

# CORRELATION AND PREDICTION OF THE SOLUBILITY OF BORAGE OIL IN DENSE CARBON DIOXIDE USING A CUBIC EQUATION OF STATE

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**Abstract** Amongst all the potential CO<sub>2</sub>-based techniques intended for polymer processing, the CO<sub>2</sub>-based impregnation/deposition (supercritical solvent impregnation/deposition - SSID) has proved to be a feasible and advantageous method for bioactive substances incorporation into biopolymers and so to develop polymeric-based controlled release system. Borage oil has been studied and applied for the treatment of wounds and several skin diseases mainly due to its high content in bioactive C16-C20 fatty acids. Prior to understand the complete phase behavior of ternary system composed of polymer-CO<sub>2</sub>-bioactive substance and to proceed to undergo any experimental, it is usually necessary to perform a preliminary evaluation on the feasibility and efficiency potential of the specific SSID process. Phase equilibrium data of CO<sub>2</sub>-bioactive substance binary system is usually hard, costly and time-consuming. In addition, current experimental data on the solubility of borage oil in compressed CO<sub>2</sub> is scarce. However, as an alternative strategy this limited experimental solubility data can be correlated and interpolated to predict the solubility of borage oil in compressed CO<sub>2</sub> under other conditions. In this paper, the borage oil solubility in compressed CO<sub>2</sub> were correlated and calculated using the Peng-Robinson equation of state from 283.15 K to 328.15 K and 6.0 MPa to 30.0 MPa. The van der Waals classical mixing rules and combining rules (with one and two adjustable parameters) and the LCVM mixing rule with the UNIFAC method were employed. Obtained correlation results showed a good agreement between experimental and calculated data for classical mixing rule with two adjustable parameters.

**Keywords:** Borage oil, Solubility, Peng-Robinson EOS, Mixing rules, High-pressure and Supercritical CO<sub>2</sub>.

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## 1. Introduction

The conventional impregnation process of biopolymers with bioactive substances requires three procedures: dissolution of bioactive substance (solute) in an appropriate solvent, the diffusion of the solute through the polymeric matrix, and elimination of residual solvent (Duarte et al. 2007). Amongst possible techniques for incorporation of bioactive principles in biopolymer, supercritical impregnation using carbon dioxide (scCO<sub>2</sub>) is a possibility and presents advantages beyond traditional techniques used to develop controlled delivery systems (Kikic and Vecchione 2003).

The present work is part of research project aimed at preparing polyurethane-based wound dressing loaded with borage oil using impregnation method with scCO<sub>2</sub>. Borage oil is extracted from the seeds of *Borago officinalis L.* It has been studied and applied for the treatment of wounds and several skin diseases mainly due to its high content in bioactive C16-C20 fatty acids, namely oleic (15-20%), linoleic (30-40%) and  $\gamma$ -linolenic (18-25%) acids (weight %) (Gaspar et al. 2003; Farahpour and Mavaddati 2012)

However, before investigating the behavior of the polyurethane-CO<sub>2</sub>-oil borage system and carrying out any experimental, one must firstly evaluate binary systems. The study of CO<sub>2</sub>-polymer system important in determining the maximum quantity of CO<sub>2</sub> that can be assimilated by the polymer and the polymer swelling, and solute-CO<sub>2</sub> system to know the high solubility of solute in CO<sub>2</sub> in pre-established conditions of both temperature and pressure.

The determination of the solubility of borage oil in CO<sub>2</sub> requires phase equilibrium data at high pressure, which is difficult to obtain, expensive and time-consuming. It is no coincidence that the experimental data of borage oil solubility in supercritical CO<sub>2</sub> in the literature are scarce. Therefore, an alternative is to have robust models that correlate a limited number of experimental data, and after validation, predict the solubility of borage oil in CO<sub>2</sub> for other pressure and temperature conditions.

In this paper, the borage oil solubility in compressed CO<sub>2</sub> and the corresponding binary mixture densities, were correlated and calculated using the Peng-Robinson equation of state from 283.15K to 328.15 K, and 6.0 MPa to 30.0 MPa. In order to evaluate the influence of the mixing rule in this approach, the van der Waals classical mixing rules

and combining rules (with one and two adjustable parameters) and the LCVm mixing rules with the UNIFAC method for excess Gibbs free energy calculation were employed.

## 2. Materials and Methods

### 2.1 Materials

The experimental data of borage oil solubility ( $C_{\text{exp}}^*$ ) in CO<sub>2</sub> at high pressure at different pressures (P), temperatures (T) and density ( $\rho$ ) were taken from literature (Gaspar et al. 2003) and are presented in Table 1.

**Table 1.** Experimental solubility borage oil ( $C_{\text{exp}}^*$ ) in dense CO<sub>2</sub>

P bar	T °C	$\rho$ kg.m <sup>-3</sup>	$C_{\text{exp}}^*$ kg.m <sup>-3</sup>
60	10	883.8	1.90
	25	190.5	0.11
	40	149.2	0.00
	55	129.6	0.00
100	10	921.9	2.80
	25	819.5	1.75
	40	629.3	0.26
	55	327.1	0.13
200	10	980.8	5.07
	25	915.2	5.77
	40	840.8	4.39
	55	755.5	2.05
300	10	1020.2	6.93
	25	966.8	9.87
	40	910.3	9.90
	55	850.6	9.96

### 2.2 Methods

The prediction of the solubility of a substance in dense CO<sub>2</sub> can be performed with the assistance of the model parameter estimation and validation of a model capable of describing the binary system behavior for different temperature and pressure conditions, in which the experimental data were measured. Due to the limited phase equilibrium data

for the CO<sub>2</sub>-borage oil system, an alternative methodology was developed to employ an equation of state to the solubility data presented in Table 1.

The solubility coefficient may be associated with the density and mass fraction of solute as shown in Equation (1).

$$C_i^f = \alpha_i^f \rho^f \quad (1)$$

where  $C_i^f$  is the solubility coefficient of the solute in the fluid phase,  $\alpha_i^f$  is the mass fraction of the solute and  $\rho^f$  is the fluid phase density. The description of the system requires the properties of each component involved. Although borage oil is a mixture of fatty acids, in this paper it was considered a pseudo component and the system considered as a binary system.

**Borage Oil Properties.** The oil composition was considered based on data given in Table 2 (Gaspar et al. 2003). Only oleic, linoleic and  $\gamma$ -linolenic acids were evaluated with the standard mass fractions equals to 0.21, 0.50 and 0.29, respectively.

**Table 2.** Bioactive C16-C20 fatty acids in borage oil

Fatty acid	Composition (% wt.)
Palmitic	9 - 12
Stearic	3- 5
Oleic	15 - 20
Linoleic	30 - 40
$\gamma$ -Linolenic	18 - 25

The critical properties  $T_c$  and  $P_c$ , normal boiling temperature and acentric factor,  $w$ , of borage oil were estimated by several group contribution methods, namely the Lydersen, Joback and Edmister methods (Reid, Prausnitz, and Sherwood 1977). The estimated properties are shown in Table 3 and MM denotes the molecular weight.

**Table 3.** Borage oil and carbon dioxide properties

	T <sub>c</sub> (K)	P <sub>c</sub> (atm)	w	MM (g.mol <sup>-1</sup> )
Borage oil	934.0	13.67	0.240	280.29
CO <sub>2</sub>	30.2	72.830	0.224	44.01

**Equation of State.** There are several empirical and theoretical equations of state used to describe the actual behavior of fluids under high pressure. Among the empirical cubic equations of state, the equations of Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR) are frequently used to model the phase equilibria of the binary systems involving supercritical CO<sub>2</sub> and produce results with good accuracy (Vieira de Melo et al. 1999). In this study, the Peng-Robinson cubic equation of state was selected to describe the behavior of this system, Equation (1).

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

Pure component parameters for the Peng-Robinson equation of state (PR EOS) are obtained by the following expressions:

$$a_i = 0.45724 \frac{R^2 T_{ci}^2}{P_{ci}} f(T_{ri}) \quad (3)$$

$$b_i = 0.07780 \frac{RT_{ci}}{P_{ci}} \quad (4)$$

$$\alpha_i = \frac{a_i}{b_i RT} \quad (5)$$

The terms,  $f(T_{ri})$ ,  $T_{ri}$  and  $m_i$  are calculated by the equations (6), (7) e (8), respectively.

$$f(T_{ri}) = [1 + m_i(1 - \sqrt{T_{ri}})]^2 \quad (6)$$

$$T_{ri} = T/T_{ci} \quad (7)$$

$$m_i = 0,37464 + 1,54226w_i - 0,26992w_i^2 \quad (8)$$

where  $T_{ci}$  is the critical temperature,  $P_{ci}$  is the critical pressure and  $w_i$  is the acentric factor of component  $i$ . The parameters  $a$  and  $b$  of the Peng-Robinson equation of state are calculated using mixing rules. Two types of mixing rule were employed to evaluate the performance of these two approaches to fit the experimental data.: classical (with one and two adjustable parameters) and LCVM - Linear Combination of Vidal and Michelsen Rules (Boukouvalas et al. 1994).

**Classical Mixing Rule.** Based on a previous experience (Vieira de Melo et al. 1999), classical mixing rules are used to calculate the parameters  $a$  and  $b$  of the mixture, taking into account one or two fitted parameters, as follows:

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad (9)$$

$$b = \sum_i \sum_j x_i x_j b_{ij} \quad (10)$$

where  $x_i$  and  $x_j$  are the molar fraction of the component in the mixture and the interaction  $a_{ij}$  and  $b_{ij}$  are given by:

$$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij}) \quad (11)$$

$$b_{ij} = \frac{b_i + b_j}{2} (1 - l_{ij}) \quad (12)$$

The binary interaction parameters,  $k_{ij}$  and  $l_{ij}$ , are determined by minimizing the difference between experimental and calculated solubility of borage oil in dense carbon dioxide. To calculate this solubility is necessary to determine the fugacity coefficient. The fugacity coefficient using Peng-Robinson Equation and classical mixing rule is shown in Equation (13).

$$\ln \hat{\phi}_i = \frac{b_i}{b} (1 - Z) - \ln(Z - B) - \frac{A}{2\sqrt{2}B} \left( \frac{2 \sum_i y_i a_{ij}}{a} - \frac{b_j}{b} \right) \ln \left( \frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B} \right) \quad (13)$$

**LCVM Mixing Rule.** The linear combination of Vidal and Michelsen rules (LCVM) is another way to calculate the interaction parameter of the cubic equation of state coupled with the UNIFAC model for the activity coefficient (Boukouvalas et al. 1994). Equation (14) calculates the fugacity coefficient using the Peng-Robinson equation and LCVM mixing rule.

$$\ln \hat{\phi}_i = \frac{b_i}{b} \left( \frac{Pv}{RT} - 1 \right) - \ln \frac{P(v-b)}{RT} - \frac{\bar{\alpha}_i}{2\sqrt{2}} \ln \left[ \frac{v(1+\sqrt{2})b}{v(1-\sqrt{2})b} \right] \quad (14)$$

The other terms of the Equation (14) are calculated as follows:

$$\alpha = \left( \frac{\lambda}{A_v} + \frac{1-\lambda}{A_M} \right) \frac{G^E}{RT} + \frac{1-\lambda}{A_M} \sum_i x_i \ln \frac{b}{b_i} + \sum_i x_i \alpha_i \quad (15)$$

where  $A_V$  and  $A_M$  are constants related to Vidal and Michelsen mixing rules, respectively. As the Peng-Robinson equation of state,  $A_V = -0.623$  e  $A_M = -0.52$ .  $G^E$  is related to the activity coefficient  $\gamma_i$  calculated by the UNIFAC group contribution model and  $\lambda$  is the LCVM parameter that weighs Vidal and Michelsen mixing rules contribution. In this work,  $\lambda$  is estimated by fitting to experimental data. The parameter  $\bar{\alpha}_i$  is expressed by Equation (16). The parameter  $b$  is calculated with the conventional linear mixture rule shown in Equation (17)

$$\bar{\alpha}_i = \left( \frac{\partial n\alpha}{\partial n_i} \right)_{T,P,n_j \neq n_i} = \left( \frac{\lambda}{A_V} + \frac{1-\lambda}{A_M} \right) \ln \gamma_i + \frac{1-\lambda}{A_M} \left( \ln \frac{b}{b_i} + \frac{b_i}{b} - 1 \right) + \alpha_i \quad (16)$$

$$b = \sum_i x_i b_i \quad (17)$$

**Solubility Modeling.** The molar fraction of borage oil in dense phase is calculated from the solute isofugacity criteria between CO<sub>2</sub> dense phase and oil phase. Due to low solubility of CO<sub>2</sub> in the oil phase, one can assume that the supercritical fluid does not dissolve in oil phase. Therefore, the solubility of borage oil in dense CO<sub>2</sub> is expressed by the Equation (18) by assuming that the fugacity coefficient of pure borage oil is unity at a given temperature and vapor pressure:

$$x_2 = \frac{P_2^{sat}}{\hat{\phi}_2 P} \exp \left[ \frac{v_2^L (P - P_2^{sat})}{RT} \right] \quad (18)$$

where  $x_2$  is the molar fraction of borage oil,  $P_2^{sat}$  is the vapor pressure of pure borage oil,  $v_2^L$  is the molar volume of borage oil phase and  $\hat{\phi}_2$  is the fugacity coefficient of the borage oil in CO<sub>2</sub> dense phase.

The estimation of vapor pressure of oil was obtained by Equation (19). A and B parameters were estimated from normal boiling temperature and critical temperature obtained by group contribution presented in Table 3.

$$P_2^{sat} = A - \frac{B}{T} \quad (19)$$



The molar volume ( $v_2^L$ ) is estimated from Gunn and Yamada equation (Reid, Prausnitz, and Sherwood 1977).

**Objective Function.** Borage oil-CO<sub>2</sub> binary interaction parameters were calculated by fitting the experimental solubility data available in the literature (Gaspar et al. 2003). The following objective function (*OF*) was adopted:

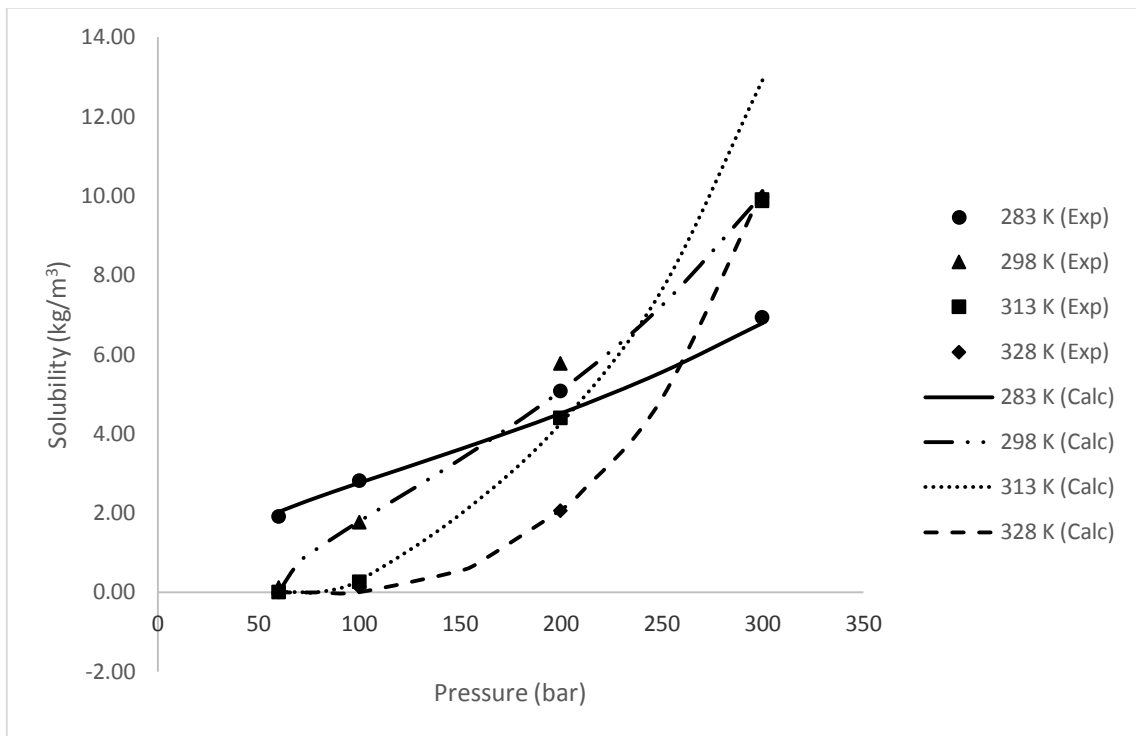
$$OF = \min \sum_{i=1}^{NEP} \frac{|C_i^{exp} - C_i^{calc}|}{C_i^{exp}} \quad (20)$$

where *NEP* is number of experimental points,  $C_i^{exp}$  is the experimental solubility coefficient and  $C_i^{calc}$  is the calculated solubility coefficient.

### 3. Results

The classical mixture rule was used with two approaches: only one interaction parameter,  $k_{ij}$ , and two parameters,  $k_{ij}$  and  $l_{ij}$ . During the first tuning attempts the interaction parameters were considered as temperature independent and were estimated to range from 283 to 328 K. The calculated results not show good agreement with experimental data for both approaches.

Thus, we performed the parameter estimation for each temperature. The approach in which we use the estimation of a single parameter,  $k_{ij}$ , for each temperature did not provide a good fit. However, the estimation of two interaction parameters ( $k_{ij}$  and  $l_{ij}$ ) for each temperature leads to satisfactory results, as shown in Figure 1.

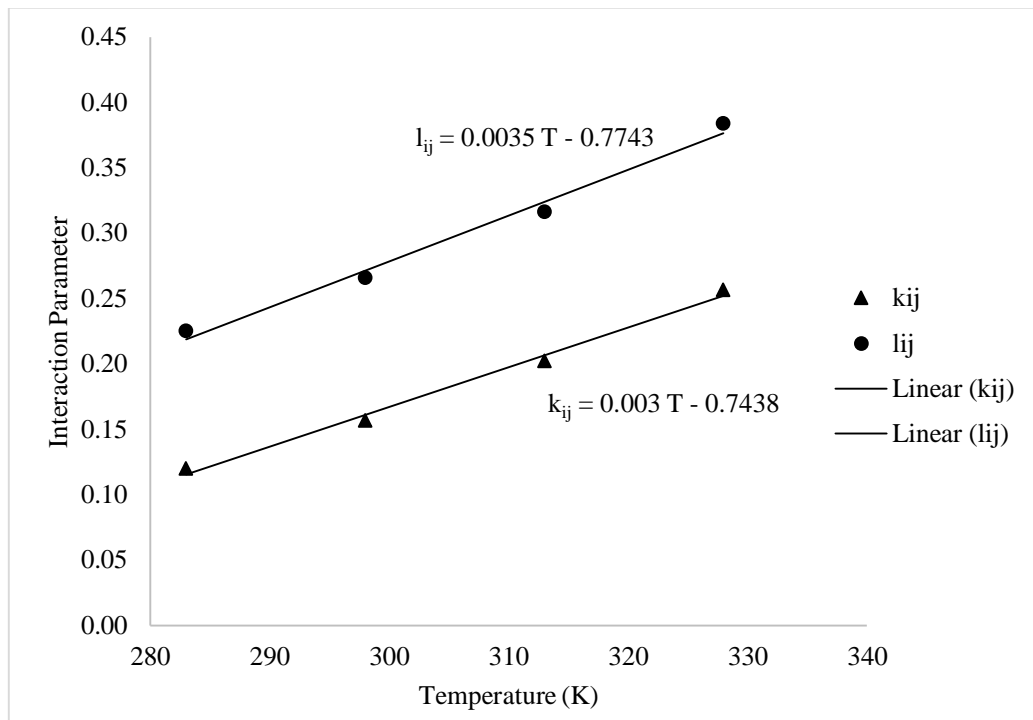


**Fig 1.** Borage oil solubility in dense CO<sub>2</sub> calculated by the Peng-Robinson equation and classical mixing rule with two parameters.

The  $k_{ij}$  and  $l_{ij}$  values are displayed in Table 4 and we observed that their values increase with increasing temperature, as shown in Figure 2. This allows the proposal of a correlation of these parameters under different conditions as a function of the temperature range from 283 to 328 K.

**Table 4.** Estimated two interaction parameters at several temperatures

T (K)	$k_{ij}$	$l_{ij}$
283	0.12	0.22
298	0.16	0.27
313	0.20	0.32
328	0.26	0.38



**Fig 2.** Correlation of binary interaction parameters with temperature

The relative percentage errors were obtained by Equation (21) and are showed on the Table 5. The reason for the high percentage relative error is due to the magnitude order (extremely small value) of the molar composition of the borage oil in CO<sub>2</sub>.

$$error = 100 \frac{|x_i^{exp} - x_i^{calc}|}{x_i^{exp}} \quad (21)$$

The correlation using Peng-Robinson equation with LCVM mixing rule and classical model with only one parameter did not provide a good agreement with experimental data. These results show that this system cannot be described with only one fitted parameter. One explanation for this performance is the complex nature of the mixture and extremely small mole fraction of the borage oil in CO<sub>2</sub>. Another relevant fact to be mentioned concerns the structure of the mixing rule. We can see that for this selected system the rule structure does not influence. LCVM and classical rules have very different structures. What matters is the number of parameters.

**Table 5.** Borage oil solubility in dense CO<sub>2</sub> calculated using classical mixing rule with two temperature dependent parameters

T (K)	P (bar)	C <sup>exp</sup> (kg/m <sup>3</sup> )	C <sup>calc</sup> (kg/m <sup>3</sup> )	x <sup>exp</sup> (molar)	x <sup>calc</sup> (molar)	error (%)
283	60	1.90	2.03	3.4E-04	3.7E-04	10.38
	100	2.80	2.76	4.8E-04	4.8E-04	0.63
	200	5.07	4.52	8.2E-04	7.1E-04	13.04
	300	6.93	6.80	1.1E-03	1.0E-03	5.63
298	60	0.11	0.00	9.1E-05	8.7E-08	99.90
	100	1.75	1.78	3.4E-04	3.6E-04	6.64
	200	5.77	5.08	1.0E-03	8.7E-04	12.72
	300	9.87	10.03	1.6E-03	1.6E-03	1.33
313	60	0.00	0.00	0.0E+00	5.8E-08	0.00
	100	0.26	0.29	6.5E-05	8.1E-05	25.34
	200	4.39	4.27	8.2E-04	8.1E-04	1.78
	300	9.90	12.93	1.7E-03	2.2E-03	28.27
328	60	0.00	0.00	0.0E+00	7.1E-08	0.00
	100	0.13	0.01	6.2E-05	3.9E-06	93.78
	200	2.05	2.08	4.3E-04	4.5E-04	55.48
	300	9.96	10.13	1.9E-03	1.9E-03	71.43

#### 4. Conclusion

This research of CO<sub>2</sub>-borage oil systems aimed to prescribe the conditions in which the solubility of the oil in CO<sub>2</sub> is higher, in order to identify the best conditions for the polyurethane impregnation process. Phase equilibrium data of CO<sub>2</sub>- borage oil is usually difficult, costly and time-consuming to obtain. In addition, current experimental data on the solubility of borage oil in compressed CO<sub>2</sub> is scarce. The shortage of phase equilibrium data of this system presents difficulties for such assessment and departing for the alternative system modeling from solubility coefficient data.

The modeling of this system is very difficult because the low molar fraction of borage oil in the mixture. Thus, we concluded that the modeling with only one parameter (only  $k_{ij}$  in classical mixing rule or  $\lambda$  in LCVM mixing rule) is not feasible. However, the correlation obtained with two adjustable parameters shows satisfactory and the parameter can be used for prediction in different condition of temperature and pressure.

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