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Measurement and Modeling of Water Content in Low Temperature Hydrate–Methane and Hydrate–Natural Gas Systems

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ABSTRACT: Trace water content creates potential ice or hydrate blocking risks in low temperature gas processing plants. To evaluate such risks, it is important to know the water content of the gas phase in gas mixtures at low temperature. In this work, new experimental data are reported for the water content of methane and a natural gas in equilibrium with hydrates at a pressure range from (3.45 to 13.79) MPa and temperature range from (273.15 to 238.15) K. The measurements have been made with a high-pressure variable volume hydrate cell using tunable diode laser absorption spectroscopy (TDLAS) technology. The cubic-plus-association (CPA) equation of state is used to model the fluid phases, and the hydrate-forming conditions are modeled by the solid solution theory of van der Waals and Platteeuw. Predictions of the model are in good agreement with the experimental data, supporting the reliability of the developed model.

INTRODUCTION

Low temperature technology is widely used in natural gas processing plants. For example, distillation is used to reduce the C_{2+} fraction to meet product specifications; the temperature in such systems could reach about 233 K if the cooling is provided by a single-stage propane refrigerant system. In a natural gas liquefaction plant, the temperature could reach about 110 K in the processes to produce the liquefied natural gas (LNG) product. Water, which is normally present in natural gas streams, has a high potential to form solids such as ice and hydrate at low temperature and bring the risk of blocking heat exchangers. If the heat exchangers are blocked or partially blocked, the efficiency of the whole plant will decrease; in some situations, the whole plant has to be shut down to solve the problem.

Because of the difficulty in accurately measuring trace amounts of water (down to several ppm) in gas mixtures, experimental data on water content in low temperature systems are scarce. In the literature, different test facilities have been used to measure trace amounts of water: Song et al.[1] measured water content in methane gas down to a temperature of 196.35 K using a Panametrics moisture analyzer; Folas et al.[2] measured water content in methane and a synthetic natural gas at temperatures from (253.15 to 293.15) K using a Karl Fischer coulometric titrator, and the same system was studied by Løkken et al.[3] at similar temperature conditions but at different pressures. Løkken also used a chilled mirror dew point analyzer to verify their measurements. Chapoy et al.[4] measured the water content in methane and two natural gas mixtures at temperatures from (250.55 to 288.15) K using tunable diode laser absorption spectroscopy (TDLAS) technology. A review of the different technologies for measuring trace moisture was given by Funke et al.[5]

In this work the TDLAS technology was used to extend the water content measurements of Chapoy et al.[4] to a lower temperature (temperatures down to 238.15 K in this work, and temperatures down to 251.65 K by Chapoy[4]), and a new composition of natural gas mixture was used in this work. The water contents have been measured in methane and a natural gas mixture in equilibrium with hydrates at pressures up to 13.79 MPa.

A thermodynamic model using the well-proven cubic-plus-association equation of state (CPA-EoS) has been employed to model the phase equilibria.[4,6] The thermodynamic model is based on uniformity of fugacity of each component throughout all of the phases. The hydrate phase is modeled by the solid solution theory of van der Waals and Platteeuw[7] using the previously reported Kihara potential parameters.[8] Good agreement between experimental data and predictions is observed, supporting the reliability of the developed model.

EXPERIMENTAL SECTION

Materials. Ultra high pure grade methane (99.995 % pure) and a synthetic natural gas supplied by BOC were used. The gas composition was checked using gas chromatography (GC), and no significant differences were found. The composition of the gas mixture is listed in Table 1. Deionized water was used for hydrate formation during the experiments.

Experimental Bath Apparatus. Figure 1 shows the schematic of the experimental apparatus, which consists of three major parts, an equilibrium variable-volume cell, an ethanol cooling bath, and the TDLAS to measure the water content; this apparatus is similar to that used and described by Chapoy et al.[4]

The equilibrium cell is a piston-type variable volume (maximum effective volume of 300 mL, maximum working pressure 70 MPa) titanium cylindrical pressure vessel with a mixing ball, mounted on a horizontal pivot with associated stand for pneumatic controlled rocking 180 degrees. The cell is surrounded by a jacket through which ethanol is circulated, and the temperature of the ethanol is controlled by a cooling thermostat, which could control the

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Table 1. Synthetic Natural Gas Composition

component	mol %
methane	90.85 (± 0.1)
ethane	6.13 (± 0.05)
propane	1.1 (± 0.05)
i-butane	0.13 (± 0.02)
n-butane	0.11 (± 0.02)
carbon dioxide	0.03 (± 0.005)
nitrogen	1.65 (± 0.05)

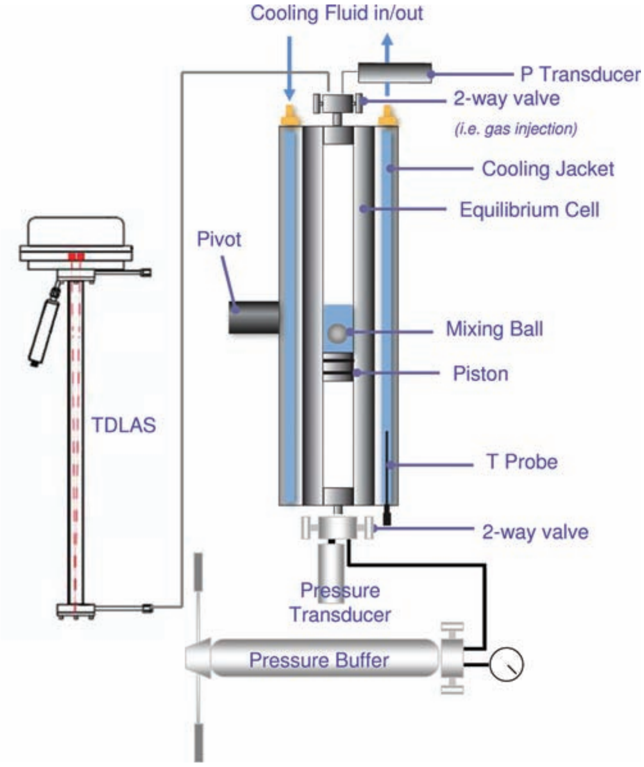

Figure 1. Schematic of the experimental apparatus.

temperature from (205.15 to 323.15) K. The equilibrium cell temperature is measured by a platinum resistance thermometer submerged in the jacket. The accuracy of the measured temperature is ± 0.05 K. The temperature probe was calibrated against a Prema 3040 precision thermometer. A Quartzdyne pressure transducer is connected to the pressure control cell to measure the equilibrium pressure; the accuracy of the measured pressure is ± 3 kPa, and the pressure transducer was checked regularly using a dead weight tester. A gas buffer is used to maintain the equilibrium pressure during measurement of the water content.

The water content is measured by SpectraSensors SS2000 TDLAS with an accuracy of 4 ppm or 2 % of the reading (whichever is greater). TDLAS is a spectroscopic technique that utilizes a diode laser as its light source, which is being used increasingly for trace moisture analysis where sensitivity, specificity, and fast response are required.[5] It works according to the fundamental principle of Beer's law. The principle involves concentrating near-infrared light at a harmonic wavelength of the measured molecule. The molecule will absorb energy from the light and vibrate at very specific frequencies. For moisture analysis, the system has to be tuned to the absorbing wavelength of moisture. The narrow bandwidth of the laser means the analyzer is highly specific, so for applications like natural gas there is no effect from contaminates like methanol, glycol, and condensates. The stated standard error for the SpectraSensorsTM SS2000 TDLAS setup is the greater of 4 ppmv or 2 % of the reading. The sensor was calibrated by SpectraSensors using a NIST traceable reference dewpoint sensor.

Table 2. Experimental and Predicted Water Content, y_w (ppm mole), of Methane in Equilibrium with Hydrates

T/K (± 0.1)	p/MPa (± 0.03)	y_w/ppm exp.	y_w/ppm pred.	dev[a] pred.
272.95	3.45	197.8	197.3	0.5
267.95	3.45	129.5	127.6	1.9
263.15	3.45	83.2	81.2	2.0
257.95	3.45	58.7	50.8	7.9
253.15	3.45	34.9	31.2	3.7
248.15	3.45	21.7	18.8	2.9
243.15	3.45	15.1	11.1	4.0
238.15	3.45	10.5	6.4	4.1
272.95	6.89	105.3	103.6	1.7
267.95	6.89	69.9	67.6	2.3
263.15	6.89	43.8	43.4	0.4
257.95	6.89	29.9	27.5	2.4
253.15	6.89	19.8	17.1	2.7
248.15	6.89	13.0	10.4	2.6
243.15	6.89	9.6	6.3	3.3
238.15	6.89	7.7	3.7	4.0
272.95	10.34	78.5	76.7	1.8
267.95	10.34	51.4	50.6	0.8
263.15	10.34	33.7	32.9	0.8
257.95	10.34	23.8	21.1	2.7
253.15	10.34	16.2	13.3	2.9
248.15	10.34	11.3	8.3	3.0
243.15	10.34	8.6	5.1	3.5
238.15	10.34	7.1	3.1	4.0
272.95	13.79	68.4	65.3	3.1
267.95	13.79	45.2	43.6	1.6
263.15	13.79	29.4	28.7	0.7
257.95	13.79	21.2	18.7	2.5
253.15	13.79	15.5	12.0	3.5
248.15	13.79	10.9	7.6	3.3
243.15	13.79	7.7	4.7	3.0
238.15	13.79	6.9	2.9	4.0

[a] dev = exp. − pred.

The tube between the equilibrium cell and the TDLAS is made of stainless steel with a length about 40 cm, and the tube is kept at 323.15 K to avoid water adsorption to the wall during the measuring. The valve at the outlet of the equilibrium cell is also kept at 323.15K to avoid cooling due to the Joule−Thompson effect.

Experimental Procedures. Similar procedures are used to that in Chapoy et al.[4] About 2 mL of distilled water is introduced into the equilibrium cell. Then the equilibrium cell and the loading line are vacuumed (water will still be inside the equilibrium cell due to its low vapor pressure, and the TDLAS is

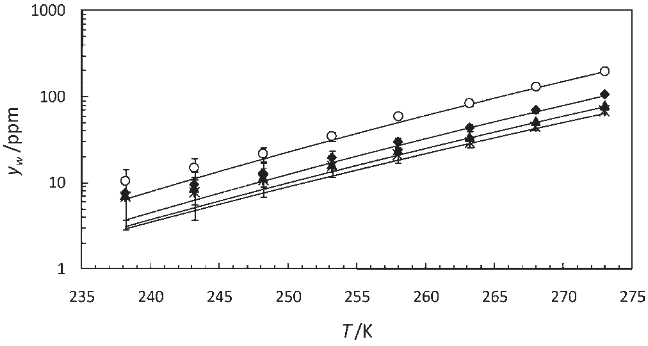

Figure 2. Experimental and predicted water content, y_w (ppm mole), of methane in equilibrium with hydrates (○, 3.45 MPa; ♦, 6.89 MPa; ▲, 10.34 MPa; ∗, 13.79 MPa). Solid lines: model predictions (error bars: ± 4 ppm).

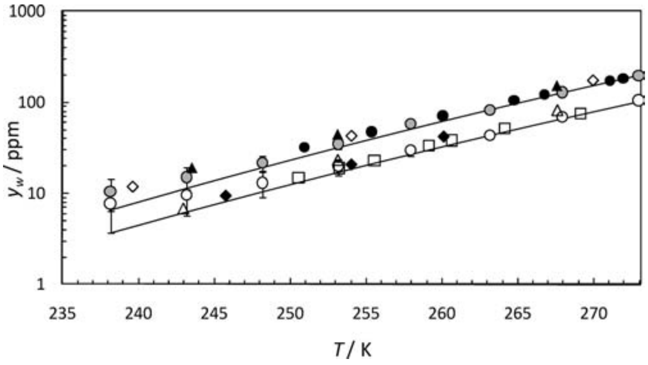

Figure 3. Comparison with literature data on water content in methane−hydrate systems (data at 3.45 MPa: gray circle, this work; ▲, Aoyagi et al.;[9] ◇, Song et al.;[1] ●, Chapoy et al.;[4] data at 6.89 MPa: ○, this work; △, Aoyagi et al.;[9] ♦, Song et al.;[1] □, Chapoy et al.[4]). Solid lines: model predictions (error bars: ± 4 ppm).

Table 3. Experimental and Predicted Water Content, y_w (ppm mole), of the Natural Gas in Equilibrium with Hydrates

		y_w/ppm		dev.
T/K (± 0.1)	p/MPa (± 0.03)	exp. (± 4)	pred.	pred.
273.15	3.45	180.5	174.8	5.7
268.15	3.45	111.8	112.5	−0.7
263.15	3.45	71.5	71.1	0.4
258.15	3.45	47.1	44.2	2.9
253.15	3.45	29.8	26.9	2.9
248.15	3.45	17.6	16.1	1.5
243.15	3.45	9.8	9.4	0.4
238.15	3.45	9.0	5.4	3.6
273.15	6.89	93.9	94.5	−0.6
268.15	6.89	60.6	61.4	−0.8
263.15	6.89	39.5	39.3	0.2
258.15	6.89	27.1	24.8	2.3
253.15	6.89	16.1	15.3	0.8
248.15	6.89	12.1	9.3	2.8
243.15	6.89	7.7	5.6	2.1
273.15	10.34	71.5	72.0	−0.5
268.15	10.34	44.6	47.5	−2.9
263.15	10.34	31.9	30.9	1.0
258.15	10.34	21.2	19.9	1.3
253.15	10.34	12.5	12.6	−0.1
248.15	10.34	10.0	7.9	2.1
243.15	10.34	6.6	4.9	1.7
238.15	10.34	5.6	3.0	2.6
273.15	13.79	63.7	63.0	0.7
268.15	13.79	42.2	42.2	0.0
263.15	13.79	28.8	28.0	0.8
258.15	13.79	19.3	18.3	1.0
253.15	13.79	12.3	11.8	0.5
248.15	13.79	9.6	7.6	2.0
243.15	13.79	6.9	4.8	2.1
238.15	13.79	5.2	3.0	2.2

disconnected temporary for loading), and the desired gas (methane or synthetic natural gas) is introduced to the equilibrium cell. After loading the equilibrium cell, the temperature is set to the desired conditions. The gas buffer is filled with the same working gas, and the equilibrium pressure could be adjusted by injecting or releasing gas inside the pressure control cell.

The temperature and pressure are set well inside gas hydrate equilibrium conditions; sufficient time (about 15 h, tests have been conducted to check the necessary time, for the system in this work to reach equilibrium, it needs no more than 10 h to get equilibrium state) is given to allow the gas and hydrate to achieve equilibrium (stable pressure and water content). The water content in the gas phase is measured by opening the valve to the TDLAS. It normally takes less than 1 min to get a stable reading from the TDLAS. (Due to the atmospheric pressure, air occupies the connecting tube before flowing the sampled gas though it, and at the start of the water measuring, the sampled gas needs to expel the air inside the tube totally.) Meanwhile, the valve connected to the gas buffer is controlled to maintain the pressure in the equilibrium cell during measurements. Equilibrium in the cell is assumed to have been achieved when the same reading is obtained at different time intervals when measuring the water content.

Thermodynamic Modeling and Correlation. Details of the thermodynamic models used in this work can be found elsewhere.[4,6] The thermodynamic model is based on the uniformity of the fugacity of each component throughout all of the phases. The CPA-EoS is used to calculate the fugacities in the fluid phase, and the solid solution theory of van der Waals and Plateeuw[7] is used to calculate the fugacities of the hydrate phase; the potential function is calculated by applying the Kihara model for spherical molecules.

■ RESULTS AND DISCUSSION

Hydrate−Methane Systems. Water content in the gas phase has been measured in the methane−hydrate system for temperatures range from (272.95 to 238.15) K at (3.45, 6.89, 10.34, and 13.79) MPa. The experimental data and the comparison with calculation from the model are given in Table 2 and Figure 2. Below 40 ppm of the measured water content, the maximum absolute deviation is less than 4 ppm and within the error band of the experimental equipment.

At (3.45 and 6.89) MPa, the results are compared to literature data[1,4,9] in Figure 3. The experimental data in this work agree quite well with literature data at 3.45 MPa. However, at 6.89 MPa, the experimental data are several ppm higher than the

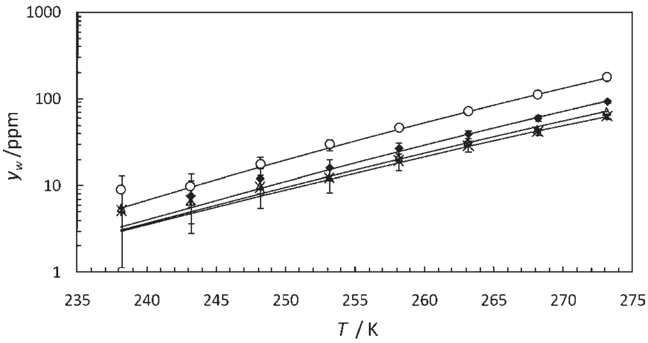

Figure 4. Experimental and predicted water content, y_w (ppm mole), of natural gas in equilibrium with hydrates (○, 3.45 MPa; ♦, 6.89 MPa; ▲, 10.34 MPa; ∗, 13.79 MPa). Solid lines: model predictions (error bars: ± 4 ppm).

available literature data and the model predictions at (243.15 and 238.15) K.

Hydrate−Natural Gas Systems. Water content in the gas phase has been measured in the natural gas−hydrate systems for temperatures ranging from (238.15 to 273.15) K at (3.45, 6.89, 10.34, and 13.79) MPa. The experimental data and the model predictions are given in Table 3 and Figure 4. Again, below 40 ppm of the measured water content, the absolute deviation is less than 4 ppm and within the reported accuracy of the experimental equipment.

Discussion. The above results show that, although the experimental data and model predictions are in quite satisfactory agreement, for systems in the low temperature area (lower than 250 K), relatively high deviations are observed. This could be explained as the following:

On the experimental side, an accurate measurement of trace amount water in gas (< 50 ppm) is very challenging due to the high polarity of water, which makes it extremely adsorptive. Besides the uncertainty in the moisture analyzer itself (such as TDLAS and chilled mirror), some other uncertainty sources exist, for example, the adsorption of the water on the connecting tubes. The design of the whole experimental measurement system (such as equilibrium cell, connecting tubes, choices of moisture analyzers) at low temperature is very demanding and requires accumulated experiences.

On the modeling side, the model of CPA-EoS for the fluid phases combined with the solid solution theory of van der Waals and Platteeuw for hydrates shows good capability in correlating and predicting the hydrate behaviors,[2,4,6] but because experimental data in the low temperature area are limited, more data are still needed for systematically tuning the parameters for prediction hydrate behaviors at low temperature conditions.

■ CONCLUSIONS

Measurements of water content in the gas phase in methane−hydrate and natural gas−hydrate systems from (238.15 to 273.15) K have been carried out using a TDLAS moisture analyzer. Experimental data in the methane−hydrate systems at (3.45 and 6.89) MPa are in good agreement with literature data. All of the experimental data are compared to the model prediction results using the CPA-EoS, and predictions of the model are in good agreement with the experimental data. Below 40 ppm of the measured water content, the maximum absolute deviation is less than 4 ppm and within the reported accuracy of the experimental measurements.

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