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Determination of the effective mass diffusivity for the system clove (Eugenia caryophyllus) + CO_2

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Article Outline

Discussion
Author comments 05 Dec 2002 19:58:17, Caciano Zapata-Noreña
Supplementary material.

Discussion

Author comments 05 Dec 2002 19:58:17, Caciano Zapata-Noreña

Additional material related to Supercritical Technology Applied to the Processing of Natural Products can be found in: http://www.fea.unicamp.br/deptos/dea/lasefi

Supplementary material.

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Determination of the effective mass diffusivity for the system clove (*Eugenia caryophyllus*) + CO_2

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ABSTRACT

The effective mass diffusion coefficient for the system clove + CO_2 was experimentally determined at 64.7 and 69.7 bar and temperatures from 10 to 20°C. The experimental apparatus was a fixed bed extractor. The fixed bed was formed with ground and compacted clove buds. Particulate solid was shaped as cylinders of approximately 2.17cm diameter and length varying from of 6.2 to 7.2 cm of uniform density. Each cylinder was treated as one solid element. Each experiment required 9 cylinders that were weighed and placed inside the extractor (with length of 60.5 cm and diameter of 2.17 cm). The effective mass diffusion coefficient was evaluated by fitting the experimental solid-phase concentration profile to the unsteady state mass balance equation for unidirectional diffusion in semi-infinite solid medium. The diffusion coefficient was considered dependent on concentration. A potential and an exponential concentration dependence models were tested. The mass balance was solved by finite difference using the explicit method. The average relative errors for both pressures and all temperature were smaller than 3.5% for the potential concentration dependence model and smaller than 5% for the exponential concentration dependence one. Predicted values for the initial effective mass-diffusion were in the range of 3.25×10^{-10} and 5.25×10^{-10} m^2/s, and at constant temperature they were not affected by pressure. Fourier numbers were smaller than 0.003, which indicate, that the experimental system behaved as a semi-infinite medium. Clove essential oil was analyzed by GC-FID being identified the following substances eugenol, β-caryophyllene, α-humulene and eugenol acetate.

Keywords: Supercritical extraction, effective diffusion coefficient, mass transfer, clove oil, clove oil composition

1. Nomenclature

D(X)	: variable diffusion coeficient (m^2/s)	k_1^e	: constant defined by Eqn. 6
D_{ef}	: effective diffusion coeficient (m^2/s)	X	: mass ratio of solute in the solid phase (kg/kg)
D_o	: effective diffusion coefficient when X = 0 (m^2/s)	X_O	: initial mass ratio in solid phase
D^+	: variable diffusion coefficient when X = X_0 (m^2/s)	X_S	: mass ratio at the solid/fluid interface
F_o^+	: Fourier number defined by D^+	t	: time (s)
k	: constant defined by Eqn. 5	z	: axial coordinate (m)
k_1	: constant defined by the Eqn. 5	ψ	: dimensionless concentration

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2. Introduction

The conventional or low-pressure extraction of natural products from plant materials can be conducted in solid-fluid equipments that operate continuously. For supercritical fluid extraction (SFE) due to the difficulties in handling the solid-fluid system at high pressure the process is most likely to be accomplished semi-continuously. A considerable amount of work has been published in the nineties relative to the SFE of essential oils [1], [2], [3], [4]. The majority of the works have focused on understanding the process from a semi-empirical point of view, although lately some efforts have been devoted to understand and measure thermodynamics and mass-transfer data. The system plant material/carbon dioxide is very complex, thus, the resulting extract composition will depend on the solvent conditions (pressure and temperature), and on the biological material itself as well as on the type of treatment it was subjected prior to extraction [3], [4].

It is generally accepted that SFE of essential oils in fixed bed can be described by a three-step process [4], [5]. For the constant or fast extraction rate period the convection is the predominating mechanism. In the falling or decreasing rate periods both convection and diffusion in the solid must be considered. For the diffusion-controlled rate period the diffusion in the solid controls the rate of mass transfer. Depending on the plant material and how it was treated prior to extraction, one of the mass transfer mechanism or even local thermodynamics constraints can be the rate-limiting step.

Goto *et al.* [6] calculated the effective diffusion of peppermint oil using a model that considers the local adsorption equilibrium. Taking the *l*-menthol as the key component the estimated effective mass diffusivity varied from 0.17×10^{-8} to 1.46×10^{-8} m^2/s. Reverchon *et al.* [7] reported that the effective mass diffusivity of basil, marjoram, and rosemary essential oils in CO_2 vary from 1.4×10^{-13} to 2.8×10^{-13} m^2/s at 100 bar and 40°C. Roy *et al.* [8] using experimental data for extraction of ginger essential oil estimated for the effective diffusion coefficient a value of 2.5×10^{-10} m^2/s. The effect of bed compactness has been studied by del Valle and Aguillera [9]. These authors evaluated the effective diffusion coefficient for the system mushroom powder/CO_2. Their estimated mass diffusivity varied from 1.0×10^{-8} to 1.5×10^{-8} m^2/s for CO_2 densities from 538.3 to 678.7 kg/m^3 and temperatures of 63 to 90°C.

Even considering the differences in the plant material used and the corresponding differences in essential oil and/or oleoresin composition the discrepancy in the values reported for the mass diffusivity are large. Another aspect to be evaluated is the definition of the mass diffusion coefficient. The diffusion step that is complex for any solid-fluid system can be even more complex for the system plant material and carbon dioxide. Diffusion in biological systems is a phenomenon of difficult explanation because of the cellular structure and interaction among solutes, being possible that the effective mass diffusivity depends on solute concentration. It would be worthwhile to pay some attention to the mechanisms included in the definition of this parameter as well as to the methodology used for its determination by the various authors. Therefore, a systematic study on effective mass diffusivity is an exciting area because one will deal with a very complex multi-component system with variable composition. The idea would be to establish a correlation for the effective mass diffusivity as a function of temperature, pressure, and solute composition.

The objective of this work was the determination of the effective mass diffusivity for the system CO_2/clove buds at 64.7 and 69.7 bar and temperatures of 10, 12, 14, 16, 18 and 20°C.

3. Effective mass diffusivity in compacted solids

The amount of soluble material present in plant material varies enormously from about 1.5% (m/m) for lemongrass to as much as 24% (m/m) in clove buds. The complexity of the chemical composition of the extracts also varies a lot. Compare for instance, the composition of clove oil [10], a relatively simple multi-component mixture, with that of ginger oleoresin [3], or black pepper oil [4], [11]. To understand the diffusion phenomena and to measure the effective mass diffusivity in a real situation the system chosen was clove buds and carbon dioxide. Germer [12] and Rodrigues [13] showed that about 90% of clove oil is extracted during the constant or the convection-controlled extraction rate period. Since clove buds have up to 24% of oil this leaves as much as 2.4% to be extracted in the falling and diffusion-controlled extraction rate periods. As already mentioned the chemical composition of clove oil is relatively simple. With this picture, the real system clove buds/carbon dioxide was used as a “model” system.

To get an insight in the role of pressure, temperature and composition over the effective mass diffusivity we can take a look in the behavior of the binary diffusion of the substances present in the clove oil in carbon dioxide. Using the correlation of Wilke-Chang [14] and the clove oil composition of Rodrigues *et al*. [10] the binary diffusion coefficients were calculated (Figure 1). The results show that as expected, the binary diffusion coefficients are larger at lower pressure, increase almost linearly with temperature, and are inversely proportional to molecular weight. From these results it may be expected that the effective mass diffusivity will be influenced by the oil composition. The influence will in some way be related to the effects of temperature and pressure in the extracts chemical composition.

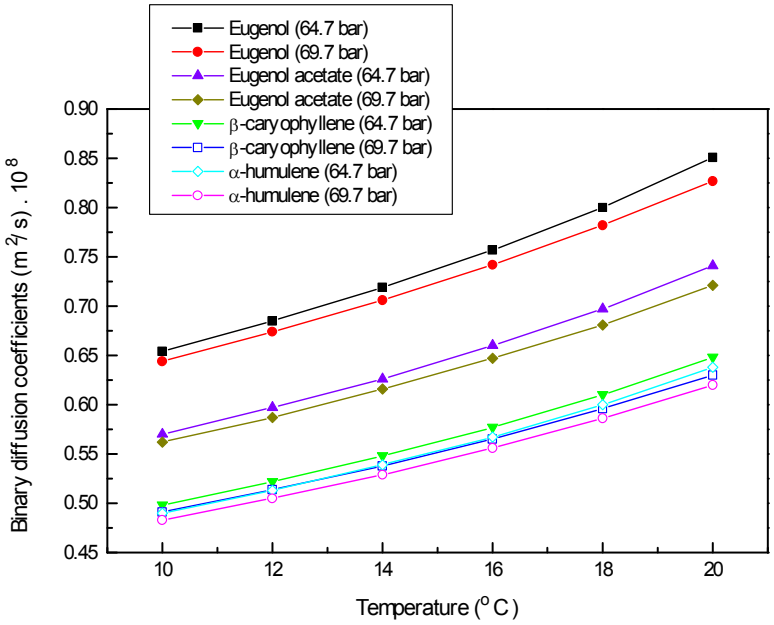


Figure 1. Binary diffusion coefficients for substances present in clove oil in carbon dioxide.

A convenient system to study the effective diffusion would be the use of a bed of clove particles that simulated a semi-infinite solid media. The clove bed would have to be formed with compacted solid particles and treated as a porous solid as suggested in literature [9]. del Valle and Aguilera [9] observed for powdered mushroom that previous densification of the solid resulted in the extraction kinetics being controlled by the diffusion in the solid matrix. They predicted the extraction rate using models for transient diffusion in solids. Considering a cylindrical bed with a diameter several times smaller than the length the mass balance for the solid phase is given by the unidirectional, transient mass transfer equation, or Fick's Second Law, and could be written as:

$$\frac{\partial X}{\partial t} = \frac{\partial}{\partial z}\left[D(X) \frac{\partial X}{\partial z} \right] \qquad \text{Eqn. 1}$$

Where X is the mass ratio of solute (clove oil) in the solid phase (clove particles), t is time, and z is the axial direction. D(X) is the effective mass diffusion coefficient that is expected to be a function of the solute concentration in the solid due to the complex nature of the solid phase. The effective mass diffusivity for the system clove/CO_2 defined by Eqn.1 embodies the following process: *i*) The solvent movement into the solid phase; *ii*) The solutilization of the solute mixture; *iii*) The diffusion of the mixture solute/solvent up to the solid-fluid interface. For a semi-infinite solid with initial homogeneous concentration of solute the initial and boundary conditions are [15], [16]:

I.C.: Initially the clove oil was evenly distributed within the solid:

$$X(0,z) = X_o \qquad \text{Eqn. 2}$$

B.C.(1): At the solid-fluid interface the solid surface concentration was:

$$X(t,L) = X_S \qquad \text{Eqn. 3}$$

B.C.(2): At the sealed solid end:

$$\left.\frac{\partial X}{\partial z}\right|_{(t,0)} = 0 \qquad \text{Eqn. 4}$$

To express the concentration dependence of the effective mass diffusivity a potential function was chosen [15]:

$$D(X) = D_o(1+kX)^{k_1} \qquad \text{Eqn. 5}$$

Zapata-Noreña and Meireles [17] used the following exponential function to express the solute concentration dependence of the effective mass diffusivity [18]:

$$D(X) = D_o \exp(k_1^e X) \qquad \text{Eqn. 6}$$

4. Material and Methods

4.1.Raw material preparation and characterization

Clove buds bought from a local store (Campinas, São Paulo, Brazil) were cleaned to remove all foreign and deteriorated material. Clove buds were stored in plastic containers hermetically closed and placed in a domestic freezer (Metalfrio, 620L, horizontal, Brazil). The amount of soluble oil was determined by the method described by Pearson [19].

The amount of material required for each experimental run was ground in a laboratory helix-type mill (Marconi, model MA 345, Brazil) with water circulation. The solid was ground frozen to avoid thermal degradation of the volatile oil. Particles with meshes of –32 to +65 were used to form the fixed bed. The particulate solid was manually compacted with the aid of a rod of glass (1 cm of diameter) into a surgical tubular cloth (T M Orthopaedic, 15 m of length, and 4 cm of width, 100% cotton) that was placed inside a hollow cylindrical matrix (made of disposable hypodermic syringes). Compacted solids with cylindrical shape (2.17 cm of diameter and length between 6.2 and 7.2 cm) and uniform densities were obtained. Each experiment required 9 compacted clove cylinders that were weighed in an analytic balance (Sartorius, model A 200 S, ±0.0001g, USA) and placed inside the fixed bed extractor (with length of 60.5cm and inside diameter of 2.16cm).

4.2.Experimental procedure

The experimental apparatus is shown in Figure 2 [17]. Valves V_1 and V_2 were always open to guarantee that reservoir-II was always full of CO_2 (Liquid Carbonic do Brasil, 99% pure, Brazil). System pressure was controlled with the aid of a heating tape (Fisaton, model 5, 2.5 cm width, Brazil) wrapped around reservoir-I and linked to an automatic temperature controller (Dyna-sense, Model 2156-00, USA). One hour before connecting the extractor to the extraction line, the re-circulating water bath (Tecnal, Model TE-184, ±1°C, Brazil) for reservoir-II was turned on. Ninety minutes later, having reached pre-selected operational conditions, valve V_3 was opened and CO_2 began to flow. Up to this point valve V_4 was opened. Once extractor pressure was equilibrated, its upper end was isolated closing valve V4. Thereafter, valve V_5 and the micro-metering valve used to expand and to control the CO_2 flow rate were opened. These valves were heated with a heating tape (Fisaton, Model 5, 2.5 cm of width, Brazil) linked to an electronic temperature controller (Dyna-Sense, Model 2156-00, USA). They were opened in such a way so as to maintain the CO_2 flow rate constant and at a minimum $(0.020\pm0.002)\times10^{-3}$kg/s. This care was taken to avoid the possibility of oil accumulation in the fluid phase. Oil was collected in 20 cm^3 glass flasks. CO_2 flow was maintained for seven hours. After this valve V_3 was closed. After complete depressurization, clove cylinders were removed from the extractor and placed in a desiccator; afterwards, they were weighted.

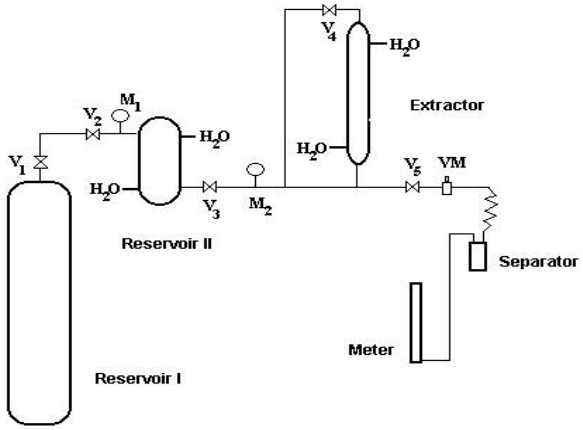


Figure 2. Experimental apparatus

4.3.Chemical composition of clove oil

The composition of clove oil was determined by gas chromatography using the procedure described by Rodrigues *et al*. [10].

4.4.Parameters fitting and other calculations

For estimation of X_s, k_1 and D_o parameters, the modified simplex method of Nelder and Mead [20] was used. Quality of model fitting was evaluated through average relative errors given by:

$$\%\,\bar{e}_r = \frac{\sum_{1}^{N_p}\left[\frac{|\psi_{pred} - \psi_{exp}|}{\psi_{exp}}\right]}{N_p} \qquad \text{Eqn. 7}$$

Where N_p is the number of experimental points and predicted and experimental concentrations are expressed dimensionless; ψ is the dimensionless mass ratio of solute in the solid phase.

For the solution of the mass balance equations using the explicit method 60 nodal points were used with increments of 5 second to avoid numerical oscillation [21]. The stability criteria used was:

$$\frac{D\Delta F_0^+}{(\Delta Z)^2} \leq \frac{1}{2} \qquad \text{Eqn. 8}$$

Intervals for the Fourier number were in the order of magnitude of 10^{-5}.

Parameters were fitted for both models at 64.7 and 69.7 bar. In addition, the data was also fitted to the concentration-independent model using two boundaries conditions: $X_S = 0$ and $X_S \neq 0$. For the potential concentration dependence model parameters were calculated at all temperatures while the exponential concentration dependence model was applied for temperatures of 14, 16, 18, and 20°C, since values at 10 and 12°C were reported by Zapata-Noreña and Meireles [17].

5. Results and discussion

The particles mean diameter calculated as suggested in the ASAE-319.2 method [22] was 3.40×10^{-4} m (-32 +65 mesh). The cylindrical bed had a density of 882±28 kg/m^3, a value slightly below the range of 889 and 1212 kg/m^3 used by del Valle and Aguilera [9] obtained with particles of mean diameter of 2.85×10^{-4} m (-35 + 100 mesh).

5.1.Extracts composition at working conditions

Table 1 shows the composition of the clove oil for the various operating conditions. The following substances were identified: eugenol, eugenol acetate, β-caryophyllene, and α-humulene, the substances associated with the characteristic flavor of the clove essential oil [23], [24]. The amounts of β-caryophyllene and α-humulene remain almost constant while the amount of eugenol is always larger at 64.7 bar as compared to 69.7 bar. For the eugenol acetate the amounts were larger at 69.7 bar at all temperatures. These results show that the assumption of a quasi-binary system for SFE of solute from a natural substratum should be carefully considered once it may not be always acceptable.

5.2.Determination of the effective mass diffusivity

In despite of the fact that the solute composition varies with pressure and temperature the system clove/CO_2 was treated as a quasi-binary system.

The experimental data were first fitted to the concentration-independent effective mass diffusivity model for semi-infinite solid [25] with the surface concentration set equal to zero (Table 2). The magnitude of the errors indicated that this model poorly described the experimental data. In addition, the residual analysis showed a non-random distribution of the residues.

Table 1. Mean composition of clove essential oils as a function of temperature and pressure.

	64.7 bar					69.7 bar				
Temp. (°C)	Eugenol	Eugenol acetate	β-caryophyllene	α-humulene	Non-identified	Eugenol	Eugenol acetate	β-caryophyllene	α-humulene	Non-identified
10	50.14	27.60	19.77	2.10	0.39	48.41	28.19	19.86	2.49	1.05
12	58.62	19.50	19.81	1.60	0.47	49.34	27.64	19.91	2.23	0.88
14	60.14	19.08	18.90	1.53	0.35	50.28	27.70	19.10	2.09	0.83
16	49.67	26.77	20.44	2.34	0.78	48.01	26.61	21.78	2.58	1.02
18	58.69	19.28	20.02	1.63	0.38	51.57	26.14	19.72	2.12	0.45
20	53.43	24.97	18.86	2.05	0.69	51.35	26.76	19.06	2.18	0.65

Table 2. Estimated concentration-independent effective diffusion coefficient, $X_S \neq 0$

	64.7 bar		69.7 bar	
Temp. (°C)	$D_o.10^8$ (m^2/s)	$\%\bar{e}_r$	$D_o.10^{10}$ (m^2/s)	$\%\bar{e}_r$
10	2.10	16.26	2.37	17.63
12	2.39	18.70	2.13	12.67
14	2.61	21.28	2.79	21.89
16	2.90	17.55	2.91	14.25
18	2.90	10.87	3.15	16.97
20	3.05	16.36	4.43	14.00

Next the experimental data were fitted using the concentration-independent model with non-zero surface concentration, i.e., $X_S \neq 0$ and the potential and exponential concentration dependence models. Tables 2 to 5 show the esti-

mated values for D_0, X_S, k_1, and k_1^e obtained by fitting experimental data to the models. For all calculations the parameter k of Eqn. 5 was arbitrarily set equal to unity. The interfacial solid-surface concentration X_S and the model parameters k_1 k_1^e were considered to be independent of pressure. At 64.7 bar, the parameter D_0 increased from 10 to 16°C, decreased from 16 to 18°C, and increased again from 18 to 20°C. At 69.7 bar the parameter decreased at 12 and 18°C. A similar behavior was observed for the exponential concentration dependence model. The mean relative deviations were smaller than 3.5% for the potential concentration dependence model and 5.0% for the exponential concentration dependence model.

Table 3. Estimated parameters for the concentration-independent effective diffusion model with $X_0 \neq 0$

	64.7 bar			69.7 bar		
Temp. (°C)	X_S (kg/kg)	$D_o.10^{10}$ (m^2/s)	$\%\bar{e}_r$	X_S (kg/kg)	$D_o.10^{10}$ (m^2/s)	$\%\bar{e}_r$
10	0.160	6.1	3.14	0.155	6.1	3.20
12	0.155	6.1	3.98	0.160	3.6	0.68
14	0.145	6.1	3.23	0.135	6.1	3.23
16	0.145	4.1	1.63	0.155	4.1	1.50
18	0.145	4.1	5.13	0.145	4.1	3.51
20	0.145	4.1	2.20	0.145	4.1	1.93

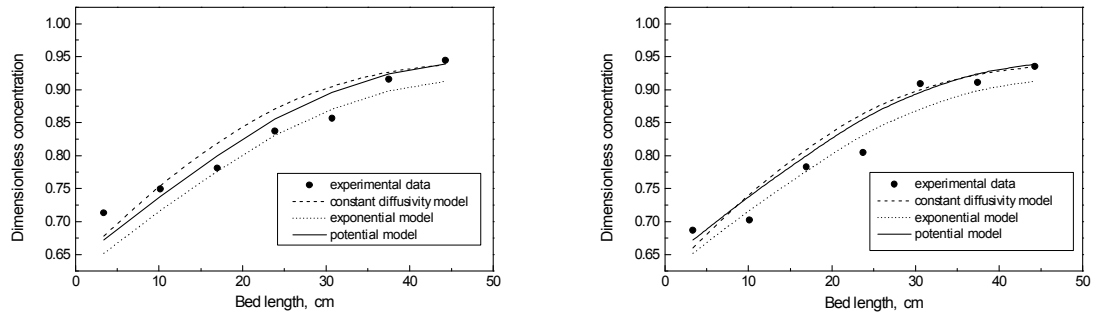
Table 4. Estimated parameters for the potential concentration dependence model

	64.7 bar				69.7 bar			
Temp. (°C)	k_1	X_S (kg/kg)	$D_o.10^{10}$ (m^2/s)	$\%\bar{e}_r$	k_1	X_S (kg/kg)	$D_o.10^{10}$ (m^2/s)	$\%\bar{e}_r$
10	-1.1	0.160	5.25	2.58	-1.1	0.160	5.25	2.71
12	-1.1	0.160	5.25	3.39	-1.1	0.160	3.71	1.22
14	-1.2	0.145	5.25	2.46	-1.2	0.145	5.25	2.52
16	-1.4	0.145	4.21	1.93	-1.4	0.145	4.21	1.95
18	-1.4	0.145	3.26	2.69	-1.4	0.145	3.25	3.11
20	-1.4	0.145	4.21	2.22	-1.4	0.145	4.21	1.60

Figures 3 to 5 show the concentration profile as a function of temperature, for both pressures. Comparison of the average relative errors shows the exponential concentration dependence model to be the poor one, although this is not clearly seen from the concentration profiles. The residual analysis showed a slight tendency towards a non-random behavior for larger concentration, or away from the solid-fluid interface for all models. In the average, the exponential concentration dependence model represented the experimental data better than the potential concentration dependence or the concentration-independent models.

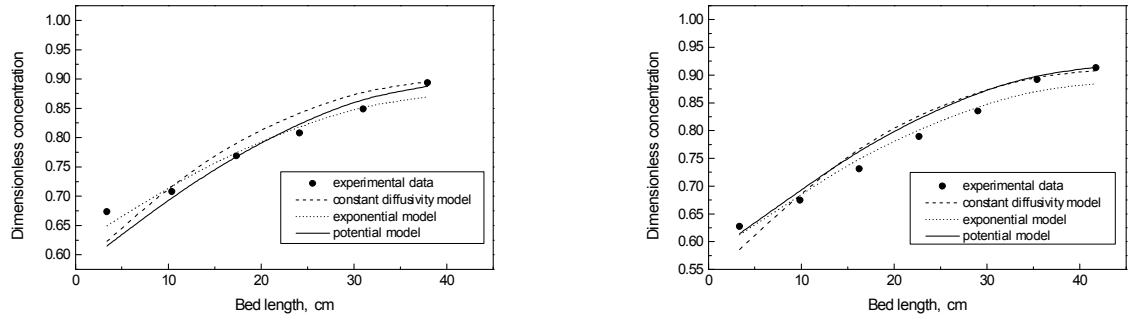
Table 5. Estimated parameters for the exponential concentration dependence model

	64.7 bar				69.7 bar			
Temp. (°C)	$k_1^e.10^6$ (kg/kg)	X_S (kg/kg)	$D_o.10^{10}$ (m^2/s)	$\%\bar{e}_r$	$k_1^e.10^6$ (kg/kg)	X_S (kg/kg)	$D_o.10^{10}$ (m^2/s)	$\%\bar{e}_r$
10	1.93	0.155	4.97	3.05	1.93	0.155	4.97	2.75
12	1.93	0.155	4.97	1.83	1.32	0.155	3.64	0.81
14	1.93	0.155	4.97	1.64	1.93	0.145	4.97	2.02
16	1.32	0.145	3.64	3.43	1.32	0.145	3.64	4.16
18	1.32	0.145	3.64	2.00	1.32	0.145	3.64	4.97
20	1.32	0.145	3.64	3.24	1.32	0.145	3.64	3.13



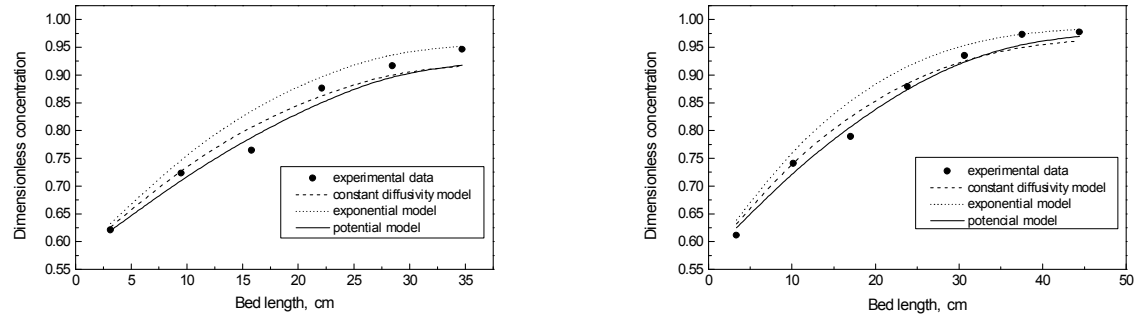
(a) (b)

Figure 3. Comparison of experimental and calculated concentration profile at 10°C. (a) 64.7 bar; (b) 69.7 bar. (•) Experimental data; (—) potential concentration dependence model; (….) exponential concentration dependence model; (---) constant diffusivity model.



(a) (b)

Figure 4. Comparison of experimental and calculated concentration profile at 14°C. (a) 64.7 bar; (b) 69.7 bar. (•) Experimental data; (—) potential concentration dependence model; (….) exponential concentration dependence model; (---) constant diffusivity model



(a) (b)

Figure 5. Comparison of experimental and calculated concentration profile at 20°C. (a) 64.7 bar; (b) 69.7 bar. (•) Experimental data; (—) potential concentration dependence model; (….) exponential concentration dependence model; (---) constant diffusivity model.

Figures 6 and 7 show the behavior of the effective mass diffusion coefficient as a function of temperature for both pressures. As expected the diffusion coefficient decreases with concentration; this is typically observed in drying of porous or granular products where the diffusivity increases with concentration up to a point of maximum and then decreases [26]. The temperature dependence is in accordance with a retrograde condensation behavior. Germer [12] has reported a maximum in solubility near 16°C at the 70 bar; Rodrigues *et al* [27] have reported a maximum in solubility at 66.7 bar and 10°C, thus, the observed behavior is in accordance with a retrograde condensation for the conditions studied.

As discussed before, the diffusion in the solid substratum/SCF system is subjected to various phenomena and the explanation of this behavior can only be completed considering the combined effect of all of them. The effective diffusion coefficient can be associated to the interaction of the solute in the solid phase as well as in the fluid phase. The thermodynamic limitations of the system can to some extent interfere with the measurement of the effective diffusion coefficient due to local saturation conditions, however this phenomenon was not considered in the model. There also exists the possibility that the operational conditions used were close to the "crossover" region, because results in the literature report a minimum value of solubility at 16°C for pressures of 60.5 and 70 bar [12]. Another phenomenon that should be considered is the observed modification in the composition of the extract, for the pressures and temperatures in study. The composition was affected by temperature at 64.7 bar, even so that was not observed at 69.7 bar (Table 1). Thus, the possible conversion of eugenol in eugenol acetate could be responsible, at least partially, for the behavior observed for the effective diffusion coefficient.

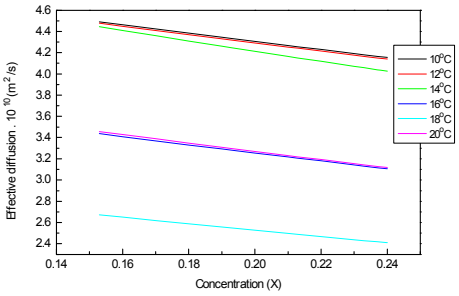


Figure 6. Effective diffusion coefficient estimated with the potential concentration dependence model at 64.7 bar

Considering the values of effective mass diffusivity the estimated Fourier numbers were smaller than 0.003 for all conditions. It is generally accepted that for Fourier numbers smaller than 0.05 the solid can be treated as a semi-infinite solid. Therefore, the boundary condition at the sealed solid end of Eqn. 5 in this work truly represented the condition of a semi-finite solid.

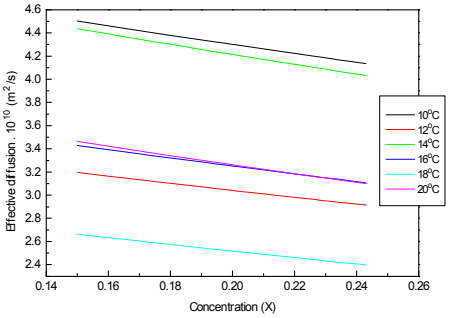


Figure 7. Effective diffusion coefficient estimated with the potential concentration dependence model at 69.7 bar.

6. Conclusion

The concentration profiles for the system clove/CO_2 calculated using the potential and exponential concentration dependence models were not distinctively different. Considering the mean relative deviation the potential concentration dependence model was preferred. The effective mass diffusivity decreased with oil concentration in the solid. Even though a clear behavior of the effective mass diffusivity could not be drawn for the influence of temperature and pressure, the largest values of the mass diffusivity were obtained at 10°C at both pressures while the lowest at 18°C. Further experiments should be designed to elucidate the solute/inert-solid as well as the solute/solvent interactions. Considering the shape of the concentration profile it might be interesting to use other functions to express the concentration-dependence of the mass diffusivity.

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