Abstract

For more efficient, robust and inexpensive CCS systems, improvements of the models describing the behavior of fluids involved in CCS are required. Accurate models in turn require experimental data of high quality, which are still lacking for many important properties when impurities are present. SINTEF Energy Research and the Norwegian CCS Research Centre (NCCS) are addressing the lack of phase equilibrium data in CCS by performing accurate measurements of important systems using a purpose-built setup. So far, the binary mixtures of CO$_2$ + N$_2$, CO$_2$ + O$_2$, CO$_2$ + CH$_4$, CO$_2$ + Ar, and CO$_2$ + CO have been investigated. In the present paper, some examples from the measurements on CO$_2$ + Ar and CO$_2$ + CO systems are provided, illustrating that trusting models could lead to serious consequences if they are not supported by independently verified data.

Keywords: Type your keywords here, separated by semicolons

1. Introduction

It is well known that high costs and perceived technology risks are major barriers for large-scale global deployment CCS prescribed by IEA [1] and others to mitigate anthropogenic climate change in a cost-efficient manner. In order to optimize the costs of robust and safe CCS systems, accurate knowledge of the properties of the fluids in all parts of the CCS chain is absolutely necessary. The properties of pure CO$_2$ are relatively well known, but in real-life CCS applications, the CO$_2$ product will not be pure [2]. Even small amounts of some impurities may significantly change the fluid properties compared with pure CO$_2$, which in turn will affect the different processes involved [3-5]. The impact of impurities must hence be known to optimize the CO$_2$ specifications and to predict fluid behavior in the parts of CO$_2$ chain where impurities are unavoidable, for instance prior to and in the purification process or in geological storage.

Unfortunately, there are still major data gaps for CCS-relevant thermophysical properties, conditions, and fluids, which prevent the development and verification of precise modeling tools [6]. Hence, unless these data gaps are closed, CCS processes will have to be designed and operated with excessive and costly margins. Still, undesirable incidents, such as breakdown of rotating machinery, leakage caused by corrosion, or reduced reservoir injectivity, may occur.

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Hence, SINTEF Energy Research has with international partners for many years now worked to provide highly accurate property data [7, 8] in the most important gaps using advanced facilities. The workhorse for this activity, as well the activity to improve models based on the new data, is currently the Norwegian CCS Research Centre (NCCS) [9].

Highly accurate phase equilibrium measurements of the binary mixtures CO$_2$ + N$_2$ [9], CO$_2$ + O$_2$ [10], CO$_2$ + CH$_4$ [11], CO$_2$ + Ar [12], and CO$_2$ + CO [13] have been important results of this work so far, using a facility specifically designed for accurate phase equilibrium measurements for CCS called CO$_2$Mix [14]. In total, more than 23 isotherms have been measured with this setup, ranging in temperature from -60 to 30 °C and up to 182 bar in pressure, mostly in areas without data or with data in need of verification.

The focus on these measurements has so far been on binary systems because these are most useful to build models. Hence, a significant improvement of models for CO$_2$ with these impurities have been enabled. For all systems investigated, the new VLE data enable an accurate description of the full isotherms investigated, including the critical region, which has a high technological interest for CCS transport [4], but also is the hardest region to both measure and model. Equations of state (EOSes) have already fitted to the new data for all investigated systems.

The present paper will draw attention to some of the more enlightening examples of the most recent phase equilibrium measurements on CO$_2$ + Ar and CO$_2$-CO will be shown. These measurements have been produced in a temperature span from -60 to 26 °C.

2. Phase equilibrium data

Some examples of the new data are provided below. Each figure presents the phase equilibrium data at a given temperature with other data from the literature and with prediction from existing models. A pure substance as water, liquid and vapor can at equilibrium in a closed container only coexist at a single pressure, the boiling point, for a given temperature. This is different for a mixture, where vapor and liquid typically can coexist over a range of pressures between the dew point (red) at low pressure and boiling point (blue) at high pressure. The dew and boiling point pressure is shown as a function of composition, and the area enclosed between the dew point and boiling point curves are called phase envelopes.

2.1. Vapor liquid phase equilibrium (VLE) measurements on the CO$_2$ + CO system

CO is produced in oxygen-lean processes and can in CCS be found in captured CO$_2$ from e.g. refineries and pre-combustion processes, in concentrations up to 0.2% [2]. CO is a highly poisonous gas, and it is therefore of high interest knowing where any CO in the CCS process stream ends up. Such predictions in general requires accurate VLE measurements. Of course, the poisonous nature of CO also required that proper safety measures had to be taken during the measurement campaign, with multiple barriers including an external supply of fresh air for operators of the setup as illustrated in Fig. 1.

Four isotherms have recently been measured of the CO$_2$-CO-system [13]. At 25 °C, only a single experimental point was identified prior to our work. As expected, the existing models hence did not make a very good fit to the new data. This is illustrated in Fig. 2, where our new data and the previous literature data point are plotted together with model prediction of the simple cubic model of Soave, Redlich and Kwong (SRK) [15] as well as the recent Helmholtz reference model for CO$_2$-rich mixture EOS-CG from Ruhr-Universität Bochum [16]. In our work [13], the parameters of the Peng-Robinson (PR) cubic EOS [17] with the alpha correction by Mathias and Copeman [18] (MC), the mixing rules by Wong and Sandler [19] (WS), and the NRTL [20] excess Gibbs energy model were fitted to the new data. In addition, a scaling law was fitted and applied to predict the critical point of each isotherm to great accuracy. However, for a consistent prediction of all thermodynamic properties, a reference equation of state should be used. Improvement of EOS-CG using our and other data will be developed.
Argon is an important impurity from various capture processes, in particularly in oxy-fuel plants, where there can be several percent in the CO₂ product prior to additional purification [2].

Phase equilibria was recently measured for 7 different temperatures on the CO₂+Ar system from -60 to 26 °C, providing a fairly good coverage of the VLE properties of this system [12]. The new data provided by the CO₂Mix facility enabled a significant improvement of the existing reference models. As two examples, the measured isotherms at 0 °C and -60 °C are provided in Figs. 34. Unlike the case of CO₂ + CO at 25 °C discussed above, more literature data were found at 0 °C for CO₂ + Ar. As seen in Fig. 3, however, the prior data were scattered and in need of verification. GERG-2008 is a very popular EOS for natural gas [21] which is implemented in many process simulation tools. At the time when this EOS was developed, only a single phase equilibrium data set was available at this temperature [22]. As seen in the figure, the GERG team fitted those measurements perfectly, but the problem is that the data set available had a large deviation from later measurements. Consequently, at 25 °C, the GERG phase envelope is two times bigger than the data supports. Such large inaccuracies may lead to expensive overdesign or, worse, negative surprises and this example illustrate that property data always should be verified by independent measurements. In comparison, the new binary Helmholtz reference EOS model developed by Ruhr-Universität Bochum in reference [12] has much higher confidence as it is built on verified data sources.

Impurities also affect the formation of solids of a fluid, as illustrated in Fig. 4 providing phase equilibrium data for CO₂ + Ar at -60 °C. For pure CO₂, this temperature is below the triple point temperature at −56.6 °C where dry ice, liquid, and CO₂ may coexist. Addition of some Ar enables the presence of liquids below the triple point temperature of pure CO₂. Determining the temperature where dry is formed is very important for a number of
processes, for instance for low-temperature separation processes where the CO$_2$ will coexist with impurities. Very little data exist for dry ice formation. Phase diagrams involving solids could be quite complex, but both equilibrium between vapor and solids (frost points), liquid and solids (freezing points), vapor-liquid equilibria (dew and bubble points), and vapor, liquid and solids (three phase line) were measured. Due to the lack of data, it is not a surprise that prior models did not predict the data very well. In fact, a common EOS, the SRK cubic equation of state, with typical parameters, did not predict the co-presence of two fluid phases at all!

4. Conclusions

In order to develop efficient and robust CCS systems at optimal cost, it is important that accurate models and experimental data on the properties of relevant fluids at relevant conditions are available. For pure CO$_2$, many important properties are fairly well known and described with accurate models, but this is not the case when impurities are present. This situation could lead operators to include expensive, and perhaps unnecessary purification steps in their processes to reduce uncertainty, or worse even, to expensive surprises if the impact of impurities is underestimated. In parts of the CCS chain, e.g. capture, storage / injection, and leakage situations, impurities can sometimes simply not be avoided.

In the last few years, SINTEF Energy Research has improved the data situation greatly for some common impurities found in CCS with respect to phase equilibria. These measurements are still ongoing and conducted as part of the Norwegian CCS research Centre. The present paper provides some data example of the most recently published measurements, illustrating the need to measure where there are no data, and that trusting a single data set could be risky if not independently verified.

Fig. 2: VLE measurements of the CO$_2$ + CO system at 25 °C. Data are further described in reference [13].
Although some common impurities have been addressed during the last few years, there is still a number of important binary systems and conditions that lack verified data or any data at all. With regards to conditions, this is particularly true with respect to phase equilibria involving dry ice which are important in depressurization situations and in liquefaction processes. Some recent data on such phase equilibria involving argon was presented in the present paper. In addition to binary phase equilibrium data, also more high-quality data on systems with three or more components are needed in order to provide verification of models built on data from measurements on binary systems. For many systems there is also a need for better measurements close to the critical point of mixtures to better pin-point conditions that could lead to two-phase flow.

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Fig. 4: Phase equilibria of the CO₂ + Ar system at -60 °C. Data and models are further described in reference [12].

References


