MATHEMATICAL MODEL FOR FIXED BED SORBENT CHROMATOGRAPHY: CHROMATOGRAPHIC SEPARATOR

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Abstract

Chromatographic separation is based on the different affinity of the components of a mixture for the stationary and mobile phases. A deterministic model for chromatographic separation of two components using a granular fixed bed as a stationary phase was developed. The species to be separated were adsorbed onto the fixed bed until its saturation (saturation or sorption stage) and then they were desorbed using a fluid as an eluent (elution or desorption stage). The overall sorption rate of components was expressed as a difference between sorption and desorption rates and a plug flow with axial dispersion of mobile phase was assumed. Process dynamics were calibrated based on data reported in the related literature on the sorption/desorption of diosgenin and sclareol onto/from fixed bed imprinted polymer pearls. Good species separability for saturation stage was obtained at low levels of liquid superficial velocity and high values of fixed bed height. To obtain a desired separation in the elution stage, a mobile phase with a higher affinity for a component should be used.

Key words: chromatography, modelling, fixed bed, sorption, elution, imprinted polymer

1. Introduction

The first researches on chromatographic separation were published by the Russian botanist Mikhail Semyonovich Tsvet (also spelled Tswett), who separated plant pigments in a column filled with calcium carbonate [1]. The term of chromatographic elution, introduced by Tadeus Reichstein and Joseph von Euw, refers to the chromatographic separation of sample components by passing them through a stationary phase [2]. From 1937 until now, 12 Nobel prizes have been awarded for researches in which chromatography had an essential role, *e.g.*, Archer John Porter Martin and Richard Laurence Millington Synge won the

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Nobel Prize in Chemistry (1952) for the invention of partition chromatography [3].

As shown in Fig. 1, the chromatographic separation is based on the different affinity of the components of a sample (mixture) for the stationary phase (packed in a column) and the mobile phase (eluent flowing through the stationary phase). Concentrations of sample components along the column containing the stationary phase (Fig. 1) are shown in Fig. 2. For each mixture component, the surface under the curve that describes the variation of component concentration along the fixed bed is the same whatever the position in the bed (*e.g.*, S_A area in Fig. 2 is the same regardless of position, because this area is proportional to the amount of *A* component in the mixture).

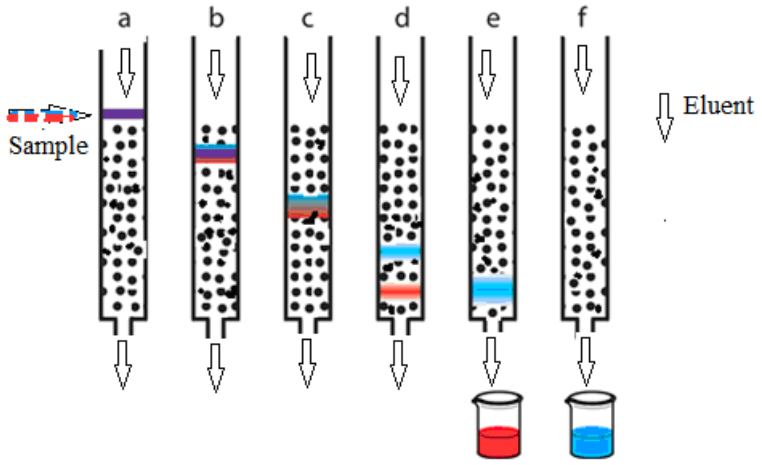

Fig. 1. The principle of chromatographic separation of two components (blue and red) by passing them through a column containing a solid stationary phase which is eluted with a mobile phase.

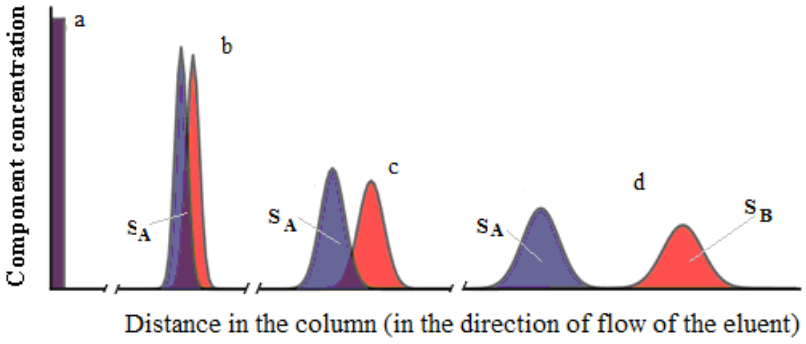

Fig. 2. Concentration of two components of a sample along the column containing the stationary phase.

As the peak of a component is completely separated from the peak of the other component (case *d* in Fig. 2), the composition of the mixture can be calculated by measuring the areas of these peaks. This is the basic principle of chromatographic analysis, a modern instrumental analysis method, which has heavily evolved over the last 10 years [4]. A scheme of a gas chromatograph and a picture of Buck Scientific Gas Chromatograph (Mass Transfer Laboratory, Faculty of Applied Chemistry and Materials Science (FACMS), UPB) are shown in Fig. 3.

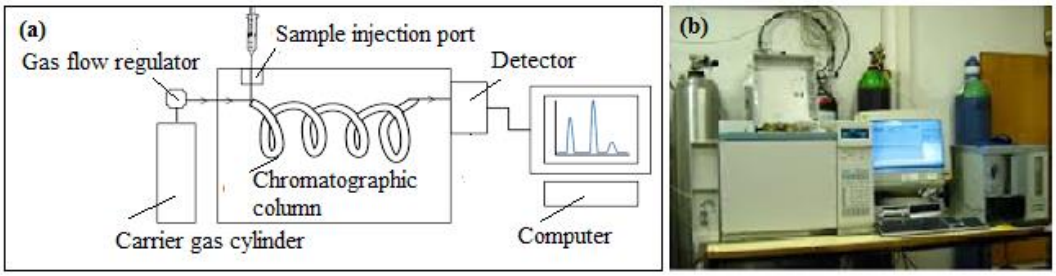

Fig. 3. Scheme of a gas chromatograph (a) and a picture of Buck Scientific Gas Chromatograph (Mass Transfer Laboratory at FACMS, UPB) (b).

Mechanisms of component separation are mainly based on adsorption, ion exchange, and size-exclusion. Often, chromatographic processes can occur through a combination of them.

The present work focuses on the modelling of the chromatographic separation of two compounds using a granular fixed bed as a stationary phase. The compounds to be separated are sorbed onto the fixed bed until its saturation and then they are desorbed using a fluid as an eluent.

2. Modelling

For a stationary phase consisting in fixed bed particles, the model selected to predict *i* (*A* and *B*) species sorption from a mobile phase has been based on the following simplifying assumptions [5-10]:

- plug flow with axial dispersion of mobile phase along the stationary phase;
- a monolayer sorption of *i* species molecules occurs onto the surface of stationary phase particles and pores walls;
- internal and external diffusion resistance is negligible;
- overall sorption rate of *i* species depends on the competition between sorption and desorption processes.

Model equations, initial and boundary conditions for sorption of *i* species from the mobile phase onto stationary phase are as follows [5-10]:

- mass balance equation for *i* species in the mobile phase flowing through the fixed bed:

$$\frac{\partial c_i}{\partial \tau} + w\frac{\partial c_i}{\partial z} = D_{li}\frac{\partial^2 c_i}{\partial z^2} - \frac{\partial c_{Si}}{\partial \tau} \quad (1)$$

- overall sorption rate equation of *i* species:

$$\frac{\partial c_{Si}}{\partial \tau} = k_{ai}\left(1 - \frac{a_1 c_{SA} + a_2 c_{SB}}{Q}\right)c_i - k_{di}c_{Si} \quad (2)$$

- initial conditions:

$$\tau = 0 \qquad 0 < z \le H \qquad c_i = 0 \quad (3)$$

$$\tau = 0 \qquad z = 0 \qquad c_i = c_{i0} \quad (4)$$

- boundary conditions:

$$\tau > 0 \qquad z = 0 \qquad \frac{\partial c_i}{\partial z} = \frac{w}{D_{li}}(c_{i0} - c_i) \quad (5)$$

$$\tau > 0 \qquad z = H \qquad \frac{\partial c_i}{\partial z} = 0 \quad (6)$$

An adequate modification of initial and boundary conditions as well as of model parameters (D_{li}, a_i, k_{ai}, k_{di}, Q, w), transforms the sorption model into the desorption (elution) model of the species retained in the stationary phase [6].

3. Results and discussions

Sorption and elution dynamics are mainly affected by superficial velocity of mobile phase flowing through stationary phase (fixed bed particles), fixed bed height, operating temperature, and characteristic parameters of solid phase [5-16].

Data from the related literature were used to predict the dynamics of sorption process of *i* species from mobile phase onto stationary phase. Table 1 contains values of characteristic parameters of sorption of diosgenin (A) and sclareol (B) from mobile phase (75% vol. alcoholic solution at 25 °C) onto fixed bed imprinted polymer (based on acrylonitrile-acrylic acid copolymer) pearls [5,6]. Axial dispersion coefficient was determined using Eq. 7 [7-10], where w (cm/s) is mobile phase superficial velocity and d_P mean particle diameter (cm).

$$D_{li} = D_l = \frac{w d_P}{2} \quad (7)$$

Graphical representations in Figs. 4-6 show the effects of superficial velocity of mobile phase (w), fixed bed height (H), and initial concentration of B species in the mobile phase (c_{B0}) on the breakthrough curves for fixed bed imprinted polymer pearls. Depicted data emphasize the following issues: (i) a good species separability is obtained at low levels of w and high values of H; (ii) separability efficiency does not depend by the values of c_{B0}; (iii) if the aim is a fast saturation of the fixed bed, *e.g.*, in order to concentrate the processed mixture, then high values of w and H are needed. Species separability in Figs. 4-6 can be quantified by a separability coefficient, $C_{sep,br}$, defined by Eq. 8 as a ratio between the period when a single component exits the fixed bed, τ_1, and the total bed breakthrough time, τ_{br}.

$$C_{sep,br} = \frac{\tau_1}{\tau_{br}} \tag{8}$$

Table 1

Characteristic parameters of sorption of A and B species from mobile phase onto stationary phase

Parameter	Symbol	Unit	Value	Value*
Sorption rate constant	k_{aA}	s^{-1}	2×10^{-2}	2×10^{-2}
	k_{aB}	s^{-1}	3×10^{-2}	3×10^{-2}
Desorption rate constant	k_{dA}	s^{-1}	1×10^{-4}	1×10^{-2}
	k_{dB}	s^{-1}	1×10^{-2}	5×10^{-2}
Constants in Eq. (2)	a_1	-	2×10^{-2}	2×10^{-2}
	a_2	-	3×10^{-2}	3×10^{-2}
Maximum monolayer sorption capacity	Q	mol/L	5×10^{-2}	5×10^{-2}

* mobile phase with higher affinity for A species

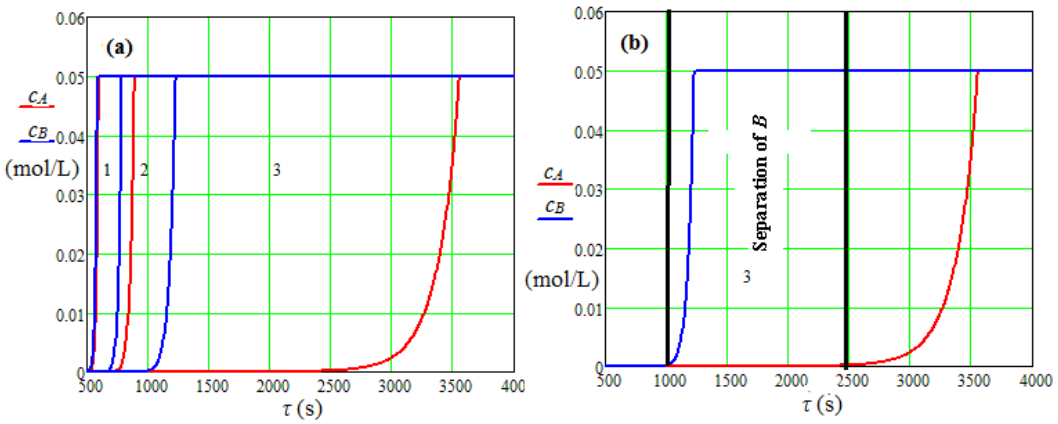

Fig. 4. Effect of superficial velocity of mobile phase on the breakthrough curves (a) and species separability (b) for fixed bed imprinted polymer pearls (H = 10 cm, d_P = 0.1 cm, $c_{A0} = c_{B0}$ = 0.050 mol/L): (1) $w = 5 \times 10^{-2}$ cm/s; (2) $w = 3 \times 10^{-2}$ cm/s; (3) $w = 1.5 \times 10^{-2}$ cm/s.

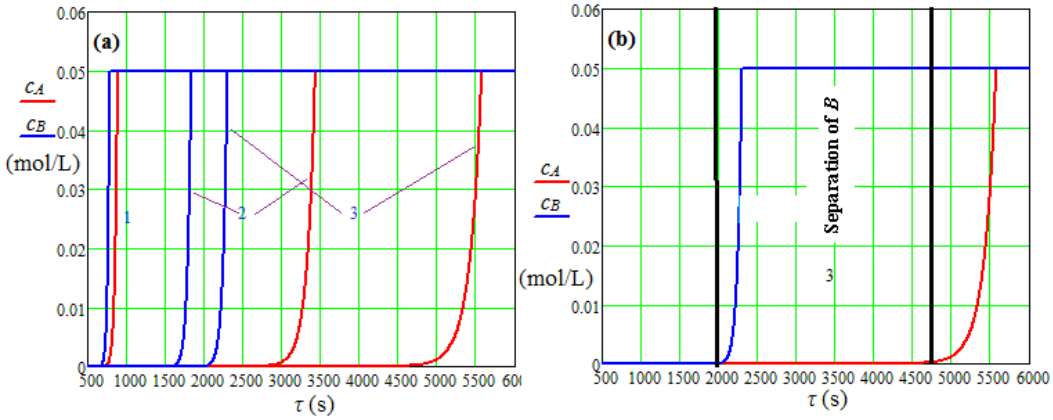

Fig. 5. Effect of fixed bed height on the breakthrough curves (a) and species separability (b) for fixed bed imprinted polymer pearls ($w = 3 \times 10^{-2}$ cm/s, $d_P = 0.1$ cm, $c_{A0} = c_{B0} = 0.050$ mol/L): (1) $H = 10$ cm; (2) $H = 20$ cm; (3) $H = 24$ cm.

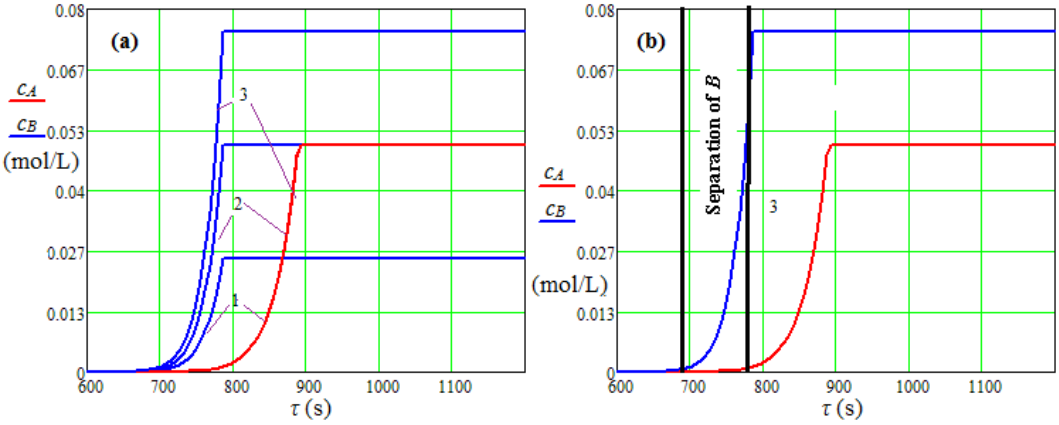

Fig. 6. Effect of initial concentration of *B* species in the mobile phase on the breakthrough curves (a) and species separability (b) for fixed bed imprinted polymer pearls ($H = 10$ cm, $d_P = 0.1$ cm, $c_{A0} = 0.050$ mol/L, $w = 3 \times 10^{-2}$ cm/s): (1) $c_{B0} = 0.025$ mol/L; (2) $c_{B0} = 0.050$ mol/L; (3) $c_{B0} = 0.075$ mol/L.

Plots in Figs. 7 and 8 show the effects of superficial velocity of mobile phase (w) and fixed bed height (H) on the elution curves for fixed bed imprinted polymer pearls. It was considered that the washing of diosgenin and sclareol retained by the stationary phase was performed using either 75% vol. alcoholic solution (the same mobile phase as in the saturation stage) at 65 °C or a mobile phase with higher affinity for A species [5,6]. A separability coefficient, $C_{sep,el}$, is defined by Eq. 9, where τ_{el} is the elution time.

$$C_{sep,el} = \frac{\tau_1}{\tau_{el}} \tag{9}$$

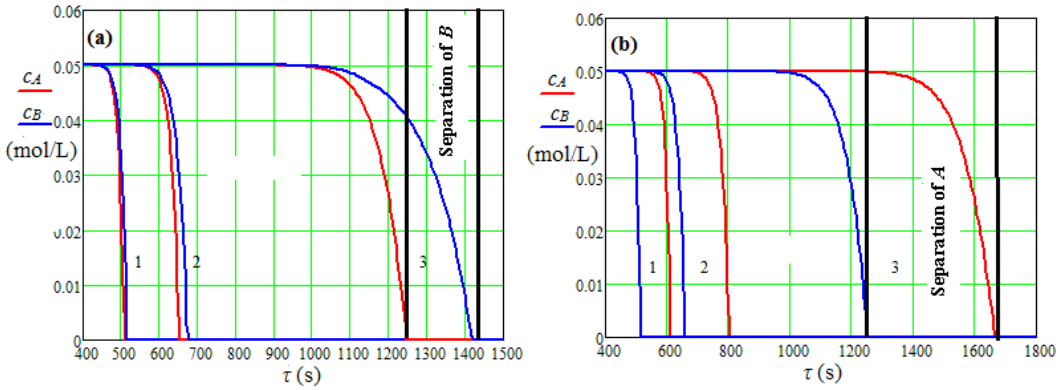

Fig. 7. Effect of superficial velocity of mobile phase on the elution curves for fixed bed imprinted polymer pearls (H = 10 cm, d_P = 0.1 cm, c_{SA0} = 0.014 mol/L, c_{SB0} = 0.048 mol/L):
(1) $w = 5 \times 10^{-2}$ cm/s; (2) $w = 3 \times 10^{-2}$ cm/s; (3) $w = 1.5 \times 10^{-2}$ cm/s ((a) the same mobile phase as in the saturation stage; (b) mobile phase with higher affinity for A species).

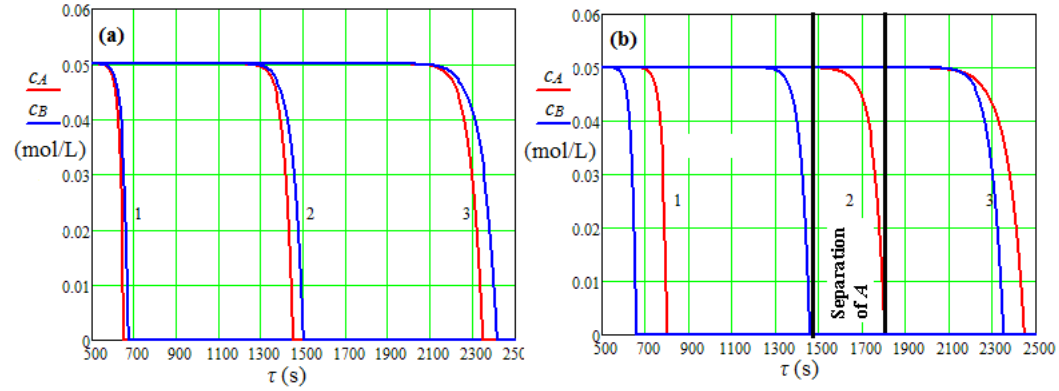

Fig. 8. Effect of fixed bed height on the elution curves for fixed bed imprinted polymer pearls ($w = 3 \times 10^{-2}$ cm/s, d_P = 0.1 cm, c_{SA0} = 0.014 mol/L, c_{SB0} = 0.048 mol/L):
(1) H = 10 cm; (2) H = 20 cm; (3) H = 24 cm ((a) the same mobile phase as in the saturation stage; (b) mobile phase with higher affinity for A species).

Table 2

Values of separability coefficient for breakthrough and elution of stationary phase

Figure	Operating conditions	τ_1 (s)	$\tau_{br/el}$ (s)	C_{sep} (%)
4	H = 10 cm d_P = 0.1 cm $c_{A0} = c_{B0}$ = 0.050 mol/L $w = 1.5 \times 10^{-2}$ cm/s	2500 – 1000 = 1500 (B species)	3600	41.7
5	H = 24 cm d_P = 0.1 cm $c_{A0} = c_{B0}$ = 0.050 mol/L $w = 3 \times 10^{-2}$ cm/s	4750 – 2000 = 2750 (B species)	5600	49.1
6	H = 10 cm d_P = 0.1 cm	775 – 695 = 80 (B species)	900	8.9

	c_{A0} = 0.050 mol/L c_{B0} = 0.075 mol/L $w = 3 \times 10^{-2}$ cm/s			
7a	H = 10 cm d_P = 0.1 cm c_{SA0} = 0.014 mol/L c_{SB0} = 0.048 mol/L $w = 1.5 \times 10^{-2}$ cm/s	1420 –1200 = 220 (B species)	1420	15.5
7b	H = 10 cm d_P = 0.1 cm c_{SA0} = 0.014 mol/L c_{SB0} = 0.048 mol/L $w = 1.5 \times 10^{-2}$ cm/s	1680 – 1200 = 480 (A species)	1680	28.6
8a	H = 20 cm d_P = 0.1 cm c_{SA0} = 0.014 mol/L c_{SB0} = 0.048 mol/L $w = 3 \times 10^{-2}$ cm/s	1500 – 1450 =50 (B species)	1500	3.33
8b	H = 20 cm d_P = 0.1 cm c_{SA0} = 0.014 mol/L c_{SB0} = 0.048 mol/L $w = 3 \times 10^{-2}$ cm/s	1800 – 1480 = 320 (A species)	1800	17.8

4. Conclusions

A model for chromatographic separation involving saturation of stationary phase (saturation or sorption stage) followed by elution with a mobile phase until the total washing of solid phase (elution or desorption stage) was developed. A plug flow with axial dispersion of mobile phase along the stationary phase was assumed. The overall sorption rate of species was expressed as a difference between sorption and desorption rates.

Data from the related literature on the sorption/desorption of diosgenin and sclareol onto/from fixed bed imprinted polymer pearls were used to simulate the process dynamics at various levels of superficial velocity of mobile phase, fixed bed height, and initial concentration of *B* species in the mobile phase.

Characteristic simulations of sorption stage indicated that good species separability was obtained at low levels of superficial velocity and high values of bed height. Moreover, it was proved that separability efficiency for sorption stage did not depend by the values of initial *B* species concentration. In order to obtain a desired separation in the desorption stage, it should be used a mobile phase having a higher affinity for a component.

Nomenclature

a_i constants in Eq. (2)
c_i concentration of *i* species in the mobile phase, g/cm^3
c_{Si} concentration of *i* species in the stationary phase (fixed bed particles), g/cm^3
C_{sep} separability coefficient
d_P mean particle diameter, cm
D_{li} axial dispersion coefficient, cm^2/s
H bed height, cm
$k_{ai/di}$ sorption/desorption rate constant, s^{-1}
Q maximum monolayer sorption capacity, g/cm^3
w superficial velocity of mobile phase, cm/s
z axial distance in the fixed bed, cm

Greek letters
τ time, s

Subscripts
a adsorption
br breakthrough
d desorption
el elution
i component in the mixture
0 initial

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