



# Vapor - liquid equilibrium of the carbon dioxide/methane mixture at three isotherms

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## ARTICLE INFO

### Article history:

Received 21 September 2017

Received in revised form

6 January 2018

Accepted 13 January 2018

Available online 3 February 2018

### Keywords:

Vapor – liquid equilibrium

Carbon dioxide

Methane

Equations of state

UMR-PRU

## ABSTRACT

Experimental vapor – liquid equilibrium data for the CO<sub>2</sub>/CH<sub>4</sub> mixture have been measured at 293.13 K, 298.14 K and 303.15 K, with emphasis on the mixture critical area. The maximum estimated standard uncertainties are 3 mK in temperature, 2 kPa in pressure and 0.0008 in mole fraction. The scaling law of statistical thermodynamics has been fitted to the critical region data of each isotherm and very good estimation of the critical point is achieved with a maximum uncertainty of 10 kPa in critical pressure and 0.0009 in critical molar composition. The measurements have been validated against experimental data taken from the literature, where available, and against the prediction of the GERG-2008 model. The Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR) Equations of State using the classic van der Waals one fluid mixing rules, the perturbed chain statistical association fluid theory (PC-SAFT) and the Universal Mixing Rule – Peng Robinson (UMR-PRU) model have been fitted to the data of each isotherm with very satisfactory results. UMR-PRU yields the lowest deviation, especially concerning the critical point area, with an overall absolute average deviation (AAD) of 0.18% in bubble point pressure and 0.43% in CO<sub>2</sub> mole fraction of the vapor phase. In the critical points, UMR-PRU results in an average % AAD equal to 1.55 in critical pressure and 0.99 in the critical point composition.

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## 1. Introduction

The knowledge of vapor – liquid equilibrium (VLE) of binary mixtures is very important for validating thermodynamic models and tuning model parameters, rendering possible the accurate process design and operation. The carbon dioxide/methane mixture (CO<sub>2</sub>/CH<sub>4</sub>) is important both for carbon capture and storage (CCS) and the natural gas (NG) industry. In the case of CCS, methane can be found as an impurity in CO<sub>2</sub> captured from natural gas sweetening process, as well as from pre-combustion carbon capture in power plants [1]. On the other hand, CO<sub>2</sub> is one of natural gas components with typical concentration ranging, depending on the NG field, from 2% up to 30% [2]. Due to its importance for the natural gas industry the CO<sub>2</sub>/CH<sub>4</sub> mixture has been studied since 1970 and according to NIST literature report [3], twenty three publications of VLE data are available in the literature covering a

temperature range from close to the triple point up to the critical point of CO<sub>2</sub>, i.e. from 153 K to 301 K, and pressures from 0.27 up to 8.74 MPa. Especially the region from 210 K up to 273.15 K is considered well covered with measurements over the whole phase boundary. However, from temperatures above 273.15 K, few experimental data are available and in most cases there is only one publication per isotherm, so no explicit validation of the data can occur. More specifically, experimental data covering both the liquid and vapor phase are reported in the work of Kaminishi et al. [4] for 283.15 K, without covering the critical mixture area and Nasir et al. [5] who reported several VLE measurements along the bubble and dew point lines. Despite that fact, much scattering is observed between those publications, as well as with the reported bubble points by Devlikamov et al. [6]. At the isotherm of 288.15 K, four data sources are available, Arai et al. [7], Xu et al. [8], Shi et al. [9] and Nasir et al. [5] which are in very good agreement with each other, especially in the area away from the critical point. Xu et al. [8] also reported data for the isotherm of 293.15 K, covering the whole phase boundary. Recently, Nasir et al. [5] reported the VLE of the

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CO<sub>2</sub>/CH<sub>4</sub> binary for several isotherms ranging from 240 K up to 293 K. Yet, in their work a few data have been reported above 287 K. Meanwhile, the critical mixture area is not covered sufficiently in those isotherms. Finally, Bian et al. [10] measured the CO<sub>2</sub>/CH<sub>4</sub> VLE close to the critical temperature of CO<sub>2</sub>, at 301.15 K, but away of the critical mixture area. Apart from the publications covering both phases, Devlikamov et al. [6] reported the bubble points of CO<sub>2</sub>/CH<sub>4</sub> mixture at four isotherms, which are stated at 278.15 K, 283.15 K, 293.15 K and 298.15 K.

According to Li et al. [1], CCS capture typically involves temperatures above 298.15 K, while the operating window for pipeline transportation is from 273.15 K to 317.15 K [11]. Therefore, new experimental data are required to cover the gaps in the higher temperature area and also to be used in order to extend the applicability of thermodynamic models. In the present work, VLE data for the CO<sub>2</sub>/CH<sub>4</sub> mixture at three isotherms, 293.13 K, 298.14 K and 303.15 K are measured, following the work by Westman et al. [12,13]. Emphasis is given in capturing the mixture behavior in the critical region. The experimental data obtained in this study are validated against the existing literature data at the isotherms of 293.13 K and 298.15 K, as well as against the prediction of the state-of-the-art model for natural gas mixtures, GERG-2008 [14,15] as calculated through the NIST RefProp software. The results and analysis are presented in accordance to the IUPAC guidelines for reporting phase equilibrium measurements [16], by performing estimation of the standard uncertainty as described in the Guide for the estimation of the Uncertainty in Measurements (“GUM”) [17]. Finally, binary interaction parameters have been fitted to each isotherm of the experimental data obtained in this work using in-house software. For the correlation of the obtained experimental data, the Soave – Redlich – Kwong (SRK) [18,19] and the Peng – Robinson (PR) [20,21] Equations of State (EoS) combined with the van der Waals one fluid mixing rules (vdW1f) [22,23] are examined. The above EoSs are selected since, due to their simplicity, they are commonly used in industrial practice. Furthermore, two more sophisticated approaches for the thermodynamic modelling of the VLE are also fitted to the experimental data obtained in this work. That is the Universal Mixing Rule – Peng Robinson (UMR-PRU) model, which combines the PR EoS with the UNIFAC [24] activity coefficient model, and an EoS with a more theoretical background derived from statistical thermodynamics, the Perturbed Chain – Statistical Associating Fluid Theory (PC-SAFT) [25,26]. The performance of the different models is studied by fitting the model parameters to the liquid phase experimental data and comparing the description of the vapor phase solubility, as well as the critical point estimation.

The structure of the paper is as follows. In Section 2 the experimental apparatus and procedure are briefly described and in Section 3 the most important parameters for the uncertainty analysis are presented. The VLE experimental data are presented and the results of the thermodynamic modelling are discussed in Section 4. Finally, the conclusions reached are presented in Section 5. The models used to correlate the experimental data are briefly presented in Appendix A, while the detailed experimental data are given in tabulated form in the Supplementary Material.

## 2. Experimental procedure

The apparatus used in this work [27] has been described in detail by Westman et al. [12]. The phase equilibrium cell has an internal volume of 100 ml and consists of a sapphire cylinder sealed by two titanium flanges, enclosed in a thermostatic bath. CO<sub>2</sub> and methane are injected separately into the cell using syringe pumps, enabling dynamic control of both the cell pressure and total composition. The injection pipelines are connected to valves

embedded in the titanium flanges to minimize the dead volume of the cell. In order to monitor the temperature and ensure thermal uniformity, 25 Ω standard platinum resistance thermometers (SPRTs) are placed in each flange. The gas phase pressure inside the cell is measured by isolating a pressure sensor array from the fluid under test at various temperatures and level of aggressiveness using a differential pressure sensor setup. For composition measurements, small samples can be extracted from the cell using two capillaries. One capillary is used for the vapor sampling and has its inlet close to the top of the cell, while the other can be adjusted to the appropriate height to be used for the liquid sampling. To compensate for the cell pressure drop caused by sampling, a bellows inside the cell can be expanded to decrease the cell volume. In order to reduce the time needed to reach equilibrium, the cell is equipped with a magnetic stirrer.

The temperature and pressure calibration was the one described by Ref. [12] and has been performed in-house in the SINTEF ER facilities. The temperature sensors have been calibrated against fixed point cells according to the International Temperature Scale of 1990 (ITS-90) [28] while the pressure sensors against a recently calibrated dead weight tester. The analytical procedure along with the respective uncertainty analysis are given in detail in Ref. [12]. The gas chromatograph (GC) has been calibrated against gravimetrically prepared calibration gas mixtures, which have been prepared in-house using a custom-built apparatus for such preparation. The purity of the source gases as given by the manufacturer is reported in Table 1, while no further analysis has been performed. Details about the GC calibration are given in Section 3.3.4.

### 2.1. General

The measurements have been performed using an isothermal analytical method with a variable volume cell with the temperature and the pressure as independent variables. The equilibrium cell is kept at constant temperature using a thermostat bath and is filled with CO<sub>2</sub> and a mixture of CO<sub>2</sub>/CH<sub>4</sub> until the target pressure is obtained. The coexistence of the two phases is confirmed visually through a borescope, which is directly connected to a monitor. The experimental procedure is similar to the one followed by Westman et al. [12,13] and will be briefly described in the following. Before the start of a VLE experiment, the whole system is evacuated through a vacuum pump to ensure no contamination of the pipelines, the pumps or the equilibrium cell. More specifically, the CO<sub>2</sub> pump, the impurity mixture pump and their respective lines are evacuated once and then are flushed with their respective gas. The flushing and evacuation procedure is repeated five times in total to remove any impurities remaining in the cell. After the final flushing and evacuation, the gases are filled to their respective lines and pumps and remain at a pressure of at least 0.5 MPa to prevent any contamination. Then, the same procedure is repeated for the equilibrium cell. After setting the required temperature of the thermostatic bath, the cell is filled with CO<sub>2</sub> until the liquid level is about 40% of the cell volume. The stirrer runs until the temperature and pressure are stabilized. If the measured vapor pressure is within the uncertainty limits of the Span-Wagner [29] EoS, the setting of the bath is deemed appropriate.

After the CO<sub>2</sub> vapor pressure measurements, methane, in the form of a CO<sub>2</sub>/CH<sub>4</sub> mixture, is injected to the cell by an injection pump, until the specified pressure is obtained. The liquid level of the cell is adjusted either by injecting more CO<sub>2</sub> or by venting out some liquid from the bottom of the cell. The mixture is stirred to equilibrium and when the temperature and the pressure indications are stabilized for about thirty minutes, the stirrer is turned off and the mixture is left to settle before starting the sampling. The settling time ranges from thirty minutes to three

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