



High-pressure phase behaviour of the carbon dioxide + *n*-heptane system: a model system with experiments, modelling, and critical literature assessment

Sergiu Sima , Catinca Secuianu *

Department of Inorganic Chemistry, Physical Chemistry and Electrochemistry, Faculty of Chemical Engineering and Biotechnologies, National University of Science and Technology POLITEHNICA Bucharest, 1-7 Gh. Polizu Street, S1, 011061 Bucharest, Romania

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ABSTRACT

New isothermal vapour – liquid equilibrium data in the temperature range 313.15–383.15 K and vapour – liquid critical points are reported for the carbon dioxide + *n*-heptane system. All available experimental data for this mixture were also collected and critically reviewed, showing that previous modelling efforts reported in the literature were largely limited to reproducing the specific isothermal data measured in each study, while only two works addressed the vapour – liquid critical behaviour in the pressure–temperature projection.

The phase behaviour of the system was modelled using the Peng–Robinson (PR), Soave–Redlich–Kwong (SRK), and General Equation of State (GEOS), employing both constant binary interaction parameters and temperature-dependent k_{12} with constant l_{12} . The interaction parameters were transferred from the carbon dioxide + *n*-hexane system without further optimisation. The models reproduce the critical behaviour with reasonable accuracy, although deviations remain in phase compositions and upper critical endpoint predictions.

The combined experimental, literature, and modelling results provide a consistent description of the phase behaviour of the carbon dioxide + *n*-heptane system.

1. Introduction

Throughout the twentieth century, experimental and theoretical investigations of carbon dioxide + hydrocarbon (alkane) systems constituted a major focus of researchers all over the world, especially across Europe, the Americas, and Asia [1–13]. These studies laid the foundations of modern fluid phase equilibria, establishing reference data, experimental techniques, and thermodynamic models that continue to be widely used. Despite this long history, carbon dioxide + hydrocarbon mixtures have retained and even increased their relevance in the twenty-first century, as renewed scientific and industrial challenges have emerged [14–29].

Carbon dioxide + *n*-hydrocarbon systems are of sustained importance due to their role in energy-related processes, enhanced oil and gas recovery, subsurface engineering, carbon capture, utilisation, and storage (CCUS), separations, etc. [30–36]. At the same time, they constitute a well-established benchmark family for the validation of high-pressure experimental techniques and thermodynamic models. The systematic variation of molecular size along the *n*-alkane series allows trends in

phase behaviour to be explored in a controlled manner, making carbon dioxide + *n*-alkane systems particularly suitable for methodological assessment. Within this family, the carbon dioxide + *n*-heptane system has been repeatedly selected as a model system in the literature [37–43]. Owing to its intermediate molecular complexity and pronounced near-critical behaviour, it has been widely used to validate new experimental apparatuses, confirm measurement protocols, and test emerging thermodynamic frameworks. Consequently, high-quality data for carbon dioxide + *n*-heptane serve not only applied purposes but also play a critical role in establishing experimental reliability and model robustness. High-pressure vapour – liquid equilibrium (VLE) data for this system are therefore especially valuable.

In the present work, vapour – liquid measurements are reported along isotherms from 313.15 to 383.15 K, covering pressures up to 131 bar, together with the experimental determination of the vapour – liquid critical curve. Importantly, these results provide a direct and independent validation of the authors' previous high-pressure measurements, demonstrating the reproducibility and internal consistency of the experimental methodology across different systems and conditions.

* Corresponding author.

E-mail addresses: sergiu.sima@upb.ro (S. Sima), catinca.secuianu@upb.ro (C. Secuianu).

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From a modelling perspective, carbon dioxide + hydrocarbon mixtures have been addressed in the literature using a wide range of approaches [44–52]. Specifically for the carbon dioxide + *n*-heptane mixture, previous studies have reported experimental data without thermodynamic modelling [49,53–56], employed empirical correlations [54] or correlations based on molecular bond indices [57], applied classical equations of state such as SRK [37], PR [53,58], or extended BWR formulations [37], and one-fluid corresponding states models [59] or more advanced frameworks, including PPR78 [39,40,42,60], PR2SRK [39], SAFT-VR [41], and SAFT- γ Mie [40], have also been proposed, often involving increased complexity or system-specific parameterisation.

The present study adopts a deliberately simple yet physically grounded semi-predictive strategy. The carbon dioxide + *n*-heptane system is modelled using three cubic equations of state (EoSs): Peng–Robinson (PR) [61], Soave–Redlich–Kwong (SRK) [62], and the General Equation Of State (GEOS) [63–65] in conjunction with classical van der Waals mixing rules. Binary interaction parameters are not adjusted to the system under investigation but are transferred from the carbon dioxide + *n*-hexane system, thereby explicitly testing parameter transferability along the *n*-alkane homologous series. Also, temperature-dependent binary interaction parameters $k_{12}(T)$ are employed together with a constant volume correction parameter l_{12} . This approach enables a rigorous assessment of the capability of cubic equations of state to reproduce both vapour – liquid equilibria and critical behaviour at high pressures without resorting to extensive system-specific fitting.

Also, we critically review and discuss the available literature on the carbon dioxide + *n*-heptane system with respect to its phase equilibrium behaviour. Previously reported experimental data and modelling approaches are carefully examined, highlighting agreements, discrepancies, and methodological differences among the various studies. This critical comparison helps to clarify remaining discrepancies and to place the present results within the broader context of fluid phase equilibrium data for this widely used model system.

Beyond its technical objectives, this contribution is dedicated to the memory of Professor Maurizio Fermeglia (University of Trieste) whose scientific work profoundly influenced experimental thermodynamics, equation-of-state modelling and simulations, and energy-related applications. Professor Fermeglia's research combined rigorous measurements of thermophysical properties, such as density, viscosity, refractive index, excess volumes, and deviation functions for complex hydrocarbon mixtures [66], with a sustained interest in applied thermodynamics for energy systems [67]. In later years, his work increasingly addressed topics directly connected to energy transition and carbon capture, utilisation, and storage (CCS/CCUS) [68]. His contributions to the assessment and development of cubic equations of state, including studies dedicated to the legacy and continued relevance of the Soave–Redlich–Kwong (SRK) equation of state, reinforced the importance of physically sound and industrially applicable thermodynamic frameworks [69–72].

We gratefully acknowledge the lasting scientific influence of Professor Evelyne Neau (University of Aix-Marseille), whose collaborations and contributions to predictive thermodynamics, closely intersected with Professor Fermeglia's work [73] as well as Professor Karel Aim (The Czech Academy of Sciences), whose contributions to experimental measurements, thermodynamic modelling, and molecular simulations include an early professional association with Professor Fermeglia.

Their professional paths and scientific contributions reflect the strong personal and scholarly connections that have long characterised this community.

2. Experimental section

2.1. Materials

Carbon dioxide with a mass fraction purity of at least 0.99995 was supplied by Linde Gaz Romania (Bucharest, Romania), while *n*-heptane (Reagentplus®, mass fraction purity ≥ 0.990) was purchased from Sigma-Aldrich (see Table 1). The chemicals were used as received.

2.2. Apparatus and procedure

The experimental measurements were carried out using a high-pressure phase equilibrium apparatus identical to that employed in our earlier studies, which has been described in detail elsewhere [74–78]. Briefly, vapour – liquid equilibrium measurements were performed using an analytical technique, namely the *AnTVisVarCap* method developed by Dohrn and co-workers [3,4,14–17], which enables sampling and analysis of both coexisting phases.

The core of the apparatus is a variable-volume, high-pressure equilibrium cell fitted with two sapphire windows, allowing full visual observation of phase behaviour. The cell is coupled to an on-line sampling and analytical system. Phase sampling is achieved using two high-pressure electromechanical Rapid On-Line Sampler Injector (ROLSI™) valves (MINES ParisTech/CEP-TEP, Fontainebleau, France) [79], which connect the equilibrium cell to a gas chromatograph (GC) through heated capillary transfer lines. The injector expansion chambers are electrically heated to ensure instantaneous vaporisation of withdrawn liquid samples, while the transfer lines are maintained at elevated temperature using a linear heating resistor regulated by an Armines/CEP/TEP controller to prevent condensation.

Compositional analyses were performed using a Perichrom gas chromatograph (France) equipped with a thermal conductivity detector (TCD) and an HP-Plot/Q capillary column (30 m length, 0.530 mm internal diameter). Helium served as the carrier gas at a flow rate of 30 mL·min⁻¹.

Since the experimental procedure for vapour – liquid equilibrium measurements and critical curve determination follows that reported in our previous publications [76–78,80–83], only a concise summary is provided here. Prior to each experiment, the entire system, including the equilibrium cell, was flushed repeatedly with carbon dioxide and subsequently evacuated using a vacuum pump. Carbon dioxide was introduced into the equilibrium cell using a Teledyne ISCO 500D syringe pump, allowing precise control of the injected amount. The organic component was then introduced under vacuum conditions while applying vigorous stirring. Carbon dioxide was added incrementally using the syringe pump until the desired pressure was reached, after which the cell temperature was adjusted to the target value. The mixture was continuously stirred for several hours to facilitate equilibration. Once equilibrium was presumed to be established, stirring was stopped and the system was allowed to rest for approximately one hour to ensure complete phase separation. Samples of both liquid and vapour phases were subsequently withdrawn through the ROLSI valves and analysed by GC. For each experimental condition, at least six liquid-phase samples were analysed to evaluate repeatability. Owing to the very small volume of each sample, pressure variations during sampling were negligible. Calibration of the TCD response for carbon dioxide and *n*-heptane was performed by injecting known amounts of each

Table 1
Description of substances.

Substance	Chemical formula	CAS Registry Number	Manufacturer	Minimum mass fraction purity
Carbon dioxide	CO ₂	124-38-9	Linde Gaz Romania	0.99995
<i>n</i> -Heptane	C ₇ H ₁₆	142-82-5	Sigma-Aldrich	≥ 0.99

component using GC syringes. The detector response was correlated with the injected mole numbers using quadratic and third-degree polynomial fits for carbon dioxide and *n*-heptane, respectively, yielding correlation coefficients of 0.9999 and 0.9983.

Measurement uncertainties for all experimental variables and derived properties were evaluated according to the procedures described in our earlier works [84–86] and in Refs. [39,41,87]. Temperature was measured using a platinum resistance thermometer connected to a digital display and calibrated against a certified Digital Precision Thermometer (PT100 sensor) traceable to the Romanian Bureau of Legal Metrology. The combined standard uncertainty in temperature, dominated by the calibration uncertainty, was estimated to be ± 0.1 K. Pressure measurements were obtained using a pressure transducer connected to a digital multimeter and calibrated at 323.15 K with a precision hydraulic dead-weight tester (Model 580C, DH-Budenberg SA, Aubervilliers, France). The combined pressure uncertainty was estimated as ± 0.015 MPa over the range 0.5–20 MPa.

Critical points were determined using a visual observation technique, following procedures described previously [49,77,82]. The method starts from a homogeneous single-phase mixture of known composition at a selected temperature and pressure. System pressure is gradually adjusted by varying the cell volume until the appearance of a bubble or dew point (BP, DP) is detected. Upon observation of a bubble point, temperature is slowly increased until the corresponding dew point is reached. Pressure is then increased to restore homogeneity, after which the phase composition is sampled. Subsequently, pressure is gradually reduced until the first appearance of liquid droplets, followed by controlled decreases in temperature and volume to approach the boundary between homogeneous and heterogeneous regions. Cooling is continued until gas bubbles are observed. This sequence is repeated with incremental additions of carbon dioxide and successive cooling steps, enabling accurate determination of the vapour – liquid critical point.

3. Modelling

The phase behaviour of the carbon dioxide (1) + *n*-heptane (2) binary mixture was modelled in a semi-predictive manner using the SRK [62], PR [61], and GEOS [63–65] cubic equations of state combined with van der Waals mixing rules (two-parameter conventional mixing rules, 2PCMR), with binary interaction parameters tuned for the carbon dioxide + *n*-hexane system [78]. Although these models are well known, the relevant information is provided here for the reader's convenience.

The GEOS equation of state is defined by eq. (1), in conjunction with the classical van der Waals mixing rules (eqs. (2–5)) and the combining rules for a_{ij} , b_{ij} , and c_{ij} (eqs. (6–8)), where a “+” sign is used if $c_i, c_j > 0$ and a “–” sign if $c_i, c_j < 0$. The c parameter for pure compounds typically has negative values.

$$P = \frac{RT}{V-b} - \frac{a(T)}{(V-d)^2 + c} \quad (1)$$

$$a = \sum_i \sum_j X_i X_j a_{ij} \quad (2)$$

$$b = \sum_i \sum_j X_i X_j b_{ij} \quad (3)$$

$$c = \sum_i \sum_j X_i X_j c_{ij} \quad (4)$$

$$d = \sum_i X_i d_i \quad (5)$$

$$a_{ij} = (a_i a_j)^{\frac{1}{2}} (1 - k_{ij}) \quad (6)$$

$$b_{ij} = \frac{b_i + b_j}{2} (1 - l_{ij}) \quad (7)$$

$$c_{ij} = \pm (c_i c_j)^{\frac{1}{2}} \quad (8)$$

The parameters a , b , c , and d for a pure component are defined as follows:

$$a(T) = \frac{R^2 T_c^2}{P_c} \beta(T_r) \Omega_a \quad (9)$$

$$b = \frac{RT_c}{P_c} \Omega_b \quad (10)$$

$$c = \frac{R^2 T_c^2}{P_c^2} \Omega_c \quad (11)$$

$$d = \frac{RT_c}{P_c} \Omega_d \quad (12)$$

Four critical conditions are imposed, using α_c as the Riedel criterion (eqs. (13–16)) at $T_r = 1$ and $V_r = 1$.

$$P_r = 1 \quad (13)$$

$$\left(\frac{\partial P_r}{\partial V_r} \right)_{T_r} = 0 \quad (14)$$

$$\left(\frac{\partial^2 P_r}{\partial V_r^2} \right)_{T_r} = 0 \quad (15)$$

$$\alpha_c = \left(\frac{\partial P_r}{\partial T_r} \right)_{V_r} \quad (16)$$

From these conditions, the equations for the parameters Ω_a , Ω_b , Ω_c , and Ω_d are derived:

$$\Omega_a = (1 - B)^3 \quad (17)$$

$$\Omega_b = Z_c - B \quad (18)$$

$$\Omega_c = (1 - B)^2 (B - 0.25) \quad (19)$$

$$\Omega_d = Z_c - \frac{(1 - B)}{2} \quad (20)$$

$$B = \frac{1 + m}{\alpha_c + m} \quad (21)$$

where Z_c is the critical compressibility factor and P_r , T_r , V_r are the reduced variables.

The function describing the temperature dependence is given by:

$$\beta(T_r) = T_r^{-m} \quad (22)$$

The m and α_c parameters of the GEOS equation of state were determined by constraining the equation of state to reproduce the experimental vapour pressures and liquid volumes along the saturation curve, from the triple point to the critical point [48].

The SRK equation of state, with the constants a and b , is formulated as follows:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)} \quad (23)$$

$$a = 0.42748 \frac{R^2 T_c^2}{P_c} \alpha(T) \quad (24)$$

$$b = 0.08664 \frac{RT_c}{P_c} \quad (25)$$

$$\alpha(T_R, \omega) = [1 + m_{\text{SRK}}(1 - T_R^{0.5})]^2 \quad (26)$$

$$m_{\text{SRK}} = 0.480 - 1.574\omega - 0.176\omega^2 \quad (27)$$

The Peng–Robinson equation of state with the two constants, a and b , is expressed as:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b) + b(V-b)} \quad (28)$$

$$a = 0.45724 \frac{R^2 T_c^2}{P_c} \alpha(T) \quad (29)$$

$$b = 0.077796 \frac{RT_c}{P_c} \quad (30)$$

$$\alpha(T_R, \omega) = [1 + m_{\text{PR}}(1 - T_R^{0.5})]^2 \quad (31)$$

$$m_{\text{PR}} = 0.37464 - 1.54226\omega - 0.26992\omega^2 \quad (32)$$

The two-parameter conventional mixing rules (2PCMR) are given by the following expressions, where a_{ij} and b_{ij} are defined in eqs. (6) and (7):

$$a = \sum_i \sum_j X_i X_j a_{ij} \quad (33)$$

$$b = \sum_i \sum_j X_i X_j b_{ij} \quad (34)$$

4. Results and discussion

4.1. Experimental results

The vapour – liquid critical curve determined in this study is reported in Table 2, while the eight vapour – liquid isotherms measured between 313.15 K and 383.15 K are presented in Table 3 together with their associated standard uncertainties. Temperatures are reported to two decimal places (including the 0.15 K from converting °C to K), and mole fractions are given to four decimal places, which is customary and consistent with the experimental uncertainties ($u(T) = 0.1$ K, $u(X_1) = 0.001$, $u(Y_1) = 0.005$); this ensures that variations near the critical point are properly represented and allows meaningful comparison with modelled VLE and critical-point behaviour. For clarity and easier interpretation, the isothermal data are also illustrated in Fig. 1.

The new data are compared with our previous measurements for the carbon dioxide + *n*-hexane (n-C6) [78] and carbon dioxide + 2,4-dimethylpentane (2,4-DMP) [81] systems in Figs. 2 and 3, respectively, at temperatures corresponding to those investigated in the earlier studies. For improved clarity and visualisation, the temperatures were divided

Table 2
VLE critical curve for the CO₂ (1) + *n*-heptane (2) binary system.

<i>T</i> /K	<i>P</i> /bar	<i>X</i> ₁	<i>T</i> /K	<i>P</i> /bar	<i>X</i> ₁
304.21 ^a	73.83	1.0000	343.15	108.80	0.9196
313.15	81.70	0.9761	344.95	109.70	0.9171
318.85	86.20	0.9652	346.35	110.50	0.9142
323.15	89.10	0.9575	353.15	115.40	0.9045
328.65	94.60	0.9456	356.05	117.10	0.8992
331.35	97.20	0.9407	360.75	120.10	0.8903
333.05	99.30	0.9376	363.15	122.60	0.8846
333.15	99.60	0.9371	367.55	124.70	0.8762
337.15	102.90	0.9309	373.15	127.50	0.8667
338.95	104.40	0.9286	383.15	130.80	0.8485
340.85	106.50	0.9242	540.20 ^a	27.40	0.0000
342.55	108.30	0.9219			

Standard uncertainties: $u(T) = 0.1$ K, $u(P) = 0.1$ bar, $u(X_1) = 0.001$;

^a DIPPR [88] values

Table 3

VLE for CO₂ (1) + *n*-heptane (2) at various temperatures.

<i>P</i> /bar	<i>X</i> ₁	<i>Y</i> ₁	<i>P</i> /bar	<i>X</i> ₁	<i>Y</i> ₁
<i>T</i> /K = 313.15 ± 0.1					
5.7	0.0809	0.9754	71.0	0.8254	0.9940
13.9	0.1682	0.9883	75.8	0.9108	0.9918
22.6	0.2575	0.9914	77.5	0.9506	0.9912
31.5	0.3499	0.9935	79.4	0.9599	0.9885
42.8	0.4754	0.9949	81.1	0.9795	0.9813
51.2	0.5605	0.9955	81.7	0.9761	0.9761
63.4	0.7032	0.9950			
<i>T</i> /K = 323.15 ± 0.1					
12.5	0.1392	0.9791	70.3	0.7094	0.9914
20.1	0.2115	0.9854	74.3	0.7608	0.9897
30.4	0.3076	0.9885	77.5	0.7956	0.9875
40.3	0.4054	0.9907	81.4	0.8459	0.9835
50.6	0.5013	0.9915	85.1	0.8895	0.9713
60.3	0.6043	0.9918	89.1	0.9575	0.9575
<i>T</i> /K = 333.15 ± 0.1					
10.3	0.1061	0.9697	70.2	0.6265	0.9886
20.4	0.1971	0.9793	80.7	0.7286	0.9842
30.5	0.2819	0.9839	90.6	0.8256	0.9735
40.5	0.3685	0.9861	94.7	0.8727	0.9645
50.4	0.4534	0.9878	99.6	0.9371	0.9371
60.5	0.5379	0.989			
<i>T</i> /K = 343.15 ± 0.1					
12.7	0.1237	0.9636	70.5	0.5693	0.9852
20.3	0.1803	0.9725	80.3	0.6464	0.9839
30.5	0.2629	0.9781	90.5	0.7306	0.9770
40.6	0.3402	0.9815	100.6	0.8080	0.9617
50.7	0.4199	0.9838	108.2	0.8866	0.9411
60.2	0.4913	0.9851	108.8	0.9196	0.9196
<i>T</i> /K = 353.15 ± 0.1					
12.8	0.1154	0.9515	70.2	0.5234	0.9808
22.3	0.1871	0.9668	80.5	0.5891	0.9792
32.1	0.2555	0.9728	90.7	0.6579	0.9745
40.5	0.3169	0.9766	100.4	0.7218	0.9650
50.3	0.3833	0.9792	110.7	0.8128	0.9482
60.5	0.4536	0.9809	115.4	0.9045	0.9045
<i>T</i> /K = 363.15 ± 0.1					
20.4	0.1555	0.9523	80.2	0.5524	0.9731
30.1	0.2256	0.9642	90.3	0.6136	0.9684
40.3	0.2916	0.9703	100.5	0.6783	0.9565
50.4	0.3603	0.9736	110.7	0.7454	0.9426
60.3	0.4272	0.9758	121.0	0.8502	0.9101
70.4	0.4891	0.9757	122.6	0.8846	0.8846
<i>T</i> /K = 373.15 ± 0.1					
11.2	0.0739	0.9256	80.3	0.5127	0.9654
20.4	0.1347	0.9425	90.5	0.5691	0.9559
30.2	0.1996	0.9538	100.1	0.6237	0.9442
40.2	0.2663	0.9634	110.2	0.6864	0.9324
50.5	0.3317	0.9675	120.4	0.7586	0.9054
60.4	0.3943	0.9698	123.8	0.7936	0.8902
70.3	0.4545	0.9692	127.5	0.8667	0.8667
<i>T</i> /K = 383.15 ± 0.1					
10.4	0.0505	0.9126	80.8	0.4744	0.9579
20.1	0.1174	0.9325	89.7	0.5229	0.9491
30.5	0.1809	0.9444	100.1	0.5823	0.9352
39.8	0.2407	0.9543	109.3	0.6386	0.9212
51.3	0.3092	0.9619	119.5	0.7086	0.8945
61.0	0.3624	0.9633	126.8	0.7690	0.8699
72.1	0.4274	0.9622	130.8	0.8485	0.8485

Standard uncertainties: $u(T) = 0.1$ K, $u(p) = 0.1$ bar, $u(X_1) = 0.001$, $u(Y_1) = 0.005$

into two subfigures. In Fig. 2a, the odd temperatures (313.15, 333.15, 353.15, and 373.15 K) are presented, comparing the results for the carbon dioxide + *n*-heptane and carbon dioxide + *n*-hexane systems. In Fig. 2b, the even temperatures (323.15, 343.15, 363.15, and 383.15 K) are shown for the same systems. Similarly, Fig. 3a compares the pressure–composition data for the CO₂ + *n*-heptane, CO₂ + *n*-hexane, and CO₂ + 2,4-dimethylpentane systems at 323.15 and 363.15 K, while Fig. 3b presents the corresponding comparisons at 343.15 and 383.15 K. In these systems, the organic components represent a lower homologue of the *n*-alkane series and a branched alkane isomer, respectively.

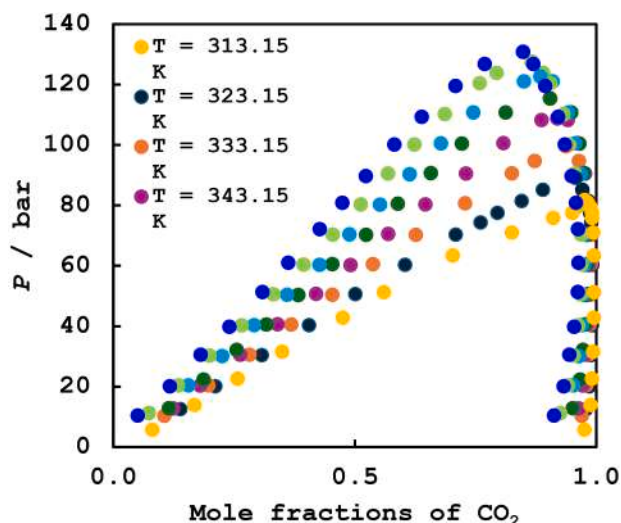


Fig. 1. VLE data measured at eight temperatures for the carbon dioxide (1) + *n*-heptane (2) binary system.

Consistent with previous reports [42,45,47,78], no clear systematic trend can be identified when comparing the solubilities of two consecutive *n*-alkanes in carbon dioxide at the same temperatures; nevertheless, *n*-heptane tends to exhibit a higher solubility in carbon dioxide than *n*-hexane over the investigated temperature range (Fig. 2). As previously observed [80], the branched alkane exhibits a significantly lower solubility than both *n*-heptane and *n*-hexane in carbon dioxide over the same temperature range (Fig. 3). Furthermore, the new isothermal data are compared with all available literature data under comparable conditions in Figs. 1S–8S (Supplementary Information). It should be noted that the vapour – phase compositions are not reported for all previously published data. Overall, the new data agree well with most literature isotherms within experimental uncertainty, with a few exceptions discussed further. Fig. 1S compares the bubble points reported by Lay [58] with the pressure–composition data of Liu et al. [57] and those obtained in the present work. It can be seen that the liquid–phase compositions reported in the present study agree very well with those of Lay [58], whereas the data of Liu et al. [57] indicate higher carbon dioxide solubility than observed here. Their measurements also suggest that the critical point at this temperature is located at a higher pressure. The pressure–liquid phase composition data measured at the next temperature investigated in this study, 323.15 K (Fig. 2S), also show very good agreement with most other studies conducted at the same or a closely similar temperature. In particular, the present results are consistent with those of Mutelet et al. [60], Sanchez-Vicente et al. [40], and most of the data reported by He et al. [89], with the exception of a single point at higher pressure of the latter. At this temperature as well, the data of Liu et al. [57] indicate higher carbon dioxide solubility than those reported by the other authors and in the present study. With respect to vapour–phase compositions, the present data show compositions richer in carbon dioxide than those reported by Liu et al. [57] and by He et al. [89]. Sanchez-Vicente et al. [40] reported dew points at higher pressures, with which the present data tend to agree. Fig. 3S compares the new data obtained in this study at 333.15 K with those reported by Mutelet et al. [60] and by Liu et al. [57]. As observed at previous temperature, the present data show excellent agreement with those of Mutelet et al. [60] and lower carbon dioxide solubilities than those reported by Liu et al. [57]. The 343.15 K isotherm (Fig. 4S) was used as a validation case in several early studies, as discussed in the next section. Consequently, four research groups reported bubble points (BPs) or pressure–liquid–vapour phase compositions at this temperature. The present liquid–phase data show very good agreement with those reported by Nagahama et al. [53], Sako et al. [38], and Mutelet

et al. [60]. As observed at lower temperatures, the data of Liu et al. [57] indicate higher CO₂ solubility and a higher critical point. With respect to vapour–phase compositions, the present results agree with those of Nagahama et al. [53] and with most of the data reported by Sako et al. [38]. Fig. 5S compares the present data with measurements at 353.15 K or nearby temperatures reported by Robinson and Kalra [90], Kalra et al. [54], Mutelet et al. [60], and Al Ghafri et al. [41]. The agreement is very good for both phases, even though the data of Robinson's group [90,54] were measured at slightly lower temperatures. It should be noted that the data from Robinson's group overlap, and the “×” and “+” symbols coincide, creating the visual impression of a star. Fig. 6S compares the bubble points reported by Mutelet et al. [60] with the present VLE data at 363.15 K, showing very good agreement. Similarly, Fig. 7S compares the data of this study at 373.15 K with previous bubble points reported by Mutelet et al. [60] and by Sanchez-Vicente et al. [40] as well as with the dew points Sanchez-Vicente et al. [40]; the agreement is good within experimental uncertainty. Finally, the VLE data at 383.15 K (Fig. 8S) from the present study are compared with the bubble points reported by Mutelet et al. [60], showing good agreement except for a couple of points.

Fig. 4 shows the *P*–*T* projection of the experimental critical line measured in this work together with all available literature data. Overall, within the temperature range investigated (313.15–383.15 K) here, the agreement is good, with only a few data points showing deviations [91].

4.2. Literature comparison and analysis

The entire literature for the carbon dioxide + *n*-heptane system was reviewed, and all available data were collected. Searches were conducted in databases including NIST [92], DETHERM [90], ISI Web of Knowledge [93], and Scopus [94], as well as in high-pressure review articles [1,3,4,14–17]. Although fewer studies have been published for this system compared with other carbon dioxide + *n*-alkane systems, the available vapour – liquid equilibrium data nevertheless span a wide temperature range, from 238 K to 502 K. However, for many isotherms only liquid–phase compositions with corresponding pressures are reported [40,58–60,95], and when vapour–phase compositions are included, they are often measured at pressures different from those of the liquid phase [38,39,53,90]. In this context, the new experimental results presented here complement the existing datasets, enabling a more comprehensive comparison and assessment of solubility behaviour under comparable conditions.

Thus, in the twentieth century, as already mentioned, carbon dioxide + alkane systems attracted significant experimental attention. However, the present discussion is limited to the phase behaviour of the carbon dioxide + *n*-heptane mixture. Chronologically, the earliest work identified is that of Francis [96], who reported that the carbon dioxide + *n*-heptane system exhibits a stable miscibility gap with an upper critical solution temperature of 222.15 K. This was followed by the study of Shenderei and Ivanovskii [95], published in 1964 in a Russian journal, which reported a pressure–liquid composition isotherm at a low temperature of 238 K. Subsequently, Schneider [97] reported, to the best of our knowledge, the first high-pressure liquid–liquid critical curve for this system in 1966, at pressures exceeding 1000 bar.

In 1971, Im and Kurata [55] investigated the miscibility gap of this system and identified the upper critical solution point (UCSP), the compositions of the coexisting liquid phases along the three-phase equilibrium curve, the quadruple solid–liquid–liquid–vapour point (Q-point), as well as another quadruple (eutectic) point at 181.75 K located at the lower end of the solid–liquid locus. The following year, Hayduk et al. (1972) [98] reported the solubility of carbon dioxide in *n*-heptane at (283.15, 298.15, and 303.15) K, albeit only at atmospheric pressure. In 1974, Kurata published a report for the Gas Processors Association (GPA Research Report RR-10, 26-71), entitled “Solubility of Solid Carbon Dioxide in Pure Light Hydrocarbons and Mixtures of Light Hydrocarbons”, containing low-temperature liquid–liquid equilibrium

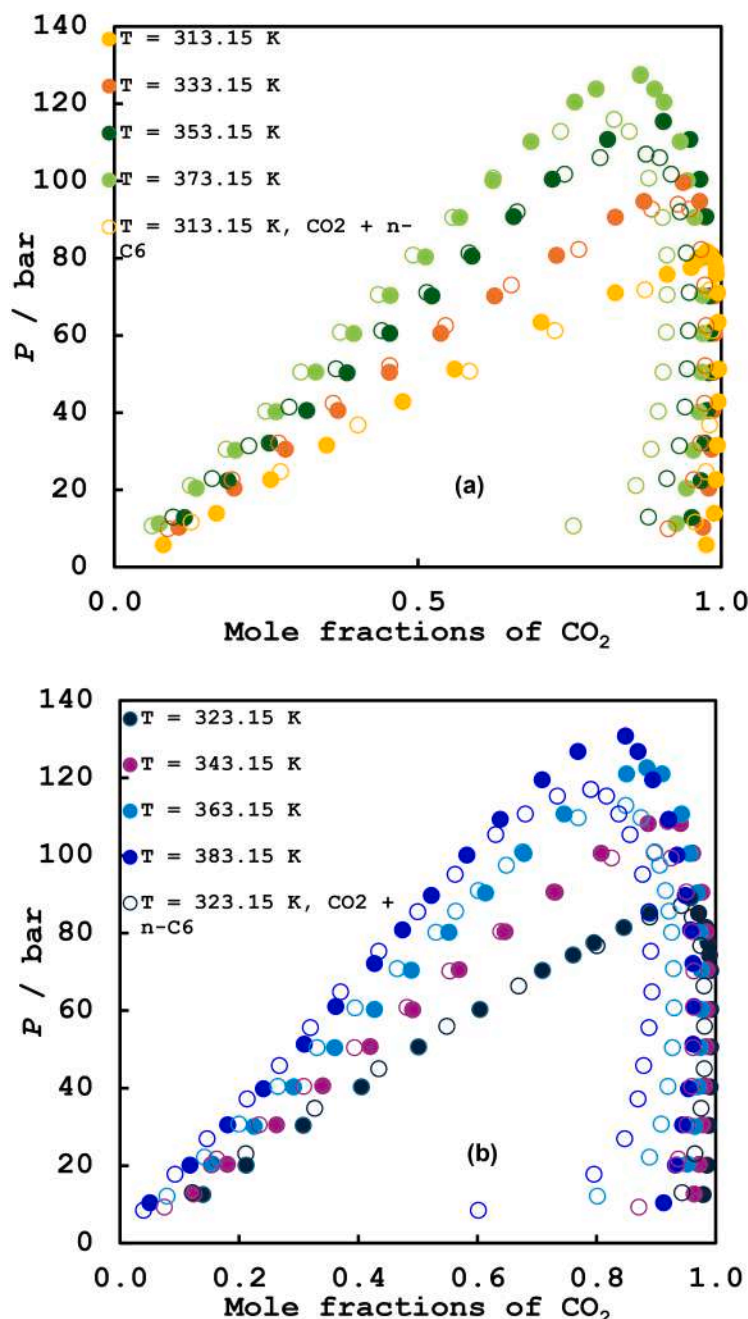


Fig. 2. Comparison of pressure-composition data for CO₂ + *n*-heptane (full circles) and CO₂ + *n*-hexane (open circles) [78] binary systems at the same temperatures: (a) (313.15, 333.15, 353.15, and 373.15) K; (b) (323.15, 343.15, 363.15, and 383.15) K.

data (accessible via the DETHERM database [90]). Two years later, Robinson and Kalra (1976) presented isothermal vapour – liquid equilibrium data at four temperatures ranging from 310 to 394 K (data accessed via the DETHERM database) in another GPA Research Report (RR-18, Project 745, Gas Processors Association). In 1977, King and Al-Najjar [99] reported the solubility of carbon dioxide in *n*-heptane at (293.15, 298.15, and 303.15) K at atmospheric pressure. Subsequently, Kalra et al. (1978) [54] published four VLE isotherms at the same temperatures as in their earlier work (GPA Research Report RR-18), but with both phase compositions reported at identical pressures.

In 1984, Nagahama et al. [53] used the carbon dioxide + *n*-heptane system to validate a newly developed experimental apparatus, reporting one isotherm at 343.1 K with compositions for both phases. In a 1985 paper, Fall and Luks [100] summarised the endpoint temperatures of liquid – liquid – vapour immiscibility loci for various binary mixtures of

carbon dioxide and *n*-paraffins, citing the measurements of Im and Kurata [55]. Another Japanese group (Inomata et al.) published two further papers in 1986: one reporting three VLE isotherms at 394, 468.4, and 502 K [101], and another using the 394 K isotherm, presented graphically, to validate their new apparatus [37].

In 1992, Gurdial et al. [102] reported the first vapour – liquid equilibrium critical points for this system over the temperature range of 305–323 K. Two years later, He et al. (1994) [89] published two isotherms (310.65 and 323.15 K) in a Chinese journal; these data were accessed via the DETHERM database [90]. In 1995, Sako et al. [38] employed the carbon dioxide + *n*-heptane system to validate their experimental procedure, presenting one isotherm at 343 K graphically (digitised by and available through the DETHERM database). In 1997, Chester and Haynes [56] cited Ziegler's PhD thesis (1996) and reproduced his pressure–temperature vapour – liquid critical data in their

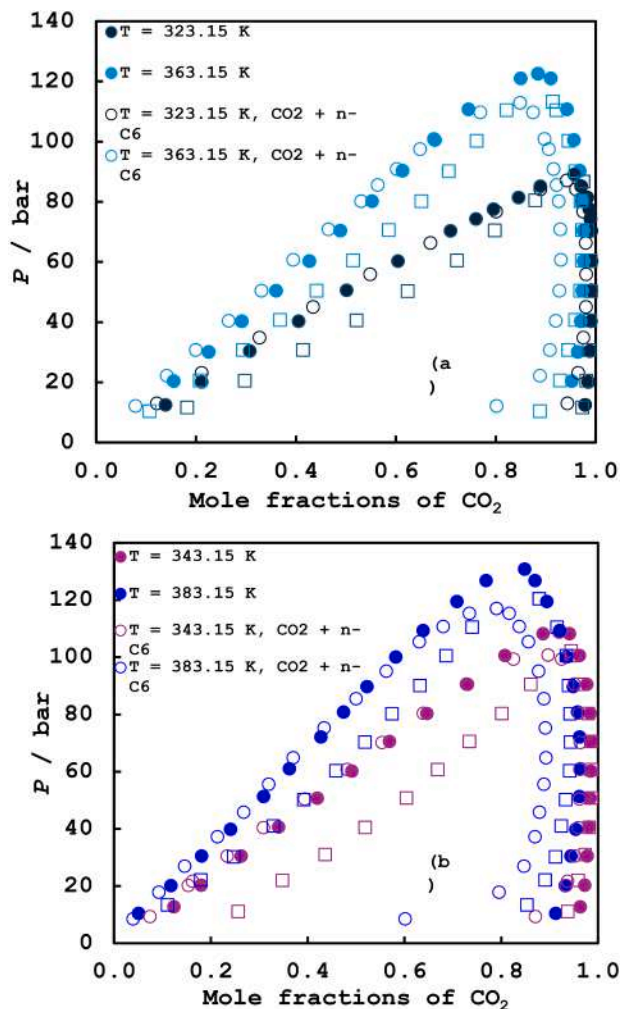


Fig. 3. Comparison of pressure-composition data for CO₂ + *n*-heptane (full circles) CO₂ + *n*-hexane (n-C6, open circles) [78], and CO₂ + 2,4-dimethylpentane (2,4-DMP, open squares) binary systems at the same temperatures: (a) (323.15 and 363.15) K; (b) (343.15 and 383.15) K.

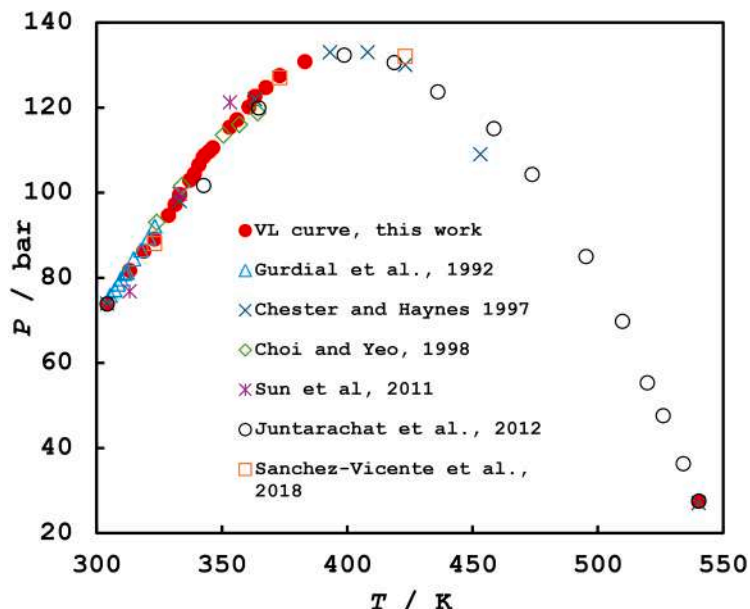


Fig. 4. *P*-*T* fluid phase diagram of the carbon dioxide (1) + *n*-heptane (2) system.

paper. One year later, Choi and Yeo (1998) [49] reported bubble points (BP), dew points (DP), and critical points (CPs) along five isopleths.

In 2001, Fenghour et al. [59] published density measurements and also reported one bubble point at each of three temperatures (approximately 301, 321, and 363 K). A valuable study covering a very wide temperature range (310.65 K to 413.15 K) and presenting bubble points was published by Mutelet et al. [60] in 2005. In 2007, Ke et al. [43] used a shear-mode piezoelectric sensor to monitor the high-pressure phase behaviour of asymmetric binary systems. The application of this sensor was demonstrated using the carbon dioxide + *n*-heptane system, with graphical data reported at fourteen temperatures between 300.31 K and 338.45 K for a fixed composition, from which the mixture critical point was identified at 322.2 K and 89.7 bar.

Five years later, Lay (2010) [58] reported bubble points along five isotherms between 293.15 and 313.15 K and summarised the pressure, temperature, and composition ranges from part of the available literature. In 2011, Sun et al. [91] estimated the critical points of this system at four temperatures. In 2012, Juntarachat et al. [42] validated a newly

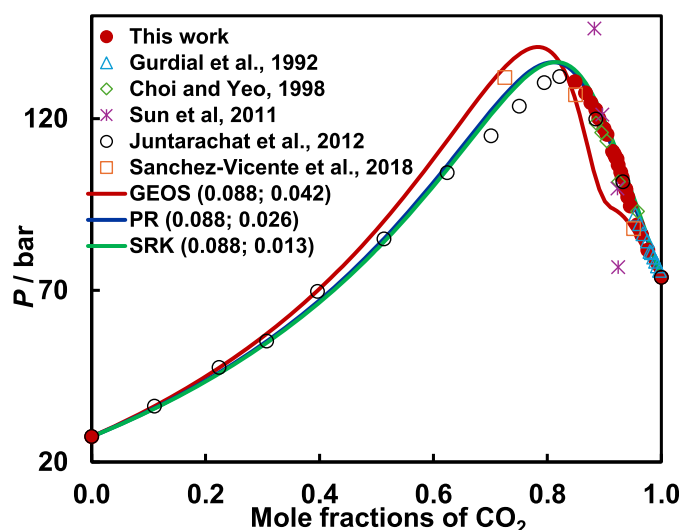


Fig. 5. *P*-*X* projection of the LV critical curve of the carbon dioxide (1) + *n*-heptane (2) system.

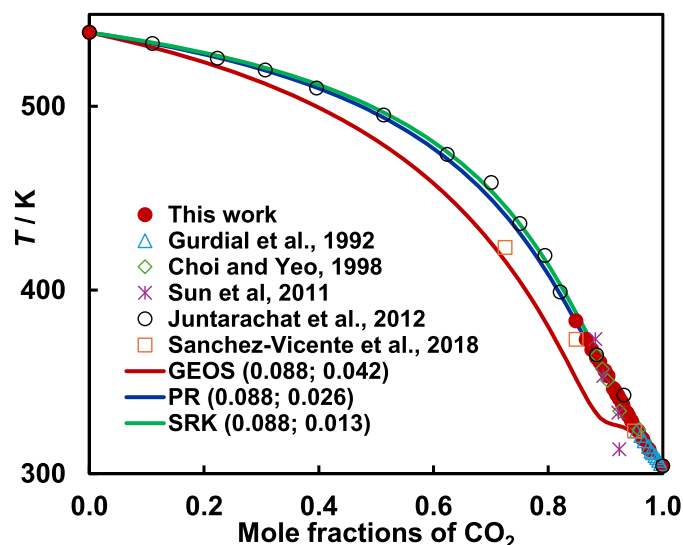


Fig. 6. T - X projection of the LV critical curve of the carbon dioxide (1) + n -heptane (2) system.

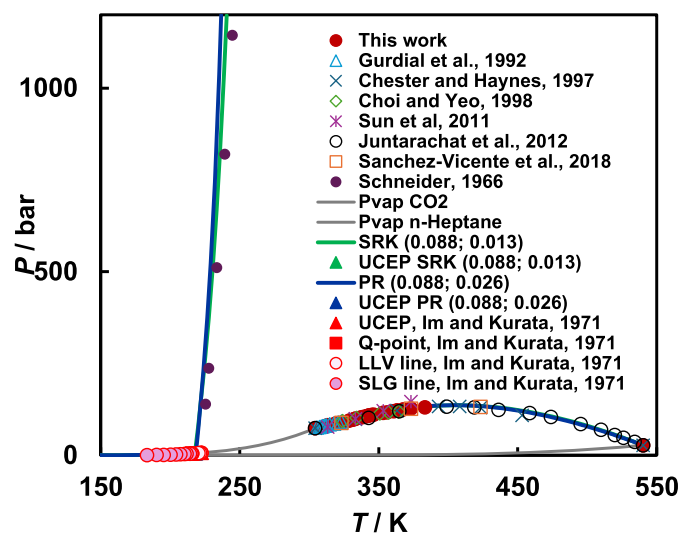


Fig. 7. P - T projection of the critical loci for the system carbon dioxide + n -heptane.

developed apparatus by measuring vapour – liquid equilibrium critical points over the entire composition range for this system and another two carbon dioxide + n -alkanes containing systems. Three subsequent studies from one of the most known research groups in the field were published in 2014, 2015, and 2018 [39–41]. In the first of these, carbon dioxide + n -heptane was used as a model system, with bubble and dew points measured at different pressures at 394 K [39]. The second study presented a ternary system containing n -heptane, carbon dioxide, and water, including two binary isotherms for the carbon dioxide + n -heptane, and a mini-review of previously published data [41]. The third study was a comprehensive investigation dedicated to this system, recognised as a model system, reporting or estimating bubble points, dew points, and corresponding critical points, as well as densities and derived thermophysical properties [40].

Finally, the most recent study identified for this system was published in 2022, in which Liu et al. [57] reported four isotherms between 313.15 K and 343.15 K, with both phase compositions measured.

The identified vapour – liquid equilibrium literature is summarised in Table 4, organised by increasing temperature and including, where

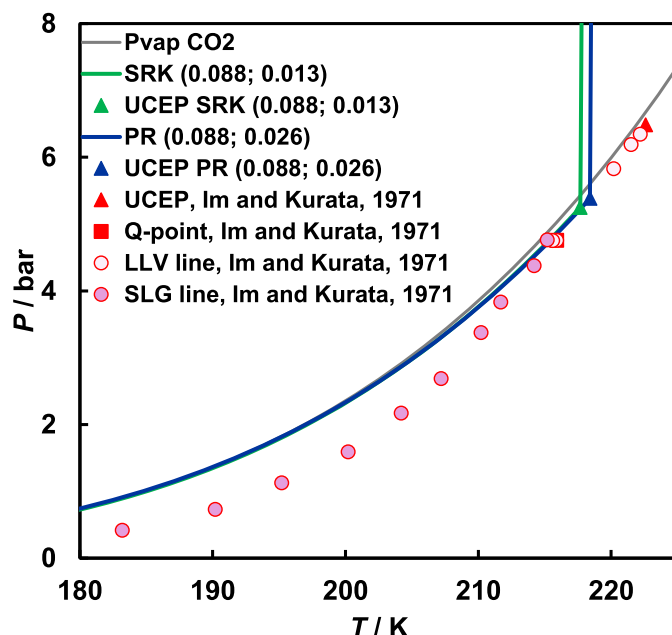


Fig. 8. Detail of the liquid – liquid – vapour (LLV) equilibrium curve in the P - T projection of the phase diagram.

available, the type of data measured and other relevant details. Some datasets were accessed directly through the DETHERM database, as indicated. Except for studies retrieved from DETHERM and the work of Sako et al. [38], where the n -heptane purity was not disclosed, all remaining studies employed heptane of high purity (at least 99%), without any additional purification being performed. It should be noted that most authors found reasonable agreement when comparing their data with previous studies, despite not identifying the full extent of the earlier literature. Certain temperatures, namely 310, 323, 343, 353, and 394 K, received greater attention over the years, as shown in Table 4. It can also be noted that most of the available data in the literature were obtained using synthetic methods (Table 4). Literature data measured at temperatures different from those investigated in the present work are also shown and compared in Figs. 9S–16S. In Fig. 9S, although the figure is relatively crowded, data measured between 238.15 and 313 K are compared. It can be seen that most datasets are consistent with one another, except for the data reported by Liu et al. [57] at 313.15 K, which exhibit a different trend. To facilitate interpretation of the data within this temperature range, the comparisons were divided into three intervals: 238–303 K (Fig. 10S), 308–313 K (Fig. 11S), and 310 K (Fig. 12S). The latter temperature was selected because it has been widely used by several authors to compare and validate their data, experimental apparatuses, and procedures. This separation of temperature intervals further confirms that the literature data are generally in good agreement, particularly for the liquid-phase compositions, with the exception of the data reported by Liu et al. [57], as noted above. For the vapour-phase compositions, only the data reported by He and et [89]. underestimate the carbon dioxide solubilities, whereas the remaining datasets show reasonable agreement. As previously noted, some data points overlap in these figures, creating the visual impression of symbols that are different from those shown in the legend. The temperature of 393.15 K (and approximately ± 1.2 K) was used as a model temperature, and the available data were compared in Fig. 13S. The agreement for both phases, liquid and vapour, among different groups is remarkable, considering the difficulties of performing measurements at such high temperatures. In Fig. 14S, the remaining available temperatures, ranging from 403.15 K to 502 K, are compared. For better visualisation, this range is further divided into two intervals: 403–448 K (Fig. 15S) and 468.4–502 K (Fig. 16S). Overall, the data are consistent, although some

Table 4Literature VLE phase behaviour for CO₂ (1) + *n*-heptane (2) binary system.

Vapour-Liquid Equilibrium Data					
<i>T</i> /K	<i>p</i> _{range} /bar	Nexp	Type	Method ^a	Reference
238.15	2.03 – 10.13	9	<i>p</i> – <i>X</i>	N.A.	Shenderei and Ivanovskii, 1964 [95]
293.15	34.8 – 50.9	5	<i>p</i> – <i>X</i>	SynVis	Lay, 2010 [58]
298.00	15.2 – 52.6	4	<i>p</i> – <i>X</i>	SynVisVar	Sanchez-Vicente et al., 2018 [40]
298.15	37.9 – 56.1	5	<i>p</i> – <i>X</i>	SynVis	Lay, 2010 [58]
298.15	2.31 – 62.54	14	<i>p</i> – <i>X</i>	SynVisVar	Sanchez-Vicente et al., 2018 [40]
301.76	34.61	1	<i>p</i> – <i>X</i>	SynNon	Fenghour et al., 2001 [59]
303.15	41.1 – 61.4	5	<i>p</i> – <i>X</i>	SynVis	Lay, 2010 [58]
308.15	43.2 – 67.8	5	<i>p</i> – <i>X</i>	SynVis	Lay, 2010 [58]
310.65	1.86 – 75.64	23	<i>p</i> – <i>X</i> , <i>Y</i>	N.A.	Robinson and Kalra, 1976 via [90]
310.65	31.3 – 65.5	8	<i>p</i> – <i>X</i> , <i>Y</i>	N.A.	He et al., 1994 [89] via [90]
310.65	23 – 71	11	<i>p</i> – <i>X</i>	SynVisVar	Mutelet et al., 2005 [60]
310.65	1.86 – 75.64	23	<i>p</i> – <i>X</i> , <i>Y</i>	AnTVisVarVal	Kalra et al., 1978 [54]
310.70	17.24 – 72.67, 1.86 – 75.50	8, 11	<i>p</i> – <i>X</i> , <i>p</i> – <i>Y</i>	N.A.	Robinson and Kalra, 1976 via [90]
310.70	8.89 – 75.64	4	<i>p</i> – <i>X</i> , <i>Y</i>	N.A.	Robinson and Kalra, 1976 via [90]
313.15	45.7 – 74.1	5	<i>p</i> – <i>X</i>	SynVis	Lay, 2010 [58]
313.15	13.8 – 87.5	8	<i>p</i> – <i>X</i> , <i>Y</i>	AnTLcirVcirValVis	Liu et al., 2022 [57]
321.08	40.4	1	<i>p</i> – <i>X</i>	SynNon	Fenghour et al., 2001 [59]
323.00	19.7 – 77.3	4	<i>p</i> – <i>X</i>	SynVisVar	Sanchez-Vicente et al., 2018 [40]
323.15	31.3 – 75.4	10	<i>p</i> – <i>X</i> , <i>Y</i>	N.A.	He et al., 1994 [89] via [90]
323.15	3.51 – 86.1, 67.6 – 85.65	14, 3	<i>p</i> – <i>X</i> , <i>p</i> – <i>Y</i>		Sanchez-Vicente et al., 2018 [40]
323.15	25.7 – 97.1	8	<i>p</i> – <i>X</i> , <i>Y</i>	AnTLcirVcirValVis	Liu et al., 2022 [57]
323.20	25 – 86	11	<i>p</i> – <i>X</i>	SynVisVar	Mutelet et al., 2005 [60]
333.15	28 – 96	11	<i>p</i> – <i>X</i>		Mutelet et al., 2005 [60]
333.15	37.7 – 102.3	8	<i>p</i> – <i>X</i> , <i>Y</i>	AnTLcirVcirValVis	Liu et al., 2022 [57]
343.00	11.2 – 103.2, 21 – 103.1	11, 10	<i>p</i> – <i>X</i> , <i>p</i> – <i>Y</i>	AnTVisVal	Sako et al., 1995 [38] via [90]
343.10	23.69 – 107.58, 23.67 – 107.62	14, 14	<i>p</i> – <i>X</i> , <i>p</i> – <i>Y</i>	AnTVisVarVal	Nagahama et al., 1984
343.10	31 – 106	10	<i>p</i> – <i>X</i>	SynVisVar	Mutelet et al., 2005 [60]
343.15	26.1 – 129.5	8	<i>p</i> – <i>X</i> , <i>Y</i>	AnTLcirVcirValVis	Liu et al., 2022 [57]
348.00	26.2 – 104.9	4	<i>p</i> – <i>X</i>	SynVisVar	Sanchez-Vicente et al., 2018 [40]
352.40	16.06 – 116.11, 4.24 – 116.11	9, 10	<i>p</i> – <i>X</i> , <i>p</i> – <i>Y</i>	N.A.	Robinson and Kalra, 1976 via [90]
352.59	4.24 – 116.11	17	<i>p</i> – <i>X</i> , <i>Y</i>	AnTVisVarVal	Kalra et al., 1978 [54]
352.59	33 – 113	13	<i>p</i> – <i>X</i>	SynVisVar	Mutelet et al., 2005 [60]

Table 4 (continued)

Vapour-Liquid Equilibrium Data					
<i>T</i> /K	<i>p</i> _{range} /bar	Nexp	Type	Method ^a	Reference
352.90	18.9 – 106.9	6	<i>p</i> – <i>X</i> , <i>Y</i>	AnTVLcirValVis	Al Ghafri et al., 2015 [41]
362.90	43.78	1	<i>p</i> – <i>X</i>	SynNon	Fenghour et al., 2001 [59]
363.15	36 – 115	9	<i>p</i> – <i>X</i>	SynVisVar	Mutelet et al., 2005 [60]
373.00	33.5 – 125.5	4	<i>p</i> – <i>X</i>	SynVisVar	Sanchez-Vicente et al., 2018 [40]
373.15	38 – 123.	9	<i>p</i> – <i>X</i>	SynVisVar	Mutelet et al., 2005 [60]
373.15	5.21 – 126.5, 96.27 – 126.5	13, 4	<i>p</i> – <i>X</i> , <i>p</i> – <i>Y</i>	SynVisVar	Sanchez-Vicente et al., 2018 [40]
383.15	40 – 129	9	<i>p</i> – <i>X</i>	SynVisVar	Mutelet et al., 2005 [60]
393.15	43 – 133	9	<i>p</i> – <i>X</i>	SynVisVar	Mutelet et al., 2005 [60]
394.00	49.6 – 128.4	5	<i>p</i> – <i>X</i> , <i>Y</i>	AnTLcirVal	Inomata et al., 1986 [101]
394.00	49.6 – 128.4	5	<i>p</i> – <i>X</i> , <i>Y</i>	AnTLcirVal	Inomata et al., 1986 [37]
394.13	30 – 131	11	<i>p</i> – <i>X</i>	SynVisVar	Mutelet et al., 2005 [60]
394.15	5.6 – 134.8, 100.2 – 131.1	10, 5	<i>p</i> – <i>X</i> , <i>p</i> – <i>Y</i>	SynVisVar	Al Ghafri et al., 2014 [39]
394.15	22.1 – 134.1	6	<i>p</i> – <i>X</i> , <i>Y</i>	AnTVLcirValVis	Al Ghafri et al., 2015 [41]
394.26	11.307 – 132.37	17	<i>p</i> – <i>X</i> , <i>Y</i>	AnTVisVarVal	Kalra et al., 1978 [54]
394.30	11.31 – 133.14, 11.31 – 132.38	9, 8	<i>p</i> – <i>X</i> , <i>p</i> – <i>Y</i>	N.A.	Robinson and Kalra, 1976 via [90]
403.15	45 – 134	9	<i>p</i> – <i>X</i>	SynVisVar	Mutelet et al., 2005 [60]
413.15	46 – 124	5	<i>p</i> – <i>X</i>	SynVisVar	Mutelet et al., 2005 [60]
423.00	44.1 – 130	4	<i>p</i> – <i>X</i>	SynVisVar	Sanchez-Vicente et al., 2018 [40]
423.15	3.75 – 131.2, 95.7 – 127.7	12, 4	<i>p</i> – <i>X</i> , <i>p</i> – <i>Y</i>	SynVisVar	Sanchez-Vicente et al., 2018 [40]
448.00	46.1 – 117.8	3	<i>p</i> – <i>X</i>	SynVisVar	Sanchez-Vicente et al., 2018 [40]
468.40	30.9 – 103.9, 99.0 – 108.8	9, 2	<i>p</i> – <i>X</i> , <i>Y</i> , <i>p</i> – <i>X</i>	AnTLcirVal	Inomata et al., 1986 [101]
477.21	17.51 – 99.22	7	<i>p</i> – <i>X</i> , <i>Y</i>	AnTVisVarVal	Kalra et al., 1978 [54]
502.00	30.4 – 76.8	7	<i>p</i> – <i>X</i> , <i>Y</i>	AnTLcirVal	Inomata et al., 1986 [101]

^a As denoted by Dohrn and co-authors

points of the 468.4 K isotherm reported by Inomata et al. [101], appears to deviate from the general trend.

It should be noted that this system exhibits type II phase behaviour [100], as classified by van Konynenburg and Scott [103] and, more recently, by Privat and Jaubert [104]. This means it has a continuous VLE curve connecting the pure components, a liquid–liquid (LL) critical curve at very low temperatures, and a three-phase equilibrium curve (LLV). The available critical and vapour–liquid–liquid equilibrium data from the literature are summarised in Table 5. In addition to the vapour–liquid critical points measured by various groups over the years, Table 5 also includes the LL critical data measured by Schneider [97] at pressures above 1000 bar, the liquid–liquid equilibrium data from the Q-point to the UCEP reported by Im and Kurata [55], and the

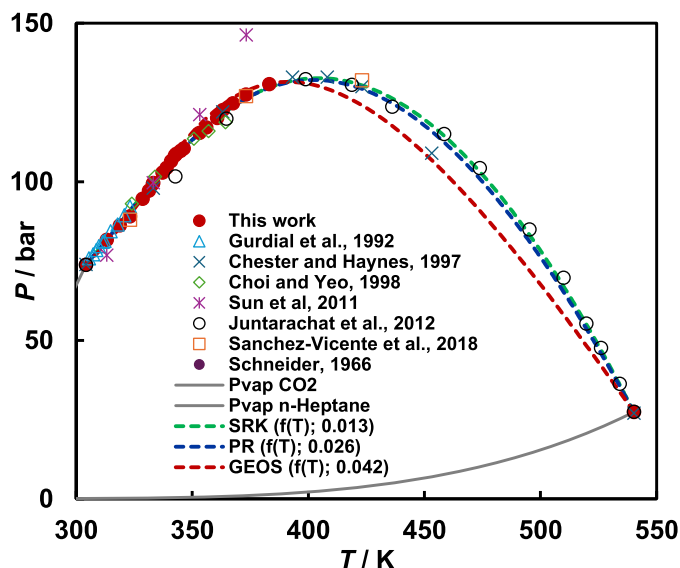


Fig. 9. P - T fluid phase diagram of CO_2 + n -heptane system with temperature-dependent k_{12} and constant l_{12} .

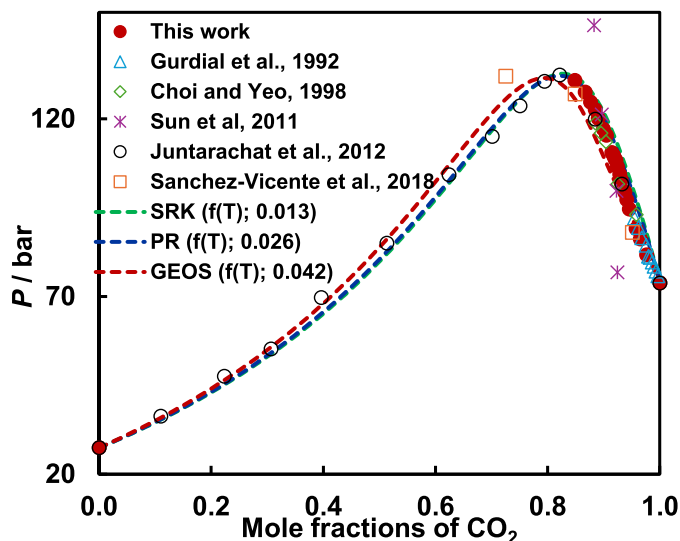


Fig. 10. P - X projection of the LV critical curve of the CO_2 (1) + n -heptane (2) system with k_{12} temperature-dependent and constant l_{12} .

corresponding P - T equilibrium line from their study.

With respect to previously reported vapour-liquid critical data, one point from Chester and Haynes [56] on the branch toward n -heptane, as well as one point from Sanchez-Vicente et al. [40] on the same branch but closer to the critical pressure maximum (CPM), shows some dispersion when compared with the data reported by Juntarachat et al. [42]. On the increasing-temperature side of the vapour - liquid critical curve, from carbon dioxide toward the critical pressure maximum, a larger number of datasets are available, including those from the present work. In this region, the data are generally consistent, with only limited scatter observed, corresponding to two points each from Sun et al. [91], Choi and Yeo [49], and Juntarachat et al. [42].

4.3. Modelling results

In previous sections, we noted that a variety of modelling strategies have been applied over the years to the carbon dioxide + n -heptane system, ranging from empirical correlations to predictive approaches.

Early studies generally did not attempt a systematic modelling of the system or used it only as a consistency test (e.g., Kalra et al. [54]), with most authors primarily focused on reproducing their measured isotherms. As a result, modelling efforts have remained fragmented, and only a couple studies [40,42] report a description of the vapour - liquid critical curve.

In this context, the objective of the present work is to provide a comprehensive and coherent description of the phase behaviour of the carbon dioxide + n -heptane system, with particular emphasis on its critical behaviour. Building on our recent successful modelling of the carbon dioxide + n -hexane system, the binary interaction parameters (BIPs - k_{12} , l_{12}) determined in that study [78] were transferred to the carbon dioxide + n -heptane system (Table 6). It should be noted that the pure-component critical properties and acentric factors were taken from the DIPPR database [88], as our internal study showed that using values from other sources did not improve the modelling. The m and a_c parameters of the GEOS equation are also reported in Table 7.

Using constant binary interaction parameters customised for each equation of state (GEOS, PR, and SRK), we first modelled the critical curves (VLE and LLE) as well as the three-phase equilibrium curve (LLV). The experimental vapour - liquid critical data obtained in this work, together with all available literature data, are compared with the model predictions in Fig. 17S. While PR and SRK exhibit similar performance, PR being marginally superior, and reproduce most features of the critical curve, both equations underestimate the critical pressure maximum (CPM), with deviations of approximately 3 bar. In contrast, the GEOS model shows a larger deviation, overestimating the CPM by about 8 bar and underestimating its corresponding temperature, and predicts a slight inflection on the left branch of the critical curve.

A comparable feature appears to be present in the SAFT- γ Mie results reported by Sanchez-Vicente et al. ("Fig. 4" in [40]). The inflection observed on the CO_2 -rich branch of the critical curve is likely a model-induced effect associated with the proximity to the pure CO_2 critical point, and in the case of GEOS, its higher functional flexibility appears to amplify this behaviour; to our knowledge, this is the first time such an inflection has been observed in systems modelled with GEOS and it should not be interpreted as a physical feature of the mixture. The critical behaviour observed in the P - T projection of the critical curve is also evident in the P - X (Fig. 5) and T - X (Fig. 6) projections. Both SRK and PR reproduce the experimental data reasonably well, although a few literature points exhibit some scatter. The GEOS model, on the other hand, shows a slightly larger overestimation of the CPM and reproduces the same unusual inflection of the critical curve observed in the P - T projection.

When the liquid - liquid (LL) critical curve and the three-phase equilibrium curve are also plotted, it can be seen that all models predict the UCEP remarkably well, with deviations of less than 5 K and 1 bar from the experimental values of 222.6 K and 6.48 bar reported by Im and Kurata [55]. Among the models, PR provides the closest prediction of the UCEP, whereas SRK better reproduces the experimental LL critical curve measured by Schneider [97], likely due to its more pronounced slope, as illustrated in Figs. 7 and 8. In Figs. 7 and 8, the solid - liquid - gas (SLG) up to the eutectic point data measured by Im and Kurata [55] that intersect the LLV curve are also displayed.

Given the unusual behaviour of the GEOS model, and noting that temperature-dependent binary interaction parameters have been shown in other studies [40,42] to reproduce the P - T behaviour well, we next employed temperature-dependent k_{12} parameters for all three models, while retaining the same constant l_{12} interaction parameters as before (Table 6). The temperature-dependent form adopted for k_{12} is based on the expression proposed in [105] and is given by

$$k_{12} = k^\infty + k' \cdot e^{-\frac{T}{T^*}} \quad (35)$$

where $k^\infty = 0.05$, $k' = 0.01$, and $T^* = 304.21$ K, corresponding to the critical temperature of carbon dioxide.

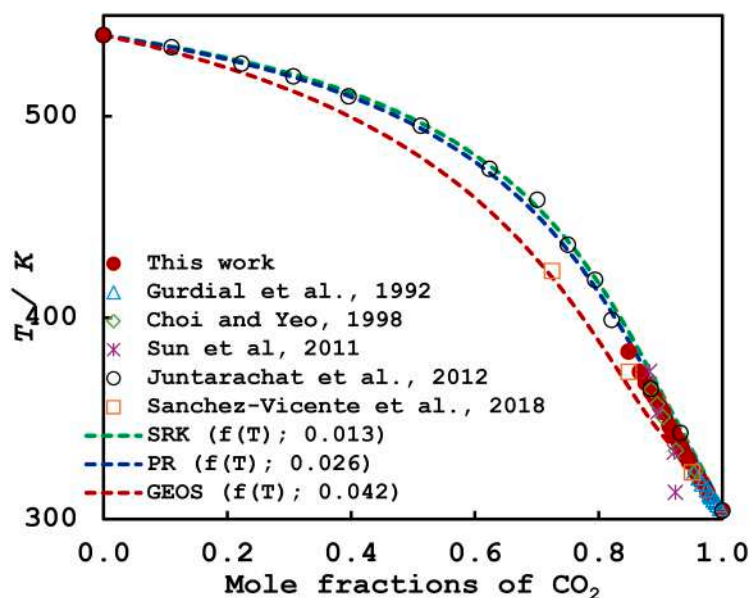


Fig. 11. T - X projection of the LV critical curve of the CO_2 (1) + n -heptane (2) system with k_{12} temperature-dependent and constant l_{12} .

Table 5

Literature critical and three-phases equilibria behaviour for CO_2 (1) + n -heptane (2) binary system.

$T_{\text{range}}/\text{K}$	$p_{\text{range}}/\text{bar}$	X_{range}	N_{exp}	Type	Reference
310.65 (310.70)	75.636 (75.6354)	(0.95) 0.95	1	VLE critical data	Kalra et al., 1978 [54], Robinson and Kalra, 1976 via [90]
305.5 – 323.2	75.8 – 92.1	0.9964 – 0.9546	10	VLE critical data	Gurdial et al., 1992 [102]
304.25 – 540.25	73.9 – 27	–	8	VLE critical data	Chester and Haynes, 1997 [56]
324 – 364.3	93.04 – 118.76	0.9580 – 0.8850	5	VLE critical data	Choi and Yeo, 1998 [49]
313.2 – 373.2	76.8 – 146.3	0.9243 – 0.8824	4	VLE critical data	Sun et al., 2011 [91]
342.75 – 534.16	101.656 – 27.457	0.93225 – 0.11006	12	VLE critical data	Juntarachat et al., 2012 [42]
323.15 – 423.15	88 – 132	0.951 – 0.725	3	VLE critical data	Sanchez-Vicente et al., 2018 [40]
225.35 – 244.55	139 – 1144	0.8572	5	LL critical data	Schneider, 1966 [97]
215.2 – 183.2	4.7623 – 0.4154	0.581 – 0.055	10	SLG equilibrium data	Im and Kurata, 1971 [55]
226.6 – 215.6 ^a	6.4848 – 4.7521	0.89 – 0.984	6	LL equilibrium data	Im and Kurata, 1971 [55]

^a Including the UCEP and Q-point

Table 6

Binary interaction parameters (BIPs) used for each model: k_{12} and l_{12} constant values and k_{12} -temperature dependent and constant l_{12} .

EoS/mixing rule	k_{12}	l_{12}
GEOS/2PCMR	0.088 ^a	0.042 ^a
	$f(T)$ ^b	0.042 ^a
PR/2PCMR	0.088 ^a	0.026 ^a
	$f(T)$ ^b	0.026 ^a
SRK/2PCMR	0.088 ^a	0.013 ^a
	$f(T)$ ^b	0.013 ^a

^a BIPs taken from Ref. [78];

^b k_{12} is expressed as function of temperature $f(T)$ given by eq. (35).

Table 7

Critical parameters (T_c , P_c), acentric factors (ω) and (m and α_c) parameters of GEOS equation for pure components.

Substance	T_c/K	P_c/bar	ω	M	α_c
CO_2	304.21	73.83	0.2236	7.0801	0.3045
$n\text{-C}_7\text{H}_{16}$	540.20	27.40	0.3495	7.7460	0.4368

As shown in Fig. 18S (results with all parameters from Table 6), and in more detail in Fig. 9 (results with one parameter temperature-dependent) all models provide improved results. The CPM is now better reproduced by all three equations of state; however, GEOS still slightly underestimates the corresponding CPM temperature.

Importantly, the unusual inflection observed in the GEOS critical curve with constant k_{12} parameter is no longer present. In the P - X projection obtained using temperature-dependent k_{12} and constant l_{12} parameters, the CPM is improved for all models (Fig. 10). However, the critical compositions are slightly overestimated by PR and SRK toward the CO_2 critical point, whereas they are underestimated by GEOS. In the T - X projection of the vapour-liquid critical curve obtained using temperature-dependent k_{12} and constant l_{12} parameters, PR and SRK predict critical compositions slightly shifted toward the CO_2 -rich side at lower temperatures, whereas GEOS predicts compositions shifted toward lower CO_2 contents (Fig. 11).

However, the improved prediction of the critical pressure maximum is accompanied by a decrease in the predicted UCEP temperature of more than 37 K for PR and 35 K for SRK (Figs. 19S and 20S). The modelling results for the isothermal data obtained using both constant binary interaction parameters and temperature-dependent k_{12} with constant l_{12} for all three equations of state are presented in Figs. 21S–28S for the temperatures investigated in this study, together with the corresponding literature data. As expected, all models reproduce the critical points reasonably well; yet, the phase compositions are generally underestimated, particularly for the liquid phase. Overall, the use of constant binary interaction parameters provides a slightly better description of the pressure-composition data than the temperature-dependent k_{12} with constant l_{12} formulation.

5. Conclusions

New isothermal vapour – liquid equilibrium data and vapour – liquid critical points for the carbon dioxide + *n*-heptane system have been reported and combined with a comprehensive review of all available experimental and modelling studies for this mixture. The literature was systematically gathered and analysed with respect to the types of measurements performed and the modelling approaches employed, revealing that most studies focused on reproducing individual isotherms, while only two works addressed the vapour – liquid critical behaviour in the *P*–*T* projection.

The phase behaviour of the system was modelled using three equations of state, GEOS, PR, and SRK, employing both constant binary interaction parameters and temperature-dependent k_{12} parameters combined with constant l_{12} . When constant interaction parameters were used, PR and SRK reproduced the vapour – liquid critical curve reasonably well, with deviations in the critical pressure maximum of approximately 3 bar, whereas GEOS showed a slightly larger deviation and an unusual inflection on the carbon dioxide-rich branch of the critical curve. This behaviour was attributed to model limitations in the vicinity of the pure carbon dioxide critical point and should not be interpreted as a physical feature of the system.

The introduction of temperature-dependent k_{12} parameters resulted in an improved prediction of the critical pressure maximum for all three models and eliminated the inflection previously observed with GEOS. However, this improvement was accompanied by a significant underprediction of the upper critical end point temperature, exceeding 37 K for PR and 35 K for SRK. Overall, the models reproduce the critical behaviour reasonably well, although slight quantitative deviations persist, which are likely related to the transfer of binary interaction parameters from the carbon dioxide + *n*-hexane system instead of being optimised for the carbon dioxide + *n*-heptane mixture.

Modelling of the isothermal vapour – liquid equilibrium data shows that all three equations of state reproduce the critical points satisfactorily, but generally underestimate phase compositions, particularly for the liquid phase. In this context, the use of constant binary interaction parameters provides a slightly better representation of the pressure–composition behaviour than the temperature-dependent k_{12} and constant l_{12} formulation.

The results underline the challenges associated with simultaneously describing critical behaviour, three-phase equilibria, and isothermal VLE data for highly asymmetric systems such as carbon dioxide + *n*-heptane. Despite these limitations, the combined experimental, literature, and modelling results presented in this work provide a coherent and comprehensive description of the phase behaviour of the carbon dioxide + *n*-heptane system and offer a consistent reference for future studies aimed at improving interaction parameter formulations or developing more advanced thermodynamic models.

CRedit authorship contribution statement

Sergiu Sima: Software, Investigation, Data curation. **Catinca Secuianu:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Secuianu Catinca reports financial support was provided by Executive Unit for Financing Higher Education Research Development and Innovation. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

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Data availability

Data will be made available on request.

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