

Vapor-liquid equilibrium, liquid density and excess enthalpy of the carbon dioxide+acetone mixture: Experimental measurements and correlations

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ABSTRACT

New vapor-liquid equilibrium data of the CO₂+acetone mixture were determined from vapor pressure measurements using a static and synthetic method from (283.15 to 383.15) K and a composition range from (4 to 85) % in CO₂ mole fraction. The fugacity coefficients approach with the Soave-Redlich-Kwong equation of state was used to calculate the composition of the phases and the binary interaction parameter. The average relative deviation between the experimental and calculated pressure values was 0.14 % and the maximum deviation was 5.0 %. Carbon dioxide shows total miscibility and good solubility in acetone in the conditions studied. The liquid density of the mixture was measured with a vibrating-tube densimeter from (283.15 to 353.15) K, at sufficient pressure to guarantee the liquid state, and a composition range from (6 to 82) % in CO₂ mole fraction. The liquid density values calculated by the equation of state with the Peneloux correction were compared with the experimental values and agreement was good with a maximum deviation of 7 % and an average deviation of 0.7 %. The excess molar enthalpies were measured by a flow-calorimetric technique at (283.30 and 298.30) K and pressures from (9.00 to 14.00) MPa. Finally, the experimental data on vapor pressure, density, and excess molar enthalpy were fitted using empirical equations, and the first two were compared with data reported in the literature. Average

deviations were between (0.07 and 30) % in the vapor-liquid equilibrium, and between (0.51 and 8.8) % in the density.

1. Introduction

Carbon dioxide + acetone is an interesting mixture that has been studied in recent decades for a variety of applications. Katayama *et al.* [1] were the first to measure the vapor-liquid equilibrium for petroleum, natural gas, and related industries. Groll and Kruse [2] and Mozurkewich *et al.* [3] studied the use of CO₂+acetone in compression refrigeration systems to reduce the high operating pressure. More recently, Hsieh and Vrabec [4] proposed acetone as a co-solvent of CO₂ in other types of applications (for example, as an extraction solvent or as a solvent in polymer synthesis processes) and measured the vapor-liquid equilibrium at higher temperatures and pressures than in ref. [1]. In recent years, acetone has also been proposed as a solvent for capturing CO₂ to reduce emissions [5-6]. However, the application that has most been studied uses CO₂ as a supercritical solvent, with acetone as co-solvent. Their properties have been measured in different working ranges [7-27].

Whatever the application, reliable vapor-liquid equilibrium (VLE) data, density, and excess enthalpy are necessary if processes containing the CO₂ + acetone mixture are to be accurately designed and optimized. Table 1 summarizes the published papers with VLE data for the CO₂ + acetone mixture, including temperature, composition and pressure ranges, the equations of state and the mixing rules used for the data modeling.

Table 1. Published papers with vapor-liquid equilibrium data of the CO₂ (1) + acetone (2) mixture

Ref.	<i>T</i> /K	<i>x</i> ₁	<i>p</i> /MPa	Modeling
[1]	298.15-313.15	0.07-0.98	0.4-0.73	RK + Redlich Kister γ -model with classic mixing rule
[4]	313.15-353.15	0.48-0.84	4.06-10.53	PR+UNIQUAC with van der Waals and Huron-Vidal mixing rules
[5]	298.2-333.2	0.09-0.89	0.81-5.36	Henry's law + PR with classic mixing rules
[6]	258.3-298.2	0.10-0.92	0.496-5.495	Predictive-SRK

[7]	313.15-333.15	0.10-0.97	0.98-9.49	PR with 6 different mixing rules
[10]	333.15-393.15	0.32-0.83	2.36-11.77	PR with classic mixing rules
[11]	298.15	0.38-0.57	2.15-3.37	Pseudocubic perturbed hard-sphere EoS with classic mixing rule
[12- 14]	291.15-313.13	0.14-0.94	0.87-7.39	PT and PR
[15]	303.0-332.9	0.15-0.80	1.05-8.10	PR modified and Generalized Bender EoS
[17]	291.15-323.15	0.12-0.53	0.70-4.02	PR and SAFT with volumen parameter-linear mixing rules
[18]	333.2-473.2	0.3-0.9	4.98-11.55	PR with van der Waals mixing rule
[19]	291.15-313.15	0.19-0.98	0.72-7.88	PR, SRK with MR-Q1 and MR-Q2 van der Waals mixing rules
[20]	308.15-333.15	1.5-6.02	0.19-0.77	SRK with Huson-Vidal mixing rule
[21]	313.11-353.18	0.29-0.81	1.93-10.78	PR with van der Waals mixing rules
[22]	288.15-318.15	0.02-0.65	0.12-5.33	SRK
[23]	323	0.06-0.79	0.49-7.11	PT with the Matthias Klotz-Prausnitz mixing rules
[24]	298.15	0.13-0.47	0.57-2.5	-
[25]	297-400	0.02-0.21	4.8-11.7	-
[26]	298.15-303.15	0-0.22	0-0.97	Berthelot equation
[27]	288.15-318.15	0.02-0.71	2.3-8.16	PC-SAFT

PR: Peng-Robinson EoS; SRK: Soave-Redlich-Kwong EoS; RK: Redlich-Kwong EoS; PT: Pater-Teja EoS

Table 2 summarizes the published papers with experimental data for the liquid density of the CO₂ + acetone mixture, including the ranges of temperature and composition.

Only one reference provides data on the molar excess enthalpies for mixtures of supercritical CO₂ and acetone [29] at (9.00 and 18.00) MPa and temperatures from (313.15 to 333.15) K.

Table 2. Liquid density data for the CO₂ + acetone mixture reported in literature

Ref.	<i>T</i> /K	<i>p</i> /MPa	ρ / kg m ⁻³
[7]	313.15-333.15	0.98-9.49	585-829
[10]	333.15-393.15	2.36-11.77	612.8-818.9
[11]	298.15	2.15-3.37	838.5-861.4
[12-14]	291.15-313.13	0.87-7.39	774.8-876.7
[16]	318.15-333.15	1.54-15.14	570-834
[17]	291.15-323.15	0.7-4.02	747.60-858.15
[28]	313.15	0.51-7.58	716.6-837.70

Despite the amount of published VLE data, most of them are limited to a temperature range between (291 and 353) K. At higher temperatures, the reported data are scarce and, in some cases, present inconsistencies, as Hsieh and Vrabec [4] have already reported. Therefore, we consider that it is necessary and of interest to make new measurements of the vapor-liquid equilibrium and liquid density, particularly at temperatures higher than 333.15 K, and provide more excess enthalpy data at temperatures lower than 313.15 K, for the CO₂ + acetone mixture to cover the working conditions of different applications, such as refrigeration and air conditioning systems [2,3] or as supercritical solvent in extraction processes [4,7,10], where VLE data and other properties at high temperature (up to 393.15 K) are necessary. All these data can also be used to evaluate the accuracy of a simple equation of state and thus model this mixture. To this end, we used an apparatus based on the synthetic, static method of measuring the vapor pressure of the CO₂ + acetone mixture in a temperature range from (283.15 to 383.15) K and composition range from (4 to 85) % in CO₂ liquid mole fraction. The phase compositions in equilibrium were calculated using a fugacity coefficient method (ϕ - ϕ approach), with the Soave-Redlich-Kwong equation of state [30], and the van der Waals mixing rule and the Peneloux correction [31], to represent the non-ideality of

the vapor and liquid phases. Also, the density of the liquid phase was measured using a vibrating-tube densimeter, in a temperature range from (283.15 to 353.15) K and CO₂ mole fractions from 0.06 to 0.82, and the results were compared with values calculated using the equation of state. Excess enthalpy was measured at (283.30 and 298.30) K and pressures from (9.00 to 14.00) MPa. These new data were obtained from the heat of mixing measurements, using a flow-calorimetric technique. Empirical equations were obtained from the experimental data to provide simple correlations to use in simulations or calculations. Finally, the vapor-liquid equilibrium and liquid density values were compared with data in the literature. The agreement between the two sets of data was good.

2. Experimental Method

2.1. Materials

Carbon dioxide (purity ≥ 99.995 % in mass fraction) was supplied by the company Abello-Linde, and acetone (purity ≥ 99.8 % in mass fraction) by Honeywell / Riedel-de Häen. Dry nitrogen (purity > 99.8 % in mass fraction) was supplied by Messer Ibérica. For excess enthalpy measurements, carbon dioxide (purity ≥ 99.995 %) was supplied by Air Products and acetone (purity ≥ 99.9 % in mass fraction) by Merck. Acetone was degassed under vacuum before being used. The chemicals were used without further purification. Table 3 shows the specification of the chemical samples used.

Table 3. Specifications of chemical samples

Chemical Name	Source	Mass fraction purity
Carbon dioxide	Abello-Linde	0.99995
	Air Products	0.99995
Acetone	Honeywell/Riedel de Häen	0.998
	Merck	0.999
Nitrogen	Messer Ibérica	0.998

2.2. Vapor pressure apparatus

The experimental device used to measure the vapor pressure of the CO₂ + acetone mixture is based on the static, isochoric method. It was designed and built in our laboratory specially for measuring the vapor pressure of mixtures at high pressure and temperature in this study. The set-up (Fig.1) consists of an equilibrium cell (1) with a volume of $(10.74 \pm 0.02) \text{ cm}^3$, built-in stainless steel to withstand high pressures and temperatures. The pressure is directly measured by four Druck pressure transducers (TP) (mod. UNIK-5000) connected to the equilibrium cell. These transducers cover different pressure ranges for better accuracy: (0-1) bar, (1-10) bar, (10-50) bar and (50-100) bar. The equilibrium cell is immersed in a thermal bath (2) of ethylene glycol + distilled water (40:60 in volume), with the temperature controlled by a JULABO thermostat (mod. EH) (3) and measured by a Pt-100 RTD (8). The quantity of CO₂ is initially introduced into an auxiliary cylinder (5) from a bottle of compressed gas (6) through a pressure gauge (7) and a series of valves (V_E , V_A , and V_B). The temperature of the CO₂ introduced into the auxiliary cylinder is measured by a Pt-100 RTD (4) and the pressure is measured with the same transducers (TP). A vacuum pump (9) COMECTA-IVYMEN is used to empty the system. A datalogger Agilent (mod. 34970A) (10) connected to a computer (11) is used to collect the temperature and pressure data. The sample in the equilibrium cell is continuously mixed by a stir bar, and a magnetic stirrer located underneath (12).

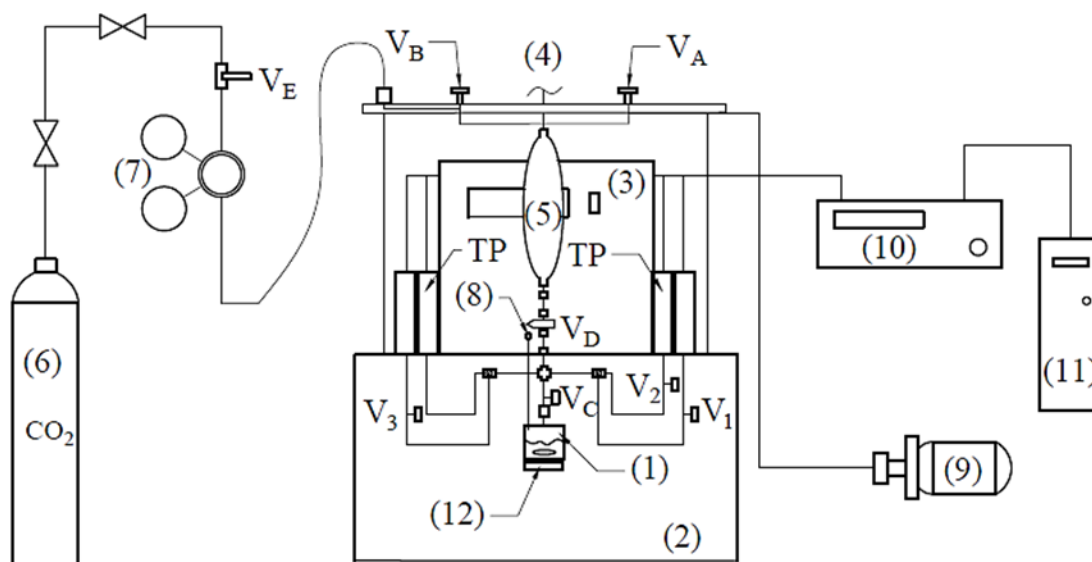


Figure 1. Diagram of the experimental device for measuring vapor pressure using the static method. (1) equilibrium cell, (2) thermal bath, (3) thermostat, (4) equilibrium cell Pt-100, (5) auxiliary cylinder, (6)

1 compressed gas bottle, (7) pressure gauge, (8) cylinder Pt-100, (9) vacuum pump, (10) datalogger, (11)
2 computer, (12) magnetic stirrer, (V) valves, (TP) pressure transducers.

3
4 The Pt-100 resistance temperature thermometer was calibrated following the ITS-90 procedure [32]. The
5 expanded uncertainty of the temperature measurement was 0.05 K. In addition, the pressure transducers
6 were calibrated using a standard procedure [33] and nitrogen gas as a reference standard. The expanded
7 uncertainty was (0.01, 0.05 and 0.08) bar for the transducers with pressure ranges of (1-10) bar, (10-50)
8 bar, and (50-100) bar, respectively. The transducer with a range up to 1 bar was not used in this study.
9 Finally, the estimated uncertainties for the phase mole fractions were 0.0005. All the uncertainties are
10 given with a confidence level of 95 % ($k = 2$), and they were estimated using GUM [34]. The transducers
11 were validated with pure CO₂, and deviations were 0.11 % lower than those of the reference data [35].

12 2.3. Density apparatus

13 The liquid density of the CO₂ + acetone mixture was measured using a set-up (Fig. 2) formed by an Anton
14 Paar HPM vibrating-tube densimeter (1) and the Anton Paar mPDS-5 evaluation unit (2), which is
15 connected to a computer (3) to acquire the data. To prepare and inject the mixture into the densimeter, a
16 variable-volume cell (4) is located between a pressure regulator (5) and the densimeter inlet. A Julabo
17 circulator bath (6) (mod. F25) controls the temperature of the experiment, which is measured directly by
18 the densimeter. An auxiliary cylinder (7) is used to transfer CO₂ gas from the compressed gas bottle to the
19 variable-volume cell, while the acetone is injected directly with a syringe (8). The fluid pressure is
20 measured with a Kulite pressure transducer (TP) (mod. ETM 200-375), calibrated from (0.1 to 7) MPa.
21 The densimeter was calibrated with water [36] and vacuum, and validated with pure acetone in the
22 temperature range from (283.15 to 353.15) K. The deviations between the experimental and reference
23 values [37] were lower than 0.1 %. The estimated expanded uncertainty [34] for the density was 0.9 kg/m³,
24 0.05 K for the temperature, 0.03 MPa for pressure, and 0.004 for the mole fraction, with a coverage factor
25 of $k = 2$ (95 % level of confidence).

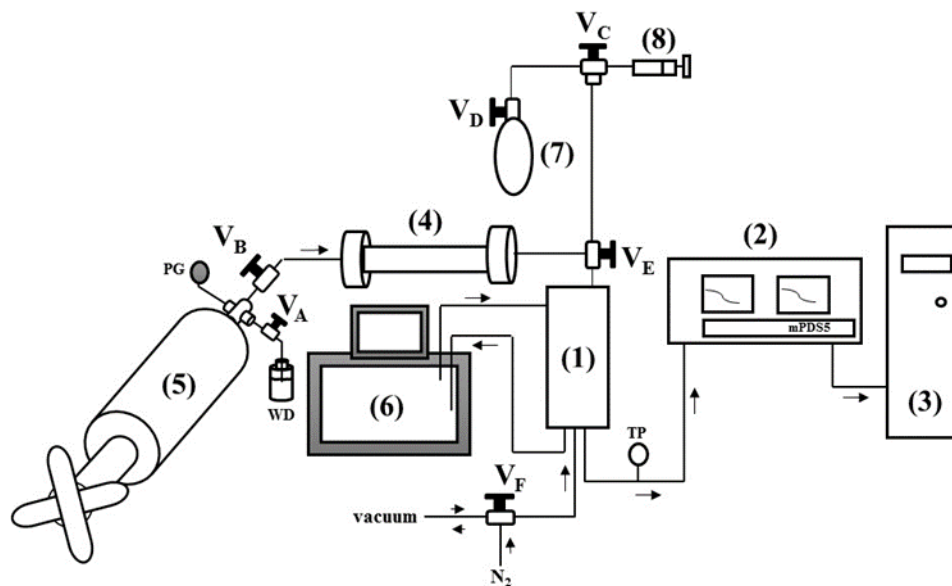


Figure 2. Diagram of the experimental device for measuring the liquid phase density. (1) external measuring cell Anton Paar HPM, (2) mPDS-5 evaluation unit, (3) computer, (4) variable-volume cell, (5) pressure regulator, (6) circulator bath.

2.4. Excess enthalpy apparatus

Excess molar enthalpies were determined from the heat of mixing measurements of pure CO₂ with acetone using a customized BT2.15 calorimeter from Setaram. The original cooling system of the calorimeter using liquid nitrogen was replaced by the continuous circulation of a fluid at sub-ambient conditions supplied by a Julabo recirculating cooler (model FL 1201). The temperature of the calorimeter is kept at 0.03 K using Setaram G11 electronics. To allow a stable thermal regulation, the cooling system is set at a temperature of around 10 K below the operating temperature. The calorimetric technique (Fig. 3) is similar to the one used for determining excess enthalpies of amines with water [38]. Experiments are performed in a dynamic mode at constant temperature and pressure. The pure fluids are supplied by two high-pressure syringe pumps (model 260DM from ISCO) and mixed in a cell designed in the laboratory. These pumps provide stable volumetric flow rates with a relative uncertainty of 0.3 % and were temperature controlled at (293.15 ± 0.03) K using a Julabo heating circulator (model F12-EH). Along the flow line, the pressure is detected using a Keller pressure transducer with a full-scale accuracy of 0.1 % (20 MPa). While measuring the heat of mixing for a given composition the pressure is kept constant at 0.02 MPa.

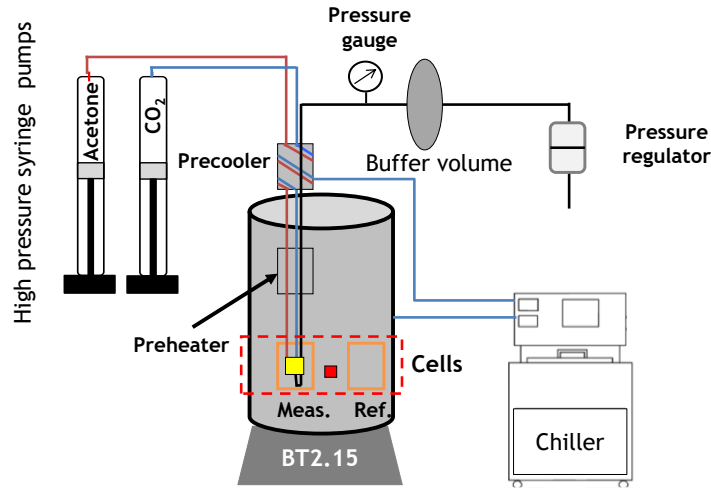


Figure 3. Schematic representation of the flow calorimetric technique

The excess molar enthalpy H^E is derived from the mixing heat power detected by a thermopile surrounding the mixing cell. The calorimetric signal Δsig (mV) is first converted into heat power using a calibration constant K ($\text{mV} \cdot \text{mW}^{-1}$) and then, into molar enthalpy using the molar flow rates of the fluids ($\dot{n}_1$ for the CO_2 and $\dot{n}_2$ for acetone) as indicated in Eq(1).

$$H^E = \frac{\Delta sig}{K \cdot (\dot{n}_1 + \dot{n}_2)} \quad (1)$$

The calorimetric signal represents the difference between the signal recorded during mixing, and a baseline signal recorded when only one of the fluids is flowing into the circuit. At 283.15 K, the calibration constant was obtained by measuring the heat of mixing heptane and toluene and comparing the results with reference values from Holzhauser and Ziegler [39]. At 298.15 K, reference values from Ott *et al.* [40] were used to determine the calibration constant. Considering uncertainties in fluid flow rates, the thermopile calibration K and calorimetric signal noises, the relative uncertainty in excess molar enthalpies is less than 5 %. However, experimental heats of mixing at very low or high molar fractions can show greater uncertainties. Indeed, these measurements require a large difference between the flow rates of the two fluids, which can cause mixing problems. Moreover, for these extreme concentrations, the mixing thermal flux is usually small and the signal-to-noise ratio increases, leading to a larger relative uncertainty in the measurement.

2.4. Sample Preparation and Measurement Procedure

The sample for the vapor pressure measurements was prepared in three steps. First, a quantity of acetone was injected into the equilibrium cell (1 in Fig. 1) and its mass was accurately determined with an analytical balance (Mettler Toledo mod. AE206), with a resolution of ± 0.1 mg. Second, the cell with the acetone was immersed in liquid nitrogen and a vacuum was created (9) for 5 min. Then, the cell was heated to room temperature. This process was repeated three times to degas the acetone and to remove the air of the measuring system. And third, CO₂ was introduced through the inlet valve (V_B) to an auxiliary cylinder (5). The mass of CO₂ was determined by an equation of state [28], measuring the pressure with the suitable transducer (TP) and the temperature with the Pt-100 (8). The volume of the cylinder is well known. The quantity of CO₂ depends on the mass of acetone injected and can be modified to obtain the desired overall composition of the mixture by filling or emptying the system through the valves V_B or V_A, respectively. When the desired mass of CO₂ and acetone was reached, the valve V_C was opened so that both components could be mixed. Then, the equilibrium cell was immersed in liquid nitrogen to ensure that the CO₂ would move to it and empty the auxiliary cylinder. When the pressure recorded was null, valve V_D was closed, and the equilibrium cell was immersed in a thermostatic bath up to the level of the transducers. The vapor pressure was measured from (283.15 to 383.15) K, with 10 K steps.

The samples for the density measurements were prepared in the variable-volume cell (4 in Fig. 2). First, acetone was directly injected (V_C) into the cell with a syringe. The mass was determined using the difference in the analytical balance. The CO₂ was introduced with the help of an auxiliary cylinder (7) previously charged with the desired mass of gas. Then, the two components were mixed in the cell by consecutive cycles of compression and expansion controlled using the pressure regulator (5). Finally, the fluid was compressed to a pressure higher than the saturation pressure at room temperature so that it could be introduced into the densimeter as a compressed liquid. The circulation bath (6) was programmed to the first experimental temperature (283.15 K), and the density value was taken when this and the temperature value were constant. Then, the next temperature was programmed, and the pressure was increased to ensure the liquid state. The process was repeated until the last temperature (353.15 K) had been tested. It was not possible to measure at higher temperatures because the working pressure is limited to 60 bar.

For excess enthalpy measurements, a sample of CO₂ was compressed in the syringe pump with a high-pressure generator to a pressure higher than the saturation pressure (Fig. 3). The flow-mixing cell makes it possible to determine excess molar enthalpies as a function of the composition. Liquid CO₂ and acetone

1 flow at constant volume flow rates because the pumps are temperature controlled. The molar flow rates
 2 were derived from the volume flow rates of the pumps using fluid densities. The densities of CO₂ and
 3 acetone were calculated as a function of temperature and pressure using the equations of state from ref.
 4 [35, 41]. Before measuring the thermopile signal S_M (μV) during the mixing process, a baseline signal S_{BL}
 5 (μV) was recorded with only one fluid flowing through the calorimeter. The baseline signal was kept close
 6 to zero by adjusting the thermoregulation of the entering fluid with a preheater. The signal was recorded
 7 for 20 min before the second fluid was injected. The heat effect due to the fluids mixing corresponded to
 8 a thermopile signal ($S_M - S_{BL}$). This signal was recorded for at least 30 min. The heat mixing was thus
 9 determined using equation 1. The experiments were repeated varying the flow rates of the fluids to obtain
 10 the entire range of compositions.

11 3. Thermodynamic Modeling

12 The composition of the liquid and vapor phases was determined by an iterative method, using experimental
 13 data of the pressure (p), temperature (T) and feed composition (z_i) for each component i , initially
 14 considering that both components are in the liquid phase. Because the vapor-liquid equilibrium of the
 15 mixture was at high pressure, the fugacity coefficient method (ϕ - ϕ approach) was selected following the
 16 recommendations of Azevedo et al. [42]. To represent the non-ideality of the liquid and vapor phases, as
 17 in previous studies the Soave-Redlich-Kwong equation of state [30] was selected [43, 44]:

$$p = \frac{R \cdot T}{V_m - b} - \frac{a\alpha}{V_m \cdot (V_m + b)} \quad (2)$$

18 The attraction and repulsion parameters of the mixture, $a\alpha$ (Pa·mol²/m⁶) and b (m³/mol), were calculated
 19 with the standard mixing rule (Eqs. 3 and 4). In this equation, a_1 , a_2 , b_1 and b_2 are the parameters for the
 20 pure components and they were calculated from the critical properties (Table 4).

21 Table 4. Properties for the pure components [37]

Compound	T_c/K	p_c/MPa	η/debye	ω	Z_{RA}
Carbon Dioxide	304.21	7.383	0	0.223621	0.27256
Acetone	508.2	4.701	2.88101	0.306527	0.24468

22 The Soave function (α) was calculated (Eq. 5) following the method proposed by Mathias *et al.* [45], valid
 23 for both supercritical and subcritical fluids, and non-polar and polar molecules. In Eq.(5) $T_{r,i}$ is the reduced

1 temperature, η_i is the dipole momentum, and m_i is a polynomial (Eq.6) which depends on the acentric
 2 factor (ω_i)

$$a\alpha = x_1^2 \cdot (a\alpha)_1 + x_2^2 \cdot (a\alpha)_2 + 2 \cdot x_1 \cdot x_2 \sqrt{(a\alpha)_1 \cdot (a\alpha)_2} \cdot (1 - k_{12}) \quad (3)$$

$$b = x_1 b_1 + x_2 b_2 \quad (4)$$

$$\alpha_i = \left[1 + m_i \cdot \left(1 - T_{r,i}^{1/2} \right) - \eta_i (1 - T_{r,i}) (0.7 - T_{r,i}) \right]^2 \quad (5)$$

$$m_i = 0.48508 + 1.55171\omega_i - 0.15613\omega_i^2 \quad (6)$$

3 The values of η_i and ω_i for carbon dioxide and acetone (Table 4) were taken from ref. [37]. The binary
 4 interaction parameter (k_{12}) in Eq.(3) was obtained by the regression of experimental data during the
 5 iteration process, and it was initially set at a guess value of 0.

6 The iterative algorithm was performed using the computer language MATLAB[®]. In a vapor-liquid
 7 equilibrium, the fugacity of each component in the liquid and vapor phases are equal ($f_i^L = f_i^V$), and they
 8 can be expressed in terms of fugacity coefficients ($\phi_i^L x_i p = \phi_i^V y_i p$). The ratio between the fugacity
 9 coefficients is known as the K -value (K_i):

$$K_i = \frac{\phi_i^L}{\phi_i^V} = \frac{y_i}{x_i} \quad (7)$$

10 From the K -values, the vapor quality (q) can be determined by solving the Rachford-Rice equation [46]:

$$\sum_{i=1}^2 \frac{z_i \cdot (K_i - 1)}{1 + q \cdot (K_i - 1)} = 0 \quad (8)$$

11 where z_i is the total mole fraction. To solve this equation, K_i initially takes the value obtained by solving
 12 the Wilson approximation [47].

$$K_i = \frac{p_{c,i}}{p} \cdot \exp \left[5.37 \cdot (1 + \omega_i) \left(1 - \frac{T_{c,i}}{T} \right) \right] \quad (9)$$

1 From the q values, the composition of the liquid (x_i) and vapor (y_i) phases can be obtained according to
 2 the Eqs. (10) and (7), respectively.

$$x_i = \frac{z_i}{1 + q \cdot (K_i - 1)} \quad (10)$$

3 When the phase compositions have been obtained, the fugacity coefficients for both phases are calculated
 4 using the Soave-Redlich-Kwong equation of state, and the K -value for each component is recalculated
 5 using Eq.(7). These new K -values are compared with the initial values and the procedure is repeated until
 6 they reach a certain tolerance, which indicates that the convergence is optimal.

7 Then, the binary interaction parameter of the mixing rule (Eq.3) was obtained by regressing the isothermal
 8 experimental data with the maximum likelihood objective function [48] for the temperature, pressure and
 9 density, according to the expression:

$$OF = \sum_{i=1}^N \left[\left(\frac{p_i^{\text{exp}} - p_i^{\text{cal}}}{\sigma_P} \right)^2 + \left(\frac{T_i^{\text{exp}} - T_i^{\text{cal}}}{\sigma_T} \right)^2 + \left(\frac{\rho_i^{\text{exp}} - \rho_i^{\text{cal}}}{\sigma_\rho} \right)^2 \right] \quad (11)$$

10

11 where superindex *exp* and *cal* means experimental and calculated values, respectively, and σ_P , σ_T and σ_ρ
 12 are the uncertainties estimated for each property. The molar volume obtained from the equation of state
 13 was corrected by the Peneloux correction [31]:

$$V_m = V_{m,SRK} - c \quad (12)$$

14 where V_m is the corrected molar volume, $V_{m,SRK}$ is the molar volume directly calculated by the Soave-
 15 Redlich-Kwong equation of state, and c is the Peneloux volume correction term, calculated for the mixture
 16 as:

$$c = x_1 \cdot c_1 + x_2 \cdot c_2 \quad (13)$$

17 where x_1 and c_i ($i=1,2$) are the mole fraction and volume correction term for the pure components of the
 18 mixture CO₂ (1) + acetone (2). The value of c_i depends on the critical properties and the Rackett parameter
 19 ($Z_{RA,i}$) of the pure components, according to the following equation:

$$c_i = 0.40768 \cdot \frac{R \cdot T_{c,i}}{P_{c,i}} (0.29441 - Z_{RA,i}) \quad (14)$$

Table 4 shows the values of the critical properties and the Rackett parameter for CO₂ and acetone. Finally, the isothermal values of the binary interaction parameter were fitted with temperature using the expression:

$$k_{12} = k_{12}^{(0)} + k_{12}^{(1)} \cdot T/K \quad (15)$$

4. Results and discussion

4.1 Vapor-liquid equilibrium data

Table 5 presents the vapor-liquid equilibrium data for the CO₂ + acetone mixture from (283.15 to 383.15) K, and the composition in mole and mass fractions of CO₂. Table 6 shows the coefficients $k_{12}^{(0)}$ and $k_{12}^{(1)}$ obtained for Eq. (15). As can be seen, the vapor pressure increases almost linearly with the liquid CO₂ mole fraction except near the critical point. As expected, the solubility of CO₂ decreases when the temperature increases. A comparison of the experimental pressure values of this study with the values calculated by the equation of state shows an average relative deviation (ARD%) of 0.14 %, with a maximum relative deviation (MRD%) of 5.0 %.

Table 5. Vapor-liquid equilibrium data for the CO₂ (1) + acetone (2) mixture at different liquid (x_1) and vapor (y_1) mole fractions and the corresponding liquid (w_1^l) and vapor (w_1^v) mass fractions from (283.15 to 383.15) K.

P/MPa	x_1	y_1	w_1^l	w_1^v
$T = 283.15 \text{ K}$				
0.099	0.0236	0.8515	0.0180	0.8131
0.257	0.0674	0.9429	0.0520	0.9261
0.472	0.1258	0.9689	0.0984	0.9594
0.664	0.1768	0.9779	0.1401	0.9711

0.882	0.2334	0.9834	0.1877	0.9782
1.261	0.3291	0.9885	0.2713	0.9849
1.515	0.3909	0.9905	0.3275	0.9875
1.737	0.4435	0.9918	0.3768	0.9892
1.803	0.4591	0.9921	0.3918	0.9896
1.917	0.4856	0.9927	0.4174	0.9904
2.072	0.5211	0.9933	0.4519	0.9912
2.44	0.6033	0.9945	0.5354	0.9928
3.162	0.7567	0.9963	0.7021	0.9952
3.546	0.8339	0.9972	0.7918	0.9963
3.634	0.8508	0.9974	0.8121	0.9965
$T = 293.15 \text{ K}$				
0.121	0.0225	0.8041	0.0172	0.7570
0.311	0.0656	0.9232	0.0506	0.9012
0.508	0.1096	0.9527	0.0854	0.9386
0.699	0.1515	0.9654	0.1193	0.9549
0.959	0.2073	0.9746	0.1656	0.9668
1.511	0.3209	0.9837	0.2639	0.9786
1.792	0.3764	0.9862	0.3141	0.9819

1.848	0.3874	0.9866	0.3243	0.9824
1.868	0.3912	0.9867	0.3275	0.9826
2.181	0.4510	0.9886	0.3840	0.9850
2.313	0.4758	0.9893	0.4079	0.9859
2.456	0.5022	0.9899	0.4333	0.9867
2.690	0.5447	0.9908	0.4755	0.9879
2.726	0.5512	0.9910	0.4820	0.9881
3.673	0.7142	0.9936	0.6544	0.9916
3.824	0.7390	0.9940	0.6824	0.9921
4.020	0.7705	0.9944	0.7181	0.9926
4.307	0.8155	0.9950	0.7701	0.9935
4.592	0.8589	0.9957	0.8218	0.9943
$T = 303.15 \text{ K}$				
0.212	0.0339	0.8254	0.0259	0.7817
0.216	0.0346	0.8284	0.0264	0.7853
0.371	0.0640	0.8993	0.0493	0.8714
0.506	0.0892	0.9255	0.0691	0.9040
0.735	0.1315	0.9482	0.1029	0.9327
0.943	0.1690	0.9591	0.1335	0.9468

1.777	0.3129	0.9774	0.2568	0.9704
2.02	0.3530	0.9799	0.2925	0.9737
2.040	0.3561	0.9801	0.2956	0.9739
2.586	0.4428	0.9839	0.3762	0.9789
2.671	0.4561	0.9844	0.3885	0.9795
2.743	0.4670	0.9848	0.3994	0.9801
2.96	0.4999	0.9858	0.4310	0.9813
4.052	0.6569	0.9893	0.5919	0.9859
4.129	0.6674	0.9895	0.6033	0.9862
4.651	0.7373	0.9906	0.6802	0.9877
5.862	0.8865	0.9931	0.8555	0.9910
$T = 313.15 \text{ K}$				
0.223	0.0275	0.7491	0.0210	0.6935
0.229	0.0286	0.7563	0.0218	0.7016
0.438	0.0624	0.8706	0.0481	0.8362
0.537	0.0781	0.8937	0.0603	0.8644
0.780	0.1165	0.9257	0.0908	0.9043
1.004	0.1509	0.9414	0.1187	0.9241
2.053	0.3048	0.9694	0.2496	0.9601

2.167	0.3208	0.9708	0.2635	0.9618
2.317	0.3415	0.9724	0.2824	0.9639
2.878	0.4170	0.9769	0.3515	0.9698
3.011	0.4344	0.9778	0.3682	0.9709
3.189	0.4574	0.9788	0.3901	0.9722
3.216	0.4610	0.9789	0.3932	0.9724
4.425	0.6091	0.9834	0.5414	0.9782
4.447	0.6117	0.9835	0.5442	0.9783
5.025	0.6778	0.9848	0.6145	0.9801
6.357	0.8199	0.9869	0.7753	0.9828
$T = 323.15 \text{ K}$				
0.236	0.0221	0.6542	0.0169	0.5891
0.245	0.0234	0.6665	0.0178	0.6023
0.513	0.0608	0.8374	0.0468	0.7963
0.568	0.0684	0.8527	0.0527	0.8143
0.825	0.1035	0.8966	0.0804	0.8679
1.062	0.1352	0.9183	0.1060	0.8950
2.308	0.2933	0.9588	0.2392	0.9463
2.335	0.2965	0.9592	0.2423	0.9469

2.519	0.3186	0.9616	0.2619	0.9500
3.076	0.3837	0.9672	0.3206	0.9572
3.443	0.4252	0.9698	0.3595	0.9606
3.460	0.4272	0.9699	0.3610	0.9681
3.646	0.4477	0.9710	0.3809	0.9621
4.780	0.5678	0.9757	0.4988	0.9682
4.791	0.5689	0.9757	0.5001	0.9702
5.428	0.6323	0.9772	0.5658	0.9702

$T = 333.15 \text{ K}$

0.252	0.0172	0.5406	0.0131	0.4714
0.263	0.0185	0.5585	0.0141	0.4894
0.600	0.0598	0.8009	0.0459	0.7531
0.603	0.0601	0.8018	0.0463	0.7543
0.868	0.0920	0.8596	0.0713	0.8227
1.118	0.1214	0.8889	0.0948	0.8584
2.443	0.2696	0.9436	0.2185	0.9269
2.612	0.2874	0.9465	0.2343	0.9307
2.726	0.2994	0.9483	0.2449	0.9330
3.265	0.3551	0.9548	0.2944	0.9412

3.690	0.3976	0.9585	0.3333	0.9460
3.879	0.4158	0.9599	0.3507	0.9478
4.108	0.4380	0.9613	0.3716	0.9496
5.126	0.5328	0.9659	0.4636	0.9554
5.150	0.5350	0.9659	0.4657	0.9555
5.860	0.5974	0.9677	0.5293	0.9579
$T = 343.15 \text{ K}$				
0.272	0.0126	0.4091	0.0096	0.3441
0.283	0.0138	0.4321	0.0105	0.3657
0.613	0.0497	0.7296	0.0382	0.6719
0.631	0.0517	0.7371	0.0397	0.6799
0.911	0.0816	0.8137	0.0631	0.7679
2.572	0.2488	0.9246	0.2006	0.9029
2.899	0.2796	0.9313	0.2275	0.9114
2.943	0.2837	0.9320	0.2311	0.9123
3.445	0.3301	0.9394	0.2719	0.9215
3.907	0.3714	0.9443	0.3093	0.9278
4.577	0.4292	0.9494	0.3633	0.9344
4.751	0.4439	0.9504	0.3772	0.9357

5.487	0.5049	0.9538	0.4359	0.9399
5.503	0.5062	0.9538	0.4372	0.9400
6.321	0.5709	0.9561	0.5020	0.9428
$T = 353.15 \text{ K}$				
0.294	0.0079	0.2616	0.0060	0.2119
0.306	0.0090	0.2884	0.0068	0.2352
0.663	0.0440	0.6600	0.0337	0.5956
0.687	0.0463	0.6712	0.0355	0.6077
0.952	0.0719	0.7576	0.0555	0.7034
1.222	0.0974	0.8070	0.0757	0.7604
2.696	0.2303	0.9014	0.1850	0.8740
3.042	0.2599	0.9100	0.2104	0.8847
3.185	0.2719	0.9130	0.2208	0.8884
3.617	0.3080	0.9205	0.2525	0.8978
4.111	0.3482	0.9269	0.2884	0.9059
5.039	0.4206	0.9349	0.3552	0.9159
5.849	0.4816	0.9392	0.4135	0.9214
5.862	0.4826	0.9392	0.4144	0.9214
6.812	0.5510	0.9419	0.4822	0.9248

$T = 363.15 \text{ K}$				
0.751	0.0414	0.5989	0.0317	0.5308
1.037	0.0664	0.7025	0.0512	0.6418
3.413	0.2604	0.8903	0.2108	0.8603
3.460	0.2640	0.8914	0.2140	0.8617
3.828	0.2919	0.8987	0.2383	0.8707
5.038	0.3806	0.9141	0.3180	0.8898
5.080	0.3836	0.9145	0.3208	0.8903
5.435	0.4087	0.9173	0.3440	0.8938
7.162	0.5000	0.8949	0.4314	0.8660
$T = 373.15 \text{ K}$				
0.835	0.0375	0.5276	0.0287	0.4584
1.128	0.0610	0.6413	0.0469	0.5753
3.482	0.2385	0.8595	0.1918	0.8226
3.740	0.2568	0.8663	0.2075	0.8308
4.080	0.2806	0.8739	0.2281	0.8400
5.418	0.3713	0.8930	0.3091	0.8635
5.569	0.3812	0.8944	0.3182	0.8652
5.859	0.4001	0.8969	0.3357	0.8682

7.849	0.4998	0.8790	0.4311	0.8463
$T = 383.15 \text{ K}$				
0.922	0.0331	0.4491	0.0253	0.3818
1.228	0.0558	0.5750	0.0428	0.5063
4.001	0.2487	0.8371	0.2006	0.7957
4.287	0.2675	0.8443	0.2168	0.8043
5.748	0.3602	0.8681	0.2990	0.8330
6.279	0.3927	0.8732	0.3289	0.8391
6.560	0.4000	0.8612	0.3356	0.8246
8.715	0.4996	0.8494	0.4311	0.8104

Expanded uncertainties ($k=2$) are $U(T) = 0.05 \text{ K}$; $U(p < 1 \text{ MPa}) = 0.001 \text{ MPa}$;
 $U(1 < p < 5 \text{ MPa}) = 0.005 \text{ MPa}$; $U(p > 5 \text{ MPa}) = 0.008 \text{ MPa}$ and $U(x_i) = U(y_i) = 0.0005$

Table 6. Coefficients of the binary interaction parameter k_{12} for the CO_2 (1) +acetone (2) mixture, Eq.(15)

Coefficient	$k_{12}^{(0)}$	$k_{12}^{(1)}$
Value	0.01181	-3.6×10^{-5}

For purposes of comparison, Figs. (4-6) show some of the data reported by other authors together with the experimental and calculated values of this study at (303.15, 333.15 and 373.15) K, respectively.

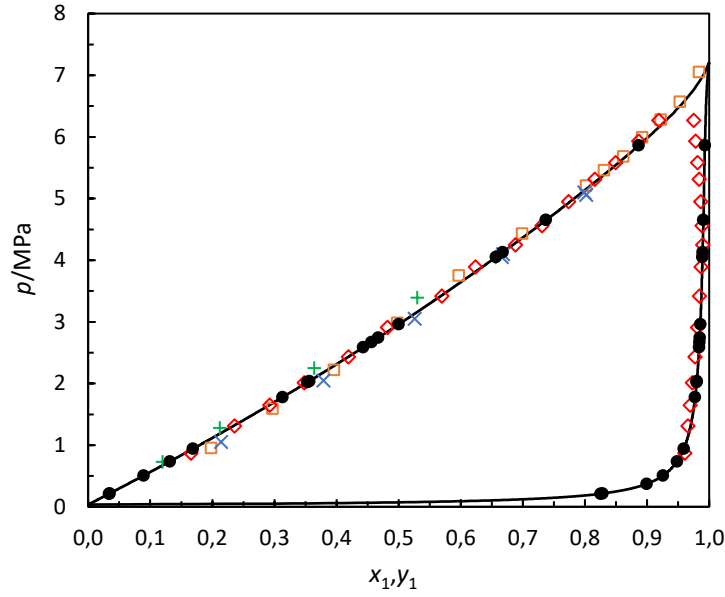


Figure 4. P - x - y phase equilibrium diagram for the CO_2 (1) + acetone (2) mixture at 303.15 K: solid line, liquid and vapor composition calculated with SRK; $\bullet$, this study; $\diamond$, Chang et al.[14]; $\times$, Bamberger and Maurer [15]; $+$, Stievano and Elvassore [17]; $\square$, Chiu et al.[19].

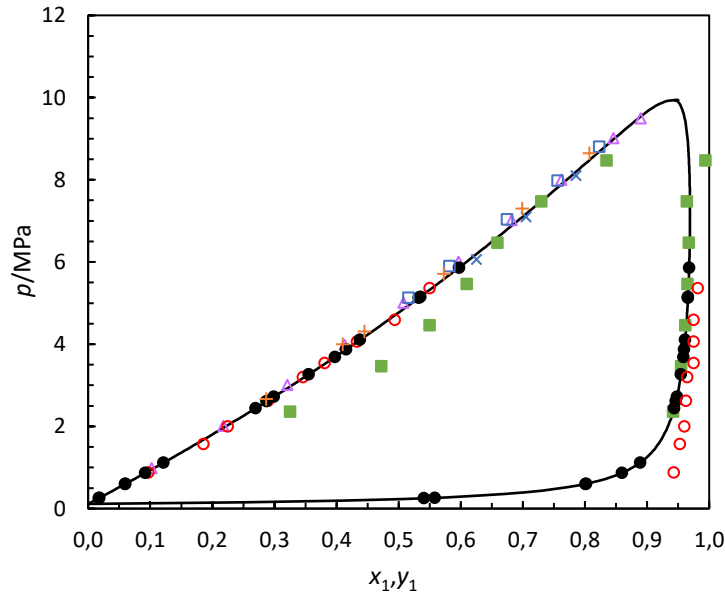


Figure 5. P - x - y phase equilibrium diagram for the CO_2 (1) + acetone (2) mixture at 333.15 K: solid line, liquid and vapor composition calculated with SRK; $\bullet$, this study; $\triangle$, Adrian and Maurer [7]; $\times$, Bamberger and Maurer [15]; $\blacksquare$, Han et al. [10]; $\circ$, Lei et al.[5]; $\square$, Hsieh and Vrabec [4]; $+$, Sato et al.[21]

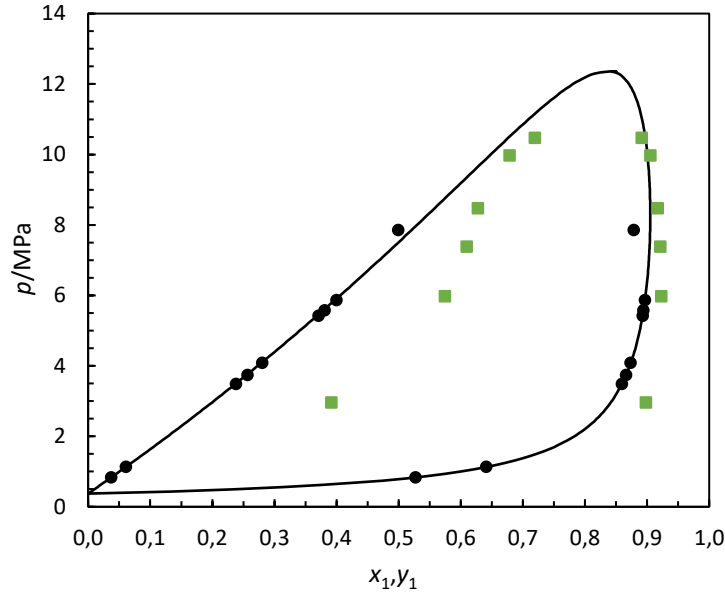


Figure 6. P - x - y phase equilibrium diagram for the CO_2 (1) + acetone (2) mixture at 373.15 K: solid line, liquid and vapor composition calculated with SRK; $\bullet$, this study; $\blacksquare$, Han et al.[10].

The deviations were evaluated by calculating the ARD% and MRD% (Table 7) for the liquid phase composition, and for the vapor phase when this was available. The deviations of the liquid phase composition in refs. [1,4,5,7,12,15,19,20,23] were low (below 5 %), while in refs. [6,11,21] they were below 7 %. However, in refs. [10,17] deviations were as high as 30 %, although at a temperature of 393.15 K, which was not measured in this study. A similar discrepancy with ref. [10] has already been mentioned by Hsieh and Vrabec [4] at 333.15 K and 353.15 K. We confirm this discrepancy in this study (Fig. 5) and affirm that it remains at 373.15 K (Fig. 6). For the vapor phase composition, most of the deviations were lower than 1 %, and the highest deviations were again found in comparison to Han et al. [10], reaching 12 % at 393.15 K.

Table 7. Comparison between the data reported in the literature and values calculated with the Redlich-Kwong-Soave equation of state for the CO_2 + acetone mixture, in terms of average (ARD%) and maximum (MRD%) relative deviation

Reference	T/K	ARD% ⁽¹⁾ (MRD% ⁽²⁾)	ARD% ⁽¹⁾ (MRD% ⁽²⁾)
		x_1	y_1

[1]	298.15	0.79 (1.3)	0.25 (0.42)
	313.15	1.1 (3.6)	0.30 (0.48)
[4]	313.15	1.8 (2.7)	-
	333.15	2.8 (3.3)	-
	353.15	2.8 (4.2)	-
[5]	298.2	2.8 (7.0)	0.25 (1.1)
	313.2	2.2 (5.2)	0.51 (1.2)
	333.2	1.8 (6.8)	2.7 (8.7)
[6]	258.3	3.9 (9.1)	-
	273.0	2.6 (9.2)	-
	288.1	6.1 (20)	-
	298.2	5.0 (25)	-
[7]	313.15	1.5 (3.4)	-
	333.15	3.5 (9.8)	-
[10]	333.15	9.7 (21)	0.63 (3.3)
	353.15	15 (31)	1.7 (3.6)
	373.15	25 (49)	6.5 (14)
	393.15	30 (36)	12 (30)
[11]	298.15	6.9 (7.3)	0.92 (1.2)
[12]	291.15	4.5 (8.9)	0.76 (2.1)
	298.15	1.6 (3.3)	0.73 (2.9)
	303.15	1.2 (5.7)	0.66 (1.9)
	308.15	2.3 (17)	0.80 (2.5)
	313.15	2.7 (18)	0.75 (1.5)
[15]	303.0	3.4 (12)	-
	323.0	3.4 (11)	-
	332.9	1.2 (1.8)	-
[17]	291.15	17 (31)	-

	303.15	7.6 (8.9)	-
	313.15	3.9 (5.9)	-
	323.15	11 (13)	-
	291.15	4.9 (18)	-
	298.15	3.1 (17)	-
[19]	303.15	2.6 (14)	-
	308.15	2.0 (9.6)	-
	313.15	1.4 (7.0)	-
	308.15	0.07 (0.13)	0.48 (0.95)
[20]	313.15	2.5 (4.4)	0.82 (1.0)
	333.15	3.6 (7.3)	0.32 (0.64)
	313.11	2.6 (4.7)	-
[21]	333.19	2.4 (4.3)	-
	353.18	5.3 (16)	-
[23]	323.0	3.5 (5.4)	0.32 (0.45)
[24]	298.15	4.5 (13)	-
	303	2.9 (5.1)	-
[27]	313	2.0 (3.8)	-
	323	2.7 (5.9)	-

$$^{(1)}ARD\% = \frac{100}{N} \sum_{i=1}^N \frac{|\xi_{RKs} - \xi_{lit}|}{\xi_{lit}}$$

$$^{(2)}MRD\% = 100 \cdot \max \left(\frac{|\xi_{RKs} - \xi_{lit}|}{\xi_{lit}} \right)$$

ξ is the mole fraction for liquid (x) and vapor (y) phases. Subscript SRK and lit refer to the calculated by Redlich-Kwong-Soave EoS and experimental value, respectively, and N the number of data

Finally, the experimental values of vapor pressure (p /MPa) were correlated with the temperature (T /K) and CO₂ liquid mole fraction (x_1) using a polynomial equation to provide a simple equation that can be used directly in simulations or calculations.

$$p = \sum_{i=0}^3 (a_i \cdot x_1^i) + \sum_{j=0}^2 (b_j \cdot x_1^j) \cdot T + \sum_{k=0}^1 (c_k \cdot x_1^k) \cdot T^2 \quad (16)$$

The values of the coefficients a_i , b_j and c_k are shown in Table 8. The ADR% of the correlation was 0.70 % with a maximum deviation of 4.8 %.

Table 8. Coefficients for the vapor pressure of the CO₂ (1) + acetone (2) mixture fitted to Eq. (16)

i/j/k	a_i	b_j	c_k
0	3.225	-0.02289	4.07×10^{-5}
1	1.91	-0.05978	2.333×10^{-4}
2	-13.72	0.04865	-
3	0.5746	-	-
ADR%		0.70 %	
MDR%		4.8%	

$$(1)ARD\% = \frac{100}{N} \sum_{i=1}^N \frac{|p_{cal}-p_{exp}|}{p_{exp}}$$

$$(2)MRD\% = 100 \cdot \max \left(\frac{|p_{cal}-p_{exp}|}{p_{exp}} \right)$$

4.2. Liquid density data

Experimental liquid densities of the CO₂ + acetone mixture are shown in Table 9, together with the corresponding composition, the CO₂ mole fraction and the measured pressure. Measurements in this study were carried out along isotherms from (283.15 to 353.15) K in steps of 5 K.

Table 9. Density for the CO₂ (1) + acetone (2) mixture at different liquid mole fractions (x_1) and the corresponding saturation pressure (P /MPa) from (283.15 to 353.15) K

x_1	$\rho/\text{kg}\cdot\text{m}^{-3}$	p/MPa	x_1	$\rho/\text{kg}\cdot\text{m}^{-3}$	p/MPa
$T = 283.15 \text{ K}$			$T = 288.15 \text{ K}$		
0.255	835.0	1.01	0.255	828.8	1.12
0.439	858.8	1.70	0.439	851.8	1.91
0.665	902.7	2.65	0.665	890.7	3.01
0.702	906.9	2.83	0.702	894.3	3.22
0.739	909.1	3.02	0.739	896.4	3.45
0.750	910.2	3.07	0.750	896.8	3.50
0.795	915.0	3.32	0.795	900.2	3.79
0.814	915.5	3.38	0.814	901.1	3.84
$T = 293.15 \text{ K}$			$T = 298.15 \text{ K}$		
0.059	797.9	0.32	0.059	792.1	0.33
0.225	814.1	1.04	0.225	807.7	1.14
0.255	822.2	1.23	0.344	817.2	1.79
0.416	836.4	2.03	0.416	828.8	2.24
0.439	843.9	2.13	0.439	835.6	2.36
0.499	848.2	2.46	0.499	839.6	2.72
0.665	878.6	3.38	0.665	866.2	3.75
0.702	881.2	3.62	0.702	868.4	4.02
0.739	882.8	3.87	0.739	868.8	4.30
0.750	882.5	3.93	0.750	868.5	4.37
0.795	883.5	4.26	0.795	865.4	4.74
0.814	883.5	4.32	0.814	865.0	4.81
$T = 303.15 \text{ K}$			$T = 308.15 \text{ K}$		

0.059	786.3	0.35	0.059	780.5	0.37
0.225	801.4	1.24	0.225	795.0	1.37
0.344	809.1	1.96	0.344	803.5	2.14
0.416	821.5	2.46	0.416	813.9	2.69
0.499	830.3	2.99	0.439	820.8	2.84
0.702	854.4	4.44	0.499	822.4	3.27
0.732	855.7	4.67	0.732	834.5	5.11
0.739	855.4	4.74	0.750	835.2	5.28
0.750	854.4	4.82			
0.814	854.8	5.30			
$T = 313.15\text{ K}$			$T = 318.15\text{ K}$		
0.059	774.5	0.40	0.059	768.6	0.44
0.225	788.2	1.46	0.225	781.2	1.59
0.255	794.6	1.74	0.255	787.3	1.89
0.344	796.9	2.32	0.344	789.7	2.51
0.416	806.2	2.93	0.416	798.4	3.17
0.439	812.6	3.08	0.439	804.2	3.33
0.499	813.8	3.56	0.499	805.4	3.85
0.685	816.6	5.09	0.665	812.2	5.31
0.750	807.6	5.74	0.732	812.1	6.01
0.814	794.8	6.31	0.739	812.3	6.10
$T = 323.15\text{ K}$			$T = 328.15\text{ K}$		
0.059	762.6	0.48	0.059	756.5	0.53
0.225	774.2	1.71	0.225	767.2	1.85

0.255	780.0	2.04	0.255	772.5	2.20
0.344	782.3	2.71	0.344	774.8	2.91
0.416	790.4	3.41	0.416	782.2	3.66
0.439	795.6	3.59	0.439	786.8	3.86
0.499	797.0	4.15	0.499	787.8	4.45
0.665	802.5	5.72	0.685	789.1	6.35
0.732	801.3	6.47	0.732	779.2	6.93
0.739	796.5	6.56			
$T = 333.15 \text{ K}$			$T = 338.15 \text{ K}$		
0.059	749.9	0.58	0.059	743.1	0.65
0.225	759.9	1.99	0.225	752.5	2.14
0.255	764.9	2.36	0.255	757.3	2.53
0.344	767.0	3.12	0.344	759.2	3.34
0.416	773.7	4.13	0.416	765.3	4.19
0.439	777.8	4.13	0.439	767.8	4.41
0.499	778.4	4.76	0.499	768.7	5.08
0.665	776.7	6.55	0.665	769.2	7.22
$T = 343.15 \text{ K}$			$T = 348.15 \text{ K}$		
0.059	736.3	0.71	0.059	729.0	0.79
0.225	744.8	2.29	0.225	737.0	2.45
0.255	749.3	2.71	0.255	741.1	2.89
0.344	751.0	3.57	0.344	742.6	3.80
0.416	755.8	4.46	0.416	747.2	4.74
0.439	757.4	4.69	0.439	748.6	4.99

0.499	758.1	5.40	0.685	749.0	8.12
0.665	759.7	7.67			
<i>T</i> = 353.15 K					
0.059	721.7	0.87			
0.225	729.0	2.62			
0.255	732.7	3.08			
0.344	734.1	4.03			
0.416	737.3	5.02			
0.439	738.7	5.28			

Expanded uncertainties (*k*=2) are $U(T) = 0.05$ K; $U(p) = 0.03$ MPa; $U(\rho) = 0.9$ kg/m³ and $U(x_i) = U(y_i) = 0.004$.

In order to evaluate the density of the liquid phase calculated by the Soave-Redlich-Kwong equation of state and using the Peneloux volume correction term, the experimental density values were compared with those calculated with the model. For the 142 data items compared, the ARD% obtained was 0.70 % and the maximum deviation (MRD%) was 7.0 % (only 5 data items have deviations higher than 3 %).

The density data ($\rho/\text{kg}\cdot\text{m}^{-3}$) were fitted with temperature (T/K) and the CO₂ mole fraction (x_1) using a polynomial equation:

$$\rho = \sum_{i=0}^3 (a_i \cdot x_1^i) + \sum_{j=0}^2 (b_j \cdot x_1^j) \cdot T + \sum_{k=0}^1 (c_k \cdot x_1^k) \cdot T^2 \quad (17)$$

The fitted values of the coefficients a_i , b_j and c_k are shown in Table 10. The ADR% for the correlation was 0.31 %, with a maximum relative deviation of 3.0 %.

Table 10. Coefficients for the density of the CO₂ (1) + acetone (2) mixture fitted to Eq. (17)

i/j/k	a_i	b_j	c_k

0	389.8	3.544	-0.007418
1	2216	-13.55	0.02091
2	995.7	-2.362	-
3	-264	-	-
ADR%		0.31 %	
MDR%		3.0 %	

$$(1)ARD\% = \frac{100}{N} \sum_{i=1}^N \frac{|\rho_{cal} - \rho_{exp}|}{\rho_{exp}}$$

$$(2)MRD\% = 100 \cdot \max \left(\frac{|\rho_{cal} - \rho_{exp}|}{\rho_{exp}} \right)$$

Density values calculated with Eq. (17) were compared with reported data (Figs. 7-9) at the different temperatures. In general, our data agree with refs. [11,12,17,21], with an ADR% below 5 %. References [7,10] show an ADR% lower than 9 % with our values, although with deviations up to 36 % in [7] for the data near the critical point. In the case of reference [16], the authors measured the dependence of density on pressure at 323.15 K for different CO₂ mole fractions. The comparison with our densities considered only the data for each composition at the lowest pressure so that the conditions were as similar as possible. The ADR% was 8.2 % with a maximum deviation of 31 %. Again, the highest deviations appear at high compositions and pressures that are near the critical point. Table 11 summarizes the deviations between the density data of this study and the data reported in the literature.

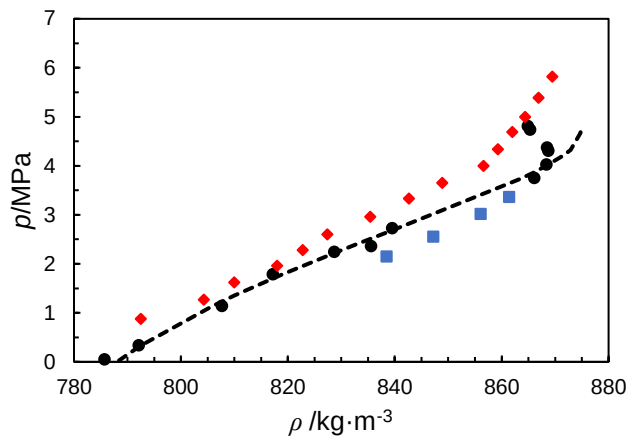


Figure 7. Liquid density (ρ) versus pressure (p) of the CO₂ + acetone mixture at 298.15 K: ●, this study; ■, Kato et al. [11]; ◆, Chang et al. [14]; ---, calculated by SRK.

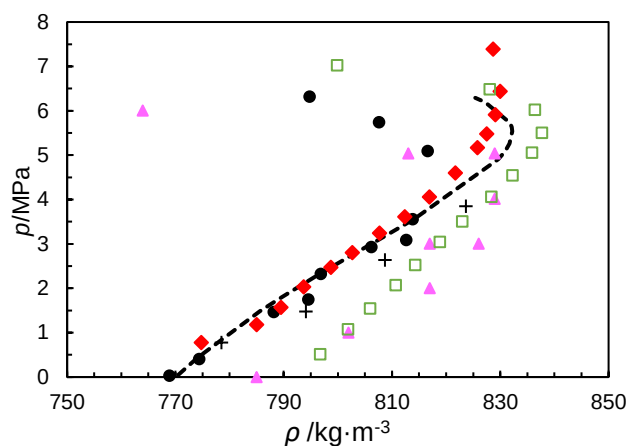


Figure 8. Liquid density (ρ) versus pressure (p) of the CO₂ + acetone mixture at 313.15 K: ●, this study; ◆, Chang et al. [16]; +, Stievano and Elsvassore [17]; ▲, Adrian and Maurer [7]; □, Aida et al. [28], ---, calculated by SRK.

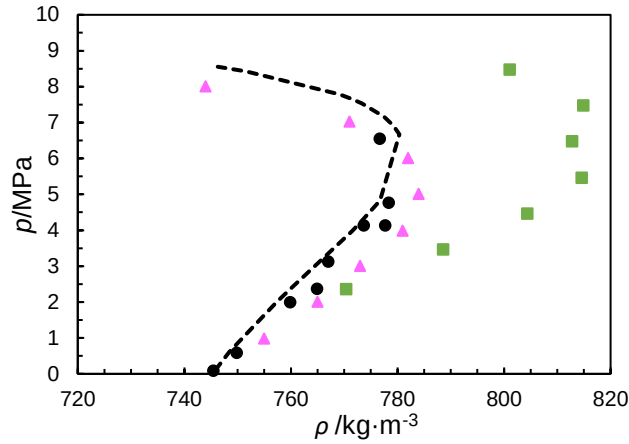


Figure 9. Liquid density (ρ) versus pressure (p) of the CO₂ + acetone mixture at 333.15 K: ●, this study; ▲, Adrian and Maurer [7]; ■, Han et al. [10], ---, calculated by SRK.

Table 11. Comparison between the data reported in the literature and values calculated with eq. (17) for the density of the liquid phase of CO₂ + acetone mixture, in terms of average (ARD%) and maximum (MRD%) relative deviation

Reference	T/K	ARD% ⁽¹⁾ (MRD% ⁽²⁾)
[7]	313.15	5.8 (36)
	333.15	4.2 (23)
[10]	333.15	3.5 (5.4)
	353.15	8.1 (10)
	373.15	6.2 (9.1)
	393.15	8.8 (9.5)
[11]	298.15	1.1 (1.3)
[12-14]	291.15	4.1 (6.4)
	298.15	0.97 (1.6)
	303.15	1.0 (2.0)
	308.15	1.3 (5.0)
	313.15	0.63 (2.6)

[16]	323.15	8.2 (31)
[17]	291.15	0.51 (0.90)
	303.15	0.56 (0.81)
	313.15	0.67 (1.0)
	323.15	1.6 (3.4)
[27]	313.15	2.5 (12)

$$(1)ARD\% = \frac{100}{N} \sum_{i=1}^N \frac{|\rho_{cal} - \rho_{exp}|}{\rho_{exp}}$$

$$(2)MRD\% = 100 \cdot \max \left(\frac{|\rho_{cal} - \rho_{exp}|}{\rho_{exp}} \right)$$

4.3. Excess enthalpy data

The excess molar enthalpies of the CO₂ + acetone system as a function of the CO₂ molar fraction were determined at 283.3 K and under pressure from (9.00 to 13.87) MPa and at 298.3 K and under pressure from (9.28 to 11.24) MPa. The experimental data are reported in Table 12 and represented in Figs. 10 and 11. Exothermic excess enthalpies were observed with minimum values located in the CO₂-rich region in each temperature and pressure condition. For a given mole fraction and pressure, mixing enthalpies are more exothermic as the temperature increases. And for a given mole fraction and temperature, mixing enthalpies are slightly less exothermic as the pressure increases. The most exothermic H^E values were observed at 9.28 MPa and 298.3 K. A minimum value of (-1240) J·mol⁻¹ was reached for a CO₂ mole fraction of 0.583.

Table 12. Excess molar enthalpies of the CO₂ (1) + acetone (2) system as a function of the CO₂ molar fraction (x_1), pressure and temperature

p	x ₁	<i>u</i> (x ₁) ^a	H ^E	<i>u</i> (H ^E) ^b
MPa			J·mol ⁻¹	
<i>T</i> = 283.30 K				
8.84	0.0801	0.0005	-204	14

8.78	0.0894	0.0005	-221	13
9.11	0.0898	0.0005	-189	11
9.12	0.1403	0.0008	-332	14
8.99	0.149	0.001	-360	16
9.01	0.149	0.001	-328	15
9.03	0.164	0.001	-385	12
9.12	0.167	0.001	-395	16
8.92	0.189	0.001	-428	20
8.99	0.196	0.001	-469	19
9.08	0.246	0.001	-555	24
8.93	0.317	0.002	-670	20
9.02	0.328	0.002	-704	28
9.01	0.378	0.002	-794	16
9.01	0.440	0.003	-868	18
8.96	0.494	0.003	-909	35
8.79	0.582	0.003	-988	40
8.93	0.582	0.003	-985	32
9.00	0.583	0.003	-963	12
8.95	0.611	0.004	-977	18

8.96	0.653	0.004	-962	20
8.99	0.653	0.004	-972	26
9.02	0.736	0.004	-895	20
9.12	0.737	0.004	-900	40
9.05	0.807	0.005	-780	29
9.08	0.807	0.005	-739	13
9.04	0.823	0.005	-741	17
9.08	0.848	0.005	-668	22
9.08	0.875	0.005	-578	28
8.96	0.893	0.005	-504	16
8.99	0.898	0.005	-485	30
8.93	0.918	0.006	-400	32
9.01	0.949	0.006	-260	20
11.01	0.0919	0.0006	-189	13
11.08	0.1189	0.0007	-253	12
11.13	0.134	0.001	-272	2
11.08	0.161	0.001	-352	21
10.95	0.223	0.001	-496	14
11.03	0.253	0.002	-551	21

10.96	0.264	0.002	-570	15
11.09	0.264	0.002	-550	14
11.04	0.301	0.002	-643	30
10.95	0.323	0.002	-667	23
11.01	0.323	0.002	-662	21
10.97	0.364	0.002	-745	16
10.95	0.417	0.003	-804	10
10.95	0.417	0.003	-799	23
10.93	0.462	0.003	-868	28
10.95	0.518	0.003	-874	21
10.99	0.518	0.003	-906	35
10.92	0.589	0.004	-923	9
10.99	0.589	0.004	-928	10
10.96	0.632	0.004	-910	12
11.01	0.651	0.004	-933	52
10.99	0.682	0.004	-885	16
10.96	0.741	0.004	-824	14
11.02	0.775	0.005	-783	15
10.87	0.788	0.005	-747	12

11.12	0.837	0.005	-629	15
11.02	0.838	0.005	-639	15
11.03	0.878	0.005	-517	25
11.01	0.891	0.005	-464	22
11.09	0.896	0.005	-445	22
11.03	0.902	0.005	-438	25
11.09	0.919	0.006	-371	23
13.88	0.125	0.001	-221	17
13.90	0.125	0.001	-214	15
13.85	0.137	0.001	-234	12
13.90	0.152	0.001	-270	12
13.98	0.152	0.001	-260	13
13.83	0.242	0.001	-518	15
13.85	0.264	0.002	-560	15
13.88	0.264	0.002	-549	15
13.91	0.264	0.002	-569	16
13.90	0.291	0.002	-613	17
13.85	0.323	0.002	-646	21
13.89	0.323	0.002	-661	14

13.87	0.365	0.002	-717	16
13.75	0.417	0.003	-785	15
13.88	0.418	0.003	-771	16
13.86	0.489	0.003	-856	16
13.89	0.589	0.004	-885	18
13.89	0.683	0.004	-850	14
13.86	0.741	0.004	-801	14
13.90	0.782	0.005	-732	12
13.87	0.811	0.005	-669	11
13.87	0.834	0.005	-613	13
13.88	0.852	0.005	-563	12
13.86	0.878	0.005	-485	15
13.86	0.935	0.006	-277	12
13.86	0.945	0.006	-240	13
$T = 293.30 \text{ K}$				
9.20	0.0804	0.0005	-205	18
9.25	0.1226	0.0007	-317	25
9.06	0.1488	0.0009	-397	20
9.24	0.218	0.001	-623	30

9.31	0.259	0.002	-700	34
9.34	0.259	0.002	-705	26
9.27	0.259	0.002	-688	20
9.26	0.318	0.002	-881	42
9.30	0.412	0.003	-1071	51
9.31	0.412	0.003	-1007	33
9.39	0.412	0.003	-1024	39
9.23	0.412	0.003	-1002	25
9.31	0.482	0.003	-1109	26
9.21	0.483	0.003	-1146	55
9.27	0.583	0.004	-1234	50
9.28	0.583	0.004	-1240	29
9.32	0.5832	0.0035	-1229	50
9.23	0.677	0.004	-1234	44
9.38	0.737	0.004	-1214	37
9.24	0.737	0.004	-1211	53
9.42	0.848	0.005	-934	21
9.35	0.849	0.005	-942	37
9.20	0.894	0.005	-687	30

11.27	0.0778	0.0005	-220	20
11.28	0.1124	0.0007	-315	30
11.21	0.152	0.001	-418	17
11.29	0.152	0.001	-426	29
11.39	0.161	0.001	-416	15
11.29	0.164	0.001	-433	10
11.22	0.181	0.001	-499	17
11.19	0.193	0.001	-527	21
11.22	0.193	0.001	-515	33
11.21	0.238	0.001	-639	22
11.16	0.264	0.002	-684	34
11.23	0.264	0.002	-678	33
11.39	0.264	0.002	-672	24
11.15	0.291	0.002	-777	27
11.39	0.324	0.002	-766	29
11.12	0.350	0.002	-866	21
11.09	0.417	0.003	-962	37
11.12	0.417	0.003	-978	42
11.21	0.418	0.003	-951	48

11.24	0.418	0.003	-958	35
11.30	0.418	0.003	-927	36
11.09	0.488	0.003	-1062	42
11.32	0.489	0.003	-1035	23
11.35	0.489	0.003	-1084	42
11.18	0.518	0.003	-1068	18
11.07	0.589	0.004	-1122	47
11.12	0.589	0.004	-1120	13
11.13	0.589	0.004	-1124	25
11.30	0.589	0.004	-1090	46
11.10	0.682	0.004	-1102	41
11.10	0.682	0.004	-1113	13
11.17	0.683	0.004	-1108	19
11.36	0.683	0.004	-1081	19
11.36	0.683	0.004	-1100	41
11.21	0.688	0.004	-1120	23
11.21	0.742	0.004	-1047	44
11.13	0.811	0.005	-931	40
11.23	0.811	0.005	-898	45

11.24	0.811	0.005	-933	27
11.22	0.847	0.005	-788	59
11.40	0.852	0.005	-784	21
11.32	0.896	0.005	-587	20
11.38	0.896	0.005	-581	30
11.31	0.910	0.006	-507	30
11.32	0.920	0.006	-440	30
11.31	0.958	0.006	-224	15
11.33	0.961	0.006	-196	15

^a $u(x_1)$ is the uncertainty in the molar fraction calculated from the uncertainties in the fluid flow rates.

^b $u(H^E)$ is the uncertainty in the experimental excess molar enthalpies.

Expanded uncertainties ($k=2$) are $u(T) = 0.06$ K and $u(p) = 40$ kPa.

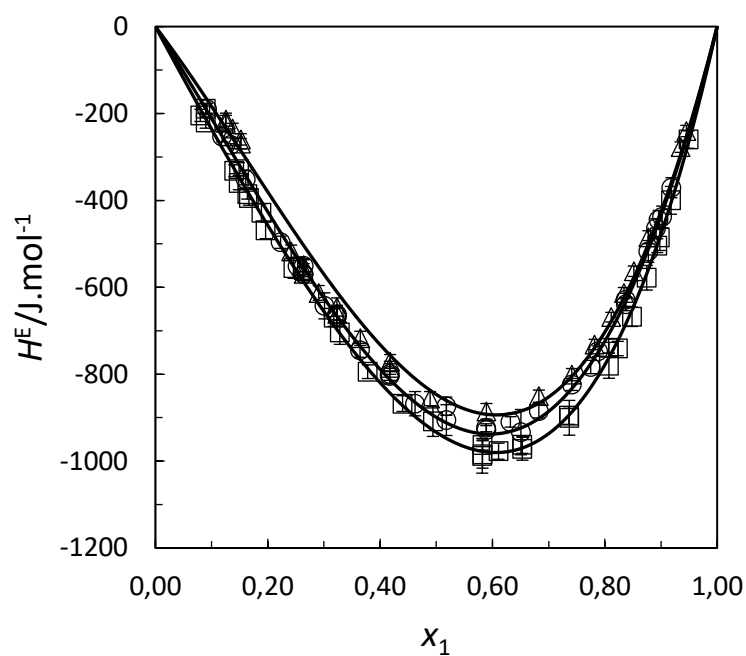


Figure 10. Excess molar enthalpies (H^E) versus CO_2 composition (x_1) of the binary system CO_2 (1) + acetone (2) at 283.15 K and: $\square$, 9.00 MPa; $\circ$, 11.01 MPa; $\triangle$, 13.87 MPa; —, calculated using Eq. (18) and coefficients given in Table 13.

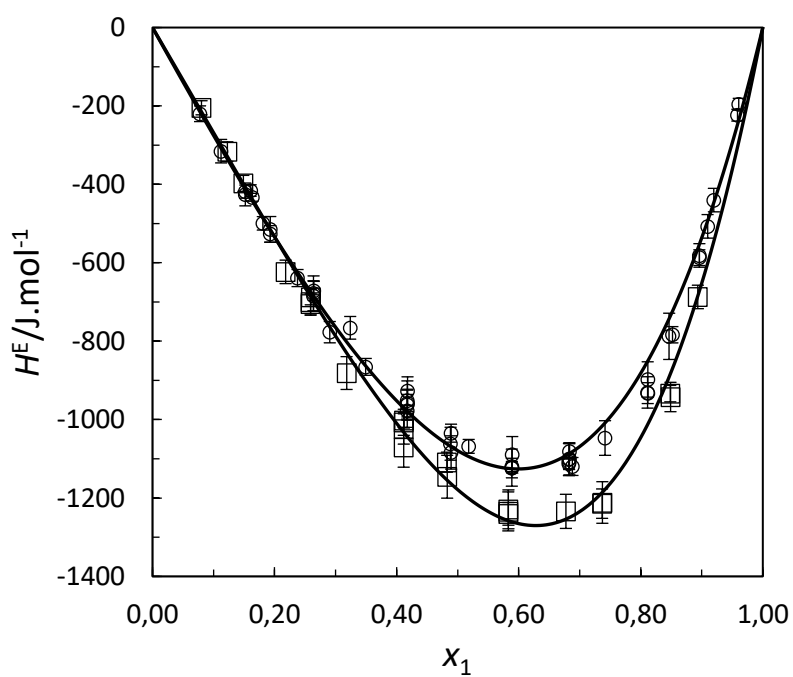


Figure 11. Excess molar enthalpies (H^E) versus CO₂ composition (x_1) of the binary system CO₂ (1) + acetone (2) at 298.15 K and: □, 9.28 MPa; ○, 11.24 MPa; —, calculated using Eq. (18) and coefficients given in Table 13.

Excess molar enthalpies were fitted to a Redlich-Kister polynomial equation:

$$H^E = x_1 \cdot (1 - x_1) \cdot \sum_{i=0}^n A_i \cdot (1 - 2 \cdot x_1)^i \quad (18)$$

where A_i are adjustable parameters. The regression of these parameters was performed using the Minuit software [49]. The minimize function method was used to optimize these parameters using the objective function F expressed in Eq.(19):

$$F = \sum_{i=1}^N \left(\frac{H_i^{E,\text{exp}} - H_i^{E,\text{cal}}}{H_i^{E,\text{exp}}} \right)^2 \quad (19)$$

where $H_i^{E,\text{exp}}$ and $H_i^{E,\text{cal}}$ are the experimental and calculated excess enthalpies; N is the number of experimental data points. The resulting A_i parameters together with the average relative deviation (ADR%) of the correlation are listed in Table 13.

Table 13. Coefficients and average relative deviation for the representation of H^E of the CO₂ (1) + acetone (2) system using Redlich-Kister Eq. (18)

T	p	A ₀	A ₁	A ₂	ARD% ^a
K	MPa	J·mol ⁻¹			
283.30	9.00	-3734.9	1673.3	-353.22	2.2
	11.01	-3596.7	1551.6	4.4128	1.7
	13.87	-3386.4	1680.3	0.00	5.4
298.30	9.28	-4730.8	2772.0	-693.18	2.8

11.24 -4316.9 1812.0 -295.06 3.4

$$^a \text{ARD}\% = \frac{100}{N} \sum_{i=0}^N \left| \frac{H_{RK} - H_{exp}}{H_{exp}} \right|$$

The Soave-Redlich-Kwong equation of state, with the binary interaction parameter obtained in the current study, estimates values lower than the experimental data, with average deviations up to 43 % and 28 % at 283.3 K and 298.3 K, respectively, which indicates that the Soave-Redlich-Kwong equation of state, with the binary interaction parameter obtained in this study, cannot properly calculate the excess enthalpy of the CO₂ + acetone mixture.

5. Conclusions

Vapor-liquid equilibrium data for the CO₂ + acetone mixture was obtained in the temperature range from (283.15 to 383.15) K and pressures up to 8.7 MPa, with an experimental device based on a synthetic and static method. The procedure was validated with pure CO₂. The density data of the liquid phase for the CO₂ + acetone mixture were measured with a vibrating-tube densimeter, in a temperature range from (283.15 to 353.15) K, compositions from 0.06 to 0.82 in the CO₂ mole fraction, and sufficient pressure to ensure the liquid state of the sample. The data obtained were used to model the vapor-liquid equilibrium by applying a Soave-Redlich-Kwong equation of state, with the classic standard mixing rule, the Boston-Mathias Soave function, and the Peneloux volume correction term. Both the experimental and calculated data were compared with data from the literature, and most of the reported data were in good agreement. The result is a simple model for estimating the vapor-liquid equilibrium of the CO₂ + acetone mixture in a wide range of compositions and temperatures, which can be used in a variety of applications. Besides, the experimental pressures and densities were correlated with the temperature and CO₂ mole fraction using polynomial equations. Finally, excess molar enthalpy data for the CO₂ + acetone mixture were obtained at (283.30 and 298.30) K and pressures (9.00 to 13.87) MPa and (9.28 to 11.24) MPa, respectively, using a flow calorimetric technique designed specifically for sub-ambient temperatures. The lowest values of the exothermic excess enthalpies were found in the CO₂-rich region for these mixtures in the temperature and pressure conditions studied. The excess molar enthalpies reported here were correlated using a Redlich-Kister polynomial equation. All these new experimental data of vapor-liquid equilibrium, density,

1 and excess enthalpy will be used in a forthcoming study on the development of thermodynamic models
2 that are representative of the CO₂ + acetone mixture.

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References

- [1] T. Katayama, K. Ohgaki, G. Maekawa, M. Goto, T. Nagano, Isothermal Vapor-Liquid Equilibria of Acetone-Carbon Dioxide and Methanol-Carbon Dioxide Systems at High Pressures, *J. Chem. Eng. Jpn.* 8 (1975) 89–92.
- [2] E.A. Groll, H. Kruse, Kompressionskälte-maschine mit Lösungskreislauf: Einsatzmöglichkeiten für die Arbeitsstoffpaare R 23/DEGDME und CO₂/acetone, *Kälite Limatech* 45 (1992) 206–218.
- [3] G. Mozurkewich, R.D. Roberts, M.L. Greenfield, W.F. Schneider, Cycle-Model Assesment of working Fluids for a Low-Pressure CO₂ climate control System, *SAE Technical Papers* 2000.
- [4] C.M. Hsieh, J. Vrabec, Vapor-liquid equilibrium measurements of the binary mixtures CO₂ + acetone and CO₂ + pentanones, *J. Supercrit. Fluids* 100 (2015) 160-166.
- [5] Z. Lei, X. Qi, J. Zhu, Q. Li, B. Chen, Solubility of CO₂ in Acetone, 1-Buthyl-3-methylimidazolium Tetrafluoroborate, and Their Mixtures, *J. Chem. Eng. Data* 57 (2012) 3458–3466.
- [6] F. Höhler, R. Deschermeier, S. Rehfeldt, H. Klein, Gas solubilities of carbon dioxide in methanol, acetone, mixtures of methanol and water, and mixtures of methanol and acetone, *Fluid Phase Equilib.* 459 (2018) 186-195.
- [7] T. Adrian, G. Maurer, Solubility of carbon dioxide in acetone and propionic acid at temperatures between 298 K and 333 K, *J. Chem. Eng. Data* 42 (1997) 668–672.
- [8] C. J. Chang, C.-Y. Day, C.-M. Ko, K.-L. Chiu, Densities and P-x-y diagrams for carbon dioxide dissolution in methanol, ethanol, and acetone mixtures, *Fluid Phase Equilib.* 131 (1997) 243-258.
- [9] J. Wu, Q. Pan, G. L. Rempel, Pressure-density-temperature behavior of CO₂/acetone, CO₂/ toluene, and CO₂/monochlorobenzene mixtures in the near-critical region, *J. Chem. Eng. Data* 49 (2004) 976-979.
- [10] F. Han, Y. Xue, Y. Tian, X. Zhao, L. Chen, Vapor-liquid equilibria of the carbon dioxide + acetone system at pressures from (2.36 to 11.77) MPa and temperatures from (333.15 to 393.15) K, *J. Chem. Eng. Data* 50 (2005) 36–39.
- [11] M. Kato, K. Aizawa, T. Kanahira, T. Ozawa, A new experimental method of vapor-liquid equilibria at high pressures, *J. Chem. Eng. Jpn.* 24 (1991) 767–771.

- 1 [12] C. Day, C.J. Chang, C. Chen, Phase Equilibrium of Ethanol + CO₂ and Acetone + CO₂ at Elevated
2 Pressures, J. Chem. Eng. Data 41 (1996) 839–843.
- 3 [13] C.J. Chang, K.-L. Chiu, C.-Y. Day, A new apparatus for the determination of P–x–y diagrams and
4 Henry’s constants in high pressure alcohols with critical carbon dioxide, J. Supercrit. Fluids 12
5 (1998) 223–237.
- 6 [14] C.J. Chang, C.-Y. Day, C.-Y. Chen, Corrections to ‘Phase Equilibrium of Ethanol + CO₂ and
7 Acetone + CO₂ at Elevated Pressures [Chany-Yih Day, Chiehming J. Chang, and Chiu-Yang Chen,
8 J. Chem. Eng. Data 1996, 41, 839-843], J. Chem. Eng. Data 44 (1999) 365.
- 9 [15] A. Bamberger and G. Maurer, High-pressure (vapour + liquid) equilibria in (carbon dioxide +
10 acetone or 2-propanol) at temperatures from 293 K to 333 K, J. Chem. Thermodyn. 32 (2000) 685–
11 700.
- 12 [16] J. Chen, W. Wu, L. Gao, T. Mu, Z. Liu, T. Jiang, J. Du, Phase Behavior, Densities, and Isothermal
13 Compressibility of CO₂ + Pentane and CO₂ + Acetone Systems in Various Phase Regions, J. Chem.
14 Eng. Data 48 (2003) 544–1548.
- 15 [17] M. Stievano, N. Elvassore, High-Pressure Density and Vapor-Liquid Equilibrium for the Binary
16 Systems Carbon Dioxide-Ethanol, Carbon Dioxide-Acetone and Carbon Dioxide-Dichloromethane,
17 J. Supercrit. Fluids 33 (2005) 7–14.
- 18 [18] W. Wu, J. Ke, M. Poliakoff, Phase Boundaries of CO₂ + Toluene, CO₂ + Acetone, and CO₂ +
19 Ethanol at High Temperatures and High Pressures, J. Chem. Eng. Data 51 (2006) 1398–1403.
- 20 [19] H.Y. Chiu, M.J. Lee, and H.M. Lin, Vapor-liquid phase boundaries of binary mixtures of carbon
21 dioxide with ethanol and acetone, J. Chem. Eng. Data 53 (2008) 393–240.
- 22 [20] P. Traub, K. Stephan, High-pressure phase equilibria of the system carbon dioxide-water-acetone
23 measured with a new apparatus, Chem. Eng. Sci. 45 (1990) 45, 751-758.
- 24 [21] Y. Sato, N. Hosaka, K. Yamamoto, H. Inomata, Compact apparatus for rapid measurement of high-
25 pressure phase equilibria of carbon dioxide expanded liquids, Fluid Phase Equilib. 291 (2010) 25-
26 29.
- 27 [22] X. Gui, Z. Tang, W. Fei, Solubility of CO₂ in Alcohols, Glycols, Ethers, and Ketones at High
28 Pressures from (288.15 to 318.15) K, J. Chem. Eng. Data 56 (2011) 2420-2429.

- 1 [23] M. J. Lazzaroni, D. Bush, J. S. Brown, C. A. Eckert, High-Pressure Vapor-Liquid Equilibria of Some
2 Carbon Dioxide + Organic Binary Systems, *J. Chem. Eng. Data* 50 (2005) 60-65.
- 3 [24] M. B. Miller, D.L. Chen, D. R. Leubke, J. K. Johnson, R. M. Enick, Critical Assessment of CO₂
4 Solubility in Volatile Solvents at 298.15 K, *J. Chem. Eng. Data* 56 (2011) 1565-1572.
- 5 [25] S. H. Page, S. R. Sumpter, S. R. Goates, M. L. Lee, D. J. Dixon, K.P. Johnston, Tri-n-
6 butylphosphate/CO₂ and acetone/CO₂ phase behaviors and utilities in capillary supercritical-fluid
7 chromatography, *J. Supercrit. Fluids* 6 (1993) 95.
- 8 [26] F. W. Giacobbe, Thermodynamic solubility behavior of carbon dioxide in acetone, *Fluid Phase*
9 *Equilib.* 72 (1992) 277-297.
- 10 [27] L. Ferreira-Pinto, P. C. Carvalho de Araujo, M. D. Aranda Saldaña, P. F. Arce, L. Cardozo-Filho,
11 Experimental Data and Thermodynamics Modeling (PC-SAFT EoS) of the {CO₂ + Acetone +
12 Pluronic F-127} System at High Pressures, *J. Chem. Eng. Data* 64 (2019) 2186–2192.
- 13 [28] T. Aida, T. Aizawa, M. Kanakubo, H. Nanjo, Dependence of volume expansion on alkyl chain
14 length and the existence of branched methyl group of CO₂-expanded ketone systems at 40°C, *J.*
15 *Supercrit. Fluids* 55 (2010) 71-76.
- 16 [29] F. Zahran, J. A. R. Renuncio, A. Caban, Excess Molar Enthalpies of CO₂ + Acetone at Pressures
17 from (9.00 to 18.00) MPa and Temperatures from (313.15 to 333.15) K, *J. Chem. Eng. Data* 55
18 (2010) 3649–3654.
- 19 [30] G. Soave, Equilibrium constants from a modified Redlich-Kwong equation of state, *Chem. Eng. Sci.*
20 27 (1972) 1197-1203.
- 21 [31] A. Peneloux, E. Rauzy, and R. Freze, A Consistent Correction For Redlich-Kwong-Soave Volumes,
22 *Fluid Phase Equilib.* 8 (1982) 7–23.
- 23 [32] H. Preston-Thomas, On the International Temperature Scale of 1990, *Metrologia*, 1990, 27, pp. 3-
24 10.
- 25 [33] Guidelines on the Calibration of Electromechanical Manometers, EURAMET/cg-17/v.01, 2007.
- 26 [34] GUM - Evaluation of measurement data — Guide to the expression of uncertainty in measurement,
27 Int. Organ. Stand. Geneva ISBN, 2008.

- 1 [35] R. Span, W. Wagner, A new EOS for carbon dioxide covering the fluid region from the triple point
2 temperature to 1100 K at pressures up to 800 MPa, *J. Phys. Chem. Ref. Data* 25 (1996) 1509-1597.
- 3 [36] W. Wagner, A. Pruß, The IAPWS formulation 1995 for the thermodynamic properties of ordinary
4 water substance for general and scientific use, *J. Phys. Chem. Ref. Data* 31 (2002) 387.
- 5 [37] R.L. Rowley, W. V. Wilding, J.L. Oscarson, Y. Yang, N. F. Giles, DIPPR Data Compilation of Pure
6 Chemical Properties, Design Institute for Physical Properties. New York: AIChE, 2010.
- 7 [38] Y. Coulier, K. Ballerat-Busserolles, J. Mesones, A. Lowe, and J.-Y. Coxam, Excess Molar
8 Enthalpies and Heat Capacities of {2-Methylpiperidine–Water} and {N -Methylpiperidine–Water}
9 Systems of Low to Moderate Amine Compositions, *J. Chem. Eng. Data* 60 (2015) 1563–1571.
- 10 [39] J.K. Holzhauser and W.T. Ziegler, Temperature dependence of excess thermodynamic properties of
11 n-heptane-toluene, methylcyclohexane-toluene, and n-heptane-methylcyclohexane systems, *J.*
12 *Phys. Chem.* 79 (1975) 590–604.
- 13 [40] J.B. Ott, C.E. Stouffer, G.V. Cornett, B.F. Woodfield, R.C. Wirthlin, J.J. Christensen, U.K. Deiters,
14 Excess enthalpies for (ethanol + water) at 298.15 K and pressures of 0.4, 5, 10, and 15 MPa, *J.*
15 *Chem. Thermodyn.* 18 (1986) 1–12.
- 16 [41] E.W. Lemmon, R. Span, E.W. Lemmon, R. Span, Short fundamental equations of state for 20
17 industrial fluids, *J. Chem. Eng. Data* 51 (2006) 785–850.
- 18 [42] E.G. Azevedo, J. Prausnitz, R. Lichtenthaler, *Molecular Thermodynamics of Fluid-phase Equilibria.*
19 Prentice Hall; 3th ed. 1998.
- 20 [43] D. Salavera, M.I. Barba, A. Coronas, Vapor-Liquid Equilibrium of Carbon Dioxide + Acetone
21 Mixture measured with a New Experimental Device based on the Isochoric Method, 6th
22 International Conference on Cryogenics and Refrigeration, April , Shanghai (China), 2018.
- 23 [44] R.J.B. Moreira-da-Silva, D. Salavera, A. Coronas, Modelling of CO₂/acetone fluid mixture
24 thermodynamic properties for compression/resorption refrigeration systems, *IOP Conf. Series:*
25 *Materials Science and Engineering* 595 (2019).
- 26 [45] P.M. Mathias, H.C. Klotz, J.M. Prausnitz, Equation-of-State mixing rules for multicomponent
27 mixtures: the problem of invariance, *Fluid Phase Equilib.* 67 (1991) 31–44.

- 1 [46] H.H. Rachford, J. Rice, Procedure for Use of Electrical Digital Computers in Calculating Flash
2 Vaporization Hydrocarbon Equilibrium, Trans. AIME 4 (1952) 19–20.
- 3 [47] G.A. Wilson, A modified Redlich–Kwong EOS. Application physical data calculation, Annual
4 AICHE National Meeting, Cleveland, OH, May 4–7, 1968, paper 15C.
- 5 [48] T. Anderson, J. Prausnitz, Computational Methods for High-Pressure Phase Equilibria and Other
6 Fluid-Phase Properties Using a Partition Function. 1. Pure Fluids, Ind. Eng. Chem. Process Des.
7 Dev. 19 (1980) 1-8.
- 8 [48] J. Fred, M. Winkler, Minuit User’s Guide, CERN, Geneva, 2004.

9