

New high-pressures vapor-liquid equilibrium data for the carbon dioxide + 2-methyl-2-propanol binary system⁺

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Abstract: New vapor-liquid equilibria (VLE) data at 323.15, 333.15, 343.15, and 353.15 K and pressures up to 112.9 bar are reported for the carbon dioxide + 2-methyl-2-propanol system. The experimental method used in this work was a static analytical method with liquid and vapor phases sampling using a rapid online sampler injector (ROLSI™) coupled to a gas chromatograph (GC) for analysis. Measured VLE data and literature data for carbon dioxide + 2-methyl-2-propanol system were modeled with the Soave-Redlich-Kwong (SRK) cubic equation of state with classical van der Waals (two-parameter conventional mixing rule, 2PCMR) mixing rules. A single set of interaction parameters that lead to a correct phase behavior was used in this work to model the new VLE data and critical points of the mixtures in a wide range of temperature and pressure. The SRK prediction results were compared to the new data measured in this study and to available literature data.

Keywords: Carbon dioxide • 2-Methyl-2-Propanol (*tert*-butanol) • SRK • High-pressures • EoS
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1. Introduction

The high-pressure phase behavior of carbon dioxide containing systems has raised considerable interest in the last years as the technology advances rapidly into new fields. Reliable and accurate experimental measurements are required in a variety of processes, such as SCF extraction, reaction, fractionation, nanoparticles formation, separation of non-volatile mixtures, supercritical fluid chromatography, hydrothermal crystal growing, hydrothermal destruction of hazardous waste, polymer processing, *etc.*, as well as in the simulation of petroleum reservoirs, enhanced oil recovery, carbon capture and storage, the transportation and storage of natural gas, refrigeration and heat-pump cycles, and the study of geological processes [1-10].

In particular, the mixtures of carbon dioxide + alcohols at high-pressures are used in the design, simulation, and optimization of extraction processes, petroleum and natural gas processing, food industries, surfactant plants, biofuels [11, 12]

This study is part of an ongoing project [13-30] on the carbon dioxide + alcohols systems at high pressures and it presents the results for the carbon dioxide + 2-methyl-2-propanol (*tert*-butanol) binary mixture. Among the binary systems previously investigated by our group are the carbon dioxide + 1-butanol [27] and + 2-butanol [20], its position isomer, respectively. Our goals were to report new experimental data for this chain isomer and to represent the phase behavior of this system with simple thermodynamic models, using a single set of binary interaction parameters.

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Table 1. Literature experimental data for the carbon dioxide + 2-methyl-2-propanol binary system.

| T/K | P _{range} /bar | NEXP ^a | Reference |
|--------|-------------------------|-------------------|-----------|
| 299.00 | 7.3-65.4 | 10 | [36] |
| 300.15 | 5.6-35.4 | 7 | [40,41] |
| 303.15 | 5.9-40.4 | 8 | [40] |
| 305.95 | 55.3-66.4 | 5 | [37] |
| 308.15 | 6.2-40.8 | 8 | [40] |
| 313.15 | 40.5-75.7 | 6 | [37] |
| 313.15 | 5.4-41.2 | 8 | [40] |
| 313.15 | 46.7-76.7 | 5 | [38] |
| 313.15 | 14.5-79.16 | 10 | [44] |
| 323.15 | 54.9-91.2 | 5 | [38] |
| 323.20 | 6.4-92.3 | 11 | [36] |
| 323.20 | 43.2-97.8 | 6 | [42] |
| 331.90 | 50.1-99.7 | 8 | [39] |
| 333.15 | 60.4-101.8 | 5 | [38] |
| 333.20 | 42.7-104.4 | 6 | [42] |
| 341.60 | 50.1-110.0 | 8 | [39] |
| 343.15 | 69.4-111.3 | 5 | [38] |
| 343.20 | 9.7-111.6 | 10 | [36] |
| 343.20 | 52.1-106.6 | 6 | [42] |
| 351.30 | 50.1-120.0 | 8 | [39] |
| 353.15 | 75.9-116.9 | 5 | [38] |
| 353.20 | 41.6-110.9 | 6 | [42] |
| 363.15 | 19.3-119.0 | 8 | [43] |
| 373.15 | 15.3-121.8 | 8 | [43] |

^aNumber of experimental points

The carbon dioxide + 2-methyl-2-propanol binary system exhibits type I or type II fluid phase behavior, according to the classification of van Konynenburg and Scott [31,32]. Type I and II fluid phase behavior are similar being characterized by a continuous critical liquid - vapor ($L = V$) locus connecting the critical points of the pure components [33]. The difference is the appearance in the type II phase diagram of a liquid - liquid ($L = L$) critical line which intersects with a liquid - liquid- vapor (LLV) locus in an upper critical endpoint (UCEP). So far, our literature review [2-5,12,34,35] showed that there are no experimental data to prove the existence of a three phase equilibrium line or a liquid-liquid critical line for the carbon dioxide + 2-methyl-2-propanol binary system. Therefore, based on the available critical data, it can be assumed that the system presents type I phase behavior.

Several papers [36-44] presented vapor-liquid equilibrium data or isothermal pressure-liquid phase compositions. The experimental conditions of the available information for the carbon dioxide + 2-methyl-2-propanol binary system is summarized in Table 1. However, there are significant deviations among the data from different sources [45]. Therefore, in this work we report new measurements using a static-analytical method, in a high-pressure visual cell, for carbon dioxide + 2-methyl-2-propanol at 323.15, 333.15, 343.15, and 353.15 K and pressures between 19.5 and 112.9 bar.

Measured and literature data for the carbon dioxide + 2-methyl-2-propanol system were modeled with the Soave-Redlich-Kwong (SRK) [46] cubic equation of state coupled with classical van der Waals mixing rules. The same modeling strategy was used as in our latest papers [13-18], meaning that a single set of binary interaction parameters was used to predict the phase behavior of the system in a wide range of pressures and temperatures.

2. Experimental procedure

2.1. Materials

Carbon dioxide (mass fraction purity >0.997) was provided by Linde Gaz Romania and 2-methyl-2-propanol (mass fraction purity >0.998) was a Sigma product. The chemicals were used without further purification, except for the careful degassing of 2-methyl-2-propanol. Gas chromatographic analysis of 2-methyl-2-propanol give a mole fraction purity of >0.999.

2.2. Apparatus and Procedure

The experimental setup was described in detail in earlier papers [13,16,29,30]. The apparatus used in this work is based on a high-pressure visual cell with variable volume [29,30], coupled with a new sampling and analyzing system [13,16]. The sampling system utilized two high-pressure electromechanical sampling valves, the so called rapid on-line sampler injector (ROLSITM, MINES ParisTech/CEP-TEP, – Centre énergétique et procédés, Fontainebleau, France [47]). The ROLSI valves are connected through capillaries to the equilibrium visual cell and to a gas chromatograph (GC). A heating resistance is used to heat the expansion chamber of the sampler injector so the liquid samples are rapidly vaporized. The transferring lines between ROLSI and the GC are heated by means of a linear resistor coupled to an Armines/CEP/TEP regulator. The GC (Perichrom) uses a thermal conductivity detector, TCD, with a HP-Plot/Q column 30 m long and 0.530 mm diameter. The

Table 2. Mole fractions of component 1 in the liquid phase x_1 and mole fractions of component 1 in the vapor phase y_1 at various pressures P and temperatures T for the binary system carbon dioxide (1) + 2-methyl-2-propanol (2).

| <i>P/bar</i> | x_1 | y_1 | <i>P/bar</i> | x_1 | y_1 |
|---------------------------|--------|--------|--------------|--------|--------|
| T/K = 323.15 ± 0.1 | | | | | |
| 21.9 | 0.1652 | 0.9823 | 65.7 | 0.6077 | 0.9903 |
| 36.0 | 0.2786 | 0.9890 | 80.7 | 0.7954 | 0.9778 |
| 51.0 | 0.4333 | 0.9840 | 89.9 | 0.9687 | 0.9687 |
| T/K = 333.15 ± 0.1 | | | | | |
| 19.5 | 0.1452 | 0.9741 | 81.9 | 0.6614 | 0.9712 |
| 35.4 | 0.2476 | 0.9746 | 92.9 | 0.7994 | 0.9612 |
| 52.7 | 0.3920 | 0.9847 | 99.2 | 0.9528 | 0.9528 |
| 71.1 | 0.5764 | 0.9836 | | | |
| T/K = 343.15 ± 0.1 | | | | | |
| 23.2 | 0.1516 | 0.9628 | 84.2 | 0.6193 | 0.9656 |
| 40.0 | 0.2673 | 0.9751 | 95.2 | 0.7164 | 0.9543 |
| 50.2 | 0.3456 | 0.9897 | 104.7 | 0.8186 | 0.9430 |
| 60.8 | 0.4204 | 0.9837 | 106.8 | 0.9408 | 0.9408 |
| 72.0 | 0.5050 | 0.9886 | | | |
| T/K = 353.15 ± 0.1 | | | | | |
| 24.4 | 0.1513 | 0.9677 | 81.0 | 0.5769 | 0.9786 |
| 35.2 | 0.2225 | 0.9715 | 95.3 | 0.6640 | 0.9614 |
| 50.7 | 0.3358 | 0.9792 | 111.7 | 0.8001 | 0.9529 |
| 65.3 | 0.4228 | 0.9817 | 112.9 | 0.9215 | 0.9215 |

GC carrier gas is helium at a flow rate of 30 mL min⁻¹. The setup was completed with a syringe pump Teledyne ISCO model 500D.

The working procedure is similar to that in our previous studies [13,16,29,30]. The entire internal loop of the apparatus including the equilibrium cell was rinsed several times with carbon dioxide. Then, the equilibrium cell was evacuated with a vacuum pump. The cell was charged with alcohol, which was degassed by using a vacuum pump and vigorously stirring. The lighter component (in this case CO₂) is introduced with the syringe pump into equilibrium cell and the pressure is set to the desired value. Then the cell was heated to the experimental temperature. To facilitate the approach to an equilibrium state, the mixture in the cell was stirred for a few hours. Then the stirrer was switched off, and about 1 h was allowed to pass until the coexisting phases were completely separated. Samples of the liquid and vapor phases are withdrawn by ROLSI and analyzed with the GC. In order to check the repeatability, at least six samples of the liquid phase were normally analyzed at the equilibrium temperature and pressure. The sample sizes being very small, the equilibrium pressure in the cell remains constant.

The calibration of the TCD for CO₂ and 2-methyl-2-propanol is done by injecting known amounts of each component using gas chromatographic syringes. Calibration data are fitted to quadratic polynomials to obtain the mole number of the component versus chromatographic area. The correlation coefficients of the GC calibration curves were 0.999 for carbon dioxide and 0.997 for 2-methyl-2-propanol.

For the phase equilibrium compositions, the relative uncertainty of the mole fraction in the liquid and vapor phase was calculated using the procedure given by Scheidgen [48] (Eqs. 5-2, 5-3, 5-4, 5-6, pp. 194-196). The average relative uncertainty was <2%. As usually in the literature [49], we report the mole fractions with four decimal places.

The uncertainties of the measurements were estimated to be within 0.1 K for temperature. The platinum temperature probe connected to a digital indicator was calibrated against the calibration system Digital Precision Thermometer with PT 100 sensor (Romanian Bureau of Legal Metrology). The uncertainty of platinum probe is estimated to be within ± 0.1 K using a similar procedure as described in [49].

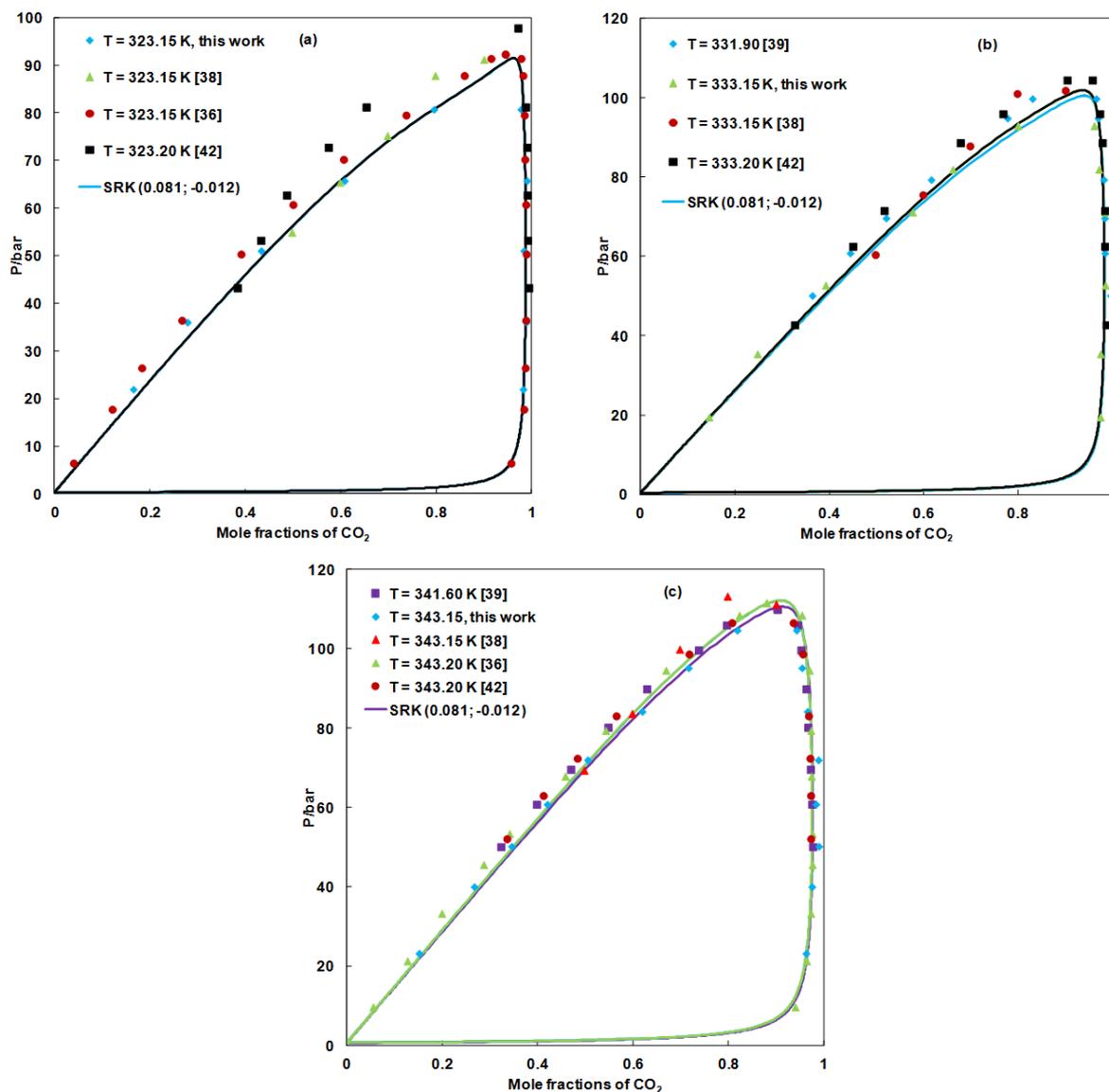


Figure 1. Comparison of new measured and literature data for the carbon dioxide + 2-methyl-2-propanol (*tert*-butanol) system and calculations by SRK model: symbols, this work and literature data at different temperatures; solid lines, predictions by SRK ($k_{12} = 0.081$, $l_{12} = -0.012$).

The pressure transducer connected to a digital multimeter was calibrated at 323.2 K with a precision hydraulic dead-weight tester (model 580C, DH-Budenberg SA, Aubervilliers, France). The uncertainty of the pressures is estimated to be within ± 0.015 MPa using a similar procedure as described in [49], for a pressure range between 0.5 and 20 MPa.

The critical points were obtained in this work following the procedure of Scheidgen [48]. At a fixed temperature (for example 353.15 K), the pressure in the cell was increased by introducing CO_2 with the syringe pump. The transition from heterogeneous (two phases) to the homogeneous range is visually observed. Then, by slowly cooling (1 to 3 K) the

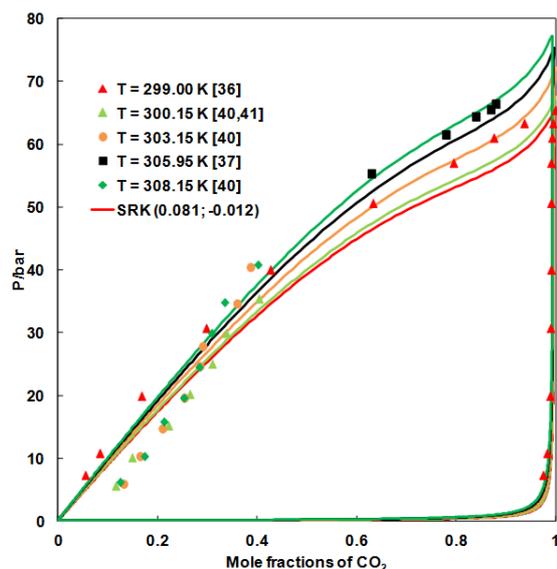
pressure in the cell decreases, and the inverse transition from homogeneous to heterogeneous range can be observed. The temperature and the pressure of the opalescence point are considered as critical data points. The composition of the critical point is obtained by sampling from the homogeneous mixture. The procedure is then repeated by introducing new amounts of CO_2 and slowly cooling.

3. Results and discussion

The vapor-liquid equilibrium compositions for the carbon dioxide + 2-methyl-2-propanol binary system

Table 3. Critical data and acentric factor [50] for carbon dioxide and 2-methyl-2-propanol (tert-butanol).

| Component | T_c /K | P_c /bar | w |
|-------------------------------------|----------|------------|-------|
| CO ₂ | 304.21 | 73.83 | 0.224 |
| tert-C ₄ H ₁₀ | 511.70 | 39.72 | 0.615 |

**Figure 2.** Comparison of literature data for the carbon dioxide + 2-methyl-2-propanol (tert-butanol) system and calculations by SRK model: symbols, literature data at different temperatures; solid lines, predictions by SRK ($k_{12} = 0.081$, $l_{12} = -0.012$).

were measured in the temperature range of 323.15 to 353.15 K and pressures up to 112.9 bar and the results are given in Table 2. The values are typically averages of six measurements.

A detailed comparison of the new experimental data measured in this study with existing literature data at nearest or same temperatures is shown in Fig. 1. As can be seen, there are very important deviations among the data from different sources. For instance, at 323.15 K (Fig. 1a) the highest difference in pressure at the same liquid composition is about 10 bar. Also, it can be noticed (Fig. 1b) that the 331.9 K [39] isotherm is located at higher pressures and compositions than most 333.15 K isotherms. The same situation can be observed in Fig. 1c for the 341.6 K isotherm [39] which is situated above most 343 K isotherms. This high degree of scatter can be observed for all available isotherms. In addition, some data sets have few experimental points or only the liquid phase composition is reported. Therefore new measurements were done in this work. Our experimental data at (323.15, 333.15, and 343.15) K (Fig. 1) agree with the measurements of Kim *et al.* [36] and Heo *et al.*

[38]. However, similar scattering of data was observed at other literature temperatures (Figs. 2-4).

Measured and literature data were modeled with Soave–Redlich–Kwong (SRK) equation of state coupled with classical van der Waals mixing rules. The Soave–Redlich–Kwong [46] equation of state is:

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

where the two constants, a and b , are:

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

$$b = 0.08664 \frac{RT_c}{P_c} \quad (3)$$

$$\alpha(T_R, \omega) = \left[1 + m_{\text{SRK}} (1 - T_R^{0.5}) \right]^2 \quad (4)$$

$$m_{\text{SRK}} = 0.480 - 1.574\omega - 0.176\omega^2 \quad (5)$$

The two parameter conventional mixing rules are given by:

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad (6)$$

$$b = \sum_i \sum_j x_i x_j b_{ij} \quad (7)$$

where

$$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij}) \quad (8)$$

$$b_{ij} = \frac{b_i + b_j}{2} (1 - l_{ij}) \quad (9)$$

The calculations were made using the software packages PHEQ (Phase Equilibria Database and Calculations) [50] and GPEC (Global Phase Equilibrium Calculations) [51]. The critical values [52] of the pure carbon dioxide and 2-methyl-2-propanol together with the acentric factors [52] used in the calculations are presented in Table 3.

The most common modeling approach in the literature is to correlate the experimental data. As it was shown previously [22], for some binary mixtures the correlations of the experimental data lead to a false liquid-liquid splitting, corresponding to a different type of phase diagram, though the errors in bubble-point pressures are small.

This is the case when correlating the experimental data for the carbon dioxide + 2-methyl-2-propanol binary system. Therefore, in the present work the modeling procedure followed the approach presented in

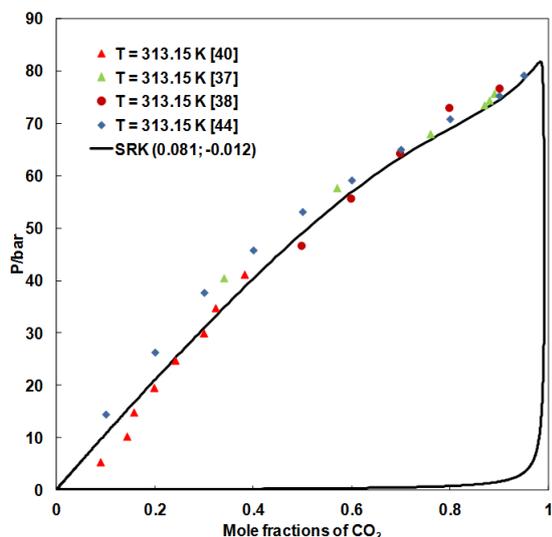


Figure 3. Comparison of literature data for the carbon dioxide + 2-methyl-2-propanol (*tert*-butanol) system and calculations by the carbon dioxide + 2-methyl-2-propanol (*tert*-butanol) system and calculations by SRK model: symbols, literature data at different temperatures; by SRK model: symbols, literature data at 313.15 K; solid lines, solid lines, predictions by SRK ($k_{12} = 0.081$, $l_{12} = -0.012$).

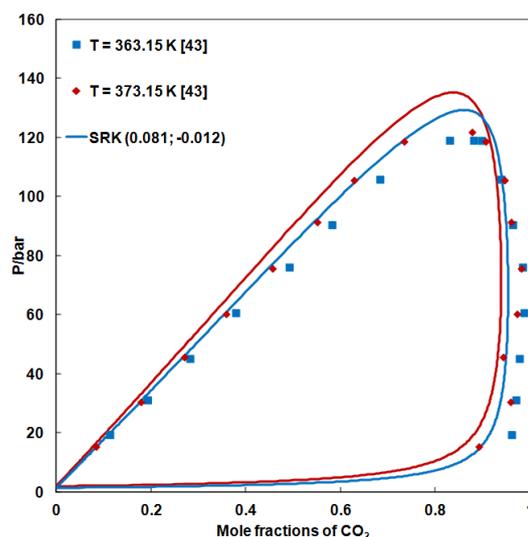


Figure 5. Comparison of literature data for the carbon dioxide + 2-methyl-2-propanol (*tert*-butanol) system and calculations by the carbon dioxide + 2-methyl-2-propanol (*tert*-butanol) system SRK model: symbols, literature data at ~ 353.15 K; and calculations by SRK model: symbols, literature data at solid lines, predictions by SRK ($k_{12} = 0.081$, $l_{12} = -0.012$).

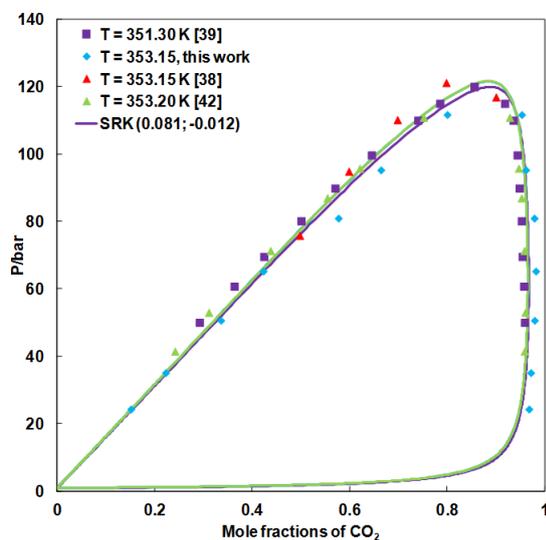


Figure 4. Comparison of new measured and literature data for the carbon dioxide + 2-methyl-2-propanol (*tert*-butanol) system and calculations by SRK model: symbols, this work and literature data at ~ 353.15 K; solid lines, predictions by SRK ($k_{12} = 0.081$, $l_{12} = -0.012$).

our last papers [13-20], where a single set of interaction parameters temperature independent was used to predict the critical and subcritical phase behavior in a large range of pressures and temperatures and the correct type of phase behavior. The same set of interaction parameters ($k_{12} = 0.081$, $l_{12} = -0.012$) was used to calculate the VLE (Figs. 1-5) and the critical curve(s)

(Fig. 6). When experimental data were available for the entire vapor-liquid critical curve, the binary interaction parameters set was obtained by a trial and error method in order to reproduce well the critical maximum pressure of the liquid – vapor critical curve [20,23]. Therefore, in this study, as the critical points available are scarce, the unique binary interaction parameters set was calculated by averaging the values of the optimized parameters for all new measured and literature temperatures from 299.0 K [36] up to 373.15 K [43], except those which lead to false liquid-liquid splitting [40,41].

Consequently, the errors in bubble-point pressures are higher for these isotherms (Figs. 1a, 2 and 3). The errors are also bigger for data sets which are not in agreement each other (Figs. 1-5). It should be remarked that experimental critical points at temperatures above 373.15 K are not available and the critical data plotted in Fig. 6 are scattered. The type of phase diagram, according to the classification of van Konynenburg and Scott [31,32], predicted by the SRK model is II (Fig. 6). Experimentally is difficult to prove this fact, as the alcohol has a melting point of 298.75 K [53] and the appearance of a solid phase will make impossible the determination of the upper critical endpoint (UCEP), if any. However, as can be seen, the calculated UCEP is located at low temperatures and the SRK model calculations are reasonably good for most experimental data.

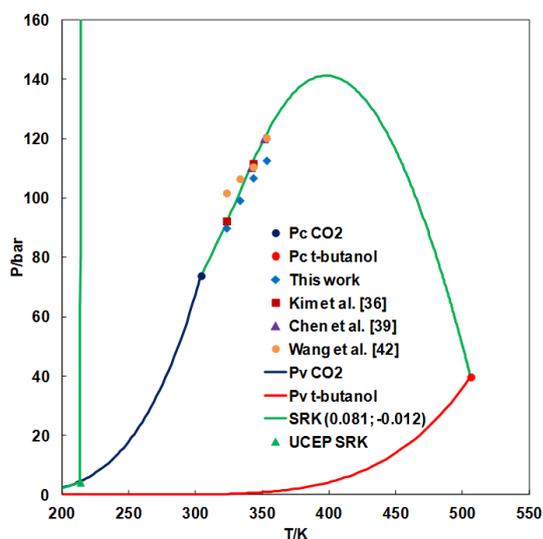


Figure 6. P - T fluid phase diagram of carbon dioxide + 2-methyl-2-propanol binary system: blue full diamond (\blacklozenge), this work orange full circle (\bullet), [42], purple full triangle (\blacktriangle), [39], dark red full square (\blacksquare), [36] - experimental critical curve; dark blue full circle (\bullet) and red full circle (\bullet), experimental critical points of pure components; dark blue and red solid lines (—, —), calculated vapor pressure curves of pure components; green full triangle (\blacktriangle), calculated UCEP and green solid lines (—), calculated UCEP and LLV lines respectively by SRK ($k_{12} = 0.081$, $l_{12} = -0.012$).

4. Conclusions

New VLE experimental data for the binary system carbon dioxide + 2-methyl-2-propanol (*tert*-butanol) were measured at 323.15, 333.15, 343.15, and 353.15 and pressures up to 112.9 bar, with a high-pressure static apparatus using ROLSI valves. Measured and literature data for carbon dioxide + 2-methyl-2-propanol system were modeled with the SRK cubic equation of state using classical van der Waals (two-parameter conventional mixing rule, 2PCMR) mixing rules. The same set of interaction parameters was used to predict the critical and sub-critical phase behavior of the binary mixture studied. The predicted results were compared both with our experimental data and the available literature data for carbon dioxide + 2-methyl-2-propanol binary systems. New experimental critical data are required especially at higher temperatures as available data are scarce and measured at moderate temperatures.

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