High-pressure densities and interfacial tensions of binary systems containing carbon dioxide + n-alkanes : (n-dodecane, n-tridecane , n-tetradecane).

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ABSTRACT

Experimental isothermal densities and interfacial tensions for the binary systems carbon dioxide + n-dodecane, carbon dioxide + n-tridecane and carbon dioxide + n-tetradecane at 344.15 K and over the pressure range 0.1 to 12, 13 and 14 MPa, are reported. Measurements are carried out on a combined device that includes a high-pressure vibrating tube densimeter and a high-pressure pendant drop tensiometer. The theoretical modeling is based on the use of Square Gradient Theory as applied to the Statistical Associated Fluid Theory (SAFT) equation of state. The experimental bulk phase equilibrium densities and interfacial tensions obtained are in very good agreement with the theoretical modeling. By seamlessly combining experimental and modelling approaches we are able to simultaneously predict phase equilibrium and interfacial properties. For the systems and conditions studied we do not observe mass nor molar barotropic inversion; the interfacial tensions decrease as the pressure (or liquid mole fraction of carbon dioxide) and/or as the n-alkane molecular chain length increases. The surface relative Gibbs adsorption of the species along the interfacial region is reported; carbon dioxide is adsorbed along the interfacial region, whereas n-alkanes (n-dodecane, or n-tridecane or n-tetradecane) do not exhibit any special adsorption activity. The adsorption of carbon dioxide increases with pressure and with the chain length of the n-alkane.

Keywords: High-pressure interfacial tension; waxes, high-pressure density; CO₂ + hydrocarbon mixtures; Square gradient theory; SAFT-EoS; EOR

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1. Introduction

The interfacial tensions (IFT) amongst carbon dioxide (CO_2), hydrocarbons and water within a crude oil reservoir are crucial properties for the understanding and eventual improvement of oil recovery and gas injection in Enhanced Oil Recovery (EOR) processes [1,2,3,4,5]. Important properties such as phase wettability (or distribution of gas, oil, water in a the reservoir), capillary pressure (or pressure across the interface), and relative permeability (or selectivity for multiphase flow in a reservoir) are influenced by the magnitude and change in IFT's with pressure, temperature and composition. Certainly, a controlled reduction of the IFT value between the injected fluid and reservoir oils improves displacement efficiencies and reduces oil saturation in EOR operations [6]. It is also worth noting also that the vanishing values of IFT are fundamental for establishing the minimum miscibility pressure, which is the main parameter required for designing and optimizing CO_2 flooding processes (see Ref. [7] and references therein). Similarly, the magnitude of IFTs dramatically affects the gravity-drainage recovery. In fact, Firoozabadi et al [8] pointed out that a reduction of 0.5 mN/m may increase the drainage recovery performance from 14 to 41% in stock-tank oil contents of reservoirs. In general, EOR proceeds at extreme temperature and pressure conditions where the values of IFTs happen to be very sensitive. Therefore, the accurate characterization and eventual tunability of IFT in a broad range of temperature and pressure is required to control the EOR efficiency.

In order to measure the interfacial properties of the mixtures as those considered in this work, by far the most common technique is the use of pendant drop tensiometry [9,10,11,12,13,14,15,16,17, 18,19,20,21]. On the other hand, theoretical descriptions of these mixtures have been made by employing Density Functional Theory (DFT) [13,14,22], Density Gradient Theory (DGT) or Square Gradient Theory (SGT) [23,24,25,26,27,28,29,30,31,32,33,34,35,36,37,38]. Furthermore, molecular simulations based either on Molecular Dynamics or Monte Carlo schemes have also been employed [19,30,31,39,40,41] to garner information on the interfacial properties of these systems. An analysis of the above mentioned references reveals that there are key points that must be taken into account: First, an unequivocal full description of interfacial properties requires -at least- two independent approaches, as some previous works have demonstrated (see for instance [13-35] and references therein). For example, while experimentation may provide bulk phase densities and interfacial tensions, classical measurements themselves do not provide detailed information at the molecular level or an accurate determination of the adsorption of species along the interfacial region. On the other hand, although theoretical models and molecular simulations are still deemed to have limited predictive capability due to the uncertainties associated their parameters, this situation is changing, and appropriately fitted

forcefields are able to discern between experimental data sets and even provide qualitative results rivaling the precision of experiments [42]. Second, most of the experimental determinations of IFT consider the use of pure bulk phase densities rather than the bulk phase densities of the mixture. This approximation has been successfully tested for several authors at moderate pressure and temperature (see for instance [43,44] and references therein). However, near to the critical state or close to a barotropic transition [45,46] the density difference between phases becomes negligible and very different to that of the pure fluids, thus affecting the accuracy of IFT determinations. This issue is important for CO₂ -containing mixtures, where the critical point is close to ambient temperature and the high pressure densities close to those of room-temperature organics. Third, DFT is less used than SGT or DGT for predicting interfacial properties in spite the fact that in principle, the theoretical framework is solid. The difficulties arise in the implementation of DFT to energetically or geometrically anisotropic models of fluids. On the other hand, in using SGT, an equation of state (EoS) can be employed directly, providing a route for determining interfacial properties with a simultaneous description of accurate PvT properties.

As part of our ongoing research work, which is devoted to the description of interfacial properties for CO₂ + n-alkanes mixtures [28-31], this work is focused on the experimental determination and theoretical modeling of bulk phase equilibrium densities and interfacial tensions of the CO₂ + n-dodecane (n-C₁₂H₂₆), CO₂ + n-tridecane (n-C₁₃H₂₈), and CO₂ + n-tetradecane (n-C₁₄H₃₀) binary mixtures at 344.15 K and over the pressure range 0.1 to 12, 13, and 14 MPa, respectively.

CO₂ + n-alkane mixtures exhibit interesting and complex bulk phase and interfacial behavior and some results are available for the above-mentioned mixtures. For the mixtures analyzed here, Fall and Luks [47] have measured and classified the phase behavior according to the van Konynenburg and Scott's [48] nomenclature. Complementarily to the work of Fall and Luks on the characterization of phase equilibria, we have characterized the thermodynamic conditions for the density inversions (mass or/and molar) observed in these mixtures [45,46]. Specifically, CO₂ + n-C₁₂H₂₆ is classified as a Type II non-barotropic mixture, CO₂ + n-C₁₃H₂₈ belongs to Type IV and displays molar barotropy, while CO₂ + n-C₁₄H₃₀ classifies as Type III and exhibits both mass and molar barotropy. Depending of the particular thermo-physical (T , p , x) conditions, these mixtures may exhibit subcritical vapor – liquid, liquid – liquid, or vapor – liquid – liquid phase equilibrium and, in some cases and conditions, display density inversions. These sub-critical phase behavior are able to promote different patterns of interfacial behavior, as we exemplified previously.[49,50] Our choice of systems is dictated by the change in barotropic behavior exhibited by these mixtures and the presumption that this volumetric effect might have an influence over interfacial properties.

For a complete discussion concerning the modeling and availability of experimental information of phase equilibrium data for CO₂ + n-alkane series, the reader is referred to Refs. [45,46,51,52,53,54,55]. Specifically, IFTs for CO₂ + n-C₁₂H₂₆ have been reported by Georgiadis et al. [13,14] as a function of temperature and pressure (297.85 to 443.05 K and 120 to 1518 kPa). Georgiadis et al. measured the IFT by using a pendant drop tensiometer and the corresponding theoretical modeling was carried out by the combination of the Statistical Associating Fluid Theory (SAFT) of Variable Range (VR) EoS [56,57] and DFT. The experimental tensiometry and SAFT-VR + DFT modeling showed good agreement with each other in spite of the fact that the reported IFT data were based on bulk phase densities of the pure components rather than on the actual density of the mixture, which may result on a displacement of the true value of the IFT, as the authors point out. For the case of CO₂ + n-C₁₃H₂₈ no experimental or theoretical values are available in the open literature. Finally, bulk phase equilibria and IFTs for CO₂ + n-C₁₄H₃₀ were measured by Gasem et al. [12] and theoretically modeled by using the DFT + SAFT-VR EoS [22] and the Square Gradient Theory (SGT) using cubic [26], quartic [28] and SAFT [33,34] EoSs.

This paper is organized as follows; we first describe the experimental equipment and measurement details (section 2). We then summarize the main expressions of the square gradient theory and the SAFT-VR-Mie EoS model (section 3). Following, we present and discuss the main results of both bulk phase equilibrium densities and interfacial properties (interfacial tension, surface activity and relative Gibbs adsorption isotherm) in section 4. Finally, we summarize the main conclusions of this work in section 5.

2. Experimental Section

2.1 Purity of Materials.

n-alkanes (i.e. n-dodecane, n-tridecane, n-tetradecane) were purchased from Aldrich and used without further purification. Table 1 reports the purity of the components (as determined by gas chromatography, GC), together with the mass densities ($\hat{\rho}$), and the interfacial tensions (γ) of pure fluids at 344.15 K and atmospheric pressure. The experimental values are also compared with those previously reported by NIST-REFPROP [58]. Carbon dioxide was purchased from Linde S.A. (Chile) with a certified purity greater than 99.9 %.

2.2 Apparatus and procedure

2.2.1. Density measurements

The mass density ($\hat{\rho}$) of pure fluids is measured at 344.15 K and atmospheric pressure using a DMA 5000 densimeter (Anton Paar, Austria). For the case of mixtures (CO₂ + n-alkane) at pressures over the atmospheric pressure, $\hat{\rho}$ in the liquid and vapor phases are measured at the experimental temperature and pressure using a DMA HP densimeter (Anton Paar GmbH, Austria). In both cases (atmospheric and high pressure) the mass density is measured with an accuracy of $5 \times 10^{-3} \text{ kg m}^{-3}$.

In both densimeters, the mass density determination is based on measuring the period of oscillation of a vibrating U-shaped tube filled with the fluid mixture sample. During the operation, the temperature of the apparatus is maintained constant to within $\pm 0.01 \text{ K}$. Pressure, in turn, is measured by means a Swagelok type S pressure transducer connected to the densimeter, and maintained constant to within $\pm 0.001 \text{ kPa}$ by means of the high-pressure syringe pump (Teledyne Isco Pump. Model 100DM, USA). The density measurements are repeated 25 times for each condition and averaged accordingly.

2.2.2. Interfacial Tension Cell.

A pendant drop tensiometer model IFT-10, manufactured by Temco Inc. (USA) is used for interfacial tension measurements. The pendant drop cell is a stainless steel cylindrical chamber (with an inner volume of $\sim 42 \text{ cm}^3$), with two injection orifices one at the top and the other at the bottom of the chamber. On the top orifice a stainless steel needle (1.4 mm i.d. and 2.45 mm o.d.) is placed for generating pendant drops. The bottom orifice is connected to the high-pressure syringe pump (Teledyne Isco Pump. Model 100DM, USA), which is used to compress CO₂ from a commercial ultra high purity CO₂ cylinder and maintained the experimental pressure constant within $\pm 0.001 \text{ kPa}$.

The chamber is equipped with appropriately sealed borosilicate glass windows, which allow visualization of the inner space during operation. The light beam source, located at one side of the visualization axis, is a quartz halogen bulb (SII P/N 240-350, Scientific Instrument Inc, USA) covered by a white diffuser made of Teflon. The camera, located at opposite side of the visualization axis, is a monochrome video camera model CS8320Bi (Toshiba Teli, Corp., Japan) connected to a personal computer through a frame grabber card. The temperature of the cell is measured by means a K-type thermocouple, and maintained constant to within $\pm 0.1 \text{ K}$ by means of electric band heaters operated by

a Watlow temperature controller model TC-211-K-989 (USA). The tensiometer, the light source and the camera are mounted on a free vibration table (Vibraplane, model 2210, USA) in order to avoid the effect of noisy measurements due to external vibrations. Interfacial tension measurements were made by analyzing images of liquid (n-alkanes) pendant drops generated at the tip of an injection needle, which is surrounded by CO₂, by using the DROPimage Advanced software version 1.5 (Ramé – Hart instruments, co. USA).[59]

The experimental procedure for determining interfacial tension is as follows. The cell is heated to the desired experimental temperature, and then it is slightly pressurized with CO₂. After degasification in an ultrasonic bath, the n-alkane (n-dodecane or n-tridecane or n-tetradecane) is pumped through a stainless steel tube to the needle tip. The pump is a positive displacement ELDEX HP Series Model B-100-S-2 CE (USA). Initially, a small portion of the pure liquid is pumped into the chamber in order to saturate the gas that fills the cell. Then, the cell is pressurized to the desired experimental pressure and a liquid drop is generated at the tip of the needle. The pressure in the IFT cell is maintained constant to within ± 0.10 kPa by means of the high-pressure syringe pump.

Once the drop is formed and the desired experimental temperature and pressure are reached, it is necessary to wait, approximately, 5 to 10 minutes until the drop reaches an equilibrium state. For the systems study here, the experiments showed that, due to the fast mass transfer processes, the interfacial tensions reaches an equilibrium state very fast (less than 5 minutes). After this equilibration step, the drop dimensions are recorded (at least during 6 hours) in order to check the stability of its geometry.

Once the shape and volume of the drop are deemed constant, the equatorial diameter of the drop, d_e (the largest one), and the horizontal diameter of the drop, d_s , which is located at a distance d_e from the apex of the drop are recorded and, simultaneously, the liquid and the gas phases are transported to the high-pressure densimeter, through a heated stainless steel tube, in order to measure the mass density of the n-alkane saturated with CO₂ ($\hat{\rho}_L$) and the mass density of CO₂ saturated with n-alkane ($\hat{\rho}_G$) both densities are measured at the experimental temperature and pressure.

Based on the experimental measurements of d_e , d_s , $\hat{\rho}_L$ and $\hat{\rho}_G$, the interfacial tension, γ , is obtained through the following expression:

$$\gamma = (\hat{\rho}_L - \hat{\rho}_G) g_c d_e^2 f(d_s, d_e) \quad (1)$$

where g_c is the local gravitational constant ($\approx 981 \text{ cm}\cdot\text{seg}^{-2}$), and $f(d_s, d_e)$ corresponds to a function related to the silhouette of the drop, whose value is determined from numerical tables.[60] In this work,

γ and $\hat{\rho}$ are measured at the isothermal condition of 344.15 K and over the pressure range 0.1 MPa to 15 MPa.

Complementarily, the experimental values of γ and $\hat{\rho}$ can be also used to predict, as a first approximation, the magnitude of the relative Gibbs adsorption isotherm of a species i on species j (Γ_{ij}). According to Masterton et al. [61] for a gas-liquid system in which the pressure is changing, Γ_{ij} can be described by the following expression:

$$\Gamma_{i2} = -\frac{\hat{\rho}_l}{M_l} \left(\frac{\partial \gamma}{\partial p} \right)_T \quad (2)$$

where the slope $(\partial \gamma / \partial p)_T$ is obtained from experimental values of $\gamma - p$. $\hat{\rho}_l$ and M_l are the molar density and molecular weight of the pure gas (here CO₂), respectively. $\hat{\rho}_l$ can be directly measured as a function of T and p or alternatively, it can be obtained from a data base [58].

Finally, it is important to recall that the chamber cleaning plays a key role in the accuracy of the pendant drop technique, since negligible impurity concentrations strongly affect γ measurements. Consequently, appropriate precautions were taken when cleaning the chamber surfaces by replicating experimental γ values of the pure fluids (see Table 1).

It is also important to recall that γ in a pendant drop tensiometer is not measured directly; therefore it is important to establish that the uncertainties of γ values are affected by the value of temperature, pressure, density difference, experimental reproducibility of γ itself and its standard uncertainties. In order to quantify these effects in the expanded or combined relative uncertainty of γ , u_c , the following relationship [62] has been considered:

$$u_c^2(\gamma) = \left[\frac{1}{\gamma} \left(\frac{\partial \gamma}{\partial p} \right)_T \delta p \right]^2 + \left[\frac{\delta \Delta \rho}{\Delta \rho} \right]^2 + \left[\frac{\sigma(\gamma)}{\gamma} \right]^2 \quad (3)$$

In Eq. (3) δp and $\delta \Delta \rho$ correspond to the standard uncertainties in pressure and density, respectively. $\sigma(\gamma)$ is the standard deviation of γ which, together with the maximum value of partial derivatives of γ in p , have directly been estimated from experimental data. For the binary systems investigated here, the average u_c value was found to be 0.77 %. Therefore, the expanded relative uncertainty of γ at 95 % confidence was 1.5 %.

Additional details concerning to the pendant drop technique have extensively described by Andreas et al. [60], Rusanov and Prokhorov [63], Ambwani and Fort [64] and Evans [65].

3. Theoretical Section

3.1. Square Gradient Theory for modeling of phase equilibrium and interfacial behavior

Simultaneous modeling of bulk phase equilibrium and interfacial tension for fluid mixtures was carried out by applying the square gradient theory (SGT) to an accurate EoS model. Invoking the SGT, the interfacial tension of a binary mixture, γ , is given by the following integral expression: [23-35,66,67]

$$\gamma = \sqrt{2} \int_{\rho_2^V}^{\rho_2^L} \sqrt{\left(a_0 - (\rho_1 \mu_1^0 + \rho_2 \mu_2^0) + p^0 \right) \left(c_2 + 2\sqrt{c_1 c_2} \frac{d\rho_1}{d\rho_2} + c_1 \left(\frac{d\rho_1}{d\rho_2} \right)^2 \right)} d\rho_2 \quad (4)$$

where a_0 is the Helmholtz energy density of the homogeneous system, ρ_i is the interfacial molar concentration of species i . ρ_i^V and ρ_i^L corresponds to the molar concentration of component i in the bulk vapor (V) and liquid (L) phases, respectively. μ_i is the chemical potential of species i and p is the pressure. The superscript 0 in p and μ_i denotes that these variables are evaluated at the phase equilibrium condition of the bulk phases (V, L). c_i is the influence parameter of species i . In this work, the subscript 1 represents CO_2 and 2 the n-alkane ($\text{n-C}_{12}\text{H}_{26}$ or $\text{n-C}_{13}\text{H}_{28}$ or $\text{n-C}_{14}\text{H}_{30}$). This selection is based on the physical fact that the less volatile component should not accumulate in the interfacial region and, therefore, it may exhibit a convenient monotonic function along the interfacial region [27,66]

Within the theoretical framework of the SGT, the isothermal bulk phase equilibrium properties (i.e. ρ_i^V , ρ_i^L , and p^0) can be found by solving the following conditions at bulk phases [67]

$$a_0 - (\rho_1 \mu_1^0 + \rho_2 \mu_2^0) + p^0 = 0 \quad (5.a)$$

$$\left(\frac{\partial a_0}{\partial \rho_i} \right)_{T^0, V^0, \rho_{k \neq i}^0} - \mu_i^0 = \mu_i - \mu_i^0 = 0 \quad i = 1, 2 \quad (5.b)$$

$$\left(\frac{\partial^2 a_0}{\partial \rho_i^2} \right)_{T^0, V^0, \rho_{k \neq i}^0} = \left(\frac{\partial \mu_i}{\partial \rho_i} \right)_{T^0, V^0, \rho_{k \neq i}^0} > 0 \quad i = 1, 2 \quad (5.c)$$

Eqs. (5) are equivalent to the necessary conditions of phase equilibrium for bulk phases. Specifically, Eq. (5.a) corresponds to the mechanical equilibrium condition ($p^L = p^V = p^0$) while Eq. (5.b) expresses the chemical potential constraint ($\mu_i^L = \mu_i^V = \mu_i^0$). Eq. (5.c) is a differential stability condition for interfaces, comparable to the Gibbs energy stability constraint of a single phase [68]

Following the formalism of the SGT, ρ_1 and ρ_2 in Eq. (4) are implicitly related by the following algebraic equation:

$$\sqrt{c_1}(\mu_2 - \mu_2^0) = \sqrt{c_2}(\mu_1 - \mu_1^0) \quad (6)$$

For the case a pure fluid, the influence parameters c_1 and c_2 can be calculated at the boiling temperature from experimental γ values (γ_{exp}) and Eq. (4) as follows

$$c_i(T^0) = \gamma_{exp}^2(T^0) \left(\int_{\rho_i^V}^{\rho_i^L} \sqrt{2(a_0 - \rho_i \mu_i^0 + p^0)} d\rho_i \right)^{-2} \quad (7)$$

where the γ_{exp} data for pure CO₂, n-C₁₂H₂₆ or n-C₁₃H₂₈ or n-C₁₄H₃₀ have been taken from the NIST REFPROP data base [58].

In Eqs (4) to (6), a_0 and μ_i can be obtained from an appropriate EoS. In this work, a_0 and its density derivative (or μ_i) were obtained from the SAFT-VR-Mie EoS proposed by Lafitte et al. [69], as we describe in the next section.

Equations (4) to (6) conform the main theoretical framework of the SGT as required to simultaneously modeling phase equilibrium, IFT and interfacial concentration profiles in the $\rho_1 - \rho_2$ projection. It is worth mentioning here that the $\rho_1 - \rho_2$ projection provides a route to evaluate the surface activity (or absolute adsorption / desorption of species along the interface region). In the quoted projection, the geometrical condition $d\rho_i / d\rho_j = \infty$ denotes the accumulation of a species i at the interface region. Furthermore, besides the surface activity, the SGT results provide the useful information for characterizing the relative Gibbs adsorption isotherm of a species i relative to a species j (Γ_{ij}), which can be calculated from the following expression [70]:

$$\Gamma_{12} = - \left(\frac{\partial \gamma}{\partial \rho_1} \right)_{T,p} \left(\frac{\partial \mu_1^0}{\partial \rho_1} \right)_{T,p}^{-1} \quad (8)$$

3.2 The Statistical Associated Fluid Theory (SAFT) Model

The Statistical Associated Fluid Theory (SAFT) is a generalized model that allows the development of physically based EoS for chain-like fluids where association -of the type found in hydrogen bonding or charge transfer processes- may be present. The reader is referred to reviews on the topic for further discussions [71,72,73,74,75,76]. Here we employ the SAFT version proposed by Lafitte et al. [69], the basis of the third-generation SAFT- γ group contribution EoS [77]. Briefly, this SAFT version is a particular case of the generic SAFT methodology for potentials of variable range for molecules conformed of segments interacting through the Mie potential, u^{Mie} , which can be represented by:

$$u^{MIE}(r) = \left[\frac{\lambda_r}{\lambda_r - \lambda_a} \left(\frac{\lambda_r}{\lambda_a} \right)^{\frac{\lambda_a}{\lambda_r - \lambda_a}} \right] \varepsilon \left[\left(\frac{\sigma}{r} \right)^{\lambda_r} - \left(\frac{\sigma}{r} \right)^{\lambda_a} \right] \quad (9)$$

In Eq. (9) λ_r and λ_a are the repulsion and attraction parameters of the intermolecular potential, respectively, r is the center-to-center distance of the interacting segments, ε is the energy scale corresponding to the potential well depth, σ length scale, corresponding loosely with an effective segment diameter.

The corresponding expression of Helmholtz energy density of SAFT EoS for non-associating chain fluid is given by [69]

$$a = (a^R + a^{ig}) \rho \frac{N_{av}}{\beta} = (a^{mono} + a^{chain} + a^{ig}) \rho \frac{N_{av}}{\beta} \quad (10)$$

where $a = A / (N k_B T)$, A being the total Helmholtz energy, N the total number of molecules, N_{av} the Avogadro constant, T the temperature, k_B the Boltzmann constant, $\beta = 1 / (k_B T)$, and ρ the molar density of the mixture. a^R is the residual Helmholtz energy density, and a^{ig} is the ideal gas reference. a^R embodies two additive contributions to the Helmholtz energy density: a^{mono} which represents monomer (unbounded) contribution for a chain composed of m_s tangential segments, while a^{chain} accounts for the

formation of chain molecules. In this SAFT model, pure components are characterized by five parameters: the molecular chain length (or number of segments) m , the repulsion and attraction parameters of the intermolecular potential λ_r and λ_a , the energy scale or potential well depth ε , and the length scale, roughly equivalent to a segment diameter σ . These five parameters can be obtained by forcing from the EoS the best overall fit to experimental fluid phase equilibria data (e.g. vapor pressure and saturated liquid density) or alternatively these parameters can be found by representing the molecules that conform the pure fluids and their mixtures as coarse-grained (CG) beads corresponding to “super”-united-atoms and using critical data and a corresponding states principle, as proposed recently.[78] Both approaches are essentially equivalent and resulting in mapping the free energy of the fluid to the best approximate fit to experimental data. In that sense, the molecular parameters provide an effective coarse-grained representation of the average best compromise parameters that can describe the whole fluid phase range.

In this work we modeled CO₂ as a single sphere [79]; n-C₁₂H₂₆ and n-C₁₃H₂₈ are formed by three tangential spheres whereas n-C₁₄H₃₀ is represented using four tangential spheres [78]. These tangential spheres interact each other through the Mie potential (see Eq. 9). Table 2 summarizes the SAFT parameters for pure fluids as used in this work. Additionally, Table 2 also includes the fitted values for c_i , which has been obtained from Eq. (7) and SAFT-VR-Mie EoS model.

The SAFT EoS is extended to mixtures by using a number of unlike parameters which are defined by applying combination rules [69]. The unlike size parameter, σ_{ij} is obtained using an arithmetic mean:

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \quad (11)$$

while the unlike Mie attractive interaction energy (or cross potential well depth), ε_{ij} is obtained using a Berthelot-like geometric average:

$$\varepsilon_{ij} = (1 - k_{ij}) \frac{\sqrt{\sigma_{ii}^3 \sigma_{jj}^3}}{\sigma_{ij}^3} \sqrt{\varepsilon_{ii} \varepsilon_{jj}} \quad (12)$$

where k_{ij} is a binary interaction parameter, which can be obtained from experimental data of phase equilibria. The cross attractive and repulsive exponents involved in the Mie potential are calculated as:

$$(\lambda_{ij} - 3) = \sqrt{(\lambda_{ii} - 3)(\lambda_{jj} - 3)} \quad (13)$$

where the same functional form applies to both the repulsion and attraction.

Finally, from Eq. 10 and using its mathematical definition [68], it is possible to obtain the following expression for the chemical potential of species i in a mixture:

$$\mu_i = \left(\frac{\partial a}{\partial \rho_i} \right)_{T,V,\rho_{j \neq i}} = \left(\frac{\partial a^R}{\partial \rho_i} \right)_{T,V,\rho_j} + RT \ln(\rho_i \Lambda_i^3) \quad (14)$$

where Λ_i corresponds to the thermal de Broglie's wavelength. In this work, Eq. (14) will be used to calculate the phase equilibrium between the bulk phases as well as the set of required interfacial properties (see Eqs. 4 – 8).

As we can observe in this section, the key parameter involved in the SGT + SAFT-VR-Mie EoS approach is k_{ij} . Pure component parameters are directly obtained employing a principle of corresponding states [78]. In order to provide a *full predictive scheme* for both bulk phase densities and IFT experimental determinations of the mixtures reported in this work, the corresponding k_{ij} values have been regressed from $p - x,y$ experimental data reported in [12,80,81], thus yielding the deviation statistics shown in Table 3. For an excellent and updated compilation of $p - x,y$ experimental data for CO₂ + n-alkanes, the reader is referred to a recent work by Cismondi et al. [55].

4. Results and discussions

4.1 Carbon dioxide + n-dodecane mixture

Vapor – liquid phase equilibrium data (p , T , x , y) for carbon dioxide + n-dodecane at 344.15 K have been reported by Camacho-Camacho et al [80] and Nieuwoudt and du Rand [82]. New and complementary data about bulk phase equilibrium densities have been measured in this work. Table 4 summarizes the experimental determinations for the bulk phase mass densities, and Figure 1 shows the corresponding phase diagram together with the predictions of the SAFT-VR-Mie EoS. Inspection of the Figure reveals that the mixture densities of carbon dioxide + n-dodecane behave ordinarily (i.e. they do not exhibit barotropic inversion, see Fig. 5.a in Ref. [45]), and that the SAFT-VR-Mie model is reliable for predicting the phase equilibria up to 12 MPa with an absolute average deviation (AAD) in liquid

and vapor mass density of 2.36 % and 2.88 %, respectively. When the mixture approaches its critical state, however, the EoS fails in accurately predicting the phase behavior due to its mean field structure. It is important to remark that these deficiencies can be overcome by using a crossover methodology (see for instance Ref. [83]).

Interfacial tension data for the binary mixture under consideration have been recently measured and modeled by Georgiadis [13,14], where the reported data were calculated from the densities of pure fluids rather than from mixture densities (see Eq. 1). The DFT + SAFT-VR-EoS approach was used then by Georgiadis for performing the theoretical modeling of interfacial properties. In order to complete the available information and analyze the impact of accurately measured mixture density data on the value of interfacial tensions, we measured the interfacial tension at 344.15 K and over the pressure range 0.1 to 12 MPa. The experimental data are collected in Table 4 while Figure 2 depicts the experimental and predicted interfacial tensions as a function of pressure. From the quoted Figure, it is possible to observe that γ monotonously decreases with pressure and the SGT overpredicts the experimental data of γ with an AAD γ of 8.5 %. These results can be improved by using some refinements or modifications, such as the use of renormalization-group theory in the EoS or by rescaling the phase behavior predictions to the experimental value of the critical pressure. Comparing the experimental data and theoretical modeling presented in this work with those reported by Georgiadis [13,14], it is possible to conclude that both approaches are in good agreement each other.

Besides phase equilibrium and interfacial tension, the theoretical approach presented here also describes the concentration profiles of species (ρ_i) at the interfacial zone. Particularly, Figure 3 shows the $\rho_i - \rho_b$ projections as a function of pressure, where we observe that CO₂ always exhibits positive surface activity (as reflected in the Figure by the sharp maximum observed for the concentration profile), whereas n-dodecane does not exhibit surface activity. Figure 3 also reports the point of maximum interfacial concentration for CO₂ (i.e. maximum surface activity) and clearly shows that the surface activity of CO₂ persists and increases with pressure.

The adsorption of CO₂ (1) in n-dodecane (2) can be approximately quantified by the relative Gibbs adsorption isotherm (Γ_{12}). Figure 4 depicts Γ_{12} as a function of pressure both for experimental data and theoretical modeling. It is seen how Γ_{12} increases with pressure without reaching a saturation limit. Comparing theoretical results (cf. Eq. 8) with the values obtained from experimental data and Eq. (2), it is possible to observe that both approaches –fit of experimental data and theoretical modeling- agree each other over the range 0.1 to 7 MPa. At higher pressures –however- discrepancies become evident,

as follows from the fact that Eq. (2) sub-predicts Γ_{l2} when the mass density of pure CO₂ considerably differs from the mass density of mixture.

4.2 Carbon dioxide + *n*-tridecane mixture

Experimentally, the isothermal phase equilibrium for carbon dioxide + *n*-tridecane have been reported from 268 K to 524 K [81,84,85]. Additionally, this mixture displays molar barotropy above 317. K. These data allows deducing that above 344.15 K phase equilibrium between a homogeneous liquid and a vapor could be observed. This work complements the available experimental data adding the bulk phase equilibrium densities and interfacial tensions at 344.15 K and over the pressure range (0.1 to 13 MPa). Table 5 reports the corresponding experimental data while Figures 5 and 6 depict a comparison between these values and the theoretical predictions.

According to Figure 5, it is observed that the densities of the binary mixture behave ordinarily and the predictions of the SAFT-VR-Mie model are reliable to 13 MPa with an AAD in liquid and vapor mass densities of 2.73 % and 2.46 %, respectively. Similar than in the previous mixture, SAFT-VR-Mie does not accurately predict the phase behavior close to the critical point. For the case of interfacial tension, both experimental determination and theoretical modeling are in good agreement (see Fig. 6) with an AAD γ of 7.47 %. As in the case of CO₂ + *n*-C₁₂H₂₆ mixture, discrepancies can be reduced by applying further refinements.

To supplement the bulk phase equilibrium and interfacial tensions, the population of species in the interfacial region is shown in Figure 7. As in the case of CO₂ + *n*-C₁₂H₂₆, CO₂ always exhibits positive surface activity as reflected by the sharp maximum observed for ρ_1 , whereas *n*-tridecane does not show surface activity. The surface activity (or absolute adsorption) of CO₂ increases with pressure. In order to quantify the relative adsorption of CO₂ (1) with respect to *n*-tridecane (2), Figure 8 displays the relative Gibbs adsorption isotherm (Γ_{l2}) as a function of pressure. From this latter Figure we can observe that Γ_{l2} increases with pressure from 0.1 to 11 MPa, where Γ_{l2} reaches a maximum value that seems to correspond to the saturation limit for CO₂. Beyond that pressure, Γ_{l2} starts to decrease. Comparing Γ_{l2} values, it is possible to conclude that, as in the previous binary system, that theory and Eq. (2) agree well from 0.1 to 7 MPa. For pressure higher than 7 MPa, the theoretical calculations yield higher values than the values obtained from Eq. (2).

4.3 Carbon dioxide + *n*-tetradecane mixture

The bulk phase equilibria and interfacial tensions of carbon dioxide + *n*-tetradecane have been experimentally determined by Gasem et al. [12] who reported mole fractions, densities for liquid and vapor phases as well as interfacial tension as a function of pressure. Due to the availability of experimental data for phase equilibria and interfacial tension, this binary mixture is traditionally used as a reference test case for simulating the behavior CO₂ + long or heavy *n*-alkane mixtures (see for instance Refs. [22,28,34,33]). Accordingly, the mixture has been selected in the present work for testing our approaches and for complementing the work of Gasem et al. [12] on low-pressure data. Table 6 summarizes the corresponding experimental data of bulk densities and interfacial tensions, and Figures 9 and 10 display these experimental values together to Gasem et al. [12] data and our theoretical predictions.

As seen in Figure 9, the densities of the binary system (as previous ones) behave ordinarily. However, it is expected that the mixture should display mass barotropy at 290 K while at 315 K molar barotropy should exist. [45]

It is also possible to observe an excellent agreement between the present experimental data and that reported by Gasem et al. [12]. In fact, the AADs in the liquid and the vapor mass density are 0.38 % and 3.33 %, respectively. According to our calculations, the SAFT-VR-Mie model is reliable for predicting the phase equilibrium up to 14 MPa with an AAD in liquid and vapor mass density of 3.49 % and 4.35%, respectively.

Figure 10 shows how the interfacial tension decreases with pressure and how it can be modeled by SGT + SAFT-VR-Mie EoS within $AAD_{\gamma} < 3.33$ %. In addition, the present experimental are in fair agreement with those reported by Gasem et al. [12], ($AAD_{\gamma} < 9$ %)

In order to assess the capability to model the interfacial tension data reported for this binary system, Table 7 summarizes the AAD_{γ} obtained from different EoS models, as well as the predictions obtained from DFT and SGT. According to the results report there, it is possible to conclude that SGT + SAFT-VR-Mie predict the lowest AAD_{γ} for the experimental data included here and for those measured by Gasem et al. [12]. It is also possible to observe that the theoretical modeling yields lower AAD_{γ} when predicting the present experimental data, without including that of Gasem et al. [12]. These results may be attributed to the fact that the experimental range covered by Gasem et al. only covers the vicinity of the critical region, where a mean field theory approach is not adequate.

As in the previous binary mixtures reported in this work, SGT + SAFT-VR-Mie EoS provides a route to explore the interfacial behavior of mixtures. Figure 11 shows that CO₂ always exhibits positive

surface activity that increases with pressure, whereas n-tetradecane does not show surface activity. The relative Gibbs adsorption isotherm of CO₂ (1) in n-tetradecane (2) is illustrated in Figure 12, where it is possible to observe that Γ_{12} increases with pressure and reaches a maximum value or saturation limit for CO₂ at 11 MPa. For higher pressures, Γ_{12} starts to decrease with pressure. It is also possible to observe that for pressures higher than 8 MPa, the theoretical calculations over-predict the values obtained from Eq. (2).

Finally, it is important to remark that the interfacial tension reported in Tables 4 to 6 have been obtained from Eq. (1) using the actual mass densities of the mixture. The common practice of using the mass densities of the pure components instead of mixture densities is a convenient approximation that may be useful for treating extremely immiscible systems or for facing cases where no experimental mixture density data have been reported. However, the impact of such an approximation on the accuracy of experimentally determined data requires careful assessment. For the CO₂ + n-alkane mixtures explored in this work, the density approximation produces a deviation from 0.5 % at low pressure to 4 % at higher pressures. Consequently it is always advisable to use mixture mass densities rather than pure component mass densities when they are available.

5. Conclusions

In this work, bulk phase mass densities and interfacial tension of CO₂ + n-alkane (n-C₁₂H₂₆ or n-C₁₃H₂₈ n-C₁₄H₃₀) have been determined and theoretically modeled. According to experimental and modeling results, the bulk phase densities do not exhibit barotropic inversion and the model results adequate for describing the phase behavior with a maximum deviation of 3.5 % for the liquid phase and 4.3% for the vapor phase. Experimental data of interfacial tensions are in good agreement with previously reported data (when available) and theoretical predictions. The SGT + SAFT-VR-Mie -EoS model provides a reliable route for predicting the interfacial tension (showing an AAD γ < 10 %) and the related interfacial properties (surface activity and isothermal relative Gibbs adsorption). For the CO₂ + n-alkane mixtures considered here, it is possible to conclude that interfacial tension decreases as the pressure or the n-alkane chain length increase. Finally, CO₂ is always adsorbed along the interfacial zone, showing a surface activity that increases with pressure or n-alkane chain length.

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List of symbols

a_0	=	Helmoltz energy density
A	=	Helmholtz energy
c_i	=	influence parameter
d_e	=	equatorial diameter of the drop
d_s	=	horizontal diameter of the drop
f	=	Laplace Capillary function
g_c	=	local gravitational constant
k_B	=	Boltzmann's constant
k_{ij}	=	interaction parameter for the EoS mixing rule
m	=	molecular chain length
M	=	molecular weight
N	=	number of molecules
N_{av}	=	Avogadro constant
p	=	absolute pressure
r	=	center-center distance
T	=	absolute temperature
u_c	=	combined standard uncertainty
V	=	Volume
x, y	=	mole fractions for liquid and vapor phases, respectively

Greek

β	=	$1 / (k_B T)$
$\delta\Delta\rho$	=	standard uncertainty in density
δp	=	standard uncertainty in pressure
ε	=	potential well depth
Γ_{ij}	=	Gibbs adsorption of a species i relatives to a species j
γ	=	interfacial tension
Λ	=	thermal de Broglie's wavelength
λ_a	=	attraction parameter of the intermolecular potential

λ_r	=	repulsion parameter of the intermolecular potential
μ	=	chemical potential
ρ	=	molar concentration
$\hat{\rho}$	=	mass concentration
σ	=	effective segment diameter
$\sigma(\gamma)$	=	standard deviation of γ

Superscripts

<i>chain</i>	=	chain contribution in SAFT - EoS
<i>mono</i>	=	monomer contribution in SAFT - EoS
<i>ig</i>	=	ideal gas contribution in SAFT - EoS
<i>R</i>	=	residual contribution in SAFT - EoS
<i>V</i>	=	vapor bulk phase
<i>L</i>	=	liquid bulk phase
<i>0</i>	=	equilibrium state

Subscripts

<i>exp</i>	=	experimental
<i>L</i>	=	liquid bulk phase
<i>V</i>	=	vapor bulk phase

Table 1 Gas chromatography (GC) purities (mass fraction), liquid mass densities ($\hat{\rho}$) and interfacial tensions (γ) of pure n-alkanes at 344.15 K and 101.3 kPa^a

component (purity / mass fraction)	$\hat{\rho}$ (kg m ⁻³)		γ (mN m ⁻¹)	
	<i>Exp.</i>	<i>Lit.</i> ^b	<i>Exp.</i>	<i>Lit.</i> ^b
carbon dioxide or CO ₂ (0.999)	1.5630	1.5629	---	---
n-dodecane or n-C ₁₂ H ₂₆ (0.999)	712.10	712.30	20.72	20.79
n-tridecane or n-C ₁₃ H ₂₈ (0.999)	720.20	720.20	21.56	21.50
n-tetradecane or n-C ₁₄ H ₃₀ (0.999)	727.10	727.40	22.07	22.08

^a Measurement uncertainties are: $\hat{\rho} \pm 5 \times 10^{-3}$ kg m⁻³; $\gamma \pm 0.01$ mN m⁻¹; $p \pm 0.10$ kPa; $T \pm 0.10$ K

^b Experimental data have been taken from NIST- REFPROP data base [58].

Table 2. Thermophysical properties of the pure components^a

<i>Fluid</i>	m_{si}	ε_i/k_B / K	$\sigma_i/\text{\AA}$	λ_{ri}	λ_{ai}	$10^{20} \times c_i / (\text{J m}^5 \text{mol}^{-2})$ ^b
carbon dioxide (CO ₂)	1	353.55	3.741	23.00	6.66	2.768
n-dodecane (n-C ₁₂ H ₂₆)	3	494.73	4.920	27.90	6.00	119.198
n-tridecane (n-C ₁₃ H ₂₈)	3	533.52	5.093	32.49	6.00	139.082
n-tetradecane (n-C ₁₄ H ₃₀)	4	438.11	4.619	22.22	6.00	167.675

^a Pure n-alkane parameters of the SAFT-VR-Mie EoS have been taken from Mejía et al. [78], and from Avendaño et al. [79] for CO₂. c_i were fitted from experimental γ data which have been taken from NIST-REFPROP data base [58]

Table 3. Binary parameters for mixing rules and statistic deviations in vapor pressure for VLE correlations and interfacial tensions predictions

<i>System</i>	<i>T / K</i>	<i>k_{ij}</i>	<i>AADP %</i>	<i>Ref.</i>
CO ₂ + n-C ₁₂ H ₂₆	344.15	0.050	2.94	[80]
CO ₂ + n-C ₁₃ H ₂₈	313.15	0.060	3.25	[81]
CO ₂ + n-C ₁₄ H ₃₀	344.15	0.065	2.27	[12]

Table 4 Experimental bulk phase mass densities and interfacial tensions for CO₂ (1) + n-C₁₂H₂₆ (2) at $T = 344.15$ K.^a

p (MPa)	$\hat{\rho}_G$ (kg m ⁻³)	$\hat{\rho}_L$ (kg m ⁻³)	γ (mN m ⁻¹)
0.10	1.702	712.109	20.72
1.00	15.480	727.014	18.54
2.00	33.789	729.249	16.53
3.00	52.283	728.841	14.74
4.00	71.883	730.270	13.03
5.00	93.970	733.681	11.31
6.00	119.002	737.708	9.57
7.00	146.718	741.052	7.82
8.00	177.146	743.119	6.12
9.00	211.629	744.015	4.57
10.00	253.074	744.215	3.24
11.00	304.649	744.202	2.26
12.00	366.129	744.393	- - -

^a Measurement uncertainties are: : $\hat{\rho} \pm 5 \times 10^{-3}$ kg m⁻³; $\gamma \pm 0.01$ mN m⁻¹; $p \pm 10^{-4}$ MPa; $T \pm 0.10$ K

Table 5 Experimental bulk phase mass densities and interfacial tensions for CO₂ (1) + n-C₁₃H₂₈ (2) at $T = 344.15$ K.^a

p (MPa)	$\hat{\rho}_G$ (kg m ⁻³)	$\hat{\rho}_L$ (kg m ⁻³)	γ (mN m ⁻¹)
0.10	1.365	720.650	21.56
1.00	15.718	735.265	19.68
2.00	32.801	738.868	17.65
3.00	51.268	739.281	15.67
4.00	71.410	740.199	13.77
5.00	93.616	741.803	11.94
6.00	118.373	743.154	10.18
7.00	146.265	743.618	8.52
8.00	177.975	743.476	6.95
9.00	214.283	743.866	5.49
10.00	256.066	746.210	4.13
11.00	304.300	751.271	2.89
12.00	360.058	757.994	1.77
13.00	424.511	762.280	0.78

^a Measurement uncertainties are: : $\hat{\rho} \pm 5 \times 10^{-3}$ kg m⁻³; $\gamma \pm 0.01$ mN m⁻¹; $p \pm 10^{-4}$ MPa; $T \pm 0.10$ K

Table 6 Experimental bulk phase mass densities and interfacial tensions for CO₂ (1) + n-C₁₄H₃₀ (2) at $T = 344.15$ K.^a

p (MPa)	$\hat{\rho}_G$ (kg m ⁻³)	$\hat{\rho}_L$ (kg m ⁻³)	γ (mN m ⁻¹)
0.10	1.694	727.098	22.07
1.00	12.768	728.281	20.41
2.00	30.997	730.234	18.55
3.00	52.049	732.045	16.70
4.00	74.023	733.325	14.87
5.00	96.355	734.050	13.06
6.00	119.506	734.457	11.31
7.00	144.635	734.937	9.61
8.00	173.280	735.931	8.00
9.00	207.041	737.827	6.48
10.00	247.256	740.852	5.07
11.00	294.682	744.970	3.78
12.00	349.174	749.776	2.63
13.00	409.364	754.390	1.64
14.00	472.346	757.357	0.82

^a Measurement uncertainties are: : $\hat{\rho} \pm 5 \times 10^{-3}$ kg m⁻³; $\gamma \pm 0.01$ mN m⁻¹; $p \pm 10^{-4}$ MPa; $T \pm 0.10$ K

Table 7 Absolute average deviation (AAD) in interfacial tension predictions for CO₂ (1) + n-C₁₄H₃₀ (2) at 344.15 K

EoS Model	Inhomogeneous Model	AAD γ^a	AAD γ^b	Refs.
SAFT-VR	DFT	4.96 %	19.36 %	[22]
SAFT-VR-Mie	SGT	3.27 %	14.70 %	This work
PCP-SAFT	SGT	- - -	20.28 %	[34]
PC-SAFT	SGT	27.21 %	> 100 %	[33]
Peng - Robinson	SGT	14.18 %	48.87 %	[26]
Quartic	SGT	18.20 %	44.62 %	[28]

Experimental data taken from: a. Table 6; b. Gasem et al. [12]

Figure Captions

- [1] Pressure (p) vs. bulk mass density ($\hat{\rho}$) diagram for CO₂ (1) + n-C₁₂H₂₆ (2) at 344.15 K. (○) experimental data; (—) predicted from SAFT-VR-Mie –EoS with $k_{ij} = 0.05$.
- [2] Interfacial tension (γ) as a function of pressure (p) for CO₂ (1) + n-C₁₂H₂₆ (2) at 344.15 K. (○) experimental data; (—) predicted from SGT + SAFT-VR-Mie –EoS with $k_{ij} = 0.05$.
- [3] Concentration profiles in the $\rho_1 - \rho_2$ projection at three pressures for CO₂ (1) + n-C₁₂H₂₆ (2) mixture at 344.15 K. (—) predicted from SGT + SAFT-VR-Mie –EoS with $k_{ij} = 0.05$. (●) bulk phase equilibrium densities, (○) maximum CO₂ surface activity.
- [4] Relative Gibbs adsorption isotherm for CO₂ (1) + n-C₁₂H₂₆ (2), Γ_{12} , as a function of pressure (p) at 344.15 K. (○) experimental data; (—) predicted from SGT + SAFT-VR-Mie –EoS with $k_{ij} = 0.05$.
- [5] Pressure (p) vs. bulk mass density ($\hat{\rho}$) diagram for CO₂ (1) + n-C₁₃H₂₈ (2) at 344.15 K. (○) experimental data; (—) predicted from SAFT-VR-Mie –EoS with $k_{ij} = 0.06$.
- [6] Interfacial tension (γ) as a function of pressure (p) for CO₂ (1) + n-C₁₃H₂₈ (2) at 344.15 K. (○) experimental data; (—) predicted from SGT + SAFT-VR-Mie –EoS with $k_{ij} = 0.06$.
- [7] Concentration profiles in the $\rho_1 - \rho_2$ projection at three pressures for CO₂ (1) + n-C₁₃H₂₈ (2) at 344.15 K. (—) predicted from SGT + SAFT-VR-Mie –EoS with $k_{ij} = 0.06$. (●) bulk phase equilibrium densities, (○) maximum CO₂ surface activity.
- [8] Relative Gibbs adsorption isotherm for CO₂ (1) + n-C₁₃H₂₈ (2), Γ_{12} , as a function of pressure (p) at 344.15 K. (○) experimental data; (—) predicted from SGT + SAFT-VR-Mie –EoS with $k_{ij} = 0.06$.
- [9] Pressure (p) vs. bulk mass density ($\hat{\rho}$) diagram for CO₂ (1) + n-C₁₄H₃₀ (2) at 344.15 K. Experimental data: (○) this work; (●) Gasem et al. [12]; (—) predicted from SAFT-VR-Mie –EoS with $k_{ij} = 0.065$.

[10] Interfacial tension (γ) as a function of pressure (p) for CO₂ (1) + n-C₁₄H₃₀ (2) at 344.15 K. Experimental data: (○) this work; (●) Gasem et al. [12]; (—) predicted from SGT + SAFT-VR-Mie – EoS with $k_{ij} = 0.065$.

[11] Concentration profiles in the $\rho_1 - \rho_2$ projection at three pressures for CO₂ (1) + n-C₁₄H₃₀ (2) at 344.15 K. (—) predicted from SGT + SAFT-VR-Mie –EoS with $k_{ij} = 0.065$. (●) bulk phase equilibrium densities, (○) maximum CO₂ surface activity.

[12] Relative Gibbs adsorption isotherm for CO₂ (1) + n-C₁₄H₃₀ (2), Γ_{12} , as a function of pressure (p) at 344.15 K. (○) experimental data; (—) predicted from SGT + SAFT-VR-Mie –EoS with $k_{ij} = 0.065$.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

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Figure 10

Figure 11

Figure 12

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