Bulk and Interfacial Properties of the Decane+Water System in the Presence of Methane, Carbon Dioxide, and Their Mixture

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Abstract

Molecular dynamics simulations are carried out to study the two-phase behavior of the n-decane+water system in the presence of methane, carbon dioxide, and their mixture at reservoir conditions. The simulation studies were complemented by theoretical modeling using the perturbed-chain statistical associating fluid theory (PC-SAFT) equation of state (EoS) and density gradient theory. Our results show that the presence of methane and carbon dioxide decreases the interfacial tension (IFT) of the decane+water system. In general, the IFT increases with increasing pressure and decreasing temperature for the methane+decane+water and carbon dioxide+decane+water systems, similar to what has been found for the corresponding decane+water system. The most important finding of this study is that the presence of carbon dioxide decreases the IFT of the methane+decane+water system. The atomic density profiles provide evidence of the local accumulation of methane and carbon dioxide at the interface, in most of the studied systems. The results of this study show the preferential dissolution in the water-rich phase and enrichment at the interface for carbon dioxide in the methane+carbon dioxide+decane+water system. This indicates the preferential interaction of water with carbon dioxide relative to methane and decane. Notably, there is an enrichment of the interface by decane at high mole fractions of methane in the methane/decane-rich or methane/carbon dioxide/decane-rich phase. Overall, the solubility of methane and carbon dioxide in the water-rich phase increases with increasing pressure and temperature. Additionally, we find that the overall performance of the PC-SAFT EoS and the cubic-plus-association EoS is similar with respect to the calculation of bulk and interfacial properties of these systems.

1 Introduction

Currently, more than 30 Gt of anthropogenic carbon dioxide is emitted per year, mainly from the combustion of fossil fuels.¹ The emission of carbon dioxide into the atmosphere plays a key role in global warming and leads to important environmental problems.²⁻⁵ For instance, the melting of ice sheets and glaciers due to global warming likely contributes to sea level rise. Notably, carbon capture and storage (CCS) is regarded as an important technology for the reduction of anthropogenic carbon dioxide emissions. Many materials such as zeolites,^{6,7} metal-organic frameworks,^{7,8} polymers,^{6,9-11} and geological formations¹²⁻²² have been used for CCS.

Interestingly, enhanced oil recovery (EOR) techniques have been considered for sequestering carbon dioxide and improving oil recovery.¹⁵⁻²² In 2015, CO₂-EOR delivered approximately 3% of the U.S. crude oil supply and its involvement will continue to grow in the coming decades.²² Currently, the water-alternating-gas (WAG) method has been used in the CO₂-EOR projects to reduce the unfavorable mobility of carbon dioxide in the formations.^{20,21} During the WAG process, water is injected alternately with carbon dioxide for mobility control. Therefore, bulk and interfacial properties of the CO₂+oil+water system play an important role in the CO₂-EOR projects. For instance, the oil recovery efficiency can be correlated to the interfacial tension (IFT) using the capillary number defined as the ratio of the viscous forces to capillary forces.¹⁸ The capillary number increases as IFT decreases and/or viscosity increases. A lower IFT is desirable for the CO₂-EOR techniques which may help to improve oil recovery. Traditionally in the U.S, carbon dioxide from natural sources were employed for approximately 90% of CO₂-EOR supply.¹⁹ Whereas, CO₂-EOR utilizing anthropogenic emissions would be required to obtain the desired environmental benefits. Notably, impurities are present in the carbon dioxide stream obtained from industrial and power sectors.²³⁻²⁵ In general, techniques used for the removal of impurities from the gas streams are expensive. Thus, it is significant to investigate the properties of the CO₂+oil+water system in the presence of impurities such as CH₄ for improving

the performance of CCS and EOR.

Many experimental,^{26–36} theoretical,^{26,30–32,35} and simulation^{37–41} works have been done to obtain the bulk and interfacial properties of ternary mixtures of CH₄ or CO₂ with water and alkanes (e.g., n-decane which is the model oil in this study) at reservoir conditions. In these studies, large regions of two- and three-phase equilibria were observed for such ternary systems, and the three-phase region decreased with increasing pressure. Furthermore, it was shown that the IFT of, for instance, the decane+water system generally decreases in the presence of CH₄ and CO₂.^{26–28} This can be attributed to the local enrichment of the interface by CH₄ and CO₂.^{37–41} Also the IFT generally increases with increasing pressure and decreasing temperature for the CH₄+decane+water and CO₂+decane+water systems in the two-phase region.^{26–28} Notably, the study of quaternary mixtures containing CH₄, CO₂, water, and higher alkanes has not been reported so far.

Molecular simulations give important insights into the interfacial and bulk environments of different systems.^{11–14,42–49} In this study, molecular dynamics (MD) simulations were carried out to understand the properties of CH₄+decane+water, CO₂+decane+water, and CH₄+CO₂+decane+water systems at reservoir conditions. The simulation studies were complemented by theoretical modeling because of the general lack of experimental data for such systems, especially the quaternary case.

2 Simulation details

MD simulations were carried out utilizing the LAMMPS code⁵⁰ to study the two-phase behavior of the n-decane+water system in the presence of CH₄, CO₂, and their mixture over broad ranges of temperature (323–443 K) and pressure (up to about 100 MPa). The simulation models and methods implemented here were the same as described in our previous studies.^{47,48} Additionally, the transferable potentials for phase equilibria (TraPPE)⁵¹ united atom force field is employed to model the n-decane molecules and the Lennard-Jones (LJ) parameter for unlike atoms ε_{ij} is estimated using an extended

version⁵² of the Lorentz-Berthelot combining rule:

$$\varepsilon_{ij} = k_{ij}^{\text{LJ}} \sqrt{\varepsilon_i \varepsilon_j}, \quad (1)$$

where k_{ij}^{LJ} is an adjustable parameter. In our simulations, the parameter $k_{ij}^{\text{LJ}} = 1$, unless otherwise stated. Each simulation box contained 2048 water molecules and up to 625 CH₄/CO₂/decane molecules (Fig. 1 and Table 1). In all cases, the box dimensions parallel to the interface were about 36×36 Å. The MD runs are carried out with periodic boundary conditions in all three dimensions. The box dimensions are sufficiently large so that the finite-size effects are negligible in the estimations of the bulk and interfacial properties.^{47,53} Each system is subjected to 5 ns equilibration run in the *NPT* ensemble followed by 5 ns production run in the *NVE* ensemble. Only the box size in the z direction (normal to the interface) was allowed to vary during the *NPT* simulations. We have employed a velocity Verlet algorithm with a constant step size of 1 fs to integrate the equations of motion. The Nosé-Hoover thermostat with a relaxation time of 0.1 ps and the Nosé-Hoover barostat with a relaxation time of 1.0 ps are employed to control the temperature and pressure, respectively. The long-range electrostatic interactions were evaluated by the particle-particle particle-mesh method with a precision of 10^{-5} . We chose a cutoff of 15 Å for both LJ and electrostatic interactions. The error bars are based on the standard deviation of the mean of four independent MD trajectories.

The IFT is evaluated as follows.^{47-49,53,54}

$$\gamma = \frac{1}{2} L_z \left[P_{zz} - \frac{1}{2} (P_{xx} + P_{yy}) \right], \quad (2)$$

where L_z denotes the box size in the z direction, and P_{xx} , P_{yy} , and P_{zz} represent the three diagonal components of the pressure tensor. The components of the pressure tensor are calculated using the virial route as implemented in LAMMPS.⁵⁰ A better agreement between simulation and experimental results was found by tuning the k_{ij}^{LJ} parameter (see eq. (1), and Figures S1 and S2). In this study, we chose $k_{ij}^{\text{LJ}} = 1.1$ for

Figure 1: Equilibrium snapshot of the $\text{CH}_4+\text{CO}_2+\text{n-decane}$ system ($x_{\text{CH}_4} = x_{\text{CO}_2} \approx 0.25$) at 443 K and 30 MPa.

both water (O)-carbon dioxide (C) and water (O)-decane pairs.

3 Theoretical details

The familiar perturbed-chain statistical associating fluid theory (PC-SAFT) equation of state (EoS) was employed to calculate bulk properties (e.g., solubility) of the system. More details of the PC-SAFT EoS can be found elsewhere.^{55,56} In brief, the PC-SAFT EoS can be expressed via the compressibility factor Z :

$$Z = 1 + Z^{\text{hc}} + Z^{\text{disp}} + Z^{\text{assoc}}, \quad (3)$$

where Z^{hc} is the hard-chain term, Z^{disp} is the dispersive part, and Z^{assoc} represents the contribution due to association. Water is modeled using the 4C association scheme⁵⁷ and CO_2 is allowed to cross-associate with H_2O (solvation).⁵⁸ The PC-SAFT EoS parameters used in this study are given in Tables S1 and S2. These parameters were obtained from literature^{55,59} and in the absence of literature data, they were regressed from the experimental data.^{60–63}

In addition, the PC-SAFT EoS was coupled with the density gradient theory (DGT)

for the estimation of the interfacial properties. Briefly, for a planar interface of area A , the Helmholtz free energy is given as^{64,65}

$$F = A \int_{-\infty}^{+\infty} \left[f_0(n) + \frac{1}{2} \sum_i \sum_j c_{ij} \frac{dn_i}{dz} \frac{dn_j}{dz} \right] dz, \quad (4)$$

where f_0 denotes the Helmholtz free energy density of the homogeneous fluid at the local density n , dn_i/dz represents the local density gradient of the i th component. The cross influence parameter c_{ij} is defined as

$$c_{ij} = (1 - \beta_{ij}) \sqrt{c_{ii} c_{jj}}, \quad (5)$$

where c_{ii} and c_{jj} represent the pure component influence parameters, and β_{ij} denote the binary interaction coefficient. The pure component influence parameters and the binary interaction coefficients used in this study are given in Tables S3 and S4. These parameters were obtained from literature⁶⁶ and in the absence of literature data, they were identified by fitting the experimental data.^{27,67–69}

In equilibrium, the density profiles across the interface is evaluated through the minimization of the free energy by solving the corresponding Euler-Lagrange equation:

$$\sum_j c_{ij} \frac{d^2 n_j}{dz^2} = \mu_i^0(n_1(z), \dots, n_{N_c}(z)) - \mu_i \text{ for } i, j = 1, \dots, N_c, \quad (6)$$

where $\mu_i^0 \equiv (\frac{\partial f_0}{\partial n_i})_{T, V, n_j}$, μ_i represents the chemical potential of the i th component and N_c denotes the total number of components. These equations were solved together with the Dirichlet boundary conditions:

$$\begin{aligned} n_i &= n_i^I \text{ at } z = 0 \\ n_i &= n_i^{II} \text{ at } z = l, \end{aligned} \quad (7)$$

where n_i^I and n_i^{II} represent the bulk densities of the coexisting phases and l denotes the

Figure 2: Interfacial tension as a function of pressure for the decane+water system. The open symbols represent the results from the MD simulations and the estimates obtained using DGT with the PC-SAFT EoS are shown as lines. The experimental results of Georgiadis et al.²⁷ are shown as solid symbols.

interfacial thickness. The bulk properties are calculated employing the PC-SAFT EoS as described above. Once the equilibrium density profiles are available, the interfacial tension γ is estimated as follows:

$$\gamma = \int_{-\infty}^{+\infty} \sum_i \sum_j c_{ij} \frac{dn_i}{dz} \frac{dn_j}{dz} dz \quad (8)$$

4 Results and discussion

4.1 Decane+water system

Fig. 2 provides the IFT of the decane+water system obtained using MD (open symbols) and theoretical (lines) calculations. Our results are also compared with the corresponding experimental²⁷ quantities (solid symbols). Other experimental results^{70–74} agree with the ones reported here and are omitted for clarity. It is seen that our simulation and theoretical results are consistent with the experimental observations. The overall absolute average deviation, for instance, between the experimental and theoretical IFT data was less than about 2.3%. From these results it is clear that the IFT almost linearly increases with increasing pressure. We find that the linear slope of the IFT versus pressure plot increases with increasing temperature. For instance, the simulated slope changes from about 0.03 mN/(m MPa) at 323 K to 0.07 mN/(m MPa) at 443 K. Also, for a given pressure, the IFT decreases almost linearly with increasing temperature. For instance, the slope changes from about -0.10 to -0.07 mN/(m K) in the pressure range 30-100 MPa (Figure S3). These results are consistent with other theoretical^{75–77} and simulation^{52,78–80} studies.

The atomic density profiles can be readily obtained using molecular simulations and/or DGT, in comparison to experiments. For instance, Figure S4 provides the density profiles of water and decane as predicted by MD (solid lines) and theoretical (dashed lines) calculations for the decane+water system. An overall agreement between the simulation and theoretical results has been obtained. The theory shows that the density profiles of water and decane vary monotonically across the interface. Notably, in contrast to the theoretical prediction, there are oscillations present near the interface for the simulated density profile of decane at low temperatures. This may be due to the finite size of the simulated system.^{81,82} These density profiles of water and decane can also be described approximately by a hyperbolic tangent function.⁸¹ Furthermore, we see that the estimated water and decane liquid densities (Figure S5) away from the interface are in good agreement with the corresponding experimental liquid densities

of pure cases.⁶⁷ These results show that decane is less dense than water, and the densities of both water and decane increase with increasing pressure and decreasing temperature. Such agreement indicates the low mutual solubility of water and decane under the studied conditions. For example, Figure S6 shows our calculated solubilities of water and decane at 0.1 MPa and the corresponding experimental data.⁶⁰ A good quantitative agreement is obtained between the theoretical and experimental data. However, the simulated solubility values, for example, of water in the decane-rich phase differ by about an order of magnitude from the experimental data. A similar finding was reported for the water solubility in other alkanes.⁵² The agreement between the experimental and simulated solubility data may be improved by using, e.g., the TIP4P water model with the TraPPE united atom model for alkanes.⁵² Notably, the simulation of the IFT using the TIP4P/2005 water model performs better than that with most of the frequently employed water models.^{47,52}

The IFT can be understood in detail by means of the surface excess Γ_i and the relation is given by the Gibbs adsorption equation:^{48,49,53,69}

$$-d\gamma = \sum_i \Gamma_i d\mu_i. \quad (9)$$

The surface excess of the i th component relative to water is expressed as

$$\Gamma_{i,\text{water}} = -\alpha_i \int_{-\infty}^{+\infty} \Delta C(z) dz, \quad (10)$$

with

$$\Delta C(z) = \frac{n_{\text{water}}(z) - n_{\text{water}}^{II}}{\alpha_{\text{water}}} - \frac{n_i(z) - n_i^{II}}{\alpha_i}, \quad (11)$$

where

$$\alpha_i = \frac{n_i^{II} - n_i^I}{n_i^{II} - n_i^I + n_{\text{water}}^{II} - n_{\text{water}}^I}, \quad (12)$$

and

$$\alpha_{\text{water}} = \frac{n_{\text{water}}^{II} - n_{\text{water}}^I}{n_i^{II} - n_i^I + n_{\text{water}}^{II} - n_{\text{water}}^I}. \quad (13)$$

Here, I denotes the decane-rich phase and II represents the water-rich phase. Figure S7 provides the surface excess of decane as calculated from simulations (symbols) and from theoretical modeling (solid lines) for the decane+water system. We see that our simulation results are qualitatively consistent with the theoretical calculations. The maximum deviation (about a factor of 2) between the simulated surface excess values and the theoretical ones is found at the lowest studied temperature and at high pressures. We observe a negative surface excess for decane, which explains the increase in the IFT with pressure (see, e.g., eq. (9) and Fig. 2). We also notice that, at a given pressure, the surface excess of decane decreases with increasing temperature. This can explain the fact that the slope of the IFT versus pressure plot increases with increasing temperature. The negative surface excess of decane is expected because of the effects of the unfavorable hydrophobic-hydrophilic interaction between decane and water.^{78,80}

4.2 Decane+water system in the presence of CH₄

Fig. 3 provides the IFTs as obtained from the MD calculations (open symbols) and the corresponding theoretical results (lines) for the decane+water system in the presence of methane (mole fraction of methane in the decane/CH₄-rich phase $x_{\text{CH}_4} \approx 0.2, 0.5$, and 0.8) under geological conditions. The simulated IFT values at different pressures were replotted as a function of temperature and mole fraction of methane x_{CH_4} in Figures S8 and S9, respectively. It is seen that our simulation results are consistent with the theoretical predictions. Note that our results are in qualitative agreement with the only available experimental²⁸ data (solid symbols). The difference may be due to, for example, the force-field model employed in our simulations. As in the case of the decane+water system, the IFT almost linearly increases with pressure and the linear slope of the IFT versus pressure plot increases with temperature for the methane+decane+water system. Also, the linear slope of the IFT versus pressure plot

Figure 3: Interfacial tension as a function of pressure for the CH_4 +decane+water system with (a) $x_{\text{CH}_4} \approx 0.2$, (b) $x_{\text{CH}_4} \approx 0.5$, and (c) $x_{\text{CH}_4} \approx 0.8$. The open symbols represent the results from the MD simulations and the estimates obtained using DGT with the PC-SAFT EoS are shown as lines. The experimental results of Jennings and Newman²⁸ are shown as solid symbols.

Figure 4: Equilibrium distributions of different species in the CH_4 +decane+water system ($x_{\text{CH}_4} \approx 0.8$) at (a) 323 K and 30 MPa, (b) 443 K and 30 MPa, (c) 323 K and 100 MPa, and (d) 443 K and 100 MPa. The black and red colors represent MD simulation and DGT, respectively. The solid, dashed, and dotted lines denote water, decane, and methane, respectively.

decreases with increasing mole fraction of methane x_{CH_4} . For instance, the simulated slope ($T=443$ K) changes from about 0.07 mN/(m MPa) at $x_{\text{CH}_4} \approx 0.2$ to 0.03 mN/(m

MPa) at $x_{\text{CH}_4} \approx 0.8$. It is worth noting that, the IFT shows a nonmonotonic dependence on pressure in the methane+water system and, at low pressures, it decreases with pressure as discussed in previous studies.^{47,69} Also, for a given pressure, the IFT generally decreases almost linearly with increasing temperature and increasing mole fraction of methane x_{CH_4} . It can be seen that, independent of the mole fraction of methane x_{CH_4} , the slope of the IFT versus temperature plot varies from about -0.11 to -0.08 mN/(m K) in the pressure range 30–100 MPa (see Figure S8). The slope of the IFT versus mole fraction of methane x_{CH_4} plot is in the range of about -4 to -1 mN/m (see Figure S9). Note that these results are consistent with the work of Pereira et al.²⁶

It is interesting to explore the atomic density profiles to gain more insights into the bulk and interfacial properties of the methane+decane+water system. For example, Fig. 4 provides the density profiles of methane, decane, and water as predicted by MD and theoretical calculations for the methane+decane+water system ($x_{\text{CH}_4} \approx 0.8$). Also, Figures S10 and S11 provide these profiles at $x_{\text{CH}_4} \approx 0.2$ and $x_{\text{CH}_4} \approx 0.5$, respectively. An overall agreement between the simulation and theoretical results has been obtained. Here the shape of the density profiles of decane and water is, in general, similar to that observed for the decane+water system. An important finding of this study is the enrichment of the interface by decane at high values of x_{CH_4} (see, e.g., Fig. 4). Overall, these effects seem to be more pronounced at low pressures and temperatures. This is consistent with the fact that, CH_4 and decane are immiscible at low pressures and temperatures.⁴⁹ The water-water and decane-decane interactions are stronger compared to water-decane interaction and this may result in the negative surface excess of decane at low values of x_{CH_4} (see above). The stronger interaction of a water molecule with a decane molecule than with a CH_4 molecule (simulated binding energy of decane-water and CH_4 -water are about -0.74 and -0.24 kcal/mol, respectively) may favor the enrichment of decane at the interface at high values of x_{CH_4} . Such enrichment is important with regards to the IFT (see, e.g., eq. (9)) and is also believed to influence the diffusion profile and the mass transfer across

interfaces.^{27,38,39,68} Notably, the density profiles display a systematic adsorption of methane in the interface. We see that this local enrichment of methane at the interface increases with increasing pressure and decreasing temperature. It is worth noting that, the local enrichment of methane shows a nonmonotonic dependence on pressure in the methane+water system as discussed in previous studies.^{47,69} Our results also show that the enrichment of the interface by methane generally increases with increasing mole fraction of methane x_{CH_4} . Furthermore, Figures S12, S13, and S14 show our calculated solubilities of CH_4 in the water-rich phase, decane in the water-rich phase, and water in the decane/ CH_4 -rich phase, respectively, under the studied conditions. Our results show that these solubilities are affected by pressure, temperature, and mole fraction of methane x_{CH_4} . For example, the solubility of methane increases with pressure, whereas that of decane and water shows an opposite trend. The solubilities of the different species generally increase with temperature. The solubility behavior of decane is consistent with the fact that the density of water-rich phase increases with increasing pressure and decreasing temperature. In general, the solubility of methane increases with increasing mole fraction of methane x_{CH_4} , whereas that of decane and water shows an opposite trend.

It is also interesting to explore the surface excess in order to quantify, for example, the local enrichment of methane at the interface. Figures S15 and S16 provide the surface excess of methane and decane, respectively, as calculated from simulations (symbols) and from theoretical modeling (solid lines) for the methane+decane+water system under the studied conditions. We see that our simulation results are qualitatively consistent with the theoretical calculations. In general, we observe a positive surface excess for methane. Our results show that the surface excess of methane increases with increasing pressure and decreasing temperature. Also the surface excess of methane generally increases with increasing mole fraction of methane x_{CH_4} . In general, we observe a negative surface excess for decane, similar to case of the decane+water system. The dependence of this surface excess of decane on pressure and temperature is also, in general, similar to the decane+water system. As expected, the surface

excess of decane generally decreases with increasing mole fraction of methane x_{CH_4} . However, we find a positive surface excess for decane at high values of x_{CH_4} . These effects seem to be more pronounced at low pressures and temperatures. Also, methane seems to show negative values of surface excess, for example, in this region. As mentioned above, the stronger interaction of a water molecule with a decane molecule than with a CH_4 molecule may favor the enrichment (depletion) of decane (methane) at the interface. Note that the simultaneous enrichment of the interface with CO_2 and CH_4 has been observed.^{47,48,69} However, the relatively high density of decane may not allow the simultaneous enrichment of the interface with decane and CH_4 (entropic factor). Furthermore, the surface excess of methane shows a nonmonotonic dependence on pressure and shows negative values at high pressures in the CH_4 +water system.^{47,48,69} As demonstrated above, the IFT generally increases with pressure for the CH_4 +decane+water system under the studied conditions (see Fig. 3). This may suggest that the behavior of the IFT is dominated by the negative surface excess of decane (see eq. (9)).

4.3 Decane+water system in the presence of CO_2

Fig. 5 shows the IFTs as obtained from the MD calculations (open symbols) and the corresponding theoretical results (lines) for the decane+water system in the presence of carbon dioxide (mole fraction of carbon dioxide in the decane/ CO_2 -rich phase $x_{\text{CO}_2} \approx 0.2, 0.5$, and 0.8) at reservoir conditions. The simulated IFT values at different pressures were replotted as a function of temperature and mole fraction of carbon dioxide x_{CO_2} in Figures S17 and S18, respectively. It is seen that our simulation results are consistent with the theoretical predictions. Note that our results are in good qualitative agreement with the available experimental²⁷ data (solid symbols). The overall absolute average deviation, for instance, between the experimental and theoretical IFT data was less than about 10%. As in the case of the decane+water system, the IFT almost linearly increases with pressure at low values of x_{CO_2} , and the linear slope of the IFT versus pressure plot increases with temperature for the CO_2 +decane+water

Figure 5: Interfacial tension as a function of pressure for the CO₂+decane+water system with (a) $x_{\text{CO}_2} \approx 0.2$, (b) $x_{\text{CO}_2} \approx 0.5$, and (c) $x_{\text{CO}_2} \approx 0.8$. The open symbols represent the results from the MD simulations and the estimates obtained using DGT with the PC-SAFT EoS are shown as lines. The experimental results of Georgiadis et al.²⁷ are shown as solid symbols.

Figure 6: Equilibrium distributions of different species in the CO₂+decane+water system ($x_{\text{CO}_2} \approx 0.8$) at (a) 323 K and 30 MPa, (b) 443 K and 30 MPa, (c) 323 K and 100 MPa, and (d) 443 K and 100 MPa. The black and red colors represent MD simulation and DGT, respectively. The solid, dashed, and dotted lines denote water, decane, and carbon dioxide, respectively.

system. Also, the linear slope of the IFT versus pressure plot decreases with increasing mole fraction of carbon dioxide x_{CO_2} . For instance, the simulated slope ($T=443$

K) changes from about 0.07 mN/(m MPa) at $x_{\text{CO}_2} \approx 0.2$ to 0.04 mN/(m MPa) at $x_{\text{CO}_2} \approx 0.5$. The IFT is almost independent of pressure for the CO_2 +decane+water system at high values of x_{CO_2} . It is interesting to note that the IFT shows a non-monotonic dependence on pressure in the CO_2 +water system and, at low pressures, it decreases with pressure as discussed in previous studies.^{47,53,54} Also, for a given pressure, the IFT decreases almost linearly with increasing temperature and increasing mole fraction of carbon dioxide x_{CO_2} . It can be seen that, independent of the mole fraction of CO_2 , the slope of the IFT versus temperature plot varies from about -0.09 to -0.07 mN/(m K) in the pressure range 30–100 MPa (see Figure S17). The slope of the IFT versus CO_2 mole fraction plot is in the range of about -20 to -15 mN/m (see Figure S18).

It is important to consider the atomic density profiles to gain more insights into the bulk and interfacial properties of the CO_2 +decane+water system. For example, Fig. 6 provides the density profiles of carbon dioxide, decane, and water as predicted by MD and theoretical calculations for the CO_2 +decane+water system ($x_{\text{CO}_2} \approx 0.8$). Also, Figures S19 and S20 provide these profiles at $x_{\text{CO}_2} \approx 0.2$ and $x_{\text{CO}_2} \approx 0.5$, respectively. An overall agreement between the simulation and theoretical results has been obtained. Here the shape of the density profiles of decane and water is, in general, similar to that observed for the decane+water system. In contrast to the behavior of the CH_4 +decane+water system, no decane enrichment at the interface is obtained in the CO_2 +decane+water system under the studied conditions, probably due to the stronger interaction of a water molecule with a CO_2 molecule than with a decane molecule (simulated binding energy of the CO_2 -water dimer is about -2.29 kcal/mol). Notably, the density profiles display a systematic adsorption of carbon dioxide in the interface. We see that this local enrichment of carbon dioxide at the interface increases with increasing pressure and decreasing temperature. It is worth noting that, the local enrichment of CO_2 shows a nonmonotonic dependence on pressure in the carbon dioxide+water system as discussed in previous studies.^{47,53,54} Our results also show that the enrichment of the interface by CO_2 generally increases with increasing mole fraction

of carbon dioxide x_{CO_2} . Furthermore, Figures S21, S22, and S23 show our calculated solubilities of CO_2 in the water-rich phase, decane in the water-rich phase, and water in the decane/ CO_2 -rich phase, respectively, under the studied conditions. Our results show that these solubilities are affected by pressure, temperature, and mole fraction of carbon dioxide x_{CO_2} . Overall, the solubility behavior in the CO_2 +decane+water system is similar to that observed for the CH_4 +decane+water system. As an exception, decane solubility increases with pressure (see, e.g., Figure S22). We found that, at a fixed temperature and pressure, the density of the water-rich phase decreases as the values of x_{CO_2} /solubility of CO_2 in the water-rich phase increases (see, e.g., Figure S21). Therefore, at high values of x_{CO_2} , an increase in pressure may favor the solvation of decane in water outweighing any unfavorable entropic cost. Also, we find that the solubility of water increases with increasing mole fraction of carbon dioxide x_{CO_2} at all pressures due to the relatively strong CO_2 -water interactions.^{38–40}

It is also important to consider the surface excess in order to quantify, for example, the local enrichment of carbon dioxide at the interface. Figures S24 and S25 provide the surface excess of carbon dioxide and decane, respectively, as calculated from simulations (symbols) and from theoretical modeling (solid lines) for the CO_2 +decane+water system under the studied conditions. We see that our simulation results are qualitatively consistent with the theoretical calculations. Here we observe a negative surface excess for decane, similar to case of the decane+water system. The dependence of this surface excess of decane on pressure and temperature is also similar, in general, to the decane+water system. As expected, the surface excess of decane generally decreases with increasing mole fraction of carbon dioxide x_{CO_2} . However, an opposite trend is observed at high values of x_{CO_2} . Overall, these effects seem to be more pronounced at low pressures and high temperatures. This is consistent with the fact that, CO_2 and decane are immiscible at low pressures and high temperatures.⁴⁹ We also observe a positive surface excess for carbon dioxide. Our results show that the surface excess of CO_2 increases with increasing pressure and decreasing temperature. In general, the surface excess of CO_2 increases with increasing mole fraction of carbon dioxide x_{CO_2} .

Figure 7: Interfacial tension as a function of pressure for the $\text{CH}_4 + \text{CO}_2 + \text{decane} + \text{water}$ system at (a) 323 K with $x_{\text{CH}_4} + x_{\text{CO}_2} \approx 0.5$, (b) 443 K with $x_{\text{CH}_4} + x_{\text{CO}_2} \approx 0.5$, (c) 323 K with $x_{\text{CH}_4} + x_{\text{CO}_2} \approx 0.8$, and (d) 443 K with $x_{\text{CH}_4} + x_{\text{CO}_2} \approx 0.8$. The symbols represent the results from the MD simulations and the estimates obtained using DGT with the PC-SAFT EoS are shown as lines.

As in the $\text{CH}_4 + \text{decane} + \text{water}$ case, the IFT generally increases with pressure for the $\text{CO}_2 + \text{decane} + \text{water}$ system under the studied conditions (see Fig. 5). This result may indicate that the behavior of the IFT is dominated by the negative surface excess of decane (see eq. (9)).

4.4 Decane+water system in the presence of CH_4 and CO_2

Fig. 7 provides the IFTs as obtained from the MD calculations (symbols) and the corresponding theoretical results (lines) for the decane+water system in the presence

Figure 8: Equilibrium distributions of different species in the $\text{CH}_4 + \text{CO}_2 + \text{decane} + \text{water}$ system ($x_{\text{CH}_4} = x_{\text{CO}_2} \approx 0.25$) at (a) 323 K and 30 MPa, (b) 443 K and 30 MPa, (c) 323 K and 100 MPa, and (d) 443 K and 100 MPa. The black and red colors represent MD simulation and DGT, respectively. The solid, dashed, dotted, and dot-dashed lines denote water, decane, methane, and carbon dioxide, respectively.

of methane and carbon dioxide ($x_{\text{CH}_4} + x_{\text{CO}_2} \approx 0.5$ and 0.8) under geological conditions. The simulated IFT values at different pressures were replotted as a function of the mole

fraction of carbon dioxide x_{CO_2} in Figure S26. It is seen that our simulation results are consistent with the theoretical predictions. Among all studied systems, the maximum difference between the simulated IFT values and the theoretical ones is found in the case of the water+decane system in the presence of CO_2 ($x_{\text{CO}_2} = 0.8$) and at the lowest temperature (see, e.g., Fig. 5). For this case, the simulated values are higher by a factor of about 1.2 than the theoretical ones at all pressures. An important finding is that the presence of CO_2 decreases the IFT of the CH_4 +decane+water system. As in the binary and ternary cases discussed above, the IFT almost linearly increases with pressure for the CH_4 + CO_2 +decane+water system at low values of $x_{\text{CH}_4} + x_{\text{CO}_2}$. The IFT is almost independent of pressure for the CH_4 + CO_2 +decane+water system at high values of $x_{\text{CH}_4} + x_{\text{CO}_2}$. It is worth noting that, at low pressures, the IFT decreases with pressure in the CH_4 + CO_2 +water system as discussed in our previous study.⁴⁷ Also, the IFT decreases almost linearly with increasing mole fraction of carbon dioxide x_{CO_2} . For instance, the simulated slope is in the range of about -18 to -8 mN/m (see Figure S26).

Fig. 8 provides the density profiles of methane, carbon dioxide, decane, and water as predicted by MD and theoretical calculations for the CH_4 + CO_2 +decane+water system ($x_{\text{CH}_4} = x_{\text{CO}_2} \approx 0.25$). Also, Figures S27-S31 show these profiles at different mixture compositions. An overall agreement between the simulation and theoretical results has been obtained. Here the shape of the density profiles of the different species is similar to that observed for the CH_4 +decane+water and CO_2 +decane+water systems. As in the case of the ternary systems, we could observe the local enrichment of the interface by methane, carbon dioxide, and decane. Note that the enrichment of the interface by decane is observed only at high values of x_{CH_4} . The results show the preferential dissolution in the water-rich phase and enrichment at the interface for CO_2 in the CH_4 + CO_2 +decane+water system. This indicates the preferential interaction of water with CO_2 relative to methane and decane. Similar local accumulation of methane and carbon dioxide at the interface was also observed in the CH_4 + CO_2 +water system as discussed in our previous study.⁴⁷ Furthermore, Figures S32, S33, S34, and S35

show our calculated solubilities of CH₄ in the water-rich phase, CO₂ in the water-rich phase, decane in the water-rich phase, and water in the decane/CH₄/CO₂-rich phase, respectively, under the studied conditions. The overall dependence of the solubilities on pressure, temperature, and mole fractions is similar to that observed for the ternary systems. For example, as in the case of the ternary systems, the solubility of CH₄ and CO₂ increases with pressure, whereas the solubility of water shows an opposite trend.

Figures S36, S37, and S38 provide the surface excess of CH₄, CO₂, and decane, respectively, as calculated from simulations (symbols) and from theoretical modeling (solid lines) for the CH₄+CO₂+decane+water system under the studied conditions. We see that our simulation results are qualitatively consistent with the theoretical calculations. The overall dependence of the surface excess on pressure, temperature, and mole fractions is also similar to that observed for the ternary systems. The strong preference of water for CO₂ over CH₄ may result in a relatively higher surface excess for CO₂. Notably, we find a positive surface excess for decane and a negative surface excess for methane at high values of x_{CH_4} . These effects seem to be more pronounced at low pressures and high temperatures. As in the binary and ternary cases, the IFT generally increases with pressure for the CH₄+CO₂+decane+water system under the studied conditions (see Fig. 7). This may suggest that the behavior of the IFT is dominated by the negative surface excess of decane (see eq. (9)). The increasing contributions of the positive surface excesses of methane and/or CO₂ may affect the above behavior at high mole fractions of CH₄/CO₂.

4.5 Alternative theoretical model

We also applied the cubic-plus-association (CPA) EoS to compute the bulk and interfacial properties of our mixtures. The details of the DGT with the bulk phase properties evaluated using the CPA EoS have been reported in our previous study.⁴⁸ Additionally, the parameters to account for the interaction of decane with other species are given in Tables S5-S8. These parameters were obtained from literature⁸³⁻⁸⁵ and in the absence of literature data, they were identified by fitting the experimental data.^{27,60,67}

For example, Figure S39 shows the IFT of the decane+water system obtained using the DGT with the CPA EoS. The overall absolute average deviation between the experimental and theoretical IFT data was less than about 3.7%. Figure S40 shows the calculated solubilities of water and decane at 0.1 MPa. A good quantitative agreement is obtained between the theoretical and experimental data. Furthermore, Figures S41 and S42 show the estimated IFTs of the CH₄+decane+water and CO₂+decane+water systems, respectively. It is seen that our theoretical results are qualitatively consistent with the experimental observations. For instance, for the CO₂+decane+water system, the overall absolute average deviation between the experimental and theoretical IFT data was less than about 12%.

Furthermore, Figure S43 provides the estimated IFTs of the CH₄+CO₂+decane+water system. Figure S44 shows the atomic density profiles for the CH₄+CO₂+decane+water system. Figures S45, S46, S47, and S48 show our calculated solubility data for the CH₄+CO₂+decane+water system. An overall agreement between the simulation and theoretical results has been obtained. Thus, we find that the overall performance of the PC-SAFT EoS and the CPA EoS is similar. Notably, the adsorption peak in the density profile of CO₂ estimated using DGT with the CPA EoS has a slightly asymmetric shape across the interface (see, e.g., Figure S44). Also, the PC-SAFT EoS is relatively more sensitive to the change in the k_{ij} value. For example, a 1% change in the k_{ij} value results in about a 1% difference for the absolute average deviation between the experimental and theoretical (CPA EoS) solubility data of decane (see, e.g., Figure S40). By following the same procedure but using the PC-SAFT EoS, the difference is about 10% .

The bulk and interfacial properties of the studied systems play a key role in the CO₂-EOR projects. For instance, the oil recovery efficiency can be correlated to the IFT using the capillary number.¹⁸ The capillary number increases as IFT decreases and/or viscosity increases. A lower IFT is desirable for the CO₂-EOR techniques which may help to improve oil recovery. Our results show that both methane and CO₂ can lower the IFT between water and decane, and CO₂ has a more significant effect

than methane. This indicates that the advantage of CO₂-EOR may be negatively affected by the presence of impurities such as methane. Note that an important part of the phase diagram of the CO₂+decane+water system is occupied by a region of three phase equilibria.³⁰ As shown by us previously,⁴⁹ at elevated pressures and temperatures, CO₂ and decane become miscible, which may improve the flow properties of the highly viscous oil phase. The molecular simulation method is more time consuming than the DGT method. However, in comparison with DGT, properties such as the atomic radial distribution function, the chain size, and the molecular orientation can be readily calculated from the molecular simulations.^{37,49} These molecular details and the bulk and interfacial properties of the decane+brine system in the presence of gas mixtures will be presented in a future publication. Recently, we studied the bulk and interfacial properties of the CH₄+CO₂+decane system below the minimum miscibility pressure.⁴⁹ Here we extended this study to examine the bulk and interfacial properties of the CH₄+CO₂+decane+water system. This may be important, e.g., for the better understanding of the WAG method used in the CO₂-EOR projects. The phase behavior of the CH₄+CO₂+decane system is significantly affected by the presence of water. For example, the CH₄+CO₂+decane system is completely miscible at rather low pressures of a few hundred bars.⁴⁹ However, we are able to explore the bulk and interfacial properties of the CH₄+CO₂+decane+water system at much higher pressures due to the immiscibility between the water and the CH₄+CO₂+decane phases.

In reality, CO₂ may react with water to produce small amounts of, e.g., carbonic acid. For example, the simulated IFTs of the water/CO₂ system with and without reaction differed by less than about 6% at 333 K.⁸⁶ Such effects may be neglected, since the addition of decane decreases the solubility of CO₂ in water (see, e.g., Fig. S21). The most important finding of this study is that the presence of CO₂ decreases the IFT of the CH₄+decane+water system. This may be explained by the preferential interaction of water with CO₂ relative to CH₄ and decane and, as a consequence, the preferential enrichment at the interface for CO₂ in the CH₄+CO₂+decane+water system. Interestingly by tuning, for example, the mole fraction $x_{\text{CH}_4} + x_{\text{CO}_2}$, we obtained

an enrichment of decane at this interface. Additionally, the simulation studies were complemented by theoretical modeling and reasonable agreement is obtained.

The simulated binding energy of decane-water is about -0.57, -0.67, and -0.74 kcal/mol when k_{ij}^{LJ} is equal to 0.9, 1.0, 1.1, respectively. These values for CO₂-water are about -2.26, -2.27, and -2.29 kcal/mol, respectively. The simulated binding energy of the CO₂-water dimer is consistent with the value of about -2.85 kcal/mol obtained from quantum chemical calculations.⁸⁷ Furthermore, the simulated water-methane binding energy is about -0.24 kcal/mol (about -0.90 kcal/mol from quantum chemical calculations⁸⁸). The difference may be due to the use of nonpolarizable models in our simulations.⁸⁹ We see that the magnitude of binding energy increases with increasing k_{ij}^{LJ} indicating stronger dimer interactions, and that water interacts preferentially with CO₂ than with decane.

Overall, for decane+water, CO₂+water and CH₄+water systems, our results of the IFTs were in good agreement with the experiments (see, e.g., Figs. 2 and S2). But for both CH₄+water and CO₂+water systems the IFTs obtained from theoretical calculations deviate from experiment at low temperatures (the theory overestimates the IFTs of the CO₂+water system also at very high temperatures, however, the maximum temperature studied was 443 K). This is due to the fact that we employed a temperature-independent binary-interaction parameter β_{ij} , for simplicity and as in previous studies^{48,69} (see Tables S4 and S8). The simulated IFTs of the decane+water system in the presence of CH₄ and/or CO₂ are in reasonable agreement with the theoretical estimates except at low temperatures and high-pressures, probably because we used a temperature-independent (and also a pressure-independent) β_{ij} .

In our simulations, the factor contributing to the deficiencies in reproducing solubility may be the use of nonpolarizable models. Xue et al.⁵² improved the accuracy of both IFT and solubility with nonpolarizable models by adjusting the mixing parameters and they found that TIP4P is a useful candidate, though it is not as accurate as TIP4P/2005 in estimating the IFT. Also, the Exp-6 water model with modified cross-interaction parameters provided accurate results for the solubilities in the CO₂+water

system.⁹⁰ However, this model is not accurate for systems with added salt.⁹¹ The simulated IFTs for the CH₄+CO₂+water system obtained using the flexible F3C water model are in poor agreement with experiment.⁴⁷ Furthermore, polarizable models provided accurate results for the solubilities in the CO₂+water and alkane+water systems.⁸⁹ We hope to explore the effects of, e.g., polarizable models on the interfacial properties of the decane+water+CH₄/CO₂ system in a future study.

As shown in Figure S5, our results are in good agreement with the experimental bulk densities. Also, the bulk solubilities of decane in the water-rich phase and water in the decane-rich phase are rather small (see, e.g., Figure S6). Therefore, their contribution away from the interface (see, e.g., Figure S4) to the integral in eq. (10) (surface excess) is relatively negligible. For the decane+water system, the simulated surface excess is in reasonable agreement with the theoretical calculations, except at low temperatures (see Figure S7). This can be explained by noting that, in contrast to the theoretical prediction, oscillations are present near the interface for the simulated density profile of decane at low temperatures (see, e.g., Figure S4), which may be due to the finite size of the simulated system.^{81,82} As with the IFTs, the simulated surface excesses of the decane+water system in the presence of CH₄ and/or CO₂ are in reasonable agreement with the theoretical estimates except at low temperatures and high pressures, probably due to the use of a temperature-independent (and also a pressure-independent) β_{ij} and/or finite size of the simulated system.

5 Conclusions

MD simulations were carried out to study the two-phase behavior of the n-decane+water system in the presence of CH₄, CO₂, and their mixture over broad ranges of temperature (323-443 K) and pressure (up to about 100 MPa). The simulation studies are complemented by theoretical modeling using the PC-SAFT EoS and density gradient theory. Our simulation and theoretical results for the IFT of the CH₄+decane+water and CO₂+decane+water systems are qualitatively consistent with the available exper-

imental^{27,28} data. We find that the presence of CH₄ and CO₂ decreases the IFT of the decane+water system. The IFT increases with increasing pressure and decreasing temperature for the decane+water system. Generally, similar results are obtained in the presence of CH₄ and CO₂. The key finding from this work is that the presence of CO₂ decreases the IFT of the CH₄+decane+water system.

We have compared the atomic density profiles obtained using molecular simulations and DGT, in all studied systems. An overall agreement between the simulation and theoretical results has been obtained. The local enrichment of CH₄ and CO₂ at the interface is usually observed in these systems. Another interesting finding is the preferential dissolution in the water-rich phase and accumulation at the interface for CO₂ in the CH₄+CO₂+decane+water system. This suggests an enhanced interaction between water and CO₂ compared to the interactions between water and CH₄/decane. Interestingly, an enrichment of decane at the interface is observed at high mole fractions of CH₄ in the CH₄/decane-rich or CH₄/CO₂/decane-rich phase. Consistent with these results, the systems show in general a positive surface excess for CH₄ and CO₂ and a negative surface excess for decane. However, we found a positive surface excess for decane and a negative surface excess for methane at high values of x_{CH_4} . Furthermore, we calculated the solubilities of CH₄, CO₂, and decane in the water-rich phase, and water in the decane/CH₄/CO₂-rich phase. For example, we found that the solubility of CH₄ and CO₂ in the water-rich phase generally increases with increasing pressure and temperature in the studied systems. Finally, we demonstrated that the general performance of the PC-SAFT EoS and the CPA EoS is similar with respect to the evaluation of bulk and interfacial properties of the decane+water system in the presence of CH₄, CO₂, and their mixture.

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Supporting Information

Additional details of simulation analysis and theory are provided in the Supporting Information. Tables S1-S4 and S5-S8 provide parameters for PC-SAFT/DGT and CPA/DGT theories, respectively. Figs. S1-S2 provide parameters for the extended Lorentz-Berthelot combining rule. Figs. S3-S7, S8-S16, S17-S25, S26-S38 provide IFT, solubility, density profiles, and surface excess for decane+water, CH₄+decane+water, CO₂+decane+water, and CH₄+CO₂+decane+water systems, respectively. Figs. S39-S48 provide the same data obtained using CPA/DGT theory.

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Table 1: Number of molecules used in MD simulations.

System	Water no.	Decane no.	CH ₄ no.	CO ₂ no.
Water + Decane	2048	200	-	-
Water + 80% Decane + 20% CH ₄	2048	200	50	-
Water + 50% Decane + 50% CH ₄	2048	200	200	-
Water + 20% Decane + 80% CH ₄	2048	120	480	-
Water + 80% Decane + 20% CO ₂	2048	200	-	50
Water + 50% Decane + 50% CO ₂	2048	200	-	200
Water + 20% Decane + 80% CO ₂	2048	120	-	480
Water + 50% Decane + 10% CH ₄ + 40% CO ₂	2048	200	40	160
Water + 50% Decane + 25% CH ₄ + 25% CO ₂	2048	200	100	100
Water + 50% Decane + 40% CH ₄ + 10% CO ₂	2048	200	160	40
Water + 20% Decane + 16% CH ₄ + 64% CO ₂	2048	125	100	400
Water + 20% Decane + 40% CH ₄ + 40% CO ₂	2048	125	250	250
Water + 20% Decane + 64% CH ₄ + 16% CO ₂	2048	125	400	100

TOC Graphic