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Thermodynamics of carbon dioxide-hydrocarbon systems

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HIGHLIGHTS

- A comprehensive thermodynamic study of a prototype hydrocarbon-CO_2 system.
- Density and phase behavior measurements.
- Comparison with predictive thermodynamic models: PPR78 and SAFT-γ Mie.
- Both models perform well for phase behavior.
- SAFT-γ Mie generally superior for density.

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ABSTRACT

Understanding the thermophysical properties for mixtures of CO_2 and hydrocarbons at reservoir conditions is very important for the correct design and optimization of CO_2-enhanced oil recovery and carbon storage in depleted oil or gas fields. In this paper, we present a comprehensive thermodynamic study of the prototype system (CO_2 + n-heptane) comprising highly-accurate measurements of the saturated-phase densities, compressed-fluid densities, and bubble and dew points at temperatures from 283 K to 473 K and pressures up to 68 MPa over the full range of composition. We use these results to examine the predictive capability of two leading thermodynamic models: the Predictive Peng-Robinson (PPR-78) equation of state and a version of the Statistical Associating Fluid Theory for potentials of the Mie form, known as SAFT-γ Mie. Both of these models use group contribution approaches to estimate interaction parameters and can be applied to complex multi-component systems. The comparison shows that both approaches are reliable for the phase behavior. Neither model is entirely satisfactory for density, with each exhibiting absolute average relative deviations (AARD) from the experimental data of about 4% for the saturated-phase densities and 2% for the compressed-fluid densities; however, SAFT-γ Mie is found to be much more accurate than PPR-78 for the compressibility, with an overall AARD of 6% compared with 18% for PPR-78.

1. Introduction

Largely as a consequence of the combustion of fossil fuels, carbon dioxide concentrations in the atmosphere have been rising steadily and have recently surpassed 400 ppm [1]. This rising trend is the major driver of a continuing process of climate change that has so far seen the global mean surface temperature increase by about 1 °C since pre-industrial times [2,3]. Clearly, there is now an urgent need to stabilise CO_2 levels in the atmosphere to mitigate further dangerous climate change. In December 2015, an action plan was agreed in Paris with the aim of limiting the global average temperature increase by 2100 to $<$ 2 °C above pre-industrial levels [4]. To achieve this, a massive reduction in CO_2 emissions is required. The pathway to decarbonization will probably include a mix of technologies. As it is generally accepted that fossil fuels will continue to be part of the global energy mix during the 21st century, carbon capture and storage (CCS) will be a crucial technology in the drive to reduce anthropogenic CO_2 emissions from the power and industry sectors over the short and medium term, thereby protecting the security and stability of the energy system. According to an IEA report in 2015 [5], in all sectors, the amount of CO_2 captured and stored needs to be about 6 Gt per year by 2050 as a part of the overall strategy needed to achieve the 2 °C target. An advantage of CCS technologies is that they can be retrofitted to many industrial processes such as natural gas processing, hydrogen production, steel

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and cement making, as well as to power generation. Furthermore, if biomass firing is adopted power generation with net-negative CO_2 emissions is possible [6].

The CCS process comprises three main steps: capture (typically separation of CO_2 from other gaseous substances), transport (*e.g.* by pipeline), and finally storage in a geological formation (CO_2 injection and long-term monitoring to ensure permanence) [7]. Potential geological storage sites for CO_2 include active and depleted hydrocarbon reservoirs, un-minable coal seams and deep saline aquifers [8]. Potentially, the cheapest storage solution would be injection into partially-depleted oil reservoirs to enhance oil recovery (CO_2-EOR) while also storing large amounts of CO_2 [9]. CO_2-EOR could be beneficial economically as a means of reducing the high cost of CCS. Moreover, the geological properties of the oil and gas reservoirs are usually better known, as a result of their previous exploitation history, than is the case for other storage sinks. The largest commercial CCS projects have been achieved by combining CCS with EOR technology [10]. The recently published white paper, “Can technology unlock unburnable carbon?” [11] estimates that, worldwide, 1000 Gt of CO_2 can be stored in hydrocarbon reservoirs alone. The analysis in the white paper suggests that, in the period 2010 to 2050, between 100 Gt and 500 Gt of CO_2 storage would be required to meet the 2 °C objective; therefore, the available oil and gas fields potentially have the capacity to store all of the targeted CO_2, possibly at a lower cost than other options.

In the CO_2-EOR process, some of the residual oil trapped in the reservoir after secondary recovery is extracted with a tertiary CO_2 flood. The performance of the CO_2 flood relies strongly on the physical properties of the mixture of CO_2 with crude oil. Depending upon the oil composition and the temperature and pressure in the reservoir, CO_2 flooding can be either miscible, where complete miscibility of oil and CO_2 is possible, or partially miscible. The miscibility of CO_2 with the crude oil is characterized by the minimum miscibility pressure (MMP) at the reservoir temperature. This MMP is often determined in the laboratory using bottom-hole oil samples with CO_2 in the slim-tube experiment [12]. However, in the field, 100% sweep efficiency is not achieved, even above the MMP, as the CO_2 can pass along high-permeability paths between the injection and production wells, bypassing some of the residual oil. Therefore, under typical reservoir conditions, two non-aqueous phases will be present during CO_2 injection: one phase rich in CO_2, containing light hydrocarbons extracted from the oil, and the other rich in heavier hydrocarbons. The CO_2-rich phase will have a low viscosity and flow more freely towards the production well, contacting fresh oil from which it may extract further hydrocarbons. In addition, dissolution of CO_2 in the oil-rich phase results in swelling and a reduction in viscosity; this expanded oil can then also flow more easily towards the production wells [13]. At the surface, CO_2 dissolved in the produced oil is separated and re-circulated back into the process, while CO_2 not transported to the production wells is permanently stored during the process. In some fields, 40% to 50% of the injected CO_2 remains in the reservoir permanently [14], and a significant portion of the residual oil is extracted [15]. For example, since 2008, the Wasson Field’s Denver Unit CO_2 EOR project has recovered 15% of the residual oil saturation after waterflooding [16]. Enhanced gas recovery with CO_2 injection and sequestration has also been proposed and, like CO_2-EOR, may offer an economically advantageous way of achieving carbon storage [17,18].

Understanding of the phase behaviour and thermophysical properties for CO_2 + hydrocarbon systems at reservoir conditions is very important for the correct design and optimization of both CO_2-EOR and carbon storage processes. In addition to phase behaviour, the thermophysical properties of interest include (but are not limited to) the saturated-phase and compressed-fluid densities. These properties are essential to determine the amount of CO_2 that can be stored in a depleted oil reservoir as well as to model convective transport through the reservoir [19]. The saturated-phase and compressed-fluid densities are also necessary for calculating the oil swelling during CO_2 reservoir flooding. Moreover, such data are important in downstream processing and in a wide range of industrial applications such as supercritical extraction and separation processes [20,21]. Since these processes cover large ranges of operating conditions and involve multicomponent systems, reservoir/process simulations are employed in design. The design of robust and safe processes can only be achieved if the equation-of-state (EOS) models used in these simulations are optimized and/or validated with accurate experimental data [22]. In oilfield applications, the parameters of the EoS models may be optimized against measured properties of bottom-hole reservoir-fluid samples taken from the production zones of interest. However, both the generic understanding of phase behaviour and properties, and the interpretation of field data, rely greatly upon a thorough understanding of simpler systems that present the essential features of the actual reservoir fluids. For CO_2-EOR and carbon storage applications, such systems comprise mixtures of CO_2 with one or more hydrocarbon components. In order to construct reliable EOS models, it is necessary to have a substantial database of experimental information pertaining to phase behaviour and properties at reservoir conditions. Unfortunately, the available phase-behaviour, saturated-phase and compressed-fluid density data for the mixtures of interest are extremely limited at reservoir conditions [23,24].

In both petroleum and chemical engineering applications involving carbon dioxide and hydrocarbons, cubic equations of state (CEOS) are very widely deployed [25,26]. These are modifications of the van der Waals EOS and include such well-known models as the Peng-Robinson (PR) [27] and Soave-Redlich-Kwong (SRK) [28] CEOS. In connection with these, experimental data (especially vapor-liquid equilibrium data) for binary mixtures are used in the optimization of binary interaction parameters. Therefore, the performance of traditional CEOS models is limited in part by the accuracy and extent of the experimental data used in these optimizations. Several previous studies have explored the application of CEOS to mixtures of CO_2 with hydrocarbons. For example, Kariznovi have measured the bubble-curves and saturated liquid densities of ternary mixtures containing CO_2, decane and either tetradecane of octadecane [29–32]. CEOS models investigated provided a good description of the bubble-curve data when the binary interaction parameters were regressed against the binary VLE data. However, they obtained a generally poor description of the saturated-liquid densities unless volume translation terms fitted to experimental mixture data were incorporated. Other studies show similar results [33,34] and it can be concluded that, while conventional CEOS models can offer a good representation of phase behaviour, they perform relatively poorly in the prediction of density and fail in the critical region. Volume translation can be used to improve the representation of liquid density in the subcritical region somewhat, typically by making a temperature-dependent adjustment to the molar volume chosen to fit the saturated liquid density [35]. Additionally, the crossover approach may be applied to improve the representation of the critical region for both pure fluids and binary mixtures [36–38]. In the context of hydrocarbon-CO_2 mixtures, Shen et al. [39] have studied the performance of the SRK equation with both a temperature-independent volume translation and a crossover model. This approach was found to represent the saturation properties of both CO_2 and light hydrocarbons very well. When compared with experimental data for mixtures of CO_2 with C_2 to C_5 alkanes, absolute average relative deviations (AARD) in bubble pressure of between 0.4% and 1.7% were found, while the AARDs for pressure in single-phase compressed-fluid regions were between 0.4% and 16%. Unfortunately, crossover models are not easily extended to multi-component systems and volume translation does not correct the CEOS at conditions far from saturation.

Multi-Fluid Helmholtz Equation of State (MFHEOS) [40], notably the GERG-2008 EOS [41], exploit highly-accurate Helmholtz models for pure substances together with specially developed mixing rules and binary-specific departure functions for mixtures [42]. These models contain many parameters but can perform well when fully optimized by comparison with extensive experimental data. The component slate of