



Interfacial tension measurements and modelling of (carbon dioxide + *n*-alkane) and (carbon dioxide + water) binary mixtures at elevated pressures and temperatures

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ABSTRACT

Supercritical carbon dioxide (CO₂) is often used as a process fluid for enhanced oil recovery. The storage of carbon dioxide in underground formations is a potential way of mitigating climate change during a transition period to more sustainable energy sources. Combining injection with subsequent trapping of the non-wetting supercritical carbon dioxide phase in the pores of a depleted reservoir is a promising scheme for allowing the continued use of fossil fuels with minimal environmental consequences. The design of such processes is ultimately linked to the confined behaviour of the fluids in question at reservoir conditions, which is largely controlled by interfacial forces. Measurements of the relevant interfacial tensions for systems containing alkanes, carbon dioxide and water are currently limited and inconsistent while models usually fail to capture the pressure dependence of the interfacial tension. In this work, a density functional theory based on the SAFT-VR equation of state was used to predict the interfacial tension of (H₂O + CO₂ + *n*-alkane) binary systems over wide ranges of temperature and pressure. The comparison with a new set of reported experimental data of three (*n*-alkane + CO₂) systems at pressures up to the critical points, as well as with the (H₂O + CO₂) system at pressures up to 60 MPa, for a temperature range of (298–443) K, is discussed.

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1. Introduction

Carbon dioxide (CO₂) is one of the long-lived greenhouse gases (GHGs) emitted by human activity. Although it has a lower global warming potential (GWP) than the other major GHGs, it remains the most significant in terms of both emissions and impact [1]. In 2004, the amount of CO₂ produced from burning fossil fuel accounted for 57% of the world's total annual equivalent CO₂ emissions. This represents an increase since 1970 of 70% [2]. Carbon capture and storage (CCS) [3,4] is widely seen as an attractive approach for mitigating CO₂ and is projected to play a major role in emissions reduction [3].

Sequestration can be achieved by injection of CO₂ in underground formations at depths of approximately 800 m or more,

where it would be in a supercritical state with a density of $\rho \geq 300 \text{ kg m}^{-3}$. Storage would be feasible as long as buoyancy forces can be balanced by capillary forces, trapping CO₂ in rock pores, and/or CO₂ is retained below an impermeable cap rock. Porous formations such as deep saline aquifers and depleted oil or gas reservoirs can serve as sites for CO₂ storage [3]. A range of trapping mechanisms applies in such formations. Dissolution of CO₂ in the aqueous phase occurs over the medium-term (hundreds of years), while the consequent mineralisation over the long-term (millions of years) [5]. However, over the short-term (decades) the storage of CO₂ in porous reservoirs must rely on capillary trapping, i.e., the injection into μm -sized pores where interfacial tension causes the non-wetting CO₂ phase to be retained between narrow pore throats. CO₂ is also used as a process fluid in oil and gas reservoirs [6] for enhanced oil recovery (EOR) which provides the potential for CO₂ to be trapped by capillary forces in the pores of the reservoir after displacing the in situ oil or gas, so liberating at the same time valuable hydrocarbons.

Capillary trapping is largely linked to the interfacial properties of CO₂ with the reservoir fluids, mainly brine and hydrocarbons.

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The interfacial tension of CO₂ with these fluids at conditions representative of those in underground formations is therefore an important thermophysical property for the design of such processes. The data currently available are limited in extent and accuracy, especially at elevated pressures and temperatures. Such high-pressure, high-temperature (HPHT) interfacial tension data for (H₂O + *n*-alkane + CO₂) systems are required as inputs for reservoir flow models to extend their predictive capability over a wide pressure and temperature range.

The two main methods for measuring interfacial tension at elevated pressures are: the pendant drop method, using either selected plane (SP) [7] or drop shape analysis (DSA) [8,9], and the capillary rise method [10]. The DSA of pendant drops has been applied in our current work; the theoretical background for the determination of interfacial tension with the DSA approach is described extensively by Song et al. [8,9]

To our knowledge only a very limited number of experimental studies of the interfacial tension of (*n*-alkane + CO₂) systems have been undertaken at elevated pressures. Nagarajan and Robinson [11] have employed a high pressure apparatus consisting of an interfacial tension view cell and a gas chromatograph for the simultaneous determination of the fluid phase behaviour. Shaver et al. [12] also applied the pendant drop method for measuring interfacial tensions of (*n*-alkane + CO₂) systems with increasing pressure, using the same apparatus as Nagarajan and Robinson [11], after having implemented various adjustments/improvements. They used a combination of the previously published methodologies of Roush [13] for the conversion of the drop profile to cartesian values and that of Jennings and Pallas [14] for the subsequent determination of the interfacial tension. In both of these studies the densities were determined, using gas chromatography for the analysis of the two phases, at the same time as the interfacial tension, with the option of choosing different capillary sizes for the measurement of a wide range of interfacial tensions. We should also point out that a completely different technique, based on the restoring forces produced by capillary waves on the fluid surface after interacting with a laser beam, has been used to measure the surface tension of mixtures of (*n*-heptane + CO₂) and (diesel fuel + CO₂) [15]; the estimates of the vapour–liquid surface tension of pure *n*-heptane were found to be in good agreement with those obtained with the more traditional techniques based on capillarity. Several experimental studies of the interfacial tension of the (H₂O + CO₂) system have addressed the effect of elevated pressures and temperatures [16–29], and a detailed comparison has been presented in previous work [30].

From a modelling perspective, numerous studies have been made using different techniques to describe the interfacial properties and surface tension. An extensive literature review describing the differing methodologies and applications to inhomogeneous systems has already been presented [31]. Among the many methodologies, density gradient theory (DGT) and density functional theory (DFT) are the most popular and accurate theoretical approaches used for interfacial calculations.

DGT is a theory based on the van der Waals theory for inhomogeneous fluids [32]. Rediscovered by Cahn and Hilliard [33], it presents an expansion of the Helmholtz free energy density about a step density profile, that is truncated after the second term. The local free-energy density is obtained from an equation of state. This type of approach has been used to model the interfacial properties of (*n*-alkane + CO₂) and (H₂O + CO₂) systems [34–40]. However, the main limitation of the DGT approach is the need to introduce the so-called “influence parameter”. The parameter is adjusted to provide an optimal description of the surface tension data of pure fluids and it is then transferred to mixtures by using simple mixing rules.

One of the most successful predictive approaches for the study of interfacial phenomena comes from the development of DFT

methods that are based on the construction of a free energy functional from which the properties of the inhomogeneous system can be calculated. The methods for the construction of the DFT, and the different approximations commonly employed are described in detail in the excellent reviews of Evans [41] and Davis [42].

Previous applications of DFT for the prediction of (*n*-alkane + CO₂) and (H₂O + CO₂) mixtures is very restricted. To our knowledge, the only work devoted to the study of one of these mixtures is the work of Sarman et al. [43] for the (*n*-decane + CO₂) system.

Any interfacial treatment needs to be coupled to an equation of state. The evaluation of the interface requires, as a necessary prerequisite, an accurate calculation of the properties of the bulk fluid phases. Consequently, the choice of the equation of state is of crucial importance for an accurate representation of the interfacial properties. In this work, we use the SAFT-VR equation of state [44,45] as it has been shown to provide a good description of the bulk fluid phases of a wide range of systems. The SAFT-VR approach has already been used to accurately represent both the vapour–liquid and liquid–liquid phase equilibria of mixtures comprising alkanes, water, and carbon dioxide [46–71], which are the main focus of our current study. SAFT-VR is one of the variants of the original statistical associating fluid theory (SAFT) [72,73], based on Wertheim’s first order perturbation theory for associating systems [74–77]. In any SAFT-type equation of state, the Helmholtz free energy is made up of a sum of terms that contribute to the thermodynamic properties of the system and is firmly grounded in statistical mechanics. The reader is referred to comprehensive reviews for more information about the general SAFT approach and its capabilities [78–81].

The goal of this paper is twofold: first, to present a new set of measurements for three different (*n*-alkane + CO₂) systems over a wide range of pressures and temperatures; and second, to compare the new data and the recently published measurements of the (H₂O + CO₂) system [30] with predictions of the SAFT-VR-DFT approach [31] in order to check its capability for the representation of the fluid phase interfacial properties of these complex systems. We should note that the SAFT-VR approach for Mie potentials has also been used recently within a DGT formalism to successfully describe the high pressure interfacial tension of both the VLE and LLE in aqueous mixtures of CO₂ [82].

The rest of this contribution is presented as follows: in Section 2 we provide a description of the experimental setup and the conditions employed; in Section 3 we summarise the main features of the DFT approach applied to SAFT-VR to represent the interfacial properties; Section 4 is devoted to the comparison of the experimental data with the SAFT-VR-DFT. Finally, some concluding remarks are provided in Section 5.

2. Experimental

2.1. Materials

The CO₂ used in our studies was of CP grade, supplied by BOC, with a mole fraction purity >0.99995. The normal alkanes (Sigma–Aldrich, Dorset, UK) investigated (*n*-decane, *n*-dodecane and *n*-hexadecane) were of mole fraction purities >0.990; no further purification treatment was applied. Hexane (BDH, Hull, UK), iso-propanol (Sigma–Aldrich, Dorset, UK) and toluene (Sigma–Aldrich, Dorset, UK) used in this work for cleaning purposes were of mole fraction purities >0.95, 0.999 and 0.999, respectively.

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