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Solubility of *β*-Carotene from Crude Palm Oil in High-Temperature and High-Pressure Carbon Dioxide

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The solubility of *β*-carotene from crude palm oil using a phase equilibrium loading recirculating high-pressure-type apparatus at temperatures of (353.2, 373.2, and 393.2) K was studied. The experimental data showed that the mole fraction solubility of *β*-carotene was $2.27 \cdot 10^{-2}$ at a temperature of 393.2 K and at pressure of 5.4 MPa. The experimental data were compared with a set of theoretical data that was calculated using the regular solution theory model (RSTM). The theoretical data showed that the RSTM was able to correlate the solubility of *β*-carotene from crude palm oil in carbon dioxide. The mole fraction solubility of *β*-carotene based on the RSTM was $5.30 \cdot 10^{-3}$ at temperature of 393.2 K and at pressure of 3.3 MPa.

Introduction

Crude palm oil (CPO) is one of Malaysia's main commodity products. It contains approximately $w = 0.455$ of saturated fatty acids, $w = 0.396$ of monounsaturated fatty acids, $w = 0.099$ of polyunsaturated fatty acids, and $w = 0.01$ of minor components [carotenoids $w = (5 \text{ to } 7) \cdot 10^{-4}$, tocopherols and tocotrienols $w = (6 \text{ to } 10) \cdot 10^{-4}$, sterols $w = (3.26 \text{ to } 5.27) \cdot 10^{-4}$, phospholipids $w = (0.05 \text{ to } 1.30) \cdot 10^{-4}$, triterpene alcohol $w = (0.40 \text{ to } 0.80) \cdot 10^{-4}$, methyl sterols $w = (0.40 \text{ to } 0.80) \cdot 10^{-4}$, squalene $(2 \text{ to } 5) \cdot 10^{-4}$, aliphatic alcohols $w = (1 \text{ to } 2) \cdot 10^{-4}$, and aliphatic hydrocarbons $w = (0.5 \cdot 10^{-4})$].[1] CPO has a significant mass fraction of *β*-carotene, which is about $(2.7 \text{ to } 3.8) \cdot 10^{-4}$,[2] and is a precursor of vitamin A in human and animal metabolism. It is used in the food processing industry for coloring purposes.[3]

Various methods for extracting carotenes from palm oil have been developed. The methods include the saponification process,[4] adsorption using selective solvent extraction,[5,6] and a combination of the transesterification and the molecular distillation processes.[7]

Gast et al. studied the mutual solubility of *β*-carotene in CO_2 at a temperature of 310 K and at pressures of (20, 25, and 30) MPa in a dynamic system. They found that the distribution factor for *β*-carotene ($K_{\beta\text{-carotene}}$) was always constant at around 0.25.[8] Many researchers have also studied the solubility of *β*-carotene in the supercritical extraction process.[9–13]

Chuang and Brunner studied the recovery of minor components such as *β*-carotene and tocochromanols in CPO. They used three-step supercritical fluid extraction using the static system with three-step transesterification in the mixer-settler. They conducted the study in a two-stage process that involved the transesterification of triglycerides and the enrichment of minor components such as *β*-carotene up to 200-fold in CPO.[12]

Research was carried out on the solubility of carotenoid pigments such as lycopene and astaxanthin in supercritical CO_2 in a static system and was compared with obtained data and those reported in the literature for *β*-carotene over a temperature range of (313 to 333) K and over a pressure range of (10 to 42) MPa by de la Fuente et al.[13]

Saldaña et al. studied the solubility of *β*-carotene from pure *β*-carotene (binary system) in CO_2 using a quartz crystal microbalance (QCM) static technique at temperatures of (313 and 323) K and at pressures ranging from (120 to 327) bar.[14] In addition, they measured the solubility of *β*-carotene from a multicomponent system (carrot) in CO_2 using a dynamic extraction method, which was the same as the operating conditions. In this study, the solubility in both systems increased with temperature and pressure.

The solubilities of pure *β*-carotene (solid phase) in various gases were measured up to 180 MPa in a static system by Kraska et al.[15] They also compared their results with the theoretical data obtained from the Carnahan−Starling−van der Waals equation of state. In this study, *β*-carotene solubility was studied in three compressed gases (CO_2, $CClF_3$, and N_2O). *β*-Carotene solubility maxima, which were found experimentally as a function of pressure or density at constant temperature, were also modeled by a simplified form of an equation of state.[15]

Sovová et al. carried out research on the solubility of *β*-carotene in carbon dioxide at temperatures of (313.2, 323.2, and 333.2) K and at pressures up to 28 MPa using a one-pass flow apparatus (a static system).[16] In this study, the maximum solubility for *β*-carotene was found at maximum operating pressure and at maximum operating temperature. In addition, they correlated their results with the density-based equation proposed by Chrastil and modeled using the Soave−Redlich−Kwong cubic equation of state.

Choudhari and Singhal concluded that the solubility of any supercritical solute depends on a complex balance between fluid density and solute vapor pressure, both controlled by operating temperature and pressure.[17]

Furthermore, Diaz and Brignole have done a comprehensive review on thermodynamic modeling, simulation, and optimization of supercritical fluid processes in the last 20 years.[18]

In this study, the solubility of *β*-carotene from CPO in carbon dioxide at high temperature was carried out. It is also shown that this method is able to recover vitamins and edible derivatives. However, these data are necessary in several unit operation process calculations, but sometimes, because of the lack of appropriate apparatus and the other limitations, they are not measurable experimentally. Therefore, an accurate predict-

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able method for multicomponent systems (such as CPO) is required. In this article, a predictable thermodynamic model based on the regular solution theory (RST) is studied, and its accuracy is compared with the experimental data.

Thermodynamic Model

Regular Solution Theory Model (RSTM). The RST, which is adapted as a model for any system, is based on the activity coefficients by applying the following equations. The procedure for obtaining these final equations is described in detail in the literature.[19–21] However, the derived equations are slightly similar to some well-known equations such as UNIFAC, but UNIFAC equations were also obtained from the RST. (Both of them are based on the random mixing assumption.)

$$\ln \gamma_i = (\ln \gamma_i)^{\mathrm{V}} + (\ln \gamma_i)^{\mathrm{L}} \qquad (1)$$

Equation 1 showed a summation of the molar excess enthalpy of mixing (residual or energy-related contribution) and the molar excess entropy of mixing [combinatorial or entropic contribution to the nonideality of the mixture (related to size and shape differences between molecules)] in ref 19. In the current research, residual and combinatorial contributions were assumed to be vapor (extracted) phase and liquid (solute) phase properties, respectively. According to the UNIFAC, activity coefficients for vapor phase (residual contribution) and for solute phase (combinatorial contribution) are calculated by applying eqs 2 and 3 and eq 7, respectively. According to the RST, activity coefficients for vapor phase and for solute phase are calculated by applying eqs 4 and 8, respectively. King et al. showed the following equations[19]

$$(\ln \gamma_i)^{\mathrm{V}} = \sum_{k=1}^{N} \upsilon_k^{(i)} (\ln \Gamma_k - \ln \Gamma_k^{(i)}) \qquad (2)$$

whereas in eq 2, N is the number of groups present in the solution and $\upsilon^{(i)}{}_k$ is the number of groups of type k present in each molecule of type i.

$$\ln \Gamma_k = Q_k \left[1 - \ln(\sum_{m}^{N} \theta_m \Psi_{mk}) - \sum_{m=1}^{N} \frac{\theta_m \Psi_{km}}{\sum_{n=1}^{N} \theta_n \Psi_{nm}} \right] \qquad (3)$$

where

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

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

According to the RST, Walas suggested the following equations for residual contribution[22]

$$(\ln \gamma_i)^{\mathrm{V}} = \frac{1}{RT} \left(\frac{\mathrm{d}(nH_{\mathrm{mixing}}^{\mathrm{excess}})}{\mathrm{d}n_i} \right)_{T,P,n_{j \neq i}} = \left(\frac{\phi^2 V_{mi}}{RT} \right) (d_i - \zeta_{ij} d_j)^2 + 2 l_{ij} d_i d_j \zeta_{ij} \qquad (4)$$

where

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

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

d_i is the known solubility parameter of component i. U_{mi} and $U^0{}_{mi}$ are the molar internal energies of the compressed fluid component, i, and the same fluid at the same temperature but at a very low pressure. These parameters can also be calculated by the same equations for component j.

It only differs from eq 4 in terms of ζ (which is usually close to unity) and in the replacement of the area fraction by the volume fraction (ϕ_j^{υ}) as shown in the following

$$\phi_j^{\upsilon} = \frac{(x_j \cdot V_{mj})}{(x_i \cdot V_{mi} + x_j \cdot V_{mj})}$$

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

Eq 4 may be compared with the expression given by the van der Waals approach[19]

$$(\ln \gamma_i)^{\mathrm{V}} = \left(\frac{\phi_j^{\upsilon 2} \cdot V_{mi}}{RT} \right) ((d_i - d_j)^2 + 2 l_{ij} d_i d_j) \qquad (5)$$

For a nonspherical 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 the nearest neighbor molecules. (Using the X-ray diffraction information for simple fluids, Z is normally given a value of 10.) q_i is the area function for the molecule. For a linear molecule, King et al. showed[19]

$$q_i = r_i - \left(\frac{2(r_i - 1)}{Z} \right) \qquad (6)$$

where r is the number of segments, and it is calculated as a function of the number of carbon atoms. For example, n for alkanes can be determined by following calculation

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

For combinatorial contribution, King et al. showed the following equations[19]

$$(\ln \gamma_i)^{\mathrm{L}} = \ln\left(\frac{\phi_i}{x_i} \right) + \left(\frac{Zq_i}{2} \right) \ln(\theta_i / \phi_i) + l_i - (\phi_i / x_i) \sum_{j=1}^{M} x_j l_j \qquad (7)$$

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

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

where M is the number of components in the solution, θ_i is the area fraction for component i in the solution, ϕ_i is the segment fraction, Z represents interactions with nearest neighbor molecules, which almost are equal to 10, and q_i is the area function for the molecule.

According to the RST, Walas suggested the following equation for combinatorial contribution[22]

$$(\ln \gamma_i)^{\mathrm{L}} = \ln\left(\frac{\phi_i}{x_i}\right) - \left(\frac{Zq_i}{2}\right)\ln[1 + (2\phi_j/Zq_i)((r_i/r_j) - 1)] \tag{8}$$

Therefore, we can calculated y_i (CO_2 mole fractions in the vapor phase) and x_i by the iteration method from the activity coefficients data by applying thermodynamic equilibria conditions for vapor and liquid phases, which is by the distribution factor definition and a guessed initial value of the distribution factor. Two equilibrium phases are assumed to be nonideal. Activity coefficients for vapor and liquid phases were calculated using the regular solution equations. The activity coefficient of the vapor phase was divided to the activity coefficient of the liquid phase and named distribution factor. Therefore, in regular solution calculations, the distribution factor is a symbol of nonideality in both phases. The procedure for calculating all parameters on the basis of regular solution equations and the solubility data based on the interaction parameters have been given in detail in the literature.[19–21]

Experimental Section

Materials. CPO was obtained from United Oil Palm Industries Sdn. Bhd, liquefied CO_2 (mole fraction 0.999) was supplied by Mox Sdn. Bhd, β-carotene ($w = 0.960$) was from Fluka (Germany), and the acetone (volume fraction 0.998) and the hexane (volume fraction 0.998) were obtained from J. T. Baker (Germany).

Analysis. According to literature review, Chuang and Brunner used UV spectroscopy at a wavelength of 450 nm to analyze the CPO samples, which were dissolved and diluted in a solvent mixture of 30 % acetone and 70 % hexane in terms of β-carotene.[12]

The concentration of β-carotene in the palm oil samples was measured using a spectrophotometer at 446 nm. Prior to analysis, they homogenized the triglyceride fractions collected by heating them to (60 to 70) °C and then diluting them in hexane by dissolving a 0.1 g sample in 25 mL of hexane.[10]

De França et al. analyzed the extracts in terms of β-carotene using a spectrophotometer. For this purpose, the samples were diluted in 25 or 50 mL of a 70 % hexane and 30 % acetone solvent mixture, and absorbance was read at 450 nm.[23]

In this study, spectroscopy using a calibrated spectrophotometer (model UV-120-020, Shimadzu, Tokyo, Japan) which was able to indicate β-carotene absorption up to three decimal places was used to analyze the samples in terms of β-carotene. By using blank solution which was containing 70 % hexane and 30 % acetone as a reference solution with a standard solution of β-carotene, the absorbance was measured at a wavelength 400 to 500 nm. The absorbance for each 5 nm of increasing wavelength was measured. It was confirmed that maximum wavelength for β-carotene absorption was 450 nm. A 100 mL stock solution was prepared with 0.1 g of β-carotene in a volume ratio of 7:3 solvent mixture of hexane/acetone. Aliquots were taken from this solution and diluted to five different concentrations. Absorbance was read at 450 nm. The CPO samples were diluted in a solvent mixture of 70 % hexane and 30 % acetone, and absorbance was read at 450 nm wavelength. We calculated carotenes in the samples in terms of β-carotene by using a standard absorbance curve calibrated with β-carotene.

Experimental Procedure. As shown in Figure 1, the equipment used in this study was a custom fabricated recirculation high-pressure type phase equilibrium apparatus that was described in detail, and the reliability of the data was already proposed in the literature.[20,21,24,25]

The operating temperatures were set at (353.2, 373.2, and 393.2) K, and the system pressure was allowed to increase. The

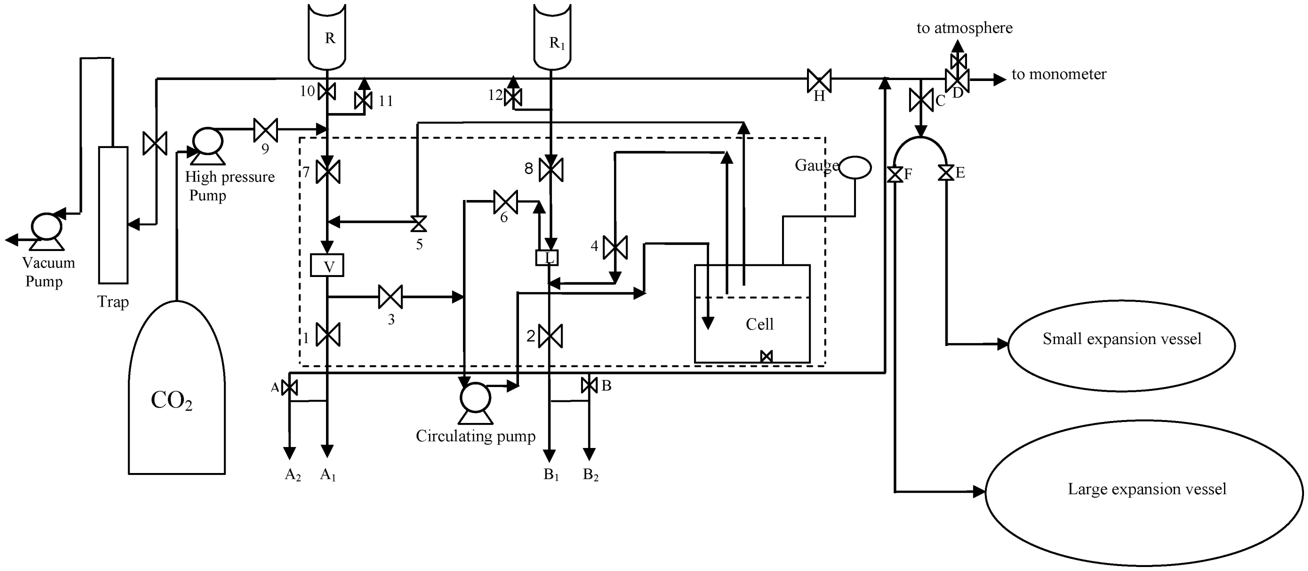

Figure 1. Schematic diagram of supercritical extraction apparatus.

Table 1. Operating Conditions, Two-Phase Equilibrium Data for *β*-Carotene from Experiment, Distribution Factor Based on *β*-Carotene (K_1), and Uncertainties (U)

P/MPa	$(y_1)^{\mathrm{average}}$	$(x_1)^{\mathrm{average}}$	K_1	$(y_1)^{\mathrm{first\ run}}$	$(x_1)^{\mathrm{first\ run}}$	$(y_1)^{\mathrm{second\ run}}$	$(\mathrm{x}_1)^{\mathrm{second\ run}}$	$100\vert U_{y_1}\vert$	$100\vert U_{x_1}\vert$
T/K = 353.2									
10.8	0.0218	0.0874	0.250	0.0220	0.0880	0.0216	0.0870	1.99	1.12
7.0	0.0186	0.0744	0.250	0.0188	0.0752	0.0184	0.0738	1.90	1.92
4.8	0.0148	0.0594	0.250	0.0150	0.0598	0.0147	0.0590	1.97	1.33
2.7	0.0110	0.0438	0.250	0.0110	0.0442	0.0109	0.0434	1.12	1.85
1.7	0.0010	0.0040	0.251	0.0014	0.0040	0.0010	0.0040	0.90	0.08
T/K = 373.2									
11.1	0.0076	0.0303	0.250	0.0076	0.0304	0.0075	0.0302	1.95	0.78
7.6	0.0114	0.0459	0.250	0.0115	0.0460	0.0114	0.0459	0.80	0.28
6.1	0.0034	0.0138	0.250	0.0034	0.0136	0.0344	0.0133	1.30	1.94
4.2	0.0012	0.0049	0.250	0.0012	0.0050	0.0012	0.0048	2.00	1.32
1.1	0.0009	0.0036	0.250	0.0009	0.0037	0.0091	0.0036	1.70	1.79
T/K = 393.2									
7.4	0.0208	0.0836	0.250	0.0210	0.0840	0.0208	0.0831	1.21	0.98
5.4	0.0226	0.0908	0.250	0.0229	0.0909	0.0224	0.0906	1.85	0.30
4.4	0.0160	0.0642	0.250	0.0162	0.0648	0.0160	0.0638	1.29	1.50
3.3	0.0094	0.0378	0.250	0.0095	0.0382	0.0094	0.0375	1.68	1.70
0.6	0.0022	0.0088	0.250	0.0022	0.0090	0.0022	0.0088	0.30	2.00

operating temperatures and the relevant pressures in each run are illustrated in Table 1. The liquid samples [from liquid sample bomb (40 cm^3) and from vapor sample bomb (50 cm^3)] were separately collected and analyzed by a UV−vis spectrophotometer (Shimadzu, Japan) at a wavelength of 450 nm in terms of *β*-carotene. The vapor samples (from both sample bombs) were separately conducted to the large expansion vessel (35 L) for vapor sample bomb and to the small expansion vessel (7 L) for liquid sample bomb. Eventually, pressure increments during the expansion process, which were a necessary item in the compositions determinations, were measured. The number of moles and the mole fractions based on CO_2 in both phases can be calculated by applying the procedure mentioned in the calculations procedure section.

The apparatus was equipped with a pressure gauge (model: stainless steel miniature gauge, brand: Swagelok, England, pressure range: $0 < P/\mathrm{bar} < 250$, ± 2.5 % of span ASME B40.1 grade C, EN 837-1 class 2.5, JIS B7505 class 2.5). This apparatus was also equipped with two sensitive digital temperature controllers [model: E5CN, brand: Omron, Japan, (± 0.3 % of indicated value or ± 1 °C, whichever is greater) ± 1 digit max].

The experimental data were produced on the basis of the average of the two repeated runs that were performed for each data point. The repeated runs ensured that the experiments could be repeated within a maximum experimental error of ± 2 %. (The experiments' uncertainties were illustrated in Table 1 in detail.) The precision of the effective parameters in composition determinations such as samples mass (which is determined by a digital balance up to six places), operating temperature, and pressure increment (expansion vessels pressures before and after expansion process, which are read from a mercury manometer) caused the mentioned error. The experimental equilibrium compositions were calculated using a calculator (brand: CASIO, model: fx-4500PA, Japan) up to 10 decimal points. All calculated data were fixed up to four decimal points because this number of points could show the equilibrium compositions well.

Calculation Procedure. The *β*-carotene concentration from the initial CPO was obtained using a UV−vis spectrophotometer with the calibration curve obtained from the standard solutions of *β*-carotene.[3] The *β*-carotene mass fraction in the initial CPO was around $2.57 \cdot 10^{-4}$.

After reaching the equilibrium condition (when circulating pump was working, temperature and pressure were constant around 30 min) and then by isolating the vapor and liquid equilibrium phases in the vapor sample bomb and liquid sample bomb (Figure 1), respectively, two phase compositions were obtained. Each sample bomb contains two phases (liquid and vapor phases) whose compositions should be determined carefully. Therefore, liquid-phase composition was determined using UV spectroscopy, and vapor-phase composition (after conducting to the expansion vessel and flashing process) was calculated using pressure increment data during expansion process and virial equation (eqs 13 and 14).

The carbon dioxide + heavy component (*β*-carotene) system was studied at temperatures of (353.2, 373.2, and 393.2) K, and the compositions of the equilibrium phases were noted at each pressure. The mole fractions of the heavy component in the vapor (y_1) and liquid (x_1) phases on the carbon-dioxide-free basis were calculated from the following equations

$$x_1 = \frac{(nx_1)^{\mathrm{L}}}{[(nx_1)^{\mathrm{L}} + (nx_2)^{\mathrm{L}}]} \tag{9}$$

$$y_1 = \frac{(nx_1)^{\mathrm{G}}}{[(nx_1)^{\mathrm{G}} + (nx_2)^{\mathrm{G}}]} \tag{10}$$

where $(nx_1)^{\mathrm{L}}$ is the number of moles of *β*-carotene in the liquid phase on a carbon-dioxide-free basis, $(nx_1)^{\mathrm{G}}$ is the number of moles of *β*-carotene in the vapor phase on a carbon-dioxide-free basis, $(nx_2)^{\mathrm{L}}$ is the number of moles of palm oil in the liquid phase on a carbon-dioxide-free basis, and $(nx_2)^{\mathrm{G}}$ is the number of moles of palm oil in the vapor phase on a carbon-dioxide-free basis.

The calculations for the mole fraction of carbon dioxide in the liquid phase (x) and in the vapor phase (y) of this system were carried out using the following equations

$$y = \frac{(ny)^{\mathrm{G}}}{[(nx)^{\mathrm{G}} + (ny)^{\mathrm{G}}]} \tag{11}$$

$$(1 - x) = \frac{(nx)^{\mathrm{L}}}{[(ny)^{\mathrm{L}} + (nx)^{\mathrm{L}}]} \qquad (12)$$

where $(ny)^{\mathrm{G}}$ is the number of moles of carbon dioxide in the vapor sample bomb, $(nx)^{\mathrm{G}}$ is the number of moles of heavy component (except β-carotene) in the vapor sample bomb, $(ny)^{\mathrm{L}}$ is the number of moles of carbon dioxide in the liquid sample bomb, and $(nx)^{\mathrm{L}}$ is the number of moles of heavy component (except β-carotene) in the liquid sample bomb.

To calculate $(ny)^{\mathrm{G}}$ and $(ny)^{\mathrm{L}}$, it is necessary to consider the deviation from the ideal gas law pressure of about 1 bar, and this was conveniently expressed by the following equation[22]

$$PV = n(RT + B_{\mathrm{v}}P) \qquad (13)$$

where P = pressure, V = system volume, n = number of moles of gas, and B_{v} = second virial coefficient.

This equation leads directly to the expression of

$$\begin{aligned}(ny)^{\mathrm{G}} &= V\left[\frac{P_2}{RT + B_{\mathrm{v}}P_2} - \frac{P_1}{RT + B_{\mathrm{v}}P_1}\right] \\ &= VP_2\left[\frac{1 - \left(\frac{P_1}{P_2}\right)\left(\frac{RT + B_{\mathrm{v}}P_2}{RT + B_{\mathrm{v}}P_1}\right)}{(RT + B_{\mathrm{v}}P_2)}\right] \qquad (14)\end{aligned}$$

for the number of moles of gas in the vapor sample bomb, where P_1 and P_2 are the expansion vessel pressure before and after expansion and V is the volume of the system.

The second virial coefficient can be calculated for the solvent, CO_2, from the literature.[26]

We calculated the number of moles of CO_2 in the liquid sample bomb, $(ny)^{\mathrm{L}}$ by using the exact procedure as that given above.

According to the apparatus design, the volumes of the systems for the calculations of the number of moles of CO_2 in the vapor sample bomb and the number of moles of CO_2 in the liquid sample bomb were assumed to be around 35 and 7 L, respectively.[20,21,24,25]

Results and Discussion

The solubility of β-carotene from CPO in carbon dioxide at various temperatures was obtained using experimental data and the equations described in the Calculation Procedure section. The results obtained are illustrated in Figure 2, and it can be seen that there was a maximum of β-carotene solubility at 393.2 K and at a reduced pressure of 0.737. This also confirms that high admissible temperature and a slightly subcritical pressure increased the solubility of β-carotene in carbon dioxide.

The highest solubilities of β-carotene were first observed at 393.2 K and then at 353.2 K. A middle solubility of β-carotene was observed at 373.2 K. It seems that a low temperature (e.g., 353.2 K according to this research) has a good effect on β-carotene solubility in CO_2, particularly in high pressures, as shown in Figure 2; a sharp slope is observable at high pressures. This was in agreement with Markom et al. that a high pressure and low temperature have a desirable effect on the β-carotene extraction using CO_2.[10] Furthermore, an admissible high temperature (e.g., 393.2 K according to this research) increases β-carotene solubility in CO_2. This subject has been concluded by Davarnejad et al. in the β-carotene extraction process from CPO using CO_2.[3]

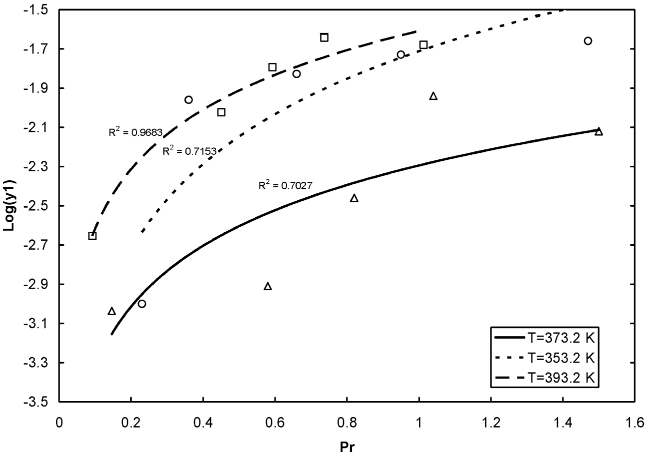

Figure 2. Solubility of β-carotene in high-pressure carbon dioxide based on the experiment at various temperatures: ○, 353.2 K (P_{r} = 0.23, 0.36, 0.66, 0.95, and 1.47); △, 373.2 K (P_{r} = 0.146, 0.58, 0.82, 1.04, and 1.5); □, 393.2 K (P_{r} = 0.0921, 0.451, 0.593, 0.7369, and 1.013).

Table 1 shows the two-phase equilibrium data for β-carotene from the experiment, the distribution factor based on β-carotene, and the uncertainties involving the two-phase equilibrium data from two repeated runs for each phase. This table clearly shows that β-carotene solubility decreased with decreasing operating pressure, and CPO was enriched from β-carotene by increasing the operating pressures. However an unpredicted slight increase in the two-phase equilibrium data was observed at a temperature of 373.2 K with a pressure of 7.6 MPa and at a temperature of 393.2 K at a pressure of 5.4 MPa. Sometimes this irregularity is observed under some operating conditions in the extraction process using CO_2.[27]

Furthermore, the calculation of the distribution factors based on β-carotene ($K_{\beta\text{-carotene}} = y_{\beta\text{-carotene}}/x_{\beta\text{-carotene}}$, where $y_{\beta\text{-carotene}}$ and $x_{\beta\text{-carotene}}$ are β-carotene mole fractions in the vapor phase and liquid phase, respectively) shows that this parameter was always constant and equal to 0.250. Gast et al. also concluded that the β-carotene distribution factors showed a constant trend ($K_{\beta\text{-carotene}} = 0.25$) at pressures of (20 to 30) MPa.[8] However, the distribution factor shows that β-carotene was always enriched in the liquid phase because it was less than one, and considerable purification of β-carotene in the vapor phase was not achieved.

Although the β-carotene solubility study showed a mole fraction range of $10^{-4} \le y \le 10^{-2}$ for β-carotene, as reported in the current research, the reported data in the literature showed very large variations.[13] This phenomenon has also been observed by others, for example, Güçlü-Üstündağ and Temelli, who reviewed the literature on the subject and reported the measured solubility values of β-carotene in supercritical CO_2.[28] These differences were attributed to differences in the purity of the sample or the limitations of the experimental and calculation techniques used.[28] In the present research, most of the results were obtained under subcritical and slightly supercritical conditions, whereas most of the reported data in the literature was based on supercritical conditions. In addition, the sampling and calculation methods are different in the various researches. Sample impurities may act as co- or antisolvents and thus affect the measured solubility values.[29] Furthermore, β-carotene is susceptible to oxidize or isomerize during testing or immediately afterward, and this effect is compounded with one of the impurities.[28,30] Solubility may also be affected by the crystalline nature of the solute. (β-carotene melts at a much higher temperature than the uppermost 353.2 K tested in the experiments, but it can be in an amorphous state.)[31] Regarding the

Table 2. Interaction Parameters Calculated on the Basis of the RSTM and Two-Phase Experimental Equilibrium Data Based on the Hexadecane + CO_2 System

P/MPa	a_{CH_3/CO_2}	a_{CO_2/CH_3}	P/MPa	a_{CH_3/CO_2}	a_{CO_2/CH_3}	P/MPa	a_{CH_3/CO_2}	a_{CO_2/CH_3}
	T/K = 353.2			T/K = 373.2			T/K = 393.2	
10.8	644.666	88.853	11.1	645.419	88.598	7.4	630.486	93.491
7.0	628.251	94.204	7.6	630.486	93.491	5.4	620.458	96.661
4.8	616.731	97.783	6.1	623.589	95.679	4.4	614.646	98.458
2.7	605.211	101.362	4.2	614.245	98.592	3.3	608.833	100.256
1.7	598.918	103.270	1.1	594.986	104.454	0.6	529.304	105.258

Table 3. Comparison of the CO_2 Mole Fractions of the Vapor Phase Based on Experiment and Model

P (MPa)	$(y_{CO_2})^{exptl}$	$(y_{CO_2})^{RSTM}$	100|RD|
	T/K = 353.2		
10.8	0.9781	0.9981	2.04
7.0	0.9814	0.9984	1.74
4.8	0.9852	0.9986	1.36
2.7	0.9890	0.9987	0.98
1.7	0.9990	0.9988	0.02
	T/K = 373.2		
11.1	0.9924	0.9973	0.48
7.6	0.9886	0.9977	0.92
6.1	0.9965	0.9979	0.14
4.2	0.9988	0.9981	0.07
1.1	0.9990	0.9983	0.08
	T/K = 393.2		
7.4	0.9792	0.9969	1.80
5.4	0.9773	0.9971	2.02
4.4	0.9840	0.9959	1.20
3.3	0.9905	0.9947	0.42
0.6	0.9978	0.9977	0.01

experimental technique, problems may arise if true equilibrium is not reached because it may occur in systems that use a dynamic procedure.[16,30–33] Because sampling may be associated with the precipitation of the solute in valves and tubing (measured solubility below true solubility) or its entrainment by the loaded fluid phase (measured solubility above true solubility), online analysis techniques,[15,31,33–36] without a change in the temperature and pressure conditions of the supercritical fluid phase, are typically preferred over off-line analysis techniques.[9,16,27,32,37] However the use of a spectrophotometric online analysis [30,34] is susceptible to errors due to the potential saturation of a UV—vis detector at high solute concentrations.[28] Expansion vessels should be equipped with heaters, and their temperatures should be set to be the same as the operating temperatures.

According to the modeling, because the β-carotene molecular formula is $C_{40}H_{56}$, it is distributed to 3 CH_3, 10 CH_2, and 27 CH. Then, we calculate the required parameters based on RSTM (such as interaction parameters and solubility data) by considering CO_2 group interactions on CH_3, CH_2, and CH groups. (These interactions for CH_3, CH_2, and CH groups are the same.) The other necessary parameters such as group area functions and volume parameters for these groups are obtained from ref 38. Regular solution equations can legitimize a component structural formula on the basis of the mentioned parameters (such as groups distribution, number of groups, groups interaction, groups area function, and volume parameters).[19]

Therefore, by applying the regular solution equations with the two-phase equilibrium data obtained from the CO_2 + hexadecane system (which includes the same groups as those for the CO_2 + β-carotene system) at a temperature of 25 °C,[39] the interaction parameters were calculated and illustrated in Table 2. The tabulated results clearly showed that the interaction parameters depend on pressure. In particular, a_{CO_2/CH_3} decreased with increasing pressure, whereas a_{CH_3/CO_2} increased with increasing pressure.

Because vapor phase data show solubility, it seems that consideration of the accuracy of the predictable method (RSTM) is necessary. Therefore, relative deviation [RD = (experimental data − theoretical data)/experimental data] of vapor-phase data based on CO_2 (solvent) as an output of the regular solution equations were compared with the experimental data and illustrated in Table 3. This theoretical method was able to predict the solubility data with relative deviations of less than 2 %.

Figures 3, 4, and 5 show β-carotene solubility in carbon dioxide on the basis of the experimental data and the RSTM data at temperatures of (353.2, 373.2, and 393.2) K respectively. The experimental data showed that the mole fraction solubility of β-carotene was $2.27 \cdot 10^{-2}$ at a temperature of 393.2 K and at a pressure of 5.4 MPa. According to the literature, pressure increment normally increases β-carotene solubility in CO_2 at a constant temperature;[13–16] however, a regular trend was not observed by Sovová et al.[16] They concluded that maximum β-carotene concentration was obtained at a pressure of 60 MPa, whereas the operating pressure increased up to 180 MPa for an isotherm of 307.6 K. All of the operating temperatures performed by Sovová et al. were less than the those in the current research. It seems that a moderate pressure with a high temperature has a good effect on the β-carotene solubility from CPO in CO_2. These Figures also confirmed that deviation between the experimental data and theoretical data from RSTM was quite severe at higher reduced pressures.

Figure 3 shows β-carotene solubility data against carbon-dioxide-reduced pressure based on the experiments and the RSTM at 353.2 K. The Figure clearly shows that the maximum β-carotene solubility ($2.18 \cdot 10^{-2}$) is experimentally observed at the reduced pressure of 1.47, whereas under the same operating conditions, solubility is theoretically reported at $1.90 \cdot 10^{-3}$.

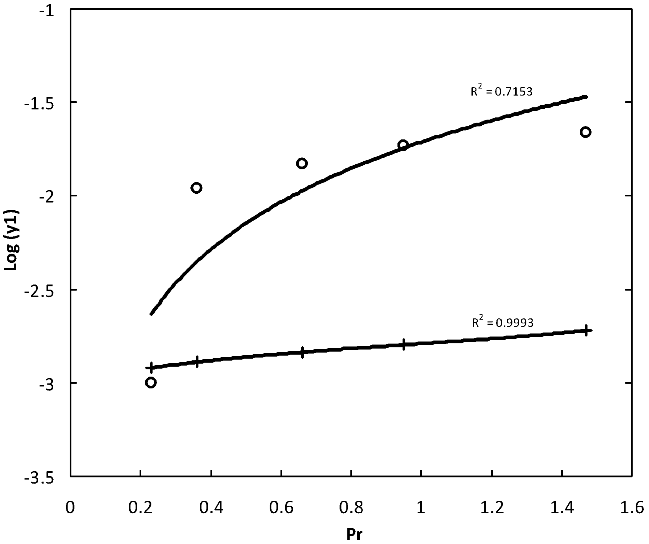

Figure 3. Solubility of β-carotene in high-pressure carbon dioxide (P_r = 0.23, 0.36, 0.66, 0.95, and 1.47) based on the experiment and RSTM at temperature of 353.2 K: ○, experimental; +, RSTM.

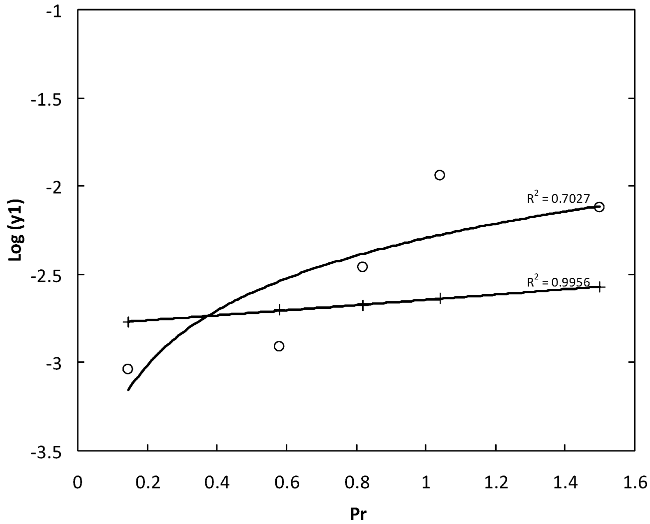

Figure 4. Solubility of β-carotene in high-pressure carbon dioxide (P_r = 0.146, 0.58, 0.82, 1.04, and 1.5) based on the experiment and RSTM at temperature of 373.2 K: ○, experimental; +, RSTM.

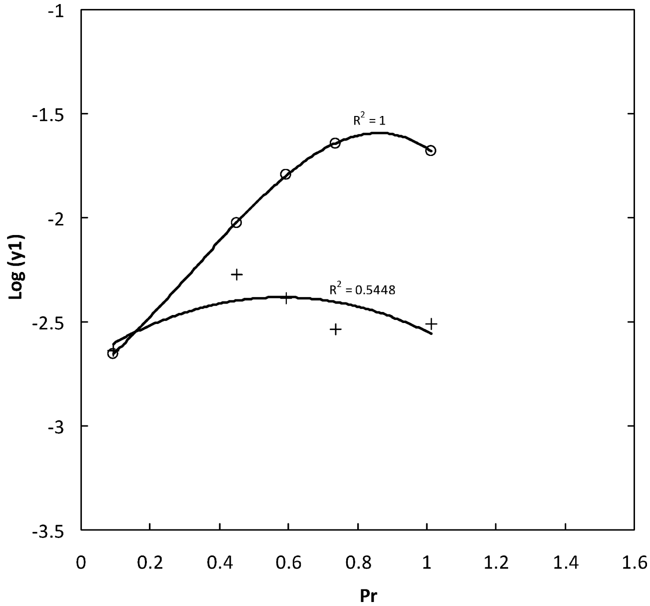

Figure 5. Solubility of β-carotene in high-pressure carbon dioxide (P_r = 0.0921, 0.451, 0.593, 0.7369, and 1.013) based on the experiment and RSTM at temperature of 393.2 K: ○, experimental; +, RSTM.

Figure 4 shows the β-carotene solubility data against the carbon-dioxide-reduced pressure based on the experiments and the RSTM at 373.2 K. This Figure also shows that the maximum β-carotene solubility is observed at the reduced pressure of 1.04, whereas under the same operating conditions, solubility is theoretically reported at $2.30 \cdot 10^{-3}$. Furthermore, maximum solubility is theoretically obtained at $2.70 \cdot 10^{-3}$ at a reduced pressure of 1.50.

Figure 5 shows the β-carotene solubility data against the carbon-dioxide-reduced pressure based on the experiments and the RSTM at 393.2 K. The Figure clearly shows that the maximum β-carotene solubility is observed at a reduced pressure of 0.737, whereas under the same operating conditions, solubility is theoretically reported at $2.90 \cdot 10^{-3}$. Furthermore, maximum solubility is theoretically obtained at $5.30 \cdot 10^{-3}$ at a reduced pressure of 0.451.

The RSTM also showed that there were maximum and minimum β-carotene solubilities at 393.2 and 353.2 K, respectively. Mid-β-carotene solubility was observed at 373.2 K. The calculated interaction parameters based on the related pressures caused this.

The highest solubility of β-carotene based on the RSTM was observed at 393.2 K and at a reduced pressure of 0.451, even though the highest solubility of β-carotene based on the experimental work was observed at 393.2 K and at a reduced pressure of 0.737.

Conclusions

In this article, the solubility of β-carotene from CPO in sub- and supercritical carbon dioxide solvent at temperatures of (353.2, 373.2, and 393.2) K was studied. The experimental data were compared with the theoretical data obtained from the RSTM.

It seems that the RSTM was able to justify the effects of the various components by the interaction and other parameters such as shape and size of molecules. The RSTM, which is based on physical chemistry, could considerably legitimize the obtained results from this research. Some differences between experimental and theoretical data were observed because of uncertainties (according to experiments) and interaction parameters calculated from two-phase equilibrium data obtained from another system.

According to the literature, pure β-carotene solubilities in supercritical carbon dioxide [pressure ranging from (12 to 20) MPa] and at low temperatures [(313.3 and 323.2) K] were reported in the range of [$(4.3 \text{ to } 9.4) \cdot 10^{-7}$], whereas β-carotene solubilities from carrot in supercritical CO_2 under the same conditions were in the range of [$(2.4 \text{ to } 24) \cdot 10^{-8}$].[14] According to the current research, β-carotene solubilities from CPO in CO_2 under the operating conditions were in the range of $(2.27 \cdot 10^{-2})$ to $(9.2 \cdot 10^{-4})$. The higher solubility values of β-carotene in CO_2 from CPO in comparison with CO_2 + carrot system are due to having 15 times more retinol equivalent than carrot.[40] However, the effect of the cell structure, which is not negligible at low temperatures, on mass transfer resistance may cause an enhancement in the solubility of β-carotene from CPO in comparison with the solid matrices such as pure β-carotene and carrot. The interaction of the other compounds such as lipids (e.g., fatty acids with their high solubilities in CO_2) may increase β-carotene solubility from CPO,[10] whereas hydrates may decrease it from the carrot matrix.[14]

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