CALCULATION OF SOLUBILITIES FOR SYSTEMS CONTAINING BIXIN, β-CAROTENE AND SUPERCRITICAL CARBON DIOXIDE

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Thermodynamic modelling of solid solubility in supercritical fluids is normally limited to pure solids. Even in the presence of solid mixtures, it is considered that the different solids in the mixture behave as if they were alone, that is, they do not interact. Results in the literature show that this hypothesis is true if the molecules of the solutes have some symmetry, both in size or polarity. The aim of this work is to present a thermodynamic model for a very asymmetric system consisting of two solids (β-carotene and bixin) and supercritical solvent (carbon dioxide). This system is very complex and the nonideallity happens due to the difference of the sizes of the molecules and their polarities. The model is based on Peng-Robinson equation of state and depends on the critical properties and the binary interaction parameters. These parameters between carbon dioxide and β-carotene and between carbon dioxide and bixin were obtained from binary experimental data presented in the literature. For the solid mixture, β-carotene and bixin, the model without any solid interaction describes poorly the available experimental data (approximately 75% of average deviation). Then, a model considering an interaction between the components in the solid phase and relaxing the constraint of equal interaction parameters between the solutes was tested and able to better describe the experimental data behaviour, with a deviation of 20% for bixin and 45% for the β-carotene.

INTRODUCTION

Annatto (*Bixa orellana*) is a tropical tree whose seeds produce pigments which have a widespread use in the food industry, namely for colouring butter, margarine, cheese, oils and sauces, with hues ranging from yellow to red [1]. Bixin, which is represented in figure 1, is a carotenoid of molecular weight 394.0 g/mole, found only in the seeds of Annato (2-3% wt.), and chemically is the mono-methyl ester of the dicarboxylic acid norbixin [2]. That compound is one of the main natural colouring materials [3] being easily degraded when exposed to light, but its sensibility to heat is better up to 125 °C [4]. While the bixin is soluble in oils upon heating, other important pigment found in annatto seeds, the norbixin, is soluble in water and insoluble in supercritical CO_2 [5]. β-Carotene, which is also represented in figure 1, is another carotenoid of high molecular weight (536.9 g/mole) with colours ranging from light orange to dark red. It appears largely distributed in nature in plants (carrots, tomatoes, annatto, etc.), fungi and algae. This compound has important applications as provitamin A, anti-oxidant and colouring material.

Measurements of solid and liquid solubility in supercritical fluids continue to be an important part of supercritical fluid (SCF) research. Despite the extensive progress that has occurred, equations of state (EOS) and related models used to describe supercritical fluid

phase behaviors are still not capable of being completely predictive across all solute-SCF systems [6].

The importance of studies of solubility in supercritical fluids of mixtures of two solid compounds has recently been emphasized [7]. These authors reviewed many examples already studied. The presence of a second solute can alter the solubility obtained in binary systems, solid-supercritical fluid, enhancing it as was the case for instance of naphthalene and benzoic acid mixtures in supercritical CO_2 [8] and hydroxybenzoic acid isomers mixtures in the same supercritical solvent [9] or lowering it as happened in mixtures of β-carotene and capsaicin, in which the latter compound showed lower solubility when compared with that obtained in the binary system [10].

The aim of this work is to present a thermodynamic model for the calculation of phase equilibrium to a very asymmetric system consisting of two solids (β-carotene and bixin) and supercritical carbon dioxide.

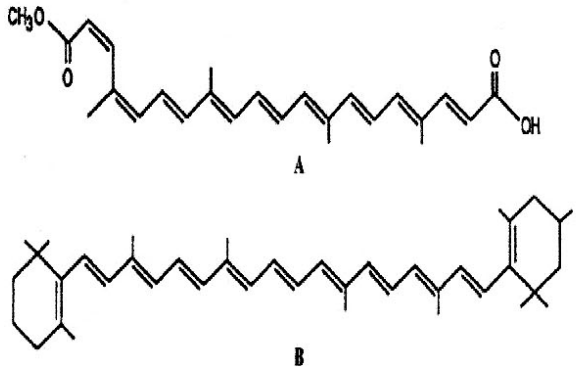

Figure 1: Structural formulae of *cis*-bixin (A) and *trans*-β-carotene (B).

THERMODYNAMIC MODEL

The assumptions of the thermodynamic model applied in this work are: the supercritical phase is a dense gas phase; the solubility of the gas in the solid phase can be neglected; one component solid phase is considered as pure solid phase; solid mixture is considered to behave like-very heavy liquid phase and the interaction between the components in this phase exists.

Under these conditions, the solubility of a solid, y_1, in the supercritical fluid phase is calculated using the following equation:

$$y_1 = \frac{P_1^{sat}}{P} \frac{\phi_1^{sat}}{\hat{\phi}_1^{G}} \exp\left[\frac{V_1^{sat}\left(P - P_1^{sat}\right)}{R\,T}\right] \quad (1)$$

where the symbol G represents the gas phase; y_1 is the molar fraction of pure solid in the gas phase, superscript *sat* represents the saturation condition, P^{sat} represents the sublimation pressure, V^{sat} the molar volume of solid and ϕ the fugacity coefficient.

Considering the solid mixture, the solubility of each solid in the gas phase is given by:

$$y_1 = \frac{\phi_1^{S}}{\hat{\phi}^{G}_1} x_1 \quad (2)$$

where S indicates mixture solid phase.

The thermodynamic model is based on the Peng-Robinson cubic equation of state (PR EOS) [11] to calculate the fugacity coefficient and it is given by

$$P = \frac{R\,T}{V - b} - \frac{a}{(V + C_1\,b)(V + C_2\,b)} \tag{6}$$

where P is the absolute pressure, T is the absolute temperature, R is the gas universal constant, a is the energy parameter and b is the co-volume parameter which can be obtained by:

$$b = b_i = \Omega_b \frac{R\,Tc_i}{Pc_i} \tag{7}$$

$$ac_i = \Omega_a \frac{R^2\,Tc_i^2}{Pc_i} \tag{8}$$

$$a = a_i = ac_i\ (F\alpha)_i \tag{9}$$

$$(F\alpha)_i = \left[1 + K_i(1 - Tr_i^{1/2})\right]^2 \tag{10}$$

$$K_i = 0{,}37464 + 1{,}54226\ w_i - 0{,}26992\ w_i^2 \tag{11}$$

$$Tr_i = T / Tc_i \tag{12}$$

$$C_1 = 1 + \sqrt{2}\,;\ C_2 = 1 - \sqrt{2} \tag{13}$$

and Tc is the critical temperature, Pc is the critical pressure, w is the acentric factor, and Ω_a=0.7780, Ω_b=0.45725.

The cubic form of the PR EOS for the compressibility factor, z, is

$$z^3 - (1 - B)\,z^2 + (A - 3\,B^2 - 2\,B)\,z - (A\,B - B^2 - B^3) = 0 \tag{14}$$

where

$$A = \frac{a\,P}{R^2\,T^2} \tag{15}$$

$$B = \frac{b\,P}{R\,T} \tag{16}$$

For mixtures, the mixing rules are given by

$$b = b_m = \sum_i \sum_j z_i\,z_j\,b_{ij} \tag{17}$$

$$a = a_m = \sum_i \sum_j z_i\,z_j\,a_{ij} \tag{18}$$

where m represents mixture, j a component and the summation is over all the components presents in the mixture. The parameters a_{ij} and b_{ij} are given through the following combination rule:

$$a_{ij} = (a_i\ a_j)^{1/2}(1 - k_{ij}) \tag{19}$$

$$b_{ij} = \frac{1}{2}(b_i + b_j)(1 - L_{ij}) \tag{20}$$

where $k_{ij} \neq k_{ji}$, $k_{ii} = 0$, $L_{ij} = L_{ji}$ *and* $L_{ii} = 0$.

The fugacity coefficient ($\hat{\phi}_i$) of the component i in the mixture, from the PR EOS, is given by

$$\ln(\hat{\phi}_i) = \frac{b_i}{b_m}(z - 1) - \ln(z - B) + \frac{A}{2\sqrt{2}\,B}\left[\frac{b_i}{b_m} - \frac{2}{a_m}\sum_j z_j\,a_{ij}\right]\ln\left[\frac{z + \alpha\,B}{z - \beta\,B}\right] \tag{21}$$

RESULTS AND DISCUSSION

Experimental data were obtained in the literature to the following systems: β-carotene + carbon dioxide [12] and bixin + carbon dioxide and β-carotene + bixin + carbon dioxide [13]. It is observed from the experimental data that the bixin solubility in the ternary system, with the presence of carotene, is higher than in the binary system, bixin + carbon dioxide, while the β-carotene solubilities are similar in both systems. The increasing of the bixin solubility is from 2.5 to 5.5 times in the same condition of temperature and pressure. The physical properties of the β-carotene (1) and of the bixin (2) were not available. It was necessary to estimate them. Joback's method was used to estimate the critical properties [14], but the results show that it is not possible to adjust adequately the solubility data. Then, the critical properties and the acentric factor were estimated minimising the deviation between the calculated and experimental results table 1 and table 2 show the physical properties calculated using Joback method [14] and the values obtained in this work for β-carotene and for bixin, respectively.

Table 1: Physical properties of β-Carotene

	Joback method [14]	Present Work
Pc (bar)	6.07	10.0
Tc (K)	1481.1	648.0
w	0.4844	0.411
Tb (K)	1209.6	-
Vm (cm^3/mol)*	536.5	536.5

* Handbook of Chemistry (1985)

Table 2: Physical properties of Bixin

	Joback method [14]	Present Work
Pc (bar)	10.9	18.5
Tc (K)	1244.1	946.0
w	0.9289	1.2301
Tb (K)	1012.1	-
Vm (cm^3/mol)*	407.38	407.38

* Calculated by Rackett method [14]

The interaction parameters k_{ij} and the vapour pressures for the systems CO_2 + β-carotene and CO_2 + bixin were estimated by minimising the deviations between the calculated and the experimental data, considering L_{ij}=0. Two strategies were adopted. In the first one, the interaction parameter was considered temperature independent. In the second one the parameter was considered temperature dependent. The results demonstrate that even with the same value of the interaction parameter, the representation of experimental data is good (mean deviation of 10%). In figures 1 and 2 are represented the calculated and experimental solubility results for β-carotene and bixin, respectively. In table 3 are shown the estimated sublimation pressures for both compounds.

This model was also used to represent the ternary system and the interaction parameter between β-carotene (2) and bixin (3) was obtained. The results show that this model does not

represent well this system, leading to a mean deviation of 70% in relation to experimental data. A second model is proposed that considers the interaction between the solids in the solid phase, which is considered like liquid. The composition of the solid phase must be informed. This molar composition for the experimental data was of 42,37% for the β-carotene and of 57,63% for the bixin. The interaction parameters were obtained and their values are k_{23} =- 1,998 and k_{32} = - 1,925 leading to a deviation of 20% for β-carotene and 45% for bixin, (figures 3 and 4).

Table 3: Estimated sublimation pressures (bar)

T(°C)	β-carotene	Bixin
40	$0.9x10^{-15}$	$1.2x10^{-15}$
50	$7.6x10^{-15}$	$7.4x10^{-15}$
60	$34.8x10^{-15}$	$46.7x10^{-15}$

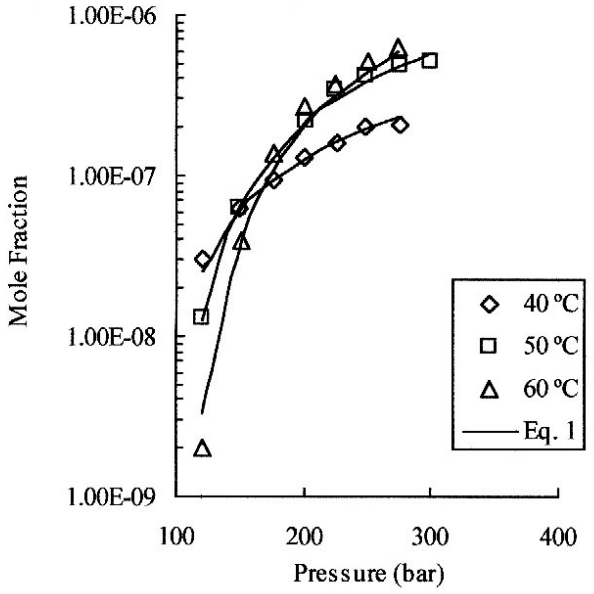

Figure 1: Calculated and experimental solubility of β-carotene in supercritical CO_2 as a function of pressure, k_{ij} = -0.437.

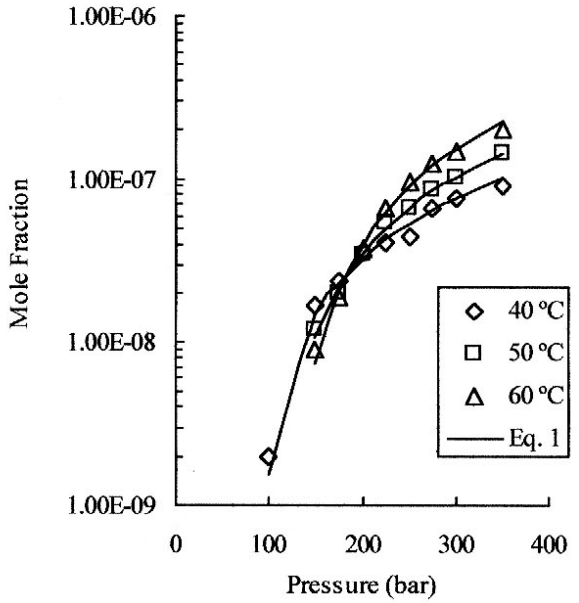

Figure 2: Calculated and experimental solubility of bixin in supercritical CO_2 as a function of pressure, k_{ij} = 0.153.

CONCLUSION

The system containing two solids (β-carotene and bixin) and supercritical carbon dioxide is very complex and the nonideallity happens due to the difference of the sizes of the molecules and their polarities. The proposed model is based on the Peng-Robinson equation of state and it is very dependent on the critical properties and the binary interaction parameters. The binary interaction parameters between carbon dioxide and β-carotene and between carbon dioxide and bixin were obtained from binary experimental data presented in the literature. For the solid mixture, β-carotene and bixin, the model without any solid interaction describes poorly the available experimental data (approximately 75% of average deviation). Then, a model considering interaction between the solids in the solid phase and relaxing the constraint of equal interaction parameters between the solutes was tested and was able to better describe the experimental data behaviour, with a deviation of 20% and 45% for bixin and β-carotene, respectively.

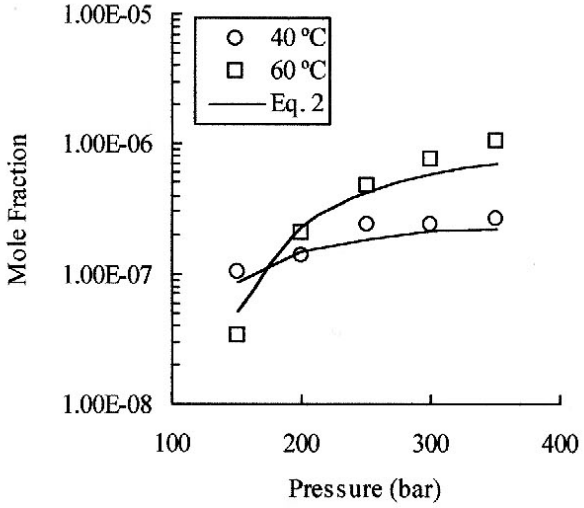

Figure 3: Calculated and experimental solubility of β-carotene from a solid mixture of bixin and β-carotene, in supercritical carbon dioxide.

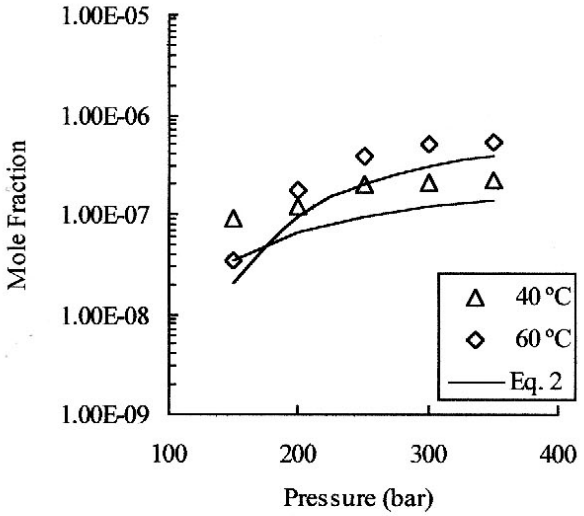

Figure 4: Calculated and experimental solubility of bixin from a solid mixture of bixin and β-carotene, in supercritical carbon dioxide.

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