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Development of Experimental Techniques, Equipment and Thermodynamic Modelling for Investigating Systems with High CO₂ Concentrations

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Abstract

In this communication we present experimental techniques, equipment and thermodynamic modelling for investigating systems with high CO₂ concentrations, including gas reservoirs with high CO₂ content and/or CO₂-rich systems from capture processes. The experimental equipment consists of high pressure (1,000 bar) equilibrium cells operating over a wide temperature (-80 to 200 °C), GC, chilled mirror and Laser Hygrometer for water content measurements. A thermodynamic model based on Cubic-Plus-Association (CPA) equation of state has been used in modelling phase behaviour of CO₂-rich systems. The hydrate-forming conditions are modelled by the solid solution theory of van der Waals and Platteeuw. The reliability of the thermodynamic model was evaluated using vapour - liquid equilibrium data.

CO₂ is a partially polar compound present in many hydrocarbon reservoirs. Its concentration in some hydrocarbon reservoirs is very high, demanding accurate experimental data and thermodynamic modelling. Another important application is modelling phase behaviour and properties of CO₂-rich systems from capture processes for transportation and storage.

The results show that the developed model, combined with a reliable database, is a powerful tool for modelling complex systems. The resulting thermodynamic model is able to conduct various calculations, including; gas solubilities in aqueous and non-aqueous phases, water content in CO₂-rich systems, hydrate stability zone in the presence of methanol and/or glycols, dehydration requirements for preventing hydrate formation in gas or CO₂-rich phase, and a large number of other calculations. The results of the predictions are compared with experimental data, demonstrating reliability of the techniques developed in this work.

CO₂ coming from capture processes is generally not pure and can contain impurities such as water. In a typical gas sweetening unit, the acid gas stream will be saturated with water. The presence of water can result in ice and/or gas hydrate formation at low temperature conditions and cause blockage.

Introduction

It is now estimated that a third of the proven natural gas reserve are sour and with increasing energy demand, development of these reserves are being given new attention. For example, in Malaysia alone over 13 Tscf of hydrocarbon gas remains undeveloped in high CO₂ content fields, where the CO₂ content is even higher than 70 mole% in some gas fields (Darman and Harum, 2006). During production, sour hydrocarbon fluids are normally saturated with water. Consequently during production, transportation and processing, the unprocessed well gas streams coming from a production field can contain water, light hydrocarbon molecules (methane, ethane, propane etc.) and some hydrogen sulphide and carbon dioxide. Given the correct temperature and pressure conditions, this can lead to hydrate formation during the transport through pipelines. The formation of gas hydrates in gas and oil sub-sea pipelines often results in their blockage and shutdown. Gas hydrates could form in numerous hydrocarbon production and processing operations, causing serious operational and safety concerns, therefore making it essential to gain a better understanding of the behaviour of gas hydrate.

However limited data are available on the phase and hydrate behaviors of CO₂-rich systems to validate existing thermodynamic models. Therefore the applicability of the existing models and their uncertainties can lead to over or

undersized designs. In this communication we present experimental techniques, equipment and thermodynamic modelling for investigating systems with high CO₂ concentrations, including gas reservoirs with high CO₂ content and/or CO₂-rich systems from capture processes.

The thermodynamic modelling is based on the Cubic-Plus-Association Equation of State (CPA EoS) for fugacity calculations in all phases, which have been used for modelling all fluid phases with previously reported binary interaction parameters (Haghighi *et al.*, 2011). The hydrate-forming conditions were modelled by the solid solution theory of van der Waals and Platteeuw (van der Waals and Platteeuw, 1959). Langmuir constants have been calculated using Kihara potential (Kihara, 1953).

In this communication, some examples of experimental measurements for CO₂-rich systems are reported. New experimental measurements are presented on the locus of incipient hydrate-liquid water-vapour (H-L_W-V) and hydrate – liquid water – CO₂ rich liquid (H-L_W-L) curves for a CO₂-rich system with water over a wide range pressure and temperature. New experimental measurements are reported for the water content of CO₂ in equilibrium with hydrates at 137.9 bar and used for evaluation of the model. Bubble point measurements were carried out for mixtures of hydrogen (2 mole%) and CO₂ (98 mole%) from -20 °C to 30 °C. The results of the predictions are compared with the experimental data, demonstrating reliability of the techniques developed in this work.

Experimental Equipment and Methods

Materials

Ultra high purity grade carbon dioxide (99.995% pure), hydrogen (99.995% pure) and a multicomponent natural gas supplied by BOC were used. Deionised water was used in all tests. The CO₂ and H₂ mixture (98 mol% CO₂ / 2 mol% H₂) was prepared by combining pure components gravimetrically. The high CO₂ natural gas was prepared by combining pure CO₂ with natural gas, the composition of the mixture is given in Table 1.

Table – 1. Composition of carbon dioxide rich test gas

Component	Mole%
Methane	6.053
Ethane	0.383
Propane	0.107
i-Butane	0.012
n-Butane	0.021
i-Pentane	0.004
Carbon Dioxide	93.266
Nitrogen	0.147
n-Pentane	0.004
n-Hexane	0.003

Experimental Equipment

Vapour-Liquid Apparatus, The apparatus (Figure 1) is based on a static-analytic method with fluid phase sampling. The set-up is comprised of a titanium cell with two windows and surrounded by an integral water jacket (Figure 1). The cell volume is about 150 ml and it can be operated up to 200 bar between -30 and 100 °C. The equilibrium cell is held in a jacket heated or cooled by a constant temperature liquid bath. The temperature of the cell is controlled by circulating coolant from a cryostat within the jacket surrounding the cell.

The cryostat is capable of maintaining the cell temperature to within 0.05 °C. A platinum resistance probe monitors the temperature and is connected directly to a computer for direct data acquisition. The pressure is measured by means of a DRUCK pressure transducer mounted directly on the cell and connected to the same data acquisition unit. This system allows real time readings and storage of temperatures and pressures throughout the different isothermal runs. To achieve a fast thermodynamic equilibrium and to provide a good mixing of the fluids, a high pressure magnetic stirrer (Top Industrie S.A.) was used to agitate the test fluids at around 1,000 RPM with a Rushton type impeller.

The cell is fitted with a moveable capillary sampler. A schematic of the set-up is shown in Figure 1. The sampling is carried out using the capillary sampler, which is connected to the top of the cell through 0.1 mm internal diameter capillary tube. Combining the visual capabilities with the moveable capillary sampler allows for small, microlitre samples of any chosen phase to be taken and passed to a GC for analysis as shown in the schematic flow diagram for the set-up in Figure 2. The withdrawn samples are swept into a Varian 3800 gas chromatograph for analysis through heated lines (T=180 °C) to avoid any condensation (Figure 2). The capillary inlet of the sampler can be displaced directly into the vapour/liquid HC phase and the outlet of the capillary is closed by a movable micro-stem operated by a magnet. When the magnet is energised it opens the outlet of the capillary, then the sample can flow inside the expansion room which is flushed with the carrier gas. The carrier gas sweeps the sample to the GC column for analysis. The sampler allows direct sampling at the working pressure without

disturbing the cell equilibrium due to the relatively small size of the sample. The mass of samples can be adjusted continuously from 0.01 to several mg thanks to an electronic timer. The expansion room of the sampler is heated independently from the equilibrium cell to allow the samples to remain in vapour state and/or vaporize a liquid sample. The GC is equipped with a Flame Ionisation Detector (FID) and a Thermal Conductivity Detector (TCD).

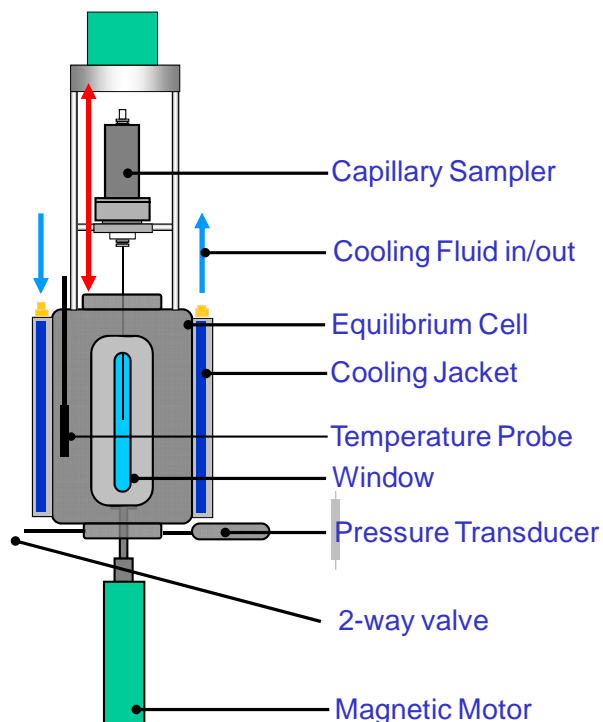


Figure – 1. Schematic of the VLE cell.

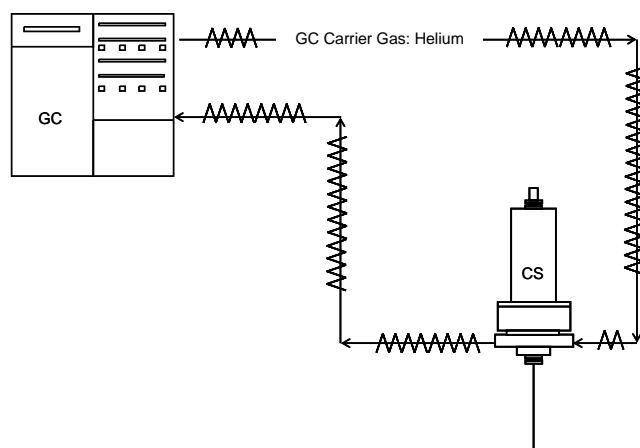


Figure – 2. Flow diagram of apparatus for on-line compositional analysis (GC: Gas Chromatograph, CS: Capillary sampler).

Bubble point Apparatus, The experimental set-up used consists of an equilibrium cell, cryostat, rocking/pivot mechanism, and temperature/pressure recording equipment controlled by a PC (Figure 3). The equilibrium cell is a piston-type variable volume (maximum effective volume of 300 ml), titanium cylindrical pressure vessel with mixing ball, mounted on a horizontal pivot with associated stand for pneumatic control and rocking through 180 degrees. Rocking of the cell, and the subsequent movement of the mixing ball within it, ensures adequate mixing of the cell fluids. For the tests reported here, the cell was rocked through 180 degrees at a rate of 8 times per minute. Cell volume, hence pressure, can be adjusted by injecting/withdrawal of liquid behind the moving piston.

The rig has a working temperature range of -80 to 50 °C, with a maximum operating pressure of 700 bar. System temperature is controlled by circulating coolant from a cryostat within a jacket surrounding the cell. The cryostat is capable of maintaining the cell temperature stability to within better than 0.05 °C. To achieve good temperature stability, the jacket is insulated with polystyrene board, while connecting pipe work is covered with plastic foam. The temperature is measured and monitored by means of a PRT (Platinum Resistance Thermometers) located within the cooling jacket of the cell, which is calibrated regularly against a Prema 3040 precision thermometer. Cell temperature can be measured with an accuracy of ± 0.05 °C. A Quartzdyne pressure transducer with an accuracy of ± 0.08 bar was used to monitor pressure. Temperature and Pressure are monitored and recorded by the PC through an RS 232 serial port.

Hydrate Apparatus, Clathrate dissociation PT conditions are determined by standard constant volume cell isochoric equilibrium step-heating techniques. This method, which is based upon the direct detection (from pressure) of bulk density changes occurring during phase transitions, produces very reliable, repeatable phase equilibrium measurements. The experimental set-up used consists of an equilibrium cell, cryostat, magnetic mixer, and temperature/pressure recording equipment controlled by a PC (Figure 4). The phase equilibrium is achieved in a cylindrical cell made of Hastelloy C276. The cell volume is about 80 ml and it can be operated up to 400 bar between -77 and 50 °C. The equilibrium cell is immersed in a constant temperature liquid bath (Lauda Proline AP1290). The cryostat is capable of maintaining the cell temperature to within 0.02 °C. A platinum resistance probe monitors the temperature and is connected directly to a computer for direct acquisition. The pressure is measured by means of a Quartzdyne pressure transducer mounted directly on the cell and connected to the same data acquisition unit. This system allows real time readings and storage of temperatures and pressures

throughout the different isothermal runs. To achieve a fast thermodynamic equilibrium and to provide a good mixing of the fluids, a high pressure magnetic stirrer (Top Industrie S.A – wetted parts made of Hastelloy C276) was used to agitate the test fluids at around 1,000 RPM with a Rushton type impeller.

The calibration of the pressure transducer was checked regularly using a dead weight tester. The pressure transducer is accurate to less than ± 0.05 bar. The temperature probe was calibrated against a Prema 3040 precision thermometer. The uncertainty on temperature measurements is estimated to be better than ± 0.1 °C.

Water Content Apparatus, The equipment is comprised of an equilibrium cell and a set-up for measuring the water content of equilibrated fluids in the cell. The equilibrium cell was the same as that used for bubble point measurements (Figure 3). The moisture content set-up is comprised of a heated line, a chilled mirror hygrometer and a flow meter. The hygrometer is an EdgeTech DewMaster, and can measure dew/frost point at temperatures from -75 to 100 °C, at pressures up to 20 bar, with a resolution of 0.1 °C and stated accuracy of ± 0.2 °C.

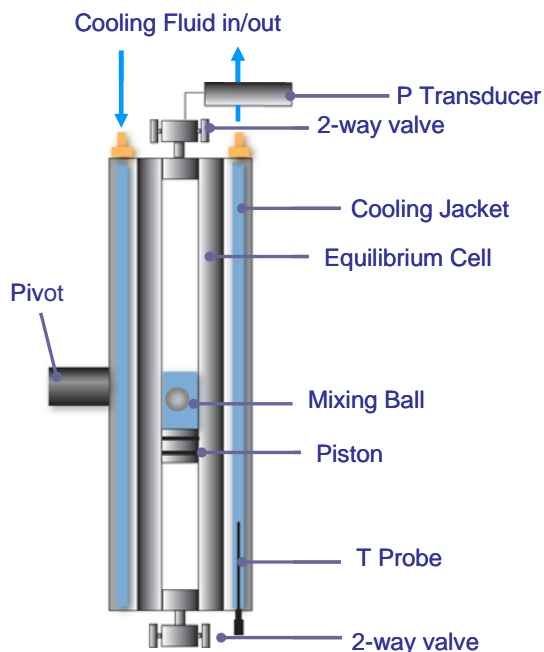


Figure – 3. Schematic illustration of equilibrium rig used for bubble point measurements

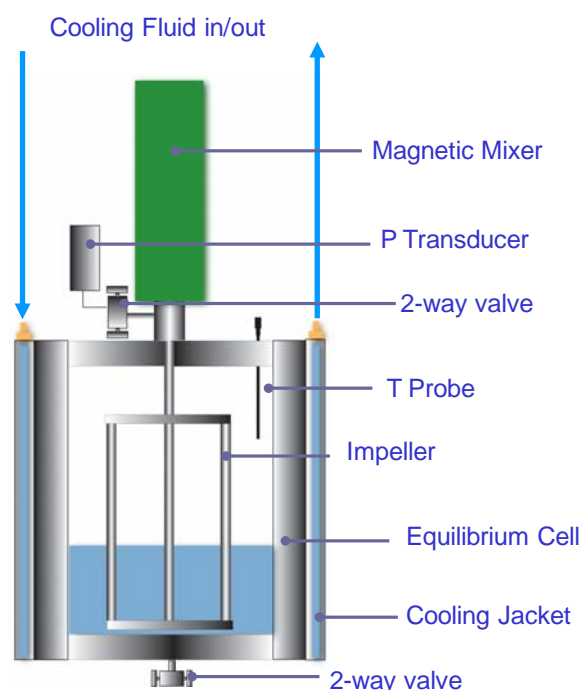


Figure – 4. Schematic illustration of equilibrium rig used for Clathrate dissociation measurements

Methods

- A typical test to determine the bubble point of the CO₂/H₂ mixture is as follows:
The cell was charged with the test sample and set to the desired temperature for the measurement. The sample volume was then reduced by pumping liquid into the cell (behind the moving piston), at the opposite end to the sample. By this means the sample pressure was increased such that the sample was at a pressure significantly higher than the expected bubble point pressure. The cell was then rocked to mix the contents and ensure equilibrium. The sample volume was then increased step-wise by removing measured quantities of the pumped liquid behind the piston. At each step mixing was continued until equilibrium was achieved, indicated by a constant pressure. The stabilized equilibrium pressures and change in sample volumes were plotted and the bubble point was indicated by a sharp change in the pressure versus volume plot.

- A typical test to determine the hydrate dissociation of a gas/liquid phase in equilibrium with liquid water is as follows:
Dissociation point measurements are made using a method known as step-heating. This method has been previously demonstrated as being considerably more reliable and repeatable than conventional continuous heating and/or visual techniques (Tohidi et al., 2000). A typical test to determine the hydrate dissociation point of a system is as follows: the equilibrium cell (Figure 4) is first cleaned and vacuumed, the cell then is charged with the test components at desired pressure. Three quarter of the volume of the cell (60 cm³) is initially preloaded with the solution then the gas is injected. The system

temperature is set to a point well outside the expected hydrate stability zone for the system under study. The temperature is then lowered to form hydrates, growth being detected by an associated drop in the cell pressure (as gas becomes trapped in hydrate structures), and/or by means of visual observation. The cell temperature is then raised step-wise (usually 0.5 °C intervals), allowing enough time at each temperature step for equilibrium to be reached. At temperatures below the point of complete dissociation of hydrates, gas is released from decomposing hydrates, giving a marked rise in the cell pressure with each temperature step. However, once the cell temperature has passed the final hydrate dissociation point, and all clathrates have disappeared from the system, a further rise in the temperature will result only in a relatively small pressure rise due to thermal expansion of the fluids. This process results in two traces with very different slopes on a pressure versus temperature (P/T) plot, one before and one after the dissociation point. The point where these two traces intersect (i.e., an abrupt change in the slope of the P/T plot) is taken as the dissociation point.

- A typical test to determine the water content of a gas/liquid phase in equilibrium with hydrate is as follows:

At the start of the test around 10 ml of 0.1 mm glass beads are placed in a cup shaped depression at the top of the piston (Figure 3). 5 ml of deionised water was then mixed with the glass beads. The glass beads have been found to aid in formation and dissociation of hydrates in previous work, helping to achieve equilibrium. The cell was then closed and the temperature reduced to -10 °C and evacuated before injecting CO₂. The cell temperature and pressure were then adjusted to achieve the desired test conditions. The cell temperature was then cycled to lower and higher temperatures than the set point over at least 20 hours. This was confirmed as being sufficient time for equilibrium to be achieved by conducting water content measurements over a number of days in one test. It was found that the water content remained stable.

The key to getting a reliable and stable water content measurement was to achieve a steady flow rate of equilibrated sample through the measurement set-up. The valve at the top of the cell (Figure 3) was sufficiently opened to achieve a flow rate of between 0.5 and 1 litre per minute through the hygrometer at the same time nitrogen was introduced into the base of the cell (below the moving piston) in order to maintain the pressure constant. The water content reading from the hygrometer was then monitored until it was stable for at least 10 minutes. This was then taken as the moisture content of the equilibrated fluid passing from the cell. During sampling the heated line was maintained at a temperature of 195 °C. The repeatability was found to be good, within the estimated experimental accuracy of ±5 ppm mole or 4% of the reading, whichever is the greater.

Thermodynamic Modelling

A general phase equilibrium model based on the uniformity of component fugacities in all phases is used to predict the phase behaviour of CO₂ rich systems. A description of the thermodynamic model can be found elsewhere (Haghighi *et al.*, 2011). In summary, the statistical thermodynamics model uses the Cubic Plus Association Equation of State (CPA EoS) for fugacity calculations in all fluid phases. The CPA EoS combines the well known Soave-Redlich-Kwong (SRK) EoS (Soave, 1972) for describing the physical interactions with the Wertheim's first-order perturbation theory (1987), which can be applied to different types of hydrogen-bonding compounds. The CPA-EoS in terms of pressure P is given by:

$$P = \frac{RT}{V_m - b} - \frac{a(T)}{V_m(V_m + b)} - \frac{1}{2} \frac{RT}{V_m} \left(1 + \rho \frac{\partial \ln(g)}{\partial \rho} \right) \sum_i x_i \sum_{A_i} (1 - X^{A_i})$$

where the physical term is that of the SRK EoS and the association term is taken from the SAFT EoS, x_i is the mole fraction of the component i and is the mole fraction of molecule i not bonded to the site A which is rigorously related to the association strength. Both depend on the structure of the molecule and the number and type of sites

The hydrate phase is modelled using the solid solution theory of van der Waals and Platteeuw (van der Waals and Platteeuw, 1959), as developed by Parrish and Prausnitz (Parrish and Prausnitz, 1972). The equation recommended by Holder *et al.* (Holder *et al.*, 1980) is used to calculate the heat capacity difference between the empty hydrate lattice and pure liquid water. The Kihara model for spherical molecules is applied to calculate the potential function for compounds forming hydrate phases (Kihara, 1953).

Validation

The model has been previously evaluated for the carbon dioxide –water system (Chapoy *et al.*, 2004). The main conclusions from this work are that the resulting thermodynamic model has been used for predicting CO₂ solubility in water, as well as water content of CO₂-rich phase and finally CO₂ hydrate phase equilibria over a wide range of temperature and pressure conditions and the predictions were found to be in good agreement with the experimental data, demonstrating the reliability of the model used in this work (see Figure 5 for CO₂ hydrate phase equilibria).

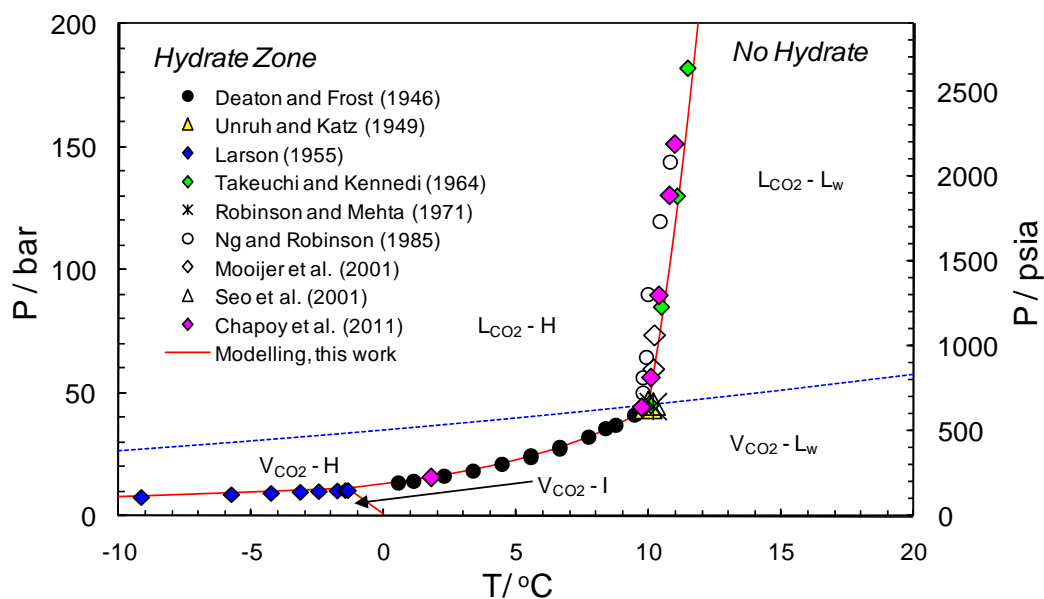


Figure – 5. Hydrate stability of CO₂ in the presence distilled water – Comparisons with experimental data (Chapoy *et al.*, 2011)

Results

Hydrate stability zone of the synthetic CO₂-rich natural gas

Measurement of the locus of incipient hydrate-liquid water-vapour (H-L_w-V) and hydrate – liquid water – CO₂ rich liquid (H-L_w-L) curves for a CO₂-rich system with water were carried out. The experimental data along with the calculated CO₂ and CO₂-rich natural gas hydrate dissociation conditions in the presence of water up to about 270 bar are presented in Figure 6 and listed in Table 2. The model predictions are seen to agree well with the experimental data. It should be noted that these data could be regarded as independent as hydrate dissociation data were not used in the development and optimisation of the thermodynamic model.

Table – 2. Experimental hydrate dissociation points for carbon dioxide rich gas mixture (Table 1) with deionised water

T/°C ±0.1	P/ bar ±0.04	P/ psia ±0.6	Phases present
4.2	20.0	290	Lw-V-H
9.4	37.0	537	Lw-V-H
11.0	50.6	734	Lw-V-H
12.5	84.8	1230	Lw-L-H
13.5	165.9	2406	Lw-L-H
14.9	268.4	3893	Lw-L-H

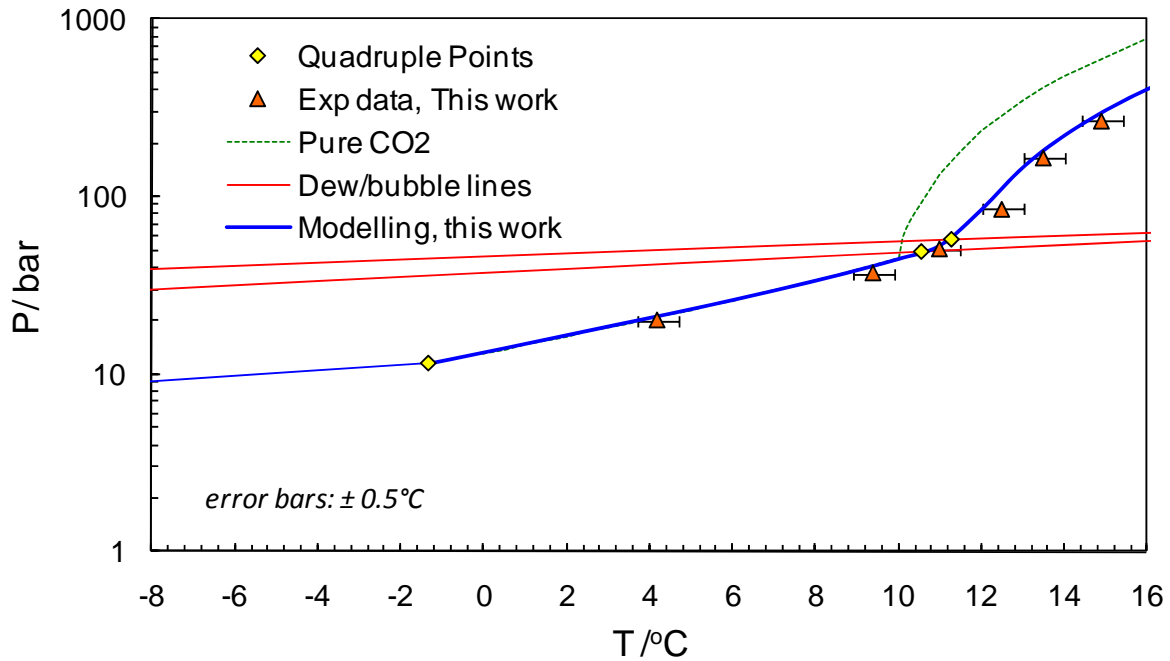


Figure – 6. Predicted and experimental hydrate stability of CO₂-rich natural gas in the presence distilled water – comparisons with experimental data and pure CO₂

Water content in liquid CO₂ in equilibrium with hydrates

The experimental data on water contents for CO₂ in equilibrium with hydrates at 137.9 bar over a wide range of temperature from -20 to 4 °C have been generated in this work and are presented in Figure 7. These data have been measured to compare with the data set reported by Song and Kobayashi (Song and Kobayashi, 1987) at the same pressure.

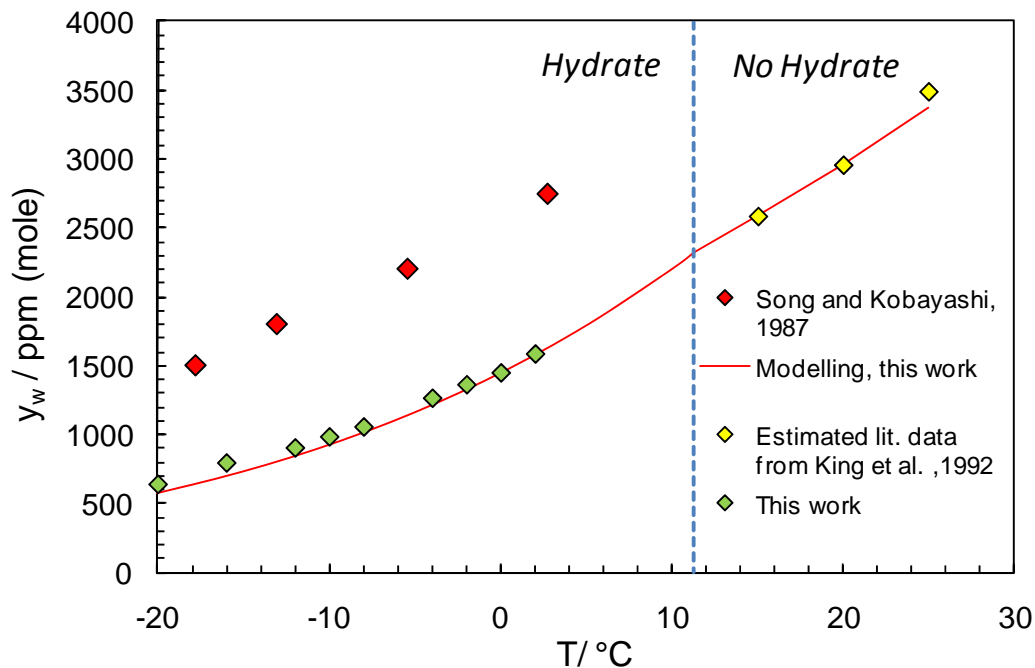


Figure – 7. Plot showing experimental water content data and predictions for the water content of CO₂ in equilibrium with hydrates at 137.9 bar and different temperatures along with data from Song and Kobayashi, 1987. The dashed blue lines delimit the hydrate stability zone.

Predictions using the previously described model, along with the experimental data from this work and from Song and Kobayashi (Song and Kobayashi, 1987) are presented in Figure 7. As can be seen from Figure 7 the experimental from this

work and predictions are in good agreement (AAD \approx 5%). The predictions of the model are also in good agreement with the available data just outside the hydrate stability zone. However, as can be seen from the figure, the deviations for the data from Song and Kobayashi (Song and Kobayashi, 1987) are significantly higher. A complete discussion on this system can be found in Haghighi *et al.*, 2011

Bubble point measurements of the CO₂-H₂ mixture

Bubble point measurements were carried out for the carbon dioxide – hydrogen mixture from -20 °C to 25 °C. A full discussion on the results was detailed in Chapoy *et al.*, 2011. The results are listed in Table 3 and plotted in Figure 8. Our experimental data are in good agreement with the work of Kaminishi and Toriumi (1966), Barrick *et al.* (1966) and Spano *et al.* (1968), however, the data of Tsang and Streett (1981) in this temperature range are not in agreement with our work and the other available literature data.

Table – 3. Bubble point of the CO₂ (98 mole%) – H₂ (2 mole%) system

T / °C	P / bar	P / psia
-20	61.2	887.6
-10	62.4	905.0
-5	63.4	919.5
0	64.0	928.2
10	70.3	1019.6
20	77.0	1116.8
25	79.2	1148.7

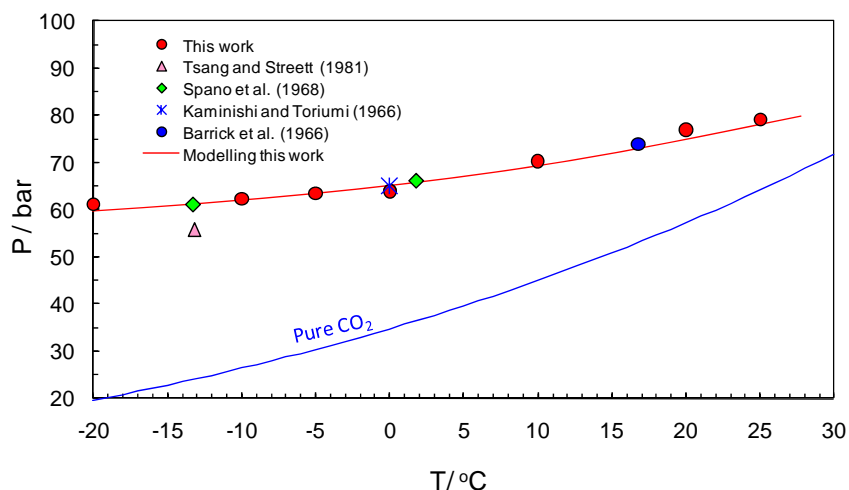


Figure –8. Bubble point of the CO₂ (98 mole%) – H₂ (2 mole%) system. The pure CO₂ vapour pressure line has been added for comparison only.

Conclusions

The principal objective of this work was to present a wide range of experimental techniques, equipment and thermodynamic modelling for investigating systems with high CO₂ concentrations. Some of the experiments carried out were:

- Hydrate stability of a saturated CO₂-rich test gas
- Phase behaviour of CO₂-rich systems
- CO₂ hydrate formation in undersaturated conditions

The predictions of the developed model are compared against these independent experimental data for a wide range of scenarios and over a wide range of temperature and pressure. A good agreement between predictions and experimental data is observed, demonstrating the reliability of the developed model.

Knowledge of the phase behaviour and properties of CO₂-rich systems is currently of great importance for both the energy industry and ultimately the environment and it is therefore planned to extend this work to different systems and to a wider range of temperature/pressure to generate new experimental data (including viscosity, density, IFT) and further validate/improve the developed thermodynamic model.

Acknowledgments

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