Phase Equilibria of (CO_2 + Butylbenzene) and (CO_2 + Butylcyclohexane) at Temperatures between (323.15 and 423.15) K and at Pressures up to 21 MPa

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Abstract

Experimental measurements of the phase equilibria of (CO_2 + butylbenzene) and (CO_2 + butylcyclohexane) have been made with an analytical apparatus at temperatures of (323.15, 373.15 and 423.15) K at pressures from 2 MPa to the mixture critical pressure. These are the first results to be published for (CO_2 + butylcyclohexane), while for (CO_2 + butylbenzene) they are the first at pressures above 6 MPa. To model the data, we use the Peng-Robinson equation of state with Wong-Sandler mixing rules incorporating the NRTL equation. The model describes the measured bubble point curves very well at all temperatures, except close to the mixture critical points at high pressures. The dew point curves are described well only at the lowest temperature; otherwise, deviations increase in the approach to the mixture critical point.

Keywords: Phase equilibria; CO_2, butylbenzene; butylcyclohexane; Peng-Robinson equation of state; Wong-Sandler mixing rules.

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1. Introduction

The injection of carbon dioxide into hydrocarbon-bearing reservoir formations is of interest in the fields of carbon storage and, especially, enhanced oil recovery (EOR). Two benefits of these processes are obvious: mitigate the effects of greenhouse gas emissions, and prolonging the productive lifespan of the oil fields. From a fundamental scientific point of view, CO_2-EOR works on a very straightforward principle, namely, that given the right physical conditions, CO_2 will mix with the oil forming a low-viscosity, low-interfacial-tension fluid that can be more easily displaced [1]. Additionally, CO_2 has the capability of invading flooding zones not previously flooded by water, as well as releasing and reducing trapped oil [2]. In terms of industrial practice, slim tube experiments are widely used to determine the conditions at which miscible displacement can be achieved. The term ‘minimum miscibility pressure’ is used to describe the lowest pressure at which full miscibility is achieved [3]. In addition to such experiments, modelling and optimization of CO_2-EOR processes is of great value and, to achieve these objectives, fluid properties, especially phase behavior, of (CO_2 + hydrocarbon) mixtures are required.

Thermodynamic models for the phase behavior of complex mixtures are typically built-up by optimization of binary interaction parameters against experimental phase-equilibrium data for the binary sub-systems. Such experimental data are available for many binary mixtures of CO_2 with normal alkanes, branched alkanes, cycloalkanes or aromatics. However, fewer data are available for mixtures of CO_2 with more complex molecules such as alkyl-substituted cycloalkanes and alkyl-substituted aromatic molecules. In order to help address these gaps in the literature, the present work focuses on the phase behavior of (CO_2 + butylbenzene) and (CO_2 + butylcyclohexane). Measurements have been made with an analytical apparatus on three isotherms at temperatures of (323.15, 373.15 and 423.15) K and at pressures ranging from 2 MPa to the mixture critical point. The experimental results have been modeled with the Peng-Robinson equation of state (EoS) [4] coupled with the Wong-Sandler mixing rules [5] incorporating the NRTL solution model [6].

2. Experimental Section

2.1. Chemicals

The chemical used are detailed in Table 1. No purification was carried out in the course of this work.

2.2. Experimental setup and procedure

The circulation-type analytical apparatus shown in Fig. 1, and described previously in detail [7], was used in this work. The vapor and liquid phases present in the equilibrium cell were recirculated by means of a dual-channel magnetically-coupled pump through lines fitted with Rolsi Evolution IV sampling valves that permitted small samples of both phases to be withdrawn and transferred to an on-line gas chromatograph (GC) for analysis. The apparatus also included a fluid injection system and temperature and pressure measuring systems. It was installed within a thermostatic air bath where the temperature was controlled with a stability of ±0.03 K or better.

The temperature was measured with a platinum resistance thermometer (PRT) inserted into a thermowell in the wall of the equilibrium vessel. This was calibrated by comparison in a constant temperature bath with a standard PRT that had itself been calibrated of ITS-90. The overall standard uncertainty of the temperature was estimated to be 0.05 K, including the uncertainty of the temperature sensor itself, calibration uncertainties and the effects of temperature fluctuations in the oven. The pressure was measured by means of a pressure transducer that was calibrated against a high-pressure pneumatic controller/calibrator at pressures up to 50 MPa. The overall standard uncertainty was estimated to be 0.04 % of reading.

Starting with the empty system under vacuum and controlled at the desired temperature, a selected amount of hydrocarbon was first charged into the cell using one of the high-pressure syringe pumps. Next, a selected amount of CO_2 was injected into the vessel from a second syringe pump that was fitted with a cooling jacket and filled from a dip-tube cylinder of liquefied CO_2. The magnetic circulation pump along with the stirrer inside the vessel were operated to accelerate the process of equilibration. The attainment of equilibrium state was judged first from the approach of the pressure to a steady value and then validated by checking the reproducibility of the vapor and liquid sample compositions. In the present experiments, equilibrium was achieved following approximately two hours of circulation and agitation. Once equilibrium was reached, several small samples of each phase, typically between (1 and 10) µmol, were taken and transferred to the GC for analysis. Pressure changes during such a sequence of sampling and analysis were negligible. Following a set of composition measurements at a particular pressure, a further quantity of CO_2 was injected into the vessel and equilibrium was re-established at the next higher pressure. If necessary, some fluid was discharged from the vessel prior to further injections of CO_2 to ensure that the liquid level remained between the inlet ports of the liquid- and vapor-recirculation loops. Isothermal measurements were continued until the mixture critical point was reached, and the whole procedure was repeated for other isotherms.

2.3. Gas Chromatography

For the (CO_2 + butylbenzene) system, a HP-INNOWAX capillary column (length 30 m, o.d. 0.32 mm, 0.25 μm film thickness) was used while, for (CO_2 + butylcyclohexane), a DB-1 capillary column (length 30 m, o.d. 0.32 mm, 1.5 μm film thickness) was employed. A thermal conductivity detector (TCD) was used for all components. To facilitate calibration, a four-port sampling valve (model ED2CI4UW1, Vici AG International) with a 1.0 μL internal sample loop was connected in series with the sampling valves. This valve was used to inject the individual pure components, or diluted solutions of each pure component, in sequence. The sampling valve with a temperature sensor and connected in the filling configuration with a pressure transducer; thus the thermodynamic state of the samples used for calibration could be known. In the case of CO_2, the calibration loop was filled by injecting from one of the syringe pumps and the amount was varied by changing the filling pressure. In the case of the two hydrocarbon components, the sampling loop was filled at ambient pressure and the amount was varied by using gravimetrically prepared dilutions in hexane. In each case, the amount of substance injected was computed from the density and composition of the calibration sample assuming a loop volume of exactly 1.0 μL. For CO_2, the equation of state of Span and Wagner [8] was used while, for dilutions of butylbenzene in hexane, a density correlation based on the measurement of Rice and Teja [9] was used. Since there were no literature values for the density of (hexane + butylcyclohexane) mixtures, measurements were made with a vibrating tube densimeter (DMA 5000, Anton Paar) calibrated with air and ultrapure water. The measured densities are given in the supplementary data [10]. The calibration results, relating the chromatographic peak area to the amount of substance injected, are plotted in Figs S.1 and S.2 in the supplementary data [10]. In fact, the calibration loop volume was not known accurately but this term cancels out when the chromatographic response factors are applied to determine the composition of a mixture. For (CO_2 + butylbenzene), the gas-chromatograph operating temperatures during both calibration and sample analysis were as follows: oven, 423 K; inlet, 473 K; TCD, 523 K. For (CO_2 + butylcyclohexane), the corresponding temperatures were: oven, 473 K; inlet, 483 K; TCD, 523 K. In the measurements, at least five samples of each phase with good composition reproducibility were taken and used to form an average. In many cases, this sequence of sampling and analysis was repeated with different sample sizes, realized by varying the opening times of the sampling valves. The compositions obtained in this way were found to be independent of the sample size within the calibrated range of the TCD. The uncertainty of the composition analysis is attributed mainly to the repeatability of the measurements because the uncertainty arising from the GC calibration was much smaller. The standard deviations for both the vapor- and liquid-phase compositions are reported together with the measured values.

3. Results and Discussion

3.1. Experimental results

The experimental data, comprising pressure, temperature, liquid- and vapor-phase compositions and their standard deviations are listed in Table 2 for the (CO_2 + butylbenzene) system and in Table 3 for the (CO_2 + butylcyclohexane) system. The data are also plotted in Figs 2 and 3. As mentioned in the introduction, very limited phase-equilibrium data have been reported previously for the mixtures studied in this work. For the (CO_2 + butylbenzene) binary, Zarah et al. [11] reported bubble-point data at temperatures of (310.15, 323.15, 348.15 and 373.15) K, while Tiffin et al. [12] reported bubble points at T = (273.15 and 293.15) K. Additionally, Gironi and Lavecchia [13] report the solubility of CO_2 in butylbenzene at p = 0.1 MPa and T = (283 to 303) K. All these data relate to pressures below 6 MPa, no dew points were reported and only the results of Zarah et al. [11] overlap the temperature range of the present work. As shown in Fig. 2, the data of Zarah et al. [11] are in good agreement with our results at pressures up to about 4 MPa but, at higher pressures, they tend to fall below our measurements. In other words, data of Zarah et al. imply a slightly larger solubility of CO_2 in the liquid phase at given temperature and pressure. These workers used a synthetic method in which it was assumed that the vapor phase was pure CO_2; however, it is not possible to identify definitively the source of the discrepancy between their data and our results. For the (CO_2 + butylcyclohexane) binary, no data were identified in the literature.

3.2. Modelling results

To model the phase behavior of the systems studied, the Peng-Robinson equation of state (EoS) together with the Wong-Sandler mixing rules has been used. The required properties for the pure compounds, namely, critical temperature, critical pressure and acentric factor, are listed in Table 4. For CO_2, the values are taken from REFPROP 9.0. [14] The critical temperatures and pressures for butylbenzene and butylcyclohexane were taken from NIST Chemistry WebBook, [15] while the acentric factors were calculated from the vapor pressure correlation provided in the same source.

The Wong-Sandler mixing rules energy and co-volume parameters, a_m and b_m, of the mixture are given by [5]:

$$a_\mathrm{m} = b_\mathrm{m}\left(\sum_i x_i \frac{a_i}{b_i} + \frac{A_\infty^\mathrm{E}}{C}\right) \tag{1}$$

$$b_\mathrm{m} = \frac{\sum_i\sum_j x_i x_j \left(b - a/RT\right)_{ij}}{1 - A_\infty^\mathrm{E}/CRT - \sum_i x_i \left(a_i/b_i RT\right)} \tag{2}$$

with

$$\left(b - a/RT\right)_{ij} = \frac{1}{2}\left[\left(b_i - a_i/RT\right) + \left(b_j - a_j/RT\right)\right]\left(1 - k_{ij}\right) \tag{3}$$

where a_i and b_i are the energy and co-volume parameters of pure component i, $C = \ln(\sqrt{2}-1)/\sqrt{2}$, and A_∞^E is the excess Helmholtz energy of the mixture at infinite pressure, which is approximated by the excess Gibbs function at low pressures. In this work, we use the NRTL solution model [6]:

$$\frac{A_\infty^\mathrm{E}}{RT} = \frac{G^\mathrm{E}}{RT} = \sum_i x_i \left[\sum_j x_j G_{ji}\tau_{ji} \Bigg/ \left(\sum_k x_j G_{ji}\right)\right], \tag{4}$$

with

$$G_{ij} = \exp\left(-\alpha_{ij}\tau_{ij}\right). \tag{5}$$

Here, τ_{ij} and τ_{ji} are interaction parameters and α_{ij} is the non-randomness parameter which, in this work, it is taken to be 0.3. In this work, the parameters k_{ij}, τ_{ij} and τ_{ji} were represented as linear functions of inverse temperature as follows:

$$k_{12} = A + B(1000\mathrm{K}/T), \tag{6}$$

$$\tau_{12} = C + D(1000\mathrm{K}/T), \tag{7}$$

$$\tau_{21} = E + F(1000\mathrm{K}/T). \tag{8}$$

Thus, for each system studied, a total of six binary parameters (A to F) were regressed simultaneously against the experimental data on all isotherms studied. The objective function to be minimized was based on the pressure as follow:

$$S = \sum_{i=1}^{N} \left(\frac{p_i^{\text{exp}} - p_i^{\text{cal}}}{p_i^{\text{exp}}} \right)^2 . \qquad (9)$$

Here, p_i^{exp} and p_i^{cal} are the experimental and calculated pressure at the i^{th} state point, and N is the number of experimental data points. The calculated pressure and vapor phase composition are listed in Table 2 and 3 for (CO_2 + butylbenzene) and (CO_2 + butylcyclohexane), respectively, and the calculated results are also plotted in Figs 2 and 3.

The regressed parameters are given in Table 5 for the two mixtures, while the calculated average absolute relative deviations of pressure, Δ_p, and vapor-phase mole fraction, Δ_y, for each isotherm are summarized in Tables 6. For (CO_2 + butylbenzene), the Δ_p are below 1.0% for all the three isotherms, while for the (CO_2 + butylcyclohexane) binary system, slightly larger deviations up to 1.7 % are found. In terms of the vapor-phase composition, Δ_y increases with increasing temperature and, for both mixtures, the largest deviations occur as the mixture critical points are approached.

4. Conclusions

With our analytical apparatus, phase equilibira of CO_2 + butylbenzene and CO_2 + butylcyclohexane mixtures were measured at temperature 323.15 K, 373.15 and 423.15 K, and at pressure up to 21 MPa. For the CO_2 + butylbenzene system, our measurement are compared with the literature values, while for the CO_2 + butylcyclohexane system, no literature data is reported. The measured data are correlated using PR EoS with Wong-Sandler mixing rules. The model performs quite well at low pressures, at high pressures close to the mixture critical points, the model performs slightly worse, especially in terms of dew points calculation.

Nomenclature

a	energy parameter in equation of state
A	Helmholtz function
AAD	average absolute deviation
b	co-volume parameter in equation of state
C	mixing rule parameter
G	Gibbs function, NRTL solution model interaction parameter
i	component i, data point i
k	interaction parameter
N	number of data points

n	mole amount
p	pressure
R	universal gas constant
S	objective function
T	temperature
x	molar fraction in the liquid phase
y	molar fraction in the vapor phase

Greek letters

α	nonrandomness parameter
Δ	absolute average relative deviation
τ	NRTL solution model interaction parameter

Subscripts

i, j	component i, j and data point i
m	mixture
∞	infinite pressure

Superscripts

E	excess function
cal	calculated value
exp	experimental value

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Table 1. Description of chemical samples.

Chemical name	CAS number	Source	Specified mole fraction Purity
Carbon dioxide	124-38-9	BOC	0.9995
Butylbenzene	104-51-8	Sigma-Aldrich	0.99
Butylcyclohexane	1678-93-9	Sigma-Aldrich	0.99

Table 2. Experimental liquid composition x_1 and vapor composition y_1 for [CO_2 (1) + butylbenzene (2)] at temperatures T and pressures p together with associated standard uncertainties $u(x_1)$ and $u(y_1)$. Calculated value p^{cal} and y_1^{cal} are also given. [a]

T (K)	p (MPa)	x_1	$u(x_1)$	y_1	$u(y_1)$	p^{cal} (MPa)	y_1^{cal}
323.15	2.120	0.1563	0.0013	0.99240	0.00012	2.092	0.99934
323.15	4.533	0.3317	0.0024	0.99680	0.00005	4.539	0.99928
323.15	6.315	0.4718	0.0021	0.99648	0.00013	6.350	0.99893
323.15	7.533	0.5716	0.0019	0.99652	0.00019	7.436	0.99853
323.15	8.386	0.6755	0.0041	0.99559	0.00017	8.333	0.99801
323.15	8.995	0.7710	0.0023	0.99337	0.00017	8.969	0.99743
323.15	9.554	0.8975	0.0017	0.98903	0.00021	9.635	0.99594
323.15	9.658	0.9327	0.0015	0.98533	0.00011	9.763	0.99501
373.15	2.124	0.1034	0.0021	0.98963	0.00013	2.123	0.99451
373.15	5.330	0.2478	0.0025	0.99294	0.00017	5.412	0.99561
373.15	8.484	0.3843	0.0016	0.98958	0.00032	8.720	0.99415
373.15	11.567	0.5107	0.0018	0.98470	0.00017	11.693	0.99125
373.15	15.543	0.6973	0.0018	0.96993	0.00045	15.459	0.98454
373.15	16.287	0.7411	0.0026	0.96185	0.00027	16.197	0.98254
373.15	17.359	0.8260	0.0021	0.92973	0.00035	17.339	0.97778
423.15	2.186	0.0830	0.0012	0.96453	0.00014	2.166	0.97363
423.15	5.780	0.2088	0.0027	0.97652	0.00049	5.740	0.98309
423.15	9.384	0.3256	0.0041	0.97697	0.00042	9.344	0.98195
423.15	13.576	0.4618	0.0018	0.96304	0.00110	13.607	0.97609
423.15	16.258	0.5486	0.0011	0.95816	0.00059	16.170	0.97032
423.15	19.120	0.6534	0.0013	0.94306	0.00105	18.928	0.96171
423.15	20.988	0.7559	0.0012	0.90423	0.00051	21.015	0.95251
423.15	21.420	0.8269	0.0026	0.86804	0.00104	21.548	0.94605

[a] Standard uncertainties are $u(T) = 0.05$ K and $u(p) = 0.0004p$.

Table 3. Experimental liquid composition x_1 and vapor composition y_1 for [CO_2 (1) + butylcyclohexane (2)] at temperatures T and pressures p together with associated standard uncertainties $u(x_1)$ and $u(y_1)$. Calculated value p^{cal} and y_1^{cal} are also given. [a]

T (K)	p (MPa)	x_1	$u(x_1)$	y_1	$u(y_1)$	p^{cal} (MPa)	y_1^{cal}
323.15	2.351	0.1505	0.0010	0.99561	0.00006	2.289	0.99920
323.15	5.024	0.3387	0.0014	0.99864	0.00002	5.074	0.99906
323.15	7.253	0.5105	0.0021	0.99710	0.00003	7.209	0.99846
323.15	8.604	0.6400	0.0033	0.99541	0.00006	8.422	0.99780
323.15	9.208	0.7307	0.0034	0.99087	0.00017	9.095	0.99724
323.15	9.506	0.8109	0.0022	0.98593	0.00008	9.597	0.99657
323.15	9.741	0.9441	0.0008	0.97506	0.00023	9.883	0.99391
373.15	2.413	0.1085	0.0003	0.99021	0.00006	2.405	0.99422
373.15	4.957	0.2227	0.0003	0.99354	0.00005	5.129	0.99527
373.15	7.517	0.3289	0.0016	0.99102	0.00012	7.744	0.99448
373.15	10.292	0.4452	0.0020	0.98683	0.00006	10.513	0.99248
373.15	12.561	0.5431	0.0031	0.98238	0.00026	12.657	0.99010
373.15	15.178	0.6631	0.0041	0.97118	0.00014	15.034	0.98640
373.15	17.107	0.7930	0.0027	0.94049	0.00017	17.358	0.98099
423.15	2.339	0.0849	0.0003	0.96923	0.00027	2.265	0.97270
423.15	5.994	0.2131	0.0006	0.97940	0.00008	5.968	0.98265
423.15	8.784	0.3066	0.0006	0.98034	0.00031	8.843	0.98223
423.15	12.285	0.4173	0.0008	0.97256	0.00049	12.252	0.97876
423.15	15.383	0.5178	0.0012	0.96004	0.00035	15.184	0.97373
423.15	18.103	0.6134	0.0007	0.94813	0.00037	17.745	0.96761
423.15	20.208	0.7155	0.0009	0.91374	0.00025	20.184	0.96030

[a] Standard uncertainties are $u(T) = 0.05$ K and $u(p) = 0.0004p$.

Table 4. Critical temperature T_c, critical pressure p_c and acentric factor ω for the pure compounds [14, 15].

Compound	T_c (K)	p_c (MPa)	ω
CO_2	304.13	7.3773	0.22394
butylbenzene	660.48	2.887	0.39267
butylcyclohexane	653.10	2.560	0.37042

Table 5. Regressed model parameters for [CO_2 (1) + butylbenzene (2)] and [CO_2 (1) + butylcyclohexane (2)].

System	*A*	*B*	*C*	*D*	*E*	*F*
CO_2 (1) + butylbenzene (2)	0.8927	-0.0704	0.5852	0.8010	-1.7196	0.4358
CO_2 (1) + butylcyclohexane (2)	0.9715	-0.0811	0.4578	0.9621	-2.1422	0.6686

Table 6. Calculated absolute average relative deviations of pressure (Δ_p) and vapor-phase mole fraction (Δ_y) for [CO_2 (1) + butylbenzene (2)] and [CO_2 (1) + butylcyclohexane (2)].[a]

System	*T* (K)	Δ_p	Δ_y
CO_2 (1) + butylbenzene (2)	323.15	0.8 %	0.0046
	373.15	1.0 %	0.0146
	423.15	0.6 %	0.0239
CO_2 (1) + butylcyclohexane (2)	323.15	1.4 %	0.0062
	373.15	1.7 %	0.0112
	423.15	1.1 %	0.0135

[a] $\Delta_p = \frac{1}{N}\sum_i \frac{\left|p_i^{\mathrm{exp}} - p_i^{\mathrm{cal}}\right|}{p_i^{\mathrm{exp}}}$, $\Delta_y = \frac{1}{N}\sum_i \left|y_i^{\mathrm{exp}} - y_i^{\mathrm{cal}}\right|$

Figures

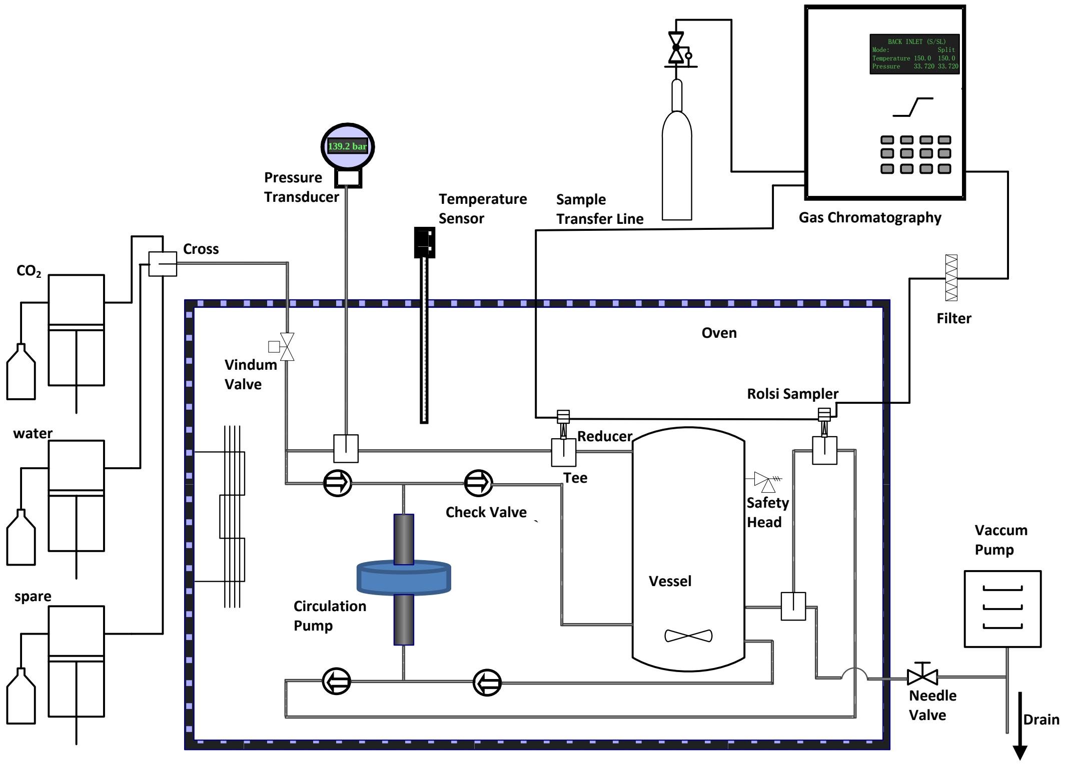

Fig. 1. Schematic diagram of the experimental setup

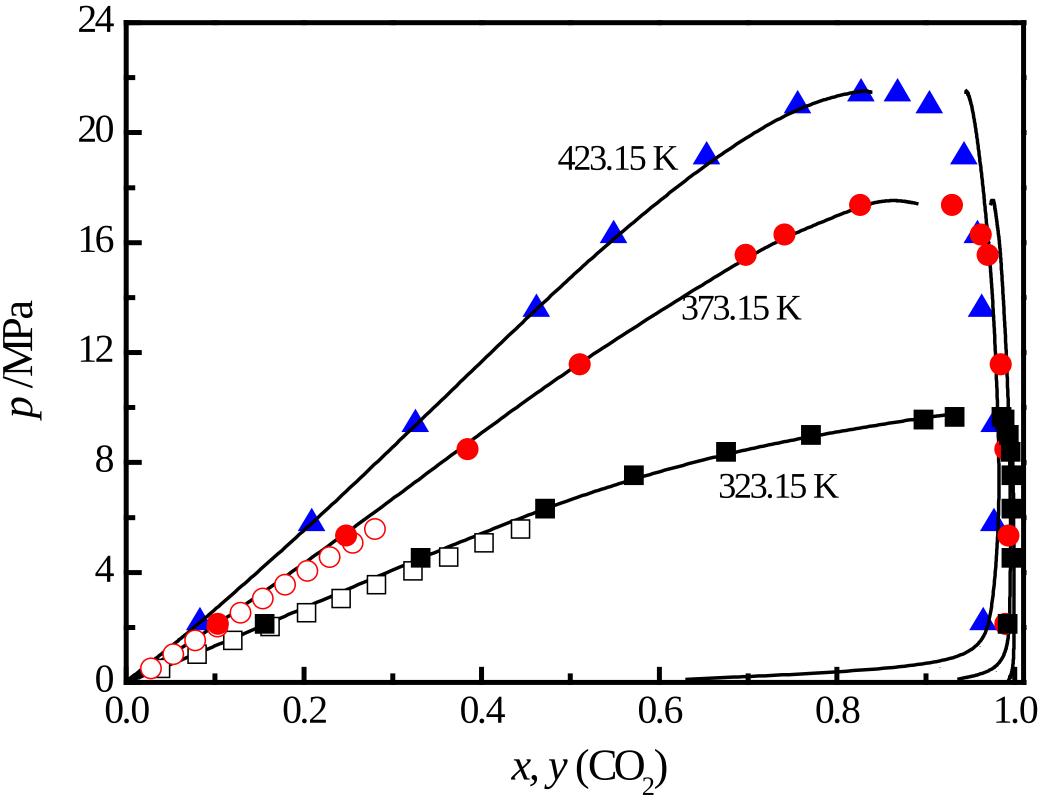

Fig. 2. *pxy* diagram for (CO_2 + butylbenzene). This work: ■, T = 323.15 K; ●, T = 373.15 K; ▲, T = 423.15 K. Zarah et al. [11]: □, T = 323.15 K; ○,T = 373.15 K. ———, calculated bubble and dew point curves.

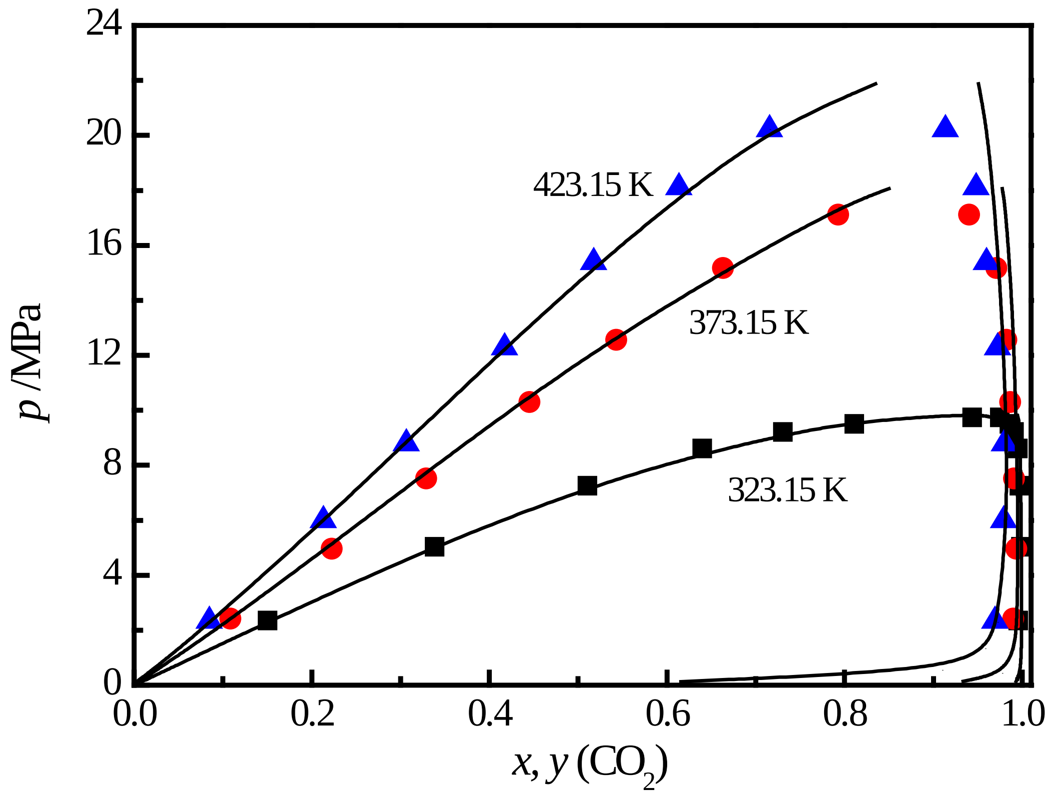

Fig. 3. *pxy* diagram for (CO_2 + butylcyclohexane). This work: ■, T = 323.15 K; ●, T = 373.15 K; ▲, T = 423.15 K; ———, calculated bubble and dew point curves.