

Measurement and mathematical modeling of solubility of buttery-odor substance (acetoin) in supercritical CO₂ at several pressures and temperatures



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ABSTRACT

The solubilities of acetoin (3-hydroxy-2-butanone), a frequently used buttery-odor compound in supercritical carbon dioxide (SC-CO₂) at several pressures and temperatures were measured in this work. The measurements were conducted in a static-analytic mode at several pressures ranging from 8 MPa to 28 MPa and four temperatures of 313.15 K, 323.15 K, 333.15 K, and 343.15 K. The equilibrium was established for 3–4 h. The solubilities of acetoin in SC-CO₂ increased with increasing both pressure and temperature beyond the crossover pressure at 8 MPa. Two density-based models namely Chrastil and Del Valle-Aguilera and Peng–Robinson equation of state (PR-EOS) with quadratic and Stryjek–Vera mixing rules were used to represent experimental solubilities and to describe phase behavior of the system. Both Chrastil and Del Valle-Aguilera models were able to correlate experimental solubility data satisfactorily with absolute average relative deviation (AARD) of 0.27%. Similarly, the phase equilibrium behavior of acetoin + supercritical CO₂ binary system can be well interpreted by PR-EOS with quadratic (AARD of 0.11%) and Stryjek–Vera mixing rules (AARD of 0.08%).

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1. Introduction

Currently, food and beverage industries are growing rapidly because of the increasing demand from the market and their importance for sustaining the economic growth of country. In this modern age, human needs for foods are not limited to only staple foods, but also on the processed food products. A large variety of processed food products and beverages have been well-known, such as butter, milk, cheese, coffee, pickles, and cookies. For attracting the consumers, most of the manufacturers use flavorings to impart a distinctive organoleptic in their food products. Acetyl methyl carbinol, commonly known as 3-hydroxy-2-butanone or acetoin, is a colorless or pale yellow liquid that is frequently used in the production of powdered flavorings for yoghurt, coffee, milk, and butter, as well as an additive in the pharmaceuticals and chemicals manufacturing [1]. This substance has a somewhat creamy taste and a pleasant buttery-odor that can be found in several fruits

and vegetables, such as apple, grape, broccoli, blackcurrant, and strawberry. Acetoin is also produced from the metabolic activity of glucose by a number of fermentative bacteria such as Enterobacteriaceae, Bacillus, and Leuconostoc sp. [2–4].

In recent years, research devoted to the applications of supercritical fluids (i.e., the fluids that exhibit a gas-like mass transfer rate and a liquid-like solvent power) for diverse applications, such as fractionation [5], extraction [6], reactions [7], biotechnology advances [8], production of fine chemicals [9], and nanomaterials processing [10] becomes increasingly popular. The main advantages of using supercritical fluids (SCFs) are the tunable solvation power by manipulating pressure and temperature and highly selective dissolution ability without damaging or contaminating the target compound. Carbon dioxide (CO₂) is by far the most extensively used supercritical solvent, owing to its practical advantages, such as cheap, readily available in high purity, safe handling and storage (non-flammable and non-explosive), environmentally friendly, has relatively low critical pressure (7.38 MPa) and critical temperature (304.25 K), and ease separation from the product. Furthermore, carbon dioxide is regarded as a non-toxic substance based on The U.S. Food and Drug Administration (FDA) approval [11].

When dealing with the effective design and optimization of supercritical-based processes of flavorings for scale-up operation,

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the knowledge about equilibrium solubility data of solute in supercritical solvent over a wide range of pressures and temperatures are of crucial importance. In the present work, the solubilities of acetoin in co-solvent free supercritical CO₂ (SC-CO₂) were experimentally measured using a static-analytic method at elevated temperatures from 313.15 K to 343.15 K and several pressures ranging from 8 MPa to 28 MPa. Previous research dealing with acetoin only attempted to isolate and identify this volatile compound from various food-stuffs and beverages, such as rice cakes [12], raw and cooked pine-mushrooms [13], kefir [14], beer [15], wine [16], and marine animals [17–19], using the combination of headspace solid-phase microextraction (SPME) and gas chromatography–mass spectrometry (GC–MS) techniques. The supercritical CO₂ extraction and process optimization for the recovery of various aroma-active compounds in Zhenjiang aromatic vinegar has been carried out by Lu and colleagues [20]. To the best of our knowledge, the solubility measurement and the evaluation of phase behavior of acetoin + supercritical CO₂ system is not available in the literature. Because acetoin has a fairly low dipole moment (i.e., 2.35) and CO₂ behaves as a lipophilic solvent in supercritical state, therefore acetoin is readily soluble in supercritical CO₂ and the addition of modifiers (co-solvent) is not required. The solubility data are correlated by two density-based models (i.e., Chrastil and Del Valle–Aguilera) and phase equilibrium behavior of the system were investigated by Peng–Robinson equation of state with quadratic and Stryjek–Vera mixing rules.

2. Materials and methods

2.1. Chemicals

Acetoin (purity 98%, $T_m = 15^\circ\text{C}$, CAS Number: 513-86-0) was purchased from Sigma–Aldrich, Singapore as crystalline dimer form with molecular weight of 88.11 g/mol and used without further purification. Liquid carbon dioxide (99.98% pure) was supplied by Aneka Gas Pty Ltd. as food grade in a dip-tube supply cylinder. Ethanol (96%, Sigma–Aldrich) was used as a liquid medium for trapping acetoin.

2.2. Solubility measurements

The solubilities of acetoin in supercritical CO₂ at various pressures and temperatures were experimentally measured in a

bench-scale supercritical apparatus using static-analytic method [21,22]. The schematic diagram of equipment set-up is shown in Fig. 1. The maximum working pressure and working temperature of the system are 40 MPa and 423.15 K, respectively. All tubings and fittings are made from 316SS-grade stainless steel (Swagelok). Briefly, a piece of cotton (± 1 g) was wetted with liquid acetoin (1 ml) and packed in a 150 cm³ high-pressure double-ended equilibration cylinder. The system was evacuated thereafter by a vacuum pump (GAST DOA-P504-BN). The system was heated from room temperature to desired temperatures (313.15 K, 323.15 K, 333.15 K, and 343.15 K) using a thermostated oven. Then, liquid CO₂ was compressed and delivered to the equilibration cylinder using an Eldex AA-100-S-2 horizontal reciprocating pump with dual inlet ports by opening valve V-1. The flow rate of liquid CO₂ was held constant at 10 ml/min until the preset pressure was reached. To maintain isothermal and isobar conditions, the system pressure was monitored real-time by a digital pressure indicator connected to pressure transducer (Druck PTX 611) and the system temperature was controlled with uncertainties of ± 1 K. Preliminary experiments showed that equilibrium was established within 3–4 h. The equilibrated supercritical phase was swept out from the sample cylinder at the same condition by fresh CO₂ into a receiving vial filled with 100 ml 96% ethanol. Ethanol was used as a trapping solvent because it can readily dissolve acetoin, cheap, and safer than methanol. Care was taken to prevent sample precipitation during depressurizing high-pressure stream by gently heating the discharge line. The receiving vial was equipped with a vent needle to allow the expanded gas to exit and total volume of solute-free ambient gas was recorded using a calibrated wet gas flow meter (ZEAL DM3B) at a known pressure and temperature (± 0.05 L). The ethanol containing acetoin was subjected to gas chromatography for analysis. The mass of cotton was weighed before and after each experimental run. All experimental data were reproduced by three replicate experiments at the identical conditions and presented as mean \pm SD ($n = 3$).

2.3. Analysis of acetoin content

The concentration of acetoin in the trapping solvent (wt%) was quantified by gas chromatography technique on a Shimadzu GC-2014 equipped with a split/splitless injection port and a flame ionization detector (FID). The stationary phase was an Agilent DB-1 dimethylpolysiloxane capillary column (30 m \times 0.53 mm \times 3 μm).

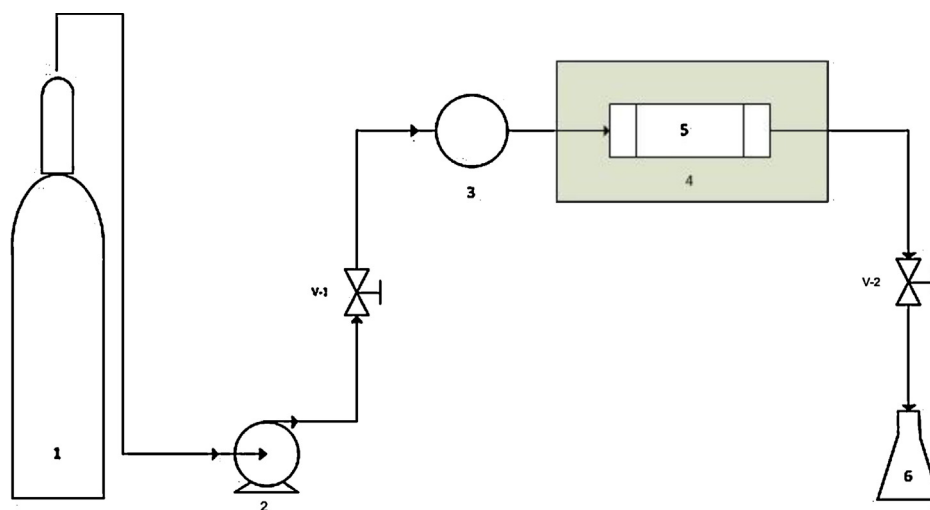


Fig. 1. Experimental set-up for solubility measurement (Dip-tube liquid CO₂ cylinder (1); Reciprocating pump (2); Pressure transducer (3); Thermostated oven (4); High-pressure equilibration column (5); Receiving vial (6)).

The analysis conditions were given in detail as follows: (1) mobile phase (carrier gas): Helium at 29.4 kPa and a constant linear velocity of 30 cm/s; (2) detector temperature of 300 °C; (3) injection port temperature of 250 °C; (4) temperature profile of the column oven: 40 °C for 5 min, followed by a first ramp to 260 °C at 10 °C/min, and a final isotherm at 260 °C for 1 min. Total program time was 28 min. The injection volume was 1 µl with a split ratio of 10:1. The calibration curve was prepared by measuring five standard solutions of acetoin with different concentrations ranging from 1 mg/l to 20 mg/l. The solubility of acetoin, in the unit of mole fraction, was calculated by the following equation:

$$y_2 = \frac{(m_2/M_2)}{(\rho_1 V_1/M_1)} \quad (1)$$

where y_2 is the mole fraction of acetoin in supercritical CO₂, m_2 is the mass of acetoin in trapping solvent (g), ρ_1 is the density of liquid CO₂ at 303.15 K (g/L), V_1 is the volume of liquid CO₂ supplied to the equilibration cylinder (L), M_1 and M_2 are the molecular mass of CO₂ (44.01 g/mol) and acetoin (88.11 g/mol), respectively.

3. Results and discussion

3.1. Solubilities of acetoin in supercritical CO₂

Generally speaking about supercritical fluids (SCFs), the tunable properties of supercritical fluids associated to their penetration ability to be a gas-like and solvent power to be a liquid-like strongly depend on the applied pressure and temperature. The densities of supercritical CO₂ at various pressures and temperatures were calculated by Peng–Robinson with Stryjek–Vera modification (PRSV) equation of state [23] and the results are tabulated in Table 1. The original Peng–Robinson equation of state has the following mathematical form [24]:

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

where P is the absolute pressure (atm), V is the molar volume (dm³/mol), T is the absolute temperature (K), R is the universal gas constant (8.314 J/mol K), $a(T)$ and b are Peng–Robinson constants. For pure component system, a and b values are given as follows:

$$a(T) = \alpha \cdot \alpha(T_r, \omega) \quad (3)$$

$$\alpha = 0.4572 \frac{R^2 T_c^2}{P_c} \quad (4)$$

$$\alpha(T_r, \omega) = (1 + \kappa(1 - \sqrt{T_r}))^2 \quad (5)$$

$$\kappa = 0.3746 + 1.5423\omega - 0.2669\omega^2 \quad (6)$$

$$b = 0.0778 \frac{RT_c}{P_c} \quad (7)$$

where P_c and T_c are pressure (MPa) and temperature (K) of the pure compound at critical point, T_r is reduced temperature or the ratio of operating temperature to critical temperature, ω is the acentric factor and κ is an adjustable parameter characteristic of each compound. The critical pressure, critical temperature, and acentric factor for pure carbon dioxide is 7.39 MPa, 304.25 K, and 0.225, respectively. The mathematics modification proposed by Stryjek and Vera (1986) on Peng–Robinson equation of state improved the model's accuracy for predicting the vapor-liquid equilibria (VLE) data by introducing two additional adjustable pure compound parameters and changing the polynomial fit of the acentric factor [23]:

$$\alpha(T_r, \omega) = ((1 + (\kappa + \kappa_1(1 + \sqrt{T_r}))(0.7 - T_r))(1 - \sqrt{T_r}))^2 \quad (8)$$

$$\kappa = 0.3789 + 1.4897\omega - 0.1713\omega^2 + 0.0196\omega^3 \quad (9)$$

Table 1
Experimental solubilities of acetoin in supercritical CO₂ at several pressures and temperatures.

P (MPa)	313.15 K			323.15 K			333.15 K			343.15 K		
	ρ CO ₂ ^a (g/L)	y_2 ^b ($\times 10^{-5}$)	S^c ($\times 10^{-2}$ g/L)	ρ CO ₂ (g/L)	y_2 ($\times 10^{-5}$)	S ($\times 10^{-2}$ g/L)	ρ CO ₂ (g/L)	y_2 ($\times 10^{-5}$)	S ($\times 10^{-2}$ g/L)	ρ CO ₂ (g/L)	y_2 ($\times 10^{-5}$)	S ($\times 10^{-2}$ g/L)
8	284	0.68 ± 0.03	0.39 ± 0.02	225	0.98 ± 0.05	0.44 ± 0.04	196	1.51 ± 0.12	0.60 ± 0.02	178	2.36 ± 0.14	0.84 ± 0.04
10	565	1.74 ± 0.09	1.96 ± 0.08	376	1.99 ± 0.08	1.50 ± 0.03	293	2.58 ± 0.06	1.51 ± 0.09	251	3.87 ± 0.07	1.94 ± 0.11
12	667	2.20 ± 0.14	2.93 ± 0.18	535	3.12 ± 0.15	3.33 ± 0.11	415	4.36 ± 0.09	3.62 ± 0.18	342	5.91 ± 0.05	4.04 ± 0.26
14	726	2.38 ± 0.07	3.46 ± 0.09	625	3.94 ± 0.23	4.93 ± 0.18	521	6.07 ± 0.18	6.33 ± 0.12	435	7.97 ± 0.03	6.93 ± 0.19
16	768	2.69 ± 0.15	4.13 ± 0.14	684	4.62 ± 0.19	6.32 ± 0.15	596	7.05 ± 0.08	8.40 ± 0.15	514	10.53 ± 0.34	10.83 ± 0.31
18	802	2.82 ± 0.08	4.53 ± 0.22	728	4.70 ± 0.14	6.84 ± 0.23	652	7.81 ± 0.25	10.20 ± 0.28	577	12.58 ± 0.27	14.52 ± 0.28
20	830	2.91 ± 0.15	4.84 ± 0.16	764	5.23 ± 0.27	7.99 ± 0.15	695	8.47 ± 0.22	11.78 ± 0.24	627	13.36 ± 0.16	16.76 ± 0.14
22	855	3.02 ± 0.11	5.16 ± 0.19	794	5.31 ± 0.21	8.44 ± 0.26	731	9.56 ± 0.06	13.98 ± 0.19	668	15.22 ± 0.44	20.34 ± 0.07
24	876	3.17 ± 0.12	5.55 ± 0.24	819	5.62 ± 0.16	9.20 ± 0.17	761	9.60 ± 0.34	14.61 ± 0.36	703	15.83 ± 0.39	22.26 ± 0.34
26	895	3.30 ± 0.05	5.90 ± 0.15	842	5.99 ± 0.26	10.10 ± 0.14	787	9.87 ± 0.17	15.53 ± 0.21	733	17.71 ± 0.28	25.97 ± 0.21
28	913	3.33 ± 0.21	6.08 ± 0.07	862	6.43 ± 0.32	11.09 ± 0.08	811	10.84 ± 0.41	17.58 ± 0.32	759	18.30 ± 0.17	27.80 ± 0.27

^a Predicted by PRSV equation of state [23].

^b Mole fraction of acetoin in supercritical CO₂.

^c Solubility of acetoin in supercritical CO₂.

The value of κ_1 can be conveniently assumed to be zero for most compounds [23]. The application of PRSV equation of state is generally superior to other equations of state in predicting the densities of various compounds, particularly the nonpolar ones and only requires little computer resources to solve the equation. As shown in Table 1, the densities of supercritical CO₂ increased at higher pressures for constant temperature, which also means greater solvent power of the fluid. A plausible explanation to this point is that increasing pressure would reduce the available volume occupied by the molecules so the molecules become closer each other. Accordingly, the ratio of mass to volume becomes higher at higher pressures and therefore the density of CO₂ rose. Meanwhile, the densities of supercritical CO₂ decreased with increasing temperature at constant pressure. This might be attributed to greater molar volume (V_m) at elevated temperatures. Since the density and molar volume is inversely proportional hence the increasing value of molar volume leads to lower value of density and vice versa.

The solubilities of acetoin in SC-CO₂ increased with increasing both pressure and temperature (Table 1). At temperature of 313.15 K, the increase of pressures from 8 MPa to 16 MPa enhanced the mole fraction of acetoin in SC-CO₂ from $(0.68 \pm 0.03) \times 10^{-5}$ to $(2.69 \pm 0.15) \times 10^{-5}$. Similar trends were observed in three other temperatures studied. This might be attributed to enhanced solvent power of the fluid toward solute at elevated pressures and temperatures. Moreover, an isobaric increase in temperature gave a positive effect on the solubilities of acetoin in supercritical CO₂. As can be seen, the mole fraction of acetoin in SC-CO₂ at 20 MPa increased progressively from 2.91×10^{-5} to 13.36×10^{-5} with temperature rise from 313.15 K to 343.15 K. These results confirm the significance of vapor pressure of solute toward solubilities at pressures beyond the crossover point (8 MPa) in which the solute tends to become more volatile at higher temperatures, allowing more acetoin to dissolve in supercritical CO₂. Furthermore, increasing temperature may also improve diffusivity (or mass transfer rate) of solute to the solvent phase thus higher solvated amounts of acetoin in supercritical CO₂.

3.2. Correlations of experimental solubility data and phase equilibria

With regards to process design and optimization of supercritical-based technologies for industrial applications, particularly in food and flavorings industries, the knowledge about equilibrium concentration of acetoin in the solvent phase over wide range of pressures and temperatures are essentially needed. For this purpose, the phase equilibria of acetoin in supercritical carbon dioxide were evaluated using two sorts of approaches: (1) density-based correlations and (2) theoretical cubic equations of state. The density-based correlations were commonly developed semi-empirically based on simple error minimization between actual and predicted values either using least-square or nonlinear regression techniques. The correlation of actual solubility data by density-based models offers an advantage because it does not require thermophysical properties of the compounds of interest such as molar volume, acentric factor, and critical point that normally cannot be measured from experiment.

3.3. Density-based correlations

In the present work, two popular semi-empirical density-based models namely Chrastil and Del Valle-Aguilera equations were applied to correlate experimental solubilities of acetoin in SC-CO₂ at several pressures and temperatures. Chrastil (1982) was the first who proposed density-based model by assuming that a solvato

complex was formed between solute and supercritical solvent at equilibrium state, as described below [25]:



From Eq. (10), it can be seen that one molecule of solute X associates with k molecules of supercritical solvent Y to form solvato complexes (XY_k) at equilibrium. The value of parameter k is not an integer in most cases based on the fact that the formation of solvato complex is not occurred stoichiometrically in which some of them become less or more stable [25]. Therefore, parameter k is often designated as an average association number for a given solute-supercritical solvent system. Chrastil model relates the solubilities of solute in supercritical solvent to that of solvent density and operating temperature in the following expression:

$$c = \rho^k \exp\left(\frac{a}{T} + b\right) \quad (11)$$

where c is the solubility of solute (kg/m^3), ρ is the solvent density (kg/m^3), T is the absolute temperature (K), a is a function of enthalpy of solvation (ΔH_{soln}) and enthalpy of vaporization (ΔH_{vap}), and b is a function of average association number that depends on the molecular mass of solute and supercritical solvent. The values of adjustable parameters k , a , and b are specific for each solute-supercritical solvent pair and not dependent on temperature and pressure. These parameters were simultaneously determined by performing nonlinear regression fitting of the model toward actual solubility data using SigmaPlot software (Version 12.3, Systat Software Inc.). In order to minimize the error between actual and predicted solubilities, the following objection function (OF) was applied:

$$\text{OF} = \sum_i^N \left| \frac{y_i^{\text{calc}} - y_i^{\text{exp}}}{y_i^{\text{exp}}} \right| \quad (12)$$

where N is the number of experimental data, y_i^{calc} and y_i^{exp} are the calculated and experimental solubility values, respectively.

The second semi-empirical density-based correlation used was Del Valle and Aguilera equation. They studied the solubilities of vegetable oils in dense CO₂ and took into account the change in enthalpy of vaporization with temperature by assuming the independency of average association number toward density and temperature [26]. Del Valle and Aguilera model, which is analog to Chrastil model, has a mathematical form as follows [26]:

$$c = \rho^k \exp\left(b + \frac{a}{T} + \frac{d}{T^2}\right) \quad (13)$$

The agreement of both models in correlating experimental solubility data was assessed from the corresponding absolute average relative deviation (AARD), defined as follows:

$$\text{AARD}(\%) = \frac{100}{N} \sum_{i=1}^N \left| \frac{y_i^{\text{calc}} - y_i^{\text{exp}}}{y_i^{\text{exp}}} \right| \quad (14)$$

The three-dimensional fittings of Chrastil and Del Valle and Aguilera models against experimental solubility data of acetoin in SC-CO₂ as a function of temperature and solvent density are shown in Fig. 2. The dot symbol and wire-mesh line represent experimental data and the model fit, respectively. The fitted parameter values of Chrastil and Del Valle and Aguilera models are listed in Table 2. From Fig. 2, it can be seen that both models satisfactorily representing experimental solubilities with the absolute average relative deviation of 0.27% for both Chrastil and Del Valle and Aguilera models. The average association number (k) regarding the formation of solvato complex between acetoin and supercritical CO₂ was 2.42 for both models. This means that one

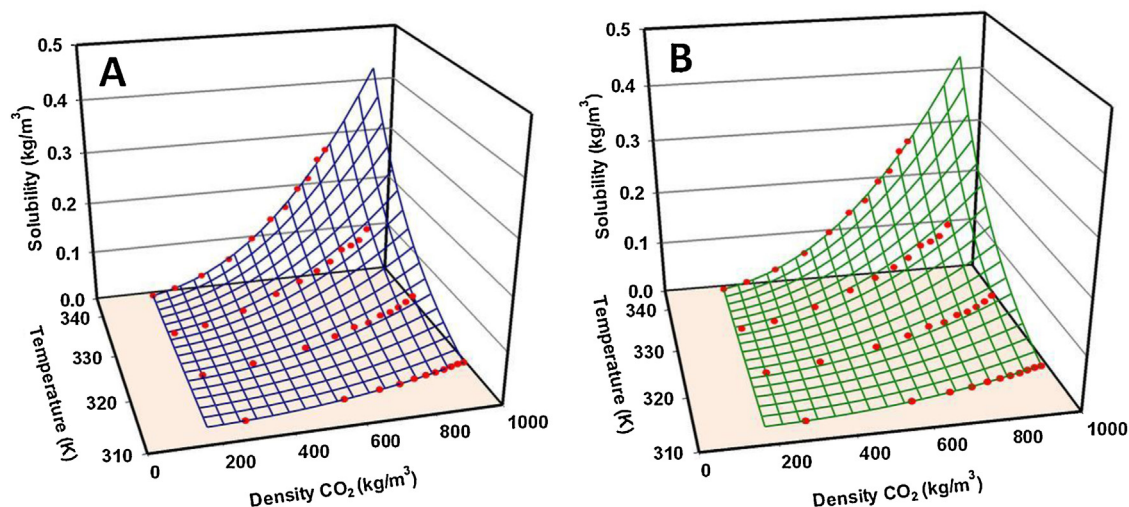


Fig. 2. Three-dimensional fittings of Chrastil (a) and Del Valle and Aguilera (b) correlation models toward experimental solubilities of acetoin in supercritical CO₂.

Table 2

The adjusted constant parameters of Chrastil and Del Valle and Aguilera models for acetoin (1)+supercritical CO₂ (2) system.

T (K)	Chrastil				Del Valle and Aguilera				
	<i>a</i>	<i>b</i>	<i>k</i>	AARD (%)	<i>a</i>	<i>b</i>	<i>d</i>	<i>k</i>	AARD (%)
313.15									
323.15									
333.15	-7,005.70	3.08	2.42	0.27	-11,237.87	9.46	7.01×10^5	2.42	0.27
343.15									

molecule of acetoin associates with 2.42 molecules of supercritical CO₂ to form a solvato complex at equilibrium. As aforesaid, the adjustable parameter *a* is a function of enthalpy of solvation (ΔH_{solv}) and enthalpy of vaporization (ΔH_{vap}), expressed as $a = \Delta H_{soln}/R$ for Chrastil model and $a = ((\Delta H_{soln}/R) - (2d/T))$ for Del Valle and Aguilera model where ΔH_{soln} is total heat of reaction or enthalpy of solution (i.e., $\Delta H_{soln} = \Delta H_{solv} + \Delta H_{vap}$). It was found that total reaction heat to form acetoin-supercritical CO₂ solvato complexes was negative, indicating the feature of a non-ideal solution system and an exothermic dissolving process of solute in supercritical solvent. The negative value of total reaction heat may also be implicit information about greater magnitude of heat released from the associating process between acetoin and SC-CO₂ molecules to form solvato complexes than that required for the break down of intermolecular forces of solute and supercritical solvent molecules. The total heat of reaction for Chrastil model was -58.25 kJ/mol, which is comparable to that of Del Valle and Aguilera model ($\Delta H_{soln} = -57.87$ kJ/mol). The values of adjustable parameter *b*, defined as $b = \ln(M_1 + kM_2) + q - k \ln M_2$ should be similar for two models because this parameter is a function of average association number (*k*) and molecular weight of solute (*M*₁, 88.11 g/mol) and supercritical solvent (*M*₂, 44.01 g/mol). However, the fitted values of parameter *b* for Chrastil and Del Valle and Aguilera models are significantly different (i.e., 3.08 for Chrastil and 9.46 for Del Valle and Aguilera). This may be attributed to the inclusion of new adjustable parameter (*d/T*²) in Del Valle and Aguilera correlation model to compensate for the variation of the solute's vaporizing heat with temperature that leads to higher magnitude of constant *q* (i.e., 6.97 for Chrastil model vs. 13.35 for Del Valle and Aguilera model).

3.4. Cubic equations of state

The phase equilibria of acetoin-supercritical CO₂ system at various pressures and temperatures were studied based on

the theoretical approach of cubic equations of state. The critical properties (*P*_c and *T*_c) and acentric factor (ω) of pure acetoin were predicted by Joback and Lee-Kesler group contribution method [27], respectively and the results are given as follows: *T*_c of 629.92 K, *P*_c of 6.27 MPa and ω of 0.53. In this regard, Peng–Robinson equation of state with quadratic and Stryjek–Vera mixing rules was applied for evaluating phase behavior of acetoin + supercritical CO₂ mixture at equilibrium. The cross coefficients *a* and *b* of Peng–Robinson equation of state for binary component systems can be expressed in the form of one-fluid mixing rule as follows:

$$a = \sum_{i=1}^N \sum_{j=1}^N x_i x_j a_{ij} \quad (15)$$

$$b = \sum_{i=1}^N \sum_{j=1}^N x_i x_j b_{ij} \quad (16)$$

The values of adjusted binary interaction parameters *a*_{ij} and *b*_{ij} were determined by applying appropriate mixing rules. For this purpose, the classical quadratic mixing rule was selected to determine the adjusted mixing parameters *a*_{ij} and *b*_{ij} [28]:

$$a_{ij} = \sqrt{a_i a_j} \times (1 - k_{ij}) \quad \text{with} \quad k_{ij} = k_{ji} \quad (17)$$

$$b_{ij} = \frac{b_i + b_j}{2} \times (1 - l_{ij}) \quad \text{with} \quad l_{ij} = l_{ji} \quad (18)$$

where *a*_i, *a*_j, *b*_i, and *b*_j are the Peng–Robinson parameters for pure component that can be determined from Eqs. (3) and (5), respectively by introducing parameters $\alpha(T_r, \omega)$ and κ for PRSV equation of state. The following Stryjek–Vera mixing rule was also employed

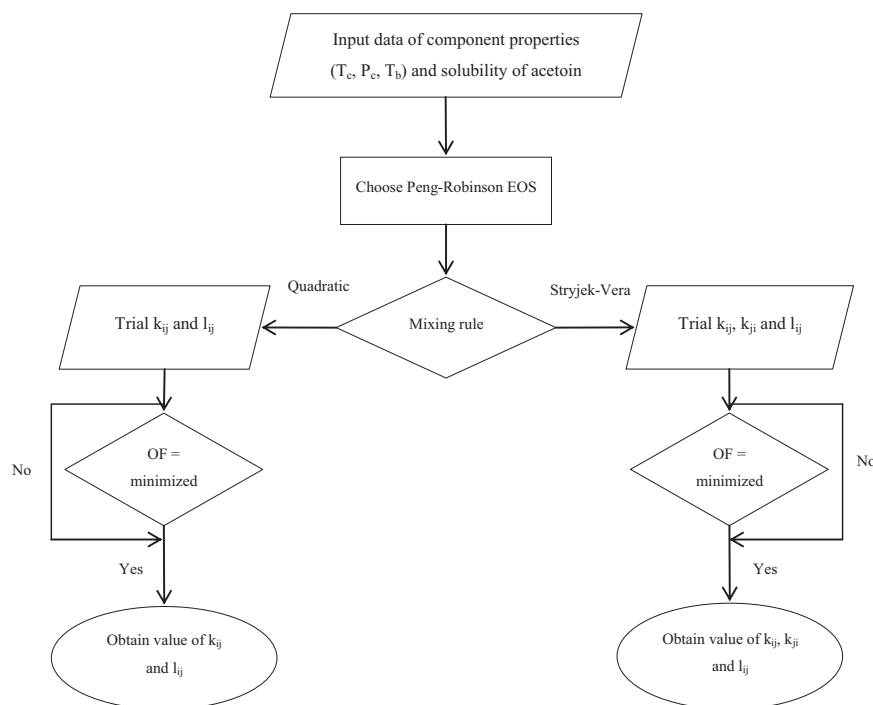


Fig. 3. The computational algorithm for determining binary interaction parameters (k_{ij} , k_{ji} , and l_{ij}) of Peng–Robinson equations of state with quadratic and Stryjek–Vera mixing rules.

for the prediction of adjusted binary interaction parameters a_{ij} and b_{ij} [29]:

$$a_{ij} = \sqrt{a_i a_j} \times \left(1 - \frac{k_{ij} k_{ji}}{x_i k_{ij} + x_j k_{ji}} \right) \quad \text{with } k_{ij} \neq k_{ji} \quad (19)$$

$$b_{ij} = \frac{b_i + b_j}{2} \times (1 - l_{ij}) \quad \text{with } l_{ij} = l_{ji} \quad (20)$$

Here, x_i and x_j represent the mole fraction of solute and supercritical solvent in the binary mixture, respectively.

The values of adjusted binary interaction parameters (k_{ij} , k_{ji} , and l_{ij}) were determined following algorithm described in Fig. 3 using PE2000 computational software (Version 2.9.9a). The computation was started by inputting the critical properties of pure component and adjusting the values of mixing parameters k_{ij} , k_{ji} , and

l_{ij} until convergence and minimized objective function satisfied. The predicted compositions of acetoin in supercritical CO₂ with optimized binary interaction parameters are plotted against actual data in Fig. 4. The change of temperatures slightly increases the values of binary interaction parameters k_{ij} and l_{ij} (Table 3) for both quadratic and Stryjek–Vera mixing rules, indicating a weak positive dependence of these parameters toward temperature. However, the increasing values of parameters k_{ij} and l_{ij} denote that higher temperature facilitates the interaction between “like” molecules (i.e., solute–solvent) to form a solvato complex. This behavior is consistent with the physical meaning of negative sign of total reaction heat obtained from density-based correlations that reflect stronger attraction forces between solute and solvent than those of solvent–solvent or solute–solute molecular interactions. The magnitude of binary interaction parameters k_{ij} and l_{ij} in this work is much lower

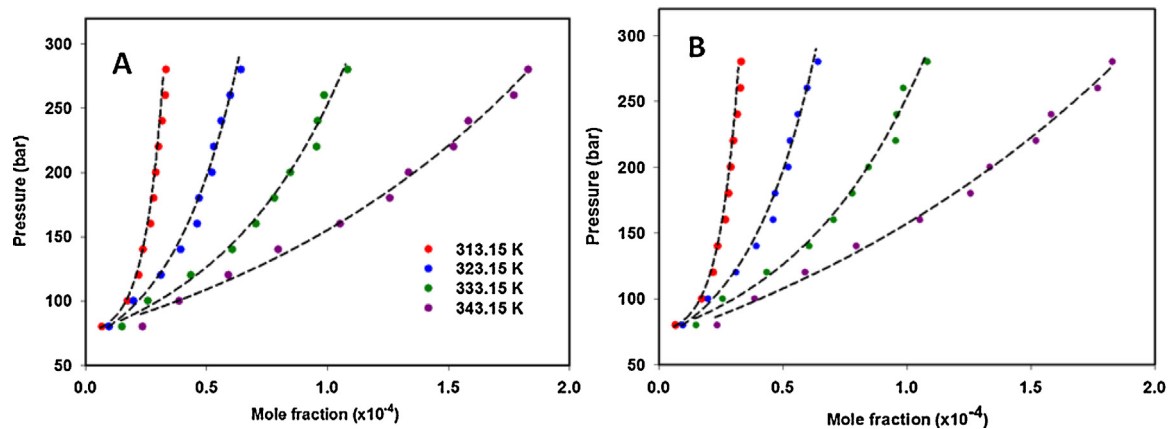


Fig. 4. Correlations between measured (dot symbols) and predicted (dashed lines) mole fraction of acetoin in supercritical CO₂ using PR-EOS with quadratic (A) and Stryjek–Vera (B) mixing rules.

Table 3The optimized binary interaction parameters of PR-EoS with quadratic and Stryjek–Vera mixing rules for acetoin (1) + supercritical CO₂ (2) system.

T (K)	Quadratic mixing rule			Stryjek–Vera mixing rule				
	k_{ij}	l_{ij}	AARD (%)	k_{ij}	k_{ji}	l_{ij}	Λ_{ij}^a	AARD (%)
313.15	0.115	0.066	0.11	0.133	0.420	0.042	-0.287	0.08
323.15	0.116	0.067		0.135	0.412	0.043	-0.277	
333.15	0.118	0.069		0.137	0.394	0.044	-0.257	
343.15	0.119	0.070		0.138	0.356	0.044	-0.218	

^a Λ_{ij} is calculated by subtracting k_{ij} and k_{ji} , which also equals to $-\Lambda_{ji}$ [29]

than that obtained by Ismadji and Bhatia [30] for the solubilities of three flavor esters namely ethyl propionate (MW of 102.13 g/mol), ethyl butyrate (MW of 116.16 g/mol), and ethyl isovalerate (MW of 130.18 g/mol) in dense CO₂. This difference is possibly due to lesser asymmetry degree of acetoin + supercritical CO₂ system because solute and supercritical solvent have similarity in terms of polarity and molecular size compared to those systems in Ismadji and Bhatia study. Additionally, the dissimilarity in molecular size between solute and solvent resulted in the negative values of mixing parameters k_{ij} and l_{ij} , as observed in Skerget et al. [31] and de la Fuente et al. [32] study for vanillin + carbon dioxide and capsaicin + carbon dioxide system, respectively. By judging the AARD values, PR-EOS with quadratic and Stryjek–Vera mixing rules both can describe the phase behavior of acetoin + supercritical CO₂ system at studied pressures and temperatures satisfactorily and shows consistency with density-based correlation.

4. Conclusions

The solubilities and phase equilibrium behavior of acetoin in supercritical CO₂ at temperatures ranging from 313.15 K to 343.15 K and several pressures up to 28 MPa have been investigated in this work. The equilibrium concentration of acetoin in supercritical CO₂ ranged between $(0.39 \pm 0.02) \times 10^{-2}$ g/L and $(27.80 \pm 0.27) \times 10^{-2}$ g/L. Beyond the crossover pressure (8 MPa), the solubilities increased with increasing both pressure and temperature due to synergistic effects between solvent power and vapor pressure of solute. The endothermicity of associating process between acetoin (X) and SC-CO₂ (Y) to form a solvato complex can be well interpreted by Chrastil and Del Valle and Aguilera models with an absolute average relative deviation (AARD) of 0.27%. Total reaction heat for the vaporization and solvation of acetoin in supercritical CO₂ was about -58 kJ/mol. The evaluation of phase behavior by Peng–Robinson equation of state with quadratic and Stryjek–Vera mixing rules reveals a weak positive dependence of adjusted binary interaction parameters k_{ij} and l_{ij} with temperature rise. To this end, the present work provides adequate information for the readership regarding solubility data of acetoin in supercritical CO₂ over a wide range of pressures and temperatures for scale-up production of this flavoring compound in the supercritical-based food, beverage, or pharmaceutical industries.

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