



Experimental and Modeling Study of the Phase Behavior of (Methane + CO₂ + Water) Mixtures

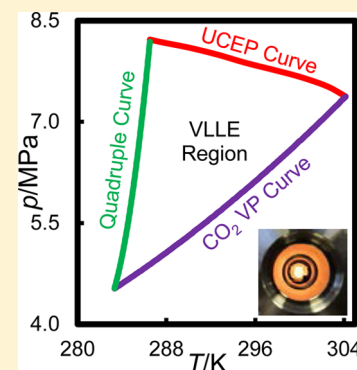
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ABSTRACT: In this work we report phase equilibrium measurements on the system (methane + carbon dioxide + water) carried out with a high-pressure quasi-static-analytical apparatus. The measurements have been made under conditions of two-phase vapor–liquid equilibrium, three-phase vapor–liquid–liquid equilibrium (VLLE), and four-phase vapor–liquid–liquid–hydrate equilibrium. The compositions of three coexisting fluid phases have been obtained along eight isotherms at temperatures from (285.15 to 303.5) K and at pressures up to either the upper critical end point (UCEP) or up to the hydrate formation locus. Compositions of coexisting vapor and liquid phases have been obtained along three isotherms at temperatures from (323.15 to 423.15) K and pressures up to 20 MPa. The quadruple curve, along which hydrates coexist with the three fluid phases, was also measured along its entire length. The VLLE data obtained for this mixture have been compared with the predictions of the statistical associating fluid theory for potentials of variable range (SAFT-VR), implemented with the square-well potential and using parameters fitted to pure-component and binary-mixture data. Specifically, we used the SAFT-VR parameters reported by Míguez and co-workers [Míguez, J. M.; dos Ramos, M. C.; Piñeiro, M. M.; Blas, F. J. *J. Phys. Chem. B* **2011**, *115*, 9604]. The pressure along the quadruple curve was compared with the predictions of two different thermodynamic models. Furthermore, a detailed study of the ternary mixtures was carried out based on comparison with available ternary data of the type (CO₂ + *n*-alkane + water) and available data for the constituent binary subsystems. In this way, we analyzed the observed effects on the solubility when the *n*-alkane component was changed or a third component was added.



1. INTRODUCTION

An understanding of the phase behavior of mixtures containing hydrocarbons, CO₂, and H₂O is required to design effective and economic processes involving reservoir fluids and CO₂. Phase behavior data for these mixtures are key inputs to reservoir simulations that are used for evaluating reservoir-development plans, interpreting well-test data, and designing surface facilities and processing plants.¹ In addition, such data play a major role in the design of CO₂-storage and CO₂-enhanced oil recovery (EOR) processes.^{2–12} In CO₂-EOR, displacement of oil by CO₂ is strongly affected by the phase behavior of the (oil + CO₂) system which, in turn, is dependent on reservoir temperature, pressure, and oil composition. In CO₂-storage processes, numerical simulations play a key role in predicting the flow of CO₂ from the injection wells into the storage formation and in determining the long-term evolution of the CO₂ plume after termination of injection. These simulations feed into larger geological/reservoir models which should provide an adequate representation of the storage process. In this way, proper selection and operation of storage sites can be accomplished with confidence. These geological/reservoir

models require detailed thermophysical property data for CO₂ and its mixtures with the reservoir fluids it encounters, especially the phase behavior. To acquire all of the experimental data required over the range of reservoir temperatures, pressures, and fluid compositions involves an enormous amount of work. If existing predictive models can be validated with suitable accuracy, or new models developed, then this would greatly enhance the feasibility of CO₂-storage processes.¹³

In addition to carbon storage and CO₂-EOR, phase equilibrium data for mixtures containing CO₂ and hydrocarbons are significant in many industrial and scientific fields such as in hydrotreatment of aqueous waste streams,¹⁴ production of coal liquids and petroleum processing,¹⁵ separation processes,¹⁶ and supercritical fluid extraction.^{17,18} Large quantities of CH₄ are typically handled in reservoir production processes and CO₂ flooding projects; hence,

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Table 1. Literature Data of Ternary Mixtures of the Type (*n*-Alkane + CO₂ + H₂O)

ref	system	equilibria	T_{\min}/K	T_{\max}/K	p_{\min}/MPa	p_{\max}/MPa
32	CH ₄ + CO ₂ + H ₂ O	VLE	324.30	375.50	10.5	50.6
33	CH ₄ + CO ₂ + H ₂ O	VLE	344.15	344.15	10	100
34	CH ₄ + CO ₂ + H ₂ O	VLE	298.75	323.15	6.2	13.8
35	CH ₄ + CO ₂ + H ₂ O	VLE	243.1	288.4	0.11	6.05
35	C ₂ H ₆ + CO ₂ + H ₂ O	VLE	252.20	288.4	0.11	2.03
136	C ₃ H ₈ + CO ₂ + H ₂ O	VLE	247.50	289.00	0.1	2.1
28	C ₃ H ₈ + CO ₂ + H ₂ O	VLLE	311.10	353.18	1.67	6.71
136	C ₄ H ₁₀ + CO ₂ + H ₂ O	VLE	252.90	288.30	0.1	2.1
29	C ₇ H ₁₆ + CO ₂ + H ₂ O	VLLE	323.15	413.15	2	13
27	C ₁₀ H ₂₂ + CO ₂ + H ₂ O	VLLE	323.08	413.16	0.94	18.12
14	C ₁₆ H ₃₄ + CO ₂ + H ₂ O	VLLE	473.15	573.15	10.1	30.1

investigation of the impact of the presence of CH₄ on the mutual solubility of H₂O and CO₂ and on the CO₂ miscibility pressure are of both technical and economic significance.

Water is always found in oil-bearing geological formations. In the oil and gas industries, the H₂O content of the hydrocarbon phases often creates problems during transportation and processing, the most severe of which is the formation of gas hydrates which may block pipelines, equipment, and instruments. Pipeline conditions are typically in the temperature range of (253.15 to 323.15) K and the pressure range of (5 to 25) MPa, an envelope that includes states in which hydrates may form. CO₂ is also an important hydrate former because of its presence as a contaminant in natural gas.¹⁹ Based on the combination and ratio of the hydrate formers, the structural and thermodynamic properties of the hydrates formed in mixed-gas systems can differ significantly from those with a single guest species. Because of this, a better understanding of the phase equilibria of mixed-hydrate systems is required in order to exploit the potential applications of hydrate formation in the presence of gas mixtures.

Methane in the form of hydrates is considered a potential source of energy, with conservative estimates suggesting that the energy stored in the form of hydrates exceeds all other hydrocarbon sources combined.²⁰ An extensive review of CH₄ hydrates as an energy source has been presented by Demirbas.^{21,22} In addition, the enormous quantities of CH₄ stored as thermally unstable hydrates also causes an environmental concern associated with the high global warming potential of methane.²³ Hydrates have also been suggested as an economically advantageous alternative to liquefied natural gas (LNG) for transportation and storage of gas.²⁴ Furthermore, the use of CO₂ to displace CH₄ from natural hydrates is currently being explored as a means of simultaneous CH₄ production and CO₂ sequestration.²⁵ In all of these processes, knowledge of the phase equilibrium properties of the mixed gas hydrates systems is essential. A number of experimental devices, methods, and mathematical models implemented for the measurements and predictions of hydrate-rich phase equilibrium of various systems have been reviewed extensively by Sloan and Koh in their recent book.²⁶

Because of the complexity of oil mixtures in which the components present are not all known, simpler systems that may represent certain characteristics of the real ones are usually studied. Unfortunately, experimental data for (hydrocarbon + CO₂ + H₂O) mixtures are scarce and typically limited to two-phase vapor–liquid equilibrium (VLE) measurements. Table 1 summarizes the published data for systems of the type (*n*-alkane + CO₂ + H₂O) together with the phases studied, and the

pressure and temperature ranges. Studies of the three-phase vapor–liquid–liquid equilibrium (VLLE) regions are extremely limited. Brunner et al.¹⁴ studied VLLE for the ternary mixture (*n*-hexadecane + CO₂ + H₂O) at temperatures of (473.15 and 573.15) K and pressures of (20.1 and 30.1) MPa using a static-analytical method. The phase compositions were all analyzed by gas chromatography. Forte et al.²⁷ measured the three-phase vapor–liquid–liquid equilibrium data of the ternary system (*n*-decane + CO₂ + H₂O) at temperatures from (323 to 413) K and pressures from (1 to 18) MPa using an analytical apparatus. The same authors²⁸ also studied the VLLE of the system (propane + CO₂ + H₂O) at temperatures from (311 to 353) K and pressures from (1.7 to 6.7) MPa, and Al Ghafri²⁹ has studied the mixture (*n*-heptane + CO₂ + H₂O) at temperatures from (323.15 to 413.15) K and pressures from (2 to 13) MPa using the same analytical apparatus. In the latter three cases, the experimental data obtained were compared with the predictions of the statistical associating fluid theory for potentials of variable range (SAFT-VR).^{30,31}

Continuing from our previous studies of (*n*-alkane + CO₂ + H₂O) mixtures,^{27–29} the present work is an experimental and modeling study of the ternary mixture (CH₄ + CO₂ + H₂O). The ternary mixture (CH₄ + CO₂ + H₂O) was the most widely studied system of the type (*n*-alkane + CO₂ + H₂O) both in the region of fluid-phase equilibria^{32–35} and fluid–hydrate equilibria.^{20,36–40} However, as shown in Table 1, previous fluid phase equilibrium measurements for this mixture were restricted to the vapor–liquid region only. The most recent study on this ternary mixture was that of Qin et al.³² in which vapor–liquid equilibria were studied for different ratios of CO₂ to CH₄ at $T = (324.3 \text{ and } 375.7) \text{ K}$ and $p = (10 \text{ to } 50) \text{ MPa}$. The effect of the gas-phase composition on the solubility of CO₂ and CH₄ in the aqueous phase was evaluated in terms of the apparent Henry's law constant $H_i = py_i/x_i$, where i denotes either CO₂ or CH₄, y_i denotes mole fraction in the gas phase, and x_i denotes mole fraction in the aqueous phase. It was found that the apparent Henry's law constant decreased with increasing ratio of CH₄ to CO₂ in the system, so that the CO₂ became more soluble by this measure upon the addition of CH₄. Similarly, it was found that, by the same measure, the solubility of CH₄ was enhanced by the presence of CO₂.

Jarne et al.³⁵ measured dew points of (CH₄ + CO₂ + H₂O) in the temperature range from (243.1 to 288.1) K at pressures from (0.11 to 6.05) MPa. The results obtained were analyzed in terms of a predictive excess-function equation of state. It was observed that the dew-point temperature at given pressure was highly dependent on the H₂O concentration but not strongly affected by ratio of CH₄ to CO₂. Dhima et al.³³ have measured

the simultaneous and separate solubilities of CH₄ and CO₂ in H₂O at $T = 344.25$ K and pressures of (10 to 100) MPa and modeled their results using a combination of the Peng–Robinson equation of state (EoS) and Henry's law. In their study, it was observed that CO₂ solubility (as measured by the apparent Henry's law constant) increased in the case of the ternary mixture compared to that of the binary mixture. Similarly in a previous study,³² it was also observed that the solubility of CO₂ increased as more CH₄ was present in the gas mixture.

Only in the work of Song and Kobayashi³⁴ were VLE states measured, but only one phase was analyzed (the gas phase). In that work, the H₂O content in the CO₂-rich phase was analyzed, and it was concluded that the presence of the CH₄ lowered the H₂O content in the gas phase by 20% to 30% from that of pure CO₂.

Although a substantial amount of research has been carried out on mixed hydrates of CO₂ and CH₄, few studies report the compositions of the gas, hydrate, and all fluid phases. Table 2

Table 2. Hydrate Equilibrium Data for the Ternary Mixture (CH₄ + CO₂ + H₂O)

ref	equilibria	T_{\min}/K	T_{\max}/K	p_{\min}/MPa	p_{\max}/MPa
38	H–V	273.06	280.46	2.0	3.5
36	H–L _w –V	273.6	284.2	1.51	7.19
37	H–L _w –V	275.14	285.34	1.92	7.47
42	H–L _w –V	273.56	283.26	1.5	5.0
39	H–L _w –V	280.3	280.3	3.04	5.46
20	H–L _w –V	274.02	280.1	1.66	4.03
40	H–L _w –V	258	274.1	0.5	3
43	H–L _w –L _{CO₂} –V	283.09	286.51	4.46	7.93
38,42	H–L _w –L _{CO₂} –V	283.32	285.56	4.53	6.72

summarizes the hydrate studies reported in the literature for the mixture of interest in this work. Blandria et al.³⁶ used a cylindrical equilibrium cell with sapphire windows for visual observation of hydrate formation. The apparatus was also fitted with a sampling device connected to a gas chromatograph for online phase composition analyses. However, only the gas phase was measured experimentally, while the compositions of the hydrate and aqueous phases were determined using a material balance approach in combination with the experimental data and the volumetric properties as evaluated from an EoS of the gas mixtures. In addition, the hydrate dissociation pressures were predicted (at the corresponding equilibrium temperature, CO₂ mole fraction in the gas feed, and H₂O mole fraction introduced to the system) using two thermodynamic models: CSMGem²⁶ (which is based on Gibbs energy minimization) and HWHYD⁴¹ (which is based on equality of fugacity for each component throughout all phases present).

Beltrán and Servio³⁷ also used a high-pressure pVT cell consisting of a very narrow glass tube for full visualization of the entire contents of the cell. They observed the hydrate, aqueous liquid, and vapor phases in equilibrium (H + L_w + V) at temperatures from (275.15 to 285.34) K and pressures from (1.92 to 7.47) MPa. However, they only measured the corresponding gas-phase compositions. Seo et al.^{38,42} measured three-phase H + L_w + V equilibrium conditions at different gas feed compositions. They also measured the quadruple points at which four phases (H + L_w + L_{CO₂} + V) coexisted. In addition, two-phase equilibrium states of hydrate and vapor were

measured and the concentration of CO₂ in the hydrate phase was also analyzed. Recently, Bi et al.⁴³ measured the four-phase (H + L_w + L_{CO₂} + V) equilibrium properties of the (CO₂ + CH₄) system using a view cell in the temperature range from (273.16 to 297.15) K at pressure up to 10 MPa. In their study, it was found that the four-phase region existed in the range of (4.46 to 8.4) MPa, (283.09 to 287.9) K, and (0 to 0.225) CH₄ mole fraction in the gas phase.

Thermodynamic models based on accurate experimental equilibrium data are needed to predict phase equilibria and hydrate thermodynamic properties for potential industrial applications. To be able to treat the nonsphericity of alkanes and the hydrogen-bonding interactions of H₂O, SAFT-VR^{30,31} based on square-well potentials was used in the present study for VLE calculations. The SAFT-VR intermolecular parameters were obtained from the work of Míguez et al.⁴⁴ In their work, they used SAFT-VR to estimate the global phase equilibrium diagram of the ternary mixture over a wide pressure and temperature range. Regarding hydrates, recently, Dufal et al.⁴⁵ integrated SAFT-VR into a traditional van der Waals and Platteeuw^{46,47} (vdWP) framework for modeling clathrate hydrates; in this approach, SAFT-VR was used to describe the fluid phases while the vdWP method was used to model the hydrates themselves. In the present work, we make use of such a model to compare with experimental data. Additionally, the hydrate model (CSMHYD) developed by the Colorado School of Mines was also used.⁴⁸

The binary systems (CO₂ + CH₄),^{49–56} (CH₄ + H₂O),^{32,57–77} and (CO₂ + H₂O)^{33,60,64,66,78–110} have been covered extensively in the literature, both in terms of experimental phase equilibrium data and modeling approaches. A thermodynamic model developed by Duan et al.^{111,112} for the solubility of CO₂ in water at temperatures of (273 to 533) K and pressures of (0 to 200) MPa was able to represent the CO₂ solubility data considered almost to within the experimental uncertainties. However, it is worth noting here that Hou et al.¹¹⁰ in their recent VLE measurements of (CO₂ + H₂O), found that the model gives increasing deviations from their data at temperatures above about 400 K. Spycher et al.¹¹³ developed an alternative model for the mutual solubility of CO₂ and water at temperatures of (285 to 383) K and pressures up to 60 MPa. This model is able to represent the compositions of both the water-rich and the CO₂-rich phases to within the experimental uncertainties. In addition, Duan and Mao¹¹⁴ developed a thermodynamic model for the binary mixture (CH₄ + H₂O) at temperatures of (273 to 523) K and pressures of (0 to 200) MPa which was also able to predict the CH₄ solubility to within the uncertainty of the available experimental data. We make use of these models in our analysis.

In the binary system (CO₂ + H₂O), the H₂O content in the gas phase decreases monotonically as pressure increases in the subcritical region. However, in the supercritical region, it decreases as pressure increases up to a pressure around (5 to 10) MPa and then increases again as pressure increases further. In all cases, the H₂O content in the gas phase increases as temperature increases. The CO₂ solubility in the H₂O-rich phase increases as pressure increases but decreases as temperature increases. For the binary system of (CH₄ + H₂O), the H₂O content in the gas phase decreases as pressure increases and increases as temperature increases while the CH₄ solubility in the H₂O-rich phase increases as pressure increases and decreases as temperature increases, similar to the behavior

observed in the ($\text{CO}_2 + \text{H}_2\text{O}$) binary system. In this work, the effect of adding a third component on the behavior of these binaries is studied both experimentally and through modeling.

2. EXPERIMENTAL SECTION

2.1. Material. The CO_2 used in this work was CP grade supplied by BOC with a mole fraction purity higher than 99.995%. The CH_4 was supplied by BOC and was “low ethylene” grade with purity higher than 99.95%. The carrier gas used in the gas chromatography was CP grade helium from BOC with purity higher than 99.999%. The H_2O used was deionized to an electrical resistivity greater than $18 \text{ M}\Omega\cdot\text{cm}$ at $T = 298 \text{ K}$. The hydrogen was also supplied by BOC with purities higher than 99.995%. The tetrahydrofuran were supplied by Sigma-Aldrich with a purity of 99.9%. No purification was attempted.

2.2. Apparatus. In this work, we used the high-pressure quasi-static-analytical apparatus described in detail by Forte et al.²⁷ As shown schematically in Figure 1, the main components

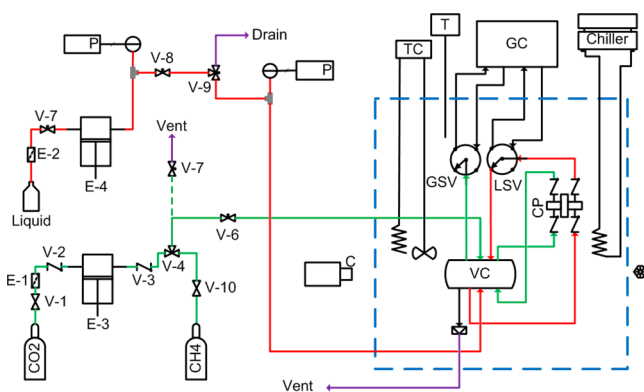


Figure 1. Schematic diagram of the analytical apparatus: E-3 and E-4, pumps; GC, gas chromatograph; VC, view cell; CP, circulating pump; TC, temperature controller; GSV, gas sampling valve; LSV, liquid sampling valve; P, pressure sensor; and T, temperature sensor. Red and green lines denote paths of liquid and gas phases, respectively.

were a high-pressure equilibrium cell, a magnetically coupled reciprocating circulation pump, electronically actuated sampling valves, a gas chromatograph (GC), and a temperature control system.

The equilibrium cell, made from type 17-4PH martensitic stainless steel, had a nominal internal volume of 35 cm^3 and was equipped with two diametrically opposite sapphire windows that enabled visual observation of the interior. The reciprocating pump was used for the circulation of both liquid and vapor, which was advantageous for promoting mass transfer between the phases. A chromatographic liquid sampling valve (LSV), with an internal $1 \mu\text{L}$ sample loop, was installed in the liquid recirculation loop and used to withdraw liquid samples for compositional analysis by GC. A chromatographic gas sample valve (GSV), with a $5 \mu\text{L}$ sample loop, was connected to the top of the equilibrium cell to enable sampling of the gas phase for analysis by GC. When two liquid phases were present, it was possible to tilt the cell such that the less-dense liquid was drawn into the recirculation loop; in that way the compositions of both liquids could be measured.

The transfer tubes connecting the sampling valves to the GC were heated by means of low-voltage mineral-insulated heater cables operating with K-type thermocouple temperature

sensors and proportional-integral-derivative (PID) temperature controllers. During sampling, the components were vaporized on the heated transfer lines and transported to the GC column by the carrier gas. The GC was equipped with a thermal conductivity detector (TCD) connecting in series with a flame ionization detector (FID); the TCD was used for the detection of CO_2 and H_2O , while the FID was used for the detection of CH_4 . A HayeSep Q column (80/100 mesh, 2 m long, 3.2 mm o.d, 2 mm i.d) was used to separate the three components. The operating conditions of the GC used in this work are listed in Table 3.

Table 3. Gas Chromatography Conditions for the Analysis of the Mixtures Used in This Work^a

injector		column		TCD		FID	
$\dot{V}/(\text{cm}^3\cdot\text{s}^{-1})$	T/K	T/K	T/K	I/mA	T/K	ϕ	
40	423.15	343.15	523.15	90	523.15	1:10	

^aTCD = thermal conductivity detector; FID = flame ionization detector; \dot{V} = He flow rate; I = current; ϕ = H_2/air flow ratio.

A manual syringe pump was used for the injection of liquid components into the equilibrium cell, while a refrigerated automatic syringe pump was used for the injection of liquefied CO_2 . The CH_4 was admitted from the supply cylinder via a pressure regulator. The valves V-4, V-7, and V-9 shown in Figure 1 were used for the purposes of flushing, draining, and venting of the system. The temperature was controlled using a bath filled with silicon oil, a controller unit, and a stirrer. The bath was equipped with two double-glazed windows, at the front and back, which were aligned with the sapphire windows of the cell. A coil connected to an additional external refrigerated circulating bath was used to provide cooling when working at temperatures near or below ambient.

Back-illumination, using a light emitting diode source fitted with a diffuser, and a camera in front mounted on an optical rail facilitated the observation of the inside of the cell. The temperature was measured by means of a platinum resistance thermometer (PRT) located in the bath close to the equilibrium cell. The pressure was measured using a pressure transducer connected to the liquid inlet line through valve V-9. Prior to use, the system was thoroughly leak tested in the whole pressure range; it exhibited a high level of integrity. The system was also checked for leakage during the course of measurements.

2.3. Calibration. The pressure transducer was calibrated previously²⁷ against a pressure balance (Desgranges et Huot, model 26000) fitted with a piston-cylinder unit having a full-scale range of 50 MPa and standard relative uncertainty of 0.005%. The calibration was done in a range of pressures from (0.1 to 50) MPa, and the final standard uncertainty of the pressure measurements was estimated to be 5 kPa. No additional calibration was done for this work, and in order to account for any sensor drift over time, the pressure readings of the transducer were periodically compared at ambient pressure against a digital barometer located in the same laboratory and small additive corrections were made to account for the observed differences.

The PRT was also calibrated previously²⁷ on ITS-90 at the temperature of the triple point of H_2O and by comparison with a standard platinum resistance thermometer in a constant-temperature bath at temperatures up to 473 K. The standard

uncertainty of the PRT was 0.01 K, but fluctuations of the bath temperature could be as much as ± 0.05 K. Consequently the overall standard uncertainty of the cell temperature was estimated to be 0.05 K.

The TCD and FID were calibrated for each component individually by an absolute method using one of the sampling valves (LSV). In this method, we assume that the volume sampled by the LSV was always constant so that the amount of substance introduced into the GC was simply proportional to the density of the fluid at the sampling conditions. The calibration was carried out at the fixed column temperature at which measurements were performed and covered a range extending beyond the experimental measurements so that no extrapolation was performed on the calibration curves for any component.

The response of the TCD to varying amounts of CO_2 was determined by adjusting the conditions of pressure and temperature in the cell. The CO_2 density was obtained from the EoS developed by Span and Wagner¹¹⁵ with an estimated relative uncertainty between 0.03% and 0.05% (which we interpret as an expanded uncertainty with coverage factor $k = 2$). For the sake of simplicity, we ascribe the value 0.025% to the standard relative uncertainty of the CO_2 density. Considering the reproducibility in the GC peak area, the standard relative uncertainty in the peak area for CO_2 was typically 1.0% while the standard relative uncertainty in the calculated amount of CO_2 at each given pressure and temperature was estimated to be 0.1%. As discussed below, the loop-volume uncertainty is excluded from this assessment.

The response of the FID to CH_4 was calibrated in the same way, and the density of CH_4 was obtained from the EoS developed by Setzmann and Wagner¹¹⁶ with an estimated uncertainty ranging from 0.03% to 0.07%. Again, the standard relative uncertainty in the peak area was typically 1.0% while the standard relative uncertainty in the calculated amount of CH_4 at each given pressure and temperature was estimated to be 0.1%.

The response of the TCD to varying amounts of H_2O was calibrated by filling the equilibrium cell with gravimetrically prepared mixtures of H_2O and tetrahydrofuran. The calibration was carried out at a pressure just above ambient and at different temperatures for various mole fractions of H_2O . The mixture density was obtained from the work of Schedemann et al.¹¹⁷ Considering the reproducibility in the response peak area, the standard relative uncertainty in the peak area response for H_2O was, on average, 2.0% while the standard relative uncertainty in the calculated amount of H_2O at each given pressure and temperature was estimated to be 0.2%.

As previously mentioned, TCD was used for both H_2O and CO_2 . A linear relationship between the amount of H_2O present and the TCD response area was observed. However, in the case of CO_2 , nonlinear behavior was observed at conditions where a large amount of CO_2 was present and a quadratic polynomial was therefore used for this component. The FID showed a very linear response for CH_4 . From time to time during the course of the measurements, and also at the end of the work, the calibration was checked to ensure that no detector drift had occurred.

2.4. Experimental Procedure. The apparatus was initially cleaned with solvents, flushed with CO_2 , and subjected to vacuum. H_2O , previously degassed under vacuum, was then loaded until it occupied approximately one-third of the cell volume, after which CO_2 was introduced slowly to the cell until

the existence of three phases was observed. Finally, CH_4 was introduced slowly through valve V-4 until the desired initial pressure was reached at the given temperature.

The system was then left for at least 2 h to equilibrate while using the circulation pump to promote mixing. Once the system was equilibrated, the vapor phase was first sampled using the GSV. The H_2O -rich phase was sampled next by means of the LSV, and finally the cell was tilted to allow sampling of the middle CO_2 -rich phase, again with the LSV. Further CH_4 was then injected so as to increase the pressure to the next state point, and the process was repeated for each isotherm. For each phase, at least six samples were taken and the results were examined to ensure reproducibility and to be sure that there was no evidence of cross-contamination or entrainment of one phase in the other or any sign of leakage. To locate precisely the UCEP at each temperature, the pressure was manipulated in very small steps by injecting or withdrawing H_2O while observing the phase state of the system. Close to the UCEP strong critical opalescence was observed. The phase compositions at the UCEP were measured by sampling at a pressure of approximately (0.01 to 0.02) MPa above the UCEP pressure.

For measurements of the four-phase $\text{H} + \text{L}_w + \text{L}_{\text{CO}_2} + \text{V}$ locus, the system was initially brought to three-phase equilibrium. The temperature was then lowered until hydrates were observed to form. An equilibration period of at least 24 h was allowed before the temperature was slowly increased in steps of 0.01 K while monitoring both temperature and pressure. The point at which the slope of the $p(T)$ locus changed sharply was considered to be the point at which the hydrate crystals were fully dissociated and is reported as the hydrate dissociation condition. Similar procedures have been implemented in the literature.^{36,118} It is worth noting here that, in hydrate measurements, there is usually a difference between the hydrate formation and dissociation conditions associated with metastability of the three-phase state during cooling. We note that, in the work of Bi et al.,⁴³ the temperatures and pressures of the four-phase states corresponding to the start and end of melting were identified. It was observed that the temperature change was small during melting but the pressure differences were considerable; our observations were similar.

During two-phase VLE measurements, the molar ratio between CO_2 and CH_4 in the gas phase was kept roughly fixed at about 0.5. This ratio was monitored by sampling the gas phase, and the composition was adjusted until the desired ratio was achieved.

2.5. Uncertainty Analysis. Using the guide to the expression of uncertainty in measurements (GUM),¹¹⁹ the combined standard uncertainty of the mole fraction of each component in a given phase $u(x_i)$ is obtained from the following equation

$$u^2(x_i) = \sum_{j=1}^n \sum_{k=1}^n \frac{\partial x_i}{\partial z_j} \frac{\partial x_i}{\partial z_k} u^2(z_j, z_k) \quad (1)$$

Here, z_j and z_k are measured input variables, $(\partial u_i / \partial z_j)$ is the sensitivity coefficient of the input variable z_j , $u^2(z_j, z_k)$ is the covariance ($j \neq k$) or the variance ($j = k$) for variables z_j and z_k . In this work, an absolute area method was used in which the peak area A_i in the chromatogram measured for component i in the mixture is related to the amount n_i of that substance in the sample. For the purposes of this uncertainty analysis, we

assume that this relationship is linear and we define chromatographic response factors f_i such that

$$n_i = f_i A_i \quad (2)$$

The mole fractions x_i of each component are given by

$$x_i = n_i / \left(\sum_{k=1}^{N_c} n_k \right) \quad (3)$$

and hence may be obtained from the chromatographic peak areas and response factors as follows:

$$x_i = A_i f_i / \left(\sum_{k=1}^{N_c} A_k f_k \right) \quad (4)$$

Then considering eqs 1 and 4, the overall combined standard uncertainty of the mole fraction arising from temperature, pressure, response factor, and chromatographic peak area uncertainties is given by

$$u^2(x_i) = (\partial x_i / \partial T)^2 u^2(T) + (\partial x_i / \partial p)^2 u^2(p) + \sum_{j=1}^{N_c} \left(\frac{\partial x_i}{\partial n_j} \frac{\partial n_j}{\partial f_j} \right)^2 u^2(f_j) + \sum_{j=1}^{N_c} \left(\frac{\partial x_i}{\partial n_j} \frac{\partial n_j}{\partial A_j} \right)^2 u^2(A_j) \quad (5)$$

The partial derivatives, sensitivity coefficients, $(\partial x_i / \partial n_j)$ are given by

$$\left. \begin{aligned} (\partial x_i / \partial n_j) &= -x_i x_j / n_j \quad (j \neq i) \\ &= (1 - x_i) x_i / n_i \quad (j = i) \end{aligned} \right\} \quad (6)$$

and the partial derivatives (or sensitivity coefficients) $(\partial n_i / \partial f_j)$ and $(\partial n_i / \partial A_j)$ are given by

$$\left. \begin{aligned} (\partial n_j / \partial f_j) &= A_j \\ (\partial n_j / \partial A_j) &= f_j \end{aligned} \right\} \quad (7)$$

It follows that the overall standard uncertainty of x_i is given by

$$u^2(x_i) = (\partial x_i / \partial T)^2 u^2(T) + (\partial x_i / \partial p)^2 u^2(p) + \sum_{j \neq i} (x_i x_j)^2 [u_r^2(f_j) + u_r^2(A_j)] + [x_i (1 - x_i)]^2 [u_r^2(f_i) + u_r^2(A_i)] \quad (8)$$

where $u_r(X)$ denotes the standard relative uncertainty of variable X . The standard relative uncertainties in the response factors are given by

$$u_r^2(f_j) = [u_r^2(n_j) + u_r^2(A_j)]_{\text{cal}} \quad (9)$$

where subscript "cal" denotes the calibration measurement for component j . We note that, in the case of a binary mixture, eq 8 reduces to the following simpler form

$$u^2(x_1) = (\partial x_1 / \partial T)^2 u^2(T) + (\partial x_1 / \partial p)^2 u^2(p) + [x_1 (1 - x_1)]^2 \sum_{j=1}^2 [u_r^2(f_j) + u_r^2(A_j)] \quad (10)$$

In this analysis, the uncertainty of the sample-loop volume is not considered as it is assumed to be constant and therefore cancels in the analysis.

From eq 8, the overall combined uncertainty in the measured mole fraction of a component is affected by the uncertainties of pressure, temperature, response factor, and peak area. From eq 9, the uncertainty of the response factor of a component in the mixture is determined by the uncertainties during calibration of both the peak area and the calculated amount of substance for that pure component, the latter being affected by the uncertainties of pressure, temperature, and the equation of state from which the density is calculated. The typical standard uncertainties of all of the input variables have been given previously, and these lead to overall combined standard uncertainties of mole fraction that vary over a wide range from 1×10^{-6} to 3×10^{-3} depending upon the component, temperature, pressure, and phase in question. It was observed that larger uncertainty occurs at lower temperatures and higher pressures.

2.6. Validation. The apparatus was validated in previous work by measuring the vapor–liquid equilibria of $(\text{CO}_2 + \text{C}_{10}\text{H}_{22})^{27}$ and $(\text{CO}_2 + \text{C}_7\text{H}_{16})^{29}$ and comparing the results with the available literature data; good agreement was found. In the present work, further validation measurements were undertaken on the $(\text{CO}_2 + \text{H}_2\text{O})$ system at $T = 323.15$ K where measurements were made of the solubility of CO_2 in the water-rich phase at pressures up to 19 MPa. The results are given in Table 4 and are compared in Figure 2 with the available literature data.^{79,80,82,87,93,99,110,120} Here, we observe good agreement over the entire pressure range.

Table 4. Experimental Solubility Data in the Water-Rich Phase for $(\text{CO}_2 + \text{H}_2\text{O})$ at Temperature of 323.15 K

p/MPa	x_1	$u(x_1)$	x_2	$u(x_2)$
2.066	0.00642	0.00015	0.99358	0.00014
3.332	0.01003	0.00024	0.98997	0.00022
4.415	0.01269	0.00028	0.98731	0.00028
5.585	0.01561	0.00035	0.98439	0.00034
6.953	0.01758	0.00039	0.98242	0.00039
9.062	0.02004	0.00044	0.97996	0.00043
13.521	0.02173	0.00048	0.97827	0.00048
18.683	0.02280	0.00050	0.97720	0.00050

3. EXPERIMENTAL RESULTS

The binary system $(\text{CH}_4 + \text{CO}_2)^{121}$ exhibits type I phase behavior while the binary systems $(\text{CO}_2 + \text{H}_2\text{O})^{108}$ and $(\text{CH}_4 + \text{H}_2\text{O})^{122}$ exhibit type III phase behavior according to the classification of Scott and van Konynenburg.^{123,124} As a consequence, the ternary mixture exhibits class IV behavior according to the global ternary diagram classification proposed by Bluma and Deiters.¹²⁵ Mixtures of this type possess an LLE immiscibility region, and hence, a VLLE region is also expected. The principal region of the present investigation is illustrated on a pressure–temperature diagram in Figure 3. The region within which three fluid phases coexist is bounded at low pressures by the three-phase $L_w + L_{\text{CO}_2} + V$ curve of the $(\text{CO}_2 + \text{H}_2\text{O})$ binary system (which is almost coincident with the vapor pressure curve of pure CO_2), and at high pressures by either the UCEP locus $L_w + L_{\text{CO}_2} = V$ or the four-phase line along which hydrate coexists with the three fluid phases. Figure 3 also shows

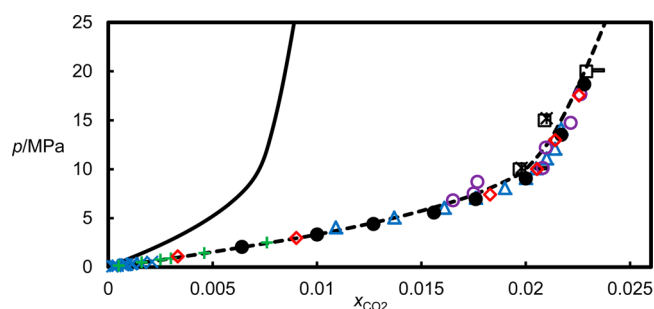


Figure 2. Isothermal pressure–composition (p, x) phase diagram at $T = 323.15$ K for the binary system ($\text{CO}_2 + \text{H}_2\text{O}$). The filled symbols correspond to the data gathered in this work at different pressures in the water-rich phase. The open symbols correspond to the binary published data for the following: \times , ref 99; \square , ref 80; Δ , ref 79; $-$, ref 87; $*$, ref 120; \circ , ref 82; $+$, ref 93; \diamond , ref 110. The dotted and solid lines correspond to the solubility in the binary system ($\text{CO}_2 + \text{H}_2\text{O}$) obtained at the same temperature and different pressures from Duan et al.¹¹² and SAFT-VR⁴⁴ models, respectively.

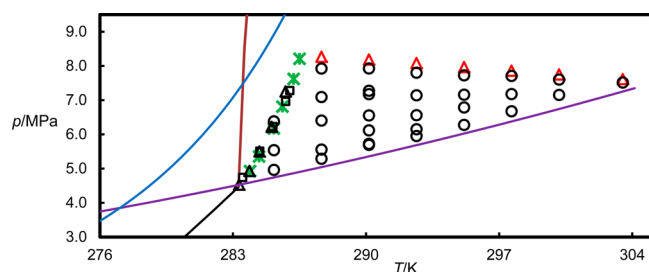


Figure 3. VLE region and its boundaries: $*$, quadruple data gathered in this work; \square , ref 43; Δ , refs 38 and 42; \circ , VLE data gathered in this work; Δ , UCEP data gathered in this work. Solid lines denote phase boundaries: CO_2 saturated vapor pressure (purple);¹¹⁵ three-phase region $L_w\text{--}H\text{--}V$ for the pure methane (blue);¹²⁸ three-phase region $L_w\text{--}H\text{--}V$ for the pure CO_2 (black);¹²⁶ and three-phase region $L_w\text{--}H\text{--}L_{\text{CO}_2}$ for the pure CO_2 (brown).¹²⁷

the vapor-pressure curve of pure CO_2 ,¹¹⁵ the $L_w + H + V$ ¹²⁶ and $L_w + H + L_{\text{CO}_2}$ ¹²⁷ hydrate equilibrium curves of the ($\text{CO}_2 + \text{H}_2\text{O}$) binary system, and the $L_w + H + V$ hydrate curve for the ($\text{CH}_4 + \text{H}_2\text{O}$) binary system.¹²⁸

The compositions of the three coexisting fluid phases have been obtained along eight isotherms at temperatures of (285.15, 287.65, 290.15, 292.65, 295.15, 297.65, 300.15, and 303.15) K and at pressures up to either the UCEP or the quadruple curve. Additionally, compositions of coexisting vapor and liquid phases have been measured along three isotherms at temperatures of (323.15, 373.15, and 423.15) K, pressures up to 20 MPa, and with the molar ratio between CO_2 and CH_4 kept roughly constant at about 0.5. The three- and four-phase states investigated are shown in Figure 3, and the experimental VLE and VLE data are given in Tables 5 and 6 together with their estimated standard uncertainties. The quadruple curve along which hydrate coexists with the three fluid phases was also measured, and the results are presented in Table 7, while the UCEP data are given in Table 8.

4. MODELING

In this work, we used the SAFT-VR model to predict the VLE using the parameters adopted by Míguez and co-workers,⁴⁴ which are based on those obtained by Clark et al.¹²⁹ for H_2O , Patel et al. for CH_4 ,¹³⁰ and Galindo and Blas for CO_2 ^{131,132}

from fits to vapor pressure and saturated liquid density data. Since, like any analytical equation of state, the SAFT approach does not reproduce the experimentally observed behavior close to the critical point, such fits are typically restricted to temperature below approximately $0.9T_c$ where T_c is the critical temperature. In order to obtain a good representation of the global phase diagram of the ($\text{CH}_4 + \text{CO}_2 + \text{H}_2\text{O}$) system, Míguez et al.⁴⁴ rescaled the parameters so as to reproduce the experimental critical temperature and pressure of each component. The resulting pure-component parameters are detailed in Table 9.

For the unlike (dispersion) energies, only the binary interaction parameter for the system $\text{CO}_2\text{--H}_2\text{O}$ was considered; the value $k_{ij} = 0.0258$ was obtained by fitting to the experimental temperature minimum of the high-temperature branch of the fluid–fluid critical line.⁴⁴ All other cross-interaction parameters were obtained in the usual manner (using the Berthelot combining rule with $k_{ij} = 0$). This set of parameters was shown to provide an excellent description of the global phase diagram of this system over a wide range of temperatures. However, the model was not optimized for a quantitative description of the low-temperature mutual solubility data of the constituent binary subsystems, and low accuracy in the high-density region is also expected as a direct consequence of the rescaling of the parameters. The aim here was to compare the general experimental trends with a rigorous molecular-based equation of state such as SAFT-VR, focusing on the agreement in the high-temperature region and critical locus of the mixture.

For the calculation of hydrate-fluid equilibria, the SAFT-VR-based approach of Dufal et al.⁴⁵ was considered, along with the CSMHYD⁴⁸ model developed by the Colorado School of Mines. It should be noted that the SAFT-VR parameters used in the hydrate calculations are different from those given in Table 9 and their values may be found in ref 45. The reason for retaining the SAFT-VR parameters from ref 45 is that these values are consistent with the other parameters present in the model of Dufal et al.

5. DISCUSSION AND COMPARISON WITH EXPERIMENT

In Figure 4, we compare the two-phase VLE data with literature data and models.^{32,112,114} In this figure, we plot the py_i/x_i for either CO_2 or CH_4 against the mole fraction of the other component, where x_i is the mole fraction of component i in the liquid phase and y_i is the mole fraction of the same component in the gas phase. This quantity is the apparent Henry's constant which we use as an inverse measure of solubility and a means of exploring the influence of adding a second nonaqueous component on the solubility of the first. Comparing our data at $y_1 \approx y_2 \approx 0.5$ with values calculated from the models of Duan et al.¹¹² at $y_1 = 0$ and Duan and Mao¹¹⁴ at $y_2 = 0$, we see that in both cases the addition of the second nonaqueous component reduces the apparent Henry's constant and thus enhances the solubility of the first nonaqueous component, although this effect is quite small. In all cases, the apparent Henry's constant increases with pressure as expected from the finite partial molar volumes of CO_2 and CH_4 in the aqueous phase; the effect is more pronounced in the case of the CO_2 . The only experimental data with which we can compare the present results are those of Qin et al.³² at temperatures of (324.7 and 375.4) K and pressures between (20 and 50) MPa. Since the pressures considered in that work are higher than in the present

Table 5. Experimental VLLE Data for $[\text{CH}_4 (1) + \text{CO}_2 (2) + \text{H}_2\text{O} (3)]$ at Temperatures T and Pressures p , Where x_i Denotes the Mole Fraction of Component i and $u(x_i)$ Denotes Standard Uncertainty of x_i ^a

phase	p/MPa	x_1	$u(x_1)$	x_2	$u(x_2)$	x_3	$u(x_3)$
$T = 285.15 \text{ K}$							
I	4.963	0.0187	0.0013	0.9809	0.0014	0.000373	0.000009
II	4.961	0.00612	0.00039	0.98990	0.00039	0.003976	0.000089
III	4.957	0.000051	0.000004	0.02830	0.00062	0.97166	0.00062
I	5.538	0.0917	0.0017	0.9080	0.0017	0.000288	0.000007
II	5.529	0.02748	0.00057	0.9699	0.0058	0.002646	0.000059
III	5.525	0.000216	0.000006	0.02797	0.00061	0.97181	0.00061
I	6.381	0.1692	0.0022	0.8306	0.0022	0.000198	0.000005
II	6.384	0.06313	0.00098	0.93469	0.00099	0.002177	0.000049
III	6.379	0.000527	0.000012	0.02743	0.00060	0.97204	0.00061
I	7.077	0.2122	0.0025	0.7877	0.0025	0.000153	0.000005
II	7.075	0.0964	0.0014	0.9018	0.0014	0.001837	0.000040
III	7.070	0.000628	0.000014	0.02685	0.00059	0.97252	0.00060
$T = 287.65 \text{ K}$							
I	5.289	0.0243	0.0029	0.9754	0.0024	0.000366	0.000009
II	5.287	0.00736	0.00043	0.98949	0.00043	0.003148	0.000070
III	5.283	0.000051	0.000004	0.02770	0.00060	0.97225	0.00060
I	5.557	0.0495	0.0014	0.9502	0.0014	0.000296	0.000007
II	5.555	0.01766	0.00050	0.97970	0.00050	0.002644	0.000059
III	5.555	0.000127	0.000005	0.02755	0.00060	0.97232	0.00060
I	6.405	0.1283	0.0019	0.8715	0.0019	0.000206	0.000005
II	6.397	0.05155	0.00086	0.94626	0.00087	0.002196	0.000050
III	6.393	0.000394	0.000009	0.02705	0.00059	0.97256	0.00060
I	7.092	0.1769	0.0022	0.8230	0.0022	0.000154	0.000005
II	7.085	0.0834	0.0012	0.9147	0.0012	0.001916	0.000043
III	7.083	0.000557	0.000013	0.02647	0.00058	0.97297	0.00059
I	7.924	0.2158	0.0025	0.7841	0.0025	0.000110	0.000003
II	7.917	0.1318	0.0018	0.8664	0.0018	0.001767	0.000041
III	7.914	0.000755	0.000017	0.02560	0.00056	0.97365	0.00057
$T = 290.15 \text{ K}$							
I	5.693	0.03276	0.0012	0.96687	0.0012	0.000369	0.000009
II	5.690	0.01080	0.00048	0.98563	0.00048	0.003562	0.000082
III	5.689	0.000076	0.000004	0.02724	0.00060	0.97269	0.00060
I	5.725	0.03454	0.0012	0.96511	0.0013	0.000355	0.000009
II	5.725	0.01161	0.00049	0.98510	0.00049	0.003299	0.000075
III	5.725	0.000085	0.000004	0.02724	0.00059	0.97267	0.00060
I	6.117	0.06994	0.0014	0.92977	0.0014	0.000300	0.000007
II	6.114	0.02749	0.00062	0.96961	0.00063	0.002901	0.000066
III	6.111	0.000194	0.000006	0.02693	0.00059	0.97288	0.00059
I	6.555	0.11458	0.0017	0.88516	0.0017	0.000262	0.000007
II	6.548	0.04552	0.00081	0.95201	0.00082	0.002468	0.000057
III	6.551	0.000293	0.000007	0.02661	0.00058	0.97310	0.00058
I	7.176	0.15567	0.0020	0.84414	0.0020	0.000193	0.000005
II	7.177	0.07453	0.0011	0.92327	0.0012	0.002205	0.000051
III	7.179	0.000431	0.000010	0.02616	0.00057	0.97341	0.00058
I	7.275	0.16277	0.0021	0.83705	0.0021	0.000180	0.000005
II	7.265	0.07839	0.0012	0.91948	0.0012	0.002125	0.000048
III	7.269	0.000475	0.000011	0.02607	0.00057	0.97346	0.00058
I	7.927	0.18401	0.0022	0.81587	0.0022	0.000121	0.000003
II	7.930	0.11863	0.0016	0.87930	0.0016	0.002073	0.000048
III	7.926	0.000598	0.000032	0.02545	0.0016	0.97395	0.00058
$T = 292.65 \text{ K}$							
I	5.954	0.0225	0.0011	0.9771	0.0011	0.000364	0.000009
II	5.952	0.00828	0.00050	0.98836	0.00050	0.003363	0.000078
III	5.954	0.000055	0.000004	0.02664	0.00058	0.97331	0.00058
I	6.151	0.0392	0.0012	0.9605	0.0012	0.00034	0.000007
II	6.143	0.01589	0.00055	0.98100	0.00055	0.003112	0.000072
III	6.141	0.000101	0.000004	0.02653	0.00058	0.97337	0.00058
I	6.561	0.0760	0.0014	0.9237	0.0014	0.000281	0.000007
II	6.554	0.03412	0.00071	0.96298	0.00072	0.002893	0.000067

Table 5. continued

phase	p/MPa	x_1	$u(x_1)$	x_2	$u(x_2)$	x_3	$u(x_3)$
$T = 292.65 \text{ K}$							
III	6.551	0.000205	0.000006	0.02621	0.00057	0.97359	0.00057
I	7.143	0.1214	0.0017	0.8784	0.0017	0.000221	0.000005
II	7.136	0.05794	0.00098	0.93959	0.00098	0.002464	0.000058
III	7.136	0.000345	0.000008	0.02574	0.00056	0.97392	0.00057
I	7.803	0.1541	0.0020	0.8459	0.0020	0.000152	0.000005
II	7.787	0.1023	0.0015	0.8955	0.0015	0.002186	0.000052
III	7.787	0.000481	0.000011	0.02497	0.00055	0.97455	0.00055
$T = 295.15 \text{ K}$							
I	6.2782	0.0207	0.0011	0.9790	0.0011	0.000370	0.000009
II	6.272	0.00803	0.00053	0.98779	0.00053	0.004176	0.000096
III	6.268	0.000046	0.000003	0.02575	0.00056	0.97421	0.00056
I	6.787	0.0632	0.0012	0.9365	0.0012	0.000302	0.000007
II	6.77	0.02843	0.00069	0.96817	0.00069	0.003399	0.000079
III	6.778	0.000160	0.000005	0.02543	0.00055	0.97441	0.00056
I	7.162	0.0920	0.0015	0.9077	0.0015	0.000247	0.000005
II	7.161	0.04523	0.00086	0.95157	0.00087	0.003196	0.000074
III	7.1595	0.000239	0.000006	0.02509	0.00057	0.97467	0.00055
I	7.7265	0.1192	0.0017	0.8806	0.0017	0.000189	0.000005
II	7.72	0.0745	0.0012	0.9226	0.0012	0.002981	0.000070
III	7.717	0.000366	0.000009	0.02457	0.00054	0.97506	0.00054
$T = 297.65 \text{ K}$							
I	6.675	0.02201	0.00098	0.97764	0.00098	0.000356	0.000009
II	6.675	0.01001	0.00058	0.98541	0.00058	0.00460	0.00011
III	6.6632	0.000056	0.000003	0.02493	0.00054	0.97502	0.00054
I	7.1773	0.0584	0.0011	0.9413	0.0011	0.000287	0.000007
II	7.1773	0.03046	0.00074	0.96556	0.00074	0.003973	0.000093
III	7.1595	0.000168	0.000005	0.02457	0.00053	0.97526	0.00053
I	7.7097	0.0856	0.0013	0.9142	0.0013	0.000219	0.000005
II	7.7019	0.0576	0.0010	0.9387	0.0010	0.003629	0.000084
III	7.6978	0.000273	0.000007	0.02407	0.00052	0.97566	0.00052
$T = 300.15 \text{ K}$							
I	7.1605	0.02751	0.00092	0.97218	0.00092	0.000313	0.000007
II	7.1528	0.01509	0.00064	0.97969	0.00065	0.00522	0.00011
III	7.153	0.000073	0.000003	0.02392	0.00052	0.97600	0.00052
I	7.612	0.0533	0.0010	0.9465	0.0010	0.000247	0.000005
II	7.603	0.03652	0.00082	0.95872	0.00083	0.00476	0.00011
III	7.602	0.000163	0.000005	0.02346	0.00051	0.97638	0.00051
$T = 300.50 \text{ K}$							
I	7.524	0.01357	0.00079	0.98611	0.00080	0.000324	0.000007
II	7.517	0.00934	0.00066	0.98503	0.00066	0.00563	0.00013
III	7.514	0.000038	0.000003	0.02307	0.00050	0.97690	0.00050

^aThe phases are labeled as I, II, and III for the gas, CO₂-rich liquid, and water-rich phases, respectively.

study, it is difficult to make a direct comparison. Nevertheless, the results of Qin et al. show a continuation of the trend whereby the apparent Henry's constant increases with pressure at constant temperature and constant y_1/y_2 . In agreement with the present study, the results of Qin et al. also show a decrease in the effective Henry's constant upon the addition of a second nonaqueous component. Turning now to the predictions of the SAFT-VR model, we observe large differences from the experimental data with the predicted solubilities being too small by a large margin. This undoubtedly reflects the fact that the model was not tuned to any solubility data. The SAFT-VR calculations do mostly reflect the trends observed experimentally and come into somewhat better agreement as the temperature increases.

The present VLLE data are compared with the predictions of the SAFT-VR model in Figure 5 where we present isothermal

(p, x_i) diagrams illustrating the compositions of the three coexisting phases. Parts a and b of Figure 5 show the solubilities of CH₄ and CO₂, respectively, in the aqueous phase under VLLE conditions. In common with the behavior observed in the two-phase region, these solubilities are strongly under-predicted by SAFT-VR. One can also observe that the mole fraction of CO₂ in the aqueous phase varies relatively little, being between 0.02 and 0.03 at all VLLE states investigated. In contrast, the mole fraction of CH₄ varies strongly with pressure across the VLLE region; at constant temperature, x_{CH_4} tends to zero at the lowest pressure and approaches its greatest value at the UCET; at constant pressure, x_{CH_4} declines monotonically with increasing temperature toward zero at the high-temperature limit of three-phase coexistence. On average, x_{CH_4} is approximately 2 orders of magnitude smaller than x_{CO_2} in the

Table 6. Experimental VLE Data for [CH₄ (1) + CO₂ (2) + H₂O (3)] at Temperatures T and Pressures p , Where x_i Denotes the Mole Fraction of Component i and $u(x_i)$ Denotes the Standard Uncertainty of x_i ^a

phase II							phase III					
p/MPa	x_1	$u(x_1)$	x_2	$u(x_2)$	x_3	$u(x_3)$	x_1	$u(x_1)$	x_2	$u(x_2)$	x_3	$u(x_3)$
$T = 323.15 \text{ K}$												
1.911	0.4971	0.0035	0.4902	0.0035	0.01267	0.00028	0.000320	0.000012	0.003121	0.000077	0.996562	0.000081
6.035	0.4868	0.0036	0.5094	0.0036	0.00378	0.00011	0.000707	0.000016	0.00851	0.00019	0.99078	0.00021
10.011	0.4913	0.0036	0.5046	0.0036	0.00411	0.00011	0.000989	0.000022	0.01159	0.00026	0.98742	0.00028
14.021	0.5018	0.0037	0.4933	0.0038	0.00487	0.00012	0.001303	0.000031	0.01310	0.00029	0.98560	0.00032
17.986	0.4961	0.0039	0.4983	0.0039	0.00556	0.00014	0.001512	0.000033	0.01420	0.00032	0.98429	0.00034
$T = 373.15 \text{ K}$												
2.009	0.4727	0.0034	0.4615	0.0034	0.0658	0.0013	0.000235	0.000007	0.001831	0.000072	0.997942	0.000056
6.059	0.4864	0.0036	0.5033	0.0036	0.01028	0.00027	0.000681	0.000018	0.00529	0.00013	0.99403	0.00014
10.207	0.4915	0.0037	0.4978	0.0034	0.01068	0.00027	0.000941	0.000033	0.00840	0.00019	0.99066	0.00022
14.051	0.4814	0.0038	0.5073	0.0038	0.01125	0.00028	0.001107	0.000034	0.00981	0.00023	0.98908	0.00025
17.912	0.4835	0.0039	0.5044	0.0039	0.01207	0.00031	0.001315	0.000044	0.01181	0.00027	0.98688	0.00030
$T = 423.15 \text{ K}$												
2.102	0.3269	0.0034	0.3286	0.0034	0.3445	0.0048	0.000281	0.000008	0.001271	0.000089	0.998452	0.000064
4.201	0.3838	0.0034	0.3981	0.0034	0.2181	0.0036	0.000573	0.000014	0.002832	0.000099	0.996601	0.000084
5.956	0.4427	0.0034	0.4428	0.0034	0.1145	0.0021	0.001029	0.000023	0.00430	0.00013	0.99467	0.00013
9.982	0.4770	0.0036	0.4541	0.0035	0.0689	0.0014	0.001635	0.000035	0.00723	0.00018	0.99111	0.00019
14.061	0.4792	0.0037	0.4719	0.0037	0.0489	0.0010	0.001811	0.000033	0.00880	0.00021	0.98939	0.00023
18.001	0.4868	0.0039	0.4662	0.0039	0.04694	0.00099	0.001915	0.000042	0.01029	0.00025	0.98780	0.00027

^aThe phases are labeled as II and III for the CO₂-rich and water-rich phases respectively

Table 7. Experimental Quadruple Data for the Ternary System [CH₄ (1) + CO₂ (2) + H₂O (3)], Together with Predictions from Thermodynamic Models

T/K	p/MPa		
	expt	CSMHYD	SAFT-VR + vdWP
This Work			
283.90	4.925	5.26	4.43
284.37	5.352	5.64	4.82
285.15	6.17	6.34	5.54
285.60	6.81	6.78	6.00
286.19	7.62	7.42	6.64
Reference 43			
283.51	4.74	4.97	4.13
284.41	5.51	5.67	4.86
285.10	6.23	6.29	5.49
285.77	6.96	6.96	6.18
285.99	7.28	7.19	6.41
References 38 and 42			
283.32	4.53	4.84	3.99
283.86	4.93	5.23	4.40
284.39	5.50	5.65	4.84
285.03	6.22	6.22	5.43
285.76	7.25	6.95	6.16

aqueous phase under VLLE conditions. Parts c and d of Figure 5 show the mole fractions of CH₄ and H₂O in the CO₂-rich liquid phase under VLLE conditions. Qualitatively, the mole fraction of CH₄ in the CO₂-rich liquid phase follows trends with temperature and pressure similar to those observed in the aqueous phase. On the other hand, the water content of the CO₂-rich liquid phase shows the reverse of these trends; for example, it decreases with increasing pressure along each isotherm under VLLE conditions. The mole fractions of both methane and water in the CO₂-rich liquid phase are slightly overestimated by SAFT-VR, but the agreement with experiment is much better than in the aqueous phase. In parts e and f

of Figure 5, we plot the mole fractions of CO₂ and H₂O in the gas phase under VLLE conditions. The gas phase is also rich in CO₂, and the experimental CO₂ mole fractions are generally in good agreement with the SAFT-VR predictions. On the other hand, SAFT-VR strongly overestimates the mole fraction of H₂O in the gas phase. The amount of H₂O present in both the CO₂-rich liquid phase and the gas phase depends on the ratio of the mole fractions of CO₂ and CH₄ in that phase. We note that increasing the amount of CH₄ has the effect of decreasing the H₂O content of that phase. The same behavior was also observed by Song and Kobayashi³⁴ who concluded that the presence of the CH₄ lowered the H₂O content in the gas phase by 20% to 30% compared with the (CO₂ + H₂O) binary system at the same temperature and pressure.

5.1. Influence of H₂O on the Phase Behavior of (CH₄ + CO₂). The amount of H₂O present in the CO₂-rich liquid and gas phases is generally small and is observed to increase as temperature increases and to decrease as pressure increases, with more H₂O dissolved in the CO₂-rich liquid phase than in the gas phase. The presence of water in the nonaqueous phases has only a small effect on their equilibrium compositions. This is illustrated in Figure 6a,b, which are pressure–composition diagrams for the coexisting CO₂-rich liquid and gas phases. Here we compare the present experimental data in the VLLE region with the predictions of the SAFT-VR model and the available experimental data for the (CO₂ + CH₄) binary system.^{55,133} Figure 6a shows the isotherms at temperatures of 287.65 and 295.15 K, while Figure 6b shows the isotherms at $T = 292.65 \text{ K}$ and $T = 295.15 \text{ K}$. As the temperatures increases, the saturated region shifts toward higher CO₂ concentration and becomes smaller in size until it vanishes at the CO₂ critical temperature. Comparing the present data with the literature results for the binary system, it can be seen that the effect of the presence of H₂O is small in the low-pressure region. However, there is a noticeable difference at higher pressures, especially close to the critical point, despite the diminishing H₂O content in both CO₂-rich liquid phase and gas phase.

Table 8. Experimental LLE Data for $[\text{CH}_4(1) + \text{CO}_2(2) + \text{H}_2\text{O}(3)]$ at the Upper Critical End Point at Temperatures T and Pressures p , Where x_i Denotes the Mole Fraction of Component i and $u(x_i)$ Denotes Standard Uncertainty of x_i ^a

T/K	p/MPa	phase II						phase III					
		x_1	$u(x_1)$	x_2	$u(x_2)$	x_3	$u(x_3)$	x_1	$u(x_1)$	x_2	$u(x_2)$	x_3	$u(x_3)$
287.65	8.268	0.1979	0.0024	0.8021	0.0024	0.000069	0.000011	0.000852	0.000019	0.02559	0.00056	0.97356	0.00057
290.15	8.186	0.1716	0.0021	0.8283	0.0021	0.000090	0.000014	0.000704	0.000016	0.02493	0.00054	0.97437	0.00056
292.65	8.084	0.1403	0.0018	0.8596	0.0018	0.000116	0.000019	0.000569	0.000013	0.02470	0.00054	0.97473	0.00055
295.15	7.964	0.1109	0.0016	0.8889	0.0016	0.000148	0.000023	0.000428	0.000009	0.02448	0.00053	0.97509	0.00054
297.65	7.861	0.0826	0.0013	0.9173	0.0013	0.000183	0.000027	0.000314	0.000007	0.02433	0.00053	0.97536	0.00054
300.15	7.751	0.05421	0.00098	0.94558	0.00098	0.000215	0.000031	0.000193	0.000005	0.02417	0.00053	0.97564	0.00053
303.50	7.615	0.01621	0.00069	0.98354	0.00068	0.000256	0.000032	0.000056	0.000003	0.02410	0.00052	0.97585	0.00053

^aThe phases are labeled as II and III for the CO_2 -rich liquid and water-rich phases, respectively.

It can be observed that the SAFT-VR predictions are excellent for the composition of the gas phase but somewhat less accurate for the coexisting liquid, especially at higher pressures and in the critical region. Deviations between theory and experiment in the composition at given conditions of temperature and pressure are of course expected at high-density conditions and in the critical region because of the limitations of the rescaling of parameters, which only ensures adjustment to the experimental critical temperature and pressure (but not density or, in the case of mixtures, composition).

The UCEP data are shown in Figure 7 in comparison with the predictions of the SAFT-VR model of Míguez and co-workers.⁴⁴ The agreement between theory and experiment is, in this case, excellent. Also plotted in Figure 7 are experimental VL critical points^{133,134,138,139} for the $(\text{CO}_2 + \text{CH}_4)$ binary system and the predicted critical curve of that binary mixture obtained from the GERG-2008 model of Kunz and Wagner.¹³⁵ It can be seen that the effect on the critical locus of water as a third component is very small indeed, again showing that small amounts of water have only a minor influence on the miscibility of CO_2 and CH_4 .

In addition, comparing the influence of H_2O on the phase behavior of the present system with that on the phase behavior of the binaries (propane + CO_2),²⁸ (n -decane + CO_2),²⁷ and (n -heptane + CO_2)²⁹ leads to the conclusion that generally addition of H_2O has a small effect on the phase behavior of (n -alkane + CO_2) mixtures at temperatures well below the critical temperature of H_2O . In these systems, it can also be observed that the water content of the nonaqueous phases decreases as one moves toward lighter n -alkanes.

5.2. Influence of CH_4 on the Phase Behavior of $(\text{CO}_2 + \text{H}_2\text{O})$. The influence of CH_4 on the mutual solubility of $(\text{CO}_2 + \text{H}_2\text{O})$ is studied by comparison with the phase behavior of the $(\text{CO}_2 + \text{H}_2\text{O})$ binary system. For purposes of this comparison, we use the models developed by Duan et al.¹¹² and Spycher et al.¹¹³ for the $(\text{CO}_2 + \text{H}_2\text{O})$ mixture. In Figure 8, we compare the K values of CO_2 and H_2O determined from the present VLE data with those predicted by the models of Duan et al. and Spycher et al. at the same temperature and pressure. Under these conditions, the binary system is in the liquid–liquid region so the K values plotted are defined as $K_i = x_i^{\text{II}}/x_i^{\text{III}}$, where x_i^{II} denotes the mole fraction of component i in phase II (CO_2 -rich liquid) and x_i^{III} denotes the mole fraction of component i in phase III (H_2O -rich liquid). Figure 8a shows K_{CO_2} as a function of pressure, and the agreement with both models is found to be good. Thus, by this comparison, the solubility of CO_2 in the aqueous phase appears to be slightly enhanced by the addition of methane.

Figure 8b shows $K_{\text{H}_2\text{O}}$ as a function of pressure in comparison with the predictions of the models of Duan et al. and Spycher et al.^{112,113} However, Duan et al. adopted an approximate treatment for the composition of the CO_2 -rich liquid phase, and they did not validate their model against experimental data in that regard. This perhaps explains the large differences observed in the calculated K values from the two models, and, for this reason, we prefer the model of Spycher et al. Thus, by comparison with the $K_{\text{H}_2\text{O}}$ values predicted by the model of Spycher et al., the presence of H_2O in the CO_2 -rich liquid phase appears to be—in general—slightly reduced by the addition of methane.

The CO_2 solubility in the H_2O -rich phase for $(\text{CH}_4 + \text{CO}_2 + \text{H}_2\text{O})$ is compared in Figure 9 with the measurements reported

Table 9. SAFT-VR Parameters Used in This Work^a

compound	ref	m	$\sigma_{ii}/\text{\AA}$	$(\epsilon_{ii}/k_B)/\text{K}$	λ_i	$(\epsilon_{ii}^{\text{HB}}/k_B)/\text{K}$	$K^{\text{HB}}/\text{\AA}^3$
CH ₄	130	1.0	4.058	156.46	1.448		
CO ₂	131,132	2.0	3.136	168.84	1.515		
H ₂ O	129	1.0	3.470	276.24	1.718	1229.27	1.3379

^a m_i 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, and $\epsilon_{ii}^{\text{HB}}$ and K^{HB} are the depth and the bonding volume of the four-site hydrogen-bonding interaction. Parameters have been rescaled to match the experimental critical temperature and pressure.

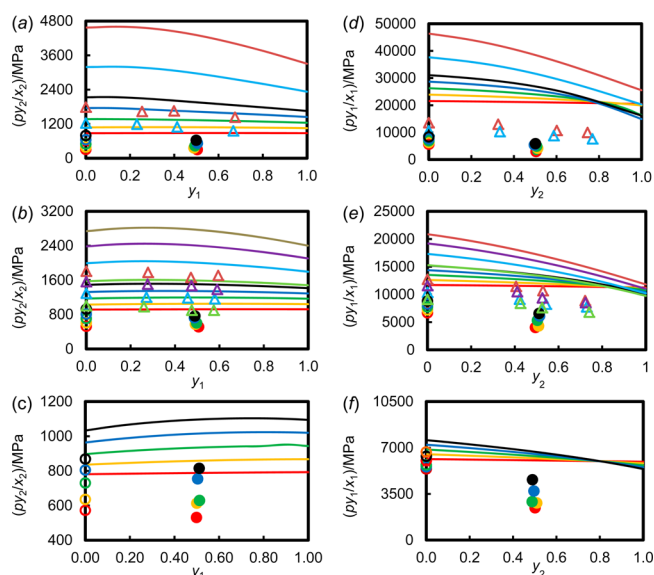


Figure 4. Apparent Henry's constant of CO₂ (a–c) and CH₄ (d–f) as a function of methane (y_1) or CO₂ (y_2) mole fraction in the gas phase under VLE conditions at $T = 323.15$ K (a and d), $T = 373.15$ K (b and e), and $T = 423.15$ K (c and f). Filled circles correspond to the data gathered in this work, open circles were obtained from the models of Duan et al.¹¹² and Duan and Mao,¹¹⁴ open triangles are data from the literature,³² and solid lines were calculated from the SAFT-VR model. Pressures are denoted by color as follows: 2 MPa (red); 6 MPa (orange); 10 MPa (green); 14 MPa (blue); 18 MPa (black); 20 MPa (light green); 30 MPa (light blue); 40 MPa (purple); 50 MPa (brown).

by Forte et al.^{27,28} for the (n -C₃H₈ + CO₂ + H₂O) and (n -C₁₀H₂₂ + CO₂ + H₂O) systems, by Brunner et al.¹⁴ for (n -C₁₆H₃₄ + CO₂ + H₂O), and by Al Ghafri²⁹ for (n -C₇H₁₆ + CO₂ + H₂O). In this figure, we plot the K value as $K_i = x_i^{\text{I}}/x_i^{\text{III}}$, where superscript I denotes the phase richest in alkane. It can be observed in Figure 9a that the K value of CO₂ decreases along an isotherm with increasing amount of alkane present in the alkane-rich phase. Thus, by this measure, the solubility of CO₂ in the aqueous phase appears to be enhanced by the addition of alkanes, and the latter can therefore be described as mild cosolvent for CO₂ in the aqueous phase. Figure 9b shows that the K value of CO₂ mostly increases with pressure along an isotherm. The present results are somewhat exceptional in this regard as they exhibit a slight decline with pressure along isotherms; however, the phase richest in alkane is in this case a gas phase whereas in the other systems is a liquid phase.

5.3. Influence of CO₂ on the Phase Behavior of (CH₄ + H₂O). The influence of CO₂ on the mutual solubility of (CH₄ + H₂O) is studied by comparison with the phase behavior of the (CH₄ + H₂O) binary system. For purposes of this comparison, we use the model developed by Duan and Mao¹¹⁴ for the (CH₄ + H₂O) mixture. In Figure 10, we compare the K values of CH₄

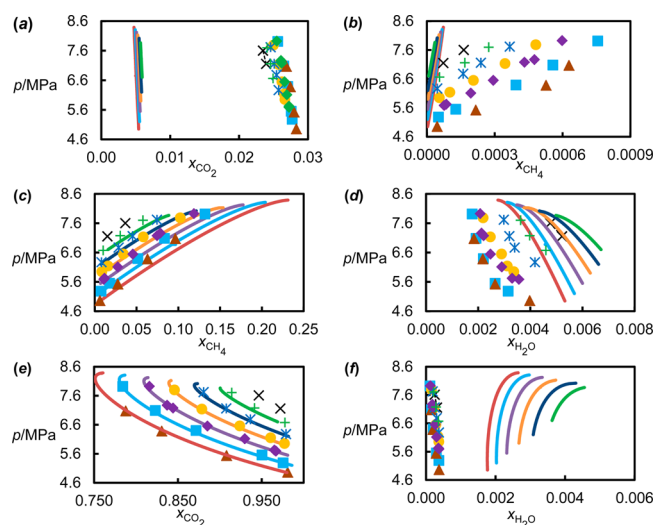


Figure 5. Isothermal pressure–composition (p, x) phase diagram for the (CH₄ + CO₂ + H₂O) system in the water-rich phase (a, b), CO₂-rich liquid phase (c, d), and gas phase (e, f) under VLE conditions. Symbols correspond to the data gathered in this work at the following temperatures: \blacktriangle , $T = 285.15$ K; \blacksquare , $T = 287.65$ K; \blacklozenge , $T = 290.15$ K; \bullet , $T = 292.65$ K; $*$, $T = 295.15$ K; $+$, $T = 297.65$ K; \times , $T = 300.15$ K. The continuous curves are SAFT-VR predictions of the three-phase equilibrium region at $T = 285.15$ K (brown), $T = 287.65$ K (light blue), $T = 290.15$ K (purple), $T = 292.65$ K (orange), $T = 295.15$ K (dark blue), and $T = 297.65$ K (green).

and H₂O determined from the present VLE data with those predicted by the model of Duan and Mao at the same temperature and pressure. Under these conditions, the binary system is in the vapor–liquid region so the K values plotted are defined as $K_i = x_i^{\text{I}}/x_i^{\text{III}}$. Figure 10a shows K_{CH_4} as a function of pressure, and we see that the experimental values in the ternary system under VLE conditions are about half those of the corresponding binary mixture at the same temperature and pressure. This large difference partially reflects the very different chemical environment of the CH₄ molecule in the nonaqueous phase. In the case of the ternary mixture under VLE conditions, we have a gas phase that is of the order of 90 mol % CO₂, whereas for the corresponding (CH₄ + H₂O) binary system the gas phase is more than 99 mol % CH₄. Calculations with the GERG-2008 model¹³⁵ show that the partial fugacity coefficient of CH₄ in the gas phase at the median VLE conditions of the present study is about one-third larger than in the gas phase of the (CH₄ + H₂O) binary system at the same temperature and pressure. However, this factor alone does not explain the large differences illustrated in Figure 10a, so we can deduce that the presence of CO₂ in the aqueous phase acts as a significant cosolvent for methane dissolution in the aqueous phase. The same observation was made with the other ternary mixtures of the type (n -alkane +

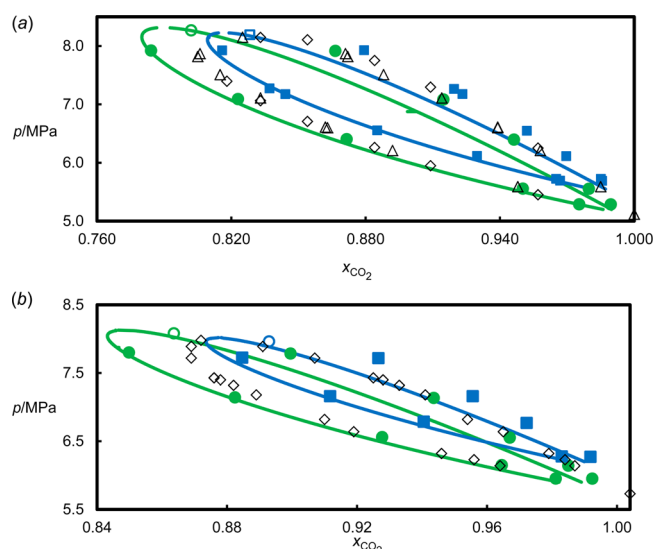


Figure 6. Isothermal pressure–composition phase diagram for the ($\text{CH}_4 + \text{CO}_2 + \text{H}_2\text{O}$) system at (a) $T = 287.65$ K (green) and $T = 290.15$ K (blue) and (b) $T = 292.65$ K (green) and $T = 295.15$ K (blue). Filled symbols correspond to the coexisting-phase data measured in this work, open colored symbols denote UCEP, and continuous curves correspond to SAFT-VR. Open black symbols correspond to published data for the binary system ($\text{CH}_4 + \text{CO}_2$): for a, (Δ) $T = 288.55$ K⁵⁵ and (\diamond) $T = 288.15$ K and for b, (\diamond) $T = 293.4$ K.¹³³

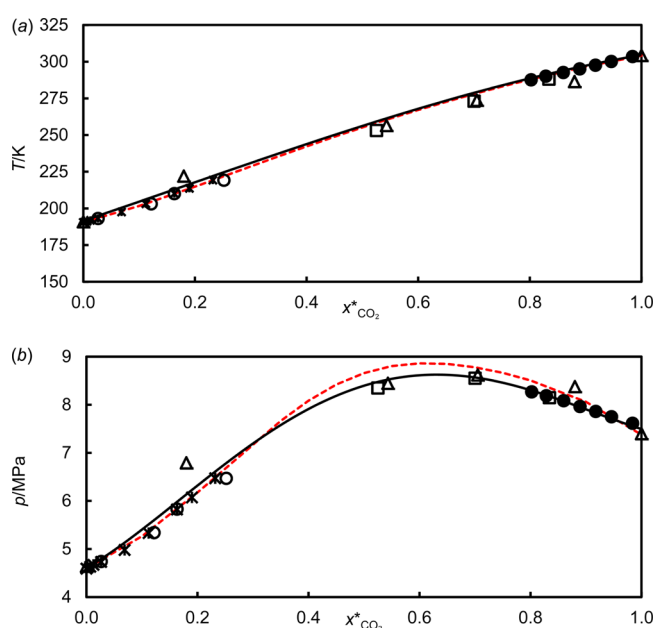


Figure 7. Plot showing the UCEP temperatures (a) and pressures (b) as a function of $x^* = x(\text{CO}_2)/[x(\text{CH}_4) + x(\text{CO}_2)]$: \bullet , this work for the ternary mixture ($\text{CH}_4 + \text{CO}_2 + \text{H}_2\text{O}$); \square , ref 133; Δ , ref 137; $*$, ref 138; \circ , ref 139. Critical data for the binary mixture ($\text{CH}_4 + \text{CO}_2$); solid and dotted lines represent the binary critical curve obtained from SAFT-VR⁴⁴ and GERG-2008,¹³⁵ respectively.

$\text{CO}_2 + \text{H}_2\text{O}$), and we conclude the presence of CO_2 generally increases the solubility of n -alkanes in water. In Figure 10b, $K_{\text{H}_2\text{O}}$ is plotted against the pressure and compared with values calculated from the model of Duan and Mao¹¹⁴ for the ($\text{CH}_4 + \text{H}_2\text{O}$) binary system. Since in both cases, the liquid phase contains more than 97 mol % water, it seems likely that the

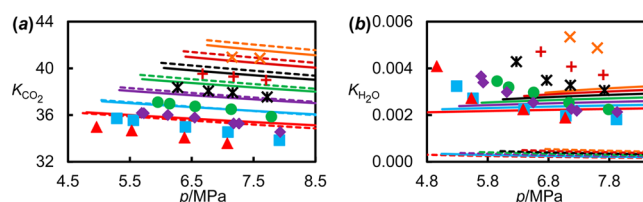


Figure 8. K factor of either CO_2 (a) or H_2O (b) as a function of pressure. Symbols correspond to the data of this work under VLE conditions at the following temperatures: \blacktriangle , $T = 285.15$ K; \blacksquare , $T = 287.65$ K; \blacklozenge , $T = 290.15$ K; \bullet , $T = 292.65$ K; $*$, $T = 295.15$ K; $+$, $T = 297.65$ K; \times , $T = 300.15$ K. Dotted and continuous curves represent binary data for the system ($\text{CO}_2 + \text{H}_2\text{O}$) obtained from the models of Duan et al.¹¹² and Spycher et al.,¹¹³ respectively, at the corresponding temperatures (indicated by color).

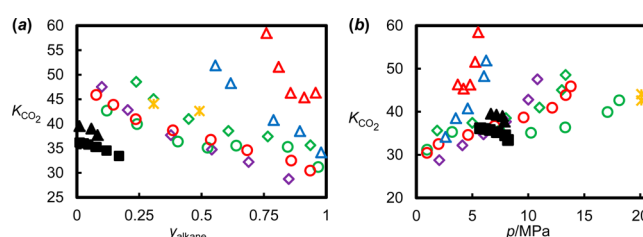


Figure 9. K factor of CO_2 in the hydrocarbon-rich phase under VLE conditions as a function of (a) alkane mole fraction and (b) pressure. Filled symbols represent VLE data gathered during this work at the following temperatures: \blacksquare , $T = 290.15$ K; \blacktriangle , $T = 297.65$ K. Open symbols represent literature data for other (n -alkane + $\text{CO}_2 + \text{H}_2\text{O}$) systems at temperatures of 338 K (blue), 343 K (purple), 353 K (red), 413 K (green), and 473 K (orange): Δ , propane;²⁸ \diamond , heptane;²⁹ \circ , decane;²⁷ $*$, hexadecane¹⁴.

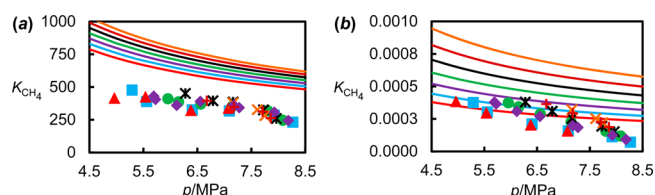


Figure 10. K factor of either CH_4 (a) or H_2O (b) as a function of pressure under VLE conditions. Symbols correspond to the data of this work at the following temperatures: \blacktriangle , $T = 285.15$ K; \blacksquare , $T = 287.65$ K; \blacklozenge , $T = 290.15$ K; \bullet , $T = 292.65$ K; $*$, $T = 295.15$ K; $+$, $T = 297.65$ K; \times , $T = 300.15$ K. Continuous curves show the model of Duan and Mao¹¹⁴ for the binary system ($\text{CH}_4 + \text{H}_2\text{O}$) at the corresponding temperatures (indicated by color).

differences observed in Figure 10b are associated mainly with molecular interactions in the gas phase where again we have very different chemical environments in the gas phases of the binary and ternary systems.

5.4. Four-Phase Line. The experimental data for the quadruple curve, including the vapor-phase composition, are given in Table 7, together with the experimental results obtained by Bi et al.⁴³ and Seo et al.^{38,42} The quadruple curve data obtained in the present study agree well with the data of Bi et al.⁴³ and Seo et al.^{38,42} At the lower end, this curve intersects the three-phase $L_w + L_{\text{CO}_2} + V$ curve of the ($\text{CO}_2 + \text{H}_2\text{O}$) binary system at its quadruple point $H + L_w + L_{\text{CO}_2} + V$ while, at its upper end, it meets the UCEP locus $L_w + L_{\text{CO}_2} = V$. The vapor compositions on the four-phase line were obtained by extrapolation of the experimental data measured in the three-

phase region. These data were first interpolated on each isotherm to the experimental four-phase pressures and then extrapolated with respect to temperature by means of fitting quadratic polynomials for each isobar. It can be clearly seen that there is good agreement between our values and literature data both in terms of equilibrium conditions and vapor compositions.

Table 7 also shows the predictions of the CSMHYD⁴⁸ and SAFT-VR-vdWP⁴⁵ models. In both of these models, structure I hydrates are predicted with the larger cavities filled mainly with CO₂. The CSMHYD model actually predicts a range of pressures at given temperature over which four phases are predicted; the values given in Table 7 relate to the lowest predicted pressure. The agreement with experiment is then quite good. The SAFT-VR-vdWP predictions are (0.5 to 1.0) MPa lower than experiment.

6. CONCLUSION

In this work, we present the first comprehensive experimental investigation of phase equilibria of the (CH₄ + CO₂ + H₂O) system in the region where three fluid phases coexist. The three-phase VLLE data were gathered on eight isotherms at temperatures from (285.15 to 303.5) K and at pressures from roughly the vapor pressure of pure CO₂ up to either the upper critical end point (UCEP) or up to the hydrate formation locus. The quadruple curve along which hydrates coexist with the three fluid phases was also measured, and compositions of the coexisting vapor and liquid phases have been obtained along three isotherms at temperatures from (323.15 to 423.15) K and pressures up to 20 MPa.

The VLLE and VLE data have been compared with the predictions of the SAFT-VR making use of the model parameters reported previously by Míguez and co-workers.⁴⁴ Although this model does not provide a very accurate quantitative description of the phase behavior in either the VLE or the VLLE regions, it does predict the global phase diagram rather well and it must be recognized that the model was not tuned to any mixture data other than the VL critical curve of the (CO₂ + H₂O) binary subsystem. No doubt, much better quantitative agreement could be obtained by means of optimizing the binary parameters. The present experimental data should provide a strong basis for tuning and validating SAFT models in the future.

A detailed analysis of the ternary mixtures was carried out based on comparison with available data and models for the constituent binary subsystems and other ternary mixtures of the type (alkane + CO₂ + H₂O). It was concluded that the presence of CO₂ significantly increases the *n*-alkane solubility in the H₂O-rich phase under both VLE and VLLE conditions as compared to the corresponding (*n*-alkane + H₂O) binary system. In addition, the presence of *n*-alkane increases the CO₂ solubility in the H₂O-rich phase compared to the binary mixture of (CO₂ + H₂O) for both VLE and VLLE measurements. It was also concluded that the H₂O content in the CO₂-rich phase decreases in the presence of *n*-alkane as compared to the binary system of (CO₂ + H₂O). It was found that the effect of H₂O on the phase behavior (*n*-alkane + CO₂) was quite small, reflecting the low mole fraction of water in the nonaqueous phases. Finally, it was observed that predictions of the CSMHYD and SAFT-VR-vdWP hydrate models agree reasonably well with the experimental hydrate locus data. However, these models predict only three phases in equilibrium which does not agree with the experimental observations.

Clearly the models require further refinement to be able to describe the full range of phase behavior observed for the (CH₄ + CO₂ + H₂O) system.

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Notes

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