

MODELING PHASE EQUILIBRIA FOR A WATER-CO₂-HYDROCARBON MIXTURE USING CPA EQUATION OF STATE IN CO₂ INJECTION EOR-STORAGE PROCESSES: A COLOMBIAN CASE STUDY

■ **MODELAMIENTO DEL EQUILIBRIO DE FASES PARA MEZCLA AGUA-CO₂-HIDROCARBONO UTILIZANDO LA ECUACIÓN DE ESTADO CPA EN PROCESOS DE EOR-ALMACENAMIENTO POR INYECCIÓN DE CO₂: UN ESTUDIO DE CASO COLOMBIANO**

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ABSTRACT

Currently, it is necessary to reduce CO₂ emissions into the atmosphere. The oil industry in Colombia can contribute through CO₂ injection processes in depleted fields. To achieve this, it is essential to know about the physicochemical interaction of CO₂ with reservoir fluids. To integrate CO₂, water and hydrocarbon phases, advanced models are necessary to capture the phenomenology of thermodynamic equilibrium. The CPA (Cubic-Plus-Association) equation of state adds an associative term to model the interaction of water with the hydrocarbon and CO₂ phase.

In this work, the CO₂ injection process is thermodynamically modelled in a case study of a depleted reservoir in Colombia. There is a compositional fluid with a gradient of PVT properties in a vertical relief of 10,000 ft, at a depletion condition of 2,000 psi @ 15,374 ft and an oil-water contact (OWC) at 17,000 ft. CO₂ injections between 10 and 80 mol% were conducted, and through the CPA equation of state, the swelling conditions of the crude oil, the solubility of CO₂ in the formation water, and the pressurization of the system were evaluated. The associative parameters of the equation were taken from literature and estimated through molecular dynamics simulations of water-CO₂-Hydrocarbon interaction.

Scheme 4C_1, at CO₂ injection conditions greater than 40%, predicts CO₂ solubility values greater than 2000 scf/bbl compared to the other literature schemes and experimental data. Scheme 2B_2 presents inconsistencies in saturation pressure calculations at high CO₂ injection contents since at 60% it reports a value of 2800 psia and at 80% a value of 2600 psia. This behavior is opposite to that reported in literature. Therefore, association schemes 4C_1 and 2B_2 presented thermodynamic problems for the calculation of properties such solubilities and saturation pressures.

This thermodynamic modelling with an advanced equation of state and use of molecular dynamics simulations enabled us to simulate different CO₂ injection scenarios in a compositional fluid. This type of studies is key to conduct successful CO₂ injection processes focused on enhanced recovery (EOR) and CO₂ storage in the porous medium in a depleted compositional reservoir in Colombia.

RESUMEN

En la actualidad es necesario reducir las emisiones de CO₂ en la atmósfera. La industria petrolera en Colombia puede contribuir mediante procesos de inyección de CO₂ en yacimientos depletados. Para ello, es fundamental tener un conocimiento de las interacciones fisicoquímicas del CO₂ con fluidos de yacimiento. Para integrar las 3 fases CO₂, agua e hidrocarburo se requieren modelos avanzados que capturen la fenomenología del equilibrio termodinámico. La ecuación de estado CPA (cubic-plus-association), es una ecuación que adiciona de un término asociativo para modelar la interacción del agua con fase hidrocarburo y CO₂.

En este trabajo se modela termodinámicamente el proceso de inyección de CO₂ en un caso de estudio de un yacimiento depletado colombiano. Se cuenta con un fluido composicional con un gradiente de propiedades PVT en un relieve vertical de 10000 ft a una condición de depletamiento de 2000 psia @ 15374 ft y un contacto agua-petróleo (OWC) a 17000 ft. Se realizaron inyecciones de CO₂ entre el 10 y 80% molar, y a través de ecuación de estado CPA, se evaluaron las condiciones de hinchamiento del crudo, solubilidad del CO₂ en el agua de formación y presurización del sistema. Los parámetros asociativos de la ecuación fueron tomados de literatura y estimados a través de simulaciones de dinámica molecular de las interacciones agua-CO₂-Hidrocarburo, mediante la descripción simplificada de un crudo vivo con contenido de asfaltenos de 1% y metano de 50% mol a 6500 psia y 255 °F.

El esquema 4C_1, en condiciones de inyección de CO₂ superiores al 40%, predice valores de solubilidad de CO₂ superiores a 2000 scf/bbl en comparación con los otros esquemas de literatura y los datos experimentales. El esquema 2B_2 presenta inconsistencias en los cálculos de presión de saturación a altos contenidos de inyección de CO₂, ya que a 60% reporta un valor de 2800 psia y a 80% un valor de 2600 psia. Este comportamiento es opuesto al reportado en la literatura. Por lo tanto, los esquemas de asociación 4C_1 y 2B_2 presentaron problemas termodinámicos para el cálculo de propiedades como solubilidades y presiones de saturación.

Este modelamiento termodinámico con ecuación de estado avanzada y uso de simulaciones de dinámica molecular, permitió simular diferentes escenarios de inyección de CO₂ en un fluido composicional. El desarrollo de este tipo de estudios es clave para llevar a cabo procesos de inyección de CO₂ exitosos enfocados en recobro mejorado (EOR) y almacenamiento de CO₂ en el medio poroso en un yacimiento composicional depletado colombiano.

KEYWORDS / PALABRAS CLAVE

CO₂ Injection | Depleted Reservoir | Compositional Gradient | Thermodynamic Equilibrium | CPA (Cubic-Plus-Association) Equation of State (EoS)
Inyección de CO₂ | Yacimiento Depletado | Gradiente Composicional | Equilibrio Termodinámico | Ecuación de Estado (EoS) CPA (Cubic-Plus-Association).

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1. INTRODUCTION

Emissions of carbon dioxide (CO_2), one of the main greenhouse gases produced by human activity, have increased in the last century due to the exploitation and use of fossil fuels (IEA, 2008). A possible solution, of great interest to industrial actors, is the processes of CO_2 capture, utilization and storage (CCUS) in deep geological formations such as saline aquifers, depleted oil and gas deposits, among others (Chabab et al., 2019). CCUS processes are considered one of the main alternatives to reduce atmospheric CO_2 emissions and mitigate climate change, along with improvements in energy efficiency and the promotion of carbon-free energy sources (renewable, nuclear, among others). The International Energy Agency (IEA) estimates that CCUS processes can reduce global CO_2 emissions by up to 20% by 2050 (IEA, 2008).

Although carbon dioxide is typically an odorless, colorless, slightly acidic, and non-flammable gas at standard temperature and pressure, it can transform into a solid, liquid, or supercritical state depending on factors such as pressure and temperature. To maximize the CO_2 storage capacity in CCUS projects, it is recommended to inject it in the form of a supercritical fluid (Survey, 1995). At such conditions (above 88°F and at pressure is 1070.3 psia), carbon dioxide most interesting properties are gas-type viscosity and behavior, volume reduction and density increase, allowing a larger volume of CO_2 to be stored in the available pore space (Van der Meer et al., 1993; Hououway & Survey, 1993). Additionally, the use of supercritical CO_2 is preferable to avoid complications with hydrate formation in the injection well, which can occur if CO_2 is in a gaseous or liquid state (Baklid et al., 1996.)

Variations in temperature and pressure exist among sedimentary basins; nevertheless, by considering average surface temperatures, geothermal and hydrostatic gradients, it is established that a minimum subsurface depth of 800 meters is necessary for carbon dioxide (CO_2) to attain its supercritical phase (Van der Meer et al., 1993; Van Der Meer et al., 1995). At this depth, 1000 m^3 of atmospheric CO_2 occupy 3.8 m^3 , and its density is about 700 g/cm^3 . According to Ennis-King and Paterson (Ennis-King & Paterson, 2002), the density of supercritical CO_2 is approximately 30–40% less than a formation water under the same conditions. The lighter CO_2 will rise upwards through the formation water by buoyancy and will accumulate at the highest possible point in the reservoir beneath the seal (Van der Meer et al., 1993; Ennis-King & Paterson, 2002).

Understanding the CO_2 solubility phenomenon is essential to increase the efficiency of CCUS processes such as CO_2 injection in enhanced recovery (EOR). The mechanism of interest occurs due to dissolution in the reservoir fluids, which depends on the phases present in thermodynamic equilibrium (Chen et al., 2022). Understanding and modeling the phase behavior of water-crude- CO_2 systems in a wide range of temperatures, pressures, and composition, will lead to the correct design and optimization of injection processes (Sun et al., 2021). Considering that experimental measurements of this type of recovery are time-consuming and expensive (Li et al., 2001), predictive thermodynamic models become an adequate and efficient alternative to predict the relevant phase equilibria in these processes and to overcome the limitations of experimental methods.

Equations of state (EoS) allow modeling the thermodynamic equilibrium of fluids in the reservoir during CO_2 injection and storage. However, it is challenging for conventional EoS to accurately model

the thermodynamic behavior of CO_2 -containing mixtures. (Chen et al., 2022). For example, the SRK EoS fails to accurately correlate the minimum water concentration in the CO_2 -rich vapor phase for the binary CO_2 + water mixture, even when using a significant binary interaction parameter. The estimation of CO_2 solubility in the aqueous phase is commonly performed using Henry's law, which may not provide accurate results for a liquid phase that is rich in CO_2 and in equilibrium with water. This phenomenon is caused by the presence of a substantial quadrupole moment in CO_2 . This quadrupole moment represents the concentration of charges at four different points within the CO_2 molecule, leading to directional interactions. Therefore, depending on the surrounding molecules, CO_2 may function as a Lewis acid (electron acceptor) or base (electron donor) (Danten et al., 2005). The thermodynamic properties and phase behavior of a CO_2 molecule can be notably affected by its quadrupole moment, especially at low temperatures. For example, the quadrupole moment of CO_2 is believed to account for the observed low temperature azeotrope in the vapor-liquid equilibrium (VLE) between CO_2 and ethane mixtures. Furthermore, in conjunction with size asymmetry, it is also responsible for the occurrence of liquid-liquid equilibrium (LLE) between CO_2 and heavy hydrocarbons (Bjørner, 2016).

The use of EoS, based on the study of molecular interactions and associative properties of the components, such as SAFT (Statistical Associating Fluid Theory) and CPA (Cubic-Plus-Association), improves the accuracy of the results compared to the modified conventional EoS used until the moment (Jindrová et al., 2016; Nasrabadi et al., 2016; Sanchez-Vicente et al., 2018). Considering the relevance of modeling thermophysical properties for hydrocarbon and CO_2 mixtures in the design and optimization of injection processes in depleted reservoirs, Sánchez-Vicente, et al. (Sanchez-Vicente et al., 2018) conducted a study of the CO_2 and n-heptane system. In this research, the densities of the saturated phase, the compressed fluids, and bubble and dew points are measured. The results compare the predictive capacity of two thermodynamic models: The Peng-Robinson predictive equation, and a version of the Statistical Association Fluid Theory (SAFT), known as SAFT- γ Mie. The two models use the group contribution method to estimate the interaction parameters, and are applied to complex multicomponent systems. Both approaches are reliable as for phase behavior, but neither model satisfactorily predicts density (Al Ghafri & Truster, 2019; Dufal et al., 2014; Papaioannou et al., 2016). Negahban, et al. (Negahban et al., 2020) perform molecular dynamics simulations with the use of SAFT- γ and coarse-grained, a model developed by Herdes, et al. (Herdes et al., 2015) in 2015, to determine the phase behavior of a binary, ternary, and multicomponent CO_2 /hydrocarbon system. These systems include CO_2 /n-hexadecane, CO_2 /n-butane/n-decane, and CO_2 /synthetic oil. The SAFT- γ model turns out to be a good candidate to simulate the phase behavior of light oils, but it can be improved for more complex systems. Molecular simulation can provide quantitative calculations of the phase behavior of petroleum mixtures when data are limited or unavailable, thereby reducing the cost and time required to fit equations of state for compositional reservoir simulators. This modeling type has succeeded in numerous industrial applications to predict phase behavior for a wide spectrum of scenarios such as vapor-liquid (VL), liquid-liquid (LL) and vapor-liquid-liquid (VLL) (Avendaño et al., 2011; Mejía et al., 2014).

In turn, using the EoS CPA, Oliveira, et al. (Oliveira et al., 2011) investigate the phase equilibrium of binary CO_2 systems with

n-alkanes, n-alcohols, esters, and n-acids over a wide range of temperatures and pressures. The compounds used represent self-associative, non-associative, and cross-associative components, to describe in detail the possible interactions of CO₂. The authors determine the importance of the self-associative and cross terms for CO₂ with n-alkanes, to adequately describe the LV Equilibrium of the system. In 2015, Tsivintzelis et al. (Tsivintzelis et al., 2015a) evaluated different associative configurations of CO₂ in mixtures with alkanes (n-C36) to determine their performance when modeling phase equilibrium. CO₂ is treated as a non-associative, self-associative fluid with schemes 2B, 3B, and 4C. CPA parameters for alkanes to date only reached n-C20; new parameters are estimated for heavier alkanes based on a correlation developed according to the Design Institute for Physical Properties database (DIPPR). The results are compared with experimental literature data for three different heavy alkanes obtaining an accurate approximation. Similar works are conducted to evaluate the associative terms of CO₂ with different compounds (Tsivintzelis et al., 2011a; Tsivintzelis & Kontogeorgis, 2015). Jidrova et al. (Jindrová et al., 2016), and compare the performance of Peng-Robinson and CPA EoS to model the phase behavior of CO₂ mixtures with bitumen and light alkanes. The results show that Peng-Robinson describes the mixtures adequately when there is no presence of a second liquid phase, or the content of asphaltene in the second phase rich in CO₂ is low. The CPA model accurately describes the phase behavior in systems with two liquid phases, even when the asphaltene content is high in the second. Due to the presence of asphaltenes, the self-associative and cross terms are relevant for describing the LV Equilibrium, which gives an advantage to the CPA model over Peng-Robinson in this type of mixtures.

Nasrabadi et al. (Nasrabadi et al., 2016), also study the presence and precipitation of asphaltenes during CO₂ injection processes through the EoS CPA. The authors highlight the poor capacity of conventional EoS to model the equilibrium in hydrocarbon phases with high asphaltene content. The use of CPA provides accurate results for 2D and 3D simulations of CO₂ injection into Weyburn oil, for multiphase flows with high asphaltene content. Other authors have modified the EoS CPA to model phase equilibrium with CO₂. Bjorner and Kontogeorgis (Bjorner & Kontogeorgis, 2016) include quadrupole interactions in the CPA, based on the work of Larsen et al. (Larsen et al., 1977). The new model evaluates the predictive capacity for binary vapor-liquid and liquid-liquid systems with high CO₂ content in mixtures with hydrocarbons, water, alcohol, and quadrupole components. The inclusion of the new term becomes relevant in mixtures of CO₂ with hydrocarbons, where it correctly predicts the binary behavior of the phases. To study the solubility of CO₂ in formation water, Bian et al. (Bian et al., 2019) present a thermodynamic model based on the CPA equation of state combined with the Wong-Sandler mixing rule (CPA-WS) and evaluate its performance in reproducing the solubility of CO₂ in water and aqueous NaCl solutions. The model confirms that the inert association scheme is more suitable for CO₂ than the 3B association scheme, in the CO₂-H₂O system. Meanwhile, the CO₂-H₂O-NaCl system can be predicted by using two adjustable parameters of H₂O-NaCl and CO₂-NaCl systems. The mean deviations of the predicted solubility of CO₂ in water and aqueous NaCl solutions from the CPA-WS model are 5.31 and 3.56%, respectively.

It can be noticed that the work performed for multiphase systems with CO₂-water-hydrocarbon at the same time is scarce, so the study of thermodynamic equilibrium is relevant to optimize the design of CO₂ injection processes in reservoirs depleted of hydrocarbons. Equations of State such as CPA offer different advantages over

conventional EoS, as they can adequately describe the associative interaction with different compounds, mainly asphaltenes present in liquid phases. Additionally, the presence of water in these systems incorporates important electrostatic interaction with CO₂ and other hydrocarbon compounds that reduce their solubility in the mixture, which can be represented by the associative interactions of the EoS CPA.

Therefore, in this work, it was decided to use the EoS CPA to study the thermodynamic behavior of systems CO₂, water, and hydrocarbon in a CO₂ injection process (10 – 80 mole%) and water contents (25 and 50 mole%) for a case study of a depleted reservoir in Colombia. The evaluation of this behavior was performed considering variables such as the swelling of the crude oil, the solubility of CO₂ in water, and the pressurization of the system. The associative parameters for the different systems were taken from the literature and, additionally, molecular dynamics (MD) simulations were conducted, focused on CO₂-hydrocarbon-water systems, to obtain the necessary association parameters for CPA.

This research introduces a broad framework for using the CPA to model the CO₂ injection process in Colombian oil reservoirs. The framework accounts for the unique characteristics of CO₂, including its quadrupole interaction, and the cross association between H₂O and CO₂ molecules, added to the association between H₂O molecules.

2. THEORETICAL FRAMEWORK

CPA EQUATION OF STATE.

All thermodynamic functions of a fluid can be derived from an equation of state. The equation of state for phase "p" can be written as follows:

$$PV_{\alpha} = Z_{\alpha} N_{\alpha} RT \quad \forall \alpha = 1, \dots, n_{\alpha} \quad (1)$$

All the complexities of non-ideal behavior are captured in the compressibility factor Z_{α} . In particular, the general form of a cubic equation of state is:

$$Z_{\alpha} = \frac{Z_{\alpha}}{Z_{\alpha} - B_{\alpha}} - \frac{Z_{\alpha} A_{\alpha}}{(Z_{\alpha} + \delta_1 B_{\alpha})(Z_{\alpha} + \delta_2 B_{\alpha})} \quad (2)$$

The non-ideal behavior comes from the temperature-dependent physical (van der Waals) interaction between the molecules (represented by A_{α}) and the temperature-independent finite volume occupied by the molecules. However, there is a very important effect whose description, so far, cannot be described using traditional cubic equations. This effect is an explicit explanation of hydrogen bonding or, in general, Lewis acid-Lewis base interactions, species that can receive and donate electrons, respectively. This phenomenon, of which hydrogen bonding is a good example, is characterized by strong short-range attractive interactions, and it is closely related to the polarity of fluid molecules.

The CPA model combines the Peng-Robinson (PR) or Soave-Reidlich-Kwong (SRK) equations of state, which consider the physical interactions between molecules, with the Wertheim association theory. An associative term is added that represents the interactions, hydrogen bond type, self, or cross between the active sites of the different types of molecules present in the fluid of interest. Equation 3 represents the CPA model:

$$Z_\alpha = Z_\alpha^{phys} + Z_\alpha^{assoc} \quad (3)$$

where Z_α^{phys} is the contribution to the compressibility factor of the cubic equation of state, and Z_α^{assoc} is the contribution to the compressibility factor of the association theory. The associative term is given by:

$$Z_\alpha^{assoc} = -\frac{1}{2} \left(1 + \rho_\alpha \frac{\partial \ln g}{\partial \rho} \right) \sum_{i=1}^{n_c} x_{\alpha,i} \sum_{j=1}^2 (1 - \chi_{Ai}) \quad (4)$$

$$X_{Ai} = \frac{1}{1 + \sum_j n_j \sum_{B_j} X_{B_j} \Delta^{AiB_j}} \quad (5)$$

$$\Delta^{AiB_j} = g \beta^{AiB_j} \left[\exp \left(\frac{\varepsilon^{AiB_j}}{RT} \right) - 1 \right] b_{ij} \quad (6)$$

where X_{Ai} is the fraction of unbound sites of the A sites in compound i, Δ^{AiB_j} is the strength of association between the association sites of compounds i and j. This strength is dependent on the terms β^{AiB_j} and ε^{AiB_j} , which correspond to the association volumes and energies between the possible association sites A and B, respectively.

Based on the foregoing, to model a system using the EoS CPA, a total of 3 parameters are required for the non-associative components (Z_α^{phys}): Critical Temperature (T_c), Critical Pressure (P_c), and Acentric Factor (ω), and, 5 for the associative components ($Z_\alpha^{phys}, Z_\alpha^{assoc}$): T_c , P_c , ω , β^{AiB_j} and ε^{AiB_j} .

The dependence of the association term on the association scheme, specifically the number and type of association sites, is evident from equation 5. The simplified notation proposed by Huang and Radosz is used in this study (Huang & Radosz, 1990). In this case, the number of the association scheme represents the total number of association sites of the molecule, and the letter represents the type of association (corresponding count of electron donor and acceptor sites). For example, the association scheme 2B represents a molecule with two association sites, one electron donor (1ed) and electron acceptor (1ea). The association scheme 3B represents a molecule with three association sites, 1ed and 2ea or 2ed and 1ea. Finally, the association scheme 4C represents a molecule with four association sites, 2ed and 2ea.

In Figure 1, the process is exemplified in the form of an algorithm that must be followed to solve the CPA equation of state and to obtain the fractions of the phases of each component, as well as their properties at the pressure and temperature conditions evaluated. The objective is to find the state that minimizes the global Gibbs free energy of the system and ensures the stability of the phases. To such end, the general equation that combines the difference in fugacity and the mass balance for all components is minimized. First, the EoS parameters must be calculated through the initial information given and the fugacity obtained. Then, it is necessary to calculate the matrix of associative terms between the different sites of the molecules to obtain the value of the associative part in the CPA model. Thus, the fractions of phases are iterated until the fugacity coefficients are determined and meet the established margin of error. This process obtains the mole fractions of all the components in the liquid or gas phase, from which it is possible to determine their properties and solubility in the total composition of the fluid.

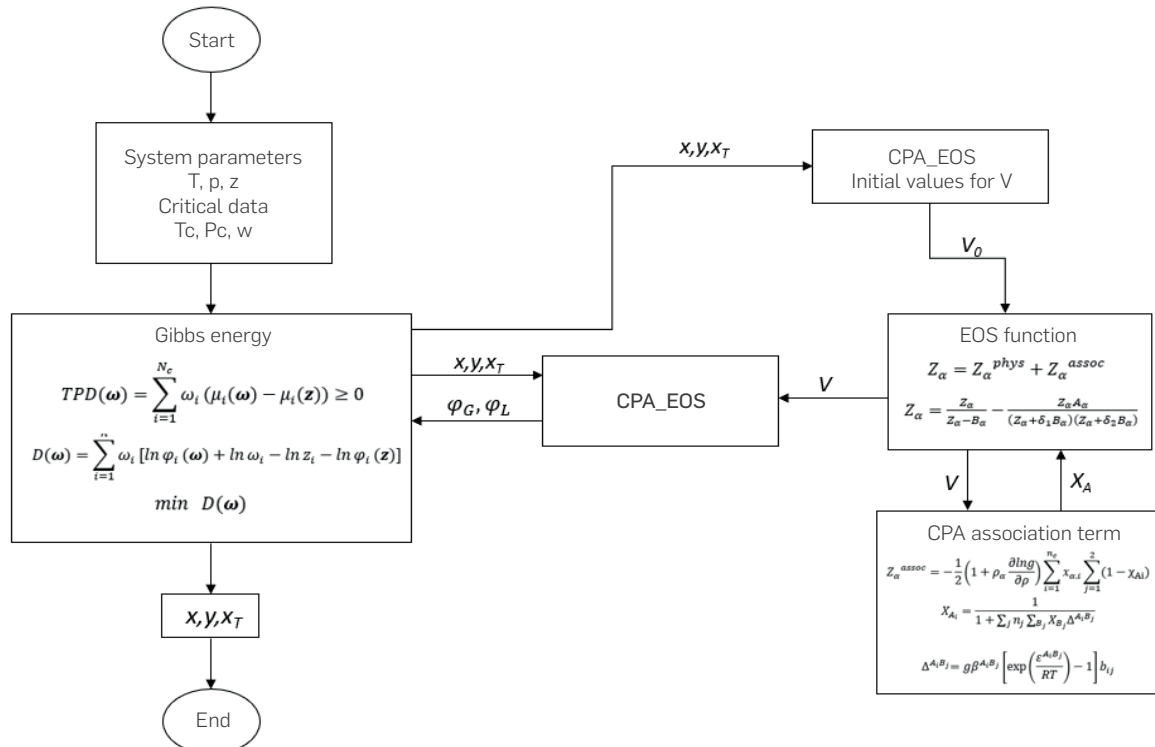


Figure 1. Example of CPA model solution algorithm.

3. METHODOLOGY

This study focuses on understanding the interactions that occur within depleted reservoirs in CO₂ injection processes in CCUS projects using the EoS CPA. Included below are some basic concepts, considerations, and simplifications to study the thermodynamic behavior of CO₂, water, and hydrocarbon systems.

Case Study. Table 1 shows a summary of the main properties of the reservoir fluid used in this study. This fluid has composition, conventional PVT experimental tests, CO₂ injection tests, minimum miscibility pressures, and asphaltene content. All this experimental information enabled us to build a robust, complete, and thermodynamically consistent fluid model for this fluid system. All simulations in this study were carried out using the EoS Peng-Robinson (Peng & Robinson, 1976) with Peneloux volume correction (Péneloux et al., 1982), independent of the temperature for modeling the physical part of the system. The EoS parameters were derived from the experimental information available. A fluid quality control (QC) included an initial simulation of Saturation Pressures, GOR and dead oil density. Small regressions were conducted on the BIC's (Binary Interaction Coefficients) between the hydrocarbons to adjust the PVT gradient properties in vertical relief (Martinsen et al., 2010), and between CO₂ and the pseudo components to adjust the gas injection tests.

Table 1. Fluid Properties

Fluid	°API	GOR (scf/STB)	Asphaltenes (% w/w)	CO ₂ (mol %)	C7+ (mol %)
Case study	40.6	1728	1.0	2,644	23,853

Table 2. Fluids at depletion conditions at 10 mole% CO₂ injection and 25 mole% water

Depth (ft)	Temperature °F	Saturation Pressure psia	CO ₂ mole%	N ₂ mole%	C1 mole%	C2 mole%	C3 mole%	C4 mole%	C5-6 mole%	C7-10 mole%	C11-14 mole%	C15-20 mole%	C21-29 mole%	C30+ mole%	Water mole%
10000	217.0	2812.21	7.9442	0.0270	7.5578	2.2876	2.1931	2.3821	4.3323	31.7430	11.4380	4.5145	0.5466	0.0337	25.0000
12000	238.1	1363.36	8.3212	0.0501	13.6926	3.6773	3.1707	3.1383	4.9006	24.0947	8.8568	4.3264	0.7064	0.0651	25.0000
13000	248.7	1624.43	8.4497	0.0634	16.3301	4.1837	3.4550	3.2930	4.8383	20.9186	8.0301	4.4671	0.8705	0.1005	25.0000
14000	259.3	1914.50	8.6147	0.0762	18.6682	4.6030	3.6662	3.3832	4.7176	18.1291	7.2786	4.5896	1.1053	0.1685	25.0000
15000	269.9	2190.07	8.7227	0.0857	20.5759	4.9787	3.8723	3.4743	4.6144	15.5837	6.4426	4.7358	1.5584	0.3555	25.0000
15374.2	273.8	2320.61	8.7454	0.0796	20.2308	5.1117	3.9922	3.5404	4.5317	13.8918	5.9883	5.1656	2.6502	1.0722	25.0000
16000	280.4	2538.17	8.8478	0.0752	19.8966	5.0647	3.8202	3.2468	3.9422	11.5444	5.7192	5.5371	4.2142	3.0915	25.0000
17000	291.0	2828.24	8.876	0.0847	21.1204	5.0907	3.6648	3.0079	3.5304	10.1782	5.4301	5.3709	4.5430	4.1028	25.0000

Table 3. CO₂ and Water Association Schemes and parameters

Reference	CO ₂				Water			
	Association Scheme	Scheme name in this job	$\varepsilon^{A_i B_j}$ (K)	$\beta^{A_i B_j}$	Reference	Association Scheme	$\varepsilon^{A_i B_j}$ (K)	$\beta^{A_i B_j}$
Tsivintzelis, 2011 (Tsivintzelis et al., 2015b)	Non-autoassociative	1B_	-	-	Tsivintzelis, 2011 (Tsivintzelis et al., 2015b)	4C	2003.13	0.0692
	2B	2B_1	939.568	0.0568				
	3B	3B_	621.568	0.0411				
	4C	4C_3	471.828	0.0297				
Oliveira, 2011 (Oliveira et al., 2011)	2B	2B_2	1237.14	0.0642				
	4C	4C_1	731.770	0.1202				
Monteiro, 2020 (Monteiro et al., 2020)	4C	4C_2	513.000	0.00257				

Studied Systems. The compositional fluid studied has a gradient of PVT properties in a vertical relief of 10,000 ft at a depletion condition of 2,000 psi @ 15,374 ft and an oil-water contact (OWC) at 17,000 ft. Considering the above and, injecting CO₂ at 10, 20, 40, 60 and 80 mole% with different amounts of water in the reservoir (25 and 50 mole%), in total, 72 fluid systems with compositions and different temperatures. In Table 2, a fluid systems example can be observed at depletion conditions, with an injection of 10 mole% CO₂ and 25 mole% water throughout the vertical relief.

The BIC's between water and hydrocarbons were maintained at 0, while the Binary Interaction Coefficients between water and CO₂ were taken from literature. (Tsivintzelis et al., 2011b)

ASSOCIATIVE PARAMETERS OF LITERATURE.

In this work, the associative components of the system are CO₂ and water. It is worth noting that although hydrocarbons are not considered associative components, they are part of the system and have a specific composition, as can be seen in Table 2. As mentioned above, 5 parameters are required for water and CO₂, as they are associative components. The critical properties and the acentric factor are already well defined, unique, and can be found in literature. (Tsivintzelis et al., 2015b) However, the parameters and associative configurations may vary depending on the author, especially those related to CO₂. Table 3 shows the different association schemes used for CO₂ and water. Considering the 72 previously mentioned systems and the 7 schemes worked for CO₂, in total, there are 504 fluid systems with different physicochemical and thermodynamic properties.

ASSOCIATIVE PARAMETERS MOLECULAR DYNAMICS (MD).

In this study, an MD model was proposed to understand the interfacial behavior of the interaction of CO₂ with the hydrocarbon and the aqueous phase. To achieve this, some simplifications were made. First, the crude oil matrix was represented by a mixture of n-heptane and toluene, widely used in the literature, known as heptol, (Moncayo-Riascos et al., 2022; Ramírez et al., 2021; Yuan Yang, (Yang et al., 2018) using a 70:30 ratio (Figure 2-a). To describe the asphaltene fraction, a molecular structure proposed in a previous work for Colombian crude oil was used (Figure 2-b), (Moncayo-Riascos et al., 2022), which was the most aggressive in terms of aggregation, with a concentration of 1% by weight. The molecular structure was proposed from petroleomics, which allows studying the "genetics of crude oil", obtaining molecular descriptors that allow us to propose reliable molecular structures that capture the structural and compositional particularities of the different fractions of crude oil (Moncayo-Riascos et al., 2022).

The gas content was represented using only methane at a molar concentration of 50%, to have a computational representation of a live crude oil. The CO₂ content was 40 mole% with respect to live crude oil (asphaltenes, heptol, and methane). Although we have a simplified system in this study, it is worth noting that the system has a considerable computational cost since there is a considerable number of molecules of each species evaluated (Figure 2-a), so the simulations were carried out using high-performance computing machines from AWS (Amazon Web Services).

Figure 2-c shows the initial configuration of the system evaluated in DM, initially with three phases (live crude oil, CO₂, and water). In a first approach, a simulation was conducted in which the boundary in the z-direction, that is, in the direction perpendicular to the interface, was considered reflective. This indicates that molecules that exceed the limits in z are reflected within the simulation box with the same speed but in the opposite direction. This was done to validate what the distribution of CO₂ is like between an aqueous phase and a model solution of a live crude oil. The results indicated that CO₂ tends to occupy the entire volume occupied by the model solution of live crude oil. Therefore, after this validation, simulations were conducted with periodic conditions in all directions, representing a water-living crude oil interface, that is, without considering reflective boundaries in the z-direction. Simulations were carried out at a pressure of 6500 psi and 255°F.

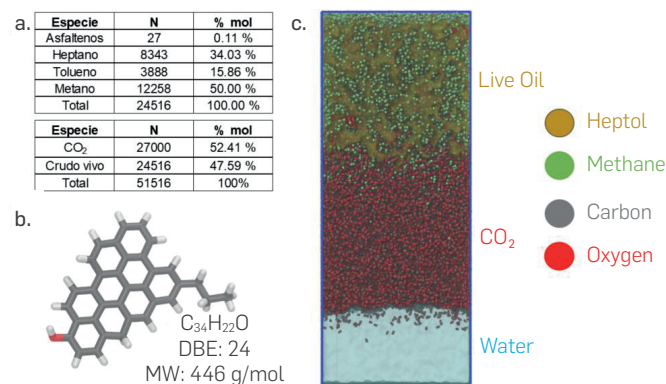


Figure 2. a) Number of molecules and mole composition of the system evaluated in DM and (b) initial configuration. Carbon atoms are shown in gray, oxygen in red, heptol in yellow (transparent), and water in blue (transparent).

All molecular dynamics simulations were performed using the free LAMMPS software (Plimpton, 1995). VMD visualization software (William et al., 1996) was used to obtain images and radial distribution functions. Temperature and pressure were controlled by the Nosé-Hoover thermostat and the barostat, respectively. The interaction parameters between atoms of different natures were defined by the geometric average mixing rules. Long-range electrostatic interactions were calculated using the particle-particle-mesh method (Hockney & Eastwood, 1988). The cutoff radius was established at 14 Å for van der Waals and electrostatic interactions, in accordance with that reported in the literature (Moncayo-Riascos et al., 2022; van Rooijen et al., 2023).

4. RESULTS

ASSOCIATIVE PARAMETERS OF LITERATURE.

As mentioned in the introduction, the evaluation of thermodynamic behavior using CPA is performed considering variables such as Gas – Oil Ratio (GOR – scf/bbl), density of crude oil and water for swelling processes, Gas – Water Ratio (GWR – scf/bbl) of CO₂ and C1 to quantify solubilities, and saturation pressures to estimate the pressurization of the various systems.

In Figure 3, the amount of CO₂ that is solubilized in the aqueous phase can be observed for different depths at three different injection contents (0, 40 and 80 mole%) and two amounts of water (25 and 50 mole%). As expected, the CO₂ content present in the aqueous phase increases with greater quantities of injected gas, and all association schemes can represent this behavior (Figure 3-a,c,e). However, scheme 4C_1, at injection conditions higher than 40%, predicts solubility values that are too high (greater than 2000 scf/bbl) compared to the other schemes and experimental data (Valtz et al., 2004). Additionally, this scheme is the only one that presents large variations in solubility with different water contents. At 40% CO₂ injection, it is observed that scheme 4C_1 predicts a value of 4500 scf/bbl at 14000 ft for 25% water (Figure 3-c), while for 50% a value of 2000 scf/bbl (Figure 3-d) is obtained. Comparing these results with the other association schemes that present minimal variations (1-8 scf/bbl) between different water contents at different depths, allows us to show that the 4C_1 scheme is not the most appropriate to work with these water-CO₂-hydrocarbons systems. Based on the above, scheme 4C_1 is not considered for subsequent analyses.

Studying the behavior of other components present in high proportions in reservoir fluids such as those studied in this work (fluids close to the critical point) is essential to understand, at a thermodynamic level, all the events that can occur in CCUS processes. Figure 4 shows the amount of C1 present in the aqueous phase for two different CO₂ injection contents (10 and 60 mole%). Similar to the behavior of CO₂, the solubility of C1 increases with depth and there is no significant change in relation with the amount of water in the system (Figure 4-a,b). It is worth keeping in mind that the soluble amount of methane in water is considerably less compared to that of CO₂. At the same injection conditions (40 mole%) and depth (17,000 ft), the methane solubility is 10 scf/bbl while CO₂ solubility is around 250 scf/bbl. A big difference with respect to CO₂ is that the amount of C1 in the aqueous phase decreases with the greater the amount of gas injected (Figure 4-a,c). This was expected because the methane present in the system is higher for 10% CO₂ injection (7 – 21 mole%) compared to 60% (3 – 9 mole%).

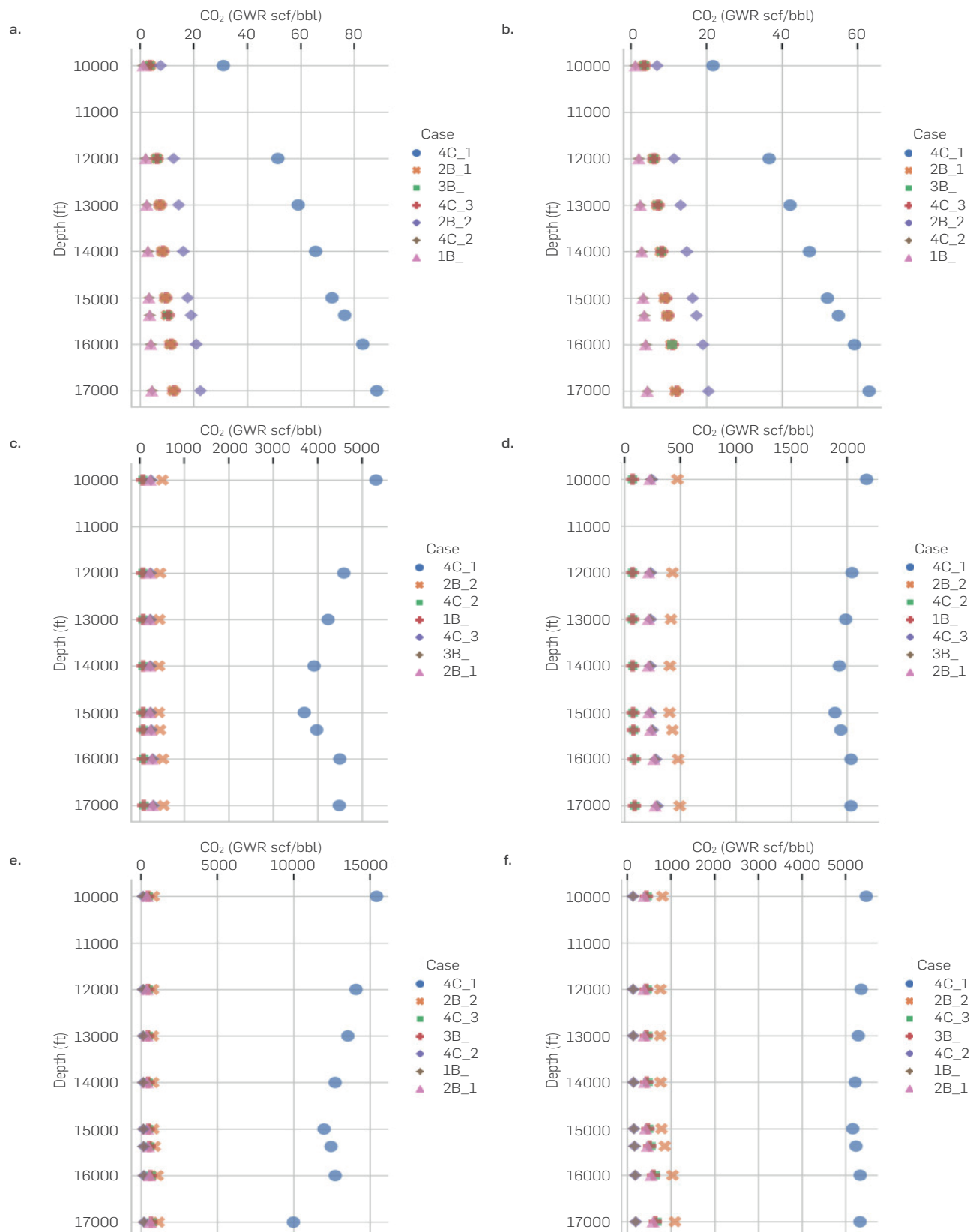


Figure 3. CO₂ content (GWR) in the aqueous phase predicted by the association schemes for different depths at three different injection contents and two amounts of water. (a) Injection Content (mole%) = 0 and Water Content (mole%) = 25, (b) Injection Content (mole%) = 0 and Water Content (mole%) = 50, (c) Injection Content (mole%) = 40 and Water Content (mole%) = 25, (d) Injection Content (mole%) = 40 and Water Content (mole%) = 50, (e) Injection Content (mole%) = 80 and Water Content (mole%) = 25 and (f) Injection Content (mole%) = 80 and Water Content (mole%) = 50.

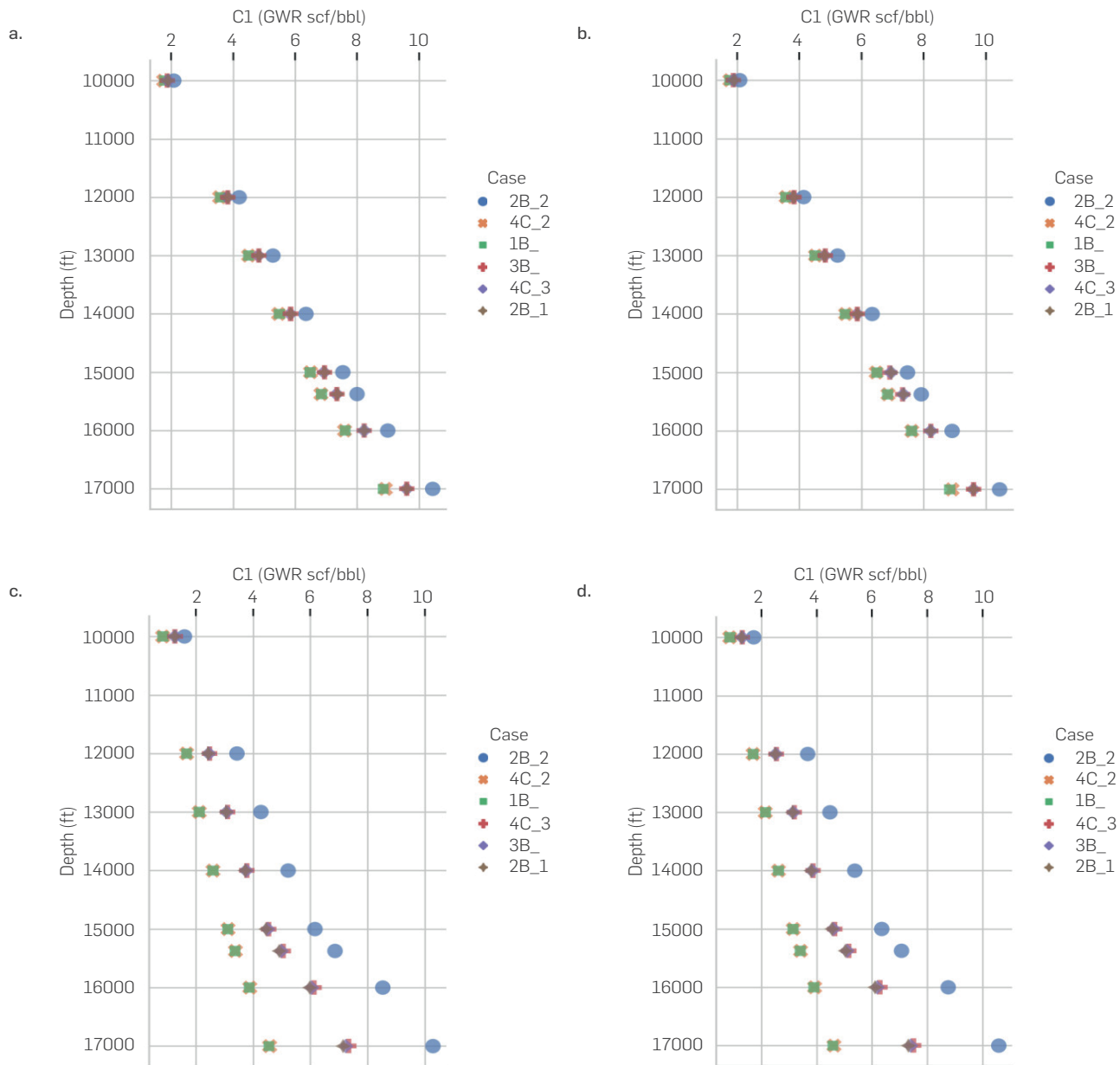


Figure 4. C1 content (GWR) in the aqueous phase predicted by the association schemes for different depths at two different injection contents and two amounts of water. (a) Injection Content (mole%) = 10 and Water Content (mole%) = 25, (b) Injection Content (mole%) = 10 and Water Content (mole%) = 50, (c) Injection Content (mole%) = 60 and Water Content (mole%) = 25 and (d) Injection Content (mole%) = 60 and Water Content (mole%) = 50

To analyze the swelling processes that occur within the crude oil, in Figure 5, saturation pressures, GOR, and oil phase density are shown for the reference depth (15374.2 ft) at different CO₂ injection conditions. Different literature studies have reported the increase in saturation pressure when injecting different amounts of CO₂ (Arya et al., 2015). This behavior is replicated by most of the association schemes used in this study; however, 2B_2 presents thermodynamic inconsistencies at high CO₂ contents, as can be seen in Figure 5-a. Hence, as occurred with 4C_1, this scheme is excluded from subsequent analyses. Regarding the GOR, very small changes can be observed with respect to the amount of CO₂ injected (Figure 5-b). The case study of this work is a fluid close to the critical point whose density under depletion conditions at the reference depth is

approximately 0.45 g/cm³. The CO₂ injection conditions (Temperature and Pressure) make this a supercritical fluid with higher densities than the original fluid in the reservoir (greater depths and CO₂ injection conditions). As CO₂ is solubilized within the original fluid, the density of the latter increases, as a consequence of a greater amount of CO₂ present in the oil phase. The phenomenon described above is observed in Figure 5-c,d. In relation with the water content in the system, there are no significant differences in the calculation of the density of the oil phase for % Injection less than or equal to 60%. For 80% contents, association schemes 1B and 4C_2 predict a lower density for systems with a greater amount of water (Figure 5-c,d). As mentioned above, schemes 4C_1 and 2B_2 present inconsistencies

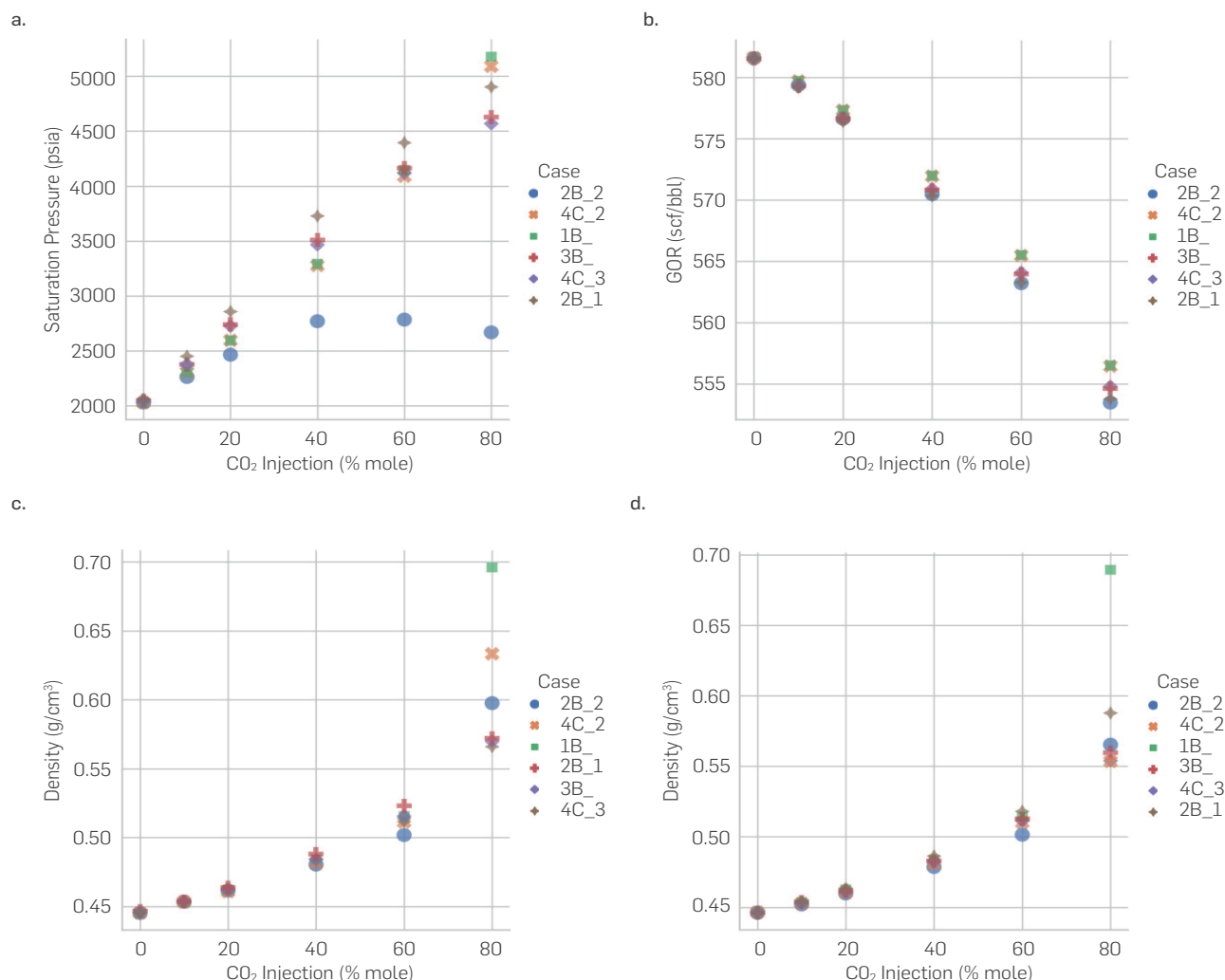


Figure 5. Saturation pressure, GOR and density of the oil phase for the reference depth (15374.2 m) at different CO₂ injection conditions. (a) Saturation Pressure (psi), (b) Gas - Oil Ratio (GOR), (c) Oil phase density (g/cm³) for 25 mole% water content and (d) Oil phase density (g/cm³) for 50 mole% water content

in the calculation of properties such as CO₂ solubility in water and saturation pressure. It should be highlighted that the SRK equation of state represents the physical component in the context of these two association schemes, while PR was selected as the equation of state for the execution of all simulations. The discrepancy in the selection of EoS to portray the physical aspect is attributed to the widespread adoption of Peng-Robinson as a fundamental framework for numerous fluid models in the industry. In this study, the focus was primarily on the association scheme as the variable of interest, which could elucidate the reasons behind the issues observed in schemes 4C_1 and 2B_2.

To overcome this drawback, it is possible to adjust the volumes and association energies of those schemes to properly calculate the phase behavior. However, it is important to note that modifying these schemes to accurately represent a singular phenomenon in this type of process, either swelling, solubility in water of formation, or system pressurization, will not correctly describe the others, resulting in new thermodynamic inconsistencies in unadjusted properties.

Associative Parameters Molecular dynamics (MD). Figure 6-a

shows the final configuration after equilibration of the raw live-CO₂-water system from the MD simulation. The results obtained led to identifying that the CO₂ molecules were mainly solubilized with the live crude oil model solution, while a few were located in the aqueous phase. Interestingly, the DM model led to establish that some methane molecules were located in the aqueous phase, while asphaltenes and heptol remained in the region occupied by CO₂ and the computational representation of live crude oil. To better visualize this distribution of the species evaluated in the DM model, some fractions were omitted. Figure 6-b only shows the location of the CO₂ molecules, allowing the CO₂ distribution in the two phases (hydrocarbon and water) to be established more clearly. Figure 6-c shows the location of the aqueous phase and the methane molecules of live crude oil to better illustrate the solubility of methane in water. Finally, in Figure 6-d, the location of the asphaltene molecules (in red) and the aqueous phase is shown, where the majority tends to remain in live crude oil and CO₂, locating a single molecule on the interface, but none within the aqueous phase (soluble), although the molecular structure of the type asphaltene used in this study (Figure 2-b), can form hydrogen bonds through the hydroxyl group (OH). In Figure 7, results of the calculation of the density profiles are

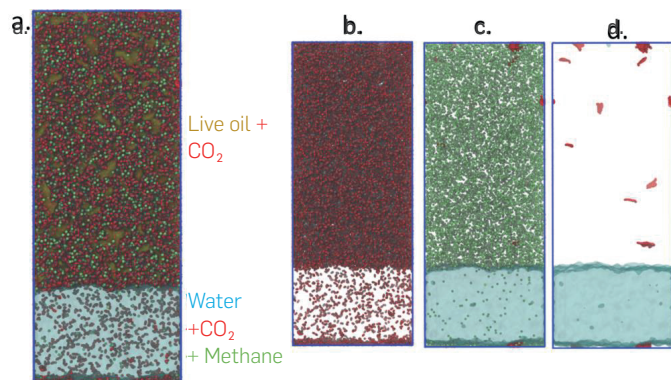


Figure 6. (a) Final configuration of the simulation of the live crude-CO₂-water system. Equilibrium location of the molecules of (b) CO₂, (c) methane and water, and (d) asphaltene and water. The color legend is the same as reported in Figure 2.

reported to have a numerical representation of the results reported in Figure 6. The results indicate that there is a reduction in the density of water of approximately 7%, due to the swelling produced by CO₂ and methane molecules, soluble in the aqueous phase. The density of the computational representation of live crude oil is only 0.3475 g/cm³ since the matrix of the model solution corresponds to 70:30 heptol, which at ambient conditions has a density of 0.7301 g/cm³. The CO₂ density at the simulation conditions (255 °F and 6500 psi) is 0.2829 g/cm³, promoting changes in the density of the live crude oil and, therefore, in the internal structure of the fluid.

Additionally, through the density profiles, it was possible to identify the interfacial region and to quantify the number of molecules located in each phase (aqueous and live crude oil). Based on these results, the mole compositions are reported in Table 4, proving that these types of computational methods are promising as complementary tools for experimental data to produce reliable data on CO₂ solubility and CO₂-water/brine interfacial tensions (Javanbakht et al., 2015), thus providing a detailed understanding of

the effect of the interaction of CO₂ with reservoir fluids (hydrocarbon and brines).

Finally, molecular dynamics simulations were used to estimate

Table 4. Mole composition of the species evaluated in the DM model in the aqueous and oil (live crude oil) phase.

Species	Live Oil (mole%)	Water (mole%)
Asphaltenes	0.05	0
Heptol	23.02	0.03
Methane	22.81	0.23
CO ₂	49.34	1.21
Water	4.77	98.53

the water-water and CO₂-CO₂ association energies. In this case, the radial distribution function (RDF) was calculated, which is widely used in DM modeling as it allows to establish the internal structure of the fluid (Headen et al., 2017; Moncayo-Riascos et al., 2021). Figure 8-a presents a diagram of the RDF calculation, where the green particle represents a reference molecule. This serves to define how the other species of the computational model are distributed, identifying, in the blue region, those molecules located in the first coordination peak. The second coordination peak corresponds to the molecules located in the red region.

In Figure 8-b, the results obtained from the radial distribution functions between the centers of mass of the water molecules (in blue) and CO₂ (in red) are reported. Additionally, using the calculation of the potential mean force (PMF), it is possible to determine the association energies from the determined RDFs. The PMF is equal to the product of the Boltzmann constant and the temperature ($-k_B \cdot T$), multiplied by the natural logarithm of the RDF (Headen et al., 2017). Figure 8-c shows association energies determined by DM for water-water (901 K) and CO₂-CO₂ (301 K) interactions, while the cross-interaction was estimated using a mixing rule (arithmetical average).

It is worth noting that the interaction energies determined in this

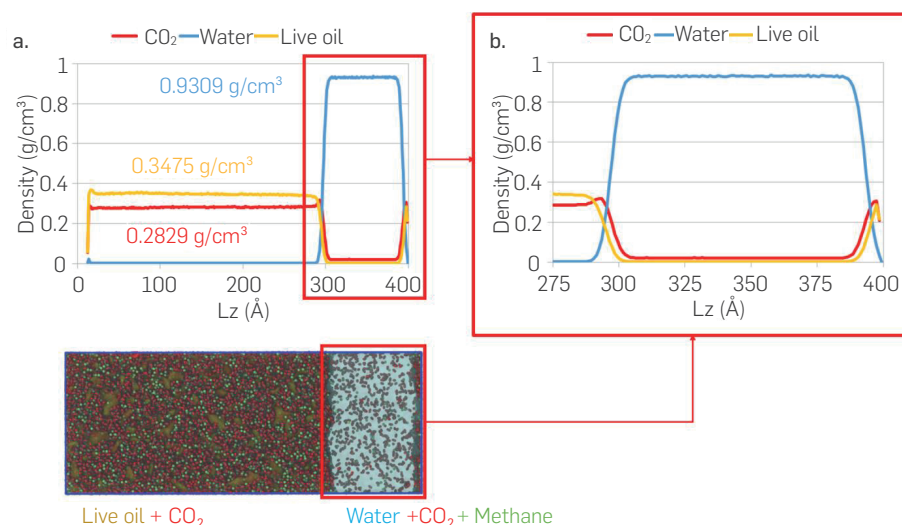


Figure 7. (a) Density profile of the equilibrium configuration of the live crude oil-CO₂-water system and (b) zoom over the live crude oil (CO₂)-water (CO₂) interfacial region highlighted in red boxes. The color legend is the same as reported in Figure 2.

study are significantly lower than those reported in the literature for the water-water interaction (2003 K) (Tsivintzelis et al., 2015b). Considering that there is no detailed description in the literature of how the association energies were obtained, this approach may be promising in acquiring association parameters with a physical description of the interactions through computational MD modeling. From the determined association energies, it is possible to find the association volumes necessary to appropriately describe the experimental data. In this study, CO₂ solubility data in water was used (Valtz et al., 2004), to adjust the association volume, finding that the association volume is 0.332 and 0.184 m³/mole, for the water-water and CO₂-water interaction respectively. The association volumes obtained are significantly higher than those reported in the literature (0.01 to 0.05 m³/mole) (Arya et al., 2016; Z. Li & Firoozabadi, 2010; Nascimento et al., 2019). This is because, having lower association energies, the

association volume must be greater to adequately describe the solubility of CO₂ in water. This means that, for lower association energies, the influence distance at which the molecules can be considered associated must be greater. Typically, the association volumes used to describe the association of asphaltene compounds is 0.05 m³/mol. Therefore, it makes physical sense to consider that the volume of association between water molecules is greater, since the region of influence of water molecules is much larger than that of asphaltenes, due to long-range electrostatic energies. This type of interaction has a fundamental role in describing the behavior of the aqueous phase, as because of it, water (18 g/mole) at ambient conditions is in the liquid phase, while molecules of higher molecular weight such as CO₂ (44 g/mole) are in the gas phase at the same conditions.

Comparison of Associative Parameters Literature and Molecular

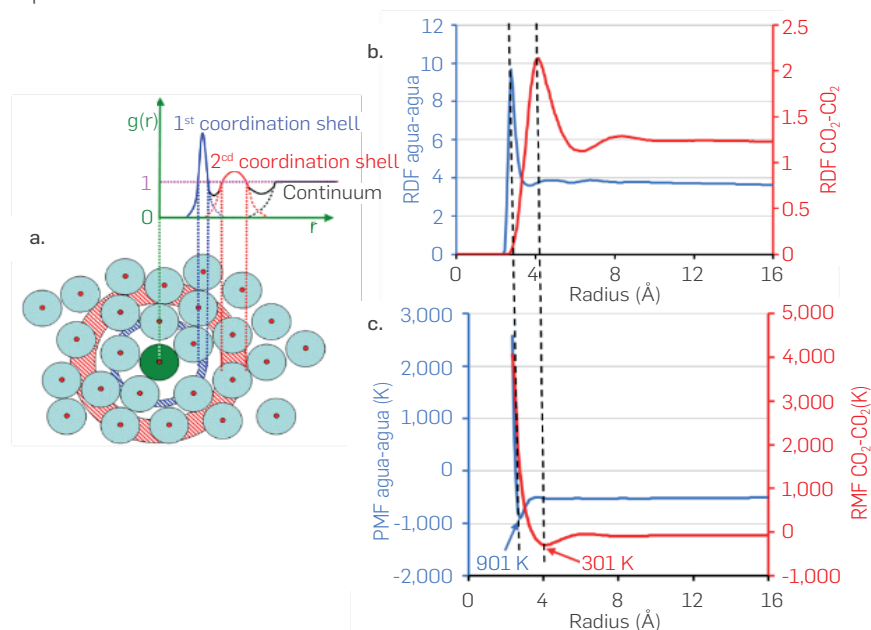


Figure 8. (a) Schematic of the calculation of the radial distribution function (RDF), and (b) zoom on the live crude oil (CO₂)-water (CO₂) interfacial region highlighted in red boxes. The color legend is the same as that reported in Figure 2.

Dynamics (MD). Once the association energies between water and CO₂ have been obtained through molecular dynamics, and the association volumes have been adjusted to experimental solubility data (Valtz et al., 2004), a new association scheme called 1B_DM is defined. It was decided to work with scheme 1B for CO₂ (CO₂ molecules do not associate with each other) because it is the most worked on in literature in recent years, as mentioned in the introduction. In turn, the water association scheme remains as 4C. Using the 1B_DM scheme and the EoS CPA, the different CO₂ injection scenarios in the case study compositional fluid are simulated. Additionally, a comparison is made between the Molecular Dynamics scheme and the literature schemes.

Figure 9 shows the saturation pressures calculated using the EoS CPA for the different Literature Association and DM schemes. As can be seen, the 1B_DM scheme correctly represents the directly proportional relationship existing between saturation pressure, CO₂ injection percentage, and depth. Both the literature and DM schemes present similar results at low injection conditions; however, as the amount of CO₂ in the system increases, the schemes predict different saturation pressures, observing a greater deviation towards the base of the formation.

As discussed earlier, the density of the oil is greater as the amount of CO₂ injected into the system is increased and this behavior is appropriately described by the 1B_DM scheme (Figure 10-a,c,e). However, compared to literature schemes, a sudden increase in crude oil density for depths 15374.2 and 16000ft is predicted for high CO₂ contents, as illustrated in Figure 10-e. This change in density does not have a clear explanation, since there is no sudden change in trend in the CO₂ content in the oil phase between 40 and 60% injection throughout the vertical relief (Figure 11). About to the aqueous phase (Figure 10-b,d,f), the trend

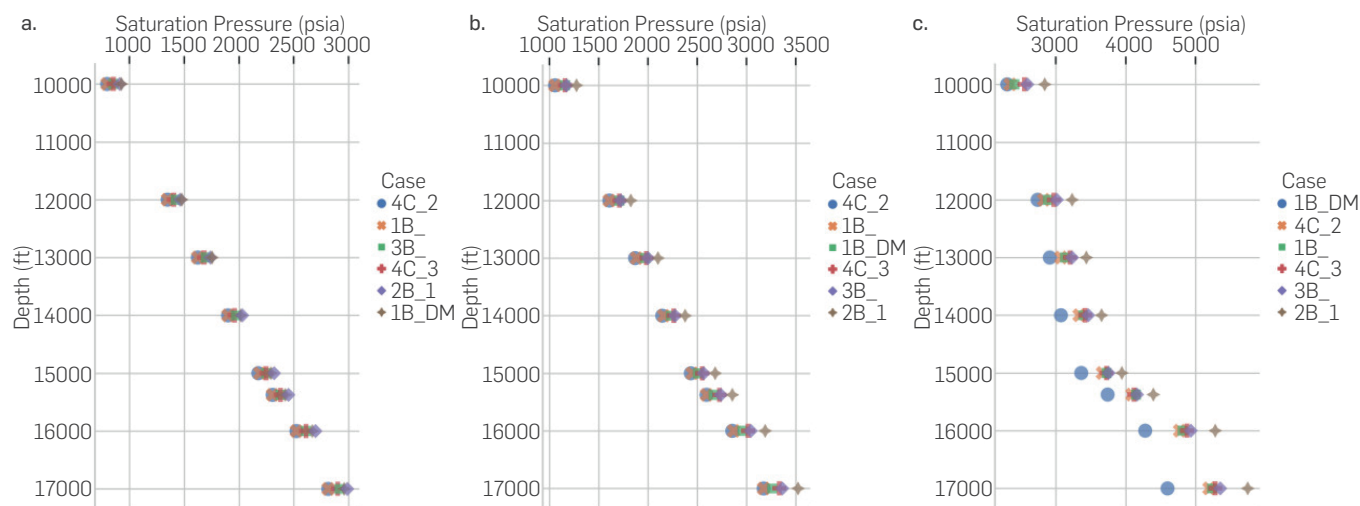


Figure 9. Saturation pressure CO₂-Water-Hydrocarbon System at different depths for CO₂ Injected at (a) 10, (b) 20 and (c) 60 mole%

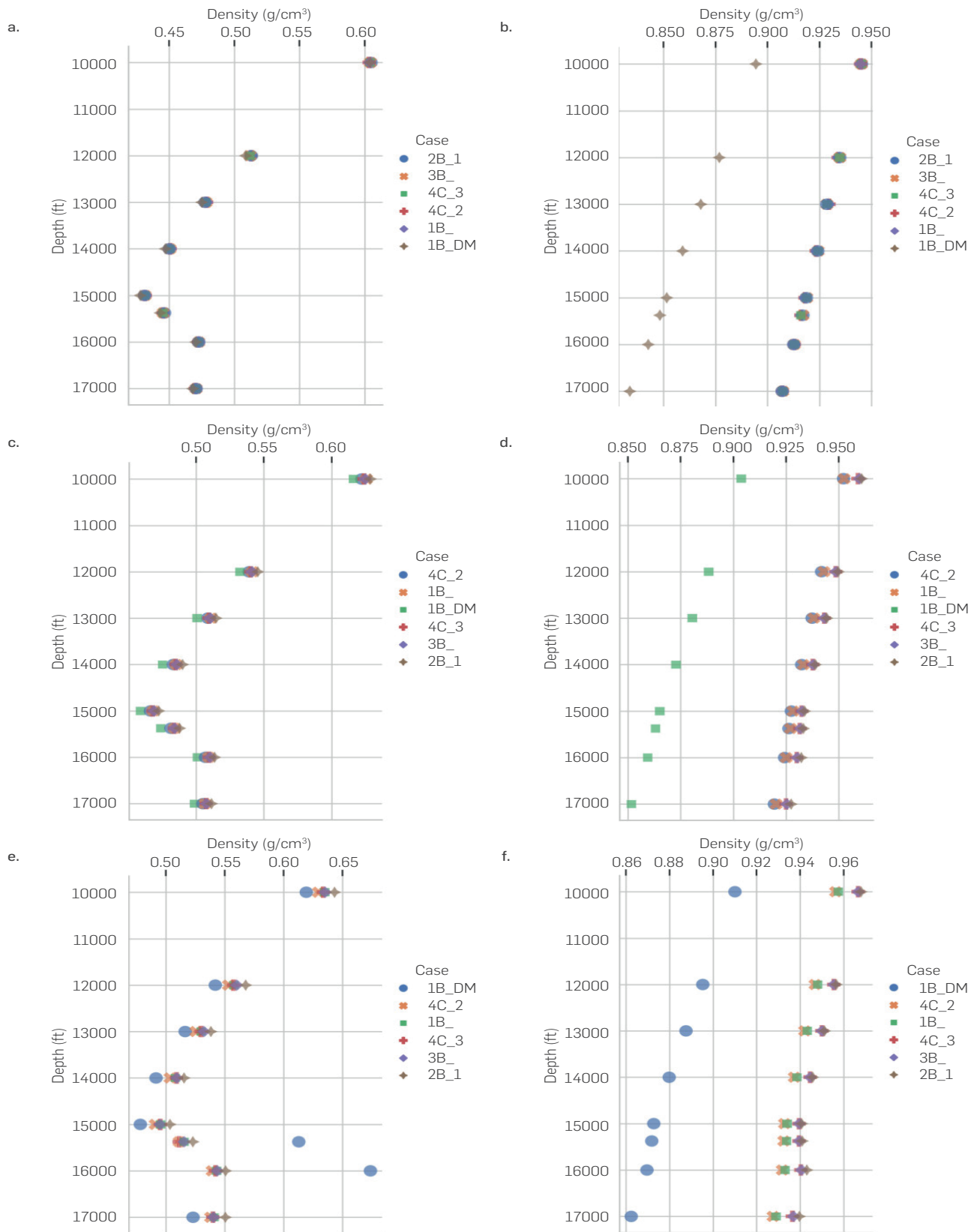


Figure 10. Density (g/cm³) at different depths for (a) Oil Phase at 0 mole% of CO₂ Injected, (b) Aqueous Phase at 0 mole% of CO₂ Injected, (c) Oil Phase at 40 mole% of CO₂ Injected, (d) Aqueous Phase at 40 mole% of CO₂ Injected, (e) Oil Phase at 60 mole% of CO₂ Injected and (f) Aqueous Phase at 60 mole% of CO₂ Injected.

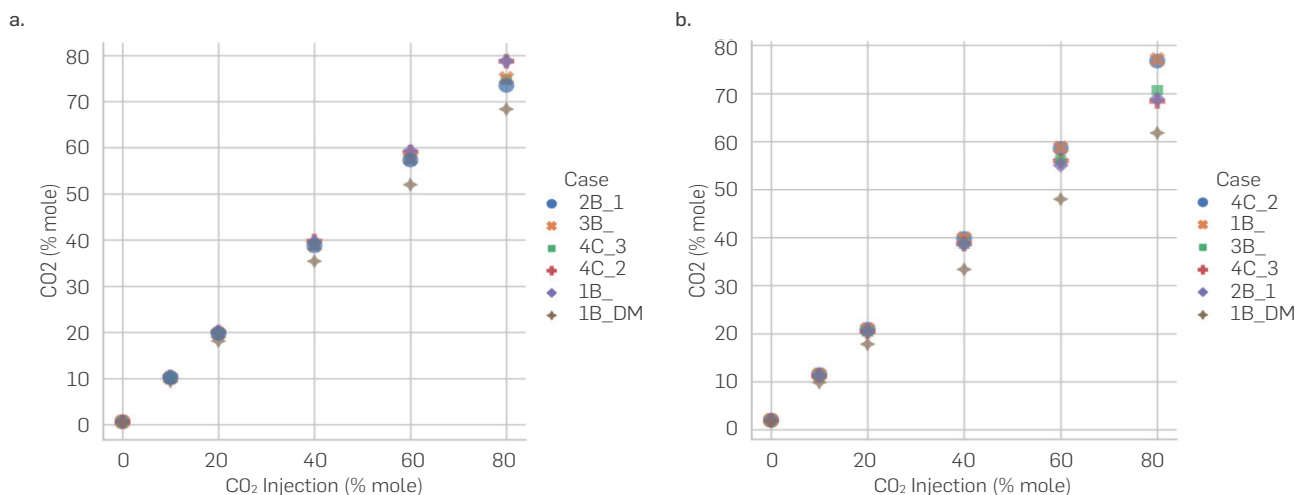


Figure 11. Mole fraction of CO₂ in the oil phase for different CO₂ injections at the (a) top (10,000 ft) and (b) bottom (17,000 ft) of the formation

of direct proportionality between the amount of CO₂ injected and its density is correctly represented with the different association schemes. However, it is worth noting that these changes are less than 2%. It can also be observed that the densities obtained by the DM association scheme are lower compared to those obtained from literature schemes.

The association scheme obtained from DM represents the increase in the CO₂ content in the crude oil with the amount of CO₂ injected into the system. Similar values of carbon dioxide present in the oil phase are calculated for injections less than 40%. However, at higher injections, there is a change in the CO₂ content for the systems that are located at the crest of the formation (10,000 ft) or in the valley of the formation (17,000 ft), as can be seen in Figure 11. It is important to note that all association schemes, including those extracted from literature, show the behavior described above. For 60% of CO₂ injected, the mole fraction at the top is 0.52 while at the bottom is 0.48 and. Also, for 80% of CO₂ injected, this difference is even greater, going from 0.69 at the top of the formation to 0.61 at the bottom. Although in theory they may be seen as small differences, these have a significant impact on important properties such as density and viscosity. It is important to note that even the association schemes extracted from literature also show the behavior described above.

Finally, to quantify the amount of CO₂ that can be solubilized in the aqueous phase, the mole fraction of CO₂ in water is calculated (later transformed into GWR) at two specific depths with amounts of CO₂ injected between 10 and 80 mole% using the different association schemes and the EoS CPA. First, the CO₂ content in the aqueous phase depends greatly on the association scheme with high injected CO₂ contents, a situation not applicable for properties such as oil density, water density (except the 1B_DM scheme), and saturation pressure. For 80 mole% injection, the solubility of CO₂ at the top (Figure 12-a) varies between 120 and 450 scf/bbl, while at the bottom, this range of variation is even greater, obtaining values of 200 to 700 scf/bbl (Figure 12-b). On the other hand, the predictions made by the DM association scheme are within the range of those calculated by the literature schemes, which makes it possible to demonstrate the coherence of the DM model to determine this type of properties. In theory, having such high CO₂ contents in water is not feasible (greater than 130 scf/bbl); however, until experimental data is available to corroborate these results, it is not possible to rule out any of the schemes studied except for cases 4C_1 and 2B_2, which showed thermodynamic inconsistencies in the calculation of basic properties.

Accurately characterizing the phase behavior of CO₂-hydrocarbon-

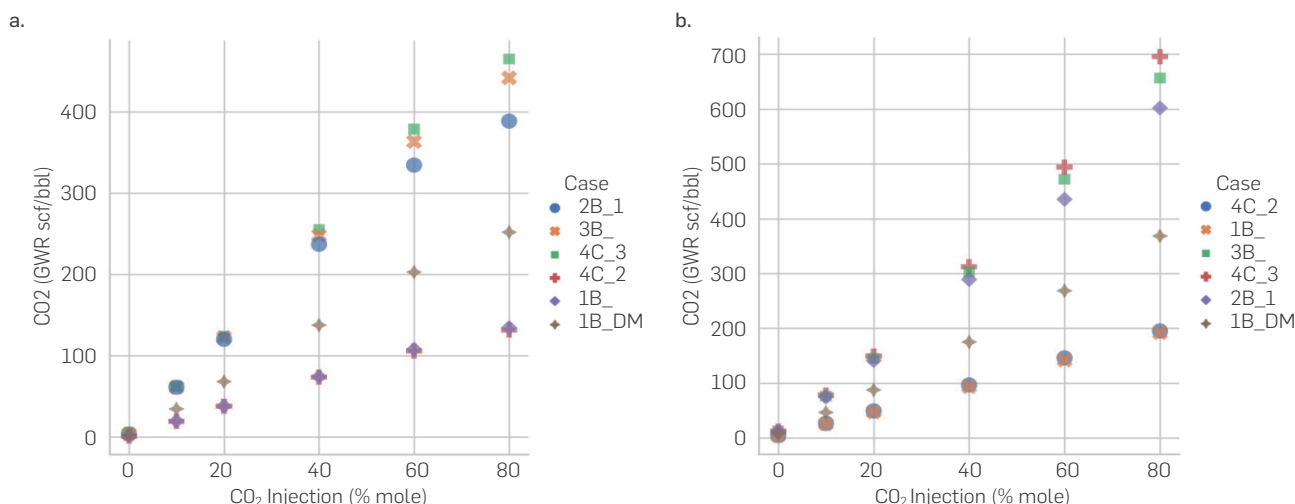


Figure 12. CO₂ content (GWR) in the aqueous phase for different amounts of CO₂ injection at the (a) top (10000 ft) and (b) bottom (17000 ft) of the formation

water systems across various temperature and pressure ranges is crucial for understanding the diverse phenomena observed in CO₂ injection EOR-storage processes. These phenomena include the effective displacement of oil by CO₂, the detrimental impact of viscous and gravitational fingering on hydrocarbon recovery, and the potential assistance in carbon sequestration within aquifers. The research conducted allows for an accurate depiction of the phase equilibria observed in the different systems examined. The complexity of this task arises from the wide range of temperature and pressure conditions, as well as the asymmetric composition of the mixtures studied. Furthermore, the presence of polar compounds with strong associative interactions adds complexity to the description of the phase equilibria in these systems. Nonetheless, the utilization of the CPA equation appropriately represents these phenomenon.

Therefore, a comprehensive understanding of the phase behavior is essential to design and optimize these processes to achieve desired outcomes. Other key parameters, such as crude oil composition and reservoir conditions, will be analyzed in future works.

This is the first time that Ecopetrol has used an advanced equation of state with the aforementioned scope, which is an important milestone in the acquisition of technical competencies and incorporation of technologies required to support the Ecopetrol Group's strategy.

CONCLUSIONS

Using CPA EoS and 8 different association schemes (7 from literature and 1 from DM), the thermodynamic behavior of CO₂, water and hydrocarbon systems was studied in a CO₂ injection process (10 – 80 mole%) and water content (25 and 50 mole%) for a case study of a depleted reservoir in Colombia. The evaluation was performed based on variables such as Gas – Oil Ratio (GOR – scf/bbl), crude oil and water density for swelling processes, Gas – Water Ratio (GWR – scf/bbl) of CO₂ and C1 to quantify solubilities and saturation pressures to estimate the pressurization of the different systems.

Association schemes 4C_1 and 2B_2 presented thermodynamic problems for the calculation of properties such as solubility and saturation pressures, as they showed unphysically trends in CO₂ injection processes. However, it is possible to adjust the volumes and association energies of the schemes to properly calculate the phase behavior.

The literature schemes, with the exception of those mentioned above, correctly represent thermodynamic behavior of water-CO₂-hydrocarbon systems in CCUS processes, whether they are swelling phenomena, CO₂ and C1 solubility in formation water or system pressurization.

The molecular dynamics computational model developed allowed us to establish an initial approach to understand the interaction of CO₂ with a model solution of a living crude oil (heptol+asphaltenes+methane) and water. The results obtained satisfactorily describe the distribution and solubility of CO₂ in the hydrocarbon phase and water. The mole fractions, determined through the computational model, are within the expected range for this type of systems, indicating that the potential use of this type of advanced modeling tools that allows reliable data and understanding the phenomena from a computational point of view

involved in CCUS processes. Additionally, the water-water and CO₂-CO₂ association energies were determined.

In general, the association scheme determined from DM presents results in accordance with those expected physically, which is corroborated when comparing the different properties determined with this scheme and those from the literature.

This work is a guide for the acquisition of experimental data of CO₂-water-hydrocarbon systems and technical competencies, plus the incorporation of technologies required to support the CCUS projects in the future and Ecopetrol Group's strategy.

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