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Water Content of CO_2 rich Mixtures: Measurements and Modeling using the Cubic-Plus-Association Equation of State

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ABSTRACT

Natural gas is well known as the cleanest fossil fuel. However, it is estimated that more than 40% of the remaining conventional natural gas reserves are deemed to be acidic, i.e., containing significant quantities of CO_2 and H_2S. As the global consumption of natural gas is expected to steadily grow, the demand will be met by sources such as sour/acid gas fields. In some specific applications that require cryogenic processes (LNG, NGL recovery), this issue is commonly addressed upstream of the gas dehydration unit, so that the gas is already sweet when arriving at the drying section. In the other cases, the effect of the acidic species on the gas water content is often not properly accounted for, even though an accurate appraisal of the water content is paramount for the sizing of dehydration units.

In this contribution, the water contents of the ternary system CO_2 + CH_4 + H_2O were determined for various CO_2 to CH_4 ratios. New experimental data were obtained using a Tuneable Diode Laser Spectroscopy (TDLS) setup, with an accuracy of +/- 1%. The Soave-Redlich-Kwong and the Peng Robinson equations of state combined with the Cubic-Plus Association were used to estimate water content on CO_2 rich gas mixtures.

Key words: Carbon Dioxide; CPA; Equation of state; Methane; Water content; Peng-Robinson; Soave-Redlich-Kwong.

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1. INTRODUCTION

The consumption of natural gas is expected to steadily grow, and the demand will increasingly be met by sources such as sour/acid gas fields. This will have an impact on the whole gas processing chain, and especially on gas dehydration. Accurate assessment of the influence of acid gases, in particular CO_2, on the gas water content, which impacts on the size of dehydration unit required, is still today incomplete, as publicly available data are scarce.

In the case of a sweet gas, the water content can be calculated by phase equilibria-based commercial softwares, or estimated using the McKetta and Wehe chart [1]. Water content assessment is much more challenging when it comes to acid gas. As both pure H_2S and CO_2 contain more water at saturation than sweet natural gas, their effect on the overall water content can be very significant.

Several sets of experimental data and charts are available to address the subject. In this regard, the GPSA Engineering Handbook gives a good overview of the available methods [2]. However and as correctly pointed out by the GPSA, most of these methods apply to a reduced range of conditions, and/or give discrete information for limited sets of compositions. Generally speaking, the literature of the past 50 years is poor on the subject. As a consequence of this, the reliability of the results is very often questionable in terms of accuracy.
In practice, in most of the cases, the problem mainly concerns CO_2, with contents sometimes up to 30-50%, while the H_2S level is generally much lower, and therefore of a very limited impact compared to CO_2. This is the reason why in this article the focus is on the influence of CO_2.

The following "*simplified*" example illustrates the importance of having a good estimation of the water content, and its influence on a molecular sieve dehydration unit. In the following discussion, it is assumed that the gas to be treated has the characteristics listed in Table 1.

Table 1. Gas compositions and properties		
Flow-rate	200 000	Nm^3/hr
Pressure	60	Bara
Temperature	25	°C
Composition (mol%):		
C_1	50	%
CO_2	40	%
C_2	8	%
C_3	2	%

Under these conditions, if the gas was considered as a sweet gas, and the water content estimated by the McKetta-Wehe chart, the design of the unit would be based on **690 ppmV** water content (***Case 1***). Taking into account the influence of CO_2, the real water content of the gas is in fact **770 ppmV**, about12% higher (***Case 2***). The dehydration unit has to meet the following outlet specifications (Table 2):

Table 2. Dehydration unit specifications	
Water content:	< 1 ppmV
Pressure drop:	< 0.35 bar (end of lifetime)
Lifetime:	> 4 years

From this very simplified Process Specification, The impact of the two water contents on the unit design will be assessed.

Table 3. Dehydration unit design		
	Case 1 (690 ppmV)	**Case 2** (770 ppmV)
# of vessels in adsorption	1	1
Vessel diameter (mm)	2 900	2950
Mole sieve quantity (kg)	11 900	13050
Adsorption time (hrs)	12	12

With an inlet water content of 690 ppmV, a typical design meeting the specification given in Table 2 would involve 11.9 metric tons of molecular sieve and 12 hours adsorption time (Table 3). If the design of ***Case 1*** was applied with the water content of ***Case 2*** was, the additional water content would lead to either one of the following scenario:

- If 12 hours adsorption time and original flow-rate were maintained, the lifetime of the unit would decrease from 4 years to only 1.5 to 2 years maximum.
- To maintain a 4 years lifetime and 12 hours adsorption time, the flow-rate would have to be decreased from 200,000 Nm^3/hr down to ~180,000 Nm^3/hr.

By taking into account the real water content of the gas, the resulting design to allow for 4 years lifetime at the stated flow-rate would be significantly different. It would involve a slightly larger vessel diameter, and ~10% more mole sieve (Table 3).

The above example stresses the fact that an incorrect water content assessment can significantly influence the operation of an existing unit. As mentioned in Terrigeol *et al.* [4] it is preferable to use a correlation in order to have a quick indication of the water content of gas mixtures containing CO_2 and CH_4.

The aim of this work is to correctly assess the water content in CO_2 rich gases, for this purpose a review of the experimental data will be made. In order to evaluate the thermodynamic models, new experimental data for water content of binary mixtures of methane and carbon dioxide were generated.

2. LITERATURE REVIEW

Phase equilibrium data are widely available for the CO_2 + CH_4, CO_2 + H_2O and CH_4 + H_2O binary systems, however data for the ternary systems to validate the thermodynamic model are rather limited, in particular water content data are scarce. Sharma [5] and Song and Kobyashi [6] have measured the water content for the ternary systems. Song and Kobyashi [6] have measured the water content for a gas mixture composed with 94.69% of CO_2 and 5.31% of CH_4. Dhima et al. [7] have measured the solubility of methane and carbon dioxide in water at 344 K and Quin et al. [8] have measured both liquid and vapour compositions at 324 and 375 K.

3. EXPERIMENTAL

3.1 Materials

The CO_2 was 99.99% pure and the CH_4 was 99.995% pure, both were supplied by BOC. The CO_2/CH_4 binary mixtures were made using gravimetric means. The accuracy of the mixture compositions is ±0.1 mole%. Deionized water was used in all tests.

3.2 Experimental setup

In order to validate the thermodynamic model, new experimental data were measured. The core of the equipment for water content measurement and the procedures have been originally described by Chapoy *et al.* [9] and Burgass *et al.* (2014) [10]. The setup is comprised of twin equilibrium cells and a device for measuring the water content of equilibrated fluids passed from the cell. The twin equilibrium cell consists of 2 piston-type variable volume (maximum effective volume of 300 ml), titanium cylindrical pressure vessel held within a single cooling jacket (Figure 1). Cell volume, hence pressure, can be adjusted by injecting/withdrawal of hydraulic liquid behind the moving piston. The rig has a working temperature range of 203.15 to 453.15 K, with a maximum operating pressure of 70 MPa. The moisture/water content measurement set-up consists of a heated line, a Tuneable Diode Laser Adsorption Spectroscopy (TDLAS) from Yokogawa and a flow meter. The unit has two measurement ranges 0-100 ppmV and 0-3000 ppmV, both having a stated standard uncertainty of ±1% of full scale ($u(y_w)$ = 1 or 30 ppmV). Taking into account the error / repeatability between samples, the expanded combined uncertainty for water content is calculated to be $U_c(y_w)$=0.0006 mole%.

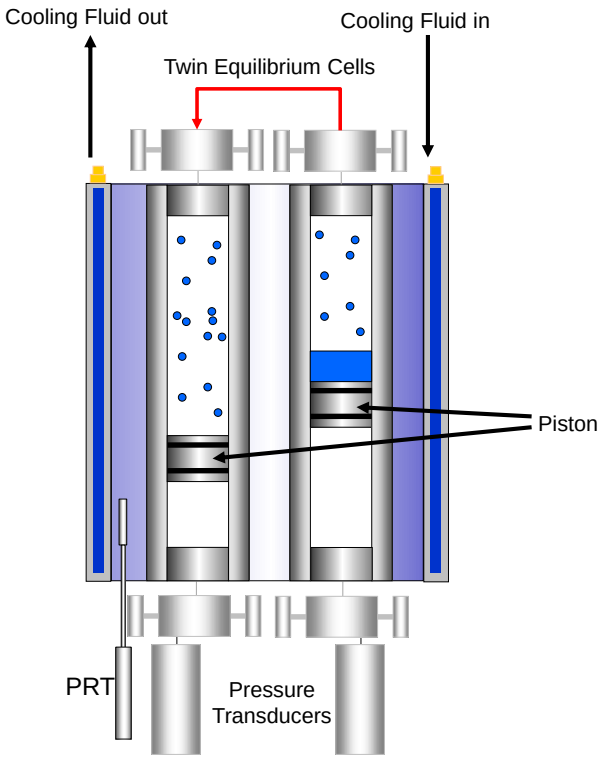


Figure 1: Schematic diagram showing equilibrium cell and water content measurement set-up.

System temperature is controlled by circulating coolant from a cryostat within a jacket surrounding the cell. The equilibrium cell and pipework were thoroughly insulated to ensure constant temperature. The temperature was measured and monitored by means of a PRT (Platinum Resistance Thermometers) located within the cooling jacket of the cell. Two Quartzdyne QS 30K-B pressures transducers connected to the bottom of the cells on the hydraulic are used to measure the pressure of the system. Both pressures transducers were previously calibrated against a deadweight tester and the temperature probe by comparison against a certified high precision probe. This calibration procedure ensures expanded uncertainties (k=2) better than $u(P)$ = 0.04 MPa and $u(T)$ = 0.1 K.

At the start of a test around 3 ml of deionized water was placed in a cup shaped depression in the bottom of the piston. The cell was then closed and evacuated before injecting the test gas. The cell temperature and pressure were then adjusted to achieve the desired test conditions. The cell was then allowed to equilibrate for at least 20 hours. This has been confirmed as being sufficient time for equilibrium to be achieved by conducting water content measurements over a number of days in previous testing.

3.3 Procedures

Once equilibrium had been achieved the valve at the top of the cell was opened in order to fill the section of heated line up to the valve prior to the hygrometer at the same time test gas was introduced into the base of the cell in order to maintain the pressure constant. Following this, the valve prior (inlet) to the hygrometer was opened sufficiently to achieve a flow rate of between 0.5 and 1 liter per minute through the hygrometer. The water content reading from the TDLS analyzer was then monitored until it was stable for at least 10 minutes. This was then taken as the moisture content of the equilibrated fluid in the cell (i.e., flowing out of the cell). During sampling the heated line was maintained at a temperature of 433.15 K.

4. THERMODYNAMIC MODELLING – THE PR-CPA

In this work, the models developed by Chapoy *et al*. [9] and Hajiw *et al*. used [11-12] have been used. In summary, the thermodynamic models are based on the uniformity of fugacity of each component throughout all the phases. The fugacities are calculated using the CPA-EoS coupled with the original Soave-Redlich and Kwong and the Peng-Robinson EoS [13].

For non-associating compounds, the CPA-EoS reduced to the SRK-EoS or PR EoS. All parameters for the CPA-SRK can be found in Chapoy *et al*. [9]. The PR-CPA parameters for water reported by Hajiw *et al*. used [11-12] were used in this work. Predictions for the CH_4 + H_2O and CO_2 + H_2O are shown in Figures 2 and 3.

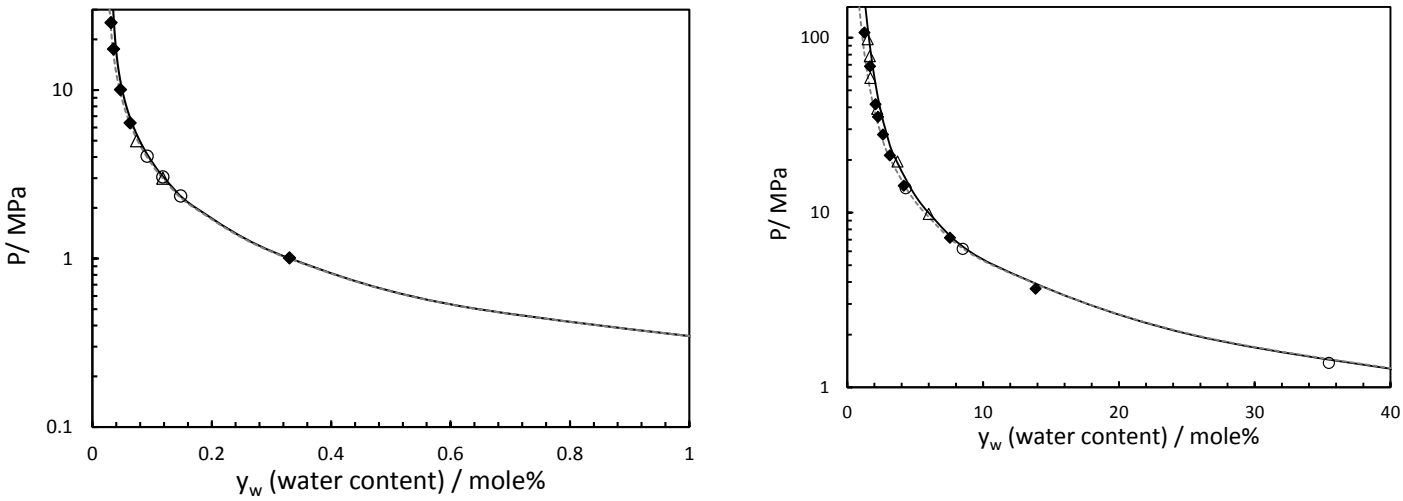


Figure 2. Py, Phase equilibria in the methane + water system at 298.15 K (left) and 423.15 K (right). Black Lines: Model predictions using the CPA-PR. Grey dashed lines: Model predictions using the CPA-SRK. At

298.15 K: (△) experimental data from [14], (○) experimental data from [15], (◆) experimental data from [16]. At about 423 K: (◆) experimental data from [17], (△) experimental data from [18], (○) experimental data from [19].

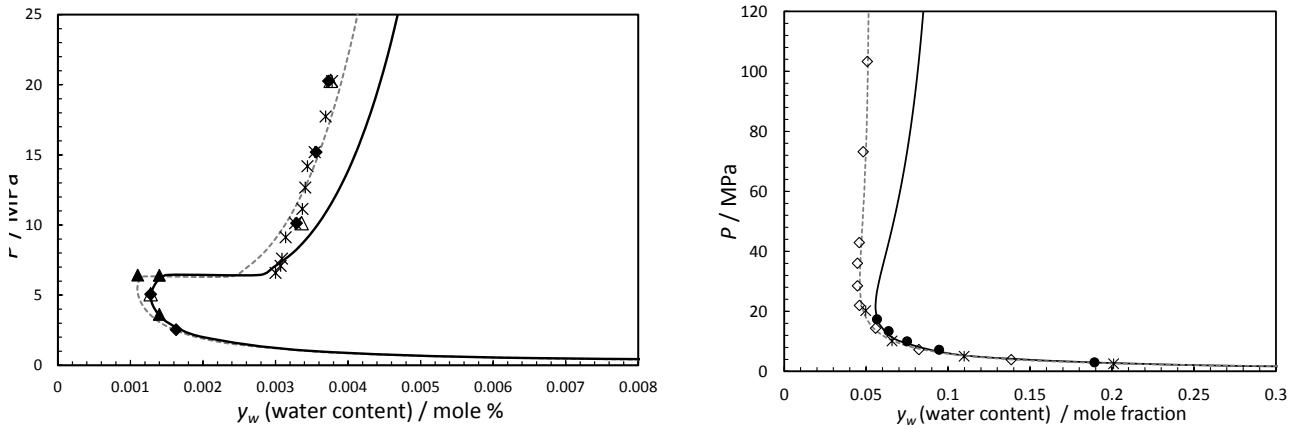


Figure 3. Py, Phase equilibria in the carbon dioxide + water system at 298.15 K (left) and 423.15 K (right). Black Lines: Model predictions using the CPA-PR. Grey dashed lines: Model predictions using the CPA-SRK. Left figure: (◆) experimental data from [20]; (△) [21]; (◢) experimental data from [22]; (✶) experimental data from [23]; (◇) experimental data from [24]. Right figure :(✶) experimental data from [21]; (◇) experimental data from [19] ;(●) experimental data from [25].

The only water content data available for the ternary system are the data presented by Song and Kobayashi [5]. They have measured the water content in 94.69 mole% CO_2 + 5.31 mole % CH_4 system. Their data at 323.15 K are shown in Figure 4 along with the predictions of the model and literature data for pure CO_2 and CH_4 at the same temperature.

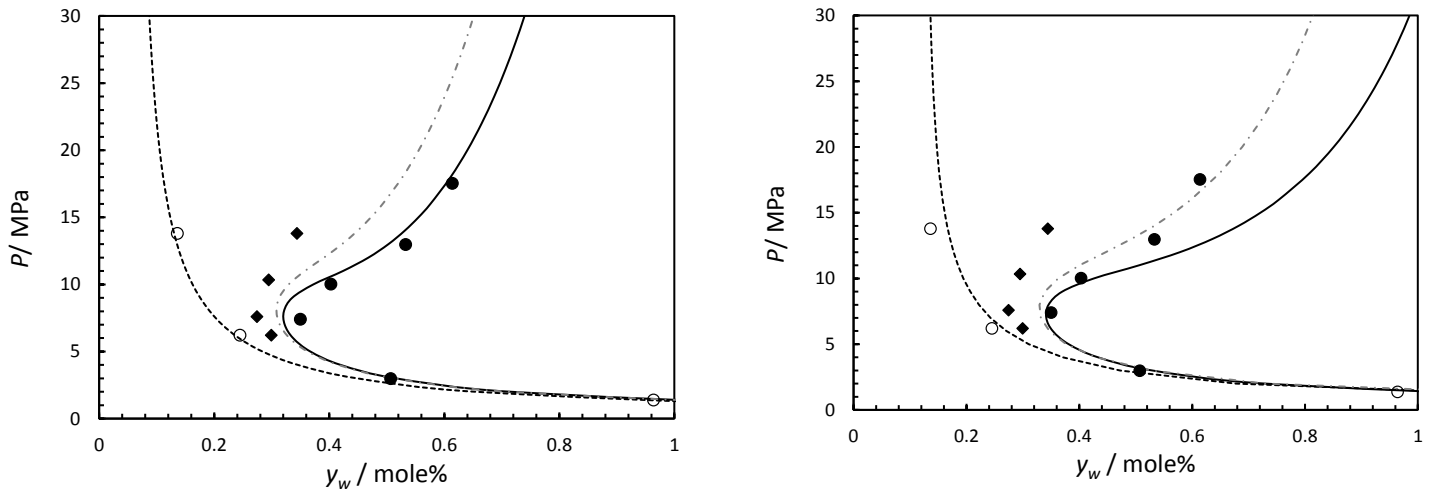


Figure 4. Py, Water content in the CH_4, 94.69 mole% CO_2 + 5.31 mole % CH_4 and CO_2 systems at 323.15 K. Left Figure: Predictions using the CPA-SRK. Right Figure: Predictions using the CPA-PR. Black Lines: Model predictions for CO_2. Dotted black lines: Model predictions CH_4. Grey broken lines: Model predictions for the 94.69 mole% CO_2 + 5.31 mole % CH_4. (◆)experimental data [6]; (○):experimental data [21] ;(●): experimental data [25].

As can be seen in the figure, the models can accurately predict the experimental water content in the pure fluids with the CPA-SRK superior to the CPA-PR in this case; however the water content predicted by the model for the ternary is higher than the one experimentally measured by Song and Kobayashi [6]. It is planned to measure water content for a similar system as the data for the binary CO_2 + water of these authors have been questioned by other researchers [9-10, 26].

5. RESULTS AND DISCUSSIONS

The new experimental water content measurements for three gas mixtures of CH_4 and CO_2 at the different test conditions are shown in Table 4. Low deviations of the new experimental data set confirm their consistency. Overall the predictions with the CPA-SRK are better than those made with the CPA-PR (Figure 5). CPA-PR seems to over predict the water content at these experiment conditions. Looking at the predictions for the binary CO_2 and water systems (Figure 3), it can be seen that higher deviations are generally observed for the CPA-PR, especially in denser phase.

Table 4. Experimental and predicted water content measurements for the three gas mixtures

Mole% CO_2	Mole% CH_4	*T*/K	*P*/ MPa	Water content Mole %		
				Exp.	PR CPA	SRK CPA
50	50	293.15	3.0	0.0989	0.1027	0.0973
			6.0	0.0636	0.0712	0.0629
		313.15	3.0	0.2961	0.3080	0.2957
			6.0	0.1791	0.1980	0.1804
30	70	293.15	3.0	0.0959	0.0975	0.0934
			6.0	0.0584	0.0627	0.0570
		313.15	3.0	0.2873	0.2949	0.2858
			6.0	0.1693	0.1791	0.1670
10	90	293.15	3.0	0.0884	0.0924	0.0894
			6.0	0.0502	0.0554	0.0516
		313.15	3.0	0.2806	0.2817	0.2756
			6.0	0.1543	0.1618	0.1541

U(T, k=2)=0.1K, U(P, k=2)=0.04 MPa and $U_c(y)$= 0.0006 mole%

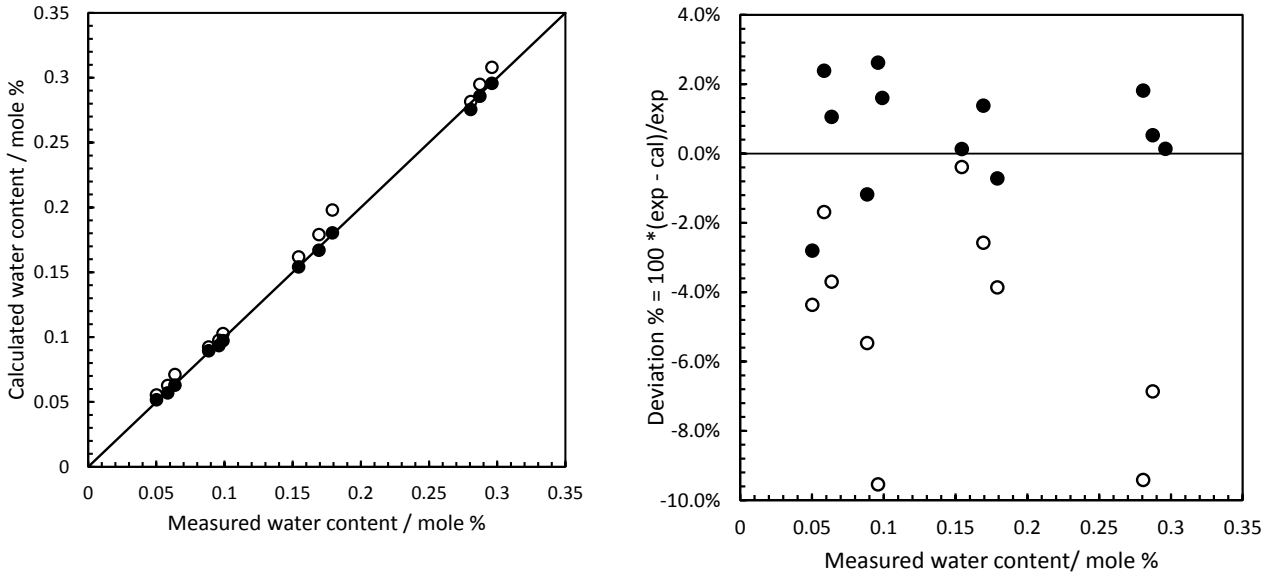


Figure 5. Comparison between experimental water content, CPA-SRK (●) and CPA-PR (○) predictions. – Left: Measured vs predicted water content; Right: Deviations between measurements and predictions.

As can be seen in Figure 5, there is an excellent agreement between the experimental data and the models.

All the experiments presented herein were in the gas phase. The experimental data follow the expected trends, i.e.:

- The water content is increasing with temperature at a given pressure (Figures 6-8)
- The water content is decreasing with pressure at a given temperature (Figures 6-8)
- The water content is increasing with the CO_2 concentration in the feed gas (Figures 9-10).

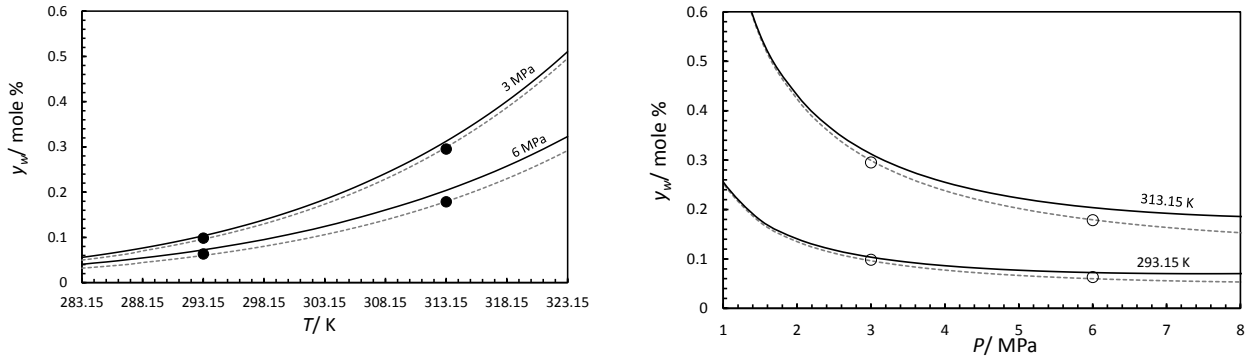


Figure 6. Predicted (Black lines: CPA-PR; Grey dotted lines: CPA-SRK) and experimental water content for the 50 mole% CO_2 + 50 mole CH_4 system – Left: Temperature dependency; Right: Pressure dependency

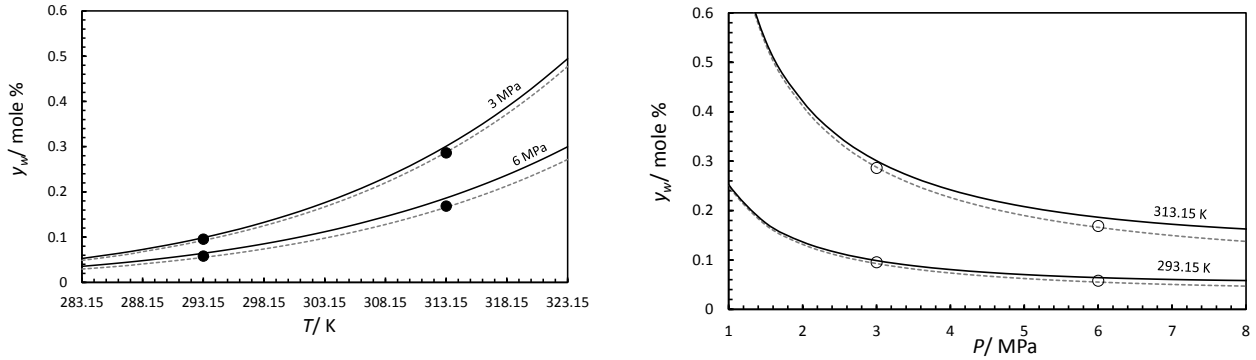


Figure 7. Predicted (Black lines: CPA-PR; Grey dotted lines: CPA-SRK) and experimental water content for the 30 mole% CO_2 + 70 mole CH_4 system – Left: Temperature dependency; Right: Pressure dependency

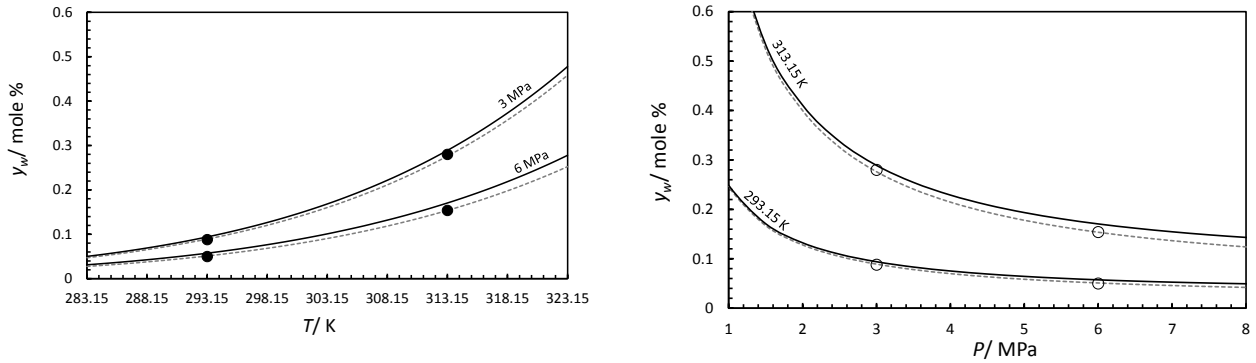


Figure 8. Predicted (Black lines: CPA-PR; Grey dotted lines: CPA-SRK) and experimental water content for the 10 mole% CO_2 + 90 mole CH_4 system – Left: Temperature dependency; Right: Pressure dependency

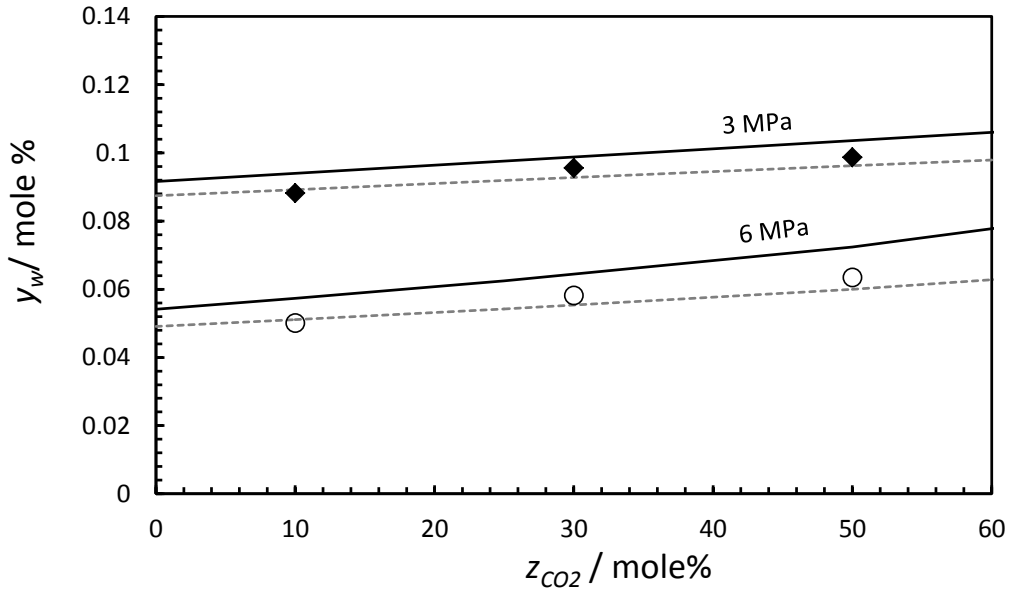


Figure 9: Predicted (Black lines: CPA-PR; Grey dotted lines: CPA-SRK) and experimental water content at 293.15 K – Effect of CO_2 in feed gas

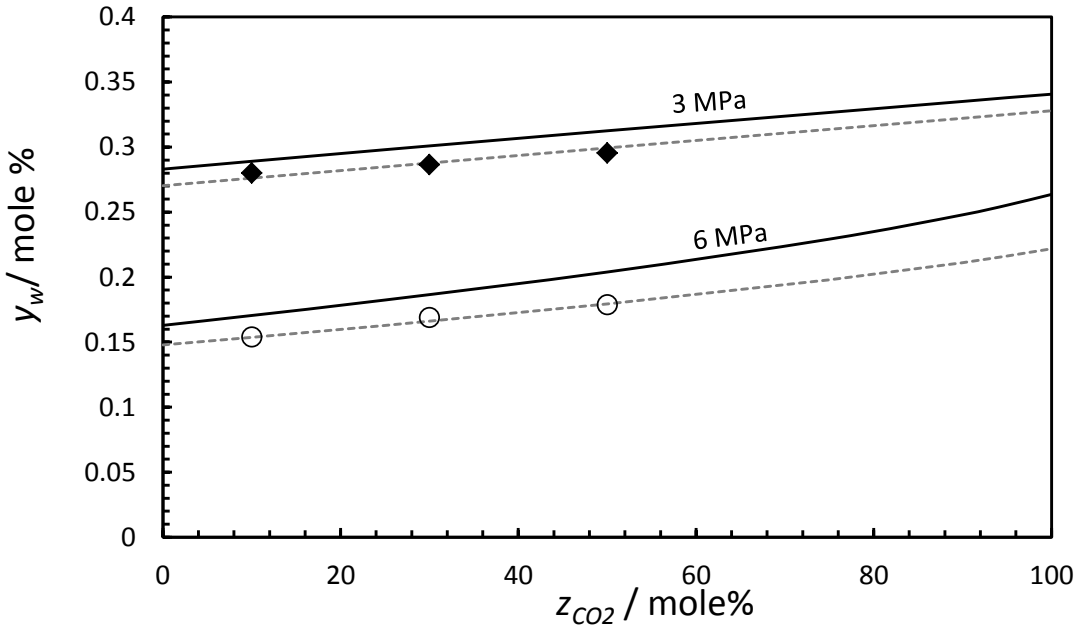


Figure 10: Predicted (Black lines: CPA-PR; Grey dotted lines: CPA-SRK) and experimental water content at 313.15 K – Effect of CO_2 in feed gas

CONCLUSION

There is a lack of water content data for multicomponent systems containing carbon dioxide. New water content of various mixtures composed of CO_2 and CH_4 were determined at conditions equivalent to those encountered in industry. Both PR-EoS and SRK-EoS combined with CPA equations can predict the water content of these mixtures with good accuracy. There is still a lack of data for these systems at higher pressure, in the liquid or supercritical regions as well as in the more complex two-phase region. In the future we are planning to fill these gaps and generate measurements for more complex mixtures including other hydrocarbons.

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