CORRELATING SOLUBILITY VALUES OF BLACK PEPPER OIL IN SUPERCRITICAL CO_2 USING EMPIRICAL MODELS

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ABSTRACT

Solubility data are important process parameters, valuable for design and scale up purposes. The equilibrium concentration, or solubility value, indicates the maximum solute concentration in the solvent phase and, for high pressure processes, is related to the solvent density.

In supercritical fluid processes, the solubility data can be obtained experimentally by dynamic or static methods, which require considerable experimental effort in order to obtain adequate equilibrium information. A valuable contribution for equilibrium data can be achieved with empirical correlations, in order to provide a better understanding of the dissolution phenomena.

Therefore, the objective of this work was to investigate the efficiency of empirical correlations, such as density based correlations like the models proposed by Chrastil and by Del Valle and Aguilera, to correlate experimental solubility data. The empirical modeling was evaluated considering experimental solubility data presented for the complex system black pepper oil (*Pipper nigrum*) and supercritical CO_2 that varied from 8.58×10^{-2} to 10.44×10^{-2} g oil/ g CO_2.and were obtained for solvent density varying from 701.00 a 948.59 kg CO_2/m^3. The comparison between experimental and correlated data indicate that the better adjustments were obtained by the enhancement factor model.

Key words: empirical modeling, solubility, black pepper oil.

INTRODUCTION

Black pepper (*Pipper nigrum* L.) is one of the most used spices in the world, especially due to its flavor and pungency. The components of the black pepper extract are responsible for its acceptance as a valuable spice, mainly because of the content in alkaloids, essential oil and terpenes. The supercritical fluid extraction of black pepper oil is a viable technology due to the increasing availability of high pressure equipment and to the product quality, free of extraction solvent. The use of low temperature, the possibility of temperature and pressure control and the selectivity of the extraction are also other advantages of the high pressure process [1, 2].

For design and scale up purpose, thermodynamic data are imperative for process modeling. Although, due to the limited amount of available experimental data, there is a main interest in thermodynamic models that are able to describe the phase behavior. The use of equations of state (EOS) and empirical correlations, density dependant are useful tools for the phase equilibrium evaluation. EOS can predict the phase behavior but are limited in the description of the near critical region. Also, these models require information such as critical properties, acentric factor and molar volume, which the experimental values normally are not available. In the other hand, empirical models are incapable to predict the phase behavior, but are helpful for experimental data correlation. Therefore, in this work, empirical density dependant correlations proposed by Chrastil and by Del Valle & Aguilera and also the correlation based on the enhancement factor were used to evaluate the system CO_2-black pepper oil, considered as a pseudo-binary system [3 - 6].

I - MATERIALS AND METHODS

The experimental values of the black pepper solubility in supercritical CO_2 were described by FERREIRA *et al*, 1999 [1] for temperatures at 30, 40 and 50^{o}C and pressures at 150, 200 and 300 bar. The solubility experimental values were obtained from overall extraction curves (OEC) describing a dynamic process. To guarantee the phase equilibrium for solubility determination, the OEC used were the ones developed at low solvent flow rate. Therefore, the solubility (y^*) was the slope of the constant extraction rate period of the OEC, resulting from a linear regression applied to the experimental data [1].

To evaluate the use of empirical model to correlate solubility data of complex mixtures in supercritical CO_2, the selected models (Chrastil, Del Vale & Aguilera, enhancing factor) were applied for the system supercritical CO_2/black pepper oil. These models are described to be appropriate for the range of temperature and pressure from which the experimental values were obtained. Also, they are mathematically simple and easy to apply, represent a linear relation between solubility and solvent density and are indicated from the literature to show good adjustment to experimental values [3, 4].

Chrastil's model (CH)

The Chrastil's model considers the formation of a solvation complex between the solvent and the solute molecules in the equilibrium, showing a linear relation between solubility, solvent density and process temperature. The equation that represents the solubility model is presented as follow [5]:

$$\ln y^* = k.\ln r + \frac{a}{T} + b \qquad (1)$$

where y* represents the solute solubility express in *g/L*, T is the system temperature (K) and ρ is the solvent density (g/L). Also, *a, b* and *k* represent the adjustable constants of the model [3, 5, 7]. The constant *k* indicate the number of CO_2 molecules present in the complex solute-solvent. The *a* and *b* parameters are vaporizing enthalpy and molecular weight dependants, respectively.

Del Valle & Aguilera's model (DVA)

The model from del Valle and Aguilera is a modification of the Chrastil's model and the changes were based on the behavior of the adjust of solubility data from several vegetable oils, such as corn, soy and sunflower. The proposed equation is adequate for a temperature range from 293 to 353 K and for pressure varying from 150 to 880 bar. The model is represented as follow [5, 6]:

$$\ln y^* = k.\ln r + \frac{a}{T} + \frac{b}{T^2} + c \qquad (2)$$

Enhancement factor's model (EF)

This model considers a linear relation between enhancement factor (E) and solvent density and also relates the solute solubility with E and the solute vapor pressure, as shown in the following equations [3]:

$$\ln E = A + Br \qquad (3)$$

$$y^* = \frac{P^S}{P}.E \qquad (4)$$

where E is the enhancement factor, ρ the CO_2 density (g/L), A and B the adjustable model parameters, P^S is the solute vapor pressure and P the system pressure [3]. In this work the solute (black pepper oil) was consider a pseudo-pure component, evaluated through the oil composition presented by Ferreira *et al.*, 1999 [1]. The solute vapor pressure for the black pepper oil was than obtained from the oil composition and using the corresponding states method from Ambrose-Walton [8].

II. RESULTS AND DISCUSSION

The use of empirical correlations for the modeling of solubility data for the system black pepper oil/supercritical CO_2 was based on the experimental data from the literature [1]. **Table 1** shows the experimental values used in this study, the operational conditions (temperature and pressure) and the solvent correspondent density, obtained according to ANGUS (1976) [9].

Table 2 presents the parameter values obtained with the adjust of the experimental data to the Chrastil's model and to the Del Valle & Aguilera's model. The vapor pressure data (P^S) for black pepper oil, calculated according to Ambrose-Walton's method [8], and the parameters for the enhancement factor model are shown in **Table 3**.

Table 1: Black pepper oil solubility in supercritical CO_2.

T (°C)	P (bar)	ρ (g/L) (*)	Solubility (**) (g solute/L CO_2)
30	150	847,79	75,453
40	150	781,27	72,814
50	150	701,00	60,145
30	200	890,87	100,579
40	200	840,40	87,737
50	200	785,12	78,119
30	300	948,59	136,976
40	300	910,61	124,298
50	300	871,21	109,336

(*) [9].
(**) [1].

Table 2: Parameter values for the empirical models Chrastil and Del Valle & Aguirela.

Empirical Model	a	b	c	k
Chrastil	-14807,9	26,123	-	3,84
Del Valle & Aguilera	70207,45	-13500128,15	-107,409	3,84

Table 3: Enhancement factor model: Parameter values and solute vapor pressure.

Temp (ºC)	P^S (bar)	A	B ($x10^3$)
30	0.0129	2.8721	12.764
40	0.0171	7.9724	6.770
50	0.0222	7.5652	7.600

Based on the adjusted parameters for the empirical correlations (**Tables 2** and **3**), the modeled solubility data were obtained for 30, 40 and 50°C as a function of solvent density, for the studied empirical models. The comparison between experimental and calculated solubility values are shown in **Figure 1**.

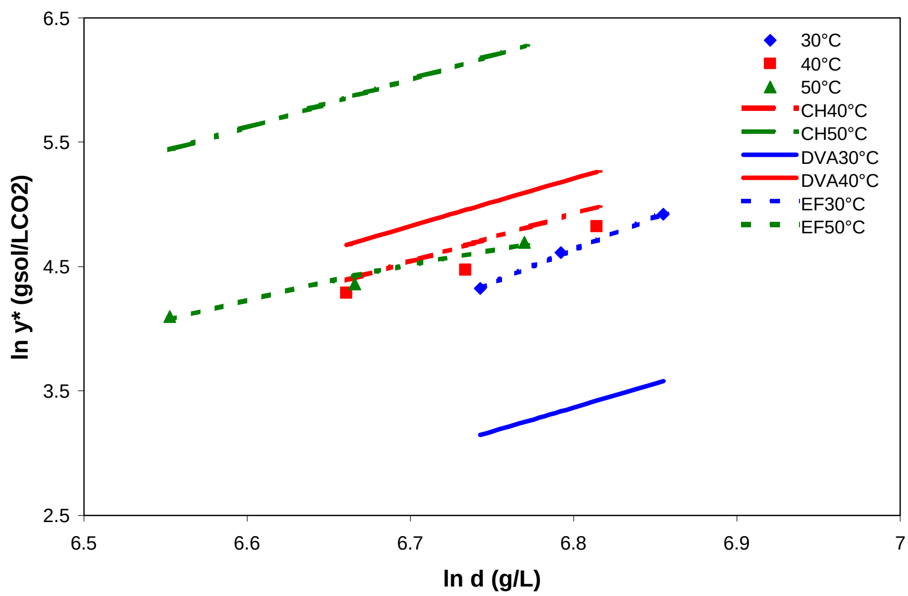

Figure 1. Black pepper solubility data:
Comparison between experimental and calculated values

The average absolute relative deviations (AARD) was calculated as an accuracy criterion for the comparison between experimental and modeled values. The AARD was calculated according to equation (5) and the results, shown in **Table 4**, were obtained for the empirical models Chrastil (CH), Del Valle & Aguilera (DVA) and Enhancement Factor (EF) for 30, 40 and 50°C. **Table 4** also presents the calculated σ-square for the empirical models CH, DVA and EF.

$$AARD = \left(\frac{100}{(n)}\right)\sum\frac{\left|y^{\exp erimental} - y^{calculado}\right|}{y^{\exp erimental}} \quad (5)$$

where *n* is the number of experimental solubility data used to obtain the empirical model parameters.

Table 4. Average absolute relative deviations (AARD) and σ-square (σ^2) for the empirical models.

T(ºC)	AARD (%) (CH)	σ^2 (CH)	AARD (%) (DVA)	σ^2 (DVA)	AARD (%) (EF)	σ^2 (EF)
30	71.734	0.998	71.744	0.998	1.0315	0.998
40	11.951	0.989	54.610	0.989	47.379	0.449
50	341.41	0.995	480.47	0.995	3.718	0.972

Evaluating **Figure 1** and **Table 4** we observe that the adjusted values from CH and DVA were similar, probably due to the fact that DVA model (3 parameters) is based on CH model (2 parameters) with the addition of one adjustable parameter and the increase of the process temperature contribution in the solubility values. The modeled results indicate good agreement between experimental and calculated values using CH and DVA, only for the 40ºC. At 30 and 50ºC, CH and DVA did not agree with the experimental values, although these temperatures are in the range of validity of both model.

The EF model produced good results at 30 and 50ºC (better agreement between experimental and calculated values), as shown in **Figure 1**. At 40ºC, the EF model indicate good adjustment only at 200 bar, but the modeled results for the set of experiments were not represented for a straight line (σ^2=0.449).

The behavior presented by the modeled results show the importance of the solute vapor pressure in the solubility data, indicating the proximity of the cross-over region. At 40ºC and for the studied range of pressure the results indicate the dominate effect of the density factor, expressed by the models CH and DVA.

CONCLUSÃO

It was observed good agreement between experimental and correlated data for the solubility of black pepper oil in supercritical CO_2, using empirical correlations. The best modeled results were obtained using the enhancement factor model (EF), for 30 and 50ºC, where the AADR (%) was 1.032 and 3.718, respectively. At 40ºC the CH model indicate better agreement (ADDR = 11.951%). It was also observed the importance of the solute vapor pressure, related to the cross-over region. Although, for the set of experiments used in this work, it was not possible to evaluate the correlations efficiency related to the process operational conditions.

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