Molecular Dynamics Simulation Study of Carbon Dioxide, Methane, and Their Mixture in the Presence of Brine

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Abstract

We perform molecular dynamics simulations to study CO_2 , methane, and their mixture in the presence of brine over a broad range of temperature (311–473 K), pressure (up to about 100 MPa), and NaCl concentration (up to about 14 wt%). The general decrease in the interfacial tension (IFT) values of the CH_4 –brine system with pressure and temperature is similar to that obtained for the corresponding CH_4 –water system. The IFT of methane and brine is a linearly increasing function of salt concentration, and the resulting slopes are dependent on the pressure. A similar behavior as methane is observed for such systems containing CO_2 and CO_2 – CH_4 mixture. The IFT of CO_2 and brine increases linearly with increasing salt content, however, the resulting slopes are independent of pressure. The simulations show that the presence of CO_2 decreases the IFT values of the CH_4 –water and CH_4 –brine systems, while the degree of reduction depends on the amount of CO_2 in each sample which is consistent with experimental evidence. These IFT values show a linear correlation with the amount of CO_2 , and the resulting slopes are dependent on temperature and pressure. Furthermore, our results for the mole fractions of the different species in the CO_2 – CH_4 –water system at 323 K and 9 MPa are in agreement with experiments. The mole fractions of methane and CO_2 in the water-rich phase decrease with increasing salt concentration, while that of H_2O in the methane- or CO_2 -rich phases remains almost unaffected in all studied cases. Our results could be useful because of the importance of carbon dioxide sequestration and shale gas production.

1 Introduction

Geologic storage of carbon dioxide offers a promising means of reducing emissions of anthropogenic CO_2 into the atmosphere.^{1–5} One unique approach to reducing emissions involves utilizing CO_2 for the extraction of oil and gas from shale formations.^{1,4} Typically carbon dioxide has a higher affinity for the shale formations and will therefore displace adsorbed CH_4 . The detailed information of interactions between methane, CO_2 , aqueous brine, and shale formations is required in simulators during natural gas production. For example, relative humidity could affect sorption of methane and carbon dioxide onto both organic and inorganic components of shales.^{1,3,5–7} The extent to which shale formations rich in expandable clays such as the smectite mineral montmorillonite swell is controlled primarily by the H_2O concentrations in the contact fluid. Swelling due to H_2O intercalation processes could lead to permeability changes that directly impact successful storage of CO_2 . Therefore the knowledge of the dissolved H_2O concentrations in contact fluids⁸ can help develop rational injection strategies to maximize geological CO_2 storage and natural gas production. Interfacial tension (IFT) is a property of great significance to CO_2 sequestration, because it controls capillary forces in the cap rock which act to avoid upward migration of the stored fluid.^{9,10} In the CO_2 -enhanced oil recovery processes, information must be obtained on important properties of the participating fluid mixtures.^{11,12} The study of interactions between CO_2 and water is important as a reference point for the understanding of a large variety of interfacial processes, for instance, those including surfactants.^{13,14}

A number of experimental,^{15–19} theoretical,^{19–21} and simulation^{21–23} studies have been carried out to determine the interfacial properties of CH_4 –water and CH_4 –brine systems. In general, the results of these studies showed a reduction of the IFT with increasing pressure. However, at relatively high pressures the IFT values exhibited a moderate increase with increasing pressures.^{16,19,21} The inversion of the IFT dependence with pressure and the observation of an IFT minimum occurred for pressures around the transition point between the positive and negative relative adsorption of

methane molecules with respect to water molecules in the interfacial region.^{19,21} The density gradient theory (DGT) was able to predict the measured increase of the IFT of the methane-water system due to the presence of up to 10 wt% NaCl.¹⁹ Several experimental,^{15,24–33} theoretical,^{28,31,33–37} and simulation^{24,37–44} studies have also been performed to determine the interfacial properties of CO₂–water and CO₂–brine systems. Overall, IFT decreased with both temperature and pressure in the low-pressure range (gaseous CO₂) but was mostly independent of pressure at high pressures (liquid or supercritical CO₂). The results of these studies also indicated that the IFT increases linearly with the molality (or ionic strength) of the salt solution.^{26,30,33,41,43}

Only few experimental,^{18,45} theoretical,³⁷ and simulation³⁷ studies have addressed interfacial properties of CO₂–CH₄–water and CO₂–CH₄–brine systems. Ren et al.¹⁸ reported the IFT of CO₂–CH₄–water system in the temperature range of 298–373 K and pressure range of 1–30 MPa. The axisymmetric drop shape analysis method was employed to measure the IFT between CO₂–CH₄ mixtures and brine over the temperature range from 298 to 398 K and the pressure range from 0.1 to 35 MPa.⁴⁵ These studies showed that the presence of CO₂ decreases the IFT of CH₄–water and CH₄–brine systems, while the degree of reduction depends on the mole fraction of CO₂ (x_{CO_2}) in the methane or CO₂-rich phases. Furthermore, a higher salinity lead to an increase in the IFT of the CO₂–CH₄–brine system. Recently, molecular simulations and density gradient theory have been used to characterize the interfacial region of CO₂–CH₄–water system.³⁷ Their analysis of the molecular density profiles showed that the preferential adsorption of CO₂ over H₂O interface is greater if compared to CH₄. However, a molecular understanding of the interfacial properties of CO₂–CH₄–brine system is lacking. In this situation, we undertake the molecular dynamics (MD) simulation study of CO₂–CH₄ mixtures in the presence of brine. This interest is enhanced by the very limited amount of experimental data⁴⁵ on the interfacial properties of such systems.

Our investigations showed that molecular simulations constitute a powerful tool to generally explore the chemical and surface interactions.^{46–50} In this work, MD simula-

tions are performed to provide molecular-level understanding of the interfacial properties of carbon dioxide, methane, and their mixture in the presence of brine (NaCl) under conditions relevant to CO₂ sequestration. Where possible, we include explicit comparison of our results with the corresponding experimental observations. The outline of the paper is as follows: In section 2, we describe the molecular models and the details of the MD simulations. The simulation results are presented in section 3 and a brief summary as well as our conclusions can be found in section 4.

2 Simulation details

All MD simulations are carried out with the LAMMPS code.⁵¹ The interactions between *i* and *j* molecular sites of different molecules are treated according to a pairwise additive Lennard-Jones (LJ) 12-6 function:⁵²

$$U_{\text{LJ}}(r_{ij}) = 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right], \quad (1)$$

where r_{ij} is the distance between the centers of *i* and *j* sites. The parameter ε_{ij} controls the strength of the short-range interactions, and the LJ diameter σ_{ij} is used to set the length scale. The LJ parameters σ_{ij} and ε_{ij} are deduced from the conventional Lorentz-Berthelot combining rules:

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}, \quad (2)$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}. \quad (3)$$

The charged sites are interacting with each other via the unscreened Coulomb potential

$$U_{\text{Coul}}(r_{ij}) = \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}, \quad (4)$$

where q_i and q_j are the partial charges of the sites *i* and *j*, respectively, and ε_0 is the dielectric permittivity of vacuum. Each water molecule is represented by the rigid TIP4P/2005 model⁵³ and CO₂ is modeled using the flexible force field developed by Cygan et al.⁵⁴ Methane (single-site) is represented by the TraPPE force field.⁵⁵ Na⁺

and Cl^- ions are modeled using the parameters proposed by Smith and Dang.⁵⁶ The LJ parameters and charges used in this study are presented in Table 1.

The simulation was initialized by placing 512 CO_2 /methane molecules and 2048 H_2O molecules in the simulation box. In this study, we adjust the number of ions according to the salt concentration and used up to about 100 Na^+/Cl^- ions. Our simulation cells are $36 \times 36 \text{ \AA}$ in directions parallel to the interface and periodic boundary conditions are employed in all three spatial dimensions. The system size is sufficiently large⁴⁰ to ensure that finite-size effects are negligible in our simulations (Fig. 1). Equilibration runs of 4 ns are performed in the *NPT* ensemble where the volume variations are achieved by changing only the box length in the z -direction L_z (see, e.g., Fig. 2). This is followed by 2 ns production runs in the *NVE* ensemble. Pressure is controlled by a Nosé-Hoover barostat with a relaxation time of 1 ps, and temperature is controlled by a Nosé-Hoover thermostat with a relaxation time of 0.1 ps. The use of the *NVE* ensemble ensures that property, such as IFT, is not biased by the extended system algorithms used to produce a constant-temperature ensemble.⁵² The long-range electrostatic interactions are handled using the particle-particle particle-mesh (PPPM) method with a relative error of 10^{-5} . The bond lengths and the angles of the water molecules are constrained using the SHAKE algorithm. A cutoff radius of $L_{\min}/2$, where $L_{\min}$ is the minimum dimension of the simulation box was applied to the LJ and Coulomb interactions. The equations of motion are integrated using a velocity Verlet algorithm with a time step of 1 fs.

The IFT is calculated from the components of the pressure tensor:⁴⁰

$$\gamma = \frac{1}{2}L_z \left[P_{zz} - \frac{1}{2}(P_{xx} + P_{yy}) \right], \quad (5)$$

where P_{xx} , P_{yy} , and P_{zz} are the three diagonal components of the pressure tensor along the x -, y -, and z -direction, respectively, and the prefactor of $1/2$ accounts for the presence of two interfaces in the simulation box. Six independent trajectories each of length 6 ns per simulation are computed to achieve good statistical averages. The differences of system temperatures from the preset value during *NVE* production runs

were mostly negligible (typically $< 1\%$). The validation of our simulation model is provided in the Supporting Information (see, e.g., Figs. S1-S3).

3 Results and discussion

3.1 CH_4 –brine and CO_2 –brine systems

Fig. 3 provides the IFT of the CH_4 –brine (NaCl) system as computed from the MD simulations (symbols) and the corresponding experimental data (smooth lines). The experimental data are taken from Kashefi et al.¹⁹ Other available experimental data^{15–18} are in agreement with the ones plotted here and not included for clarity. The surface tension of water decreases from about 70 to 38 mN/m⁵⁷ over the temperature range (311–473 K) studied here. We observe good agreement between our simulation results and the experimental data. The temperature and salt dependences of the IFT at about 7, 16, and 25 MPa as obtained from the MD simulations are replotted in Figs. S4 and S5, respectively. The general decrease in the IFT with increasing pressure or temperature in all studied cases is consistent with other studies.^{15–23} Note that the IFT values of the CH_4 –water system displayed a moderate increase with increasing pressure at relatively high pressures.^{16,19,21} The minimum in the IFT was obtained at pressures around the transition point between the positive and negative relative adsorption of methane molecules.^{19,21} The variation of the IFT values of the CH_4 –brine system with pressure and temperature is similar to that observed for the corresponding CH_4 –water system. At a fixed temperature and pressure, our results indicate that the IFT is an increasing function of salt content in all investigated cases. The IFT values exhibit a linear correlation with the temperature and the molality of the salt solution. Notably, the resulting slopes in the former case are dependent on the pressure. For example, independent of salt concentration, the slope for the temperature dependence of IFT changes from about -0.15 to -0.13 mN/(m K) in the pressure range 7–25 MPa (see Fig. S4). We also see that, independent of temperature, the slope for the salt dependence

of IFT is about $2.2 \text{ mN}/(\text{m mol kg}^{-1})$ in the pressure range 7-25 MPa (see Fig. S5).

Molecular simulations can be used to compute density profiles that are not readily accessible to experimental studies. Fig. 4a shows, as an example, the density profiles of different species in the CH_4 –water system at 373 K and 16 MPa. The appearance of a maximum in the density profile of methane (dashed line) near the interface is in agreement with other studies.^{19,21–23} These studies have shown that the local adsorption of methane molecules which is proportional to the area under the methane peak generally decreased with increasing temperature and pressure. Furthermore, the position of the peak in the density profile of methane shifted towards the methane-rich phase with increasing pressure. The density profile of H_2O (oxygen atoms) which is shown as a solid line resembles the tanh function,⁴² and no change was evident in this behavior with increasing temperature and pressure.^{19,21–23} Here the bulk density of water and methane are about 0.96 and 0.1 g/cm^3 , respectively, in good agreement with the corresponding experimental values⁵⁸ (0.97 and 0.09 g/cm^3 , respectively). Our results indicate that the salt ions homogeneously distribute in the water-rich phase and the interfacial region is largely devoid of ions (Fig. 4b). The presence of salt hardly affects the behavior of the density profiles of various species in the CH_4 –water system. Notably, there is a decrease of the methane density in the water-rich phase by the addition of salt, while that of H_2O in the methane-rich phase remains almost unaffected (see insets of Fig. 4). The former behavior is consistent with the decrease of the solubility of methane in the water-rich phase with salinity⁵⁹ at these pressure and temperature conditions.

Fig. 5 shows the IFT of the CO_2 –brine (NaCl) system as evaluated from the MD simulations (symbols) and the corresponding experimental data (smooth lines). The experimental results are obtained from the measurements of Chalbaud et al. and of Pereira et al.^{26,33} Other available experimental results^{15,24,25,27–32} are consistent with the ones plotted here and not included for clarity. The surface tension of water decreases from about 66 to 49 mN/m ⁵⁷ over the temperature range (333-423 K) studied here. The simulation results are in good qualitative agreement with the experimental

data. Simulations of the surface tension of water using the TIP4P/2005 force field perform better than most of the commonly used water models, but typically underestimate the experimental data by up to 7 mN/m (see Fig. S3). In the presence of CO₂, our simulated IFT values show similar deviations from the corresponding experimental data at both low and high pressures, which may be attributed to our chosen force field parameters.^{40–42} The temperature and salt dependences of the IFT at about 7, 16, and 25 MPa as computed from the MD simulations are replotted in Figs. S6 and S7, respectively. The overall decrease in the IFT with increasing pressure or temperature in all investigated cases is consistent with previous reports.^{15,24–31,33–43} The variation of the IFT values of the CO₂–brine system with pressure and temperature is similar to that obtained for the corresponding CO₂–water system. At a fixed temperature and pressure, the IFT increases with increasing salt concentration in all studied cases. Generally, an exponential function is required to describe the pressure dependence on the IFT values.^{40,43} Moreover, these IFT values are a linear function of temperature and molality/ionic strength of the salt solution.^{26,30,33,40,41,43} For example, independent of salt concentration, the slope for the temperature dependence of IFT is about -0.06 mN/(m K) in the pressure range 7–25 MPa (see Fig. S6). We also find that, independent of temperature, the slope for the salt dependence of IFT is about 2 mN/(m mol kg⁻¹) in the pressure range 7–25 MPa (see Fig. S7), which is consistent with previous studies.^{26,42,43}

Fig. 6a depicts the density profiles of various species in the CO₂–water system at 373 K and 16 MPa. The density profile of CO₂ (carbon atoms) which is represented as a dashed line runs through a maximum consistent with previous studies.^{24,33–43} These studies have shown that the local accumulation in CO₂ molecules generally decreased with increasing temperature and pressure, similar to the behavior obtained for the CH₄–water system.^{19,21–23} The position of the maximum in the density profile of CO₂ also moved towards the CO₂-rich phase with increasing pressure. The density profile of H₂O (oxygen atoms) which is plotted as a solid line varies monotonically across the interface. No variation was observed in this behavior with increasing temperature

and pressure.^{24,33–43} Here the bulk density of water and CO₂ are about 0.94 and 0.4 g/cm³, respectively, in good agreement with the corresponding experimental values⁵⁸ (0.97 and 0.4 g/cm³, respectively). The ions distribute uniformly in the water-rich phase but are repelled from the interface (Fig. 6b). Note that the density profiles indicated a positive surface excess of CO₂ and a negative surface excess of ions at the interface.^{40,41} In the CO₂–water system, values of the relative surface excess of CO₂ computed from simulation and those estimated from the experimental fugacity dependence of IFT showed a non-monotonic relationship with pressure.⁴⁰ It is also important to mention that, Ji et al.⁴⁴ obtained strong correlation between IFT and the number density of T- and H-type CO₂-hydrates in the CO₂–water system. The addition of salt hardly affects the behavior of the density profiles of different species in the CO₂–water system. Notably, there is a decrease of the CO₂ density in the water-rich phase by the addition of salt, while that of H₂O in the CO₂-rich phase remains almost unaffected (see insets of Fig. 6). The former behavior is consistent with the decrease of the solubility of CO₂ in the water-rich phase with salinity^{41,42,60} at these pressure and temperature conditions.

3.2 CO₂–CH₄–brine system

Once we have investigated the interfacial behavior of the CH₄–brine and CO₂–brine systems using MD simulations, the next objective is to analyze the interfacial behavior of the CO₂–CH₄–brine system. Fig. 7 shows the IFT of the CO₂–CH₄–brine (NaCl) system as computed from the MD simulations (symbols) and the corresponding experimental data (smooth lines). The experimental results are obtained from Liu et al.⁴⁵ The surface tension of water at the temperatures studied here (348 and 398 K) are about 63 and 54 mN/m,⁵⁷ respectively. We observe good qualitative agreement between our simulation results and the experimental data. The dependence of the IFT on the mole fraction of carbon dioxide x_{CO_2} at about 7, 16, and 25 MPa as obtained from the MD simulations is replotted in Fig. S8. As expected, the IFT values generally decrease with increasing pressure or temperature in all studied cases. The

presence of CO_2 decreases the IFT values of the CH_4 –water and CH_4 –brine systems, while the degree of reduction depends on the amount of CO_2 in each sample. These IFT values display a linear correlation with the mole fraction of carbon dioxide x_{CO_2} , and the resulting slopes are dependent on temperature and pressure. For example, independent of salt concentration, the slope for x_{CO_2} dependence of IFT changes from about -13 to -17 mN/m at 348 K and in the pressure range 7-25 MPa (see Fig. S8). The corresponding change in the slope is from about -9 to -14 mN/m at 398 K. Furthermore, at a fixed temperature and pressure, our results here show that the IFT values increase with increasing salt concentration in all investigated cases.

Fig. 8a displays the density profiles of different species in the CO_2 – CH_4 –water ($x_{\text{CO}_2} \approx 0.6$) system at 348 K and 16 MPa. The density profile of each species presents the same trend as discussed before. Notably, the density profiles of CO_2 (carbon atoms) and CH_4 which are plotted as dashed and dotted lines, respectively, show adsorption peaks located at the interface with relatively high intensity for the former. The density profile of H_2O (oxygen atoms) which is depicted as a solid line changes monotonically across the interface. The preferential adsorption of CO_2 over CH_4 indicates that water molecules are more likely to interact with CO_2 . These results are consistent with previous reports.³⁷ Also, the ions distribute evenly in the water-rich phase, but move away from the interface (Fig. 8b). Our simulation results show that the presence of salt hardly affects the behavior of the density profiles of various species in the CO_2 – CH_4 –water system. We point out that both CO_2 and methane densities in the water-rich phase decrease with increasing salt concentration, while that of H_2O in the methane- or CO_2 -rich phase remains almost uninfluenced (see insets of Fig. 8). Such variations will be further discussed below. Additionally, Figs. S9-S13 consider these simulated density profiles at other conditions. As before, we observe that the local adsorption of CO_2 and methane molecules generally decrease with increasing temperature and pressure in all cases. Furthermore, the position of the peaks in the density profiles of CO_2 and methane shift towards the water-poor region with increasing pressure. The monotonic behavior of the density profile of H_2O is not affected with

increasing temperature and pressure. No NaCl is found in the methane- or CO₂-rich phases in all studied cases.

The knowledge of, e.g., the concentration of H₂O dissolved in CO₂–CH₄ mixture can help develop rational injection strategies to maximize geological CO₂ sequestration and natural gas production.^{1,3,5–7,48–50} Fig. 9 presents the mole fractions of the different species in the CO₂–CH₄–water system at 323 K and 9 MPa, as computed from the MD simulations (symbols) and the corresponding experimental data (smooth lines). The experimental results are obtained from different studies.^{8,61,62} We observe good agreement between our simulation results and the experimental data. The agreement is better for the mole fractions of methane (y_{CH_4}) and CO₂ (y_{CO_2}) in the water-rich phase. The mole fraction of water ($x_{\text{H}_2\text{O}}$) in the methane- or CO₂-rich phase is, however, a factor of up to 2 lower than the corresponding experimental value. The mole fraction of methane in the water-rich phase decreases with increasing x_{CO_2} , while that of CO₂ steeply increases. This steep rise is expected, given that CO₂ interacts more strongly with H₂O than methane. Initially the mole fraction of water $x_{\text{H}_2\text{O}}$ increases almost linearly with x_{CO_2} . However, this increase is steeper at high values of x_{CO_2} , possibly because of the relatively strong quadrupole-dipole interactions between CO₂ and H₂O.

Additionally, Figs. S14-S16 consider our results for these mole fractions at other conditions. Both methane and CO₂ mole fractions in the water-rich phase increase with increasing pressure, while that of water $x_{\text{H}_2\text{O}}$ shows the opposite behavior. All these mole fractions, except for H₂O, show no significant variation with temperature. With all other conditions the same, the mole fraction of water increases with temperature. Notably, the mole fractions of methane and CO₂ in the water-rich phase decrease with increasing salt concentration (salting-out effect), while that of water $x_{\text{H}_2\text{O}}$ remains almost unaffected in all studied cases. Loring et al.⁸ performed in situ high-pressure infrared spectroscopic titrations to quantify the solubility of H₂O in CO₂–CH₄ mixture at reservoir conditions of 323 K and 9 MPa. They employed different thermodynamic models which accurately predicted the amount of dissolved H₂O concentrations at saturation in CO₂–CH₄ mixture. Therefore, these theoretical models employing the

same parameters as for the $\text{CO}_2\text{--CH}_4\text{--water}$ system could be applied to predict the corresponding water solubility in the presence of salt. We also used orientational distribution functions to look into the arrangement of molecules at the interface in the $\text{CO}_2\text{--CH}_4\text{--water}$ and $\text{CO}_2\text{--CH}_4\text{--brine}$ systems (Figs. S17-S22). The orientation angle θ is measured for both the dipole vector and the H-H vector of H_2O , and the head-to-tail vector of CO_2 molecule relative to the axis perpendicular to the interface. The results show that CO_2 molecules tend to arrange in parallel to the interface as in the pure case.³⁹ In the case of water, the orientation of the vectors at the interface is not random when compared to the bulk water phase $((1/2)\sin\theta)$. However, we find no obvious effect of salinity on the orientations of CO_2 or water molecules at the interface.

As an aside, we note that prior simulations have examined region of the phase diagram of such systems at which three phases coexist.³⁷ The temperature and pressure conditions selected for our MD simulations encompass the range of values relevant to geologic carbon sequestration. We expect that these studies could provide more insight into the rational design of practical CO_2 sequestration processes in deep saline aquifers, which involves surface wetting and migration of supercritical CO_2 through the cap rock. A knowledge of the dissolved H_2O concentrations in $\text{CO}_2\text{--CH}_4$ mixtures can be beneficial for the enhanced gas recovery processes in shales. Further improvement of the quality of predictions using molecular simulations may result from including, e.g., other choices of water model. The choice of force field parameters employed here is in a similar spirit to that used in recent simulation studies of interfacial behavior of $\text{CO}_2\text{--CH}_4\text{--water}$ system.³⁷ Fig. S23 shows simulation results obtained by replacing TIP4P/2005 water model with flexible F3C water model^{39,43} for the $\text{CO}_2\text{--CH}_4\text{--brine}$ system, and poor results are obtained. The Exp-6 models for the $\text{CO}_2\text{--water}$ system gave accurate estimate of solubilities for both water- and CO_2 -rich phases with optimized cross interaction parameters.⁶³ However, the Exp-6 water model is inaccurate for the prediction of thermodynamic properties of brine.⁶⁴ Furthermore, using polarizable force fields and accounting explicitly for strong directional interactions between

H₂O and CO₂ molecules, improved predictions are obtained.⁶⁵ In the future, we plan to study the effects of cross interaction parameters, polarizable models etc. on the interfacial properties of CO₂–CH₄–brine system. It is also worthwhile to further study the effect of ion type and chemical reactions such as carbonate formation on the phase behavior of these mixtures.

3.3 Conclusions

In this work, molecular dynamics simulations have been performed to study CO₂, methane, and their mixture in the presence of brine over a broad range of temperature (311-473 K), pressure (up to about 100 MPa), and NaCl concentration (up to about 14wt %). We find that the temperature, pressure, and salt concentration dependence of the interfacial tension predicted by our model is in agreement with experiments in all studied systems. The general decrease in the IFT values of the CH₄–brine system with pressure and temperature is similar to that observed for the corresponding CH₄–water system. The IFT of methane and brine is a linearly increasing function of salt content, and the resulting slopes are dependent on the pressure. We also show that the local adsorption of methane molecules generally decrease with increasing temperature and pressure. The presence of salt hardly affects the behavior of the density profiles of different species in the CH₄–water system.

A similar behavior as methane is obtained for such systems containing CO₂ and CO₂–CH₄ mixture. The IFT of CO₂ and brine increases linearly with increasing salinity, however, the resulting slopes are independent of pressure. The presence of CO₂ decreases the IFT values of the CH₄–water and CH₄–brine systems, while the degree of reduction depends on the amount of CO₂ in each sample. We find that these IFT values show a linear correlation with the mole fraction of carbon dioxide x_{CO_2} , and the resulting slopes are dependent on temperature and pressure. Here, the density profiles of CO₂ and CH₄ show adsorption peaks located at the interface with relatively high intensity for the former. The preferential adsorption of CO₂ over CH₄ indicates that water molecules are more likely to associate with CO₂ by virtue of strong

quadrupole-dipole interactions.

The knowledge of, e.g., the concentration of H_2O dissolved in $\text{CO}_2\text{--CH}_4$ mixture can help develop rational injection strategies to optimize geological CO_2 sequestration and natural gas production. The simulation results for the mole fractions of the various species in the $\text{CO}_2\text{--CH}_4\text{--water}$ system at 323 K and 9 MPa are consistent with experiments. We demonstrate that the mole fractions of methane and CO_2 in the water-rich phase decrease with increasing salt concentration, while that of H_2O in the methane- or CO_2 -rich phases remains almost unaffected in all studied cases. Therefore, theoretical models⁸ employing the same parameters as for the $\text{CO}_2\text{--CH}_4\text{--water}$ system could be used to predict the corresponding water solubility in the presence of salt. We believe that the above mentioned properties will be relevant to geological carbon storage and CO_2 enhanced shale gas production.

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Supporting Information

Additional details of simulation analysis are provided in the Supporting Information.

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Table 1: Charges q and LJ parameters σ and ε of water, methane, CO₂, and ions.

Force or charge site	σ (Å)	ε (kcal/mol)	q (e)
<i>Water</i> (TIP4P/2005 model) ⁵³			
O	3.1589	0.1852	
H			0.5564
M			-1.1128
<i>Methane</i> (TraPPE model) ⁵⁵			
C	3.7300	0.2941	
<i>Carbon dioxide</i> (flexible Cygan model) ⁵⁴			
C	2.8000	0.0559	0.6512
O	3.0280	0.1597	-0.3256
<i>Ions</i> ⁵⁶			
Na	2.3500	0.1300	1.0000
Cl	4.4000	0.1000	-1.0000

Figure 1: Pressure dependence of IFT for the $\text{CO}_2\text{--CH}_4\text{--brine}$ system ($x_{\text{CO}_2} \approx 0.6$, 10 wt% NaCl) at 348 K. Shown are the results obtained from the MD simulations (symbols) and the corresponding experimental data⁴⁵ (solid line). Number of water molecules/number of $\text{CO}_2\text{+CH}_4$ molecules: 4096/1024 (circles), 2048/512 (squares), 1024/256 (diamonds), and 512/128 (triangles).

Figure 2: Equilibrium snapshot of $\text{CO}_2\text{--CH}_4\text{--brine}$ system ($x_{\text{CO}_2} \approx 0.6$, 10 wt% NaCl) at $T = 348$ K and a pressure of 25 MPa.

Figure 3: Pressure dependence of IFT for the CH_4 -water and CH_4 -brine systems, as computed from our MD simulations (open symbols) and the corresponding experimental data¹⁹ (smooth lines): (a) 311, (b) 373, (c) 423, and (d) 473 K. Error bars are smaller than the symbol size. Simulation data of Biscay et al.²² are shown as solid symbols.

Figure 4: Equilibrium distributions of different species in the (a) CH_4 –water and (b) CH_4 –brine (10 wt% NaCl) systems at 373 K and 16 MPa. Solid, dashed, dotted, and dot-dashed lines represent H_2O (oxygen atoms), methane, Na^+ , and Cl^- , respectively.

Figure 5: Pressure dependence of IFT for the CO_2 –water and CO_2 –brine systems, as computed from our MD simulations (open symbols) and the corresponding experimental data^{26,33} (smooth lines): (a) 333, (b) 344, (c) 373, and (d) 423 K. Error bars are smaller than the symbol size. Simulation data of Li et al.⁴¹ are shown as solid symbols.

Figure 6: Equilibrium distributions of different species in the (a) CO_2 –water and (b) CO_2 –brine (10 wt% NaCl) systems at 373 K and 16 MPa. Solid, dashed, dotted, and dot-dashed lines represent H_2O (oxygen atoms), CO_2 (carbon atoms), Na^+ , and Cl^- , respectively.

Figure 7: Pressure dependence of IFT for the CO_2 - CH_4 -water (left panels) system and the CO_2 - CH_4 -brine (right panels) system with 10 wt% NaCl. Shown are the results obtained from the MD simulations (symbols) and the corresponding experimental data⁴⁵ (smooth lines) at 348 (top panels) and 398 K (bottom panels). Error bars are smaller than the symbol size.

Figure 8: Equilibrium distributions of different species in the (a) $\text{CO}_2\text{--CH}_4\text{--water}$ and (b) $\text{CO}_2\text{--CH}_4\text{--brine}$ (10 wt% NaCl) systems at 348 K and 16 MPa. The mole fraction of CO_2 $x_{\text{CO}_2} \approx 0.6$. Thick solid, dashed, dotted, dot-dashed, and thin solid lines represent H_2O (oxygen atoms), CO_2 (carbon atoms), methane, Na^+ , and Cl^- , respectively.

Figure 9: The mole fractions of the different species in the CO₂–CH₄–water system as a function of the mole fraction of CO₂ in the methane or CO₂-rich phase at 323 K and 9 MPa. Shown are the results obtained from the MD simulations (symbols) and the corresponding experimental data^{8,61,62} (smooth lines). The simulation uncertainties are comparable with the symbol size.

TOC Graphic