*^{3} and also for different initial injector concentrations $c_{01}= 1$ *mol/m*^{3} and $c_{02} = 10$ *mol/m*^{3} have decreased gradually that showed an acceptable separation performance.

Nomenclature

D_{eff}	effective diffusivity, m/s
c_{01},c_{02}	concentrations of components, mol/m^3
K	adsorption constant, m^3/mol
n	monolayer capacity, m^2
A	inner area of the column
t	time, s
a	normal distribution parameter, 1/m^2
u	velocity, m/s

Greek letters

ε	porosity
ρ	density, kg/m^3
φ	phase ratio, m^{-1}
υ	mobile phase flow, m^3/s

Abbreviation

HPLC	High performance liquid chromatography
FEM	finite element method
ITR	intermediate travel rate
1-D	one dimensional

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