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Experimental investigations of impurity impact on CO₂ mixture phase equilibria

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Abstract

A facility designed for precise measurements of phase equilibria of CO₂-rich mixtures relevant for CCS conditioning and transport is demonstrated. The setup aims for high accuracy in pressure, temperature, and composition measurements for pressures between 4 and 200 bar and temperatures between -60 and 150 °C.

In this paper, the test measurement of the N₂ / CO₂ system in the vicinity of the critical point for CO₂, have shown the ability to produce measurements with the high accuracy and repeatability in temperature, pressure and composition

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1. Introduction

For large-scale CCS realization, means of predicting the behavior of fluids and conditions along the value chain must be available. Currently, there are still large gaps in the available experimental data regarding the thermo-physical properties [1-3]. SINTEF Energy Research, Ruhr-Universität Bochum, and NTNU are collaborating on a

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project called CO2Mix designed to address these gaps by experimentally determine selected properties of CO₂-mixtures relevant for CCS transport and conditioning [4].

A key property in need of data is the phase state at equilibrium; and a dedicated experimental setup for the measurement of CO₂ mixture phase equilibria has been constructed in the labs of SINTEF Energy Research in Trondheim [5]. 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 concentration of different impurities. For instance, even small amounts of impurities could significantly increase the cricondenbar, the maximum pressure for which two phases can exist, compared with pure CO₂ [4]. Accurate phase equilibrium knowledge is not only important for steady state systems, but also 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. Finally, phase equilibrium (PTxy) data are prerequisites for the development of accurate equations of state from which other important thermodynamic properties can be derived.

2. Data situation

As already mentioned, there are some clear gaps in the available phase equilibrium data for mixtures relevant for CCS. In addition, a lot the data that do exists are not trustworthy. For instance, using the data situation for CO₂ – H₂, which was analyzed in [1, 2, 6-8] as an example, it is generally found that most of the data sources are quite old, pre-1970, and that the quality can be questioned. Around 300 VLE measurements have been published between 0 and 400 bar, and between 220 and 298 K. Although some gaps are present for some temperatures, the data situation superficially appear decent within the relevant range for CCS capture and transport below 200 bar. However, a closer look at the actual measurements, for instance at 290 K where there are quite a lot of measurements as shown in Figure 1, often reveals that the data situation are far from good enough for accurate process design and operation, especially in the vapor phase.

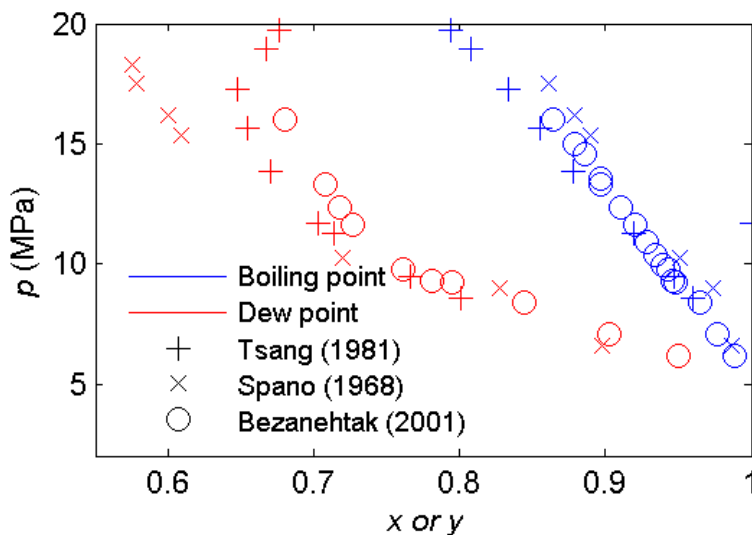


Figure 1: VLE data situation for the binary system H₂ – CO₂, data from [7, 9, 10].

A similar overview of the data situation for the CO₂ – N₂ system [1, 2] shows an apparently good data coverage over the relevant range from the triple point to the critical point of CO₂, and [1] reports 362 dew (gas phase) points and 316 boiling (liquid phase) points. A closer look at some of the isotherms especially at higher temperatures often reveals that the data situation are far from good enough for accurate process design and operation. An example of this inconsistency is shown in Figure 2 where the isotherm for 293K is shown for two different sources.

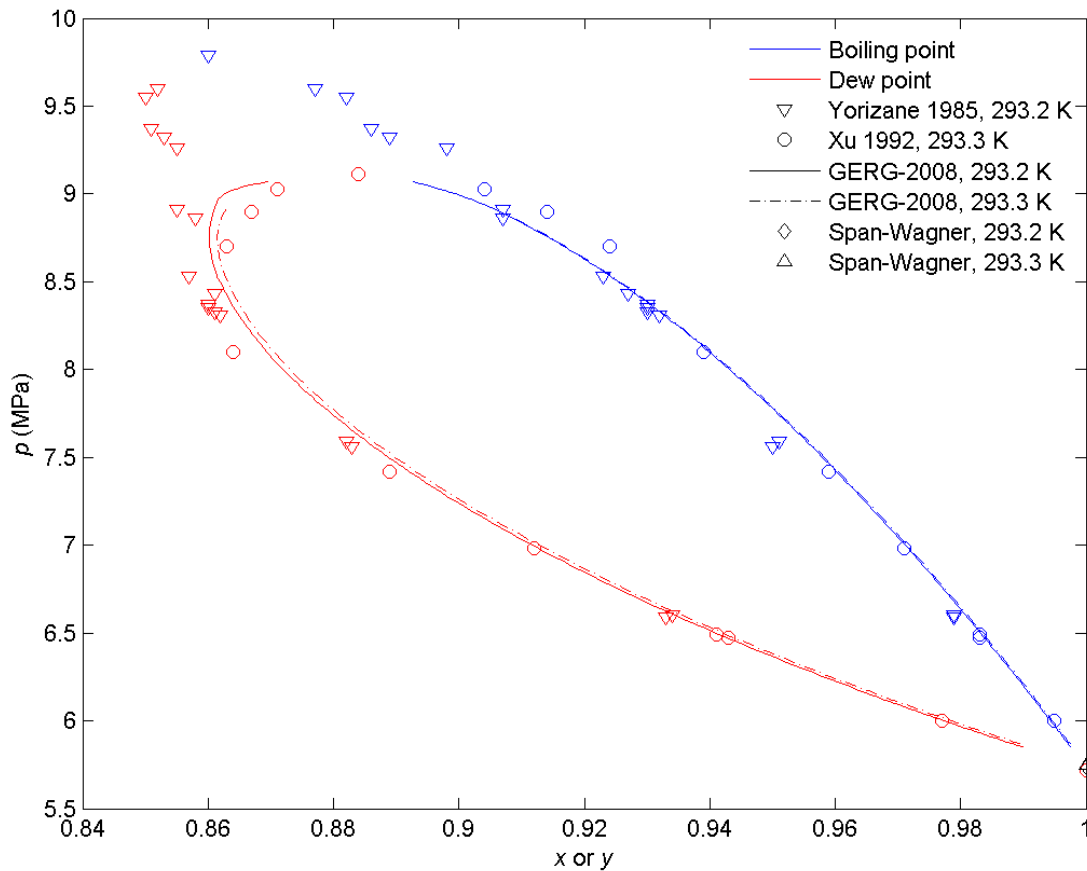


Figure 2: Models and data for the CO₂ – N₂ system around 0 °C. Data from [11, 12], adapted from [1].

3. Experimental setup

The phase equilibrium setup is using an analytic technique [13], where all fluid phase present in the test cell is measured. This improves the productivity of the setup, as, in the case of Vapor Liquid Equilibrium (VLE), both the dew point and boiling point compositions are measured simultaneously. Further, for binary mixtures, the total composition in the cell is not critical, which means that this composition can be adjusted enabling many measurement points before the cell has to be evacuated. In line with the primary objective of the setup, it is now producing vapor-liquid equilibrium data for binary mixtures. Such data are very useful in order to construct accurate equation of states by fitting binary interaction coefficients [14]. 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). Using a camera, it is possible to detect both multiple liquid phases as well as the formation of solids or hydrates.

4. Accuracy

We have gone to great lengths to assure that the measurements performed are of high enough quality to be useful to improve predictive models. The rig is designed for accuracy better than 10 mK in temperature, 0.1 % in pressure, and 100 ppm in composition. In addition to careful design and operation of the experimental facility, accurate measurement requires traceable means and adherence to systematic routines for the calibration of the different sensor systems. In particular, achieving a desirable level of accuracy regarding the composition measurements is demanding. An in-house system for gravimetric preparation of calibration gas mixtures has been made, with an estimated accuracy better than 10 ppm, since mixtures with high enough accuracy generally is not commercially available. For the compositional analysis we are using a gas chromatograph (GC), calibration of which requires particular care. To our accuracy level for quantitative measurements, the GC has a non-linear response depending both on the sample size and composition. Hence specialized calibration routines and a high degree of control of the sampling process are needed.

5. Measurement examples

Currently, a measurement campaign on the CO₂-N₂ system is being completed. This is an important system, since N₂ is present in mixtures from most capture processes. Further, the CO₂-N₂ system has fairly good and accurate data in some regions, but, as we have seen, there are gaps in others. We have been able to make very repeatable and consistent measurements even close to the critical regions. The setup has been verified by comparing the new data with existing data and models, but also produced new measurements in areas where the data situation has been unsatisfactory. Preliminary results at a given temperature are given in Figure 3. Final processed results will be submitted for publishing shortly. Quite a lot of data exist for CO₂ – N₂ at the given temperature, but as can be appreciated from the figure, not all are trustworthy. One of the most accurate equations of state for this system is GERG-2008, but seems to have convergence problems close to the critical point. This region is important in order to know at which pressures the fluids are single phase at a given temperature and composition. As shown in the insert, the CO₂Mix VLE rig is able to measure with a high fidelity and accuracy close to the critical point. A nice feature of the setup is the ability to inspect the cell content during experiments using a camera, and hence be able to see for instance transition to the critical region. Close to the critical point, minute spatial variations in temperature lead to large density and hence refractive index inhomogeneity and the mixture hence attain a milky white appearance, as shown in Figure 4.

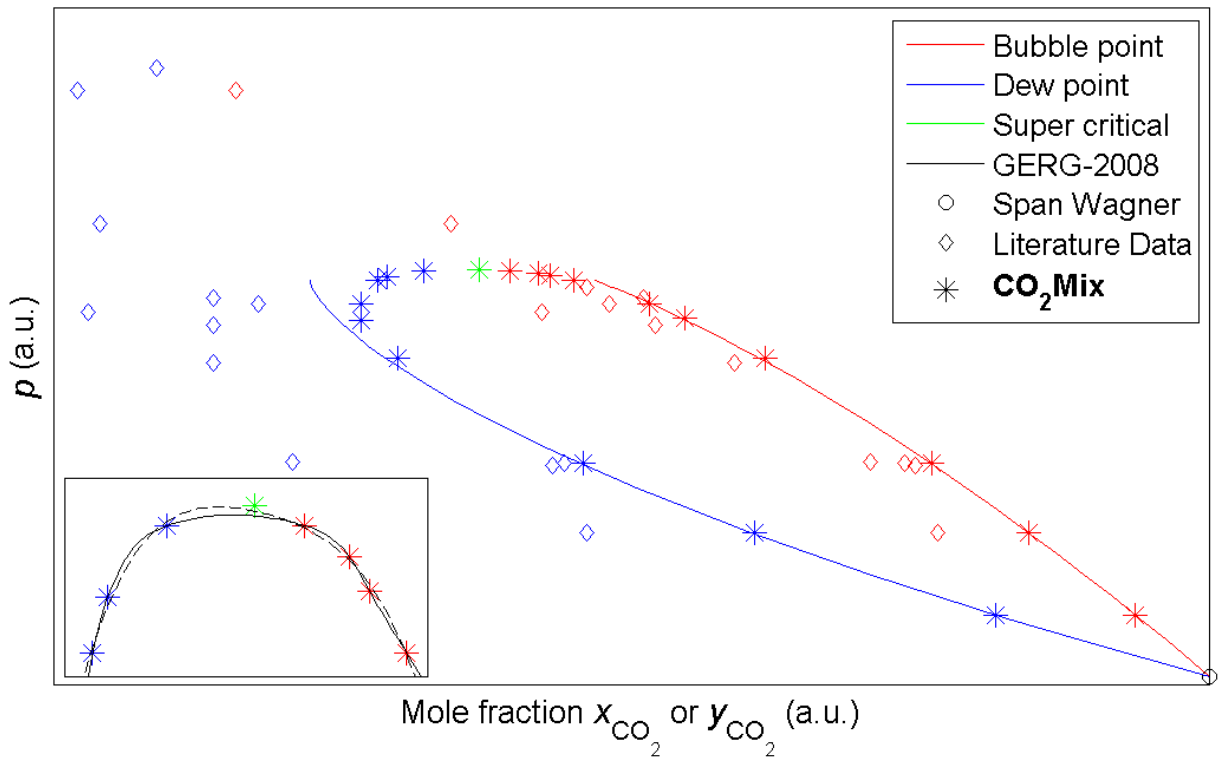


Figure 3: Example of a measured isotherm of the CO₂ – N₂ VLE series compared with data points found in existing literature. Insert shows the region close to the critical point. Measurement data will soon be published.

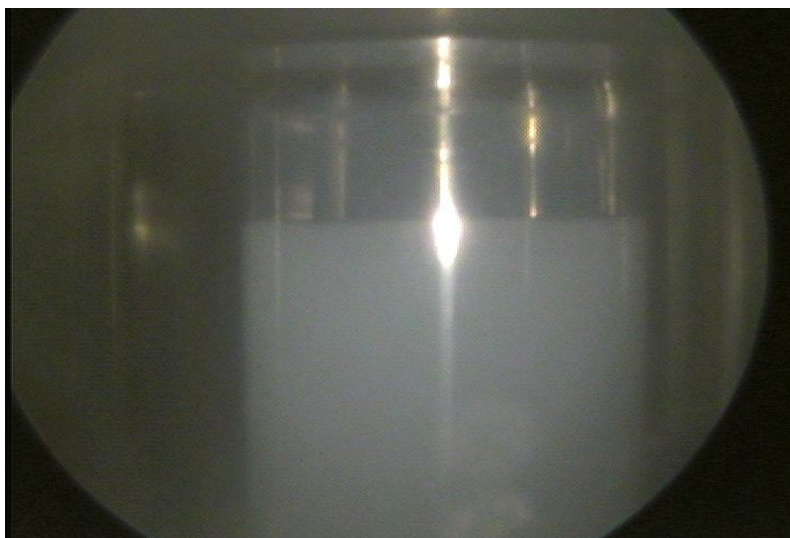


Figure 4: Approaching the critical point in VLE experiments

6. Conclusions

A new facility designed for measurements of phase equilibria of CO₂-rich mixtures relevant for CCS conditioning and transport has been established. The setup aims for high accuracy in pressure, temperature, and composition measurements for pressures between 4 and 200 bar and temperatures between -60 and 150 °C. The setup is using an analytical method, where the fluid phases present are analyzed and knowledge of the total composition inside the cell is not necessary. On the other hand, a prerequisite is that the GC used for chemical analyses has to be calibrated using mixtures with composition known to great accuracy.

In this paper, the infrastructure and routines that has been established in order to minimize and quantify the uncertainties for the setup have been described. Sophisticated calibration equipment to constrain the measurement uncertainties in pressure, temperature, and composition has been installed and is in service. For the test measurement of the N₂ / CO₂ the test rig has shown the ability to produce measurements with the specified accuracy in temperature, pressure and composition, and produced very promising results near the important critical region.

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Nomenclature

P	Pressure
T	Temperature
x	Composition in liquid phase
y	Composition in vapour phase

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