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CO₂Mix Project: Experimental determination of thermo-physical properties of CO₂-rich mixtures

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Abstract

The CO₂Mix project is established in order to fill important knowledge gaps regarding thermophysical properties of CO₂-rich mixtures relevant for CCS conditioning and transport. Even small amounts of impurities can have a large effect on these properties and hence on the design of process equipment and flow assurance calculations. Hence, accurate models backed up by experimental data of high quality are required for efficient and safe design and operation of CCS infrastructure and equipment. In the CO₂Mix project, SINTEF Energy Research, Norwegian University of Science and Technology (NTNU) and Ruhr-Universität Bochum (RUB) will perform accurate measurements of phase equilibria, density, and speed of sound. In this paper, the need for measurement of thermo-physical properties will be discussed, and the experimental setups will be described.

Keywords: CCS; Carbon-dioxid; Mixture; Vapour liquid Equilibrium;, Denstiy, Speed of Sound; Measurements

Nomenclature	
CP	Critical point
EOS	Equation of State
VLE	Vapour-liquid equilibrium
VLLE	Vapour-liquid-liquid equilibrium

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1. Introduction

In order improve the prediction of the performance of processes and process equipment in a CCS chain, it is necessary to accurate describe the behavior of the fluids that are involved. For a range of relevant conditions within the CCS chain, there are still large gaps with insufficient experimental data characterizing CO_2-rich mixtures to describe system behavior with an acceptable level of accuracy. The aim of the research project CO_2Mix is to fill these gaps for selected mixtures and physical properties. The focus will be on properties and CO_2 mixtures that are relevant for CCS conditioning and transport.

CO_2Mix is a KPN project (Knowledge-building Project for Industry) under the CLIMIT program managed by the Research Council of Norway (RCN). The duration of CO_2Mix project is between 2010 and 2014, and the project is organized under the BIGCCS research center. This project will focus on phase equilibrium, density and speed of sound measurements. The phase equilibrium measurements will be performed by SINTEF Energy Research and Norwegian University of Science and Technology (NTNU) in Trondheim, whereas the speed of sound and density measurements will take place in Ruhr-Universität Bochum (RUB).

In the current paper we will provide a motivation for the project by discussing the effect of impurities on thermophysical properties of CO_2-rich mixtures and the scarcity of experimental data for accurate property model development and verification. In addition, we will provide an overview of the different measurement setups that will be used in the project.

2. Thermodynamiceffects of impurities

The CO_2Mix project is focusing on CCS processes related to CO_2-conditioning and pipeline transport, for which typical operating ranges in pressure and temperature are listed in Table 1 and realistic mole fractions are shown in Table 2. Operation is either at low (< 4.8MPa) or supercritical pressure, but due to cooling and pressure loss both single- and two-phase might be possible in pipelines. The mole fractions of the impurities will also be dependent on the conditioning and capture technology prior to transport. For flow assurance, accurate prediction of thermodynamic and transport properties like phase behavior, density, compressibility, viscosity, and hydrate formation are important. For pipeline transport of CO_2, the pressure and temperature range should also cover abnormal operation like for instance depressurization

Thermodynamic models are often developed based on regression of parameters from experiments on vapor-liquid equilibrium (VLE) of binary mixtures. Experiments on mixtures of more than two components are useful in order to verify the developed models. For models to be more accurate and useful over a wider range, the experimental composition range must be wider than the mole-fractions listed in Table 2.

Table 1. Estimated operating conditions for temperature (T) and pressure (P) [1]

CCS process	P (MPa)	T (K)
CO_2 conditioning	< 11	219.15–423.15
CO_2 transport	< 4.8 or > 8-9	< 323.15

Table 2. Realistic mole fractions for the different components [1]

Component	Min mol%	Max mol%
CO_2	75	99
N_2	0.02	10
O_2	0.04	5
Ar	0.005	3.5
SO_2	<0.0001	1.5
H_2S+COS	0.01	1.5
NO_x	0.0002	0.3
CO	0.0001	0.2
H_2	0.06	4
CH_4	0.7	4

2.1. Effect of impurities on vapor-liquid equilibria

To do an initial evaluation of the design temperature and pressure range for the experimental facilities, an estimate of the effects of various impurities on the phase behavior has been done, using available thermodynamic models. A phase diagram for pure CO_2 is illustrated in Fig. 1a, with the vapor-liquid equilibrium forming a line between the triple point and the critical point. Thermo-physical properties for pure CO_2 are described by good models like the ones presented in refs. [2, 3]. Presence of any of the impurities shown in Table 2 will alter the phase behavior and split the equilibrium line into a bubble-point and a dew-point line, forming a phase-envelope in between. For temperature and pressure states inside this phase envelope, a liquid and gas phase will coexist.
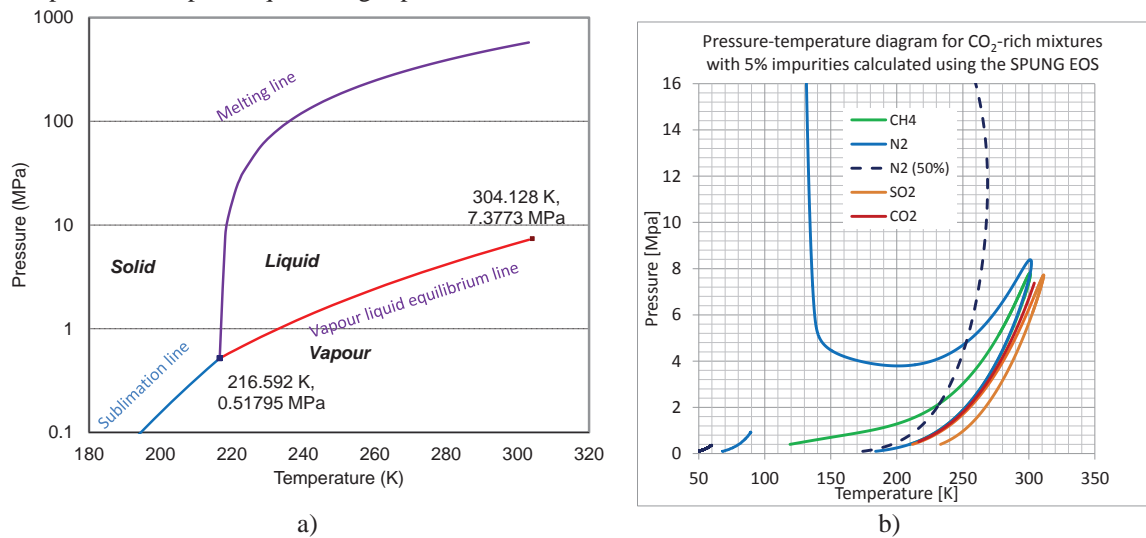

a)

b)

Fig. 1 a) Illustration of phase diagram for pure CO_2. b) and mixture of CO_2 and 5 mole% of impurity

The listed impurities can have a very different effect on the shape of the phase envelope. An illustration of typical phase envelopes for a binary mixture of CO_2 and 5 mole % of either CH_4, N_2 or SO_2 is shown in Fig. 1b. The phase diagrams are calculated using the SPUNG equation of state (EOS) [4]. This equation is based on an extended corresponding state principle. A 32-term MBWR EOS for propane is used as reference equation and the scaling factors for the temperature and density between the mixture and reference fluid models are determined from Peng-Robinson EOS. This approach was also described by Michelsen and Mollerup in [5]. This formulation is reasonably fast and utilizes the cubic equations' good behavior for prediction of VLE with an added advantage of higher accuracy on the volumetric predictions in the liquid and supercritical region.

In Fig. 1b, the pure CO_2 saturation line is shown together with conventional closed phase-envelopes of binary mixtures between CO_2 and CH_4 or SO_2. Both these phase envelopes have a higher maximum pressure, cricondenbar, than the critical pressure for either of the components in the mixture, thus extending the pressure range for the two-phase region. This is classified in the literature as a Type I phase behavior. The N_2-CO_2 mixture is a type of mixture with an atypical phase behavior – it has a separate (short) bubble-line and has a dew-line with two critical points. The dew-line extends to infinite pressure at low temperatures. For higher concentrations of N_2, the dew-line will not envelope to lower pressures but just extend toward infinite pressure with an equilibrium line between two dense high pressure phases with different compositions. The bubble-line in the displayed illustration is here hypothetical in the sense that the CO_2 in a liquid phase in that region will form solid.

When designing the experimental facility, an estimation of the two-phase regions was done by plotting the two-phase locus. The locus appears when phase envelopes for the impurity mole fraction from 1.0 to 0.0 are plotted and the cricondenbar for each envelope is connected. A diagram for CH_4-CO_2 is shown in Fig. 2a, where the maximum pressure for the two-phase region reaches 90 bar, about 15 bar above the critical pressure of pure CO_2. For temperatures below the triple point of CO_2 solid will be formed from the liquid phase – the freezing line for 75 mole% of CO_2 is shown. For higher CO_2 concentrations the freezing temperature will move slightly to the right – ending in the melting line for pure CO_2 shown in Fig. 1a.
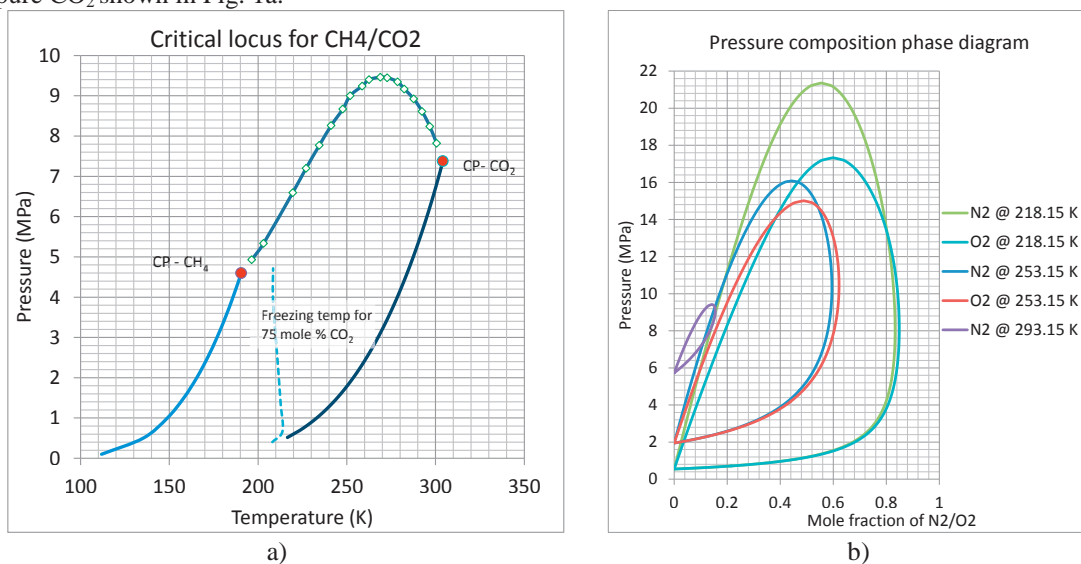

Fig. 2 a) The two-phase region with the critical locus for CO_2/CH_4 b) Pressure-composition diagram for CO_2/N_2 and CO_2/O_2 at different temperatures

For the atypical phase behavior of CO_2 and N_2, a pressure-composition phase diagram shown in Fig. 2b can be used for illustration of the two-phase region. The graphs show the predicted phase transition lines for three different temperatures: At 293.15 K, at 253.15 K and at 218.15 K. As seen for the lowest temperatures, the two-phase region extends upward to above 200 bar. The two phases can be considered as two dense phases with different composition. In Fig. 2b examples for the binary mixture of CO_2 and O_2 also show wide two-phase regions.

2.2. Effect of impurities on density

A similar analysis can be done on a CO_2 mixture with 5% impurity of relevant residuals. In Fig. 3a, the relative effect on the density compared to pure CO_2 at 90 bar over a temperature range from -30 to 50°C calculated with the SPUNG equation of state. The average deviation with this equation for pure CO_2 was 1.23% compared to the reference equation of Span and Wagner.
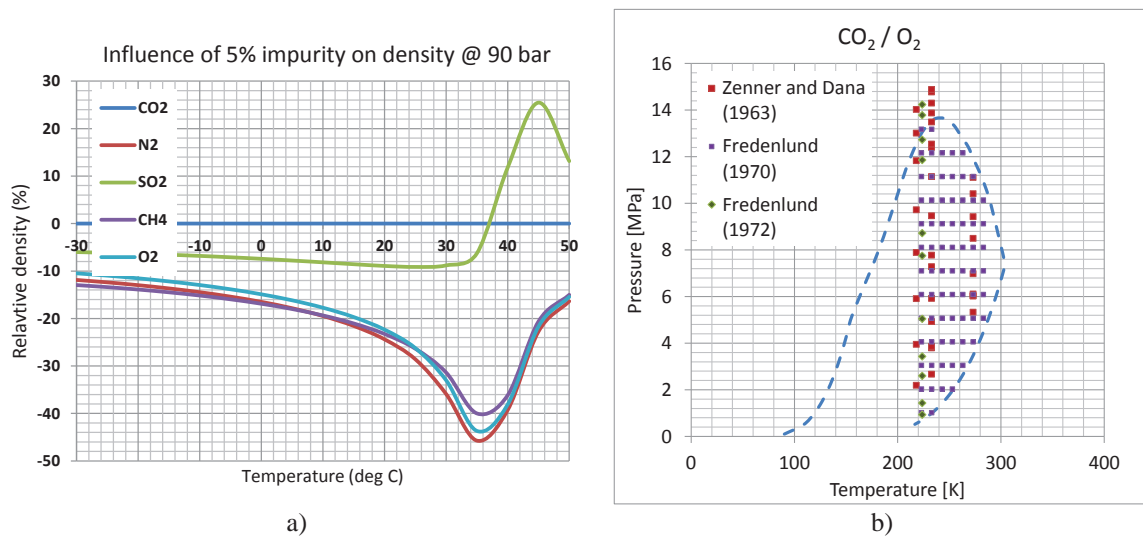

Fig. 3 a) Change in density between pure CO_2 and a mixture with 5% impurity. b) Example of reported measurements for CO_2/O_2

As seen for instance with 5% N_2, the relative density has a minimum around 35°C with a density 41% lower than pure CO_2. Disregarding the difference in viscosity and the effect on the friction factor at this point, the pressure drop ratio will be proportional to the inverse of the density-ratio, giving 1/0.59=1.69 times higher pressure drop for the same flow rate in a pipe at this condition. The theoretical power consumption will then be 2.86 times that of pure CO_2. With correction of the viscosity on the friction factor, the numbers will be lower. The maximum limit for a CO_2 transport pipeline is 4% N_2 according to [6]. At higher transportation pressure, the deviation peak will occur at higher temperature further away from the critical temperature of CO_2. This is a very good rationale for improved thermodynamic models that can predict the density of a mixture with high accuracy, but knowing the density will also be very important for instance for metering purposes and EOS development.

3. Available experimental data

In the overview from Li et.al[1] there are several gaps of missing data for density and VLE. The quality of the data was also questioned, with some of the sources for CO_2 and SO_2 being more than 100 years old. As an example, for CO_2/O_2 mixtures, phase equilibrium data are available over a large range of temperatures and pressures, while no single phase density measurements are found in the literature. This is illustrated in Fig. 3b, where each point represents one reported measurement point from [7-9] and the curves are calculated using the SPUNG EOS. Some of the measured two-phase points are predicted by the EOS to be in a single phase region. It can be mentioned that the VLE data for CO_2/O_2 were rejected in the development of the GERG-2004 equation of state because the deviations were too large from simulated results using Peng-Robinson EOS. However, the deviations are not necessarily a proof for poor data, and some of these data points should be repeated by new measurements with high accuracy. Also for the case of CO_2/CO and CO_2/COS none or very little density data have been reported. This is also true for the liquid density of CO_2/H_2

In addition, Li et.al reported inconsistencies between different data sources on phase equilibrium measurements of CO_2/CH_4 and on dew-point measurements of CO_2/H_2 at temperatures above 290 K. New measurements should be conducted for these compositions as well.

Very little speed of sound data have been reported for mixtures of CO_2 and the impurities relevant for CCS given in Table 2. Only one data set by Kachanov et al. [10] for the binary mixture of CO_2 and N_2 could be found in literature, and, unfortunately, this data set has a relative broad, unsystematic scatter. Thus, providing new and accurate speed of sound data is necessary.

4. Experimental facilities in the CO₂Mix project

In the CO₂Mix project, experimental setups have been developed to measure density, speed of sound, and phase equilibrium to a high accuracy. The phase equilibrium measurement rig is now installed and experimental results will be reported soon. The speed of sound and density measurement setups have been redesigned for the mixtures to be studied, and measurements will commence next year.

4.1. Vapor-Liquid equilibrium

The phase equilibrium measurements will be performed using an analytical technique [11], i.e. the composition of all phases present at equilibrium will be measured. The experimental setup is described in detail by Stang et al. [12].

The VL(L)E experimental test facility can be used to measure mixtures with all relevant impurities like the ones that are listed in Table 2, including explosive, corrosive, and toxic components. In addition to phase-equilibrium measurements, formation of solids and hydrates can be detected. Based on the initial predictions of phase behavior for these mixtures, the measurement equipment is designed to cover a temperature range from -60°C to 150°C with an accuracy and uniformity of 10 mK, and a pressure range from 3 to 200 bar with an accuracy of 0.10 %. The concentration range of the impurities in the CO_2 mixtures will initially be from 50 to 100 %.

4.2. Density

The density measurements in this project will be undertaken by means of a single-sinker densimeter with a magnetic suspension coupling. This kind of apparatus has been developed by Wagner et al. [13], the state of the art of this technique is described by Wagner and Kleinrahm [14]. In order to provide an

absolute determination of the density, the instrument applies the Archimedes principle. This principle says that any object which is immersed in a fluid is buoyed up by a force equal to the weight of the displaced fluid. This means that by determining the buoyancy of the object, the density of the fluid can be calculated. Therefore, the difference of the weight force of a sinker is determined employing an analytical balance (Co. Mettler, Type AT 261) in vacuum and in the fluid of interest. The sinker is made from single-crystal silicon, and has a volume of $V_s = 19$ cm^3, mass of $m_s = 44$ g and density of $\rho_s = 2329$ kg/m^3. Since the volume $V_s(T,p)$ of the sinker is well known through calibration with references fluids, the density ρ of the fluid can then be calculate by means of the following equation:

$$\rho = \frac{m_{S,vac} - m_{S,fluid}}{V_S \ T, p}$$

To be able to measure the density over a wide pressure and temperature range, the measuring cell and the analytical balance have to be separated. For this purpose the magnetic suspension coupling is applied. A schematic of the single-sinker densimeter can be seen in Fig. 4.

Fig. 4 Schematic of the single-sinker densimeter

Basically, the magnetic suspension coupling consists of an electromagnet, a permanent magnet, a position sensor and transducer, and a control system. The electromagnet is attached to the analytical balance, while the permanent magnet is part of a so-called coupling unit inside the pressure resistant measuring cell. This coupling unit reaches through the silicon-sinker and at the end the position sensor detects the vertical location of the coupling unit. Two stable positions can be realized with the magnetic suspension coupling. In the first, the so called tare position, the sinker is not lifted by the coupling unit. In this position the balance the tare weight is determined to eliminate buoyancy. In the second position, the so called measuring position, the permanent magnet is lifted up and the coupling unit elevates the sinker. In this position the weight of the sinker is recorded.

4.3. Speed of Sound

The speed of sound measurements in this project will be carried out utilizing a speed of sound apparatus with a dual path length cell, first developed by Murringer et al. [15]. The piezoelectric quartz

crystal is operated at high frequencies and serves as emitter and receiver. The crystal is mounted asymmetrical between the two reflectors at a distance of $L_1 = 20$ mm and $L_2 = 30$ mm, respectively, A schematic of the speed of sound sensor can be seen on the left side in Fig. 5.
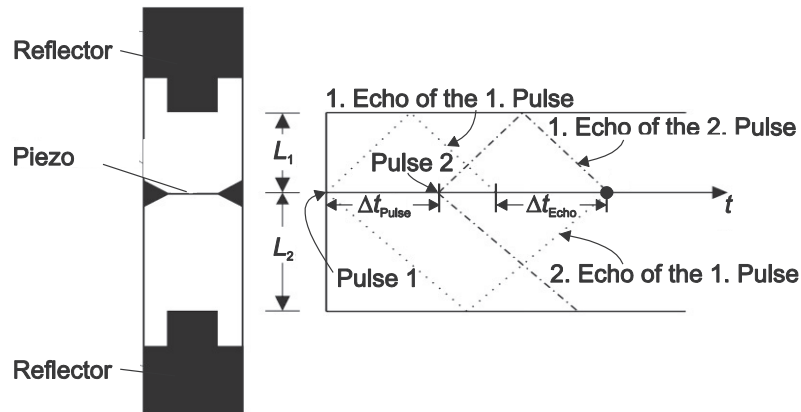

Fig. 5: Principle of the speed of sound measurement. Left: Schematic of the speed of sound sensor. Right: Illustration of the run of the sound waves of two pulses; depicted for interference.

Due to the asymmetrical path lengths the echoes of a pulse arrive successively at the piezo, separated by the time difference Δt_{Echo}. Therefore, the modified pulse-echo method [16] can be employed, whereby the cancellation of pulses is used to determine the time of flight.

As can be seen on the right side in Fig. 5 two pulses are sent out successively, separated by a time difference which is called $\Delta t_{\mathrm{Pulse}}$. The pulses have the same shape (sinusoidial) but are inverted. Furthermore, the amplitude of the second pulse is reduced to fit the higher damping on the longer path length. The time difference $\Delta t_{\mathrm{Pulse}}$ is now varied until the second echo of the first pulse and the first echo of the second pulse interfere destructively. For this case $\Delta t_{\mathrm{Pulse}}$ equals Δt_{Echo} and the speed of sound can be calculated by means of the following equation:

$$c^* = \frac{\Delta L}{\Delta t_{\mathrm{Pulse}}}$$

In this equation $\Delta L = 2\ L_2 - L_1$ describes the path length difference of the speed of sound sensor, which has to be calibrated with a reference fluid with well known speed of sound.

5. Conclusions

In CO_2Mix project, thermophysical properties of CO_2-rich mixtures relevant for CCS conditioning and transport will be measured. Current models indicate that even rather small amounts of relevant impurities can have major impact on the thermophysical properties of CO_2 rich mixtures. These properties are necessary to predict with high accuracy in order to design and operate transport CCS infrastructure in a safe and cost effective manner. Accurate predictions require that the models can be improved and verified by accurate experimental data.

Currently, there are large knowledge gaps in the reference experimental data to be covered for all these properties for a range of relevant mixtures anticipated in CCS conditioning and transport. Hence, in the CO_2Mix project, advanced measurements setups have been designed, and highly accurate measurements of phase equilibria, density, and speed of sound are under way. The measurements will be performed by SINTEF Energy Research, Norwegian University of Science and Technology (NTNU), and Ruhr-

Universität Bochum (RUB).

Acknowledgements

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