THERMODYNAMIC MODELING OF HIGH PRESSURE PHASE EQUILIBRIA FOR CLOVE ESSENTIAL OIL+CARBON DIOXIDE

Rodrigo Scopel, Eduardo Cassel*, Rubem M.F. Vargas

Laboratório de Operações Unitárias, Faculdade de Engenharia – PUCRS
Av. Ipiranga, 668/30/F/208, 90619-900 - Porto Alegre – Brazil

Email: cassel@pucrs.br

Abstract. Clove (*Syzygium aromaticum*) is widely cultivated at the eastern countries and the bud essential oil is extracted by supercritical fluid because of vegetable structure of raw material. Clove essential oil has antifungal, antibacterial, insecticidal, and antioxidant properties. The aim of this work is to modeling the solubility of clove essential oil in supercritical carbon dioxide using EoS PR with three mixing rules: van der Walls 1 (vdW1), van der Walls 2 (vdW2) and Mathias-Klotz-Prausnitz (MKP). It was performed the isothermal vapor-liquid equilibria calculation of CO_2/clove essential oil considered as a binary system and CO_2/eugenol/β-caryophyllene as a ternary system, where the oil composition is said to be the major oil compounds, i.e., eugenol and β-caryophyllene. It was developed a mathematical routine in Matlab to obtain the fitted parameters of the EOS Peng Robinson mixing rules, both for the binary mixture and for the ternary mixture at the following temperatures: 313.2 K, 318.2 K and 328.2 K. Results showed that mixing rule that best represent the experimental data for the binary system CO_2/clove oil was vdW2 with a maximum error in pressure of 3.07%. For the ternary mixture, mixing rule that best represent the experimental data was MKP with a maximum error in pressure of 2.18%.

Keywords: Clove essential oil, EoS PR, thermodynamic modeling, supercritical CO_2

1. Introduction

Clove (*Syzygium aromaticum*) is a well know spice that has been highly studied because therapeutic activities of its essential oil. Several authors have reported a powerful antioxidant activity from clove essential oil [1,2,3,4] showing that this product could be an alternative when related to synthetic products of same action. Wenquiang et al. [5] published a comparison between different extraction methods showing that Soxhlet and supercritical fluid extraction (SFE) are the most efficient methods with yield varying from 19.6% (SFE) to 41.8% (Soxhlet). When contrasting both methods, the advantage of SFE, from food industry applications, is that this one neglects the use of toxic solvents. SFE does not need a subsequent separation process and preserves thermolabile compounds [6].

Supercritical fluid extraction is a separation process that has been widely used in the extraction of active compounds present in natural matrixes [6]. It has as advantages the use of nontoxic solvents like CO_2 and provides greater selectivity with respect to interest compounds when confronted with other solvents.

In order to enable the development of mass transfer models that represents the SFE, different authors use solubility on their concepts [7]. Solubility can be calculated by a thermodynamic approach using equations of state, where an important point to be discussed is mixing rule selection. As SFE is a high pressure process, vapor-liquid equilibria (VLE) data at this condition it is necessary to fit the binary parameters of the Equation of State Peng Robinson (EoS-PR) mixing rules selected.

The objective of this work is to represent the solubility of clove essential oil in carbon dioxide using EoS-PR with three mixing rules: van der Walls 1 (vdW1), van der Walls 2 (vdW2) and Mathias-Klotz-Prausnitz (MKP).

2. Thermodynamic modelling

The isofugacity approach was used in the liquid-vapor equilibria (Equation 1):

$$\hat{f}_i^V(T,P,y_i) = \hat{f}_i^L(T,P,x_i) \tag{1}$$

For fugacity coefficients calculation it was chosen EoS-PR (Equation 2). For pure compounds, the attractive term (T) of EoS-PR was corrected by the model proposed by Soave [8] (Equation 3):

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+b(V-b)} \tag{2}$$

$$a(T) = \frac{0.45724R^2{T_c}^2}{P_c}\left[1 + (0.37464 + 1.54226\omega - 0{,}26992\omega^2)\left(1 - \sqrt{\frac{T}{T_c}}\right)\right]^2 \tag{3}$$

Mixture parameters a and b of the EoS-PR were calculated by three different mixing rules: vdW1 (Equation 4), vdW2 (Equation 5), and MKP (Equation 6):

$$a = \sum_i \sum_j z_i z_j \sqrt{a_i a_j}\,(1-k_{ij}) \qquad b = \sum_i z_i\, b_i \tag{4}$$

$$a = \sum_i \sum_j z_i z_j \sqrt{a_i a_j}\,(1-k_{ij}) \qquad b = \sum_i \sum_j z_i z_j \frac{1}{2}(b_i + b_j)(1-n_{ij}) \tag{5}$$

$$a = \sum_i \sum_j z_i z_j \sqrt{a_i a_j}\,(1-k_{ij}) + \sum_i z_i \left[\sum_j z_j (a_i a_j)^{\frac{1}{6}} (l_{ij})^{\frac{1}{3}}\right]^3$$

$$b = \sum_i \sum_j z_i z_j \frac{1}{2}(b_i + b_j)(1-n_{ij}) \tag{6}$$

and $k_{ij} = k_{ji}$, $n_{ij} = n_{ji}$, $l_{ij} = -l_{ji}$ and if $i = j$, $k_{ij} = 0$, $n_{ij} = 0$ e $l_{ij} = 0$.

Thermodynamic modeling of clove essential oil/CO_2 VLE was studied from two different approaches: as a binary mixture CO_2+clove essential oil and as a ternary mixture where essential oil is considered to be the major compounds that constitute the essential oil: CO_2+eugenol+ β-caryophyllene. Souza et al. [11] determined the clove essential oil composition by GC-MS and they found the following results in mass fraction: eugenol (75.5%), β-caryophyllene (12.5%), and other minor compounds. Thermophysical properties used for modeling the VLE experimental data are shown in Table 1.

Table 1. Pure compounds thermophysical properties.

	Pc (kPa)	Tc(K)	w	Tb(K)
CO_2	7380[a]	304.1[a]	0.239[a]	194.7[a]
β-cariophyllene	1993[c]	744.2[c]	0.4571[c]	536.15[d]
Eugenol	3510[c]	735.59[c]	0.6994[c]	527.15[d]
Clove oil	3097[b]	758.33[b]	0.6286[b]	524.15[d]

a) [8], b)[11], c)[12] e d)[13], d)Sigma-Aldrich

3. Results and discussion

The experimental VLE data of the CO_2+clove essential oil were taken from literature [11] and binary parameters of the EoS-PR mixture rules were fitted by objective function minimization (Equation 7):

$$FO = \frac{100}{N_p}\sum\left(\frac{P_{calc} - P_{exp}}{P_{exp}}\right)^2 \quad (7)$$

where N_p is the experimental data, P_{exp} is the experimental pressure, P_{cal} is the calculated pressure by EoS-PR. The pressure deviation for three EoS-PR mixture rules was calculated using the Equation 8.

$$\%\Delta P = \frac{100}{N_p}\sum\frac{\left|P_{calc} - P_{exp}\right|}{P_{exp}} \quad (8)$$

Figure 1 show results obtained for the binary system CO_2(1)/clove essential oil(2) at 313.2K. It is possible to notice that vapor phase experimental data did not were well fitted by three mixing rules used, but they represent well the liquid phase.

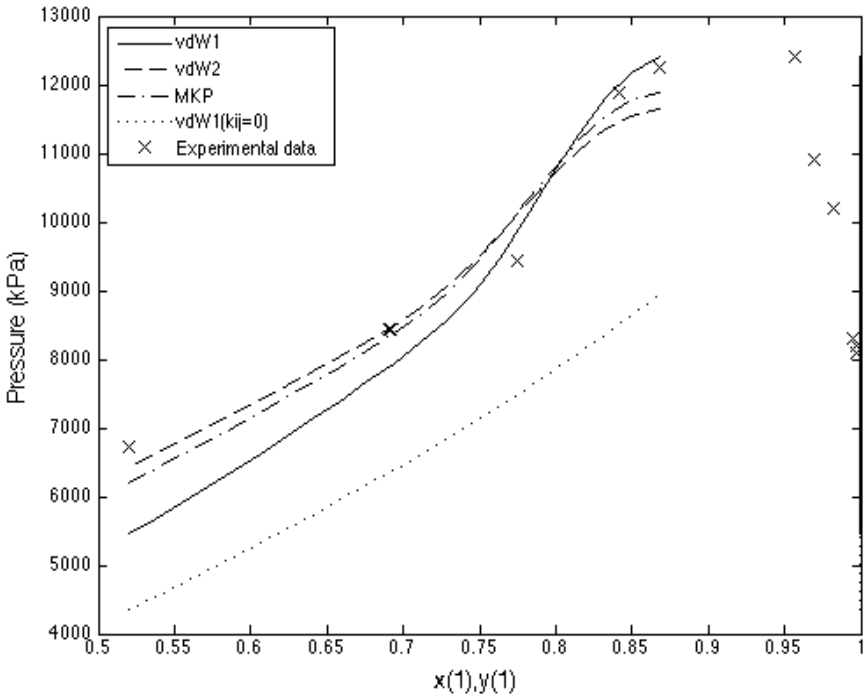

Figure 1. CO_2(1)/clove essential oil(2) VLE data at 313.2 K: Experimental [11] and calculated by EoS-PR vdW1; EoS-PR vdW2, EoS-PR MKP, and EoS-PR vdW1 (k_{ij}=0).

The parameters generated and %ΔP values for three EoS-PR mixture rules are shown in Table 2. It is possible to observe that EoS-PR vdW2 was the mixing rule that best fitted experimental data when VLE data were treated as a binary system.

Table 2. Binary parameters fitted and %ΔP values for mixture CO_2(1)/clove essential oil (2) ELV data.

	vdW1		vdW2			MKP			
T(K)	k_{12}	%ΔP	k_{12}	n_{12}	%ΔP	k_{12}	l_{12}	n_{12}	%ΔP
313	0.0370	7.53	0.0347	-0.0314	3.07	0.0357	-0.0148	-0.0240	3.29
318	0.0357	7.59	0.0329	-0.0314	1.62	0.0342	-0.0142	-0.0231	2.63
328	0.0318	6.69	0.0284	-0.0300	1.25	0.0284	-0.0211	-0.0300	1.25

In order to simulate VLE experimental data as ternary system were needed binary interaction parameters among compounds involved in ternary mixture CO_2(1)/eugenol(2)/β-caryophyllene(3). Therefore, the

CO_2(1)/eugenol(2) [14] and CO_2(1)/β-caryophyllene(2) [15] VLE were modeled by EoS-PR and their binary parameters were fitted. In Figure 2 is plotted CO_2(1)/eugenol(2) VLE data at 318 K. It is possible to notice that vdW2 and MKP were the mixing rules that best represented the VLE experimental data.

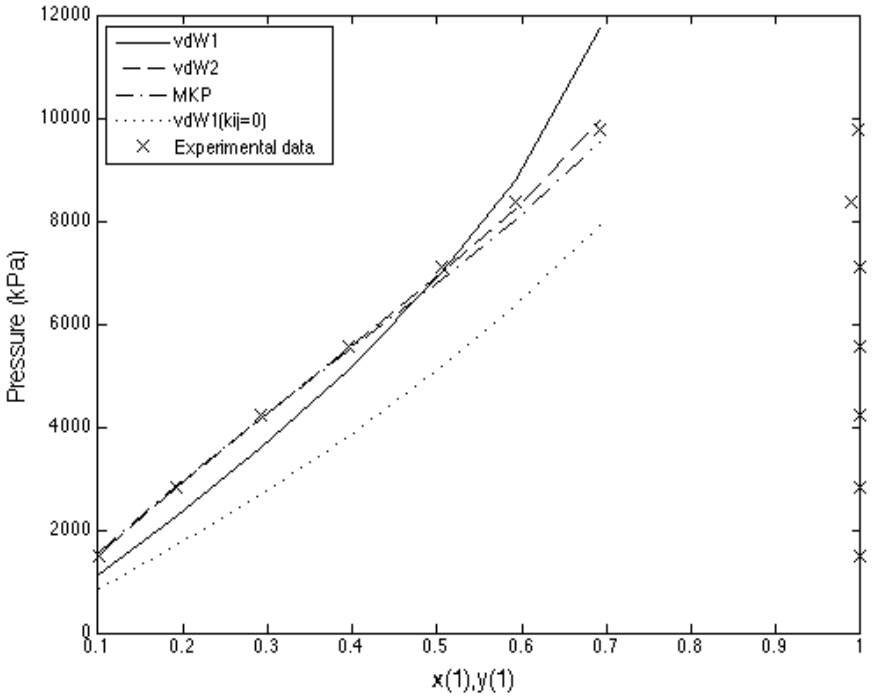

Figure 2. CO_2(1)/eugenol(2) VLE data at 318 K. Experimental [14] and calculated by EoS-PR vdW1; EoS-PR vdW2, EoS-PR MKP, and EoS-PR vdW1 (k_{ij}=0).

The parameters generated and %ΔP values for three EoS-PR mixture rules for CO_2(1)/eugenol(2) VLE data are shown in Table 3.

Table 3. Binary parameters fitted and %ΔP values for mixture CO_2(1)/eugenol(2) ELV data.

	vdW1		vdW2			MKP			
T(K)	k_{12}	%ΔP	k_{12}	n_{12}	%ΔP	k_{12}	l_{12}	n_{12}	%ΔP
308	0.0386	12.27	0.0212	-0.0245	2.55	0.0215	-0.0059	-0.0242	2.51
318	0.0441	13.24	0.0226	-0.0266	1.46	0.0171	0.0093	-0.0304	2.63
328	0.0368	11.50	0.0188	-0.0280	0.83	0.0168	0.0091	-0.0298	1.07

In Figure 3 is presented CO_2(1)/ β-caryophyllene(2) VLE data at 323 K. When analyzing the Figure 3 it is perceived that all mixing rules fitted well the pressure variable, however it appeared some error in the vapor phase composition.

The parameters generated and %ΔP values for three EoS-PR mixture rules for CO_2(1)/ β-caryophyllene (2) VLE data at 323 K are presented in Table 4. For this binary mixture the experimental data are available in the literature only at 323 K.

Table 4. Binary parameters fitted and %ΔP values for CO_2(1)/β-caryophyllene (2) ELV data.

	vdW1		vdW2			MKP			
T(K)	k_{12}	%ΔP	k_{12}	n_{12}	%ΔP	k_{12}	l_{12}	n_{12}	%ΔP
323	0.0973	1.01	0.0961	-0.0049	0.86	0.0969	-0.0011	-0.0011	0.95

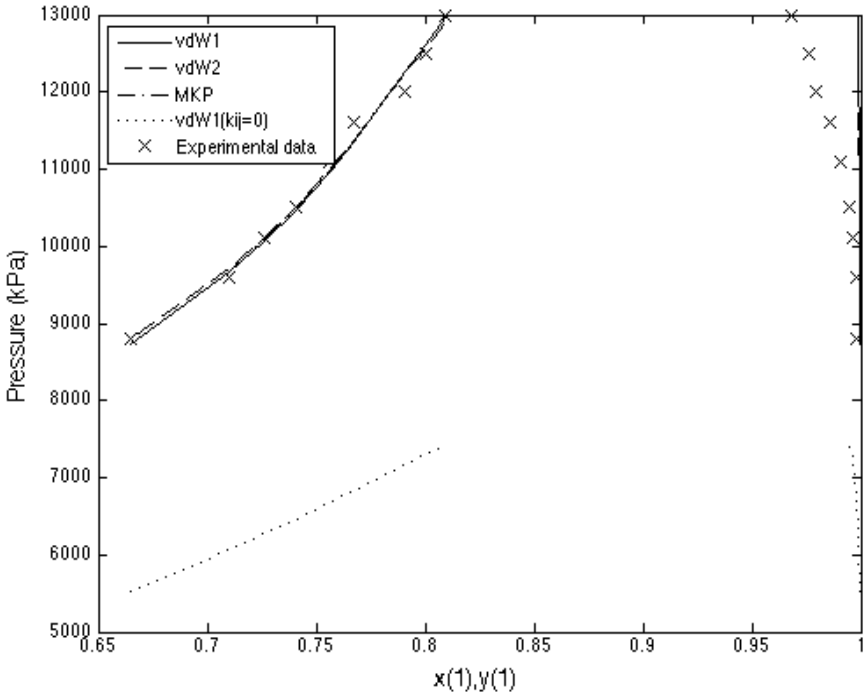

Figure 3. CO_2(1)/ β-caryophyllene (2) VLE data at 323 K. Experimental [15] and calculated by EoS-PR vdW1; EoS-PR vdW2, EoS-PR MKP, and EoS-PR vdW1 (k_{ij}=0).

In function of absence of VLE experimental data in the literature for binary mixing eugenol(1)/β-caryophyllene(2), the binary parameters of this mixture were fitted in the same way as a binary system CO_2(1)/clove essential oil(2), but keeping binary parameters of systems CO_2(1)/eugenol(2) and CO_2(1)/β-caryophyllene(2) constant. Binary parameters EoS-PR obtained to eugenol(1)/β-caryophyllene(2) binary mixture are shown in Table 5.

Table 5. Binary parameters fitted for eugenol(1)/β-caryophyllene(2) ELV data.

	vdW1	vdW2		MKP		
T(K)	k_{12}	k_{12}	n_{12}	k_{12}	l_{12}	n_{12}
308	0.0386	0.0212	-0.0245	0.0215	-0.0059	-0.0242
318	0.0441	0.0226	-0.0266	0.0171	0.0093	-0.0304
328	0.0368	0.0188	-0.0280	0.0168	0.0091	-0.0298

When considering only the major compounds (eugenol and β-caryophyllene) as clove essential oil, the CO_2(1)/eugenol(2)/β-caryophyllene ternary mixture presented the behavior similar to CO_2(1)/clove essential oil(2) at 313 K, as can be observed in Figure 4. The results to ELV modeling using EoS-PR MKP demonstrated that maximum relative error was reduced from 3.19% to 2.18%, when comparing CO_2(1)/eugenol(2)/β-caryophyllene(3) mixture with CO_2(1)/clove essential oil(2) pressure deviations (%ΔP) in relation to CO_2(1)/clove essential oil(2) experimental data [11].

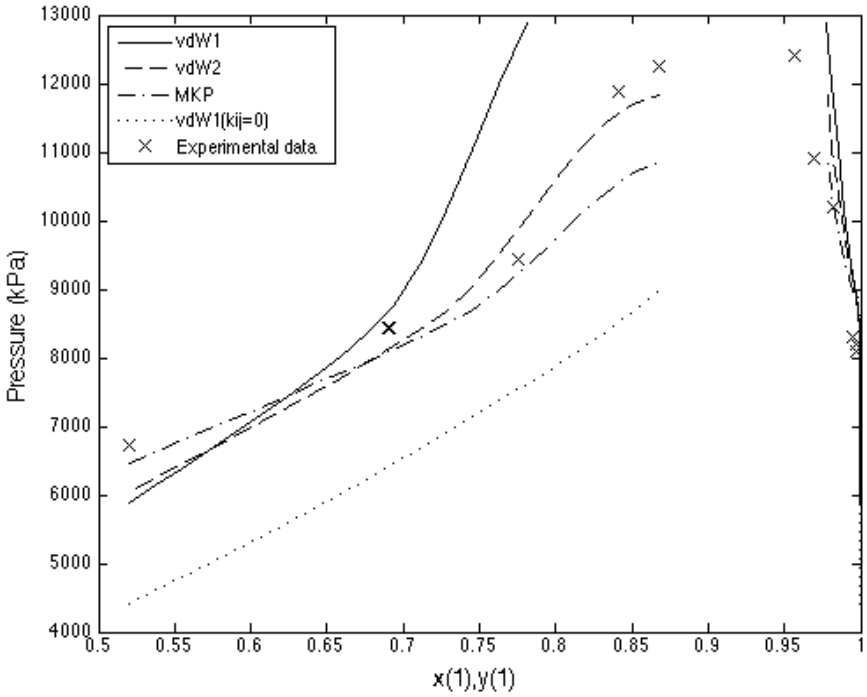

Figure 4. CO_2(1)/eugenol(2)/β-caryophyllene(3) VLE data at 313K. Experimental [11] and calculated by EoS-PR vdW1; EoS-PR vdW2, EoS-PR MKP, and EoS-PR vdW1 (k_{ij}=0).

When comparing the pressure deviation (%ΔP) shown in Table 2 with the results presented in the Table 6, it become clear that is possible to employ the major compounds to represent the colve essential oil..

Table 6. Pressure deviation (%ΔP) of CO_2(1)/eugenol(2)/β-caryophyllene(3) with regard to CO_2(1)/clove essential oil(2) VLE experimental data [11].

	%ΔP		
T (K)	vdW1	vdW2	MKP
313	11.53	4.10	2.18
318	13.31	4.06	1.28
328	13.67	1.77	1.16

4. Conclusions

By analyzing the data generated by EoS-PR with mixing rules: vdW1, vdW2, and MKP, it is possible to conclude that the number of parameters of mixing rules has directly influence in ELV modeling quality. For mixing rules studied, higher the number of parameters smaller was the deviation among calculate and experimental ELV data. Even as, the binary parameters fitted in this work can be used to calculate the solubility of clove essential oil in supercritical carbon dioxide, consequently they are fundamental information for mathematical modeling and simulation of supercritical extraction process of clove volatile compounds.

Acknowledgements

The authors thank CNPq, CAPES, FAPERGS.

References

[1] Gülçin I., Elmastaş M., Aboul-Enein H.Y. Antioxidant activity of clove oil - A powerful antioxidant source, Arabian Journal of Chemistry 5 (2012), p. 489-499.
[2] Gülçin I., Şat, I.G., Beydemir Ş., Elmastaş M., Küfrevioğlu Ö.I. Comparison of antioxidant activity of clove (*Eugenia caryophylata Thunb*) buds and lavender (*Lavandula stoechas L.*), Food. Chem. 87 (2004), p. 393-400.
[3] Scherer, R., WAGNER, R., DUARTE, M.C.T., GODOY, H.T. Composição e atividades antioxidante e antimicrobiana dos óleos essenciais de cravo-da-índia, citronela e palmarosa, Rev. Bras. Pl. Med. 11 (2009), p.442-449.
[4] Farag R.S., Badel, A.Z.M.A., Hewedi, F.M., El-Baroty G.S.A. Antioxidant activity of some spice essential oils on linoleic acid oxidation in aqueous media, JAOCS 66 (1989), p. 792-799.
[5] Wenquiang, G., Shufen, L., Ruixiang, Y., Shaokun, T., Can, Q. Comparison of essential oils of clove buds extracted with supercritical carbon dioxide and other three traditional extraction methods. Food. Chem. 101 (2007), p. 1558-1564.
[6] Cassel, E., VARGAS, R.M.F., BEDINOT, C. Unidad Piloto de Extracción Supercrítica Automatizada. In *Aplicaciones Industriales de los Taninos Vegetales: Productos y Procesos*. EDIPUCRS, 1994, Porto Alegre, Brasil. p. 95-102.
[7] Sovová H. Rate of the vegetable oil extraction with supercritical CO2 – I. modeling of extraction curves, Chem. Eng. Sci. 49 (1994), p. 409-414
[8] Soave, G. Equilibrium Constants from a Modified Redlich-Kwong Equation of State, Chem. Eng. Sci., 27 (1972) 1197-1203.
[9] Valderrama, J.O. The state of the cubic equations of state, Ind. Eng. Chem. Res. 42 (2003), p. 1603-1618.
[10] Mathias P.M., Klotz H.C., Prausnitz J.M. Equation-of-State mixing rules for multicomponent mixtures: the problem of invariance, Fluid Phase Equilibria 67 (1991), p. 31-44.
[11] Souza, A.T., Corazza, M.L., Cardozo-Filho, L., Guirardello, R., Meireles, M.A.A.M. Phase equilibrium measurements for the system clove (*Eugenia caryophyllus*) oil + CO2, J. Chem. Eng. Data 49 (2004), p. 352-356.
[12] Joback, K.G., S.M. Thesis in chemical engineering, Massachusetts Institute of Technology, Cambrige, Mass., June 1984.
[13] Lee, B.I., Kesler, M.G. AIChE J. 21 (1975), p. 510.
[14] Cheng K.W., Kuo S.-J., Tang M., Chen Y.-P. Vapor-liquid equilibria at elevated pressures of binary mixtures of carbono dioxide with methyl salicylate, eugenol and diethyl phthalate. .J. of Supercritical Fluids 18 (2003), p. 87-99.
[15] Maschietti, M. High-pressure gas-liquid equilibrium of the system carbon dioxide- β-caryophyllene at 50 and 70 ˚C. J. of Supercritical Fluids 59 (2011), p. 8-13.