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Volumetric properties and phase behavior of sulfur dioxide, carbon disulfide and oxygen in high-pressure carbon dioxide fluid

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ABSTRACT

Acid gas re-injection or carbon capture and storage are two technologies now implemented for management of produced CO_2 or reducing the industrial emission of CO_2. For both technologies, impurities such as H_2O, H_2S, O_2, and SO_2 can find a way into a CO_2 injectate stream. In addition to unwanted reactions, these impurities can alter the phase behavior and volumetric properties of the injectate stream. Measuring accurate densities associated with mixing various impurities and CO_2 fluid is one method to optimize mixing coefficients for calculating reliable phase behavior and chemical activities for these systems. In this work, the volumetric influence and/or phase behavior of SO_2, CS_2, or O_2 impurities in a dense CO_2 phase were studied through high-precision density measurements. Densities of the CO_2 mixtures were measured with a custom vibrating tube densimeter with an average uncertainty of $\pm 0.07\ kg\ m^{-3}$ for temperatures of $T = 50$ to 125 °C and pressures at $p \leq 35$ MPa. The densities were used in calculating the apparent molar volumes, which were subsequently used to (i) calibrate or verify mixing coefficients for reference quality reduced Helmholtz energy equations-of-state, and (ii) provide a fitted equation based on fluctuation solution theory which can be used to calculate fugacity coefficients and partial molar volumes of CS_2 at infinite dilution. Validating our optimized mixing coefficients for the $CO_2 + SO_2$ mixture showed more reliable vapor-liquid equilibrium phase behavior when compared to those previously estimated in the literature.

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1. Introduction

In the effort to mitigate anthropogenic emissions of carbon dioxide (CO_2) into the atmosphere, two common management strategies are implemented: acid gas injection (AGI) and carbon capture and storage or sequestration (CCS) [1]. These management strategies require the separation of CO_2 from a produced hydrocarbon or flue gas source, compression, transport, and injection into underground formations that can see conditions up to $p \approx 35$ MPa and $T \approx 200$ °C [2,3]. Furthermore, in these management strategies various impurities can end up within the CO_2 stream that can influence the phase behavior and thermochemical properties of the injectate fluid stream [4,5].

In the AGI approach, mainly H_2S and CO_2, *i.e.,* acid gas fluids already present in natural gas, are selectively removed from the sales gas in order to (i) increase the heating or caloric value of the natural gas and (ii) reduce the emission of toxic gas such sulfur dioxide (SO_2) upon combustion by the end user. To do this, the natural gas is commonly treated with an aqueous alkanolamine solution which is then regenerated by heating, resulting in the release of a low-pressure wet acid gas [6]. Based on the criteria of the storage sites, the stream will require multistage compression, which may include transition from gaseous to dense phase fluid. The impurities accompanying the CO_2 injectate stream can lead to reaction chemistry that can introduce some other potential impurities such as carbon disulfide (CS_2) and carbonyl sulfide (COS),

$$2H_2S + CO_2 \rightleftharpoons CS_2 + 2H_2O \quad (1)$$

$$H_2S + CO_2 \rightleftharpoons COS + H_2O \quad (2)$$

The volumetric behavior of the COS in high pressure CO_2 fluid has previously been investigated and reported by our group [7].

In a CCS approach, the CO_2 stream captured from the exhaust of a power plant can also contain several impurities. For example, in the oxyfuel capture process, the use of excess high purity oxygen (O_2) in a power plant to generate electricity results in a flue gas containing mainly CO_2, O_2 and H_2O and in some cases SO_2 impurity

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[8]. If one considers combining an acid gas and flue gas stream in the future, the oxidation of H_2S to form elemental sulfur could be an issue.

The presence of the above-mentioned impurities within the CO_2 streams in both management strategies can influence the phase behavior and volumetric properties. For a simple example, the density of the CO_2 rich stream can be altered by the impurities and is required for compression, wellbore head pressure and injection pressure design considerations [5]. Many accurate reference equations are available for the densities (and other properties such as enthalpies, entropies and heat capacities) for the pure fluids, but the CO_2 mixtures have received less attention due to lack of experimental data. This has led to the estimation of mixing coefficients used with reference quality reduced Helmholtz equations-of-state (EOSs) for calculating reliable mixture properties. For the $CO_2 + O_2$ binary system, the only available literature density data were the data published by Mantovani et al. [9]. These data were limited to density measurement of up to $T \approx 110$ °C and $p \approx 20$ MPa. More recently, Nazeri et al. [10] reported experimental density measurements for 0.0522 mol fraction of SO_2 dissolved in dense CO_2 phase. These density data span from $T = 0.15$ to 80 °C and pressures up to $p = 42$ MPa. To the best of our knowledge, there are no previous literature density data for $CS_2 + CO_2$.

In this work, density measurements of sub-saturated solutes (CS_2, SO_2, or O_2) dissolved in CO_2 (0.2322, 0.2392, and 0.2867 mol kg^{-1} respectively) are reported from $T = 50$ to 125 °C and up to $p = 35$ MPa. The density differences from measured pure CO_2 fluid were used to calculate the apparent molar volumes of each component. These molar volumes were then subsequently used to evaluate i) two symmetric mixing coefficients for the reference reduced pure component Helmholtz EOSs and ii) an infinite dilution correlation function for CS_2 based on the generalized Krichevskii parameter, where there was no reference EOS for CS_2. The optimization of the correlation function for the $CS_2 + CO_2$ system can be used to calculate partial molar volumes and fugacity coefficients at infinite dilution for thermochemical calculations. The newly obtained symmetric mixing parameters presented in this work and those recently published by Nazeri et al. [10] for the $CO_2 + SO_2$ system were validated by way of relative percent density difference and comparisons of calculated and experimental vapor-liquid equilibrium (VLE) data. These comparisons show that the new optimized mixing coefficients provide more accurate predictions of p-ρ-T properties versus VLE when compared to the estimated parameters. Finally, for the $O_2 + CO_2$ system, the optimized symmetric mixing coefficients were found to verify previous estimations from Kunz and Wagner [11]. This was the first of several impurities studied that showed this verification.

2. Experimental section

2.1. Materials

The details of chemicals used in this study are summarized in Table 1. The purities from suppliers, after verification with gas chromatography (GC) coupled with a thermal conductivity detector (TCD), flame ionization detector (FID) and sulfur chemiluminescence detector (SCD), were deemed sufficient and were used for density measurement without further purification.

Table 1
Purity of chemicals used in this study, chemical supplier, and the analysis procedure used for verification.

Chemical Name	Source	Analysis Method	Purity/mol %
Carbon dioxide	Praxair Inc.	GC-TCD/FID/SCD	≥99.9995
Carbon disulfide	Sigma Aldrich	GC-TCD/FID/SCD	≥99.9
Sulfur dioxide	Praxair Inc.	GC-TCD/FID/SCD	99.98
Oxygen	Praxair Inc.	GC-TCD/FID/SCD	99.993
Hydrogen sulfide	In-house	GC-TCD/FID/SCD	99.95
Nitrogen	Praxair Inc.	GC-TCD/FID/SCD	≥99.998

The distilled water used for the calibration process was polished with a water purification system (EMD Millipore model Milli-Q Type 1) to a resistivity of 18 MΩ cm. The polished water was then further degassed by stirring under vacuum for several hours before use in the vibrating tube densimeter (VTD).

2.2. Mixture preparation procedure

The CO_2 binary mixtures were prepared gravimetrically inside a well evacuated 316 stainless steel double-ended sample cylinder with an approximate inner volumes of 503 cm^3. All masses in this work were determined four times using a high-precision (Mettler Toledo XP26003L) mass comparator with a resolution of 1 mg. All mixtures were mixed using a rocking table-top, which agitated for 8 h each day for two weeks. The reported uncertainty on the molality of each mixture in Table 2 was calculated by multiplying the standard deviation by a factor of 2, providing a confidence level of approximately 90%. The binary mixture was then analyzed by GC before careful transfer into high-pressure syringe pump (Teledyne ISCO Model 260D) connected to the VTD. During the transfer procedure, the mixture in the sample cylinder, the transfer lines and the syringe pump were always maintained well above the two-phase region (by controlling the temperature and pressure) to avoid altering the composition of the fluid before measurement.

2.3. Description of the VTD used in density measurement

The single-phase CO_2 binary mixtures in the syringe pump were charged into a VTD that was built and commissioned by Deering et al. [12]. Details of the instrument and experimental procedures have been reported elsewhere, where density measurements were shown to have an average uncertainty of ±0.07 kg m^{-3} at $T = 50$ to 125 °C and up to $p = 35$ MPa [13]. In this work, only a brief description of the instrument and the measurement procedure will be given.

The vibrating tube (VT) was made of Hastelloy-C276 (H-C276) tubing as it provides good corrosion resistance. The H-C276 tube was contained in a high vacuum environment to help reduce any external surface adsorption and drag, which may result in long-term measurement drift. The vacuum chamber containing the H-C276 tube was housed in a modified Hewlett-Packard 5890 gas chromatography oven to control the temperature. Four-wire 100 Ω platinum resistance thermometers (PRT) were used in monitoring the temperatures at four different appropriate locations. These PRTs were calibrated according to the International Temperature Scale of 1990 (ITS-90) [14]. After the calibration, the overall estimated standard uncertainty in the temperature measurements was found to be ±0.005 °C. The pressure was measured with a Paroscientific 410 KR-HT-101 Digiquartz pressure transducer. This transducer was used to provide pressure measurement of fluids in this work and was re-calibrated with a deadweight tester yielding an accuracy of 0.0052% [13].

The VT behaves as a harmonic oscillator, where the change in the natural vibrational frequency of the tube is related to any change in fluid density. The vibration of the tube is driven using a coupling between a permanent magnet external to the tube, an iron tab attached to the tube and an external electromagnetic drive coil. The time period of the vibrating tube's oscillation was measured by a Berkeley Nucleonics Corporation (BNC) model 1105 universal frequency counter with a resolution of 40 ps. The density measurement of the sample fluid in the vibrating tube can be related

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