



Measurement and modelling of the vapor–liquid equilibrium of (CO₂ + CO) at temperatures between (218.15 and 302.93) K at pressures up to 15 MPa



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ABSTRACT

Precise knowledge of vapor–liquid equilibrium (VLE) data of (CO₂ + diluent) mixtures is crucial in the design and operation of carbon capture, transportation and storage processes. VLE measurements of the (CO₂ + CO) system are reported along seven isotherms at temperatures ranging from just above the triple-point temperature of CO₂ to 302.93 K and at pressures from the vapor pressure of pure CO₂ to approximately 15 MPa, including standard uncertainties of 0.006 K for temperature, 0.009 MPa for pressure and 0.011x(1 – x) for mole fraction x. The new VLE data have been compared with two thermodynamic models: the Peng–Robinson equation of state (PR-EOS) and a multi-fluid Helmholtz–energy equation of state known as EOS-CG. The PR-EOS was used with a single temperature-dependent binary interaction parameter, which was fitted to the experimental data. In contrast, EOS-CG was used in a purely-predictive mode with no parameters fitted to the present results. While PR-EOS generally agrees fairly well with the experimental data, EOS-CG showed significantly better agreement, especially close to the critical point.

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1. Introduction

Understanding the phase behavior of CO₂-rich mixtures is essential in many industrial processes such as synthesis-gas separation, CO₂-enhanced oil recovery and, more recently, carbon capture, transport and storage [1]. Phase behavior, pressure–volume–temperature relations, as well as other thermophysical properties, are required in the development of new equations of state (EOS) or in the optimization of the existing EOS.

In recent years, process design has benefited greatly from advances in computer simulation. These advances have been used to gain new insights into industrial processes as well as to estimate the performance of systems that are too complex for analytical solutions. Nevertheless, for the design, optimization and safe operation of those processes, accurate models are required to describe thermodynamic properties of the various mixtures. For instance, in gas separation processes, knowledge of phase equilibrium properties, mainly vapor–liquid equilibrium (VLE), is required for the

correct design of process equipment [2–4]. Processes such as separation of CO₂ from syngas streams and pipeline transportation of CO₂, typically containing a spectrum of impurities, occur at high pressure and/or low temperature conditions. Under these conditions, the fluids exhibit complex behavior that deviates significantly from ideality, calling for appropriate thermodynamic models for such mixtures.

Cubic EOS rooted in the van der Waals theory [5], such as the Peng–Robinson equation of state (PR-EOS) [6], have been widely and successfully applied for the past 40 years in process engineering calculations. They benefit from simplicity, low-computational requirements and straightforward implementation. Nevertheless, there remains a need for the development of more accurate EOS to address the shortcomings of cubic EOS, especially for the prediction of thermodynamic properties at high pressure. Over recent years, facilitated by advances in computing performance, the development of empirical multi-parameter Helmholtz–energy models has attracted widespread interest in the field [7–10].

A common approach is to use empirical multi-parameter multi-fluid Helmholtz–energy models, incorporating highly-accurate pure-fluid EOS, to predict the thermodynamic properties of mixtures [11]. In order to adjust the binary parameters that appear in those models, reliable and accurate experimental data on phase

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equilibria are indispensable. In fact, combining experimental phase-equilibrium data with empirical multi-parameter Helmholtz-energy EOS is a highly successful way to reduce the amount of experimental data needed to describe a system while at the same time improving the predictive capability of the EOS.

Probably the most accurate EOS currently available for the description of CO₂-rich mixtures are the GERG-2008 model of Kunz and Wagner [8] and the more recent EOS-CG model of Gernert and Span [10,12], which is an equation of state for humid combustion gases and similar mixtures. Both models use Helmholtz-energy EOS for the description of the contribution of the pure fluids to the mixture properties and contain binary parameters and some binary-specific departure functions. Both cover the main components relevant in CCS and flue-gas applications. However, GERG-2008 was developed for the prediction of thermodynamic properties of natural gases and similar mixtures, while the development of EOS-CG was focused mainly on humid and CO₂-rich gases. As with any empirical multi-parameters EOS, the success of these approaches in predicting mixture properties depends upon the availability of sufficiently-accurate experimental data against which to optimise the mixture parameters. One objective of the current work was to provide such data to facilitate future improvements to models such as EOS-CG.

Numerous high-pressure VLE experiments on CO₂-rich mixtures have been reported over recent decades [13–18]. Nevertheless, Li et al. [3], Gernert et al. [10] and Munkejord et al. [2], in their comprehensive reviews of the available VLE data for mixtures of CO₂ with substances relevant in CCS and flue gas applications, have identified significant gaps and discrepancies, especially in the critical region.

Recently, Coquelet et al. [19], Fandiño et al. [20], Tsankova et al. [21], Ben Souissi et al. [22] and Westman et al. [23–25] have studied the VLE of key binary mixtures containing CO₂, including (CO₂ + Ar), (CO₂ + H₂), (CO₂ + N₂) and (CO₂ + O₂) at temperature and pressure conditions relevant to those encountered in CO₂ pipeline transportation and low-temperature CO₂ separation processes. Nevertheless, VLE data for binary systems comprising CO₂ and toxic gases are still scarce. Experimental VLE data for the (CO₂ + CO) system were first reported by Kaminishi et al. [26], who used an analytical method but reported only a few points covering the temperature range between (223.15 and 283.15) K, with no measurements close to the critical locus. Christiansen et al. [16] used an analytical method with vapor recirculation to measure VLE of the (CO₂ + CO) system over the same temperature range. Huamin [27] reported measurements at pressures of less than 7 MPa over a temperature range from (223.15 to 261.15) K. The most-recent measurement for this system were reported by Blanco et al. [28], who used a synthetic method to study five different mixtures with CO₂ mole fractions ranging from 0.970 to 0.996 at temperatures between (253.15 and 293.15) K.

In order to check the consistency and reliability of these reported measurements [16,26–28], experimental data available at similar conditions of mole fraction, pressure and temperature have been compared. Unfortunately, as detailed further below, the agreement between the four available data sources is poor, except for the dew-point data of Kaminishi et al. [26] and Christiansen et al. [16] at 283.15 K. Significant inconsistencies between the measurements of all four authors occur even at low pressure. Therefore, new reliable and accurate VLE measurements on the (CO₂ + CO) system are needed.

The present paper reports new VLE measurements on the (CO₂ + CO) system at temperatures ranging from (218.15 to 302.93) K and pressures up to 15 MPa. The current study spans the temperature range from just above the triple-point temperature of CO₂ to just below the critical temperature of CO₂ and covers wider ranges of temperature and pressure than those reported previ-

ously. The new data gathered resolve inconsistencies between the few data available in the literature. The critical points on all isotherms were estimated by the use of scaling laws [29]. Furthermore, the new VLE data have been compared with the predictions of available thermodynamic models: the PR-EOS [6], generally incorporating a single temperature-dependent binary interaction parameter $k_{ij}(T)$, and EOS-CG [10], with no adjustable parameters.

2. Experimental

2.1. Apparatus

The low-temperature VLE apparatus used in this study was described in detail by Fandiño et al. [20] and is therefore presented here only in outline. The apparatus implemented the static-analytic method with online sampling and composition measurement, and was designed for a maximum working pressure of 20 MPa at temperatures in the range from (183 to 473) K. The apparatus, shown schematically in Fig. 1, comprised three main sub-systems: gas-handling, equilibrium cell, and quantitative compositional analysis.

The gas-handling system comprised valves V-1 to V-7, digital pressure sensors P1 to P3 and a N₂ purge. Valves V-1, V-2 and V-3 are used to introduce an approximately-known quantity of CO₂ into the equilibrium cell E-1. Valves V-4 and V-5 are used to introduce up to four further gases, thereby permitting the study of binary and multicomponent systems. The system was also used to clean the lines, reservoir E-2 and equilibrium cell by means of the venting valve V-6, the vacuum valve V-7, and a diaphragm vacuum pump. The reservoir E-2, having an internal volume of 500 cm³, was used as an intermediate CO₂ store between the supply cylinder and the equilibrium cell E-1. The amount of CO₂ introduced into the equilibrium cell was determined from changes in the reading of the pressure sensor P-3.

The high-pressure equilibrium cell E-1, fabricated from type 316L stainless steel, had an internal volume of approximately 143 cm³ and was fitted with a PTFE-coated magnetic stirrer bar. It was housed in a thermostat bath E-3 (Lauda Proline model RP890) filled with ethanol. The external permanent magnet drive, coupled with a magnetic stirrer bar, was rotated by means of a motor and gear assembly. The purpose of the N₂ purge was to create a dry and inert atmosphere inside the ethanol bath in order to avoid moisture condensation and to reduce the risk of fire or explosion, especially in the event of a leak of flammable gas.

The experimental temperature was measured with a platinum resistance thermometer (Fluke model 5615) calibrated on the International Temperature Scale of 1990 at temperatures ranging between (77 and 693) K. This was inserted into a blind hole bored in the wall of the equilibrium cell E-1. The thermometer resistance was measured and converted to a temperature reading by a digital readout unit (Fluke model 1502A). The experimental pressure was measured using a high-precision digital pressure transmitter (P-1, Keller model PA-33X, 30 MPa full scale) with manufacturer's stated expanded uncertainty of 0.05% of the full scale pressure ($k = 1.73$), corresponding to a standard uncertainty $u(p) = 0.009$ MPa. Since this measured gauge pressure, an additional absolute pressure sensor was used to obtain the atmospheric pressure (Keller model PAA-21Y, 0.2 MPa full scale) with manufacturer's stated expanded uncertainty of 1% of the full scale pressure ($k = 1.73$).

Sampling of the liquid and vapor phases was made through a pair of electromagnetic sampling valves (ROLSI Evolution IVTM, V-8 and V-9 in Fig. 1), each coupled to the equilibrium cell E-1 by a capillary tube. This arrangement permitted the withdrawal of small amounts of either phase without significantly disturbing the equilibrium. The samples were transferred to the gas

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