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Binary Mixture Phase Behavior for the 3-pentyl acetoacetate + carbon dioxide System at High Pressure

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Abstract – The demand for acetoacetate-based compounds has risen significantly in recent years due to their unique physicochemical properties and wide-ranging industrial applications. The critical-point, dew-point, and bubble-point equilibria data for the 3-pentyl acetoacetate + carbon dioxide (CO_2) binary system in the temperature range of 313.2 K to 393.2 K and pressure limited to 20.06 MPa were measured. The mole fraction responses were acquired in the range of (0.0433 to 0.7950). The pressure–temperature diagrams indicated that the critical locus of the mixture formed a continuous boundary connecting the critical points of CO_2 and pure 3-pentyl acetoacetate. The binary system 3-pentyl acetoacetate + CO_2 did not display 3-phases according to the vapor-liquid equilibria research at the test temperature. At a fixed temperature, the solubility of the system was found to increase with increasing mole fraction of 3-pentyl acetoacetate. The observed phase behavior corresponded to a Type-I system according to the classification of Van Konynenburg and Scott. Additionally, the experimentally measured bubble-point pressures were correlated using the PR EoS (Peng–Robinson equation of state) combined with vdW(van der Waals) one-fluid mixing rules. The binary interaction parameters (k_{ij}=0.005 and η_{ij}=-0.025) were optimized and determined for the 3-pentyl acetoacetate+CO_2 system. The model predictions showed good agreement with the experimental data, yielding RMSD (root mean square deviation) values of 8.14%, 5.05%, 3.37%, 3.36%, and 2.90% across the investigated temperature range.

Key words: High-pressure phase behavior, Carbon dioxide, 3-Pentyl acetoacetate, Supercritical fluids

1. Introduction

3-pentyl acetoacetate has gained significant attention due to their distinctive chemical properties and various industrial applications. Owing to their ability to dissolve a wide range of organic materials, 3-pentyl acetoacetate are widely used as solvents and chemical intermediates, fine chemicals, pharmaceuticals, agrochemicals, flavor and fragrance intermediates, and related industries [1,2]. Understanding the solubility behavior and thermodynamic of acetoacetates type solvents are essential for optimizing processes, developing fresh formulations, and new material performance [3-5]. Conventional liquid–liquid extraction methods are often unsuitable because of their high solubility in organic solvents. In contrast, supercritical carbon dioxide (Sc-CO_2) provides an efficient and environmentally friendly alternative. Sc-CO_2 is non-toxic, non-flammable, cost-effective, and chemically stable option, making it suitable for sustainable industrial applications and advanced material processing [6-10].

Sc-CO_2 has been widely applied in polymerization, chemical synthesis, material processing, and colloid formation [11,12]. Above its critical temperature and pressure, a supercritical fluid exhibits property of both gases and liquids [13]. Predicting vapor–liquid equilibrium under such conditions is challenging and typically requires experimental data combined with thermodynamic modeling. Cubic equations of state, particularly the Peng–Robinson equation of state (PR EoS), are commonly used to describe phase behavior in binary and multicomponent systems [14]. Mixing rules with adjustable interaction parameters are applied to account for solvent–solute interactions and temperature effects [15,16].

Previous studies have investigated various physicochemical properties of selected acetoacetates and 3-pentyl acetoacetate under different conditions. Reported properties included critical point behavior in CO_2, polarity and dielectric characteristics under CO_2 expansion, thermochemical properties, acoustic and density data, surface tension behavior in binary mixtures, and liquid–liquid equilibrium with CO_2 or acetoacetates. These studies collectively demonstrated the non-ideal behavior of 3-pentyl acetoacetate and provided valuable insight into their molecular interactions.

This research presents several key differentiators from previous studies on CO_2–organic solvent systems. The study provides valuable data over a wide range of temperatures, pressures, and compositions, which is important for applications involving supercritical fluids. First, the binary system of 3-pentyl acetoacetate and CO_2 has received comparatively less attention in the literature than other CO_2–organic solvent mixtures. Additionally, the study provides valuable data over a wide range of temperatures, pressures, and compositions, which is important for applications involving supercritical fluids. Second, in

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this study, Peng-Robinson equation of state (EOS) has been utilized with van der van der Waals mixing rules to correlate the VLE data, offering a clear distinction from other studies that relied on simpler experimental data or focused on more limited temperature and pressure ranges. Our work provides a deeper understanding of phase behavior in CO_2 and organic solvent systems, and the thermodynamic correlations derived from our data offer a more comprehensive foundation for future applications.

Despite this body of work, research on the phase behavior of 3-pentyl acetoacetate in the presence of supercritical fluids remains limited. Existing studies are generally restricted to a small number of compounds and narrow temperature, pressure, or composition ranges. In particular, investigations involving Sc-CO_2 have focused on only a few 3-pentyl acetoacetate derivatives and have not covered high-pressure or high-temperature conditions comprehensively. As a result, available phase equilibrium data are insufficient to fully describe the behavior of these systems or to support broader industrial applications.

To address this gap, this study examines the solution thermodynamics and phase behavior of 2-component mixtures of 3-pentyl acetoacetate and CO_2 over wide temperature, pressure, and composition ranges that have not been previously reported. Bubble-point pressures were measured and correlated using the Peng–Robinson equation of state (PR EoS) with van der Waals (vdW) mixing rules [15], and two interaction parameters were optimized to improve model accuracy. Model performance was evaluated using root mean square deviation values across the investigated temperatures. The results provide comprehensive solubility and phase equilibrium data that support the development of sustainable extraction processes, improved material formulations, and expanded use of green solvents in industrial applications.

We have studied phase behaviour of 3-pentyl acetoacetate binary mixture in CO_2 at high pressure. The experimental isotherms were presented for both the systems in (*p-x*) space. For 3-pentyl acetoacetate + CO_2 system, experimental isotherms ($313.2\ \text{K} \leq T \leq 393.2\ \text{K}$) were obtained in pressure array of $2.17\ \text{MPa} \leq p \leq 20.06\ \text{MPa}$. The critical mixture lines in (*p-T*) space confirmed type-I behavior exhibited by both binary mixes i.e., critical line existed between CO_2 critical point to 3-pentyl acetoacetate critical point. Another part of the work was to correlate obtained experimental isotherms with theoretical models. The cubic equations of state (CEoS) is one of such tool exploited widely to estimate vapor-liquid equilibria and thermodynamic properties [17-20]. The Peng-Robinson (PR) equation of state (EoS) is a simplest two parameter CEoS used and accepted widely for limitless applications [21-26]. Hence in the present study, we have employed PR EoS with vdW mixing rule to predict experimental isotherms.

2. Experimental

2-1. Materials

The 3-pentyl acetoacetate (CAS RN 13562-81-7) with purities > 0.970 were supplied by Sigma-Aldrich Co. whereas Deok Yang Gases Co. supplied pure carbon dioxide with purity > 0.999. Table 1 shows the detailed specifications of compounds used. All of the substances were used in their original form. The pictorial chemical structures of 3-pentyl acetoacetate demonstrated in Fig. 1.

2-2. Apparatus and experimental setup

High-pressure (HP) instruments were used to measure phase behavior, as discussed elsewhere [27,28]. The experimental apparatus used to determine the phase transition points of binary 3-pentyl acetoacetate and Sc-CO_2 mixtures is shown in Fig. 2. The system consisted of a hydraulic unit, water tank, digital temperature display, pressure gauge, borescope camera, high-pressure optical cell, reactor, computer monitor, and electric motor. The water tank was connected to the hydraulic system, which generated the required pressure inside a cylindrical stainless-steel reactor (inner diameter 1.6 cm, outer diameter 6.4 cm, volume 28 cm^3).

The hydraulic system (Model 65-5.75-15, High Pressure Equipment, US) was connected to both the reactor and a pressure gauge (Model

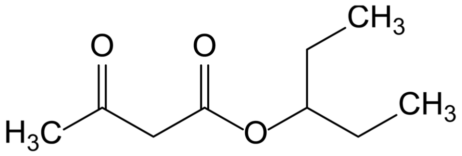

Fig. 1. Chemical configuration of 3-pentyl acetoacetate used in this work.

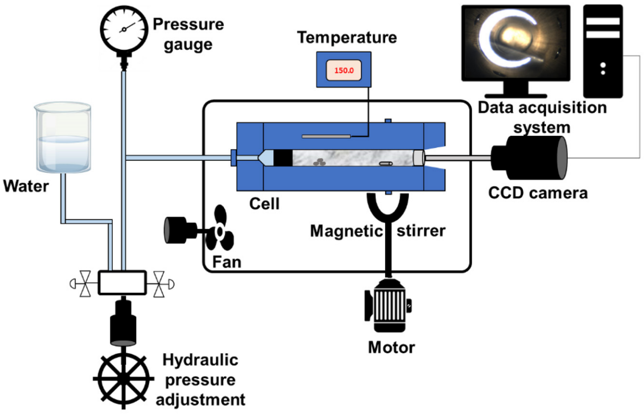

Fig. 2. The experimental apparatus of high-pressure phase behavior.

Table 1. Specifications of the chemical used in this study

Chemical Name	Source	Purity[a]	Purification Method	Analysis Method[a]
Carbon dioxide	Deokyang Gases Co.	>0.999	None	-
3-Pentyl acetoacetate	Sigma-Aldrich	>0.970	None	GC[b]

[a] Both the analysis method and the mass fraction purity were provided by the suppliers.
[b] Gas-liquid chromatography.

CM-142719, Heise, US) with an accuracy of ±0.1% and a standard uncertainty of ±0.03 MPa. The reactor was fitted with a movable piston for volume adjustment, a thermometer (Thermometrics Corp.) with an accuracy of ±0.02 K (±0.005%), and a sapphire window (1.9 cm thick) that allowed direct visual observation of phase transitions. The rear piston was isolated from the water to prevent direct contact with the sample.

A magnetic stir bar driven by an electric motor was positioned at the center of the reactor to ensure homogeneous mixing of the binary mixture, enabling precise identification of the phase transition point. On the opposite side of the piston, the reactor was connected to an additional borescope camera and a sapphire window, which was linked to a monitor for real-time observation of the phase behavior.

2-3. Experimental procedure

The experimental process was designed to ensure reproducibility and high accuracy. Before each experiment, the stirrer and reactor were thoroughly cleaned with toluene and acetone and then purged with nitrogen to remove residual impurities. A known mass of the 3-pentyl acetoacetate was weighed using an balance (Model: SECURA124-1S, Sartorius; accuracy ±0.0001 g) and injected into the reactor with a syringe. Subsequently, the required amount of CO_2 (u ± 0.002 g) was introduced from a cylinder.

Pressure and temperature were continuously monitored from a screw-in thermocouple and the pressure gauge described in the materials section. The pressure reactor was heated in a dry oven, and pressure was adjusted using a high-pressure generator until the phase transition point was reached. After achieving a stable single-phase state, the pressure was gradually fine-tuned. The system was maintained at the target temperature and pressure for at least 30 minutes before recording the phase transition data.

Following the phase transition, the system was returned to a single-phase condition and allowed to equilibrate for a minimum of 15 minutes. This procedure was repeated to verify the reproducibility of the measured transition points. Further procedural details are available in our previous publications. At least two independent measurements were performed using standard uncertainties [Pressure (p): 0.02 MPa; Temperature (T): 0.12 K]. The resulting variations yielded standard uncertainties of u(p): 0.05 MPa and u(T): 0.2 K, while the standard uncertainty in mole fraction was u(x): 0.0008 [29-31].

3. Results and Discussion

The experimental data for the binary mixture of 3-pentyl acetoacetate and carbon dioxide was analyzed to characterize phase transitions, including the dew point (DP), critical point (CP), and bubble point (BP). The binary system of 3-pentyl acetoacetate + carbon dioxide was assessed and investigational isotherms were reported in (p, x) space. The investigational isotherms of 3-pentyl acetoacetate + carbon dioxide binary system in (p, x) space are reported in Fig. 3 and Table 2 for the (2.17 MPa $\leq p \leq$ 20.06 MPa) range and (313.2 K $\leq T \leq$ 393.2 K) range of pressure and temperature, respectively. Vapor – liquid equilibrium region was observed beneath each isotherm and single-phase region reported above every isotherm. Moreover, no three-phase region was obtained at any of five temperatures. As shown in Fig. 3 and Table 2, at a constant temperature of 313.2 K, the pressure decreased from 8.31 MPa to 2.17 MPa as the mole fraction of 3-pentyl acetoacetate increased from 0.0433 to 0.7950. Under these conditions, only the BP was observed within the investigated temperature, pressure, and composition ranges. At 333.2 K, both the DP and BP were observed at mole fractions of 0.0734 and 0.1014. With further increases in the mole fraction of 3-pentyl acetoacetate, only the BP was detected. Notably, an inverse relationship between pressure and component concentration was observed at constant temperature, where the pressure decreased with increasing 3-pentyl acetoacetate concentration.

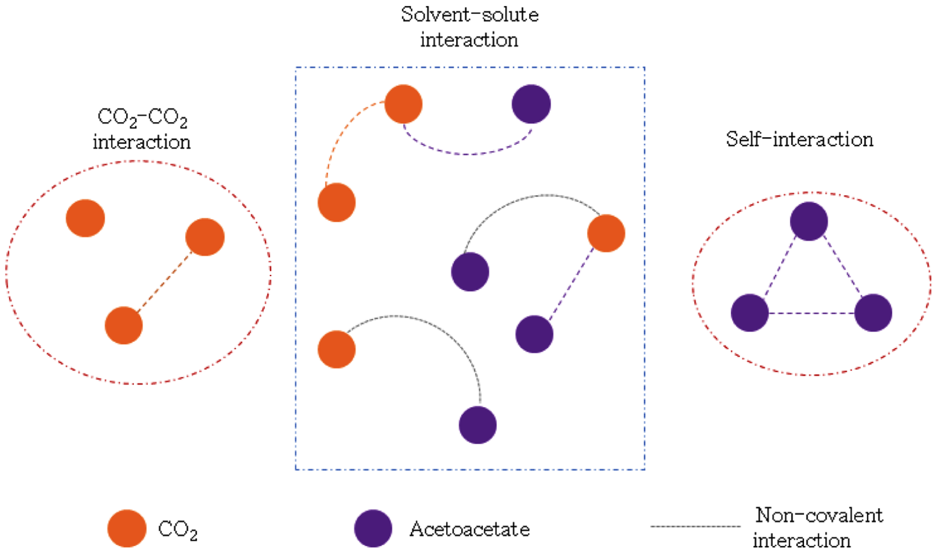

Fig. 3. Proposed mechanism for the 3-pentyl acetoacetate + CO_2 binary mixture system.

Table 2. Experimental data for the 3-pentyl acetoacetate + CO_2 system in this work. BP is bubble-point, CP is critical-point and DP is dew-point

3-Pentyl Acetoacetate Mole Fraction	p^a / MPa	Transition^b
T^a / K = 313.2		
0.0433	8.31	BP
0.0634	8.30	BP
0.0837	8.21	BP
0.0889	8.15	BP
0.1064	8.05	BP
0.1280	7.80	BP
0.1717	7.39	BP
0.2128	7.06	BP
0.2386	6.81	BP
0.2903	6.23	BP
0.3898	5.30	BP
0.5139	4.21	BP
0.5840	3.66	BP
0.7950	2.17	BP
T / K = 333.2		
0.0433	11.35	DP
0.0634	11.60	BP
0.0837	11.45	BP
0.0889	11.37	BP
0.1064	11.13	BP
0.1280	10.79	BP
0.1717	10.21	BP
0.2128	9.61	BP
0.2386	9.12	BP
0.2903	8.35	BP
0.3898	7.05	BP
0.5139	5.45	BP
0.5840	4.53	BP
0.7950	2.55	BP
T / K = 353.2		
0.0433	14.92	DP
0.0634	15.17	CP
0.0837	14.96	BP
0.0889	14.89	BP
0.1064	14.61	BP
0.1280	14.10	BP
0.1717	12.98	BP
0.2128	12.16	BP
0.2386	11.63	BP
0.2903	10.51	BP
0.3898	8.69	BP
0.5139	6.69	BP
0.5840	5.67	BP
0.7950	3.06	BP
T / K = 373.2		
0.0433	17.38	DP
0.0634	17.62	DP
0.0837	17.68	CP
0.0889	17.62	BP
0.1064	17.30	BP
0.1280	16.97	BP
0.1717	15.79	BP
0.2128	15.11	BP
0.2386	14.52	BP
0.2903	12.78	BP
0.3898	10.86	BP
0.5139	8.13	BP
0.5840	6.69	BP
0.7950	3.59	BP
T / K = 393.2		
0.0433	19.10	DP
0.0634	20.02	DP
0.0837	20.06	DP
0.0889	20.06	BP
0.1064	19.79	BP
0.1280	19.33	BP
0.1717	18.39	BP
0.2128	17.27	BP
0.2386	16.39	BP
0.2903	14.68	BP
0.3898	12.33	BP
0.5139	9.21	BP
0.5840	7.55	BP
0.7950	4.09	BP

[a] Standard uncertainties are $u(T)$ = 0.2 K and $u(p)$ = 0.05 MPa

[b] BP: Bubble-point, CP: Critical-point, DP: Dew-point

At 353.2 K, the phase behavior evolved from DP to CP and then to BP at mole fractions of 0.0433, 0.0634, and 0.0837, respectively. The corresponding pressures were measured as 14.92 MPa, 15.17 MPa, and 14.96 MPa, indicating slight variations with increasing composition.

Similarly, at 373.2 K, DP was identified at a mole fraction of 0.0433 with a pressure of 17.38 MPa, and at 0.0634 with 17.62 MPa. A slight increase in concentration to 0.0837 resulted in the appearance of the CP at 17.68 MPa. With further increases in the 3-pentyl acetoacetate concentration, the BP was observed, and a significantly lower pressure of 3.59 MPa was recorded at the highest mole fraction of 0.7950.

Finally, at 393.2 K, DP was observed in the mole fraction range of 0.0433 to 0.0837, whereas at a mole fraction of 0.0889, only the BP was detected. As the mole fraction of 3-pentyl acetoacetate increased, the pressure was found to decrease markedly across the investigated composition range. This phase behavior may be attributed to dominant self-interactions of the polar 3-pentyl acetoacetate molecules over solvent–solute interactions, resulting enhanced solubility. Similar phenomena have been reported in literature for different solvent–solute system [32-34]. Based on the Van Konynenburg and Scott classification, the phase behavior of the 3-pentyl acetoacetate + CO_2 solution aligns with Type-I region [35].

3-1. Proposed molecular interaction mechanism

Fig. 4 illustrates the proposed mechanism for the binary system of 3-pentyl acetoacetate and CO_2. In this system, the interactions between molecules were mainly driven by dipole–quadrupole interactions and hydrogen bonding. The 3-pentyl acetoacetate molecules, as polar esters, exhibited a considerable dipole moment due to their carbonyl groups, whereas CO_2, although overall non-polar, possessed a notable quadrupole moment [36]. At low concentrations of 3-pentyl acetoacetate,

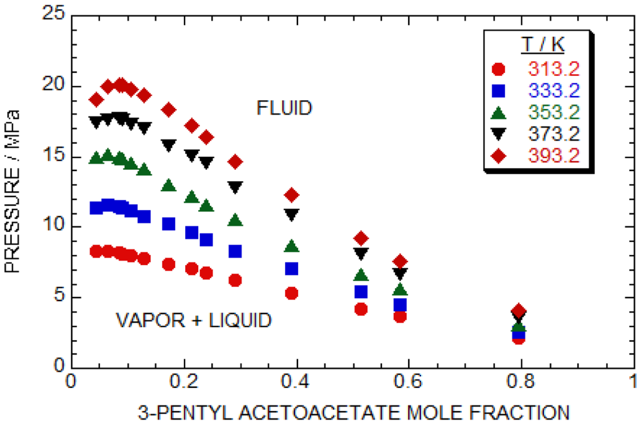

Fig. 4. Experimental isotherms (*P* vs *x*) of 3-pentyl acetoacetate + carbon dioxide system. Symbols denotes experimental data points at various temperature.

the interactions between solute molecules dominated over solute–solvent interactions, primarily because of intermolecular hydrogen bonding among the acetoacetate molecules. As the pressure raised, the density of CO_2 increased, enhancing its ability to solvate polar solutes by penetrating solute clusters and disrupting these self-associations, thereby improving miscibility. At very high pressures and temperatures, however, CO_2 density could decrease due to thermal expansion, and the kinetic energy of the molecules increased, leading to abnormal phase behavior (e.g., the appearance of DP and CP). This likely explained why complex molecular interactions occur at elevated temperatures, resulting in the observed phase behavior and solubility trends.

3-2. Thermodynamic models

Accurately describing the phase behavior of binary mixtures required correlating experimental data with the Peng–Robinson equation of state (PR EoS) using the van der Waals one-fluid mixing rule [2,37]. This methodology allowed the experimental findings to be interpreted within a thermodynamic framework and ensured alignment with theoretical predictions. The corresponding equations were presented below [13,37].

$$p = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+b(V-b)} \tag{1}$$

$$a(T) = 0.457235\frac{R^2T_c^2}{p_c}\alpha(T) \tag{2}$$

$$b(T_c) = 0.077796R\frac{T_c}{p_c} \tag{3}$$

$$\alpha(T) = [1+k(1-T_r^{0.5})]^2 \tag{4}$$

$$k = 0.37464 + 1.5422\omega - 0.26992\omega^2 \tag{5}$$

where, p_c stood for critical pressure (Pa), T_c was critical temperature (K), ω was acentric factor, α was polarizability(cm^3), R=8.314462 J/mol·K, V was molar volume (m^3/mol), *a* was attraction factor (Pa m^6/mol^2), *b* was the co-volume factor (m^3/mol).

$$a_{MR} = \sum_i\sum_i x_i x_j a_{ij} \tag{6}$$

$$b_{MR} = \sum_i\sum_i x_i x_j b_{ij} \tag{7}$$

$$a_{ij} = (a_{ii}a_{ij})^{1/2}(1-k_{ij}) \tag{8}$$

$$b_{ij} = \frac{1}{2}(b_{ii}+b_{ij})^{1/2}(1-\eta_{ij})$$

where, a_i and b_i were the PR-van der Waals one-fluid mixing rule EoS parameters of ith pure substances; k_{ij} denoted molecular energy, and η_{ij} denoted parameter for the i-j pair. The objective function (ObjF) and root mean squared deviation (RMSD%) was expressed as below [38].

$$ObjF = \sum_{i=1}^{N}\left(\frac{p_{Exp}-p_{Cal}}{p_{Exp}}\right) \tag{10}$$

$$RMSD\ \% = \sqrt{\frac{Obj\ F}{N}} \tag{11}$$

Here, *N* indicated the count of experimental data points, p_{Exp} and p_{Cal} indicated experimental and calculated pressure. The Marquardt method has been used to optimize the objective function [38]. The properties of the 3-pentyl acetoacetate was estimated employing group distribution method described by Joback and Lyderson [13]. Likewise, vapor pressure was predicted using Lee-Kesler method [13].

The pure component properties such as molecular weight, critical properties, boiling temperature, acentric factor of CO_2 and 3-pentyl acetoacetate are given in Table 3.

Fig. 5 presents a comparison between the experimental data and the simulated results for the bubble point of the binary system 3-pentyl acetoacetate + CO_2 at 353.2 K. The predicted interaction two-parameters (ITPs) for T = 353.2 K isotherm were (red solid line) k_{ij} = 0.005 and η_{ij} = -0.025 (point number used: 14). The results with ITPs set to zero (k_{ij} = 0.0 and η_{ij} = 0.0) are also illustrated in Fig. 5 by dashed blue line. The RMSD% calculated at 353.2 K for the 3-pentyl acetoacetate + CO_2 systems appeared at 3.37%. It can be clearly seen from the figures that isotherms predicted with zero ITPs were significantly deviating from investigational values. Hence, other

Table 3. The properties of pure component in carbon dioxide and 3-pentyl acetoacetate [13]

Compounds	M_w	Chemical Structure	T_b / K	T_c / K	p_c / MPa	ω
Carbon dioxide	44.01	O=C=O		304.2	7.38	0.225
3-Pentyl acetoacetate	172.22	$CH_3COCH_2COOC[CH_2CH_3]_2$	486.2^a	658.9	2.49	0.675

^{a}Sigma-Aldrich Co.

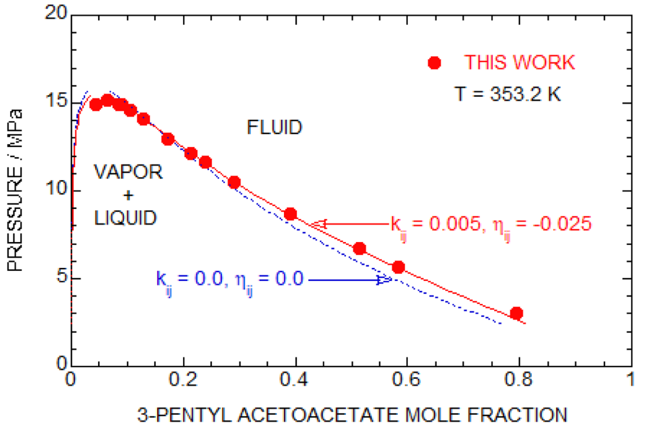

Fig. 5. Pressure vs mole fraction plot of 3-pentyl acetoacetate + carbon dioxide system with calculations obtained from PR EOS at 353.2 K. Blue broken and red solid line represent results with zero and non-zero interaction parameters (k_{ij} and η_{ij}) respectively.

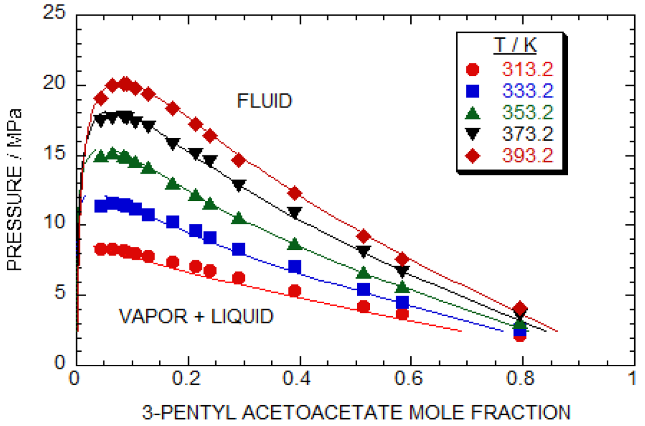

Fig. 6. Experimental and predicted isotherms of 3-pentyl acetoacetate + carbon dioxide (k_{ij} = 0.005, η_{ij} = -0.025) system at 353.2 K. Symbols denotes experimental data points at various temperature. Solid lines are predicted isotherms using PR EoS.

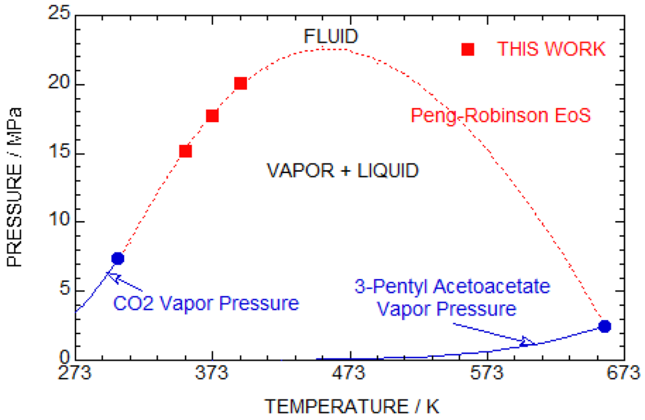

Fig. 7. Diagram in (*P* vs *T*) space for the 3-pentyl acetoacetate + carbon dioxide system. The critical-point of pure components (carbon dioxide or 3-pentyl acetoacetate) is represented by red closed circles. Red solid curves are vapor + liquid equilibrium curves. Squares denotes critical points of a mixture taken from experimental isotherms.

isotherms were calculated with non-zero ITPs. It was important to note that ITPs calculated for isotherms T = 353.2 K were used to calculate other isotherms.

Fig. 6 demonstrates the graphs of (p, x) in order to study the comparative analysis of the investigational data (symbols) of the 3-pentyl acetoacetate + CO_2 models with computational data (solid lines) achieved via PR equation applying optimum two-parameter (k_{ij} = 0.005 and η_{ij} = -0.025) at T = 353.2 K. As indicated in Fig. 6, these curves were evaluated utilizing adjusted data established at T = 353.2 K. The RMSD (%) at five T = (313.2–393.2 K) for the 3-pentyl acetoacetate + CO_2 system represented at (2.90%–8.14%) range, correspondingly (investigational counts: 70). The 3-pentyl acetoacetate + CO_2 mixtures over 313.2 K ≤ T ≤ 393.2 K, after applying the optimized interaction parameters determined at 353.2 K, was 4.92% at average error. Moreover, the lab-based investigational data and those from the simulated response exposed a good matching at all the five operated temperatures. In proportion to the simulated data, the mixture critical curve demonstrated a type-I model. It was important to note that the form of the correlation model and the range of adjustable parameters might vary depending on the thermodynamic framework, such as EoS, activity coefficient models, or empirical correlations. However, the phase behavior predicted by the PR EoS did not indicate the presence of three-phase regions under the evaluated conditions.

In Fig. 7 have compared the maximum mixture-critical lines of the investigational data with the predicted results from the P-R equation for the 3-pentyl acetoacetate + CO_2 solutions. The maximum mixture behavior for the 3-pentyl acetoacetate + CO_2 solutions exhibited the largest pressure in the (p, T) space. The colligation tendency and shapes of the critical curvesaligned well with the experimental observations from present study, confirming the reliability of the EoS (thermodynamic) model. The characteristic of the curve was identical to Type-I of Van Konynenburg and Scott [35]. According to the classification by Van Konynenburg and Scott, Type-I fluid behavior was defined by a continuous critical line that connected the critical points of both components. This behavior typically occurred in mixtures where the components have comparable vapor–liquid critical temperatures [39,40]. The predicted mixture-critical line showed type-I curve [35], which was in reasonable agreement with the investigational values at the one or two temperatures. In Fig. 7, the red solid lines mean saturated vapor pressure for pure CO_2 [13], and 3-pentyl acetoacetate [13]. The red solid curves mean the saturated vapor pressure of 3-pentyl acetoacetate [13] predicted by the Lee-Kesler method [13]. The red closed circles represented the critical-point for the pure CO_2 and 3-pentyl acetoacetate. The curve above part of the blue dashed curves was in 1-phase, while the curve below part was in 2-phase. The dashed curve represented the calculated results determined by the P-R equation, with k_{ij} = 0.005 and η_{ij} = -0.025 (for 3-pentyl acetoacetate). The blue closed squares measured in experiment represented the mixture-critical point obtained from the isotherms.

4. Conclusion

In this study, comprehensive vapor–liquid equilibrium (VLE) data were obtained for the binary system of 3-pentyl acetoacetate + CO_2 at five isothermal conditions within the range of 313.2 K ≤ T ≤ 393.2 K and pressures up to 20.06 MPa. The solubility of 3-pentyl acetoacetate was found to increase consistently with its mole fraction at constant temperature. Furthermore, its solubility also increased with rising temperature, with 3-pentyl acetoacetate exhibiting the highest solubility in CO_2. The critical mixture curves were observed to lie between the critical points of pure CO_2 and pure 3-pentyl acetoacetate, indicating Type-I phase behavior. The experimental bubble point data were successfully correlated using the Peng–Robinson (PR) equation of state combined with the van der Waals one-fluid mixing rule. The optimized binary interaction parameters were determined as k_{ij} = 0.005 and η_{ij} = -0.025 for 3-pentyl acetoacetate. The root mean square deviations (RMSD) were within acceptable limits, with a value of 4.95% for this system. This work represents the first study to provide extended high-pressure VLE data over a wide mole fraction range for this binary system. The results offer valuable thermodynamic insights and provide accurate modeling parameters that are essential for the design and optimization of separation processes involving supercritical CO_2 and 3-pentyl acetoacetate.

Conflict of Interest

The authors declare that they have no conflict of interest.

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