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Equilibrium thermodynamics and mass transfer parameters estimation of the synthesis products of piperonal from essential oil of *Piper hispidinervum* C. DC by reversed phase liquid chromatography[1]

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Resumo

A rota sintética aplicada ao óleo essencial de *Piper hispidinervum D.C* (pimenta-longa) leva a formação de uma mistura multicomponente composta, majoritariamente, por piperonal, safrol, isosafrol e terpinoleno. Foi estudado, no presente trabalho, a adsorção de tais espécies químicas utilizando-se acetonitrila/água 70/30 (v/v) como fase móvel e C_{18} como fase estacionária. O piperonal é o componente que tem a menor afinidade e o terpinoleno, a maior com a fase estacionária. A resistência externa e interna à transferência de massa controla o processo global de transferência de massa e o mecanismo de difusão na fase estacionária é descrita pelo modelo da difusão paralela.

Palavras-Chave: separação multicomponente, pimenta longa, adsorção, transferência de massa, C_{18}.

Abstract

The synthetic route applied to essential oil of *Piper hispidinervum* leads to the formation of a multicomponent mixture composed, mainly by piperonal, safrole, isosafrole, and terpinolene. In this paper, it was studied the adsorption phenomena of these compounds using acetonitrile/water 70/30 (v/v) as mobile phase and C_{18} as stationary phase. Piperonal is the component that has the lowest affinity and terpinolene, the greatest with stationary phase. The internal resistance to mass transfer controls the overall mass transfer and parallel diffusion model describes the intra-particle transport mechanism.

Key-words: multicomponent separation, long pepper, adsorption, mass transfer, C_{18}.

1. Introduction

Oil of long pepper (*Piper hispidinervum* D.C) with 86 % safrole when submitted to izomerization, followed by electrochemical oxidation and subsequent oxidation leads to piperonal's formation whose yield is 85 %. The resultant solution synthesis is a mixture, not only piperonal, but also other substances with terpinolene, safrole, cis-trans-isosafrole and other components in lower amount (CREMASCO; BRAGA, 2010; CREMASCO; BRAGA, 2012). The piperonal (3,4-(methylenedioxy)benzaldehyde) is an aromatic aldehyde, solid at room temperature and characteristic floral fragrance. This substance is very utilized with fixer in cosmetic industry, and chemical industry with substrate for synthesis various products (TORRI *et al*. 1984; SANTOS *et al*. 2004).

Reversed phase Liquid chromatography (RPLC) is ruled by equilibrium phenomena between fluid phase and solid phase, fluidodynamics in porous medium and mass

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transfer. The association of chromatographic technique and moment analysis of the response peaks is a powerful approach for adsorption studies (CREMASCO; STARQUIT, 2008). The moment analysis in chromatography and, as extension, the pulse analysis have been applied to measure the transport rate, adsorption parameters and bed characteristics for single component (YAMAMOTO et al., 2001) or multicomponent systems (CHIARA et al., 2005). Moment analysis is a useful tool for determining partition coefficient, and mass transfer parameters from pulse experiments, as verified since Schneider and Smith (1968) (CREMASCO; WANG, 2012). In this paper the moment analysis method is applied to determine adsorption constants, effective diffusion coefficients of synthesis products of piperonal from essential oil of *Piper hispidinervum* C. DC, in a fixed bed of C_{18} silica as adsorbent.

In order to obtain this mathematical model, some assumptions are fixed: the flow rate is constant; the transversal cross section is constant for and through the column; radial dispersion is negligible; the axial dispersion coefficient is a function of solute and flow rate; the external mass transfer resistance is considered; the solids are made of spherical particles with uniform radius; the solution is dilute and thus adsorption isotherm is linear (in this case, the compounds present in a multicomponent system can be considered as single component); and the parallel diffusion model describes the intra-particle transport mechanism. From these assumptions, the description of the response peaks from moment analysis is for *mass balance for bulk liquid phase* (is founded in MA et al., 1996; CREMASCO et al., 2001; PIATKOWSKI et al., 2003; LIU et al., 2006), and for *mass balance for stationary phase* is founded in MA et al., 1996; PIATKOWSKI et al., 2003; LIU et al., 2006). It's possible to apply the Laplace-Carson transform to the solute continuity equations, and obtained analytical solutions for pulse elution curves (CREMASCO; WANG, 2012). The explicit expressions for the first, μ, and second moments, σ^2,respectively,

$$\mu = \frac{L}{u}\left[1 + \left(\frac{1-\varepsilon}{\varepsilon}\right)K\right] + \frac{t_0}{2} \qquad (1)$$

$$\sigma^2 = \left(\frac{2L}{u}\right)\left(\frac{E_b}{u^2}\right)\left[1+\left(\frac{1-\varepsilon}{\varepsilon}\right)K\right]^2 + \left(\frac{2L}{u}\right) \mathrm{x} \left(\frac{1-\varepsilon}{\varepsilon}\right)K^2\left(\frac{d_p}{6k_f} + \frac{d_p^2}{60D_{eff}}\right) + \frac{t_0^2}{12} \qquad (2)$$

with

$$K = \varepsilon_p + (1-\varepsilon_p)k_p \qquad (3)$$

and (PIATKOWSKI et al., 2003)

$$D_{eff} = \varepsilon_p D_p + (1-\varepsilon_p)k_p D_S \qquad (4)$$

In this model, L is the effective length column (L); E_b, axial dispersion coefficient (L^2T^{-1}); u, liquid interstitial velocity (LT^{-1}); k_f, film mass transfer coefficient; D_P, pore diffusion coefficient (L^2T^{-1}); D_S, surface diffusion coefficient (L^2T^{-1}); D_{eff}, effective diffusion coefficient (L^2T^{-1}); ε, bed porosity (-); ε_p, adsorbent porosity (-); k_p, isotherm constant (-). The equation for the second moment of chromatographic curve shows dependency with mass transfer: k_f, E_b, D_{eff}. For convective mass transfer coefficient, the correlation of Wilson and Geankoplis (1966) can be used. The axial dispersion coefficient, E_b, can be estimated from literature (CHUNG; WEN, 1968; KOCH; BRADY, 1985; GUNN, 1987; ATHAYLE *et al.*, 1992). The pore diffusion coefficient, D_P, presents in Equation (4) can be calculated by propose of Mackie e Meares (1955) (MA et al., 1996; PIATKOWSKI et al., 2003)

$$D_p = \frac{\varepsilon_p}{(2-\varepsilon_p)^2} D_{AB} \qquad (5)$$

The free diffusion coefficient, D_{AB}, can be known by (Siddiqi; Lucas, 1986),

$$D_{AB} = 2.98 \,\mathrm{x}\, 10^{-7}\left(\frac{1}{V_{bA}^{0.5473}\eta^{0.026}}\right)\left(\frac{T}{\eta}\right) \qquad (6)$$

with V_{bA} molar volume at normal boiling point; η, dynamics viscosity; T, absolute temperature (K).

Experimental moments from chromatographic curve

The proper way to verify the performance of the proposed model is its validation by chromatographic experimental assay, using chromatographic pulse technique. From the hypothesis that allowed the obtaining of Equations (1) and (2), it is possible to establish a relationship between the efficiency of the column, through the height equivalent to a theoretical plate (HETP) and moments (GUIOCHON et al., 2006), according to

$$\mathrm{HETP} = \left(\frac{\sigma'^2}{t_R^2}\right)L \tag{7}$$

with

$$\sigma'^2 = \sigma^2 - \frac{t_0^2}{12} \tag{8}$$

$$t_R = \mu - \frac{t_0}{2} \tag{9}$$

Considering Equations (8) and (9), and substituting Equations (1) and (2) into Equation (7), as well as making appropriate algebraic manipulations, one obtains

$$\mathrm{HETP} = 2\left(\frac{E_b}{u}\right) + 2u\left(\frac{1-\varepsilon}{\varepsilon}\right)\frac{1}{K} \left(1+\left(\frac{\varepsilon}{1-\varepsilon}\right)\frac{1}{K}\right)^{-2}\left(\frac{d_p}{6k_f} + \frac{d_p^2}{60D_{eff}}\right) \tag{10}$$

Equation (10) can be rearranged according to (CREMASCO et al., 2001):

$$\mathrm{HETP}_{mod} = 2\left(\frac{E_b}{u}\right) + 2u\left(\frac{1-\varepsilon}{\varepsilon}\right)\frac{1}{K} \left[1+\left(\frac{\varepsilon}{1-\varepsilon}\right)\frac{1}{K}\right]^{-2}\left(\frac{d_p^2}{60D_{eff}}\right) \tag{11}$$

or

$$\mathrm{HETP}_{mod} = \beta + \alpha u \tag{12}$$

From the straight angular coefficient, α, it is possible to obtain effective diffusion coefficient and the intersection β, the axial dispersion coefficient.

Experimental porosities and isotherm constant from chromatographic curve

There are in the Equation (1) the column porosity, ε, and particle porosity ε_p. For the determination column porosity, someone uses a molecule whose size is larger than the particle pores, and that no presents affinity thermodynamics with the stationary phase. Thus, these molecules move only in the column interstices. In this case, the parameter K, Equation (3) is equal to zero ($k_p = 0$). Then, Equation (1), considering Equation (9), is

$$t_R = \frac{L}{u} \tag{13}$$

By relation between interstitial velocity, u, and superficial velocity, u_0, $u = u_0/\varepsilon$, with $u_0 = Q/\mathrm{Area}$; Q mobile phase volumetric flow rate; Area: column cross-sectional Area. Equation (13) becomes

$$t_R = \frac{L}{u_0}\varepsilon \tag{14}$$

From the straight angular coefficient, t_R vs. L/u_0, it is possible to obtain column porosity, ε. The particle porosity, ε_p, can be obtained using a molecule that has no interaction with stationary phase and can penetrate into all particle pores. In this situation, Equation (3) is $K = \varepsilon_p$, and Equation (1), considering Equation (9), is

$$t_R = \frac{L}{u_0}\left[\varepsilon + (1-\varepsilon)\varepsilon_p\right] \tag{15}$$

From the straight angular coefficient, t_R vs. L/u_0, it is possible to obtain the total porosity, ε_t,

$$\varepsilon_t = \varepsilon + (1-\varepsilon)\varepsilon_p \tag{16}$$

and known the value column porosity, ε, it is possible to obtain the particle porosity, ε_p.

Notice that the values of porosities particle and bed can be obtained directly from the experimental analysis of the first moment of chromatographic curve, considering that the molecules used in such tests do not show affinity with stationary phase. On the other hand, if one consider that a particular molecule presents affinity with adsorbent, isotherm constant so, it is replace u

$= u_0$□, Equations (3) and (9) in Equation (1) (FERRARI, 2014), is:

$$t_R = \frac{L}{u_0}\left[\varepsilon_t + (1-\varepsilon_t)k_p\right] \qquad (17)$$

From the straight angular coefficient, t_R vs. L/u_0, it is possible to obtain the parameter γ, according to

$$\gamma = \varepsilon_t + (1-\varepsilon_t)k_p \qquad (18)$$

it is possible to see that constant k_p is determined after porosities obtained previous.

2. Materials and Method

All experiments were carried out in chromatograph Shimadzu, that consist in system controller, detector UV and two pumps, models CBM- 20A/UFLC, SPD-20A, LC-10AD and LC-20AT, respectively. The mobile phase was composed by acetonitrile, grade HPLC, obtained from J. T. Baker, USA and water Milli Q (18.2 MΩ), whose ratio was 70/30 (v/v). The standards of piperonal (99%) and safrole (99.7%) were obtained from Sigma-Aldrich, USA; the isosafrole (99.5%), ChemService, USA; terpinolene (>85%), in Fluka, USA. Uracil (98%), from Sigma-Aldrich, USA, was used to obtain total porosity (Equation 36). An analytical column (25 cm x 0.46 cm) and a semi-preparative column (25 cm x 1.00 cm) have been used, both filled with silica C_{18} Vydac 150HC, particle size 20 µm, particle porosity 0.357, acquired from Grace Pure. The chemical species accounted for 95.1% of the species present in mixture resultant of the synthesis of the piperonal from crude essential oil of *Piper hispidinervum* (long pepper) (CREMASCO; BRAGA, 2012).

The equilibrium constants were obtained by pulse method with solution 0.20 g L^{-1} of the mixture piperonal/safrole/terpinolene. The solutions were injected in chromatographic system in the following conditions: the flow rates were 0.6 – 1.4 mL min^{-1}, temperature 25°C, wave length 245 nm and analytical column. The isosafrole was prepared in solution apart, in same concentration, due to coelution with the safrole. The total porosity was determined with injections of the solution of uracil at 0.17 g L^{-1} wave length of 254 nm at 25°C. All the injections were 20 □L and flow rates were 0.6-1.4 mL min^{-1} in the analytical column and 4.0-6.0 mL min^{-1} in semi-preparative column. The molecular diffusion coefficient (Table 1), mole fractions of the water and acetonitrile were calculated based in composition described above. Dynamic viscosity and density of the mobile phase were obtained by linear interpolation of the experimental data of Hickey and Waghorne (2001) and their values are 0.857 g mL^{-1} and 0.609 mPa s, respectively. The liquid molar volume was calculated by method described in Elbro et al., (1991). The authors use new contribution method to determine liquid molar volume as a function of the temperature.

Table 1. Liquid molar volume and free diffusion coefficient

Substance	V_b(cm^3 mol^{-1})	D_{AB}(cm^2 s^{-1})
Piperonal	56.38	1.625×10^{-5}
Safrole	79.03	1.352×10^{-5}
Isosafrole	93.17	1.235×10^{-5}
Terpinolene	142.80	9.777×10^{-6}

Mass transfer and axial dispersion parameters were obtained in semipreparative column with solution of piperonal, safrole and terpinolene in concentration 0.20 g L^{-1} each component and isosafrole solution in concentration 0.20 g L^{-1}. The retention time and half width of the chromatographic band were obtained in the flow rates 4.0 to6.0 mL min^{-1}. All injections were 20 µL, 25 °C and wave length 200 nm. The experimental values of height equivalent theoretical plate (HETP) were obtained from (VAN DEMMTER et al., 1956; GUIOCHON et al., 2006).

$$\mathrm{HETP} = \frac{L}{N} = \left(\frac{\sigma'^2}{t_R^2}\right)L \qquad (19)$$

with L, columns length; σ'^2 from Equation (8); t_R, from Equation (9), and N given by

$$N = 5.545\left(\frac{t_R}{w_{h/2}}\right)^2 \qquad (20)$$

and $w_{h/2}$ peak width at half height (the length of the line parallel to the peak base at 50% of the peak). The determination of the total porosity, equilibrium constant, and mass transfer parameter was made in replicate and retention times of all the measure were corrected by injection time without column.

3. Results and Discussion

Total porosity

The Equation (15) applied to set experimental data t_R *versus* L/u_0 provided straight line, Figure 1.

The values of the total porosities in analytical column ($R^2 = 0.9915$) and semi-preparative column ($R^2 = 0.9986$) are presented in Table 2.

Table 2. Column porosities

Column	L(cm)	ID (cm)	ε_T	ε
A	25.0	0.46	0.686	0.512
B	25.0	1.00	0.596	0.372

DI: inner diameter of the column. A:analytical. B: semipreparative.

Due to particle porosity is 0.357, the column porosity can be obtain from Equation (16). The results of column porosity are presented in Table 2.

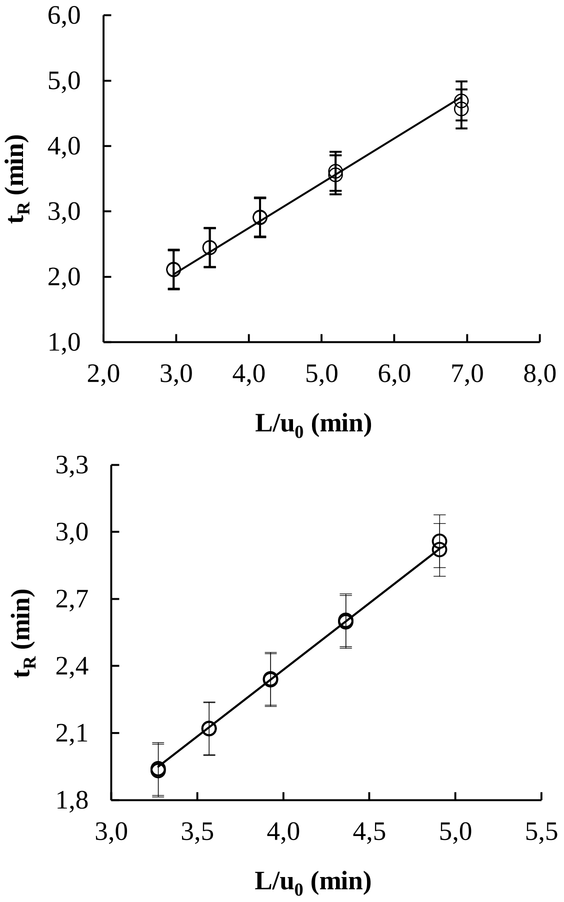

Figure 1. Total porosity: (a) analytical column. (b) semipreparative column. Experimental conditions: Flow rate = 0.6 - 4.0 mL min^{-1} in (a) and 4.0 – 6.0 mL min^{-1} in (b); Temperature = 25 ºC; Detection = 254 nm.

Isotherm constants

The thermodynamics analysis were done in analytical column (25 cm x 0.46 cm), with $\varepsilon = 0.512$ (Table 2) and $\varepsilon_p = 0.357$. By use of Equation (18), it is was possible to obtain Figure 2. The k_p values, from this figure, are presented in Table 3.

Table 3. Isotherm constants

Substance	k_p	R^2	α_{j1}
piperonal (1)	0.869	0.99997	–
safrole (2)	3.122	0.99998	3.592
isosafrole (3)	3.446	0.99998	3.965
terpinolene (4)	12.343	0.99992	14.204

component j: 2, 3 ,4.

In Table 3, the equilibrium constants showed that affinity with stationary phase C_{18} has the following ascending order: piperonal, safrole, isosafrole and terpinolene. It was also that the constant value of piperonal is very distant regarding components, mainly of terpinolene. Already the distance observed between the constants of safrole and isosafrole is tiny.

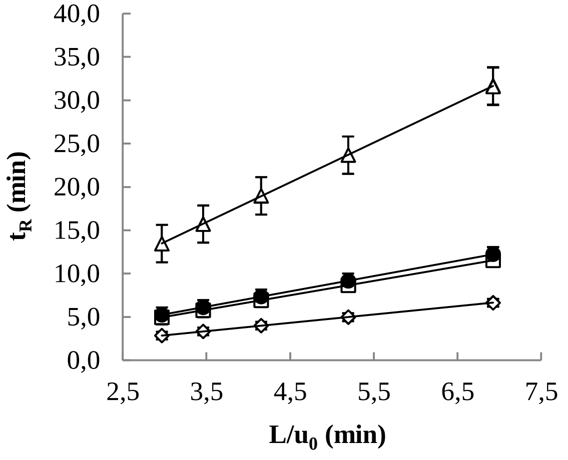

Figure 2. Equilibrium constants: (Δ) terpinolene, (●) isosafrole, (□) safrole, (◊) piperonal. Experimental conditions: Flow rate = 0.6 - 1.4 mL min^{-1}; Temperature = 25 ºC; Detection = 245 nm.

This distance can be described by rate (α) between the constants of less retained component and more retained component, which in chromatography is termed selectivity. For a stationary phase is selective, this rate must be greater than a unit. In Table 3, the rate values between the constant component and constant piperonal satisfy such requirement. On the other hand, the same does not apply at separation of pair safrole/isosafrole, because, the selectivity is lower (α_{32} = 1.104) and cannot be separated under experimental condition used. These substances are constitutional isomers, that is, structurally very similar and therefore, the difference in interaction with the stationary phase C_{18} in mobile phase acetonitrila/water is also very small. Thus, equilibrium stages will be virtually the same. This directly affects selectivity of column, hindering separation. (LANÇAS, 2009; SNYDER et al., 2010; EBERLIN; BENASSI, 2012).

However, it is necessary the determination other chromatographic parameters, besides selectivity, as efficiency and resolution to evaluate thoroughly the separation. The distillation and crystallization are example of techniques that could be utilized in piperonal separation.

Determination of axial dispersion and mass transfer coefficients

The effective diffusion and axial dispersion coefficients were obtained from slope and intercept of straight line described by Equation (12). The results are presented in modified Van Deemter graph (Figure 3) and Table 4. It is observed a linear relationship among $HETP_{\mathbf{mod}}$ *versus* u to piperonal (R^2 = 0.9553), safrole (R^2 = 0.9719), isosafrole (R^2 = 0.9949), and terpinolene (R^2 = 0.8937)

The pore diffusion coefficients, D_P, in Table 4, was calculated from Equation (5), considering ε_p = 0.357, and free diffusion coefficients from Table 1. The effective diffusion coefficients, D_{eff}, were obtained from straight angular coefficients of Figure 3;
and D_s, surface diffusion coefficient, from Equation (4), considering D_p in Table 4.

The results of D_p and D_s present same magnitude order, showing the importance of diffusive mechanism to be describe by parallel model. In some cases, surface diffusion became the main diffusive mechanism of mass transfer (PIATKOWSKI et al., 2003). Regarding obtainment of axial dispersion coefficient, it has been found, to all chemical species evaluated, values in order to 10^{-3} cm^2 s^{-1}.

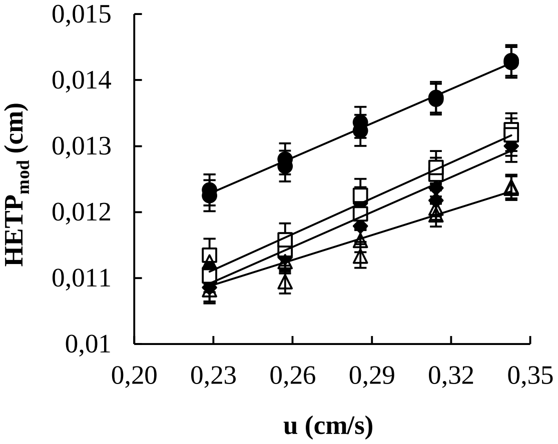

Figure 3. Obtainment mass transfer parameters: (●) isosafrole, (□) safrole, (♦) piperonal, (Δ) terpinolene. Experimental conditions: Flow rate = 4.0-6.0 mL min^{-1}; Temperature = 25 °C; Detection = 245 nm.

Table 4. Mass transfer parameters

Compound	D_P (cm^2 s^{-1})	D_{eff} (cm^2 s^{-1})	D_s (cm^2 s^{-1})	E_b (cm^2 s^{-1})
Piperonal (1)	2.150 x 10^{-6}	1.655 x 10^{-6}	1.588 x 10^{-6}	3.450 x 10^{-3}u
Safrole (2)	1.787 x 10^{-6}	2.791 x 10^{-6}	1.072 x 10^{-6}	3.485 x 10^{-3}u
Isosafrole (3)	1.633 x 10^{-6}	3.005 x 10^{-6}	1.093 x 10^{-6}	4.159 x 10^{-3}u
Terpinolene (4)	1.293 x 10^{-6}	5.466 x 10^{-6}	6.306 x 10^{-7}	4.004 x 10^{-3}u

Table 5 – Characteristic of lumped mass transfer

	k_f x 10^{-2}(cm s^{-1})	Bi_m
	lower – higher.	lower – higher.
Piperonal	5,213 – 5,968	31,5 – 36,1
Safrol	4,610 – 5,278	16,5 – 18,9
Isosafrol	4,342 – 4,970	14,4 – 16,5
Terpinoleno	3,715 – 4,253	6,80 – 7,78

In order to verify the influence of the external or internal resistance on the mass transfer phenomenon, it was used the number of mass Biot (Bi_m) given by Equation (21) and Table 5 (BAILEY; OLLIS, 1986; ZHOU et al. 2003):

$$Bi_m = \frac{k_f d_p}{2D_{ef}} \qquad (21)$$

where d_p is the particle diameter, k_f is the external mass transfer coefficient and D_{ef} is the effective diffusion coefficient. The values of k_f were calculated by Wilson and Geankoplis correlation and the values of D_{ef}, are in Table 4.

In case that $0.1 < Bi_m < 100$ indicate that the both external and internal resistance affects the lumped mass transfer (PARTI, 1994; DINCER, 1998; SARTI et al. 2001). In Table 5, Bi_m values are within the range pointed out by authors, i.e., both internal and external resistance contribute for lumped mass transfer.

The E_b results presented in Table 6 are compared with those from Literature using relative mean deviation by

$$RMD = \left(\frac{E_{b_{experimental}} - E_{b_{theoretical}}}{E_{b_{theoretical}}} \right) x100\% \qquad (22)$$

The performance of Literature's equations is showed in Table 6. Except the Gunn and Koch and Brady equations, other equations present are satisfactory to estimate the axial dispersion coefficient. According to Hong et al. (2004), Gunn correlation presented high errors for low value Reynolds number such as chromatographic separation. In this paper, the Reynolds number varied of de 2,4 x 10^{-2} a 3,6 x 10^{-2}. This values are similar that found by Hong et al., (2004). On the other hand, Koch and Brady correlation assume Peclet number must be much great than 1 for that be valid. In this paper, Peclet number varied of 10,4 to 26,0, that despite being greater than unit, can be related to large deviations.

4. Conclusion

The equilibrium constants present that the components of the mixture has the following ascending order of affinity with stationary phase: piperonal, safrole, isosafrole and terpinolene. The results indicate that the piperonal can be separated of multicomponent mixture or even binary combinations with either components of the mixture. Lumped mass transfer is controlled both internal and external resistance, which is related with parallel diffusion mechanism. The values founded to axial dispersion coefficients lie within those usually provided in literature. Athayle and coworkers correlation described more rightly the axial dispersion in column

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Divulgação

Este artigo é inédito e não está sendo considerado para qualquer outra publicação. Os autores e revisores não relataram qualquer conflito de interesse durante a sua avaliação. Logo, a revista *Scientia Amazonia* detém os direitos autorais, tem a aprovação e a permissão dos autores para divulgação, deste artigo, por meio eletrônico.

Table 6. Relative mean deviation (%).

	CHUNG; WEN 1968	KOCH; BRADY 1985	GUNN 1987	ATHAYLE *et al.* 1992
Piperonal	6.57	-25.19	-67.57	-4.02
Safrole	5.51	-22.16	-62.94	-2.01
Isosafrole	-11.60	-33,21	-66.73	-16.65
Terpinolene	-8.17	-26,37	-58.92	-9.98

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