Experimental and molecular modelling study of the three-phase behaviour of (propane + carbon dioxide + water) at reservoir conditions

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Abstract

Acquiring a comprehensive understanding of the phase behaviour of mixtures of crude-oil with carbon dioxide and water is a key input for reservoir engineering in processes of enhanced oil recovery and geological storage of carbon dioxide. To gain an insight, given the very complex nature of crude-oil mixtures, the study of simpler systems is of interest. In this work the system (propane + carbon dioxide + water) has been chosen as a model (light oil fraction + carbon dioxide + water) mixture. Phase equilibrium measurements have been carried out using a quasi-static-analytical high-pressure apparatus that was validated on the system (*n*-decane + carbon dioxide) in comparison with literature data, and used to study the system (*n*-decane + carbon dioxide + water) [Forte, E.; Galindo, A.; Trusler, J. P. M.; *J. Phys. Chem. B* 115 (49)(2011) 14591-14609]. In the present work, new experimental data have been measured for the system (propane + carbon dioxide + water) under conditions of three-phase equilibria. Compositions of the three coexisting phases have been obtained along four isotherms at temperatures from (311 to 353) K and at pressures up to the upper critical end points where the propane-rich and the carbon dioxide-rich phases become critical. The experimental data obtained for the ternary mixture have been compared to the predictions obtained with the statistical associating fluid theory for potentials of variable range (SAFT-VR). The phase behaviour of each pair of binary subsystems has been calculated using this theory and, where applicable, a modification of the Hudson and McCoubrey combining rules has been used to treat the systems predictively. Furthermore, a detailed analysis of the phase behaviour of the ternary mixture has been carried out based on comparison with available data for the constituent binary subsystems, as well as with the previous findings for the ternary (*n*-decane + carbon dioxide + water). Such comparison is useful to examine the effect that adding a third component has in the mutual solubility of each pair. Remarks relevant to reservoir processing are also highlighted.

Key words: Experimental data, Phase behaviour, SAFT-VR, Carbon dioxide, Water, Propane, Three-phase equilibria, Upper critical end point

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1. Introduction

Knowledge of phase equilibria is crucial in the design and operation of chemical processes, including separation, purification and extraction. Operations such as distillation, gas absorption or supercritical extraction are a few examples in which details of such behaviour are necessary. In particular, CO₂ plays an important role in supercritical fluid extraction [1]. Its excellent properties, such as non-toxicity, relatively low critical temperature and pressure, low cost and the possibility of being readily recovered and recycled, have made CO₂ not only the most common solvent in supercritical extraction, but also a powerful alternative to harmful organic solvents. Among the most attractive applications of carbon dioxide is its use as an injection gas for enhanced oil recovery (EOR) purposes. CO₂-EOR processes have been ongoing for around forty years [2, 3]. Furthermore, when CO₂ of anthropogenic origin is used in EOR, not only is oil recovery improved but also the CO₂ may be sequestered in the reservoir.

The importance of understanding the miscibility and, in general the phase behaviour, of carbon dioxide with oil in the context of both CO₂-EOR and CO₂ storage processes was reviewed in our previous work [4]. In summary, the CO₂ injected is likely to form two phases with the existing oil: a CO₂-rich and an oil-rich phase. In addition water is a working-fluid that may have been previously injected as a displacement fluid or in alternating steps with the CO₂ to improve the efficiency of the sweeping process. From a thermodynamic point of view the presence of water means that a third phase will typically coexist with the oil-rich and CO₂-rich phases. It is generally understood that reservoir conditions mean high temperatures and high pressures (characteristic temperatures for diverse oil reservoirs may vary from 300 K to 410 K with initial conditions of pressure from 10 MPa to 50 MPa [5–9]), although such pressure conditions will obviously vary during the life of the reservoir. The essential input for CO₂-EOR processes from phase equilibria measurements is however limited to pressures on the bubble-curve locus of hydrocarbons with CO₂ in the presence of water. Regarding the sequestration of the CO₂, although structural and capillary trapping are known to be the primary processes at play, dissolution of the CO₂ is one of the long-term mechanisms for immobilizing CO₂ in the reservoir. In numbers, solubility trapping prevails in a scale from ten to hundreds of years [10, chap.5] after injection.

Given the complexity of oil mixtures, a necessary step towards acquiring a comprehensive understanding of the behaviour of (oil + carbon dioxide + water) is the completion of a database comprising simpler hydrocarbon systems. In spite of the attention that binary combinations of alkanes, carbon dioxide and water have received, experimental data concerning ternary (*n*-alkane + carbon dioxide + water)-type mixtures are sparse. The system (*n*-hexadecane + carbon dioxide + water) is the one with the heaviest hydrocarbon that has been studied [11]. In that study, mainly VLE was measured at temperatures between (473.15 and 573.15) K and pressures between (10 and 30) MPa, but also one experimental point was reported in the three-phase equilibrium region at 473.15 K and 20 MPa [11]. The system (*n*-decane + carbon dioxide + water)

was the focus of our earlier work [4], where three-phase vapour-liquid-liquid equilibrium (VLLE) data were measured at temperatures from (323 to 413) K and pressures from (1 to 18) MPa. The remaining studies found in the literature concern lighter alkanes. Among mixtures consisting of carbon dioxide with water and an alkane of low molecular weight, the system (methane + carbon dioxide + water) has been the most widely studied, not only regarding fluid-phase equilibria [12–15] but also fluid-hydrate equilibria [16–19]. Most of these fluid-phase equilibrium studies in ternary mixtures have focused on vapour-liquid equilibrium (VLE) and, with the exception of that of Qin et al. [12], only one phase composition was measured. In the study of Song and Kobayashi [15] measurements were made along the three-phase equilibrium locus, but only the CO₂-rich phase was analyzed. Studies concerning ethane, propane or butane are fewer in number [13, 20]. The latter studies were focused on the determination of dew points of the mixtures at low temperature (below 289 K) and pressure (up to 2.4 MPa) using a semi-flow apparatus. Regarding the system (propane + carbon dioxide + water) two experimental studies are reported in the literature, both focused on phase equilibrium with hydrates [21, 22] at temperatures up to 286 K [21, 22]. There appear to be no experimental data on vapour-liquid-liquid equilibrium (VLLE) for this system. Based on this study of the literature, we choose to study in this work (propane + carbon dioxide + water) as a model (light oil fraction + carbon dioxide + water) mixture with the objective of providing new VLLE measurements.

Aqueous systems of alkanes and/or CO₂ present complex phase behaviour to be measured due to the low solubilities of these compounds in water for large temperature ranges below the critical temperature of water (647 K). The (propane + water) system exhibits type III phase behaviour in the classification of Scott and van Konynenburg [23, 24], typical of (alkane + water) mixtures as well as the system (CO₂ + water); type III phase behaviour is characteristic of very immiscible systems with a wide region of liquid-liquid equilibria that extends to high temperatures and pressures. For a comprehensive review on measurements of (carbon dioxide + water), the reader is referred to Refs. [25, 26]. Regarding systems consisting of various (hydrocarbons + water), it is worth highlighting the extensive work of Tsonopoulos et al. [27–31] as well as the IUPAC-NIST reviews [32–40], albeit both studies focused on heavier hydrocarbons than propane. For completeness, previous work on the (propane + water) mixture is here briefly reviewed. One of the earlier studies on the system (propane + water) is that of Poettman and Dean [41], who reported data on the water content of the vapour and the liquid alkane-rich phases of the system at conditions of three-phase coexistence. Data at VLLE conditions were later also obtained by Kobayashi and Katz [42] for the same system, including some VLE data at temperatures up to 420 K and 20 MPa. Sánchez and Coll [43] analysed the water-rich phase at conditions of two-phase equilibria involving high temperature, in the range from (530 to 660) K, and elevated pressure, from (20 to 330) MPa. Data for the propane-rich phase at VLE conditions were obtained by Blanco et al. [44] at low temperatures, from (250 to 280) K, and pressures < 0.5 MPa, as well as by Song and Kobayashi [45] at similar conditions. More recently, data for the water-rich phase at VLE conditions has been obtained by Chapoy et al. [46] over a temperature range from (280 to 370) K and

pressures < 4 MPa. Similarly, the water-rich phase has also been analysed by Mokraoui et al. [47] this time at VLLE conditions and at temperatures ranging from (300 to 340) K and pressures below 3 MPa. At low temperatures, the system also presents fluid-hydrate equilibria, which have been studied by a number of authors [45, 48, 49]. A further interesting feature typical of (alkane + water) systems is existence of gas-gas equilibria of the second type [50]; this was first identified in the (propane + water) system by de Loos et al. [51] at pressures up to 190 MPa. Measurements on the critical curve for this system were also carried by Brunner [50] at pressures up to 50 MPa as part of an extensive study of the family of (alkane + water) mixtures.

In our previous manuscript [4], we discussed the necessity of having a reliable sampling technique to analyse aqueous mixtures of this type involving also components of different volatility. This was tackled with the design of an experimental apparatus with re-circulation, micro sampling and on-line chromatographic analysis. The same experimental equipment was used in the present work.

The interest in studying these aqueous mixtures is not restricted to their practical application and their experimental complexity, but reflects also the challenging nature of these systems from a modelling perspective. Associating theories such as the statistical associating fluid theory (SAFT) [52, 53] prove advantageous for modeling these highly non-ideal mixtures. Previous applications of associating theories to model (alkane + water) systems [54–65] and (carbon dioxide + water) [66–71] were reviewed in detail in our previous manuscript [4], to which the reader is referred for a complete analysis. Certain challenges were highlighted in these systems, such as the difficulty of modelling mutual solubilities of phases of very different nature, as represented by large variations between the dielectric constant of each phase and/or dipole moment of the molecules. Previous attempts to model the phase behaviour of ternary systems of the type of interest here are again limited, but the work of Míguez et al. [72] and Kontogeorgis et al. [73] on the system (methane + carbon dioxide + water) are of relevance. Two different models are used in these works. Míguez et al. [72] use the SAFT-VR equation of state with a limited adjustment of cross interaction parameters to have a global estimation of the phase diagram, while in [73] the cubic plus association (CPA) equation of state is chosen along with a different interpretation of the unlike interactions between CO_2 and water, which are represented based on a cross-associating model.

In the remainder of this paper, the experimental procedure is described and new liquid-liquid equilibrium (LLE) and vapour-liquid-liquid equilibrium (VLLE) data for the system (propane + carbon dioxide + water) are presented. We compare our experimental findings with the predictions of SAFT-VR [74, 75]. We use this method as it has already been shown in a number of studies [4, 66, 68, 69, 71, 72, 76–78] to provide an accurate description of the phase behaviour of mixtures consisting of alkanes, CO_2 and water, for wide ranges of thermodynamic conditions. Finally, where possible, the agreement or deviations from published binary experimental data are further studied to analyse the effect of adding a third component and a third coexisting phase in the phase equilibria of the system.

2. Experimental

In this work we use a high-pressure apparatus based on a quasi-static analytical technique [4]. The equipment relies on recirculation of two coexisting phases using a two-channel magnetically operated micro-pump, sampling and on-line chromatographic analysis. The main components, represented in Figure 1, are a high-pressure view-cell, a magnetically coupled reciprocating pump (both fabricated in-house), electronically-actuated sampling valves (Cheminert, model C2-2206EH3Y, and Valco, model DCI4UWT1Y, VICI AG International) and a gas chromatograph (Shimadzu, model GC-2014, Shimadzu Scientific Instruments, Inc.). A manual syringe pump (Sitec model 750.1100, SITEC-Sieber Engineering AG) was used for loading water; an automatic syringe pump (Teledyne Isco, model 100DM, Teledyne Technologies Inc.) was used for loading carbon dioxide. The remaining circuits shown in Figure 1 were used for purposes of venting, flushing and draining the system (valves V2 and V5). Loading of propane was done by means of an HPLC pump (Knauer Smartline Pump 1000, Wissenschaftliche Gerätebau Dr. Ing. Herbert Knauer GmbH) connected to V5 and refrigerated to a temperature of about 273 K. The vessel, the reciprocating pump and the sampling valves were located inside a temperature-controlled oil bath.

2.1. Materials

The CO₂ used in this work was CP grade supplied by BOC with a mole-fraction purity higher than 0.99995. The water was deionised to an electrical resistivity $> 18 \text{ M}\Omega\cdot\text{cm}$ at $T = 298 \text{ K}$ and was degassed immediately prior to use. The propane was supplied by CK Gas Products Ltd. with > 0.999 purity. The carrier gas used for gas chromatography was CP-grade helium from BOC, with > 0.99999 purity.

2.2. Experimental procedure

The measurements were isothermal, with sequential analysis of each phase through composition measurements repeated a minimum of four times. The gas phase was sampled using the sampling valve GSV in Figure 1 and the liquid phases through the corresponding LSV together with a certain degree of tilt of the high-pressure cell to allow sampling of the middle phase [4]. A single column was sufficient to conduct the chromatographic analysis of the (propane + CO₂ + water) mixture. The column used was a HayeSep Q with 80/100 mesh ($2 \text{ m} \times 3.2 \text{ mm o.d.} \times 2 \text{ mm i.d.}$, silcosteel lined to reduce adsorption). The operating conditions of the GC are summarised in Table 1.

2.3. Experimental results for (propane + carbon dioxide + water)

The majority of the experimental data gathered in this work correspond to three-phase VLLE composition values. Data for four isotherms at $T = (311, 323, 338 \text{ and } 353) \text{ K}$ and pressures from the vapour pressure of propane to the critical pressure between the propane-rich and CO₂-rich phases have been obtained. The VLLE data are reported in Table 2. Additionally, in Table 3 the LLE data obtained at the critical

pressure between the propane-rich and the carbon dioxide-rich phases in coexistence with the water phase are presented.

The combined standard uncertainty in the composition measurements $u_c(x_i)$ was calculated based on estimations of the contributions arising from the calibration of the chromatograph, and from uncertainties in pressure and temperature measurements as follows [79]

$$u_c^2(x_i) = \left(\frac{\partial x_i}{\partial p}\right)^2 u^2(p) + \left(\frac{\partial x_i}{\partial T}\right)^2 u^2(T) + \sum_{j=1}^3 \left(\frac{\partial x_i}{\partial n_j} \frac{\partial n_j}{\partial A_j}\right)^2 u^2(A_j), \quad (1)$$

where $u(p)$, $u(T)$ and $u(A_j)$ are the standard uncertainties related to the pressure, temperature and calibration of the chromatograph for component j , respectively. The estimated uncertainties are $u(p) = 10$ kPa, $u(T) = 0.05$ K and $u(A_j)/A_j = 0.02$, the latter referred to the given chromatographic area. The combined standard uncertainty in the composition measurements is summarised in Table 4. Standard deviations were used to account for a second class of uncertainty, based on the repeatability of the measurements as a result of random sources of error. Both types of uncertainty were combined to obtain the overall uncertainties presented also in Table 4.

3. Models, theory and calculations

In the case of mixtures where only limited experimental data are available at the outset, such as this one, a sophisticated equation of state is an essential tool to guide experiments and choose state points to be measured. In this work we rely on the SAFT-VR approach for this purpose. Within the SAFT-VR formalism [74, 75], molecules are modelled as associating chains of tangentially bonded spherical segments interacting through attractive potentials of variable range. Chains of m tangent spheres of diameter σ_{ii} that interact through square-well potentials of well-depth ε_{ii} and range λ_{ii} are considered. Hydrogen bonding interactions are mediated by adding short-range off-center associating sites to the molecules. These interact through attractive square-well potentials of energy $\varepsilon_{ii}^{\text{HB}}$ and cut-off range r_c^{HB} ; each of these sites is placed at a distance $r_d/\sigma=0.25$ from the centre of the segment.

3.1. Pure components

The models used here for the pure components are based on previous works. Propane is modelled as a homonuclear chain comprising a number of segments based on a previous parametrization for the alkane family [80–82], CO₂ is modelled as a non-associating molecule comprising two identical spherical segments [76, 77] and water is modelled as a single sphere with four off-centre square-well association sites, as this was found to be the most appropriate model to describe the hydrogen bonding interaction based on thermodynamic and spectroscopic data [83]. The intermolecular model parameters used here were obtained in earlier works by comparison with experimental vapour pressure and liquid density data for each component in a range from the triple point to 90 % of the critical temperature.

It should be noted at this point that SAFT-VR, like any other classical equation of state, is a mean-field theory and therefore does not account for density fluctuations. Such a mean-field description is known to fail in the proximity of critical points, where long-range density fluctuations characterise the behaviour. Appropriate treatments to incorporate a description of critical fluctuations have been presented for the SAFT-VR equation [84–89], but these are not considered in this work. In practice, the mean-field description typically leads to an over-prediction of temperature and pressure in the critical region. In this work, it was considered useful to use molecular parameters re-scaled to the experimental critical point of carbon dioxide and propane. These re-scaled models for propane and carbon dioxide were obtained [76, 77] by adjusting the conformal parameters (σ_{ii} and ε_{ii}) to match the experimental critical temperature and pressure. It is worth mentioning here that in practice this re-scaling to the critical point is done at the expense of a loss in the accuracy of the calculations in the low temperature and high-density region. Because the conditions of interest are far from the critical point of water, the intermolecular parameters of this component were not re-scaled, so that a major loss of accuracy in the region of interest was avoided. The SAFT-VR parameters for the three pure components are collected in Table 5.

3.2. Mixtures

The application of SAFT-VR to mixtures requires, as any other equation of state, the determination of a number of unlike interactions [75, 90]. These are typically expressed based on simple arithmetic or geometric-mean rules. However, for an accurate representation of complex mixture phase behaviour, often two adjustable parameters need to be included. These two parameters, k_{ij} and γ_{ij} , related to the unlike depth and range of the square-well potential, respectively, are typically determined by comparison with experimental data. State independent parameters are considered throughout this work.

3.2.1. (Propane + carbon dioxide)

The system (propane + carbon dioxide) is modelled using an arithmetic-mean rule for the unlike range of the potential [75], and so the corresponding adjustable parameter is set to zero ($\gamma_{ij} = 0$). The k_{ij} parameter is not adjusted, but an appropriate value is calculated using an extended version of the Hudson and McCoubrey combining rules [90]. These are based on a generalisation of those of Hudson and McCoubrey for application to square-well potentials and incorporating a further treatment of polar interactions (e.g., the effect of dipolar, quadrupolar and association interactions are accounted for in addition to the usual London-dispersion attraction) [90]. In the calculation of the k_{ij} parameter using these combining rules, we account for the quadrupole moment of the CO₂ molecule, taken as [91] $Q = -1.4 \times 10^{-39} \text{ C} \cdot \text{m}^2$, whereas the dielectric constant of the media is assumed to be constant and equal to unity, based on actual values at the temperatures of study [92]. The ionization potentials of propane and CO₂ are taken to be [92] $I_1 = 1.8 \times 10^{-18} \text{ J}$ and $I_2 = 2.2 \times 10^{-18} \text{ J}$. The final value determined by the generalised Hudson and McCoubrey

combining rules for the binary interaction parameter is $k_{ij} = 0.082$. Use of this value allows for a successful prediction of the phase diagram of the system, as seen in Figure 2. The global phase behaviour that is predicted is also shown in Figure 2(b), as the critical curve for this system appears within the range of conditions of interest to this work.

3.2.2. Aqueous systems: (propane + water) and (carbon dioxide + water)

The application of the extended Hudson and McCoubrey combining rules to aqueous systems leads to a strong state-dependency of the k_{ij} parameter [90]. This is due to the variations of the dielectric constant in each phase and of the permanent dipole moment of water with temperature and density, as well as the temperature dependency of the Keesom term describing the permanent dipole-dipole interactions between water molecules. In this work, the unlike interaction parameters were instead adjusted by comparison with experimental data in the region of interest so as to have temperature- and phase-independent values. In the optimisation, experimental data [42] for both the aqueous and the propane-rich phase in a range of temperatures from (310 to 360) K and pressures from (0.5 to 20) MPa were used. However, as predicted by the extended Hudson and McCoubrey combining rules [90], an accurate prediction of both the aqueous and the alkane-rich phases with a single interaction parameter is not easily achieved. If only the common binary interaction parameter k_{ij} is used for (propane + water), the best agreement with experiment, obtained with $k_{ij} = 0.3006$ and shown in Figure 3, leads to a considerable underestimation of the solubility of propane in the aqueous phase (predicted in the order of $x_1 \sim 10^{-11}$). If the second interaction parameter (γ_{ij}) is adjusted, a good compromise for both phases can be obtained, albeit at the expense of some loss in the accuracy of the alkane-rich phase (see Figure 3 for the case with parameters $k_{ij} = -0.99$ and $\gamma_{ij} = 0.2225$). Although the value for the cross dispersion parameter (k_{ij}) seems excessive, we have confirmed that these values of cross interaction parameters lead to the type III phase behaviour that is expected [50, 51]. For a fairer comparison of the combined correction of both parameters, we can calculate the attractive van der Waals constant. This parameter values presented correspond to a correction for the attractive van der Waals constant (calculated with Lorentz-Berthelot combining rules) equal to 0.37. A comparable correction of 0.4 would correspond if the initial parameter set ($k_{ij} = 0.3006$ and $\gamma_{ij} = 0$) were used. Additionally, a check with the Hudson and McCoubrey combining rules suggests that large negative values (close to $k_{ij} = -0.7$) are necessary to model the water-rich phase at the temperatures of study; similar values have also been suggested for the (methane + water) system [90].

For the system (carbon dioxide + water) the second interaction parameter γ_{ij} is also used. The parameters ($k_{ij} = -0.6228$ and $\gamma_{ij} = 0.1358$) were obtained by fitting to experimental data [93–95] for the aqueous and the carbon dioxide-rich phases of the mixture at $T = 323.15$ K in a range of pressures from (0.1 to 18) MPa. As before, although these correcting factors seem rather large we have confirmed that they lead to type III phase behaviour and that they would correspond to a correction of 0.12 in van der Waals-Lorentz-Berthelot

terms. The predicted phase behaviour at $T = 308.15$ K is shown in Figure 4. Comparison with a previous set of parameters where the γ_{ij} interaction parameter is set to zero is also shown for completeness.

4. Discussion

The binary subsystems (propane + carbon dioxide), (propane + water) and (carbon dioxide + water) are known to be of type I, III and III, respectively, in the classification of Scott and van Konynenburg [23, 24]. The result of such a combination leads to a ternary system (propane + carbon dioxide + water) that may be considered of type VI in the classification of ternaries suggested by Bluma and Deiters [96]. This type of phase behaviour is characterised by a surface of liquid-liquid critical points that spans from the critical point of the less volatile component (water) and increases with pressure. At lower pressures and temperatures, a second critical surface can be found that connects the critical points of propane and carbon dioxide and ends at an upper critical end line. Regions of vapour-liquid-liquid three phase coexistence can thus be found at conditions below the upper critical end line. In Figure 5 an isotherm is plotted. For a given temperature, the VLLE region starts at the vapour pressure of propane and ends up at the upper critical end point that corresponds at that temperature. It can also be seen in the figure that regions of three phase equilibria represent only a small percentage of the diagram, which is mostly characterised by two-phase coexistence regions of vapour-liquid (i.e., in the carbon dioxide-rich side and below the upper critical end point conditions) or liquid-liquid. These VLLE regions are further presented in Figure 6 for the four isotherms measured, where both the experimental data and the corresponding SAFT-VR calculations are shown. In general, similarities in volatility and size between the molecules of propane and carbon dioxide may result in a relatively broad miscible range; this is reflected in the diagrams by a relatively narrow VLLE region. This is more obvious if the general appearance of the diagram for the (propane + carbon dioxide) system is compared with that for (*n*-decane + carbon dioxide + water) [4]; in the second case the VLLE region is markedly wider and spans to higher pressures.

Points along the upper critical end line, where the propane-rich and the carbon dioxide-rich phases become critical in presence of the water-rich phase, have also been measured for this system (cf. Table 3). The experimental upper critical end point at each temperature was observed to be associated with a colorful opalescence. The critical pressure was obtained visually, and the composition measurement of the coexisting phases was carried out at slightly higher pressure, following the procedure previously discussed [4]. To complete the analysis of the ternary mixture, the effect of adding a third component in each binary subsystem is studied in the discussion that follows, through comparison of the data measured for the ternary system with published data for each binary.

4.1. Influence of water on the phase behaviour of (propane + carbon dioxide)

In general the presence of a third aqueous phase and the dissolution of part of the water in the propane-rich and carbon dioxide-rich phases does not result in any large effect on the equilibrium between propane and carbon dioxide. This is shown in Figure 7 for two isotherms ($T = 311.10\text{ K}$ and $T = 323.01\text{ K}$) based on the available binary data at the temperatures of study.

The locus of the upper critical end points is depicted in Figure 8. A general agreement between our experimental data, which correspond to upper critical end points between the carbon dioxide-rich and propane-rich phases, and published critical points for the binary (propane + carbon dioxide) is observed. The theory predicts a gentle trend towards a higher critical pressure, if the calculations for the ternary and the binary are compared (see Figure 8), but this mild discrepancy seen with the theory seems to keep within experimental uncertainty. It can be concluded that the effect of water on the mutual solubilities of (propane + carbon dioxide) is very small under the conditions investigated.

4.2. Influence of carbon dioxide on the phase behaviour of (propane + water)

The effect of adding carbon dioxide to the water-rich phase of the (propane + water) system is first analysed. In Figure 9 the solubility of propane in the water phase of the ternary system is compared to that in the binary system. In spite of the scatter of the data, it can be concluded that the solubility of propane in water increases when carbon dioxide is also present. This observation is consistent with the effect seen in the corresponding phase of the (decane + carbon dioxide + water) system [4]. Interestingly, the theory predicts lower solubilities than for the corresponding binary. At a given temperature, the trend of experiments and theory shows some consistency as the pressure increases. This is especially obvious at the lowest temperature, where it is clear that the higher the pressure the lower the solubility for both experiments and theory for the ternary. Comparing now isotherms, there is also a general trend towards an increase in solubility as the temperature raises, an observation that is again consistent with the theory for the ternary and with the behaviour shown by the published binary data in the LLE region. Focusing now only on the solubilities of propane in the binary system, there is again a trend that is not predicted by the theory in comparison to the published experimental data. We are referring to the crossover that is experimentally seen if isotherms in the VLE region are compared with those in the LLE region. In the LLE region, the measured solubility increases with temperature, whereas in the VLE region it decreases. The theoretical calculations for the binary predict a decrease of solubility with temperature in both regions.

Regarding the effect of carbon dioxide on the solubility of water in the alkane-rich phase, the experimental results for the ternary seen in Figure 10 show a trend towards increasing solubilities when CO_2 is present, in comparison to solubility data for the binary (propane + water). The theory, however, predicts the opposite trend when the calculations for the ternary and the binary are compared at each temperature. It was already mentioned in the previous section that for (propane + water) the interaction parameters were selected based

on enhancing also the predictions of the water-rich phase; as said this was done at the expense of a loss in accuracy in the predictions of the alkane-rich phase. If the interaction parameters that reproduce best the alkane-rich phase ($k_{ij} = 0.3006$ and $\gamma_{ij} = 0$, instead of the $k_{ij} = -0.99$ and $\gamma_{ij} = 0.2225$ set) are used in the calculations of the ternary phase behaviour, the solubility of water in the alkane-rich phase is predicted to increase upon the addition of carbon dioxide with respect to that of the binary (calculated with the same interaction parameters), in agreement with the trend found experimentally. Experimentally however, measuring the water content of this phase is not exempt of difficulty, as discussed in previous work [4]. It can be concluded that carbon dioxide may act as a mild co-solvent on the mutual solubilities of (propane + water) although such findings are not supported by the theoretical approach in the aqueous phase.

4.3. Influence of propane on the phase behaviour of (carbon dioxide + water)

The influence of propane on the mutual solubility of (carbon dioxide + water) is studied by comparison to binary data for (carbon dioxide + water), where we study the carbon dioxide-rich and the water-rich phases separately. Regarding, first, the carbon dioxide-rich phase, a trend towards decreasing the solubility of water when propane is present can be seen in Figure 11. The predictions of the theory are consistent with the experimental findings. It is interesting to note that this anti-solvent effect of the alkane over the mutual solubilities of carbon dioxide and water was not observed with the ternary containing *n*-decane [4]. This behaviour may be attributed to the higher alkane content of the carbon dioxide-rich phase in the ternary system based on propane compared to that present in the system based on decane.

In the water-rich phase the addition of propane leads to a notable decrease in the saturated compositions of carbon dioxide, compared to the binary. This can be seen in Figure 12, where the isotherms for the ternary are plotted against one isotherm for the binary at the temperature closest to the lowest studied in this work; at higher temperatures the same effect could be seen, although the comparison is not plotted in the graph for sake of clarity. This anti-solvent effect of propane on the water-rich phase is seen to commence at low pressure, so that below the vapour pressure of propane the amount of carbon dioxide in water is negligible and nearly independent of pressure; the slope then changes for pressures higher than the vapour pressure of propane. This noticeable effect is quite surprising given the low solubility of propane in the water phase, but it is justified based on chemical potentials; i.e., it is related to the high solubility of propane in the coexisting carbon dioxide-rich phase. Comparing to the findings of our previous work [4], the addition of decane presented a very mild effect, only visible at high pressure (close to the upper critical end points; i.e., pressures > 10 MPa). In Figure 13, we examine the solubility of carbon dioxide in the water phase of a different ternary system, this time (methane + carbon dioxide + water) [12], again compared to solubility data in the aqueous phase of the binary (carbon dioxide + water). As in the case of propane, the anti-solvent effect of a light hydrocarbon, now methane, can be observed in this figure. Because in this case the data for this ternary are in the two phase region, the solubility of carbon dioxide in water depends on

the methane content of the gaseous CO₂-rich phase; it is clear how the solubility decreases as the methane content increases (see Figure 13), in agreement with our earlier reasoning. In Figure 13 the data for both the (propane + carbon dioxide + water) measured here and the (decane + carbon dioxide + water) system presented earlier [4] are also plotted at the same temperature for completeness; the effect of *n*-decane at this temperature is negligible.

Concerning reservoir processing, one of the roles of CO₂ in EOR is that of reducing the interfacial tension between the oil and the water by dissolution [97], hence promoting the coalescence of the drops of oil that were trapped after secondary oil recovery. The notable decrease observed in the solubility of carbon dioxide in the water-rich phase when in the presence of a light hydrocarbon suggests that the properties of the aqueous phase would be even closer to those of pure water. On the other hand, if the solubility of carbon dioxide in the alkane-rich phase is analysed for the two cases studied of propane and decane at a temperature of, for example, 323 K and pressures below the upper critical end point, it can be seen that less CO₂ is dissolved in the propane-rich phase, compared to the decane-rich one. It could then be thought that the performance of CO₂ in enhanced oil recovery is less efficient in the case of low-molecular weight hydrocarbons, where less carbon dioxide dissolves in the aqueous and the oil phase. This is in practice not a drawback, given the easier recovery of light fractions of oil because of their high volatility and the low pressure necessary to achieve conditions of total miscibility with the injected CO₂ (i.e., above the upper critical end point of these components with carbon dioxide at a given temperature). The discussion can also be extended to the topic of sequestration of CO₂ in the reservoir; if only the solubility trapping in the reservoir water is considered, it will be enhanced if the injected carbon dioxide is free of volatile alkanes. To conclude this section, it can be said that propane is observed to act as an anti-solvent on the mutual solubilities of (carbon dioxide + water).

5. Conclusions

The phase behaviour of the system (propane + carbon dioxide + water) has been studied both experimentally and theoretically, and compared in detail to the ternary mixture of (*n*-decane + carbon dioxide + water) presented in previous work [4]. Experimentally, the VLLE of the system (propane + carbon dioxide + water) has been measured along four isotherms from $T = (311.10 \text{ to } 353.18) \text{ K}$ and pressures ranging from values above the vapour pressure of propane $p = (1.67 \text{ to } 3.71) \text{ MPa}$ to the upper critical end point between the carbon dioxide-rich and the propane-rich phases in the presence of the water-rich phase, these latter found to range from $p = (6.71 \text{ to } 5.51) \text{ MPa}$ with increasing temperatures. The analysis of the system has been complemented with calculations performed with the SAFT-VR equation. Details of the models used to describe the thermodynamic properties of these fluids and their mixtures have been given. Because a classical equation is used, with a given set of intermolecular potential parameters it is not possible to predict

accurately and simultaneously the phase behaviour at conditions both far from and close to criticality. The parameters need therefore to be adjusted either at low temperature or at near critical conditions, where the latter strategy is typically followed with cubic equations of state. In a similar manner, here the intermolecular potential parameters for the most volatile components (i.e., carbon dioxide and propane) have been re-scaled to the experimental critical point. Where possible, the behaviour of the binary subsystems have been predicted and in all cases, temperature- and phase-independent binary interaction parameters have been used.

The experimental VLLE data for the ternary system (propane + carbon dioxide + water) have been compared to literature data for the corresponding binary subsystems, as well as to the phase equilibria predicted with SAFT-VR and to the observations that were earlier made in the previous study on (decane + carbon dioxide + water) [4]. Overall, the comparison between the mutual solubilities of the three components at conditions of three phase equilibria for the ternary system and the solubility of the components in the corresponding binary subsystems shows only small differences. The solubility of water in propane and that of propane in water seem to increase slightly with respect to the binary (propane + water) when CO₂ is present, although the reversed effect is seen with the theory on the water-rich side. The mutual solubilities of carbon dioxide and water decrease notably in presence of propane, compared to the binary system (carbon dioxide + water). A similar comparison with the binary (propane + carbon dioxide) system shows no appreciable differences, probably due to the relatively low pressures of study.

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Table 1: GC conditions set for the analysis of the mixture studied in this work^a.

Injector		Oven	TCD		FID	
$\dot{V}/\text{cm}^3\cdot\text{s}^{-1}$	T/K	T/K	T/K	I/mA	T/K	ϕ_r
40	473.15	373.15	503.15	90	503.15	1:10

^a TCD = Thermal Conductivity Detector, FID = Flame Ionisation Detector.

$\dot{V}$ = He flow rate, I = current, ϕ_r = H_2 : Air flow ratio.

Table 2: Experimental VLLE data and SAFT-VR calculations for (propane (1) + carbon dioxide (2) + water (3)) where I, II and III denote the propane-rich, carbon dioxide-rich and water-rich phases, respectively.

Phase	p/MPa	x_1^{exp}	x_2^{exp}	x_3^{exp}	p/MPa	x_1^{pred}	x_2^{pred}	x_3^{pred}
$T = 311.10 \text{ K}$					$T = 311.10 \text{ K}$			
I	1.67	0.9538	0.0394	0.0068	1.67	0.9580	0.0395	0.0026
II	1.67	0.8045	0.1885	0.0070	1.67	0.8598	0.1362	0.0040
III	1.67	3.5×10^{-4}	0.0015	0.9982	1.67	1.7×10^{-4}	0.0009	0.9989
I	3.47	0.7313	0.2650	0.0037	3.48	0.6700	0.3274	0.0026
II	3.48	0.4108	0.5855	0.0037	3.48	0.4204	0.5772	0.0024
III	3.48	3.0×10^{-4}	0.0077	0.9920	3.48	1.3×10^{-4}	0.0073	0.9926
I	4.97	0.5024	0.4928	0.0048	4.97	0.4369	0.5604	0.0027
II	4.96	0.2905	0.7072	0.0024	4.97	0.2787	0.7192	0.0021
III	4.98	2.7×10^{-4}	0.0126	0.9872	4.97	9.4×10^{-5}	0.0117	0.9882
I	6.43	0.2671	0.7282	0.0047	6.43	0.2230	0.7744	0.0026
II	6.44	0.2141	0.7838	0.0022	6.43	0.1817	0.8162	0.0021
III	6.43	2.0×10^{-4}	0.0162	0.9836	6.43	6.0×10^{-5}	0.0156	0.9843
$T = 323.01 \text{ K}$					$T = 323.01 \text{ K}$			
I	1.86	0.9789	0.0135	0.0076	1.86	0.9925	0.0037	0.0038
II	1.86	0.9445	0.0456	0.0098	1.86	0.9814	0.0123	0.0064
III	1.86	4.3×10^{-4}	0.0005	0.9991	1.86	1.6×10^{-4}	0.0017	0.9998

Table 2: Experimental VLLE data and SAFT-VR calculations for (propane (1) + carbon dioxide (2) + water (3)) (continued).

Phase	p/MPa	x_1^{exp}	x_2^{exp}	x_3^{exp}	p/MPa	x_1^{pred}	x_2^{pred}	x_3^{pred}
I	3.02	0.8605	0.1330	0.0066	3.02	0.8308	0.1653	0.0038
II	3.02	0.6270	0.3677	0.0054	3.02	0.6365	0.3590	0.0045
III	3.02	4.4×10^{-4}	0.0039	0.9956	3.02	1.4×10^{-4}	0.0058	0.9964
I	4.44	0.6947	0.2990	0.0063	4.45	0.6344	0.3617	0.0038
II	4.46	0.4618	0.5341	0.0041	4.45	0.4452	0.5512	0.0036
III	4.45	3.2×10^{-4}	0.0077	0.9920	4.45	1.1×10^{-4}	0.0102	0.9927
I	5.98	0.4899	0.5037	0.0064	5.99	0.4234	0.5729	0.0038
II	6.00	0.3679	0.6283	0.0038	5.99	0.3371	0.6596	0.0033
III	6.00	3.9×10^{-4}	0.0110	0.9886	5.99	7.1×10^{-5}	0.0145	0.9893
$T = 338.10 \text{ K}$					$T = 338.10 \text{ K}$			
I	2.60	0.9610	0.0205	0.0185	2.61	0.9766	0.0173	0.0061
II	2.60	0.9261	0.0635	0.0104	2.61	0.9464	0.0444	0.0092
III	2.61	4.5×10^{-4}	0.0006	0.9990	2.61	1.6×10^{-4}	0.0003	0.9995
I	3.52	0.8794	0.1040	0.0166	3.53	0.8648	0.1290	0.0061
II	3.53	0.7445	0.2476	0.0078	3.53	0.7392	0.2533	0.0075
III	3.53	4.9×10^{-4}	0.0027	0.9968	3.53	1.5×10^{-4}	0.0024	0.9975
I	4.59	0.7744	0.2079	0.0177	4.59	0.7361	0.2578	0.0061
II	4.59	0.6348	0.3591	0.0062	4.59	0.5994	0.3941	0.0065
III	4.58	5.5×10^{-4}	0.0051	0.9944	4.59	1.3×10^{-4}	0.0045	0.9953
I	6.04	0.6062	0.3766	0.0172	6.05	0.5404	0.4537	0.0059
II	6.04	0.5455	0.4495	0.0050	6.05	0.5066	0.4875	0.0059
III	6.06	4.4×10^{-4}	0.0078	0.9918	6.05	1.1×10^{-4}	0.0073	0.9926
$T = 353.18 \text{ K}$					$T = 353.18 \text{ K}$			
I	3.70	0.9317	0.0417	0.0266	3.71	0.9394	0.0510	0.0096
II	3.71	0.8924	0.0930	0.0146	3.71	0.8956	0.0921	0.0123

Table 2: Experimental VLLE data and SAFT-VR calculations for (propane (1) + carbon dioxide (2) + water (3)) (continued).

Phase	p/MPa	x_1^{exp}	x_2^{exp}	x_3^{exp}	p/MPa	x_1^{pred}	x_2^{pred}	x_3^{pred}
III	3.71	6.5×10^{-4}	0.0009	0.9985	3.71	1.6×10^{-4}	0.0008	0.9990
I	4.21	0.8865	0.0862	0.0273	4.21	0.8831	0.1073	0.0096
II	4.22	0.8281	0.1614	0.0105	4.21	0.8184	0.1703	0.0114
III	4.21	6.7×10^{-4}	0.0019	0.9975	4.21	1.5×10^{-4}	0.0017	0.9982
I	4.80	0.8323	0.1389	0.0288	4.80	0.8144	0.1759	0.0096
II	4.79	0.7744	0.2166	0.0089	4.80	0.7501	0.2393	0.0106
III	4.80	6.6×10^{-4}	0.0030	0.9964	4.80	1.4×10^{-4}	0.0027	0.9972
I	5.25	0.7866	0.1857	0.0277	5.25	0.7568	0.2336	0.0096
II	5.26	0.7453	0.2460	0.0087	5.25	0.7144	0.2756	0.0100
III	5.25	4.8×10^{-4}	0.0036	0.9959	5.25	1.4×10^{-4}	0.0034	0.9964

Table 3: Experimental LLE data for (propane (1) + carbon dioxide (2) + water (3)) at the critical point between the propane-rich and CO₂-rich phases (the combination of both phases is referred here as CO₂-rich phase) in presence of a water-rich phase, or upper critical end point. The phases are labelled as II and III for the CO₂-rich and the water-rich phases, respectively.

T/K	p/MPa	Phase II			Phase III		
		x_1^{exp}	x_2^{exp}	x_3^{exp}	x_1^{exp}	x_2^{exp}	x_3^{exp}
311.10	6.71	0.2140	0.7814	0.0046	1.6×10^{-4}	0.0168	0.9830
323.01	6.68	0.3618	0.6335	0.0048	2.8×10^{-4}	0.0125	0.9873
338.10	6.24	0.5445	0.4359	0.0195	5.2×10^{-4}	0.0084	0.9911
353.18	5.52	0.7404	0.2339	0.0258	4.5×10^{-4}	0.0040	0.9955

Table 4: Combined standard uncertainty $u_c(x_i)$, standard deviations σ_{x_i} and overall uncertainty $U(x_i)$ for the composition measurements of the system (propane (1) + carbon dioxide (2) + water (3)) in mole fraction. The phases are labelled as I, II and III for the propane-rich, CO₂-rich and water-rich phases, respectively.

	Phase I			Phase II			Phase III		
	x_1	x_2	x_3	x_1	x_2	x_3	x_1	x_2	x_3
$u_c(x_i)$	5×10^{-3}	5×10^{-3}	4×10^{-4}	7×10^{-3}	7×10^{-3}	2×10^{-4}	1×10^{-5}	1×10^{-4}	1×10^{-4}
σ_{x_i}	2×10^{-3}	1×10^{-3}	2×10^{-3}	1×10^{-3}	1×10^{-3}	1×10^{-3}	4×10^{-5}	2×10^{-4}	2×10^{-4}
$U(x_i)$	5×10^{-3}	5×10^{-3}	2×10^{-3}	7×10^{-3}	7×10^{-3}	1×10^{-3}	5×10^{-5}	2×10^{-4}	2×10^{-4}

Table 5: SAFT-VR intermolecular model parameters^a used for modelling the behaviour of the pure components.

	Reference	m	$\sigma_{ii}/\text{\AA}$	$(\varepsilon_{ii}/k_B)/\text{K}$	λ_{ii}	$(\varepsilon_{ii}^{\text{HB}}/k_B)/\text{K}$	$r_c^{\text{HB}}/\text{\AA}$
CO ₂	76, 77	2.0	3.1364 ^b	168.89 ^b	1.5157		
C ₃ H ₈	76, 77	1.6667	4.2249 ^b	204.87 ^b	1.5531		
H ₂ O	83	1.0	3.0342	250.00	1.7889	1400.00	2.10822

^a m is the number of square-well segments in the molecule, σ_{ii} is the hard-core diameter, λ_{ii} and ε_{ii} are the range and the depth of the square-well potential, respectively, and r_c^{HB} and $\varepsilon_{ii}^{\text{HB}}$ are those of the hydrogen-bonding interaction.

^b Parameters re-scaled to the experimental critical point.

Figure 1: Schematic diagram of the static-analytical apparatus. The following components are depicted: view-cell, VC; magnetic recirculation pump, MRP; liquid sampling valve, LSV; gas sampling valve, GSV; gas-chromatograph, GC; temperature controller, TC; pressure transducers, PI; pressure generators, PG1 and PG2; bursting-disc, BD; liquid reservoir, LR and gas cylinder, GS.

Figure 2: Isothermal pressure-composition (p, x) (a) and (p, T) (b) phase diagram for the (propane (1) + carbon dioxide (2)) mixture. In (a) the symbols correspond to published VLE experimental data for the system at: $\diamond$, $T = 293.15$ K [98]; $\triangle$, $T = 311.05$ K [99] and $\circ$, $T = 344.43$ K [99]. In (b) the symbols correspond to the following experimental data: $\diamond$, vapour pressure of propane [100, 101]; $\circ$, vapour pressure of carbon dioxide [102–107]; the rest of the symbols correspond to critical data points for the mixture: $\star$, Ref. [108]; $\square$, Ref. [109]; $+$, Ref. [110]; $\triangle$, Ref. [111]; $\times$, Ref. [112]; $*$, Ref. [113]. The curves in (a) correspond to predictions obtained with SAFT-VR using the $k_{ij} = 0.082$ value calculated by the extended Hudson and McCoubrey combining rules at the experimental temperatures. In (b) the continuous curves correspond to the calculated vapour pressure for the pure components, whereas the discontinuous curve corresponds to the predicted critical locus with the same k_{ij} value.

Figure 3: Isothermal pressure-composition (p, x) phase diagram for the (propane (1) + water (2)) mixture at $T = 310.93$ K showing an amplified image of both saturated phases. The open symbols correspond to published experimental VLE and LLE phase equilibrium data at: $\diamond$, $T = 310.93$ K [42]; $\circ$, $T = 310.93$ K [114]; $\triangle$, $T = 310.93$ K [115]. The continuous curve corresponds to calculations obtained with SAFT-VR using $k_{ij} = -0.99$ and $\gamma_{ij} = 0.2225$. The discontinuous curve corresponds to calculations obtained with SAFT-VR using $k_{ij} = 0.3006$ and $\gamma_{ij} = 0$. Note that the discontinuous curve corresponding to the calculations of the water-rich phase is out of range and therefore not plotted in the figure.

Figure 4: Isothermal pressure-composition (p, x) phase diagram for the (carbon dioxide (1) + water (2)) mixture at $T = 308$ K showing an amplified image of both saturated phases. The open symbols correspond to published experimental VLE phase equilibrium data at: Δ , $T = 308.15$ K [116]; $\diamond$, $T = 308.21$ K [66]; $\circ$, $T = 308.15$ K [117]; $\square$, $T = 308.20$ K [66]. The continuous curve corresponds to calculations obtained with SAFT-VR using $k_{ij} = -0.6228$ and $\gamma_{ij} = 0.1358$. The discontinuous curve corresponds to calculations obtained with SAFT-VR using $k_{ij} = -0.1966$ and $\gamma_{ij} = 0$.

Figure 5: Isothermal pressure-composition (p, x) prismatic diagram for the (propane + carbon dioxide + water) system at $T = 311.10$ K calculated with SAFT-VR. Regions of three-phase equilibria appear coloured in light red. Regions of two-phase equilibria appear delimited by continuous thick red curves with some tie-lines traced with thin dashed red lines. Small regions of one-phase equilibria appear in the outer regions delimited by the continuous thick red curves. The two phase coexisting regions for the binary subsystems appear in the lateral sides of the prismatic diagram with a continuous blue line.

Figure 6: Isothermal composition diagram for the (propane + carbon dioxide + water) system at (a) $T = 311.10$ K, (b) $T = 323.01$ K, (c) $T = 338.10$ K and (d) $T = 353.18$ K. The symbols represent VLE data points measured in this work at average pressure: (a) $\blacklozenge$, $p = 1.67$ MPa; $\blacksquare$, $p = 3.48$ MPa; $\blacktriangle$, $p = 4.96$ MPa; $\star$, $p = 6.44$ MPa; $\bullet$ and $p = 6.71$ MPa; (b) $\blacklozenge$, $p = 1.86$ MPa; $\blacksquare$, $p = 3.02$ MPa; $\blacktriangle$, $p = 4.46$ MPa; $\star$, $p = 6.00$ MPa; $\bullet$ and $p = 6.68$ MPa; (c) $\blacklozenge$, $p = 2.60$ MPa; $\blacksquare$, $p = 3.53$ MPa; $\blacktriangle$, $p = 4.59$ MPa; $\star$, $p = 6.04$ MPa and $\bullet$, $p = 6.24$ MPa; (d) $\blacklozenge$, $p = 3.71$ MPa; $\blacksquare$, $p = 4.22$ MPa; $\blacktriangle$, $p = 4.79$ MPa; $\star$, $p = 5.26$ MPa and $\bullet$, $p = 5.52$ MPa. The discontinuous curves are SAFT-VR predictions of the three-phase equilibrium region for every pressure data-point plotted and the shadowed areas emphasise the experimental three-phase regions. The continuous line is the measured tie-line between the two coexisting phases that remain slightly above the critical point between the CO_2 -rich and the propane-rich phases.

Figure 7: Isothermal pressure-composition (p, x) phase diagram for the (propane (1) + carbon dioxide (2) + water (3)) system. The filled symbols represent data gathered during this work for the propane-rich and the carbon dioxide-rich phases under VLLE conditions and temperatures: $\blacktriangle$, $T = 311.10$ K; $\blacklozenge$, $T = 323.01$ K. The open symbols correspond to measurements for the binary (propane + carbon dioxide) at: $\square$, $T = 310.93$ K [118]; $\triangle$, $T = 311.05$ K [99] and $\circ$, $T = 323.15$ K [98]. The continuous curves correspond to the SAFT-VR predictions for the propane-rich and the carbon dioxide-rich phases in the ternary system at conditions of VLLE equilibria. The discontinuous curves correspond to the SAFT-VR predictions for the binary system (propane + carbon dioxide).

Figure 8: Experimental (p, T) critical locus. The filled triangles, $\diamond$, correspond to measurements of upper critical end points between the CO_2 -rich and the propane-rich phases in the presence of a third water-rich phase visually observed in this work. The open symbols correspond to critical data points for the binary system (propane + carbon dioxide): $\diamond$, Ref. [118]; $\circ$, Ref. [119]; $\star$, Ref. [108]; $\square$, Ref. [109]; $+$, Ref. [110]; Δ , Ref. [111]; $\times$, Ref. [112]; $*$, Ref. [113]. The continuous curve corresponds to the calculations with SAFT-VR for the upper critical end line in the ternary at the conditions experimentally studied. The discontinuous curve corresponds to the calculations with SAFT-VR for the critical line in the binary.

Figure 9: Isothermal pressure-composition (p, x) phase diagram for the (propane (1) + carbon dioxide (2) + water (3)) system showing the propane content in the water-rich phase under VLLE conditions. The filled symbols represent data gathered during this work: $\blacktriangledown$, $T = 311.10$ K; $\blacklozenge$, $T = 323.01$ K; $\bullet$, $T = 338.10$ K and $\blacktriangle$, $T = 353.18$ K. The open symbols correspond to published data for the solubility of propane in the water-rich phase in the binary (propane + water) at $*$, $T = 310.93$ K [42]; $\circ$, $T = 310.93$ K [114]; $+$, $T = 310.93$ K [115]; $\times$, $T = 323.13$ K [46]; $\diamond$, $T = 338.15$ K [46]; Δ , $T = 329.26$ K [42]; $\square$, $T = 353.18$ K [46] and ∇ , $T = 360.93$ K [42]. The continuous curves correspond to the SAFT-VR predictions for the water-rich phase in the ternary system at conditions of VLLE equilibria at the same temperatures, increasing from left to right. The discontinuous curves correspond to the SAFT-VR predictions of the propane-rich phase in the (propane + water) binary system, at the same temperatures, increasing from right to left.

Figure 10: Isothermal pressure-composition (p, x) phase diagram for the (propane (1) + carbon dioxide (2) + water (3)) system showing the water content in the propane-rich liquid phase under VLLE conditions. The filled symbols represent data gathered during this work: $\blacktriangledown$, $T = 311.10$ K; $\blacklozenge$, $T = 323.01$ K; $\bullet$, $T = 338.10$ K and $\blacktriangle$, $T = 353.18$ K. The open symbols correspond to published data for the solubility of water in the propane-rich phase in the binary (propane + water) at $\triangle$, $T = 310.93$ K [42]; $\square$, $T = 310.93$ K [115]; $*$, $T = 311.98$ K [42] and $\diamond$, $T = 338.71$ K [42]. The continuous curves correspond to the SAFT-VR predictions for the propane-rich phase in the ternary system at conditions of VLLE equilibria at the same temperatures, increasing from left to right. The discontinuous curves correspond to the SAFT-VR predictions of the propane-rich phase in the (propane + water) binary system.

Figure 11: Isothermal pressure-composition (p, x) phase diagram for the (propane (1) + carbon dioxide (2) + water (3)) system showing the water content in the CO_2 -rich phase under VLLE conditions. The filled symbols represent data gathered during this work: $\blacktriangledown$, $T = 311.10$ K; $\blacklozenge$, $T = 323.01$ K; $\bullet$, $T = 338.10$ K and $\blacktriangle$, $T = 353.18$ K. The open symbols correspond to published data for the solubility of water in the CO_2 -rich phase in the binary system (carbon dioxide + water) at conditions: $\square$, $T = 323.15$ K [120]; $\circ$, $T = 323.15$ K [93]; $\triangle$, $T = 323.15$ K [95]; $\star$, $T = 323.2$ K [121]; ∇ , $T = 323.15$ K [122] and $\diamond$, $T = 353.1$ K [121]. The continuous curves correspond to the SAFT-VR predictions for the CO_2 -rich phase in the ternary system at conditions of VLLE equilibria. The discontinuous curves correspond to the SAFT-VR predictions of the CO_2 -rich phase in the (carbon dioxide + water) binary system.

Figure 12: Pressure-composition (p, x) phase diagram for the (propane (1) + carbon dioxide (2) + water (3)) system showing the solubility of CO₂ in the water-rich phase under VLLE conditions. The filled symbols represent data gathered during this work: $\blacktriangledown$, $T = 311.10$ K; $\blacklozenge$, $T = 323.01$ K; $\bullet$, $T = 338.10$ K and $\blacktriangle$, $T = 353.18$ K. The open symbols correspond to the solubility in the binary (carbon dioxide + water) at Δ , $T = 313.2$ K [123]; $\diamond$, $T = 313.0$ K [124]; $\square$, $T = 313.2$ K [125]; $\circ$, $T = 313.15$ K [94]; $*$, $T = 313.15$ K [126]. The continuous curves correspond to the SAFT-VR predictions for the water-rich phase in the ternary system at conditions of VLLE equilibria. The discontinuous curves correspond to the SAFT-VR predictions of the water-rich phase in the (carbon dioxide + water) binary system.

Figure 13: Isothermal pressure-composition (p, x) phase diagram comparing the solubility of carbon dioxide in the water-rich liquid phase of the system (methane (1) + carbon dioxide (2) + water(3)) to that of (carbon dioxide + water). Part of the open symbols correspond to published data for the solubility of carbon dioxide in the aqueous phase of (methane + carbon dioxide + water) at $T \simeq 324$ K and VLE conditions [12], where the composition of the vapour phase is around $\times$, $y(1) \simeq 0.7$; $\star$, $y(1) \simeq 0.4$ and ∇ , $y(1) \simeq 0.2$; the remaining open symbols correspond to the solubility in the binary (carbon dioxide + water) at Δ , $T = 323.15$ K [127]; $*$, $T = 323.15$ K [94]; $\circ$, $T = 323.15$ K [93]; $\diamond$, $T = 323.2$ K [121]; $\square$, $T = 323.15$ K [128]. For completeness the data gathered in this work for the solubility of carbon dioxide in the aqueous phase of each ternary is also represented in the plot as filled symbols: $\blacklozenge$, for (propane + carbon dioxide + water) at $T = 323.01$ K and VLLE conditions; $\blacktriangle$, for (n -decane + carbon dioxide + water) at $T = 323.08$ K and VLLE conditions. The continuous curve corresponds to the SAFT-VR predictions relative to the binary mixture.