



Effect of water content on the equilibrium pressure of (carbon dioxide + decane and + decalin) from $T = (313.15 \text{ to } 333.15) \text{ K}$



Inaura C.C. Rocha^a, Rosana L. Fialho^{a,*}, José J. Marques^b, Cláudio Dariva^c, Fernando L.P. Pessoa^d

^a Industrial Engineering Post Graduation Program, Federal University of Bahia, Bahia 40210-630, Brazil

^b Department of Chemical Engineering, Federal University of Sergipe, Sergipe 49100-000, Brazil

^c PEP/PBI/UNIT, NUESC/ITP, Tiradentes University, Sergipe 49032-490, Brazil

^d EQ/UFRJ, Federal University of Rio de Janeiro, Rio de Janeiro 21945-970, Brazil

ARTICLE INFO

Article history:

Received 20 February 2013

Received in revised form 7 May 2013

Accepted 10 May 2013

Available online 18 May 2013

Keywords:

Phase transitions

Carbon dioxide

Decane

Decalin

Water

ABSTRACT

Phase behaviour of mixtures containing hydrocarbons, water and carbon dioxide are of great interest to the petroleum and related industries. However, to describe the effect of water on phase equilibria remains a challenge from theoretical and experimental point of view. Phase transitions for the {decane ($C_{10}H_{22}$) + water + CO_2 } and {decalin ($C_{10}H_{18}$) + water + CO_2 } system were measured using an apparatus based on the visual synthetic method. The experimental work was carried out in a high-pressure equilibrium cell. Using this apparatus, temperatures ranging from 313 K to 333 K and pressures up to 15 MPa can be handled. Phase transitions were mainly affected by critical points of miscibility and also by the vicinity of the CEP.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

The continued interest in the use of supercritical CO_2 as at least one component of miscible displacement of hydrocarbon fluids has appeared in the petroleum industry for tertiary oil recovery since the 1980s [1]. Phase behaviour of mixtures containing hydrocarbons, water and carbon dioxide are of great interest to petroleum and related industries due to reservoir simulation and the design of transport and separator equipment [2]. However, the effect of water on equilibrium properties remains a challenge in some industrial cases.

In the literature, one can find several studies on (water + hydrocarbons) phase equilibria containing alkanes as the organic phase but little studies are found with decahydronaphthalene (decalin), as a mixture of *cis*- and *trans*- isomers. Due to the importance of decane and decalin as oil in several kinetic studies and be commonly found in the composition of fuels [3] decane and decalin were chosen as the candidate solvents to represent normal (decane) and cycloparaffins (decalin) present in petroleum. In addition, in order to do a comparison between an aliphatic and naphthenic phase behaviour, since the presence of naphthenic hydrocarbons is widely expressive in typical oils, the effect of water content on the equilibrium pressure of ($C_{10}H_{18} + CO_2$) was also investigated.

Decane and decalin are hydrocarbons with same carbon number and have almost the same molar mass. Their differences are attributed to their structures: decane has a linear chain while decalin is cyclical with two rings in its structure. For this reason, equilibrium phase behaviour can be quite complex and unlike. The perspective of complexity is apparent from the point of view of van Konynenburg and Scott [4]. According to their classification, the phase behaviour for the (carbon dioxide + decane) binary system is type II [5] while (carbon dioxide + decalin) exhibits type III [6]. The phase behaviour is even more extreme in the case of (decane + water) and (decalin + water) whereas there is also a significantly smaller amount of data.

Apparently, these systems have not been explored from the experimental point of view. Mixtures of hydrocarbons and/or carbon dioxide with water have received attention in the literature not only because of their practical interest but also because of the theoretical challenges presented in attempting to model such systems accurately. Both types of systems are known to form highly non-ideal mixtures due to the strong association of water. This contributes to the associated use of different types of experimental methods with or computational technique.

The use of experimental data and thermodynamic models has been a successful in predicting the phase equilibria behaviour of fluids of interesting. However, phase equilibrium computations are usually regarded as being difficult due to lack of experimental data. Despite the fact that the literature covers a wide range of components under various temperature and pressure conditions,

* Corresponding author. Tel.: +55 71 32839800; fax: +55 71 32839801.

E-mail addresses: rosanafialho@ufba.br, rosanalopesfialho@gmail.com (R.L. Fialho).

TABLE 1
Provenance and purity of the materials used in the study.

Chemical name	Source	Mass fraction purity	Purification method
Carbon dioxide	Linde Gas	>0.999	Chemicals used without further purification
Ethanol	Vetec Química Fina	>0.998	
Decane	Vetec Química Fina	>0.99	
Decalin	Vetec Química Fina	>0.99	

there are a few experimental data reported for the (hydrocarbons + water + CO₂) ternary systems. That is why several research groups are still working on data acquisition.

So far some researchers have published experimental measurements including water in their systems: Okafor [7] studied the (decane + CO₂ + H₂O) system at $T = (313, 343 \text{ and } 393) \text{ K}$ while Forte *et al.* [5] measured the same system between $T = (323 \text{ and } 423) \text{ K}$; Wang and Chao [8] measured the vapour-liquid (VLE) and liquid-liquid (LLE) equilibria of the (decane + O₂) system at temperatures (473, 493 and 513) K; Brunner [9] studied the global phase behaviour for 23 mixtures of (water + linear hydrocarbons) (1 to 36 carbon numbers) in the range from $T = (300 \text{ to } 600) \text{ K}$; Bidart *et al.* [10] also investigated the description of the phase behaviour of binary mixtures of (water + n-alkane) ($n = 1-36$), considering the topological approach introduced by van Konynenburg and Scott [4] Takenouchi and Kennedy [11], Bamberger *et al.* [12], Valtz *et al.* [13] are a few researchers who investigated a (CO₂ + H₂O) system under various experimental conditions. Finally, there are some review articles about experimental investigation techniques such as Schneider [14], Dohrn and Brunner [15] and Fonseca *et al.* [16] available in the literature.

Although there are some studies concerning the effect of water in (CO₂ + hydrocarbon) mixtures, there is a scarcity of experimental data mostly for decalin. So, it is of great importance to investigate mixtures with all three components in complex situations such as will be presented here. It is interesting to mention that no study has provided details of experimental phase transitions, especially with regard to the quantity of water in the mixture, either for decane or decalin.

In this study, synthetic mixtures of (C₁₀H₂₂ + H₂O + CO₂) and (C₁₀H₁₈ + H₂O + CO₂) were elaborated to represent fractions that may occur in crude oil. The phase transitions of these mixtures were measured at three temperatures (313.15, 323.15, and 333.15) K and under different proportions of water (1, 5, and 10)% w/w H₂O: Hydrocarbon in order to evaluate their influence on the (carbon dioxide + hydrocarbon) phase equilibria. To the best of our knowledge, this is the first time that the phase behaviour of these ternaries systems is studied in comparative mode.

2. Experimental

The suppliers and the purity of the chemicals used in this study are summarized in table 1. All compounds were used as received, without further purification. In the case of decalin, compound is a mixture of *cis*- and *trans*-isomers. Double distilled water was used for preparation of the solutions. The experimental work was carried out in a high-pressure equilibrium cell and the applied experimental procedure is based on the visual synthetic method, which means that no sampling is necessary. An advantage of this apparatus is that the appearance of a new phase can be safely detected by visual observation [16].

2.1. Apparatus and procedures

The apparatus in figure 1 consists of three main sections: (i) feeding pure carbon dioxide (ii) achieving phase equilibrium and (iii) observing phase transitions. The principal components of the first section include a CO₂ cylinder (CCO₂), a water thermal bath (WB) and a high-pressure syringe pump (SP). The carbon dioxide stocked in the cylinder is refrigerated by the water bath and then sent to the syringe pump. The cold water is kept circulating between the thermal bath and jacket of the syringe pump.

The second main section includes a pressure generator (SP) and measurement system (P), a heat generator (HG) and temperature measurement (T) system, a magnetic stirrer plate (MS) and a windowed variable volume cell (CELL). The view cell is cylindrical, fabricated from stainless steel (316 SS) and is composed of four major parts: a cell body (187 mm total length), a frontal window (FW) and

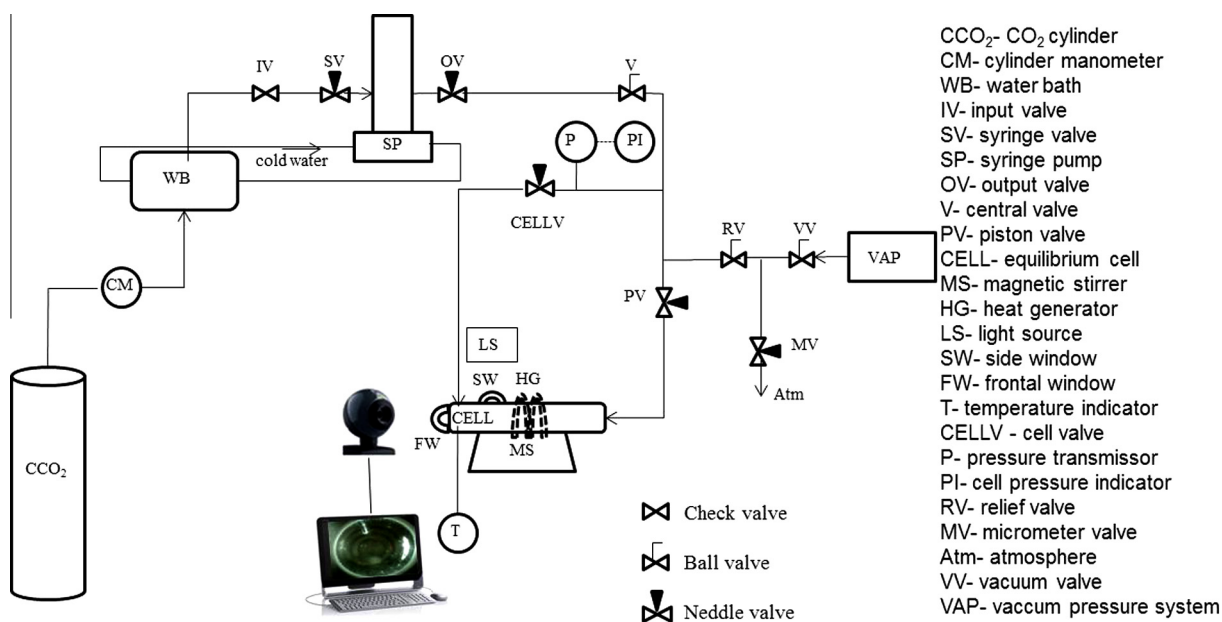


FIGURE 1. Schematic diagram of phase equilibrium apparatus.

side sapphire windows (SW) located on the top and a steel piston (40.5 mm length) to vary the internal volume of the equilibrium cell. The cell is enclosed by an electric resistance and an automatic control system that keeps the temperature constant. A magnetic stir bar inside the cell helped the mixture to reach equilibrium. The mixture in the equilibrium cell was compressed to the desired pressure by moving this piston located inside the cell. The pressure is measured by a calibrated pressure transducer (GEFRAN model MNO-6-MB35D) with uncertainty of ± 0.005 MPa. High pressure in the system is attained by pumping the gaseous component (CO_2) into the back of equilibrium cell through the piston valve (PV).

The third one is composed of a light source (LS), a webcam and a computer for better and safe visualization of all phenomena. In the frontal window, a view of the cell interior was possible due to a webcam connected to a computer. Figure 1 shows all the components mentioned and the simplified scheme of the experimental apparatus.

The experiment begins by loading the equilibrium cell with a mixture of water and liquid hydrocarbons of a known composition. In order to ensure the integrity of the mixture, the air present in the equilibrium cell was removed by drawing a quick vacuum (VAP). After this, the carbon dioxide fraction is inserted into the cell to complete the global composition of mixture. For the determination of the volume to be inserted, the density of CO_2 must be known. It can be done knowing the temperature and pressure inside the line up to CELLV valve (in this study, maintained at $T = 293.15$ K and 10 MPa). The density value was obtained using the equation in Angus *et al.* [17]. Enough CO_2 is also added by the piston valve to prevent sudden stresses on cell glass windows before heating. The magnetic stirrer is activated and the cell is heated to the experimental temperature. When the experimental temperature reaches steady state, the cell is pressurized with CO_2 until the gas and hydrocarbon is in a single phase. A time is required for equilibrium establishment (15 min) and then the pressure was slowly decreased until incipient formation of a new phase. A bubble pressure was recorded when small vapour bubbles appeared (usually in the middle or in the top) in the cell or when the piston was completely hid by a fog. Also, in experiments with high water content (when the inner visibility became quite complicated) the agitation in the cell had to be reduced otherwise the exact moment of phase transition would be lost. For each composition, the pressurization/depressurization procedure was repeated three times and standard deviations were verified. At the end of procedure, the CO_2 is released into atmosphere using relief (RV) and micrometer (MV) valves.

3. Results and discussion

3.1. Binary system

The vapour–liquid equilibrium (VLE) of (ethanol + CO_2) system has been measured in order to validate the experimental procedure by comparison with data previously reported by other authors. The results obtained are shown in table 2. In this table, compositions are expressed as mole fractions. It can be seen (figures 2 and 3) that the data obtained in this work agree well with the data in the literature [18–27] although some data measured in this work systematically deviate below the data previously reported by other authors. Possibly this can be attributed to the differences between experimental methods employed in these researches such as synthetic and analytical ones.

3.1.1. Ternary systems

To explain the final results of this experimental work, it is worth explaining the initial condition of both systems (when desired

TABLE 2

Experimental (vapour + liquid) equilibria data for temperature T , pressure p and mole fraction x for the system ($\text{CO}_2(1) + \text{ethanol}$).^a

x_1	p/MPa	
	$T/313.15$ K	$T/333.15$ K
0.259	3.84	5.07
0.268	3.99	5.19
0.512	6.13	8.42
0.518	6.34	8.53
0.709	6.67	10.05
0.712	6.88	10.01

^a Uncertainties provided are the standard deviations of each value. $u(T) = 0.1$ K; $u(p) = 0.01$ MPa; $u(x_1) = u(y_1) = 0.001$.

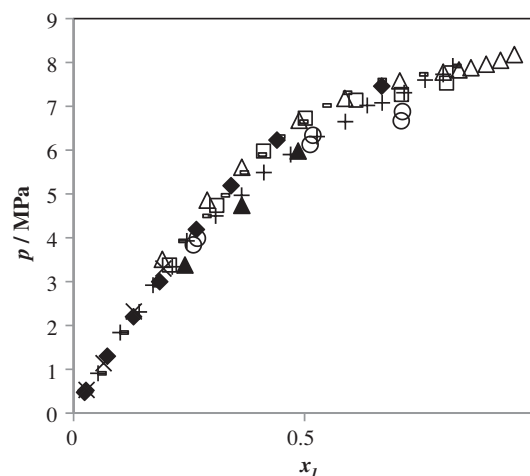


FIGURE 2. p vs. x_1 (mole fractions) in the CO_2 (1) + ethanol (2) system at 313.15 K: \circ , from this work; \square , Mehl *et al.* [18]; \triangle , Chiu *et al.* [19]; \times , Secuianu *et al.* [20]; \blacktriangle , Stievano and Elvassore [21]; \blacklozenge , Galicia-Luna *et al.* [22]; $-$, Chang *et al.* [23]; $+$, Day *et al.* [24].

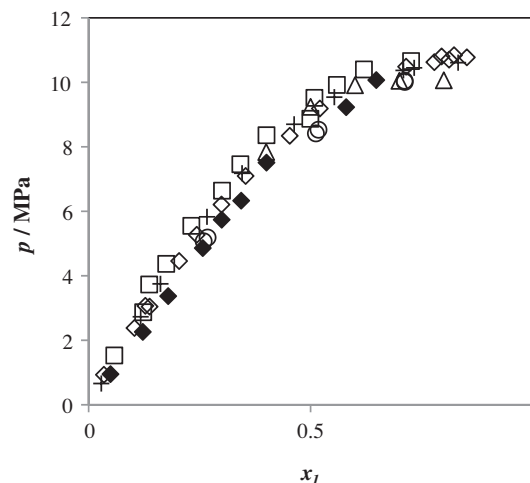


FIGURE 3. p vs. x_1 (mole fractions) in the CO_2 (1) + ethanol (2) system at 333.15 K: \circ , from this work; \square , Knez *et al.* [25]; \blacklozenge , Secuianu *et al.* [20]; \triangle Wu *et al.* [26]; $+$, Joung *et al.* [27]; \diamond , Galicia-Luna *et al.* [22].

pressures and temperatures are reached). During the initial heating of the cell, the coexistence of two liquid phases and one vapour phase were observed. As the cell was pressurized by the CO_2 injection, the disappearance of the vapour phase was confirmed by the

progressive increase in the meniscus in the cell. At the end of compression, two liquid phases were obtained which remained separated even at high pressures. This behaviour, more pronounced in poorer compositions in CO₂, was observed in the whole composition range. This is the reason why the system is classified as LLE.

It is also important to emphasize that at a given temperature and pressure, it was only possible to identify the phases present, however it was neither possible to determine their concentrations nor perform any sampling.

According to Benazzi [28], bubble pressure transitions are characterized by the formation and growth of bubbles at the top of the cell, while the dew point pressure transitions occur with the formation of a fine cloud and/or droplets in the cell background. The occurrence of transitions near the vicinity of critical point was demonstrated by changes of the optical properties of the mixture (change of colour to dark blue) [29]. The phase transitions observed in our experiments exhibited the same behaviour as described.

3.1.2. CO₂ + C₁₀H₂₂ + H₂O system

Results for the (CO₂ + C₁₀H₂₂ + H₂O) system are listed in tables 3–5. These data include measurements at $T = (313.15, 323.15, \text{ and } 333.15) \text{ K}$, and under (1, 5, and 10%) (w/w) H₂O:C₁₀H₂₂. The experimental pressures ranged from 2.27 MPa to 11.06 MPa and are the average of at least three different measurements. The standard deviations of pressure $u(p)$ determined for each composition were always less than 0.01 MPa. In the following tables, compositions are expressed as mass fractions. Bubble (BP) and dew (DP) points are also discriminated. However, in some cases it was not possible to identify if the transition was a dew type or was in the vicinity of critical point.

TABLE 3

Phase transition pressures p for temperature T and mass fraction x for the system {CO₂(1) + decane + water} with 1% (w/w) H₂O:C₁₀H₂₂.^a

x_1	$T/313.15 \text{ K}$		$T/323.15 \text{ K}$		$T/333.15 \text{ K}$	
	p/MPa	Transition	p/MPa	Transition	p/MPa	Transition
0.100	2.27	BP	2.49	BP	2.72	BP
0.251	4.76	BP	5.38	BP	6.00	BP
0.400	6.12	BP	7.15	BP	8.17	BP
0.553	7.02	BP	8.23	BP	9.52	BP
0.696	7.45	BP	8.85	BP	10.38	BP
0.799	7.69	BP	9.18	BP	10.93	BP
0.904	7.96	BP	9.43	DP	10.91	*

*Not identified.

^a Uncertainties provided are the standard deviations of each value. $u(T) = 0.1 \text{ K}$; $u(p) = 0.01 \text{ MPa}$; $u(x_1) = u(y_1) = 0.001$.

TABLE 4

Phase transition pressures p for temperature T and mass fraction x for the system {CO₂(1) + decane + water} with 5% (w/w) H₂O:C₁₀H₂₂.^a

x_1	$T/313.15 \text{ K}$		$T/323.15 \text{ K}$		$T/333.15 \text{ K}$	
	p/MPa	Transition	p/MPa	Transition	p/MPa	Transition
0.100	2.36	BP	2.61	BP	2.86	BP
0.251	4.84	BP	5.48	BP	6.15	BP
0.397	6.17	BP	7.10	BP	8.11	BP
0.549	7.06	BP	8.31	BP	9.69	BP
0.695	7.42	BP	8.82	BP	10.38	BP
0.804	7.65	BP	9.22	BP	10.91	BP
0.905	7.95	DP	9.43	DP	10.90	*

*Not identified.

^a Uncertainties provided are the standard deviations of each value. $u(T) = 0.1 \text{ K}$; $u(p) = 0.01 \text{ MPa}$; $u(x_1) = u(y_1) = 0.001$.

TABLE 5

Phase transition pressures p for temperature T and mass fraction x for the system {CO₂(1) + decane + water} with 10% (w/w) H₂O:C₁₀H₂₂.^a

x_1	$T/313.15 \text{ K}$		$T/323.15 \text{ K}$		$T/333.15 \text{ K}$	
	p/MPa	Transition	p/MPa	Transition	p/MPa	Transition
0.100	2.42	BP	2.67	BP	2.95	BP
0.251	5.02	BP	5.67	BP	6.39	BP
0.397	6.39	BP	7.35	BP	8.49	BP
0.549	7.13	BP	8.38	BP	9.80	BP
0.695	7.48	BP	9.02	BP	10.59	BP
0.804	7.73	BP	9.29	BP	11.03	BP
0.905	8.06	DP	9.46	DP	10.88	*

*Not identified.

^a Uncertainties provided are the standard deviations of each value. $u(T) = 0.1 \text{ K}$; $u(p) = 0.01 \text{ MPa}$; $u(x_1) = u(y_1) = 0.001$.

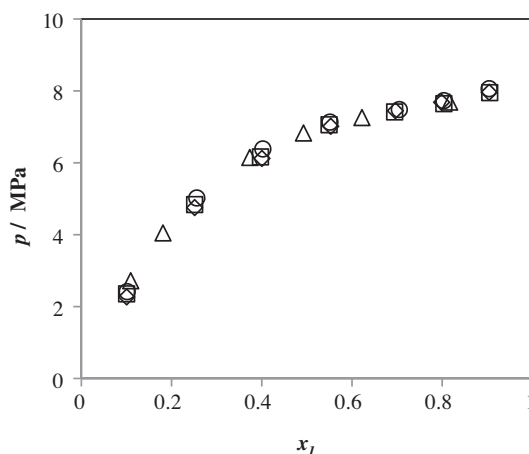


FIGURE 4. p vs. x_1 (mass fractions) in the CO₂ (1) + C₁₀H₂₂ (2) + H₂O (3) system at 313.15 K: Δ , without H₂O (data from Forte *et al.*, 2011 [5]); \diamond , 1% (w/w) H₂O:C₁₀H₂₂; \square , 5% (w/w) H₂O:C₁₀H₂₂; \circ , 10% (w/w) H₂O:C₁₀H₂₂.

The (CO₂ + C₁₀H₂₂ + H₂O) mixtures present two typical phase transitions. Before transition occurs, the entire mixture was in liquid phase, where water droplets were dispersed in another immiscible liquid. After loss of pressure, some gas bubbles appeared in the top and middle of the cell. Sometimes a cloud announces the appearance of bubbles. These may be a consequence of three immiscible liquid type phases once water is indeed immiscible with both hydrocarbons and CO₂ over the experimental range studied.

However, the appearance of bubbles was visually well defined in poor compositions in CO₂ and (w/w) H₂O:C₁₀H₂₂ ratios. When the amount of water is increased, the droplets of water in the cell as well as the cloud complicate the visual identification of the bubbles.

Another attribute of these data is the interesting behaviour shown in figures 4–6. For each composition of CO₂, phase transition pressures (p/MPa) vs. global composition (x_1) were plotted. The objective was to compare the influence of (1, 5, and 10%) (w/w) H₂O:C₁₀H₂₂ ratios in all global compositions at the same temperature. To promote a better understanding, experimental data of the binary (CO₂ + C₁₀H₂₂) at $T = 313.15 \text{ K}$ by Forte *et al.* [5] was inserted in the graph.

As can be seen, the curves almost overlap, even with the absence or increase in the amount of water and temperature in the system. This behaviour is consistent with the (CO₂ + C₁₀H₂₂ + H₂O) phase prediction at $T = 344 \text{ K}$, under pressures of 6.9 MPa and 13.8 MPa, developed by Kuan *et al.* [30]. They deduced that the

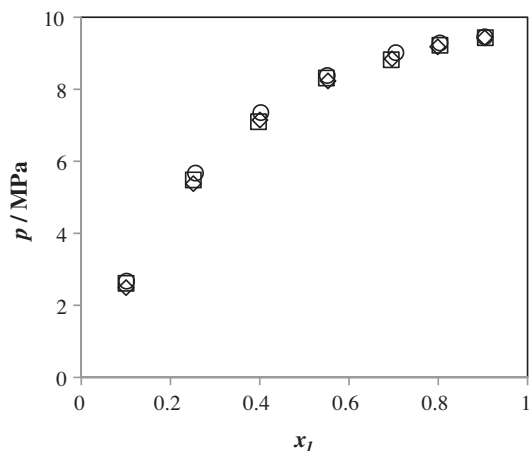


FIGURE 5. p Vs. x_1 (mass fractions) in the CO_2 (1) + $\text{C}_{10}\text{H}_{22}$ (2) + H_2O (3) system at 323.15 K: \diamond , 1% (w/w) $\text{H}_2\text{O}:\text{C}_{10}\text{H}_{22}$; \square , 5% (w/w) $\text{H}_2\text{O}:\text{C}_{10}\text{H}_{22}$; \circ , 10% (w/w) $\text{H}_2\text{O}:\text{C}_{10}\text{H}_{22}$.

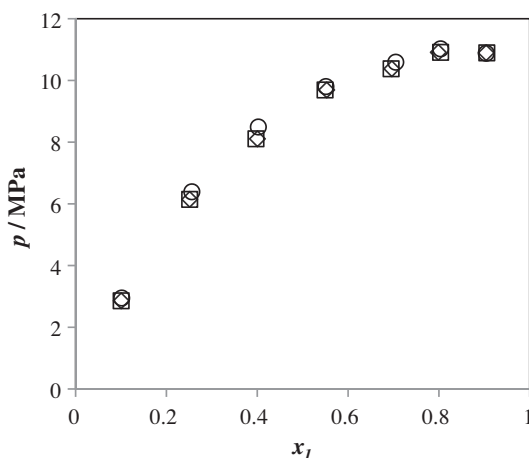


FIGURE 6. p Vs. x_1 (mass fractions) in the CO_2 (1) + $\text{C}_{10}\text{H}_{22}$ (2) + H_2O (3) system at 333.15 K: \diamond , 1% (w/w) $\text{H}_2\text{O}:\text{C}_{10}\text{H}_{22}$; \square , 5% (w/w) $\text{H}_2\text{O}:\text{C}_{10}\text{H}_{22}$; \circ , 10% (w/w) $\text{H}_2\text{O}:\text{C}_{10}\text{H}_{22}$.

presence of water does not change the CO_2 -and hydrocarbon- rich phases under these conditions.

3.1.3. $\text{CO}_2 + \text{C}_{10}\text{H}_{18} + \text{H}_2\text{O}$ system

For the $(\text{CO}_2 + \text{C}_{10}\text{H}_{18} + \text{H}_2\text{O})$ system, tables 6–8 present phase transition pressures. The standard deviations of pressure $u(p)$ determined for each composition were always less than 0.1 MPa. The pressures ranged from 3.42 MPa to 15.71 MPa.

One typical phase transition of these mixtures is the appearance of bubbles in CO_2 poor compositions. However, behaviour consistent with the presence of another phase transition was observed: this time, the transition was characterized by the formation of a mist in the system along with intense turbidity, but without visible bubbles. The cloudy aspect of the cell contents suggested the presence of three immiscible phases: one water phase and two quasi-critical organic phases.

As shown in figures 7–9, our phase transition pressure data exhibited the same tendency, followed by a small increase among pressures when the temperature is raised. According to Zuo *et al.* [31], the only significant effect of water on the phase equilibria of multicomponent hydrocarbon mixtures is a decrease in dew

TABLE 6

Phase transition pressures p for temperature T and mass fraction x for the system $\{\text{CO}_2(1) + \text{decalin} + \text{water}\}$ with 1% (w/w) $\text{H}_2\text{O}:\text{C}_{10}\text{H}_{22}$.^a

x_1	$T/313.15\text{ K}$		$T/323.15\text{ K}$		$T/333.15\text{ K}$	
	p/MPa	Transition	p/MPa	Transition	p/MPa	Transition
0.099	3.42	BP	3.79	BP	4.16	BP
0.252	6.55	BP	7.49	BP	8.47	BP
0.402	8.06	BP	9.52	BP	11.24	BP
0.550	12.70	BP	13.32	BP	14.63	BP
0.687	12.98	*	13.53	*	14.97	*
0.798	11.59	DP	12.79	DP	14.42	DP
0.901	8.32	DP	10.57	DP	12.54	DP

*Not identified.

^a Uncertainties provided are the standard deviations of each value. $u(T) = 0.1\text{ K}$; $u(p) = 0.1\text{ MPa}$; $u(x_1) = u(y_1) = 0.001$.

TABLE 7

Phase transition pressures p for temperature T and mass fraction x for the system $\{\text{CO}_2(1) + \text{decalin} + \text{water}\}$ with 5% (w/w) $\text{H}_2\text{O}:\text{C}_{10}\text{H}_{22}$.^a

x_1	$T/313.15\text{ K}$		$T/323.15\text{ K}$		$T/333.15\text{ K}$	
	p/MPa	Transition	p/MPa	Transition	p/MPa	Transition
0.102	4.19	BP	4.65	BP	5.11	BP
0.255	7.65	BP	8.7	BP	9.76	BP
0.401	10.59	BP	11.51	BP	12.83	BP
0.553	13.69	BP	13.97	BP	15.14	BP
0.705	13.65	*	14.69	*	15.71	*
0.853	9.93	DP	11.09	DP	13.32	DP
0.901	8.02	DP	10.55	DP	12.51	DP

*Not identified.

^a Uncertainties provided are the standard deviations of each value. $u(T) = 0.1\text{ K}$; $u(p) = 0.1\text{ MPa}$; $u(x_1) = u(y_1) = 0.001$.

TABLE 8

Phase transition pressures p for temperature T and mass fraction x for the system $\{\text{CO}_2(1) + \text{decalin} + \text{water}\}$ with 10% (w/w) $\text{H}_2\text{O}:\text{C}_{10}\text{H}_{22}$.^a

x_1	$T/313.15\text{ K}$		$T/323.15\text{ K}$	
	p/MPa	Transition	p/MPa	Transition
0.100	3.98	BP	4.38	BP
0.202	5.86	BP	6.62	BP
0.405	11.43	BP	12.11	BP
0.506	12.21	BP	12.8	BP
0.800	11.00	DP	12.45	DP
0.902	8.44	DP	10.43	DP

^a Uncertainties provided are the standard deviations of each value. $u(T) = 0.1\text{ K}$; $u(p) = 0.1\text{ MPa}$; $u(x_1) = u(y_1) = 0.001$.

point pressures, which is more pronounced as temperature is increased.

Thus, in order to investigate that effect more deeply, some $(\text{CO}_2 + \text{C}_{10}\text{H}_{18})$ binary data found in Mehl [32], Vitu *et al.* [33] and Silva [34] were added to the graphs. In fact, the presence of the aqueous phase causes the dew point curve to shift downward, and the dew point pressure decreases more steeply with the increase of temperature. This typical behaviour becomes evident comparing our data to those in Vitu *et al.* [33] as in figures 7–9.

On the other hand, there is an unusual instability associated with phase transition pressures between 0.2 and 0.5 mass fractions for the Mehl [32] data. This type of behaviour still remains without explanation for us.

Concerning the effect of water on the phase equilibria, Brady *et al.* [35] and Hemptinne *et al.* [36] concluded that the solubility of water in liquid hydrocarbons seems to be mostly affected by the type of hydrocarbon chain, with very little effect due to the

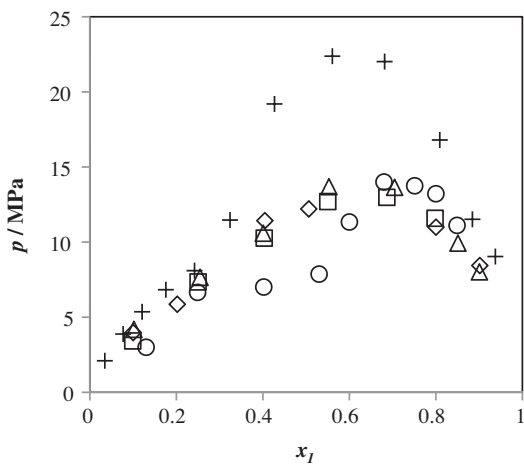


FIGURE 7. p Vs. x_1 (mass fractions) in the CO_2 (1) + $\text{C}_{10}\text{H}_{18}$ (2) + H_2O (3) system at 313.15 K: \square , 1% (w/w) $\text{H}_2\text{O}:\text{C}_{10}\text{H}_{18}$; \triangle , 5% (w/w) $\text{H}_2\text{O}:\text{C}_{10}\text{H}_{18}$; \diamond , 10% (w/w) $\text{H}_2\text{O}:\text{C}_{10}\text{H}_{18}$; \circ , without H_2O (data from Mehl, 2010 [32]); +, without H_2O (data from Vitu et al. [33]).

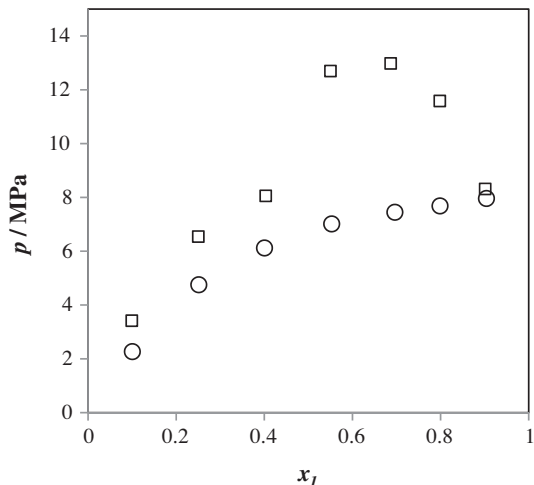


FIGURE 10. p Vs. x_1 (mass fractions) for both systems: \square , CO_2 (1) + $\text{C}_{10}\text{H}_{18}$ + H_2O ; \circ , CO_2 (1) + $\text{C}_{10}\text{H}_{22}$ + H_2O with 1% (w/w) $\text{H}_2\text{O}:\text{C}_{10}\text{H}_{22}$ and at 313.15 K.

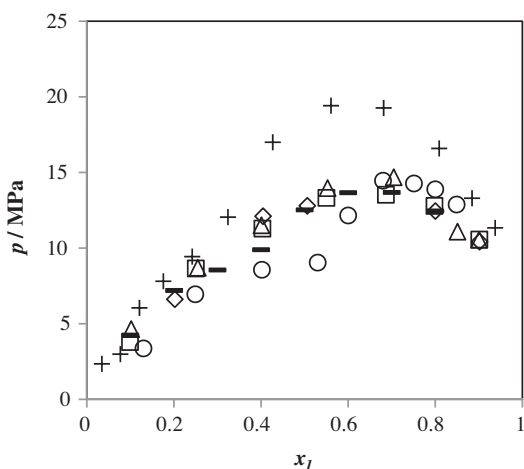


FIGURE 8. p Vs. x_1 (mass fractions) in the CO_2 (1) + $\text{C}_{10}\text{H}_{18}$ (2) + H_2O (3) system at 323.15 K: \square , 1% (w/w) $\text{H}_2\text{O}:\text{C}_{10}\text{H}_{18}$; \triangle , 5% (w/w) $\text{H}_2\text{O}:\text{C}_{10}\text{H}_{18}$; \diamond , 10% (w/w) $\text{H}_2\text{O}:\text{C}_{10}\text{H}_{18}$; —, 10% (w/w) $\text{H}_2\text{O}:\text{C}_{10}\text{H}_{18}$ (data from Silva et al., 2010 [34]); \circ , without H_2O (data from Mehl [32]); +, without H_2O (data from Vitu et al., 2008 [33]).

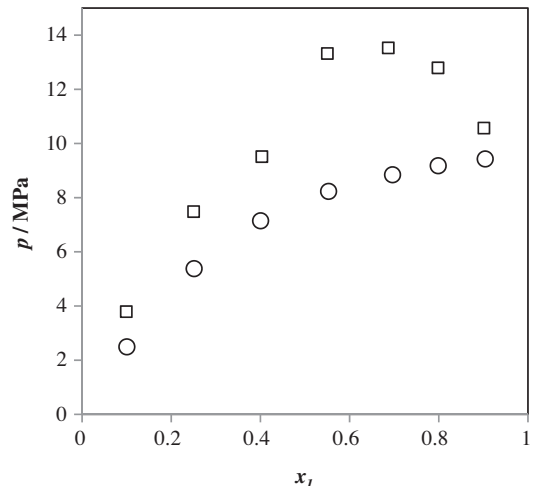


FIGURE 11. p Vs. x_1 (mass fractions) for both systems: \square , CO_2 (1) + $\text{C}_{10}\text{H}_{18}$ + H_2O ; \circ , CO_2 (1) + $\text{C}_{10}\text{H}_{22}$ + H_2O with 1% (w/w) $\text{H}_2\text{O}:\text{C}_{10}\text{H}_{22}$ and at 323.15 K.

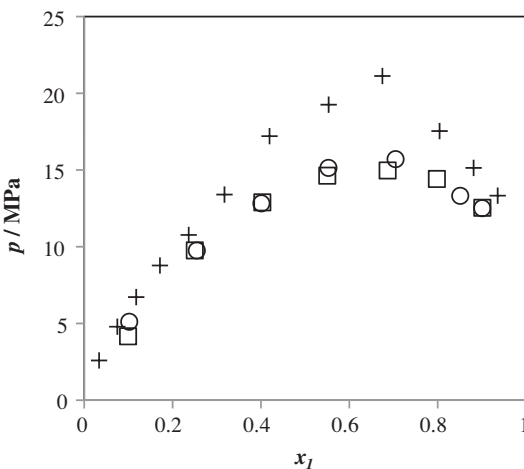


FIGURE 9. p Vs. x_1 (mass fractions) in the CO_2 (1) + $\text{C}_{10}\text{H}_{18}$ (2) + H_2O (3) system at 333.15 K: \square , 1% (w/w) $\text{H}_2\text{O}:\text{C}_{10}\text{H}_{18}$; \circ , 5% (w/w) $\text{H}_2\text{O}:\text{C}_{10}\text{H}_{18}$; +, without H_2O (data from Vitu et al., 2008 [33]).

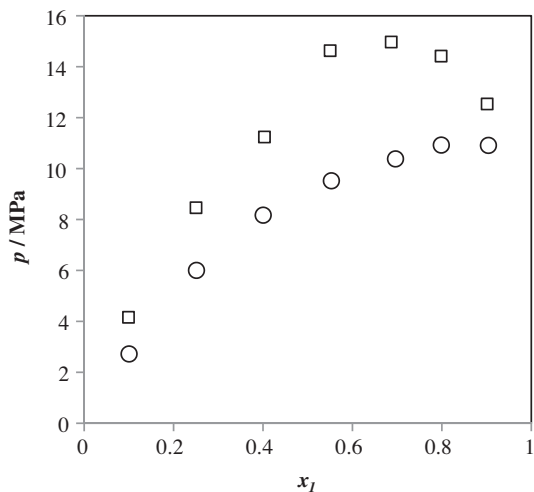


FIGURE 12. p Vs. x_1 (mass fractions) for both systems: \square , CO_2 (1) + $\text{C}_{10}\text{H}_{18}$ + H_2O ; \circ , CO_2 (1) + $\text{C}_{10}\text{H}_{22}$ + H_2O with 1% (w/w) $\text{H}_2\text{O}:\text{C}_{10}\text{H}_{22}$ and at 333.15 K.

carbon number or molecular weight. In this sense, as the phase behaviour may vary according to the hydrocarbon chain and once decane and decalin have distinct structures, different behaviours are expected.

Figures 10–12 support this argument as decane and decalin have the same carbon number, almost the same molar mass but are aliphatic and naphthenic respectively. This could be attributed to their differences in structure: the decane has a linear chain while decalin is cyclical with two rings in its structure.

Besides, (CO₂ + decane) exhibits Type II behaviour and the data reported in this work was determined over a temperature range where the quoted binary is completely miscible. The (CO₂ + decalin) system in turn exhibits Type III behaviour, and experimental measurements were performed in the vicinity of the CEP (critical end point). The trend of the equilibrium pressures for this second system, particularly the sharp inflections and maximum pressure points observed in figures 11–13, are a consequence of two facts: the determined isotherms are affected by critical points of immiscibility and also by the vicinity of the CEP.

4. Conclusions

Experimental data for the ternary systems of (CO₂ + decane + water) and (CO₂ + decalin + water) were measured at temperatures (313.15, 323.15, and 333.15) K and pressures up to 15.0 MPa. The results show that at a given composition, two different types of phase transitions could be observed, which results mainly in the appearance of bubbles or a cloud. At the same time, the contents of water remained unsolved even with increasing pressure or temperature.

The experimental pressures of both systems were compared graphically in order to observe the effect of water. The determined isotherms are affected by critical points of immiscibility and also by the vicinity of the CEP.

Acknowledgements

The authors are grateful for Brazilian financial support from the Coordination for the Improvement of Higher Level –or Education– Personnel (CAPES) and The Bahia State Research Support Foundation (FAPESB).

References

- [1] G.M. Schneider, *Pure Appl. Chem.* 63 (1991) 1313–1326.
- [2] A. Shariati, C.J. Peters, M. Moshfeghian, *J. Chem. Eng. Data* 43 (1998) 785–788.
- [3] Y. Liu, C.W. Wilson, *Adv. Mech. Eng.* 12 (2012) 1–13.
- [4] P.H. van Konynenburg, R.L. Scott, *Philos. Trans. R. Soc. London* 298 (1980) 495–540.
- [5] E. Forte, A. Galindo, J.P.M. Trusler, *Phys. Chem. B* 115 (2011) 14591–14609.
- [6] E. Brunner, M.C. Thies, G.M. Schneider, *J. Supercrit. Fluids* 39 (2006) 160–173.
- [7] M.N. Okafor, Phase equilibria from PVT measurements for carbon dioxide, water, and n-decane, Ph.D. Thesis, University of Missouri, 1987.
- [8] Q.I. Wang, K.-C. Chao, *Fluid Phase Equilib.* 59 (1990) 207–215.
- [9] E. Brunner, *J. Chem. Thermodyn.* 22 (1990) 335–353.
- [10] H. Segura, J. Wisniak, *Ind. Eng. Chem. Res.* 46 (2007) 947–954.
- [11] S. Takenouchi, G.C. Kennedy, *G.C. Am. J. Sci.* 262 (1964) 1055–1074.
- [12] A. Bamberger, G. Sieder, G. Maurer, *J. Supercrit. Fluids* 17 (2000) 97–110.
- [13] A. Valtz, A. Chapoya, C. Coquelet, P. Paricaudb, D. Richona, *Fluid Phase Equilib.* 226 (2004) 333–344.
- [14] G.M. Schneider, in: *Experimental Thermodynamics, vol. II: Experimental Thermodynamics of Non-Reacting Fluids*, International Union of Pure and Applied Chemistry, Butterworths, London, 1975.
- [15] R. Dohrn, G. Brunner, *Fluid Phase Equilib.* 106 (1995) 213–282.
- [16] J.M.S. Fonseca, R. Dohrn, S. Peper, *Fluid Phase Equilib.* 300 (2011) 1–69.
- [17] S. Angus, B. Armstrong, K.M. Reuck, V.V. Altunin, O.G. Gadetski, G.A. Chapela, J.S. Rowlinson, *International Thermodynamics Tables of the Fluid State: Carbon Dioxide*, Pergamon Press, New York, 1976.
- [18] A. Mehl, F.P. Nascimento, P.W. Falcão, F.L.P. Pessoa, L. Cardozo Filho, *J. Thermodyn.* (2011).
- [19] H.-Y. Chiu, R.-F. Jung, M.-J. Lee, H.-M. Lin, *J. Supercrit. Fluids* 44 (2008) 273–278.
- [20] C. Secuianu, V. Ferioui, D. Gean, *J. Supercrit. Fluids* 47 (2008) 109–116.
- [21] M. Stievano, N. Elvassore, *J. Supercrit. Fluids* 33 (2005) 7–14.
- [22] L.A. Galicia-Luna, A. Ortega-Rodriguez, *J. Chem. Eng. Data* 45 (2000) 265–271.
- [23] J.-S. Chang, M.-J. Lee, H.-M. Lin, *J. Chem. Eng. Data* 43 (1998) 233–237.
- [24] C.-Y. Day, C.-J. Chang, C.-Y. Chen, *J. Chem. Eng. Data* 41 (1996) 839–843.
- [25] Z. Knez, M. Skerget, L. Ili, C. Lutge, *J. Supercrit. Fluids* 43 (2008) 383–389.
- [26] J. Wu, J.M. Prausnitz, *Ind. Eng. Chem. Res.* 3 (1998) 1634–1643.
- [27] S.N. Joung, C.W. Yoo, H.Y. Shin, et al., *Fluid Phase Equilib.* 185 (2001) 219–230.
- [28] T.L. Benazzi, *Estudo do Comportamento de Fases de Sistemas Contendo Glicerol e Óleo de Oliva em Propano na Presença de Surfactante*. Thesis of Dissertation, Rio Grande do Sul, 2005.
- [29] G.V.S.M. Carrera, *Fluid Phase Equilib.* 303 (2011) 180–183.
- [30] D.-Y. Kuan, P.K. Kilpatrick, M. Sahimi, et al., *SPE Reser. Eng.* (1986) 61–72.
- [31] Y.-X. Zuo, E.H. Stenby, T.-M. Guo, *J. Petrol. Sci. Eng.* 15 (1996) 201–220.
- [32] A. Mehl, *Estudo do Equilíbrio de Fases de Hidrocarbonetos e CO₂ Supercrítico*, Ph.D. Thesis, Rio de Janeiro, 2009.
- [33] S. Vitu, J.-N. Jaubert, N. Pauly, J.-L. Daridon, *J. Chem. Thermodyn.* 40 (2008) 1358–1363.
- [34] J.N.C. Silva, *Estudo do Equilíbrio de Fases de Hidrocarbonetos, Água e CO₂ Supercrítico*, Thesis of Dissertation, Rio de Janeiro, 2010.
- [35] C.J. Brady, J.R. Cunningham, G.M. Wilson, Report RR-62, GPA; Provo, Ut., 1982.
- [36] J.C. Hemptinne, A. Dhima, H. Zhou, *Revue De L'Institut Français Du Pétrole* 53 (1998) 283–302.