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Accurate measurements of CO₂ rich mixture phase equilibria relevant for CCS transport and conditioning

H. G. Jacob Stang^a, Sigurd W. Løvseth^{a,*}, Sigmund Ø. Størset^a, Bjarne Malvik^a, Håvard Rekstad^{a,b}

^aSINTEF Energy Research, 7465 Trondheim, Norway

^bNorwegian University of Science and Technology, 7491 Trondheim, Norway

Abstract

This paper describes the experimental rig that has been constructed for the measurements of phase equilibrium of CO₂-rich mixtures under relevant conditions for CCS transport and conditioning. The rig is believed to have an accuracy better than 10 mK in temperature and 0.10 % in pressure. Measurements will be performed using the analytical technique, which means that composition of all phases will be measured. In the years to come, a comprehensive experimental plan will be executed, resulting in new and accurate phase equilibrium data relevant for CCS conditioning and transport.

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1. Introduction

As described in a separate submission to GHGT-11 [1], SINTEF Energy Research, Ruhr-Universität Bochum, and NTNU are collaborating on a project called CO₂Mix designed to experimentally determine selected thermo-physical properties of CO₂-mixtures relevant for CCS transport and conditioning.

One of the key properties that will be investigated is the phase state at equilibrium. Knowing the exact phase state as a function of mixture composition, temperature, and pressure is important in order to design process equipment and systems for conditioning and transport, and to specify the maximum allowed

* Corresponding author. Tel.: +47 7353972; fax:.
E-mail address: Sigurd.W.Lovseth@sintef.no.

concentration of different impurities. For instance, in order to avoid corrosion, it is important to be aware of the conditions under which free water will be present. In addition, accurate phase behavior knowledge is important in order to make robust routines for start-up and shut-down of the systems, as well as for the understanding of an uncontrolled depressurization, i.e. leakage. In order to set up reliable thermodynamic models that describe the equilibrium phase state, accurate experimental data is required. Large gaps in these data have been identified for a number of relevant conditions and mixtures [2].

This paper describes the experimental rig that is constructed for the measurements of phase equilibrium of CO₂-rich mixtures under relevant conditions. The set-up was installed in August this year in the lab of SINTEF Energy Research in Norway. In the years to come, a comprehensive experimental plan will be executed, resulting in new and accurate phase equilibrium data relevant for CCS conditioning and transport.

The primary objective for the measurements will be to provide vapor-liquid equilibrium data for binary mixtures. However, the rig will also be suitable for testing multicomponent mixtures and to study other types of phase equilibria, for instance with two liquid phases present (VLLE). In addition, we aim to equip the rig with instrumentation that can detect and possibly determine the composition of solid and hydrate phases.

2. Rig overview

The rig is designed to measure phase equilibria of selected CO₂ mixtures and conditions relevant for conditioning and transport in CCS [1]. The measurement range in temperature and pressure is between -60 and 150 °C and 3 and 200 bar, respectively. The rig is intended to be used to measure phase equilibria of CO₂ mixed with typical impurities found in CCS up to a concentration of 50 %, but in principle most mixtures with phase equilibria that falls into our temperature and pressure range can be measured, including corrosive, toxic, and explosive gases.

The phase equilibrium will be measured using an analytical method [3], i.e. the composition of all phases will be measured rather than depending on precise a priori knowledge of the overall composition. The core component of the rig is the 0.1 l cell, in which the different components will be injected and the phase equilibrium will be established.

The pressure is measured using an array of four precise and temperature controlled pressure transmitters. Temperature is controlled by submerging the cell into a highly precise thermostatic bath. The aim is to have a combined accuracy and uniformity better than 10 mK in temperature and 0.10 % in pressure.

To be able to extract both gas and liquid samples from the cell, two samplers will be used; one located near the top of the cell for the gas phase and one vertical movable to be used for liquid phases. Once extracted, the samples will be transferred to a gas chromatograph (GC) by a carrier gas, separated in the GC column and detected using one of several possible detectors.

During the design of the experimental rig particular care has been made in material selection and design, such that the rig can be used for corrosive mixtures at elevated pressures and temperatures. The rig and the surrounding infrastructure will be qualified for use with explosive and toxic components. The setup should thus be well prepared for experiments with the relevant gas mixtures in CCS.

3. The VLE cell

The phase equilibrium cell is the core of the phase equilibrium rig and consists of a sapphire cylinder which is placed between two titanium flanges, as seen in Fig. 1. The cell volume is approximately 100 mL. Integrated into the upper flange there are three valves meant for CO₂, other gases, and N₂/ drain /

flushing, respectively. In addition, the cell is connected to two sampling valves and a pressure measurement array through the upper flange. Connected to the upper flange, there is also a plate bellows of 1 ml for pressure compensation inside the cell which is controlled by the pressure of an external N_2 circuit. In the bottom flange, there is one inlet / outlet for water and evacuation of the cell. In both the upper and lower flange, there are pockets with 25Ω standard platinum resistance thermometers (SPRTs) for precise temperature measurements. A magnetic stirrer is used in order for the content of the cell to reach equilibrium faster after a change of either composition, pressure, or temperature has taken place. .

The rig is equipped with a real time borescope, allowing for optical access to the VLE cell and its contents while it is submerged in the thermostatic bath. This gives the opportunity to keep experiments under surveillance, thus providing information on contents (gas, liquid, dry ice etc.) and whether equilibrium is established inside the cell. Also, as described in Section 6.2 Sampling, optical access ensures correct positioning of the liquid sampler, which is critical for analysis of all phases present during equilibrium. An image of liquid-phase equilibrium as well as the establishment of the CO_2 triple point is provided in Fig. 2.

The project has also put effort into investigating possible spectroscopic techniques for composition analysis, giving the opportunity of in-situ analysis without the need of sampling. As a consequence, the cell's flanges are equipped with threaded holes for possible later attachment of optics, as seen in Fig. 1.



Fig. 1: The CO_2 Mix VLE cell.

4. Cell injection

A key feature of the phase equilibrium cell is the ability to independently inject CO_2 , other gas(es) (impurity), and liquid water using three highly accurate syringe pumps. Hence, it is possible to change the total composition and pressure inside the cell independently between to measurement points in a series, enabling the adjustment of the liquid level. Both the volume and the pressure of the pumps can be accurately controlled. The syringe pump that is normally used for impurities can also be employed for

calibration of the setup by injecting a reference mixture of known composition into the cell. Hence, this pump can be heated to 150 °C such that the composition of the mixture injected into the cell is known even for reference mixtures with relative high temperature dew point curves.

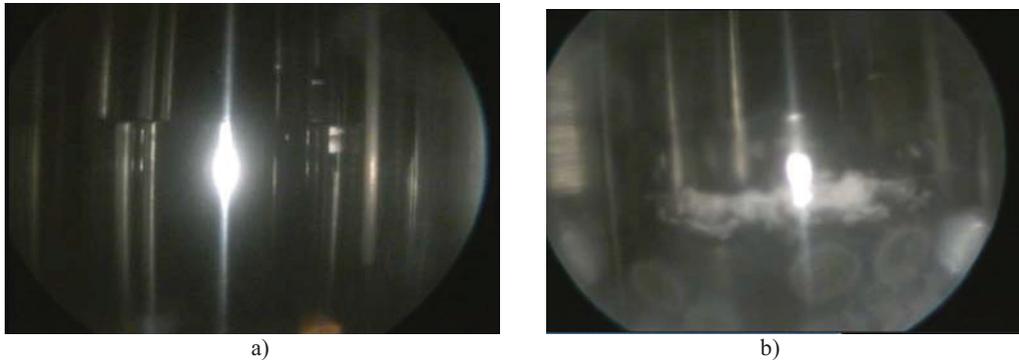


Fig. 2: Images from of the cell submerged into a thermostatic bath using a borescope. a) Vapor-liquid equilibrium. b) Video framegrab of establishment of CO₂ triple point

5. Temperature measurements and control

The temperature control is achieved by submerging the equilibrium cell in thermostatic calibration baths from Hart Scientific. HS 7080 covers the region up to 95 °C using ethanol or water as bath fluids, where as HS 6020 are suitable for higher temperatures using transparent silicone oils such that visual inspection of the cell will still be possible. The hot bath has a specified uniformity of 4 mK at 100 °C and 12 mK at 300 °C, but not specification at 150 °C. Otherwise, both baths have a specified temperature uniformity and stability well below 10 mK. To make sure that the performance is not impaired by the presence of the cell suspended into the bath, fluid temperature uniformity and stability has systematically been measured at 18 points around the cell at different temperatures.

Temperature measurements are performed using 25 Ω standard platinum resistance thermometers (SPRTs) placed both in the upper and lower flange, to allow for independent measurements as well as uniformity check. The thermometers are interrogated using an ASL FC 650 Precision Thermometry Bridge. The SPRTs are interrogated by measuring the ratio between the resistance of the SPRT and a reference resistor which is made to have minimum temperature dependence.

The temperature measurement equipment will routinely be calibrated using fixed point cells according to the international temperature scale of 1990 [4]. For this purpose, indium (157 °C) and tin (232 °C) freezing point cell, Gallium (30 °C) melting point cells and triple point cells for water (0 °C) and mercury (-39 °C) will be used. It is expected that the total uncertainty in temperature measurements will be within a few mK.

6. Pressure measurement and control

Pressure measurements will be performed using an array of four temperature controlled pressure transmitters from Keller with a rated accuracy of 0.01 % at full scales of 10, 30, 100, and 200 bar, respectively, resulting in a total accuracy better than 0.03 %. Since the fluid under test could be corrosive and at a wide temperature range, the pressure sensor array has been separated from the cell fluids using a

membrane and differential pressure sensor, such that the absolute pressure sensors only are exposed to nitrogen. The total pressure is then calculated by adding the pressure of the differential pressure sensor and the relevant absolute pressure transmitter. The pressure of the pressure sensor nitrogen circuit is regulated by a pump that controls the differential pressure sensor to zero. Hence, this sensor could have a narrow full scale and its precision will not significantly impair the total pressure measurement. The pressure measurements will routinely be calibrated using a dead-weight tester.

Although the samples extracted from the phase equilibrium cell will be small, we do not want the associated pressure decrease to affect the accuracy of our results. Hence, a plate bellows controlled by another pump and nitrogen circuit is placed installed the cell to compensate for the extracted volume, as illustrated in Fig. 3. The bellows has a total volume of 1 ml. The pump of the bellows nitrogen circuit will regulate the pressure inside the bellows in such a way that the cell pressure remains constant.

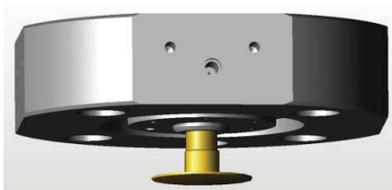


Fig. 3: Plate bellows of phase equilibrium cell

7. Sampling and chemical composition measurements

7.1. Chemical composition measurements

The chemical composition of both the gas and liquid phases will primarily be analyzed using a gas chromatograph (GC). The GC in use is an Agilent 7890, equipped with three different detectors: a thermal conductivity detector (TCD), a flame ionization detector (FID), and a flame photometric detector (FPD). For inorganic compounds, the TCD will be used, whereas for low concentrations of organic and combustible compounds (e.g. CH_4), the FID will be preferred.

The GC is equipped with a separation column in which a carrier gas, usually helium, is flushed through. When performing analysis, a sample is injected into the carrier gas flow and carried to and through the GC column. The column in use is a porous layer open capillary tube (PLOT) column (30m long, 0.53mm diameter). The micrometer thick porous layer of the column gives different retention times for different components, caused by varying chemical adhesion between components and the porous layer. The difference in retention time results in physical separation of components travelling through the column, and the different components will thus be detected at different times. Comparing the sensor signal curve for each component with established reference calibration curves gives the overall composition of each sample.

7.2. Calibration of composition measurements and calibration mixture preparation

As discussed above, the composition measurements require careful calibration of the GC which requires calibration mixtures with precisely known composition. Such mixtures are not readily available

for all the binary systems and concentrations we would like to investigate, especially since multiple concentrations are required for each system.

Hence, a setup for gravimetric preparation of calibration mixtures is being constructed adjacent to the phase equilibrium rig. Here, an accurate balance called a comparator can measure the weight of gas cylinders down to the mg range of a total mass of more than 20 kg. In order to achieve sufficiently accurate results, it is required that the comparator is calibrated continuously using weights with certified mass. In addition, other sources of error like buoyancy variations and convection has to be taken into account and minimized.

After the carefully controlled filling of different pure gases, the gas cylinders will be rotated using a lathe. This setup is combined with a heat source, such that seven mixtures with relatively high temperature dew points single phase become single phase with uniform composition. The gas mixtures prepared in-house will be compared with commercially available and certified mixtures when available.

The calibration of the GC can both be performed through direct injection into the column and via the phase equilibrium cell. For daily calibration and check of the GC, it is expected that calibration at a single concentration is sufficient.

7.3. Sampling

Sampling will be performed using samplers developed at Ecole des Mines in Paris which are called ROLSI samplers [5, 6]. These consist of a capillary with 150 microns inner diameter that goes into the fluid under test, connected to a precise piezo-controlled valve. The valve is continuously flushed by the carrier gas from the GC, which in most cases will be helium. The valve, as well as the tubing going to the GC, can be heated to 200 °C, such that we are ensured that the sample reaching the GC is in gas phase. The minimum sample size of the ROLSI is 3 µg. Two samplers are present inside the VLE cell. One is located just beneath the upper flange and is used for extraction of gas samples. The second, intended for liquid sample extraction, is located towards the lower flange, and can be adjusted along the vertical axes to ensure the tip of the sampler to be submerged in the liquid phase while extracting a sample.

Since the liquid level of the VLE cell will vary with composition, pressure and temperature, precise positioning of the liquid sampler is required to ensure sample extraction from the liquid layer only. This is especially important if two liquid layers are present (VLLE measurements), which also is within the scope of the project. This is achieved using the borescope, described in Section 3.

8. Conclusion

A new experimental facility for the measurement of phase equilibria of CO₂-rich mixtures relevant for CCS conditioning and transport has been described. The experimental setup is expected to produce data with very high accuracy both in temperature, pressure, and composition, and it is believed that it will provide data of high quality needed for safe, efficient, and economically realizable CCS transport infrastructure in the years ahead.

Currently the various systems for pressure, temperature, sampling, and composition measurements are under final testing and calibration, and we hope to commence measurements on the first real system within 2012.

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