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Prediction of β-Carotene Solubility at Supercritical Conditions Using Regular Solutions Theory

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Abstract: The objective of this paper is to model the extraction of carotenoid with supercritical carbon dioxide as the solvent used. Experimental data for the high pressure vapor-liquid phase equilibrium of the binary system carbon dioxide-carotenoid are reviewed for the elevated temperature 313.15, 323.15, 333.15 K and pressure up to 500 bar. The experimental data were correlated and modeled using Redlich-Kwong equation of state and regular solution methods. The use of equation of state as an empirical correlation for collating and predicting liquid-liquid and liquid-dense fluid equilibria is discussed. It is concluded that the estimation of some of the parameters required for these calculations would be difficult if the solute (carotenoid) was a complex substance about which little was known apart from its structural formula. An alternative procedure is to apply activity coefficient expression of the regular solution theory type to each phase. Calculations along these lines are described and the physical basis for applying these methods under the relevant conditions discussed. The regular solution theory approach in particular has been found to be encouraging for the mutual miscibility calculations for heavy components (such as carotenoid) particularly substances sensitive to temperature, though the interaction parameters for the prediction activity coefficients must be regarded as pressure dependent.

Key words: Supercritical extraction · Regular solution theory · Equation of state · Interaction parameters · Activity coefficient

Nomenclature

Symbol	Description
EOS	Equation of state
RST	Regular solution theory
x_i^E	Component *i* mole fraction in extracted phase
x_i^S	Component *i* mole fraction in liquid phase
Ratio	yield of carotene/yield of chlorophyll a
Yield	μg carotene/ mg dry weight microalgae (feed)
RD	Relative deviation
γ_i	Component *i* activity coefficient
$\partial^2 Q_i / \partial x_i^2$	Solubility parameter for component *i*

INTRODUCTION

Conventional methods based on the solvent extraction from natural matrices are time consuming. This method requires multiple extraction steps and large amounts of organic solvent, which are often expensive and potentially harmful.

Extraction with carbon dioxide under supercritical conditions constitutes an emerging technology in terms of environmental impact. The advantages in using carbon dioxide are lack of toxicity, chemical inertness, critical temperature and pressure available, low cost and availability [1]. Furthermore, the use of carbon dioxide is also beneficial in adding quality to the products obtained

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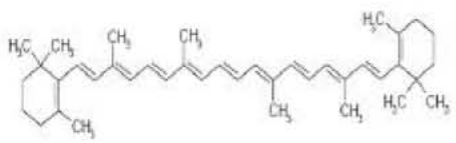

Fig. 1: Structural formula of β-carotene

since this technique does not give rise to excessive heating which usually has a negative effect on the thermolabile compounds [2].

Carotenoids are increasingly used in food technology mainly due to consumer pressure and more demanding regulations regarding the use of artificial dyes [2]. Carotene is a precursor of vitamin A in human and animal metabolism and it is used in the food processing industry for coloring purposes. This large aliphatic molecule has a molecular weight of 536.9 g/mol and one of its isomers, β-carotene, is illustrated in Figure1 [3].

Supercritical CO_2 has a low solubility for β-carotene most of which is concentrated in the raffinate. System pressure was found to be more significant rather than temperature for increasing the solubility in supercritical CO_2 [4]. The solubilities of pure β-carotene in supercritical CO_2 have been reported by several authors [3].

Usually established for pure component, the equation of state could be extended to a solution at equilibrium of a multi-component system by using suitable mixing rules that define the homogenous supercritical mixture characteristics. Numerous equation of state are proposed in the literature, their use is strongly related to the domains of operating parameters and the nature of the chemical components. The best known EOS for pure components are the cubic equations of state, such as Redlich-Kwong EOS, Redlich-Kwong-Soave EOS and Peng-Robinson EOS [5].

The objective of this study is to predict mutual solubilities for a system involving carbon dioxide and carotene as heavy component with supercritical carbon dioxide solvent. Theoretical data were calculated from regular solution equations and compared with the experimental data. These equations are described in detail by King *et al.* [6]. Calculations using the proposed equation mentioned above are defined and described in this paper, together with the physical basis for applying the proposed methods under the relevant conditions. Some of the interaction parameters that are required for the calculation of activity coefficients can be calculated from the experimental data for some equilibria systems which have been mentioned in reference [7]. The other interaction parameters have been generated by Fredenslund *et al.* [8]. The obtained data, activity coefficient, Gibbs function relationships and eventually mutual solubility data are calculated for two equilibria phases by using regular solution equations.

Prediction Phase Equilibrium Solution Using Quasi-lattice Models: The regular solution theory adopted as a model for this system is based on the activity coefficients by applying the following equations:

$$RT\ln\gamma_i = \left(\frac{d\left(nG_{mixing}^{Excess}\right)}{dn_i}\right)_{T,P,n_{j\neq i}} = \left(\frac{d\left(nH_{mixing}^{Excess}\right)}{dn_i}\right)_{T,P,n_{j\neq i}} - T\left(\frac{d\left(nS_{mixing}^{Excess}\right)}{dn_i}\right)_{T,P,n_{j\neq i}} \quad (1)$$

$$\ln\gamma_i = \left(\ln\gamma_i\right)^{Extract} + \left(\ln\gamma_i\right)^{Solute} \quad (2)$$

$$\left(\ln\gamma_i\right)^{Extract} = \frac{1}{R\times T}\times\left(\frac{d\left(nH_{mixing}^{Excess}\right)}{dn_i}\right)_{T,P,n_{j\neq i}} = \left(\frac{\phi_j^2\times V_{mi}}{R\times T}\right)\left(d_i-\zeta_{ij}d_j\right)^2 + 2l_{ij}d_id_j\zeta_{ij} \quad (3)$$

where

$$\zeta_{ij} = \left[\left(\frac{V_{mj}}{V_{mi}}\right)\left(\frac{q_i}{q_j}\right)\right]^{\frac{1}{2}} \quad (4)$$

and

$$d_i = \left[\frac{\left(U^0_{mi}-U_{mi}\right)}{V_{mi}}\right]^{\frac{1}{2}} \quad (5)$$

d_i is the well known "solubility parameter" of component (i). U_{mi} and U^0_{mi} are the molar internal energy of the compressed fluid component (i) and the same fluid at the same temperature but a very low pressure. These parameters are calculated by the same equations but for component (j), as well. Eq. (3) may be compared with the expression given by the Van der Waals approach [9],

$$\left(\ln\gamma_i\right)^{Extract} = \left(\frac{\phi_j'^2\times V_{mi}}{R\times T}\right)\left(\left(d_i-d_j\right)^2 + 2l_{ij}d_id_j\right) \quad (6)$$

It differs from this only in the term ζ (which is usually close to unity) and in the replacement of the area function ϕ_j' by the volume function,

$$\phi_j' = \frac{\left(x_j\times V_{mj}\right)}{\left(x_i\times V_{mi}+x_j\times V_{mj}\right)} \quad (7)$$

where (V_{mi}) is the molar volume of the pure liquid (i).

For a non-spherical molecule of type (i), quantity (q_i) is defined such that (Zq_i) is the number of interactions made by a molecule of this type with surrounding molecules. A monomer has (Z) interactions with nearest neighbor molecules (following X-ray diffraction information for simple fluids Z is normally given a value of 10). (q_i) is termed the area function for the molecule. For a linear molecule [10],

$$q_i = r_i - \left(\frac{2\times(r_i-1)}{Z}\right) \tag{8}$$

(r) is the number of segments and it is calculated as a function of number of carbon atoms, for example (n) for alkanes can be determined for the calculation, therefore,

$$r = 0.90 + 0.283(n-1)$$

Also, there would be an arrangement for Eq. (3) as following,

$$\ln\gamma_i^{Extract} = \sum_{K=1}^{N} v_K^{(i)}\left(\ln\Gamma_K - \ln\Gamma_K^{(i)}\right) \tag{9}$$

$$\ln\Gamma_K = Q_K\left[1 - \ln\left(\sum_m^N \theta_m\Psi_{mK}\right) - \sum_{m=1}^{N}\frac{\theta_m\Psi_{Km}}{\sum_{n=1}^{N}\theta_n\Psi_{nm}}\right] \tag{10}$$

where

$$\Psi_{mK} = Exp\left(-\frac{a_{mn}}{T}\right) \tag{11}$$

Q_k is the area function for group k and θ_m is the area fraction of group m. $\ln\Gamma_k^{(i)}$ is defined similarly except that the group area fractions refer to the pure liquid i and not to the mixture.

$$(\ln\gamma_i)^{Solute} = \ln\left(\frac{\phi_i}{x_i}\right) + \left(\frac{Zq_i}{2}\right)\times\ln(\theta_i/\phi_i) + l_i - (\phi_i/x_i)\sum_{j=1}^{M} x_j l_j \tag{12}$$

where M, θ_i and ϕ_i are the number of components in the solution, the area fraction for component i in the solution and the segment fraction, respectively.

$$l_i = (Z/2)(r_i - q_i) - (r_i - 1)$$

$$\phi_i = \frac{x_i r_i}{\sum_{i=1}^{M} x_i r_i}$$

Also there is another arrangement for Eq. (12),

$$(\ln\gamma_i)^{Solute} = \ln\left(\frac{\phi_i}{x_i}\right) - \left(\frac{Zq_i}{2}\right)\times\ln\left[1 + (2\phi_j/Zq_i)\left((r_i/r_j) - 1\right)\right] \tag{13}$$

In the present work activity coefficient is calculated using Eqs. (2), (9) and (12).

In order to present the calculations detail of the mutual solubilities for the system CO_2 (i)/heavy component (j) it is necessary to define that x_i^E is the mole fraction of component (i) based on the extract phase (carbon dioxide) and x_i^S is the mole fraction of component (i) based on the solute phase. Therefore x_i^E and x_i^S can be calculated from the activity coefficients data γ_i^E and γ_i^S for the phases and from the distribution factors k_i and k_j as:

$$\gamma_i^E x_i^E = \gamma_i^S x_i^S \tag{14}$$

$$k_i = \frac{x_i^E}{x_i^S} \tag{15}$$

The procedure is as follows:

a: Guessing initial k-values for each component given by Eq. (15).

b: Use these guessed k-values to obtain the approximate mole fraction of component (i) in each layer.

$$x_i^E = \frac{1-k_j}{k_j}{1-\frac{}{k_i}} \tag{16}$$

$$x_i^S = \frac{x_i^E}{k_i} \tag{17}$$

These values were then inserted at step b and the cycle was repeated until the mole fractions calculated in step b showed negligible change from one step to the next.

An alternative approach which was used in the regular solution theory calculations was to establish analytic expressions for a function Q and its derivatives with respect to mole fraction given by:

$$Q_i = -\left[x_i\ln(x_i\gamma_i) + x_j\ln(x_j\gamma_j)\right] = -\frac{G_m^{mixing}}{RT} \tag{18}$$

$$\left(\frac{\partial Q_i}{\partial x_i}\right)^E = \left(\frac{\partial Q_i}{\partial x_i}\right)^S = \frac{\left(Q_i^E - Q_i^S\right)}{\left(x_i^E - x_i^S\right)} \tag{19}$$

$$\frac{dQ_i}{dx_i} = -\ln\frac{\gamma_i x_i}{\gamma_j x_j} \tag{20}$$

$$\frac{d^2Q_i}{dx_i^2} = -\frac{d\left(\ln\frac{\gamma_i x_i}{\gamma_j x_j}\right)}{dx_i} \tag{21}$$

(G_m^{mixing}) is the molar Gibbs function of mixing and from standard thermodynamic relationships, it follows that ($\partial^2 Q_i / \partial x_i^2$) should be negative at all points in a completely miscible system. If the system is partially miscible there will be a region over which ($\partial^2 Q_i / \partial x_i^2$) is positive. In the latter case the points on the Q_i versus x curve corresponding to the equilibrium phase extract (E) and solute (S) have a common tangent Eq. (19).

where $(\partial^2 Q_i / \partial x_i^2)^E$ = gradient, $(\partial^2 Q_i / \partial x_i^2)^E$ taken at the mole fraction (x_i^E) of component (i) in the solvent-rich phase and $(\partial^2 Q_i / \partial x_i^2)^S$ = gradient taken at mole fraction (x_i^S) of component (i) in the solute-rich phase.

If the first assumption is as good (estimations of the) values of $(x_i^E)^0$ and $(x_i^S)^0$ (for the mole fractions (x_i^E) and (x_i^S)) which are already available, the applied procedure was found to be satisfactory for locating (x_i^E) and (x_i^S) using Eq. (19).

This procedure was repeated until no further adjustment was required. Eq. (19) was then satisfied and the mole fractions (x_i^E) and (x_i^S) specified the required calculated phase compositions

RESULTS AND DISCUSSION

Using the liquid-liquid equilibrium data for the system carbon dioxide-squalane at required pressure and temperature, Figure 2, together with the regular solution derived model [6, 11] in order to calculate effective values for the $a_{CO2/CH\ (or\ CH2\ or\ CH3)}$ and $a_{CH/CO2}$ interactions as a function of pressure as shown in Table 3. These data used to predict mutual solubility data in the carbon dioxide-carotenoid system at temperatures 313.15, 323.15, 333.15 K and at pressure up to 500 bar. Parameters other than $a_{CO2/CH2}$ and $a_{CH2/CO2}$ required in the regular solution model were evaluated using the standard methods described in [8]. Furthermore the derived model based on the regular solution theory used in the present work is given in [10].

In order to examine the behavior of the system CO_2-carotenoid at various pressures and temperatures miscible or immiscible, it is necessary to calculate the values of the activity coefficient (γ), Gibbs function (G) and its derivatives (dG/dx) and (d^2G/dx^2), using Eqs. (2), (9), (12), (18), (20) and (21).

Experimental data extracted from [2]. Table 1 shows ratio (the yield of extracted carotene per yield of extracted chlorophyll a) at different temperatures and at various pressures. Table 2 shows the yield of extracted carotene (μg carotene/ mg dry weight microalgae (feed)) and carotene mole fractions (in extracted phase) related to temperature and pressure.

Table 1: Pressure/Ratio of carotenoid at 313.15, 323.15 and 333.15 K [2]

T=313.15 K		T=323.15 K		T=333.15 K	
P (bar)	Ratio	P (bar)	Ratio	P (bar)	Ratio
200	0.524	200	0.410	200	1.389
300	0.258	300	0.230	300	0.179
400	0.115	400	-	400	0.153
500	0.129	500	0.129	500	0.120

Table 2. Experimental data extracted from Table 1, Pressure/yield of carotenoid, at temperatures 313.15, 323.15 and 333.15 K

	CO_2/Carotenoid, T=313.15 K		CO_2/Carotenoid, T=323.15 K		CO_2/Carotenoid, T=333.15 K	
P (bar)	Yield	$(x_{carotene})^{Exp}$	Yield	$(x_{carotene})^{Exp}$	Yield	$(x_{carotene})^{Exp}$
200	0.152	1.24609×10^{-5}	0.152	1.25×10^{-5}	0.125	1.03×10^{-5}
300	0.208	0.0167680	0.248	2.04×10^{-5}	0.250	2.05×10^{-5}
400	0.125	1.0300×10^{-5}	-	-	0.340	2.79×10^{-5}
500	0.104	8.6000×10^{-6}	0.180	1.48×10^{-5}	0.252	2.07×10^{-5}

Table 3: Interaction parameters $a_{CH3/CO2}$ and $a_{CO2/CH3}$ based on the calculations of the experimental data extracted form Figure 2 at temperatures 313.15, 323.15 and 333.15 K

CO_2/Squalane, T=313.15 K				
P (bar)	$(x^E_{squalane})^{Exp.}\times10^3$	$(x^S_{squalane})^{Exp.}\times10^2$	$a_{CH3/CO2}$	$a_{CO2/CH3}$
200	2.352941	9.7124943	2565.7422	74.0
300	3.5294	2.7810056	1008.8450	95.0
400	4.7059	14.5714285	754.56040	80.0
500	6.670	15.2941179	1915.6307	65.0
CO_2/Squalane, T=323.15 K				
P (bar)	$(x^E_{squalane})^{Exp.}\times10^3$	$(x^S_{squalane})^{Exp.}\times10^2$	$a_{CH3/CO2}$	$a_{CO2/CH3}$
200	3.5294118	5.57534470	2333.2239	72.0
300	5.2941200	2.78100560	2634.1658	75.0
400	7.0588240	12.9411764	2762.0835	65.2001
500	117.6470580	1.0	961.11400	60.0
CO_2/Squalane, T=333.15 K				
P (bar)	$(x^E_{squalane})^{Exp.}\times10^3$	$(x^S_{squalane})^{Exp.}\times10^2$	$a_{CH3/CO2}$	$a_{CO2/CH3}$
200	2.5	16.0	2149.3108	80.0
300	5.0	11.666700	799.55430	85.0
400	12.7780	9.2424242	1256.1367	68.0
500	26.6700	6.5151515	719.02610	70.0

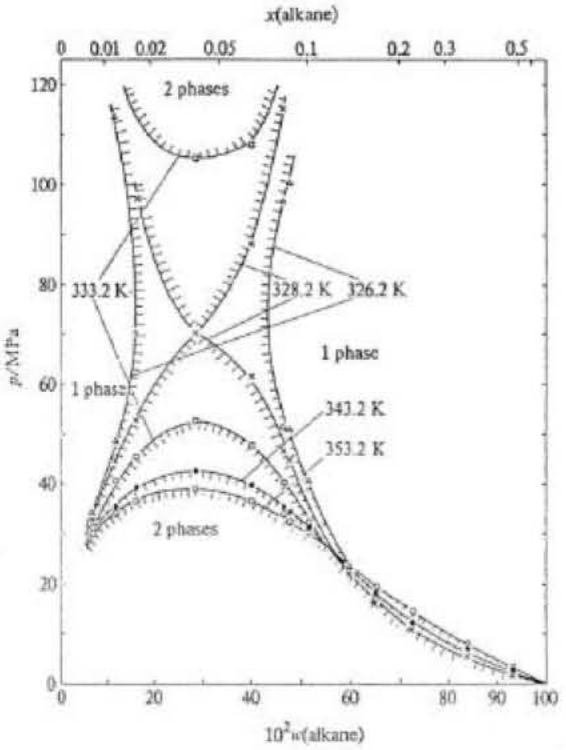

Fig. 2: Pressure/composition diagrams for carbon dioxide/squalane system [7]. w: weight percentage of squalane, x: mole fraction percentage of squalane, P=pressure (MPa).

Interaction parameters calculated by applying regular solution theory equations related to the experimental data obtained by [7] (which are shown in Figure 2). Therefore interaction parameters obtained at various temperatures and pressures are shown in Table 3.

CO_2-carotene system was also modeled by applying Redlich-Kwong equation of state. All equations are shown in reference [11]. Some necessary parameters such as critical properties and adjustable parameter (as a function of temperature) have been shown in reference [12].

All results such as experimental vapour phase data, two phases equilibrium data (based on regular solution theory) and extracted phase data (based on EOS) tabulated in Tables 4-6 at temperatures 313.15, 323.15, 333.15 K and at various pressures respectively. However, the relative deviation (RD) data are also shown in the same tables for the two models (which are EOS and regular solution equations).

$$RD = \frac{\text{Experimental data - Theoretical data}}{\text{Experimental data}}$$

A statistical analysis was employed for checking the regular solution model accuracy. Minitab software applied for this purpose. Two groups of data involving the experimental data and the data obtained from the regular solution e quations were employed. It observed

Table 4: Comparison of the experimental and theoretical (based on regular solution theory model and EOS) data at temperature 313.15 K and at pressures 200, 300, 400 and 500 bar

P(bar)	$(x^E_{CO2})^{Exp.}$	$(x^S_{CO2})^{RST}$	$(x^E_{CO2})^{RST}$	$(x^E_{CO2})^{EOS}$	RD% Based on RST	RD%Based on EOS
200	0.999987500	0.005	0.9992	0.99999786	0.0788	1.036×10^{-3}
300	0.983231902	0.3838	0.9996	0.99999929	1.6647	1.705
400	0.999989752	0.6469	0.9989	0.99999957	0.1089	9.818×10^{-4}
500	0.999991473	0.0452	0.9987	0.99999969	0.1291	8.217×10^{-4}

Table 5: Comparison of the experimental and theoretical (based on regular solution theory model and EOS) data at temperature 323.15 K and at pressures 200, 300, 400 and 500 bar

P(bar)	$(x^E_{CO2})^{Exp.}$	$(x^S_{CO2})^{RST}$	$(x^E_{CO2})^{RST}$	$(x^E_{CO2})^{EOS}$	RD%Based on RST	RD%Based on EOS
200	0.999987500	0.0144	0.9990	0.99999543	0.0988	7.930×10^{-4}
300	0.999979665	0.0055	0.9992	0.99999508	0.0779	1.542×10^{-3}
400	-	0.0043	0.9986	0.99999839	-	-
500	0.999985242	0.5813	0.9975	0.99999903	0.2485	1.378×10^{-3}

Table 6: Comparison of the experimental and theoretical (based on regular solution theory model and EOS) data at temperature 333.15 K and at pressures 200, 300, 400 and 500 bar

P(bar)	$(x^E_{CO2})^{Exp.}$	$(x^S_{CO2})^{RST}$	$(x^E_{CO2})^{RST}$	$(x^E_{CO2})^{EOS}$	RD%Based on RST	RD%Based on EOS
200	0.999989752	0.0284	0.9992	0.9999678	0.0789	2.1952×10^{-3}
300	0.999979501	0.6498	0.9989	0.99999392	0.1079	1.4419×10^{-3}
400	0.999972120	0.3393	0.9985	0.99999839	0.1472	2.6271×10^{-3}
500	0.999979337	0.7608	0.9974	0.99999906	0.2579	1.9723×10^{-3}

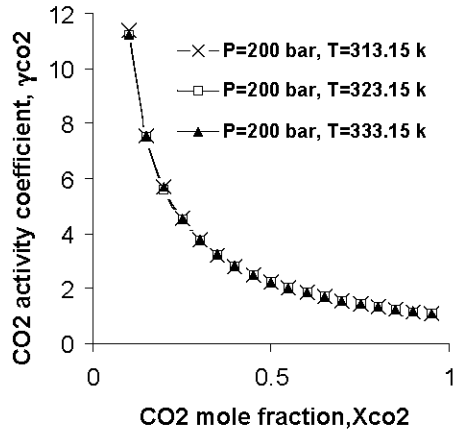

Fig. 3: CO_2 activity coefficient (γ_{CO2}) calculated from Eq. (2) against CO_2 mole fraction (x_{CO2}) at constant pressure 200 bar and at variable temperatures 313.15, 323.15 and 333.15 K.

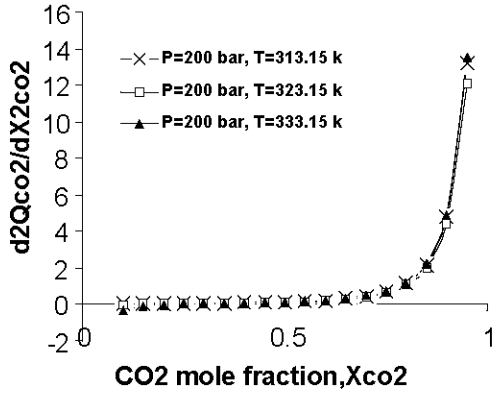

Fig. 4: Parameter (d^2Q_{CO2}/dx^2_{CO2}) calculated from Eq. (21) against CO_2 mole fraction (x_{CO2}) at constant pressure 200 bar and at variable temperatures 313.15, 323.15 and 333.15 K.

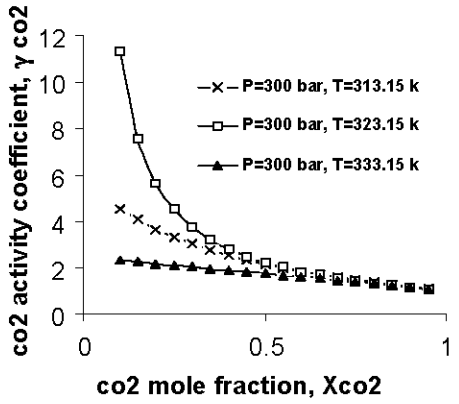

Fig. 5: CO_2 activity coefficient (γ_{CO2}) calculated from Eq. (2) against CO_2 mole fraction (x_{CO2}) at constant pressure 300 bar and at variable temperatures 313.15, 323.15 and 333.15 K.

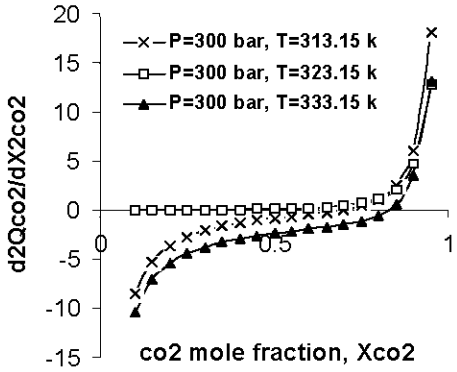

Fig. 6: Parameter (d^2Q_{CO2}/dx^2_{CO2}) calculated from Eq. (21) against CO_2 mole fraction (x_{CO2}) at constant pressure 300 bar and at variable temperatures 313.15, 323.15 and 333.15 K.

that confidence interval factor (CI) was at 95% for the range of (-0.003060, 0.002786). T-value was also obtained at -0.10. This analysis showed an acceptable P-value factor (P-value = 0.924>0.05).

Carotene solubility in supercritical carbon dioxide is predicted by applying the regular solution equations, Gibbs function relationships and activity coefficient expression.

Figure 3 shows CO_2 activity coefficient (γ_{CO2}) calculated from Eqs. (2), (9) and (12) against CO_2 mole fraction (x_{CO2}) at constant pressure 200 bar and at temperatures 313.15, 323.15 and 333.15 K. Interaction parameters $a_{CH3/CO2}$ and $a_{CO2/CH3}$ obtained from Table 3. Furthermore Figures 5, 7 and 9 show CO_2 activity coefficient (γ_{CO2}) at pressures 300, 400 and 500 bar respectively. Figure 3 showed that CO_2 activity coefficient against CO_2 mole fraction decreased exponentially with increasing CO_2 mole fractions at pressure 200 bar and at various temperatures. However, this trend observed as an exponential feature at pressure 300 bar and at temperatures 313.15 and 323.15 K, at pressures 400 bar and temperatures 323.15 and 333.15 K as well as at pressure 500 bar and at temperatures 323.15 and 313.15 K. But, activity coefficients linearly decreased with increasing CO_2 mole fractions for the other conditions.

Figure 4 shows the solubility parameter, d^2Q_{CO2}/dx^2_{CO2}, for CO_2 calculated from Eq. (21) against CO_2 mole fraction (x_{CO2}) at constant pressure 200 bar and at variable temperatures 313.15, 323.15 and 333.15 K. Interaction parameters $a_{CH3/CO2}$ and $a_{CO2/CH3}$ obtained from Table 3. Furthermore Figures 6, 8 and 10 show the solubility parameter for CO_2 calculated from Eq. (21) against CO_2

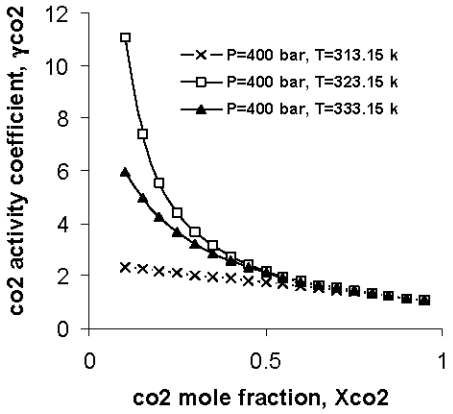

Fig. 7: CO_2 activity coefficient (γ_{CO2}) calculated from Eq. (2) against CO_2 mole fraction (x_{CO2}) at constant pressure 400 bar and at variable temperatures 313.15, 323.15 and 333.15 K.

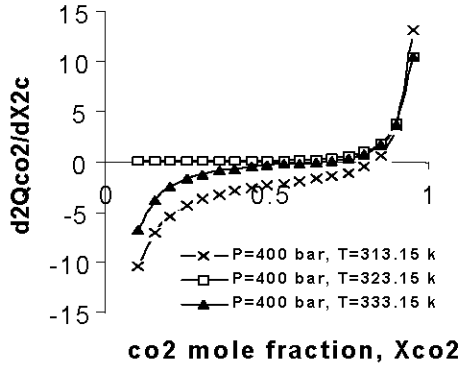

Fig. 8: Parameter (d^2Q_{CO2}/dx^2_{CO2}) calculated from Eq. (21) against CO_2 mole fraction (x_{CO2}) at constant pressure 400 bar and at variable temperatures 313.15, 323.15 and 333.15 K.

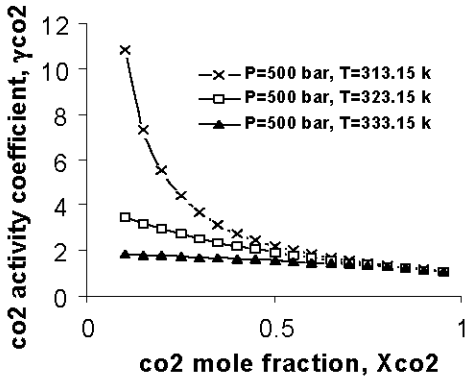

Fig. 9: CO_2 activity coefficient (γ_{CO2}) calculated from Eq. (2) against CO_2 mole fraction (x_{CO2}) at constant pressure 500 bar and at variable temperatures 313.15, 323.15 and 333.15 K.

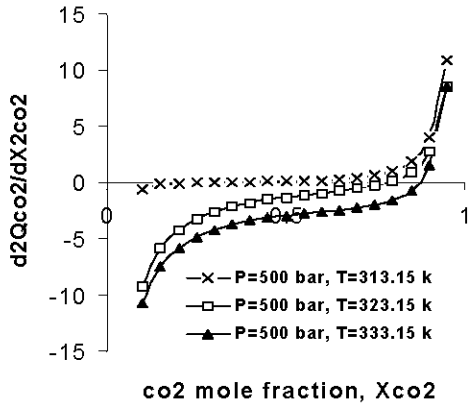

Fig. 10: Parameter (d^2Q_{CO2}/dx^2_{CO2}) calculated from Eq. (21) against CO_2 mole fraction (x_{CO2}) at constant pressure 500 bar and at variable temperatures 313.15, 323.15 and 333.15 K.

mole fraction (x_{CO2}) at pressures 300, 400 and 500 bar respectively. Figure 4 showed that this system is partially miscible at pressure 200 bar and at various temperatures because solubility parameters showed a positive sign in the range for all CO_2 mole fractions. However, this trend (as being partially miscible) observed at pressures 300 bar, 400 bar and at temperature 323.15 K as well as at pressure 500 bar and at temperature 313.15 K. But the others showed point of inflection.

This system (CO_2-carotene) is completely miscible for CO_2 mole fractions less than 0.70, therefore the conditions are at pressure 300 bar and at temperature 313.15 K. The same behavior Is observed for CO_2 mole fractions less than 0.75 at pressure 300 bar and at temperature 323.15 K. Also the same behavior observed for CO_2 mole fractions less than 0.80 at pressure 400 bar and at temperature 313.15 K. Also observed that for CO_2 mole fractions less than 0.65 at pressure 400 bar and at temperature 333.15 K as well as the same behavior observed for CO_2 mole fractions less than 0.75 at pressure 500 bar and at temperature 323.15 K and for CO_2 mole fractions less than 0.85 at pressure 500 bar and at temperature 333.15 K.

Regular solution theory data (as a described model) give the most reliable values for the carotene extraction which are carried out at various pressures and at temperatures of 313.15, 323.15 and 333.15 K. It is found that the calculated data based on regular solution theory are in good agreement with the statistical results obtained by Macánchez-Sánchez *et al.* [2].

CONCLUSIONS

This study predicted the solubility data of β-carotene at supercritical conditions using the regular solutions theory approach. The theoretical equations and associated parameters used in the modeling are clearly described. The β-carotene experimental data and Redlick-Kwong parameters obtained from published literature.

The regular solution theory as a general model can be applied for different systems and at various conditions. The significant difference between regular solution model and other models (such as equation of states) is that the later required critical constants for phase equilibria data and therefore provide vapor phase only. But for regular solution model, the data obtained are totally related to group interaction parameters and independent of temperature. It is possible to predict liquid-liquid and vapor-liquid equilibria from the knowledge of structural formula of the constituent molecular species. The system miscibility also can be obtained by applying the solubility parameter which was calculated from regular solution equations. In this study the interaction between the individual groups constituting the molecules was considered and group interaction parameters were generated together with parameters that describe the size and shape of the molecules.

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