

Phase Equilibria of (Methylbenzene + Carbon Dioxide + Methane) at Elevated Pressure: Experiment and Modelling

Saif ZS. Al Ghafri^{1,2} and J. P. Martin Trusler^{1*}

(1) Qatar Carbonates and Carbon Storage Research Centre, Department of Chemical Engineering, Imperial College
London, South Kensington Campus, London SW7 2AZ UK.

(2) Fluid Science and Resources Division, School of Mechanical & Chemical Engineering, University of Western
Australia, 35 Stirling Highway, Crawley WA 6009, Australia

* Corresponding author e-mail: m.trusler@imperial.ac.uk.

Abstract

Phase equilibria in the ternary mixture ($C_7H_8 + CO_2 + CH_4$) were measured at temperatures of (323.15, 373.15 and 423.15) K and pressures up to 31 MPa by means of a synthetic method in which both bubble- and dew-points were measured. The results were compared with calculations based on the SAFT- γ Mie and the Predictive Peng-Robinson (PPR-78) equations of state, both of which use group-contribution approaches for parameters estimations. At low pressures, good agreement was observed with both models but this deteriorated with increasing pressure and, in the critical region, both models over-predict the pressure. The deviations are more pronounced at the highest methane content in the ternary system and at the lowest temperature. SAFT- γ Mie is shown to generally give better agreement with experiment than PPR-78. The current work suggests that the interaction parameters between CH_4 and one or more of the functional groups in methylbenzene require further refinement.

Keywords: Phase equilibrium; modelling; carbon dioxide; SAFT; PPR78; methane, methylbenzene

1. Introduction

Carbon capture and storage (CCS) is recognized as an effective medium-term technology to reduce CO₂ emissions by capturing and storing anthropogenic CO₂ associated with the combustion of fossil fuels in power generation and some other industrial processes. To offset some of the additional costs associated with CCS, the captured CO₂ may be used in enhanced oil recovery (CO₂-EOR) operations. Knowledge of the phase equilibria of CO₂ with the hydrocarbons is fundamental in the design and operation of both CCS and CO₂-EOR processes [1-5]. While equilibrium data for binary (CO₂ + hydrocarbon) mixtures are reasonably plentiful, phase equilibria data of multicomponent (CO₂ + hydrocarbon) mixtures are scarce. The extensive reviews published by Dohrn, Peper, and Fonseca [6, 7] on the availability of high-pressure high-temperature (HPHT) phase equilibrium data clearly concluded that equilibrium data for ternary, or higher, (CO₂ + hydrocarbon) mixtures are very limited, especially for systems containing hydrocarbons other than alkanes. To our knowledge, there are no phase equilibria data reported in the literature for the ternary mixture (C₇H₈ + CO₂ + CH₄) which is studied in this work. However, the constitute binaries systems (C₇H₈ + CO₂) [8-19], (C₇H₈ + CH₄) [20-27] and (CO₂ + CH₄) [28-35] have been reasonably well studied in the literature.

A wide variety of approaches have been implemented for the prediction of phase behavior and other thermophysical properties of (CO₂ + hydrocarbon) mixtures, ranging from empirical and semi-empirical correlative models, such as cubic equations of state (EoS) with adjustable binary parameters, through predictive cubic equations of state such as the Predictive Peng-Robinson (PPR78) EoS [36] and similar approaches [37, 38], to molecular-based models such as the Statistical Associating Fluid Theory (SAFT) [39, 40]. Cubic equations of state are widely applied in the oil and gas industries and may provide accurate descriptions of vapor-liquid equilibria; however, the need to regress binary interaction parameters against experimental data means that their applicability is limited by the availability and quality of such data. Recently, Jaubert and coworkers developed a group contribution method allowing the estimation of the temperature-dependent binary interaction parameters $k_{ij}(T)$ in the PR EoS, thereby creating a predictive model which they designated PPR78

[36-38]. On the other hand, the SAFT approach may give better prediction of phase equilibria for complex and associating mixtures, and also other properties such as density, without such extensive fitting to experimental data. This is especially true of group-contribution SAFT approaches, wherein the total intermolecular potential energy is expressed as a sum of functional-group interactions and the parameters characterizing the interactions of these groups are considered transferrable between systems. This makes the method predictive for many systems. In this work, we implement SAFT with the generalized Mie potential and a group contribution approach, designated SAFT- γ Mie [41].

The PPR-78 and SAFT- γ Mie group-contribution methods have not yet been extensively tested against multicomponent mixture data at HPHT conditions. Therefore, one of the objectives of the present study was to facilitate such comparisons for a multicomponent (CO_2 + hydrocarbon) system, specifically the (C_7H_8 + CO_2 + CH_4) system, under such conditions. Continuing from our previous studies of (CO_2 + hydrocarbon) mixtures [42-45], new data for phase equilibria of the (C_7H_8 + CO_2 + CH_4) system have been measured covering a wide range of conditions and compositions at different fixed feed-gas mole ratios between CO_2 and CH_4 in the ternary system. The data gathered, and the comparison made, enable one to evaluate and demonstrate the predictive capabilities of these methods, as well as their potential for improvement.

2. Experimental

2.1 Apparatus

The apparatus used has been described in detail previously [43]; a summary is given here for completeness. **Figure 1** illustrates the configuration of the variable-volume static-synthetic apparatus, which permits visual observation of the co-existing phases inside the equilibrium cell under conditions of known overall composition. The apparatus supported working pressures and temperatures up to 40 MPa and 423.15 K, respectively. The equilibrium cell was fitted with a movable piston at one end and was closed by a sapphire window at the other end, allowing for visual

observation of the entire interior volume. Mixing of the injected fluids was accomplished by means of an internal PTFE-coated magnetic stirrer bar of ellipsoidal shape coupled to a rotating external magnet. Two high-pressure syringe pumps were used for quantitative injection of the components of interest into the equilibrium cell. An insulated aluminum heating jacket attached to the body of the cell was used to control the temperature, which was measured using a calibrated 4-wire platinum resistance thermometer (Sensing Device Ltd, model SD01168). A pressure transducer (DJ Instruments, model DF2) was used upstream of the equilibrium cell to measure the system pressure. A CCD camera was used to take still images and video of the mixture as an aid to visual observations of the phase transitions. The apparatus was previously validated by comparison with published isothermal vapor-liquid equilibrium data for the binary system ($\text{CO}_2 + n\text{-C}_7\text{H}_{16}$) [43].

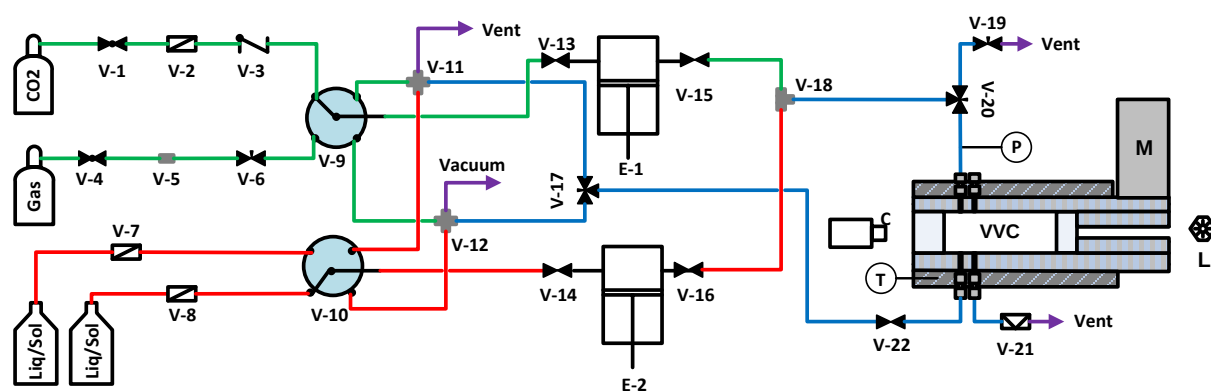


Figure 1. Schematic diagram of the variable volume cell apparatus: V-1, on/off valve; V-2, filter; V-3, check valve; V-4, on/off valve; V-5, reducer; V-6 valve; V-7 and V-8, filter; V-9 and V-10, 5 way electrically actuated valves; V-11 and V-12, union crosses; V13 to V16, check valves; V17, three way electrically actuated valve; V-18, tee; V-19, two way manual valve; V-20, three way manual valve; V-21 safety head; V-22, two way air operated normally closed valve; VVC, variable volume cell; E-1 and E-2, high pressure syringe pumps; M, motor and gear box; L light source; P and T indicates pressure transducer and temperature sensors respectively. Green colour indicates gas paths, red colour indicates liquid paths, and blue colour indicates mixture paths

2.2 Calibration and Uncertainty

The calibration and associated uncertainties have been described previously in detail [42, 43]. Here a summary is given relevant to the system studied. The overall standard uncertainty of the cell temperature was estimated to be 0.5 K; this takes into account the none-uniformity that exists at high

temperatures. The pressure transducer used to measure the sample pressure was calibrated against a hydraulic pressure balance and the standard uncertainty of the pressure was estimated to be 35 kPa.

The uncertainties of the synthetic mole fractions are detailed in Appendix 1 and are mainly affected by the uncertainty of the volume expelled from the syringe pumps, the fluid density under the pump conditions, and the mole fraction z of CO_2 in the feed-gas mixture. One syringe pump was always used to inject the liquid while a second pump was used to inject the $(\text{CO}_2 + \text{CH}_4)$ gas mixtures. However, in some cases, the gas was introduced directly into the cell at the beginning of an experiment and the amount calculated based on the filling temperature and pressure and the cell volume; consequently, in those cases, cell volume, temperature and filling pressure also affect the composition uncertainties. For the $(\text{CO}_2 + \text{CH}_4)$ gas mixtures, the density was obtained from the GERG-2008 equation of state of Kunz and Wagner [46], with an estimated relative uncertainty of 0.1% for the conditions studied in this work. For C_7H_8 , the density was obtained from the equation of state of Lemmon and Span [47] with an estimated relative uncertainty of 0.05 % at the pump conditions. In the case of the calibrated volumes, the standard relative uncertainty of the pump volumes was found to be 0.1% for both syringe pumps while the overall relative standard uncertainty in the cell volume was found to be 0.2 %. Detailed analysis of the pumps and cell volume uncertainties can be found in our previous publications [42, 43]. All gas mixtures $(\text{CO}_2 + \text{CH}_4)$ provided has a certified relative uncertainty $u_r(z)$ of 0.5% of the smaller mole fraction. Taking all of this into account, it was found that the overall standard uncertainties in the synthetic mole fraction lie within around 1% of the mole fraction for each component and over the entire measurements range. The standard uncertainties are tabulated in Table 4.

The uncertainties of the bubble- and dew-pressures were mainly determined by the subjective uncertainty in visually observing the bubble- or dew-point condition and the uncertainty of the pressure measurement itself. Except in the critical region, bubble points were easily observed visually during isothermal measurements with variation of the cell volume. Dew points were generally more

difficult to observe by this method and were only measured at high pressures. The camera was mostly focused on the interior of the cell and dew points were associated with the appearance of droplets on the interior surfaces of the cell rather than on the window. Close to the critical point, it became more difficult to detect both bubble- and dew-point conditions. Considering these factors, the uncertainty in temperature and the uncertainty of the pressure, the standard uncertainty of the bubble pressure p_b was estimated to be 0.2 MPa for p_b at all temperatures, while the standard uncertainties of the critical pressure p_c and dew pressures p_d were estimated to be 0.3 MPa.

2.3 Materials

The materials used are detailed in **Table 1**. The compositions of the gas mixtures used are quantified by the mole fraction z of CO_2 ; below we also make use of the mole ratios $Y = z/(1 - z)$ of CO_2 to CH_4 .

Table 1. Description of chemical samples ^a

Chemical name	Source	z	$u(z)$	Purity as supplied	Additional purification
Carbon dioxide	BOC			$x \geq 0.99995$	None
Methane	BOC			$x \geq 0.9995$	None
$(1 - z) \text{CH}_4 + z \text{CO}_2$	BOC	0.2500	0.0013	$x \geq 0.9995$	None
	BOC	0.5000	0.0025	$x \geq 0.9995$	None
	BOC	0.7500	0.0013	$x \geq 0.9995$	None
Methylbenzene	Sigma Aldrich			$w \geq 0.998$	None

^a x = mole fraction purity, w = mass fraction purity, z = mole fraction of CO_2 .

2.4 Experimental Procedure

The experimental procedure was similar to that described previously [42, 43]. The $(\text{CO}_2 + \text{CH}_4)$ gas mixture was loaded into one of the syringe pumps, while the other was loaded with pure liquid

methylbenzene. The temperatures of both syringe pumps were controlled at 283.15 K. Starting from a clean and evacuated system, the usual procedure was to inject methylbenzene first followed by the gas mixture. The mass of fluid introduced in each injection step was obtained from the syringe pump displacement and knowledge of the density at the pump temperature and pressure. The overall composition of the system was calculated at every stage of the experiment from the cumulative amounts of methylbenzene and the gas mixture introduced from the pumps, allowing for the dead volume that remains in the connecting tubes and fittings.

Following the injection of the components, V-20 was closed (see **Figure 1**) and the pressure inside the cell was adjusted by moving the piston until one homogenous phase was obtained at a fixed temperature. The system was then allowed to equilibrate under continued stirring for at least one hour. The pressure was then decreased in small decrements, each followed by a further equilibration period, while simultaneously recording temperature, pressure and volume, and observing the state of the system. This process continued until the appearance of a second phase. Usually, after observing a bubble or dew point, an additional quantity of the gas mixture was injected, and a new measurement was initiated. A few measurements were repeated to check the reproducibility, which was found to be within 0.1 MPa. Visual observation using the CCD camera was the primary means of detecting phase changes. In some cases, to access low mole fractions of methylbenzene and/or high pressures, the equilibrium cell was initially filled with the gas mixture followed by injection of methylbenzene.

3. Theory

The predictive cubic-EoS model considered in this work, the PPR78 EoS, uses the group-contribution approach of Jaubert and coworkers [36-38, 48, 49]. In this approach, the binary interaction parameter k_{ij} is given by

$$k_{ij}(T) = \left[\left\{ -\frac{1}{2} \sum_{k=1}^{N_g} \sum_{l=1}^{N_g} (\alpha_{ik} - \alpha_{jk})(\alpha_{il} - \alpha_{jl}) A_{kl} (T_0 / T)^{(B_{kl} / A_{kl} - 1)} \right\} - \left\{ \frac{\sqrt{a_i(T)}}{b_i} - \frac{\sqrt{a_j(T)}}{b_j} \right\}^2 \right] \times \left[\frac{2\sqrt{a_i(T)a_j(T)}}{b_i b_j} \right]^{-1}. \quad (1)$$

Here, N_g is the number of distinct functional groups present in the molecule, α_{ik} is the occurrence of group k in component i divided by the total number of groups present in that component, and A_{kl} and B_{kl} are group parameters. Additionally, $a_i(T)$ is the attractive parameter and b_i is the repulsive parameter in the Peng-Robinson equation of state for component i . With this model, the properties of arbitrary mixtures containing any number of components may be computed knowing only the critical temperature, critical pressure and acentric factor of each component. Pure component properties were obtained from the NIST Thermodata Engine (TDE) software [50, 51]. In this approach, carbon dioxide and methane are each modelled as distinct molecular groups, while methylbenzene comprises three functional groups: aCH, aC and CH₃. No further optimization was considered in the present work for this method.

The SAFT- γ Mie EoS is described in detail by Papaioannou et al. [41] and here we summarize only the interaction model and the nature and source of the parameters used. In SAFT- γ Mie, complex molecules are represented by several fused segments representing the functional groups from which the molecule may be assembled. Each distinct functional group is characterized by one or more identical segments and the interaction potential energy u_{kl} between non-associating segments k and l present in two different molecules is given by the Mie potential:

$$u_{kl}(r_{kl}) = \left(\frac{\lambda_{r,kl} \varepsilon_{kl}}{\lambda_{r,kl} - \lambda_{a,kl}} \right) \left(\frac{\lambda_{r,kl}}{\lambda_{a,kl}} \right)^{\lambda_{a,kl} / (\lambda_{r,kl} - \lambda_{a,kl})} \left[\left(\frac{\sigma_{kl}}{r_{kl}} \right)^{\lambda_{r,kl}} - \left(\frac{\sigma_{kl}}{r_{kl}} \right)^{\lambda_{a,kl}} \right]. \quad (2)$$

Here, r_{kl} is the center-to-center distance between the groups, $\lambda_{r,kl}$ is the repulsive exponent, $\lambda_{a,kl}$ is the attractive exponent, ε_{kl} is the energy-scaling parameter and σ_{kl} is the length-scaling parameter. The parameters that characterize the interactions of identical functional groups are therefore as follows:

ε_{kk} , σ_{kk} , $\lambda_{r,kk}$, $\lambda_{a,kk}$ and the number ν_k of segments that comprise the group. An additional parameter,

the shape factor S_k , is used to characterize the extent to which the segment contributes to the molecular properties of the system [41]. The parameters ϵ_{kl} , σ_{kl} , $\lambda_{r,kl}$ and $\lambda_{a,kl}$ in the unlike interaction energy may be either estimated from combining rules [41] or regressed against experimental data. Typically, combining rules alone are not sufficiently accurate and one or more parameters are regressed against experimental data while the others are obtained from combining rules.

In SAFT- γ Mie, carbon dioxide and methane are each modelled as distinct molecular groups, while methylbenzene is modelled using two aromatic functional groups: aCH and aCCH₃. In the present case, the interaction parameters were determined from experimental data for systems comprising the constituent groups, but not necessarily the constituent compounds or sub-systems of the (methylbenzene + carbon dioxide + methane) mixture itself. Thus, when applied to the current system, the method is regarded as predictive. The source and values of the like parameters used for the individual groups (CO₂, CH₄, aCH and aCCH₃) are given in **Table 2**; these were all obtained in previous work [52, 53]. The cross parameters σ_{kl} and $\lambda_{a,kl}$ were obtained from combining rules, while the source and values of the cross parameters ϵ_{kl} and $\lambda_{r,kl}$ are given in **Table 3**. The aCH-CO₂ and aCCH₃-CO₂ cross interaction parameters ϵ_{12} and $\lambda_{r,12}$ were fitted in our previous work [42] while the CO₂-CH₄ and aCH-aCCH₃ cross interaction parameters ϵ_{12} and $\lambda_{r,12}$ were previously fitted [53].

Table 2. Like group parameters used

	S_k	$(\epsilon/k_B) / K$	$\sigma \cdot 10^{10} / m$	λ_r	λ_a	Reference
CH ₄	1.0000	152.58	3.7370	12.504	6.00	[53]
aCH	0.3218	371.53	4.058	14.756	6.00	[52]
aCCH ₃	0.3166	651.41	5.487	23.627	6.00	[53]
CO ₂	0.8468	207.89	3.050	26.408	5.06	[53]

Table 3. Unlike cross interaction energies ϵ and repulsive exponent λ_r .^a

Group 1	Group 2	$(\epsilon / k_B) / K$	λ_r	Reference
CO ₂	CH ₄	144.72	11.950	[53]
aCH	aCCH ₃	471.23	18.572	[53]
aCH	CO ₂	224.33	14.155	[42]
aCCH ₃	CO ₂	309.36	24.974	[42]
aCH	CH ₄	189.40	8.994	This work
aCCH ₃	CH ₄	202.17	8.403	This work

^a indicates parameters obtained through combining rules.

To adequately describe binary vapor-liquid equilibrium (VLE) data, it was found necessary to fit the unlike terms (ϵ_{12} and $\lambda_{r,12}$) for the aCH-CH₄ and aCCH₃-CH₄ interactions. The aCH-CH₄ cross interaction parameters ϵ_{12} and $\lambda_{r,12}$ were determined by fitting experimental VLE data for (C₆H₆ + CH₄) at temperatures of 293 K [54], 313 K [54] and 333 K [54]. The aCCH₃-CH₄ cross-interaction parameters ϵ_{12} and $\lambda_{r,12}$ were determined by fitting experimental VLE data for (C₇H₈ + CH₄) at temperatures of 278 K [21], 313 K [24] and 422 K [23]. The cross-interaction parameters were obtained by minimizing the following objective function:

$$\chi^2 = N^{-1} \sum_{i=1}^N \left[\frac{p_{i,\text{exp}}(T_i, x_i) - p_{i,\text{calc}}(T_i, x_i)}{p_{i,\text{exp}}(T_i, x_i)} \right]^2 + N^{-1} \sum_{i=1}^N [y_{i,\text{exp}}(T_i, x_i) - y_{i,\text{calc}}(T_i, x_i)]^2. \quad (3)$$

Here, T_i and x_i denote the i^{th} experimental temperature and liquid-phase mole fraction at which the experimental bubble pressure and vapor-phase mole fraction were $p_{i,\text{exp}}$ and $y_{i,\text{exp}}$ and the corresponding calculated values are $p_{i,\text{calc}}$ and $y_{i,\text{calc}}$, respectively, and N is the total number of VLE data points. The minimization of χ^2 was achieved using a gradient-based successive quadratic programming algorithm with multiple starting points as detailed by Papaioannou et al. [41].

The quality and consistency of the available experimental binary data used in the parameter estimation was also assessed by the vapor-phase enhancement factor $f = y \cdot p / p^{\text{sat}}$ for the aromatic component, for which y is the vapor-phase mole fraction and p^{sat} is the vapor pressure at the temperature in question [55]. The definition of this quantity is such that $f \rightarrow 1$ as p reduces towards p^{sat} ; data which do not smoothly approach this limit can be excluded as being of low quality. The quality of the available data was assessed by plotting f for several isotherms in the temperature range of interest, as illustrated in **Figure 2** for the methane-benzene system. In the present case, all the data were considered acceptable by this criterion.

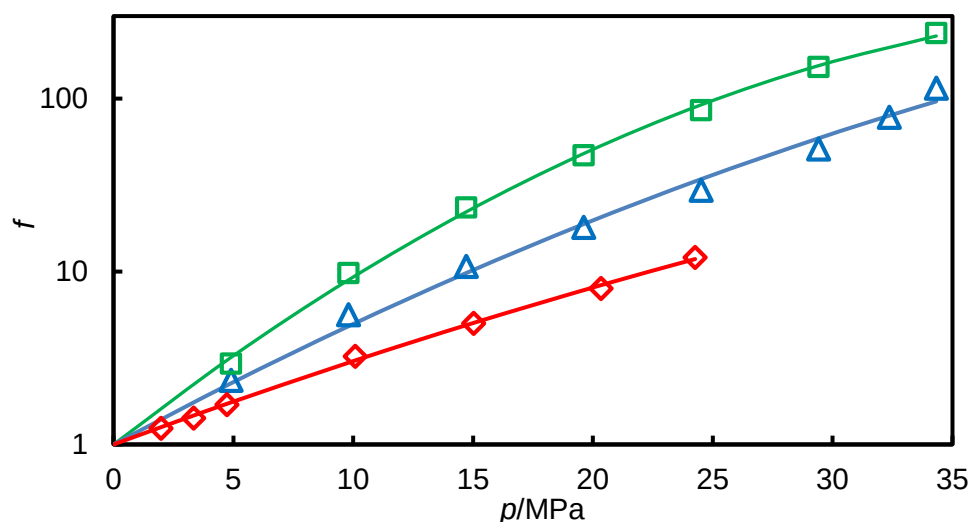


Figure 2. Enhancement factor analysis for literature data measured for the benzene + CH₄, where f is the enhancement factor and p is the system pressure at: $\square$, $T = 293$ K [54]; $\triangle$, $T = 333$ K [54]; $\diamond$, $T = 421$ K [23]. Lines represent quadratic polynomials fitted to $\ln f$ and constrained such that $\ln f = 0$ at $p = 0$.

4. Results and Discussion

In **Figures 3**, the SAFT- γ Mie and PPR78 descriptions of the vapor-liquid equilibria of (C₆H₆ + CH₄) are compared at temperatures of 293 K [54], 333 K [54], 421 K [23], 462 K [23], and 501 K [23]. Good agreement between experiment and the predictions of both models is observed only at pressures well below the critical. At high pressures, close to the critical region, both models over-predict the

pressure for given compositions and this is more pronounced at lower temperatures. SAFT- γ Mie generally shows better agreement. In **Figures 4**, the SAFT- γ Mie and PPR78 descriptions of the vapor-liquid equilibria of ($C_7H_8 + CH_4$) are compared at temperatures of 278 K [21], 313 K [24], 422 K [23], 462 K [23], and 501 K [23]. As with the ($C_6H_6 + CH_4$) system, good agreement between experiment and the model predictions is observed in the low-pressure region, while both models over-predict the critical pressure. Again, SAFT- γ Mie performs noticeably better than PPR-78.

A poor description of the near-critical region is a known difficulty of classical EoS models. However, in our previous work [42], the models considered here were able to describe the vapor-liquid equilibria of the ($C_6H_6 + CO_2$) and ($C_7H_8 + CO_2$) systems reasonably accurately across the entire temperature and pressure ranges considered, including the critical region. Additionally, SAFT- γ Mie and PPR78 were found to describe the vapor-liquid equilibria of ($CO_2 + CH_4$) adequately over the entire pressure and temperature ranges considered [53]. This suggests that the binary interaction parameter between CH_4 and C_7H_8 in PPR78 and the cross-interaction parameters between the CH_4 group and the aCH and/or aCCH₃ groups in SAFT- γ Mie may requires further refinement.

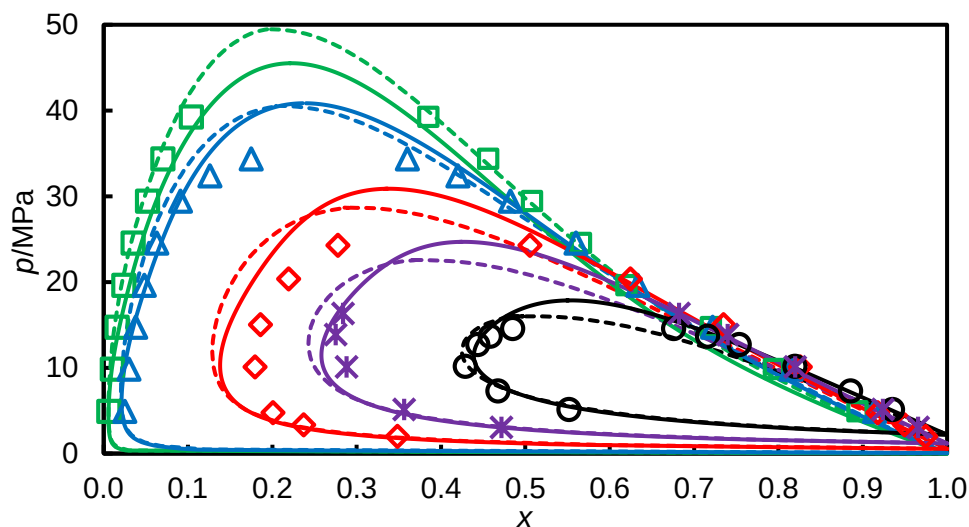


Figure 3. Isothermal p - x diagram for benzene + CH_4 , where p is pressure and x is the mole fraction of benzene. Symbols represent the experimental literature data while the continuous and dotted curves represents the description with the SAFT- γ Mie approach and PPR78 approach respectively at: $\square$, $T = 293$ K [54]; $\triangle$, $T = 333$ K [54]; $\diamond$, $T = 421$ K [23]; $*$, $T = 462$ K [23]; $\circ$, $T = 501$ K [23].

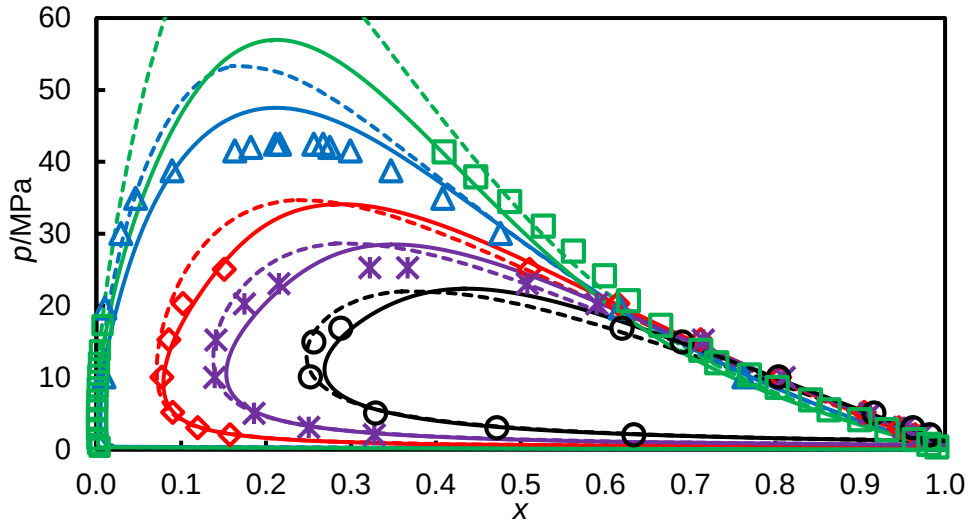


Figure 4. Isothermal p - x diagram for methylbenzene + CH_4 , where p is pressure and x is the mole fraction of methylbenzene. Symbols represent the experimental literature data while the continuous and dotted curves represents the description with the SAFT- γ Mie approach and PPR78 approach respectively at: $\square$, $T = 278$ K [21]; $\triangle$, $T = 313$ K [24]; $\diamond$, $T = 422$ K [23]; $*$, $T = 462$ K [23]; $\circ$, $T = 501$ K [23].

The experimental bubble and dew pressures obtained for the ternary mixture are given in **Table 4** for all isotherms measured over the whole composition range of methylbenzene at different mole ratios Y of carbon dioxide to methane in the feed gas: $Y = (1/3, 1 \text{ or } 3)$. The experimental results are also plotted as pressure-composition (p, x_1) diagrams in **Figures 5, 6 and 7**, where x_1 is the mole fraction of methylbenzene, for all isotherms at each of the three mole ratios Y of CO_2 to CH_4 in the feed gas.

Table 4. Experimentally VLE data and associated uncertainties for C_7H_8 (1) + CO_2 (2) + CH_4 (3) at temperatures T , pressures p , for different mole ratios Y of carbon dioxide to methane, where x_i denotes the mole fraction of component i in the mixture at a bubble or dew point. ^a

p/MPa	x_1	$u(x_1)$	x_2	$u(x_2)$	x_3	$u(x_3)$	Status	Y
$T = 323.15$ K								
8.95	0.0158	0.0001	0.7381	0.0013	0.246	0.0013	dew	3
10.95	0.0265	0.0000	0.7301	0.0013	0.2434	0.0013	dew	3
13.34	0.0952	0.0002	0.6786	0.0012	0.2262	0.0012	dew	3
13.57	0.1491	0.0003	0.6382	0.0011	0.2127	0.0011	bubble	3
13.33	0.2477	0.0005	0.5642	0.0010	0.1881	0.0010	bubble	3
12.56	0.3482	0.0006	0.4889	0.0009	0.163	0.0009	bubble	3
10.92	0.4623	0.0006	0.4033	0.0009	0.1344	0.0007	bubble	3
8.65	0.579	0.0006	0.3158	0.0010	0.1053	0.0009	bubble	3

p/MPa	x_1	$u(x_1)$	x_2	$u(x_2)$	x_3	$u(x_3)$	Status	Y
6.26	0.6996	0.0005	0.2253	0.0006	0.0751	0.0004	bubble	3
5.93	0.7123	0.0006	0.2157	0.0008	0.0719	0.0006	bubble	3
5.15	0.7512	0.0006	0.1866	0.0009	0.0622	0.0009	bubble	3
5.12	0.7549	0.0005	0.1838	0.0005	0.0613	0.0003	bubble	3
4.92	0.7676	0.0003	0.1743	0.0004	0.0581	0.0003	bubble	3
2.28	0.9082	0.0002	0.0689	0.0002	0.0230	0.0001	bubble	3
9.35	0.0176	0.0001	0.4912	0.0024	0.4912	0.0024	dew	1
16.05	0.0380	0.0001	0.4810	0.0024	0.4810	0.0024	dew	1
18.12	0.0531	0.0001	0.4734	0.0023	0.4734	0.0023	dew	1
19.91	0.0753	0.0002	0.4624	0.0023	0.4624	0.0023	bubble	1
22.35	0.1712	0.0004	0.4144	0.0021	0.4144	0.0021	bubble	1
22.41	0.2117	0.0004	0.3941	0.0020	0.3941	0.0020	bubble	1
21.83	0.2796	0.0005	0.3602	0.0018	0.3602	0.0018	bubble	1
20.32	0.3437	0.0006	0.3281	0.0017	0.3281	0.0017	bubble	1
16.97	0.4558	0.0006	0.2721	0.0014	0.2721	0.0014	bubble	1
16.55	0.4768	0.0006	0.2616	0.0013	0.2616	0.0013	bubble	1
12.66	0.5919	0.0006	0.2041	0.0011	0.2041	0.0011	bubble	1
6.72	0.7743	0.0004	0.1128	0.0006	0.1128	0.0006	bubble	1
11.45	0.0236	0.0001	0.2441	0.0013	0.7323	0.0013	dew	1/3
20.35	0.0348	0.0001	0.2413	0.0012	0.7239	0.0012	dew	1/3
26.09	0.0939	0.0002	0.2265	0.0012	0.6796	0.0012	dew	1/3
30.11	0.1510	0.0002	0.2123	0.0011	0.6368	0.0011	bubble	1/3
30.61	0.2123	0.0003	0.1969	0.0010	0.5907	0.0010	bubble	1/3
30.57	0.2849	0.0004	0.1788	0.0009	0.5363	0.0010	bubble	1/3
28.10	0.3626	0.0004	0.1594	0.0008	0.4781	0.0009	bubble	1/3
23.10	0.489	0.0005	0.1278	0.0007	0.3833	0.0008	bubble	1/3
16.95	0.6048	0.0006	0.0988	0.0005	0.2964	0.0007	bubble	1/3
15.72	0.6324	0.0004	0.0919	0.0005	0.2757	0.0006	bubble	1/3
13.40	0.6877	0.0004	0.0781	0.0004	0.2342	0.0005	bubble	1/3
5.36	0.8648	0.0002	0.0338	0.0002	0.1014	0.0002	bubble	1/3
2.25	0.9517	0.0001	0.0121	0.0001	0.0362	0.0001	bubble	1/3
$T = 373.15 \text{ K}$								
15.87	0.0728	0.0002	0.6954	0.0012	0.2318	0.0012	dew	3
17.39	0.1129	0.0001	0.6653	0.0012	0.2218	0.0012	dew	3
18.12	0.1555	0.0003	0.6334	0.0011	0.2111	0.0011	dew	3
18.45	0.2056	0.0002	0.5958	0.0012	0.1986	0.0012	bubble	3
18.19	0.2549	0.0004	0.5588	0.0011	0.1863	0.0011	bubble	3
17.83	0.3045	0.0004	0.5216	0.0011	0.1739	0.0011	bubble	3
17.25	0.3493	0.0005	0.4880	0.0010	0.1627	0.0010	bubble	3
16.85	0.3746	0.0004	0.4691	0.0011	0.1564	0.0010	bubble	3
14.26	0.4822	0.0006	0.3884	0.0009	0.1295	0.0008	bubble	3
12.00	0.5663	0.0006	0.3253	0.0009	0.1084	0.0008	bubble	3
9.65	0.6500	0.0006	0.2625	0.0008	0.0875	0.0006	bubble	3

p/MPa	x_1	$u(x_1)$	x_2	$u(x_2)$	x_3	$u(x_3)$	Status	Y
8.31	0.7002	0.0006	0.2249	0.0008	0.0750	0.0006	bubble	3
7.42	0.7291	0.0006	0.2032	0.0007	0.0677	0.0006	bubble	3
6.75	0.7553	0.0006	0.1835	0.0006	0.0612	0.0005	bubble	3
4.43	0.8324	0.0005	0.1257	0.0005	0.0419	0.0003	bubble	3
1.87	0.9285	0.0002	0.0536	0.0002	0.0179	0.0001	bubble	3
9.35	0.0447	0.0001	0.4776	0.0023	0.4776	0.0023	dew	1
11.25	0.0505	0.0001	0.4748	0.0023	0.4748	0.0023	dew	1
17.83	0.0687	0.0002	0.4656	0.0023	0.4656	0.0023	dew	1
22.06	0.1042	0.0003	0.4479	0.0022	0.4479	0.0022	dew	1
23.53	0.1514	0.0003	0.4243	0.0021	0.4243	0.0021	bubble	1
24.18	0.2056	0.0004	0.3972	0.0020	0.3972	0.0020	bubble	1
24.15	0.2789	0.0005	0.3606	0.0018	0.3606	0.0018	bubble	1
22.45	0.3668	0.0006	0.3166	0.0016	0.3166	0.0016	bubble	1
19.27	0.4771	0.0006	0.2614	0.0013	0.2614	0.0013	bubble	1
15.15	0.5919	0.0006	0.2040	0.0011	0.204	0.0011	bubble	1
14.62	0.6068	0.0006	0.1966	0.0010	0.1966	0.0010	bubble	1
13.73	0.6275	0.0006	0.1862	0.0010	0.1862	0.0010	bubble	1
9.91	0.7239	0.0004	0.1381	0.0007	0.1381	0.0007	bubble	1
6.05	0.8247	0.0003	0.0877	0.0005	0.0877	0.0005	bubble	1
3.25	0.9053	0.0002	0.0474	0.0003	0.0474	0.0003	bubble	1
14.05	0.0520	0.0001	0.2370	0.0012	0.7110	0.0012	dew	1/3
23.35	0.0771	0.0002	0.2307	0.0012	0.6922	0.0012	dew	1/3
28.45	0.1462	0.0003	0.2134	0.0011	0.6403	0.0011	dew	1/3
30.01	0.2221	0.0004	0.1945	0.0010	0.5834	0.0011	bubble	1/3
30.01	0.2849	0.0005	0.1788	0.0009	0.5363	0.0010	bubble	1/3
28.20	0.3625	0.0006	0.1594	0.0008	0.4781	0.0009	bubble	1/3
27.61	0.3855	0.0006	0.1536	0.0008	0.4609	0.0009	bubble	1/3
27.22	0.4027	0.0006	0.1493	0.0008	0.4479	0.0009	bubble	1/3
23.28	0.4930	0.0006	0.1268	0.0007	0.3803	0.0008	bubble	1/3
18.05	0.6049	0.0006	0.0988	0.0005	0.2963	0.0007	bubble	1/3
17.15	0.6224	0.0004	0.0944	0.0005	0.2832	0.0006	bubble	1/3
16.65	0.6325	0.0004	0.0919	0.0005	0.2756	0.0006	bubble	1/3
13.35	0.7007	0.0004	0.0748	0.0004	0.2245	0.0005	bubble	1/3
12.72	0.7156	0.0004	0.0711	0.0004	0.2133	0.0005	bubble	1/3
7.03	0.8442	0.0002	0.0390	0.0002	0.1169	0.0003	bubble	1/3
2.90	0.9372	0.0001	0.0157	0.0001	0.0471	0.0001	bubble	1/3
$T = 423.15 \text{ K}$								
15.65	0.1096	0.0003	0.6678	0.0012	0.2226	0.0011	dew	3
16.36	0.1278	0.0001	0.6542	0.0013	0.2181	0.0013	dew	3
19.36	0.2014	0.0004	0.5990	0.0011	0.1997	0.0010	dew	3
20.45	0.2542	0.0002	0.5594	0.0012	0.1865	0.0012	bubble	3
20.15	0.3155	0.0005	0.5134	0.0010	0.1711	0.0010	bubble	3
19.18	0.3839	0.0004	0.4621	0.0011	0.1540	0.0010	bubble	3
19.45	0.3747	0.0004	0.469	0.0010	0.1563	0.0009	bubble	3

p/MPa	x_1	$u(x_1)$	x_2	$u(x_2)$	x_3	$u(x_3)$	Status	Y
18.16	0.4141	0.0004	0.4394	0.0011	0.1465	0.0010	bubble	3
13.62	0.5743	0.0006	0.3193	0.0008	0.1064	0.0006	bubble	3
8.76	0.7293	0.0006	0.2030	0.0007	0.0677	0.0005	bubble	3
7.92	0.7557	0.0006	0.1832	0.0007	0.0611	0.0005	bubble	3
4.23	0.8667	0.0003	0.1000	0.0004	0.0333	0.0003	bubble	3
1.56	0.9647	0.0001	0.0265	0.0001	0.0088	0.0001	bubble	3
16.84	0.1010	0.0002	0.4495	0.0022	0.4495	0.0022	dew	1
19.56	0.1259	0.0003	0.4371	0.0022	0.4371	0.0022	dew	1
22.86	0.1917	0.0004	0.4041	0.0020	0.4041	0.0020	dew	1
23.95	0.2531	0.0005	0.3735	0.0019	0.3735	0.0019	bubble	1
23.65	0.3234	0.0006	0.3383	0.0017	0.3383	0.0017	bubble	1
22.68	0.3836	0.0006	0.3082	0.0016	0.3082	0.0016	bubble	1
19.34	0.5007	0.0006	0.2496	0.0013	0.2496	0.0013	bubble	1
15.67	0.6070	0.0006	0.1965	0.0010	0.1965	0.0010	bubble	1
14.87	0.6277	0.0006	0.1861	0.0010	0.1861	0.0010	bubble	1
10.56	0.7429	0.0005	0.1286	0.0007	0.1286	0.0007	bubble	1
5.23	0.8571	0.0003	0.0715	0.0004	0.0715	0.0004	bubble	1
2.45	0.9367	0.0002	0.0317	0.0002	0.0317	0.0002	bubble	1
19.75	0.1089	0.0003	0.2228	0.0012	0.6683	0.0012	dew	1/3
21.67	0.1226	0.0003	0.2193	0.0011	0.6580	0.0012	dew	1/3
24.65	0.1558	0.0003	0.2111	0.0011	0.6332	0.0011	dew	1/3
25.85	0.1670	0.0004	0.2083	0.0011	0.6248	0.0011	dew	1/3
27.02	0.1902	0.0004	0.2024	0.0011	0.6073	0.0011	dew	1/3
27.83	0.2273	0.0004	0.1932	0.0010	0.5795	0.0011	dew	1/3
28.05	0.2494	0.0005	0.1876	0.0010	0.5629	0.0010	bubble	1/3
28.15	0.2738	0.0005	0.1815	0.0009	0.5446	0.0010	bubble	1/3
28.05	0.3118	0.0005	0.1721	0.0009	0.5162	0.0010	bubble	1/3
27.75	0.3200	0.0006	0.1700	0.0009	0.5100	0.0010	bubble	1/3
27.13	0.3561	0.0006	0.161	0.0008	0.4829	0.0009	bubble	1/3
26.90	0.3625	0.0006	0.1594	0.0008	0.4782	0.0009	bubble	1/3
26.05	0.4027	0.0006	0.1493	0.0008	0.448	0.0009	bubble	1/3
22.15	0.5031	0.0006	0.1242	0.0007	0.3726	0.0008	bubble	1/3
18.17	0.6049	0.0006	0.0988	0.0005	0.2963	0.0007	bubble	1/3
17.05	0.6325	0.0006	0.0919	0.0005	0.2756	0.0006	bubble	1/3
13.17	0.7157	0.0005	0.0711	0.0004	0.2132	0.0005	bubble	1/3
8.742	0.8164	0.0004	0.0459	0.0003	0.1377	0.0004	bubble	1/3
3.55	0.9135	0.0002	0.0216	0.0001	0.0649	0.0002	bubble	1/3

^a Expanded uncertainties are $U(T) = 1 \text{ K}$, $U(p) = 0.4 \text{ MPa}$ for bubble points or $U(p) = 0.6 \text{ MPa}$ for dew points with coverage factor $k = 2$.

Also shown in **Figures 5, 6 and 7** are the predictions of the SAFT- γ Mie theory (continuous curves) and PPR78 (dashed curves). Here we observe generally good agreement between experiment and

the predictions of both models in the low-pressure region. At high pressures, close to the critical region, both models over-predict the pressure for given compositions and this is more pronounced at the lower mole ratios Y of CO_2 in the feed gas (higher methane content in the ternary system) and lowest temperature, with SAFT- γ Mie is shown to give better agreement in this region. At this mole ratio ($Y = 1/3$) and this temperature ($T = 323.15$ K), the observed deviations between experimental and predicted pressures in the critical region can be as high as 5 MPa for SAFT- γ Mie and 7 MPa for PPR78. These Figures shows that the agreement between the SAFT- γ Mie theory and the experimental data is best at the highest temperature and worst at the lowest temperature considered in the present work.

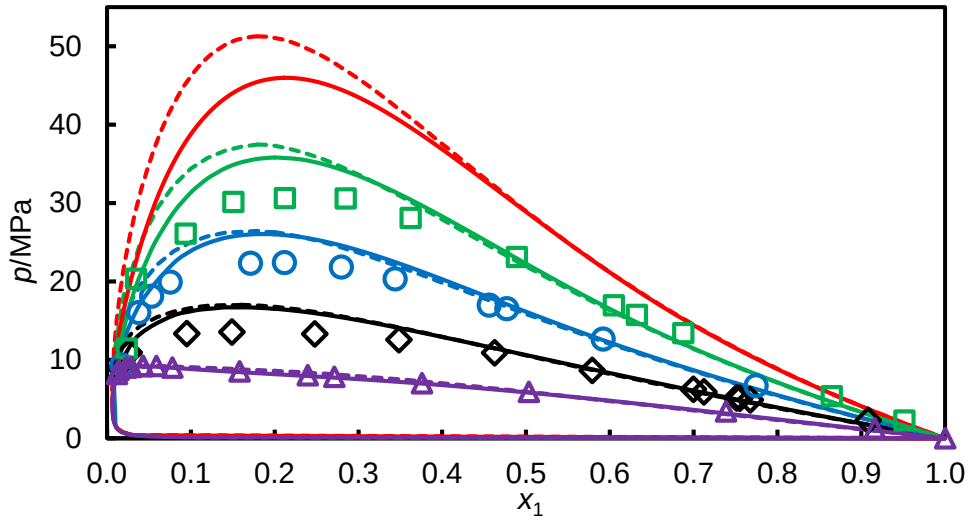


Figure 5. Bubble and dew curves for the ternary mixture (methylbenzene + CO_2 + CH_4) at temperature $T = 323.15$ K, where p is pressure and x_1 is the mole fraction of methylbenzene. Symbols represent experimental data at the following mole ratios Y of carbon dioxide to methane: $\square$, $Y = 1/3$; $\circ$, $Y = 1$ and $\diamond$, $Y = 3$. The symbol $\triangle$ corresponds to binary data for (methylbenzene + CO_2) measured previously at this temperature [42]. The solid and dashed lines represent prediction from SAFT- γ Mie and PPR78 respectively, black lines correspond to the binary mixture (methylbenzene + CH_4), and red lines refer to (methylbenzene + CO_2).

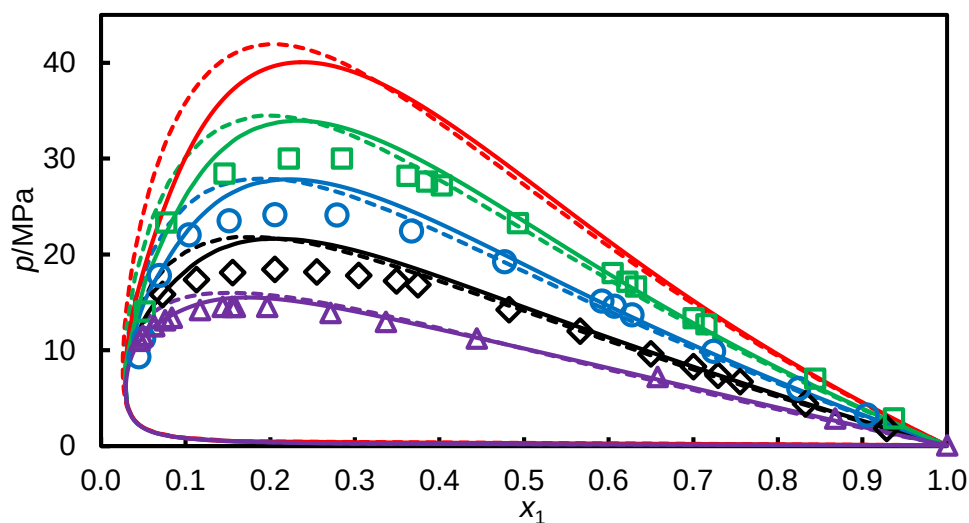


Figure 6. Bubble and dew curves for the ternary mixture (methylbenzene + CO₂ + CH₄) at temperature $T = 373.15$ K, where p is pressure and x_1 is the mole fraction of methylbenzene. Symbols represent experimental data at the following mole ratios Y of carbon dioxide to methane: $\square$, $Y = 1/3$; $\circ$, $Y = 1$ and $\diamond$, $Y = 3$. The symbol $\triangle$ corresponds to binary data for (methylbenzene + CO₂) measured previously at this temperature [42]. The solid and dashed lines represent prediction from SAFT- γ Mie and PPR78 respectively, black lines correspond to the binary mixture (methylbenzene + CH₄), and red lines refer to (methylbenzene + CO₂).

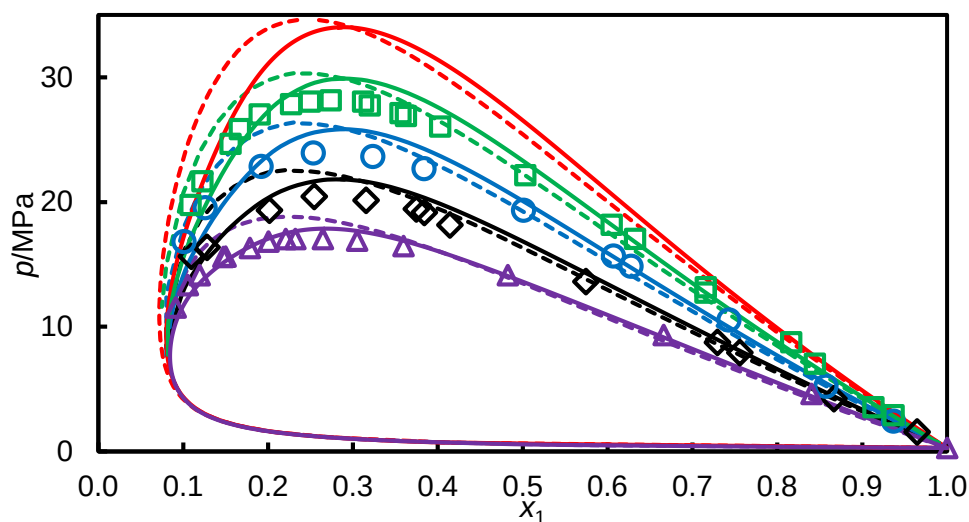


Figure 7. Bubble and dew curves for the ternary mixture (methylbenzene + CO₂ + CH₄) at temperature $T = 423.15$ K, where p is pressure and x_1 is the mole fraction of methylbenzene. Symbols represent experimental data at the following mole ratios Y of carbon dioxide to methane: $\square$, $Y = 1/3$; $\circ$, $Y = 1$ and $\diamond$, $Y = 3$. The symbol $\triangle$ corresponds to binary data for (methylbenzene + CO₂) measured previously at this temperature [42]. The solid and dashed lines represent prediction from SAFT- γ Mie and PPR78 respectively, black lines correspond to the binary mixture (methylbenzene + CH₄), and red lines refer to (methylbenzene + CO₂).

In our previous work with the PPR78 model [43], we noticed that the binary interaction parameters between two supercritical components (CO_2 and CH_4 in this case) may not be predicted well by the group contribution method, which was developed by fitting binary phase-equilibrium data only, and that such binary parameters may require further adjustments. The deterioration in the performance of both models with increasing methane content in the ternary system suggests that the interaction parameters between CH_4 and the functional groups that describe C_7H_8 also require further adjustments in both cases.

5. Conclusions

New experimental VLE data are reported for the ternary system ($\text{C}_7\text{H}_8 + \text{CO}_2 + \text{CH}_4$) at temperature between (323 and 423) K and at pressures up to approximately 31 MPa. The results span three different mole ratios of CO_2 to CH_4 and, for each ratio, three isotherms were studied. Comparison between the predictions of the SAFT- γ Mie and PPR78 approaches and the experimental data show very good agreement in the lower pressure region. At high pressures, close to the critical region, both models over-predict the pressure for given compositions and the deviation are more pronounced at the highest methane content and the lowest temperature. SAFT- γ Mie is shown to generally give better agreement. The current work suggests that the interaction parameters between CH_4 and the functional groups that describe C_7H_8 require further optimization.

Funding

This work was carried out as part of the activities of the Qatar Carbonates & Carbon Storage Research Centre (QCCSRC). We gratefully acknowledge the funding of QCCSRC provided jointly by Qatar Petroleum, Shell, and the Qatar Science and Technology Park, and their permission to publish this research.

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Appendix 1: Composition Uncertainty Analysis

In the VLE experiments, pure liquid (component 1) and gas mixture (comprising components 2 and 3) were injected in separate operations. Let n_L be the amount of liquid introduced into the cell and let n_G be the corresponding amount of gas mixture introduced. The mole fraction x_1 of component 1 is then given by

$$x_1 = \frac{n_L}{n_L + n_G} . \quad (A1)$$

Neglecting, for the purposes of the uncertainty analysis, the effect of the small dead volumes, the amounts of liquid and gas injected into the vessel are

$$\left. \begin{aligned} n_L &= \rho_L V_L \\ n_G &= \rho_G V_G \end{aligned} \right\} , \quad (A2)$$

where ρ is molar density at the pump conditions, V is cumulative injected volume and subscripts L and G denote liquid and gas, respectively. From equation (A1), the standard uncertainty of x_1 is given by

$$\begin{aligned} u^2(x_1) &= \left[n_L \left(\frac{\partial x_1}{\partial n_L} \right) u_r(n_L) \right]^2 + \left[n_G \left(\frac{\partial x_1}{\partial n_G} \right) u_r(n_G) \right]^2 , \\ &= [x_1(1-x_1)u_r(n_L)]^2 + [x_1(x_1-1)u_r(n_G)]^2 \end{aligned} \quad (A3)$$

and from equations (A2) the standard relative uncertainties $u_r(n_L)$ of the amount of liquid and $u_r(n_G)$ of the amount of gas are related to the standard relative uncertainties of the molar densities and cumulative volumes as follows:

$$\left. \begin{aligned} u_r^2(n_L) &= u_r^2(\rho_L) + u_r^2(V_L) \\ u_r^2(n_G) &= u_r^2(\rho_G) + u_r^2(V_G) \end{aligned} \right\} . \quad (A4)$$

Consequently, the combined standard uncertainty of x_1 is given by

$$u(x_1) = x_1(1-x_1) \left[u_r^2(\rho_L) + u_r^2(\rho_G) + u_r^2(V_L) + u_r^2(V_G) \right]^{1/2} . \quad (A5)$$

In a few cases, a modified filling procedure was followed in which the cell was first filled with the gas mixture and the liquid component was then injected in the usual way. In these cases, equation (A5) still applies but V_G is interpreted as the volume of the cell under the filling conditions. Note that $u_r(\rho_L)$ and $u_r(\rho_G)$ are overall combined relative uncertainties include the uncertainty of the equation of state

used to evaluate molar density and the consequences of uncertainties in the temperature, pressure and (for the gas mixture) composition under the conditions at which V_L and V_G were determined.

The two remaining mole fractions are given by

$$\left. \begin{aligned} x_2 &= z(1 - x_1) \\ x_3 &= (1 - z)(1 - x_1) \end{aligned} \right\}, \quad (\text{A6})$$

where z is the mole fraction of component 2 in the feed gas mixture. From this it follows that

$$u^2(x_2) = z^2 u^2(x_1) + (1 - x_1)^2 u^2(z) \quad (\text{A7})$$

and

$$u^2(x_3) = (1 - z)^2 u^2(x_1) + (1 - x_1)^2 u^2(z). \quad (\text{A8})$$

The relative standard uncertainty for each component is shown in Figure A1. Here it can be observed that, in the cases of carbon dioxide and methane, the relative standard uncertainties of the synthetic mole fractions fall into two groups. For the group with $u_r(x_i) \geq 0.5\%$, the mole fraction of component i in the feed-gas mixtures was ≤ 0.5 ; while for other group, in which $u_r(x_i) \leq 0.3\%$, the mole fraction of component i on the feed-gas mixture was 0.75. Overall, the relative uncertainties in the synthetic mole fractions are less than 0.6% for all the measurements.

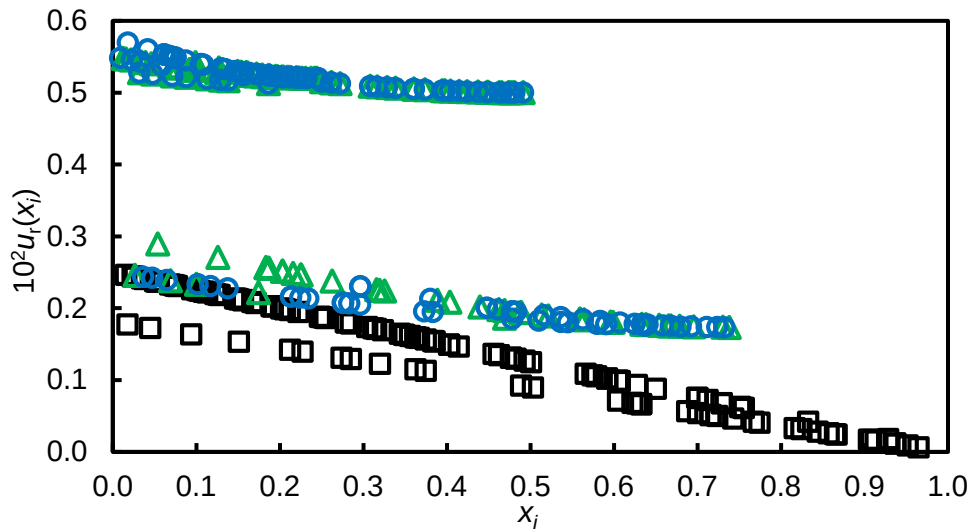


Figure A1. Distribution of the relative uncertainty $u_r(x_i)$ of the mole fractions x_i : $\square$, methylbenzene; $\circ$, carbon dioxide; $\triangle$, methane.