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J. Phys. Chem. B, **Just Accepted Manuscript** • DOI: 10.1021/acs.jpcb.8b12033 • Publication Date (Web): 07 Mar 2019

Downloaded from <http://pubs.acs.org> on March 14, 2019

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Dioxide-Methane-Brine System

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January 30, 2019

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Abstract

Molecular dynamics simulations and theoretical analysis were carried out to study the bulk and interfacial properties of carbon dioxide–methane–water and carbon dioxide–methane–brine systems under geological conditions. The density gradient theory with the bulk phase properties estimated using the cubic-plus-association (CPA) equation of state (EoS) can well describe the increase in the interfacial tension (IFT) of the CO₂–water system in the presence of methane. The theoretical estimates of species mole fractions in the carbon dioxide–methane–water system are in good quantitative agreement with the experimental results. Furthermore, simulations of carbon dioxide–methane–brine system show that the IFT of the CaCl₂ case is generally higher than that of the NaCl case. This is probably due to the stronger hydration of Ca²⁺ ions and their stronger repulsion from the interface as compared to Na⁺. While the overall shape of the ionic profiles is not much affected by the ion type, the water profiles show a local enrichment at the interface in the system with CaCl₂. In contrast to the case of NaCl, the slopes of the plots of IFT vs CaCl₂ concentration are dependent on temperature. Species mole fractions in the carbon dioxide–methane–brine system predicted by combining the CPA EoS with the Debye-Hückel electrostatic term are in good agreement with simulation results.

1 Introduction

To reduce atmospheric emissions of CO_2 , its storage in deep saline aquifers and depleted oil and gas reservoirs is considered an effective strategy.¹⁻⁷ Recently, large capacity estimates for sequestration of CO_2 in shale gas reservoirs have been reported. For example, the Marcellus shale could store up to about 18 gigatonnes of CO_2 by 2030.⁸ Therefore, the study of the interaction between CO_2 and the fluids and minerals present in subsurface formations is fundamental to the understanding of geological sequestration of CO_2 . The estimates of species mole fractions⁹⁻¹³ of the participating fluid mixtures may be essential to improve injection approaches during carbon dioxide storage and gas production. The interfacial tension (IFT) can influence the CO_2 storage in reservoirs by controlling the potential leakage of CO_2 through the caprocks.^{14,15}

In recent years there has been considerable interest in the study of properties of methane-brine^{9,16-18} and carbon dioxide-brine systems.^{10,17-29} These studies showed a linear dependence of IFT on the salt concentration under geological conditions. In general, for both of these systems, the slopes of the plots of IFT vs NaCl concentration were independent of pressure and temperature. Interestingly, this slope is higher for the CaCl_2 case compared to the NaCl case. These studies also showed that the solubilities of methane and carbon dioxide in salt solutions decrease with increasing ionic strength. In addition, experimental studies have addressed the bulk and interfacial properties of $\text{H}_2\text{O} + \text{CH}_4 + \text{CO}_2$ ternary system.^{11-13,18,30} Míguez et al.³¹ studied the interfacial properties of this ternary mixture using computer simulations and density gradient theory (DGT). It was found that the preferential adsorption of carbon dioxide over water interface is greater if compared to methane. However, the study of the carbon dioxide–methane–brine system has been rare.^{17,18}

Recently, we studied CO_2 , CH_4 , and their mixture in NaCl brine under geological conditions using molecular dynamics (MD) simulations.¹⁷ These simulations showed that the presence of methane increases the IFT values of the CO_2 –water and CO_2 –brine systems. This increase depends on the amount of methane which is

in agreement with experimental results.¹⁸ We also found that the mole fractions of methane (y_{CH_4}) and carbon dioxide (y_{CO_2}) in the H_2O -rich phase decrease with increasing NaCl concentration. However, the mole fraction of water ($x_{\text{H}_2\text{O}}$) in the CH_4 - or CO_2 -rich phases was almost independent of the NaCl concentration. To further understand the effect of ion type, in this paper we present MD simulation results for CO_2 , CH_4 , and their mixture in the presence of CaCl_2 (aq). Calcium chloride was chosen for this study because it is also a major component of natural brines.³² Given the general lack of experimental data for this system, theoretical modeling is used to complement the simulation results.

2 Molecular dynamics simulation

The LAMMPS code³³ was utilized to carry out MD simulations. The simulation model and method employed here are the same as in our previous study.¹⁷ Additionally, Ca^{2+} ion was modeled using the parameters from Koneshan et al.³⁴ (Lennard-Jones length $\sigma = 2.87 \text{ \AA}$ and Lennard-Jones energy $\varepsilon = 0.1 \text{ kcal/mol}$).

The interfacial tension was estimated as³⁵

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

where L_z is the simulation box length in the direction normal to the interface (z). P_{xx} , P_{yy} , and P_{zz} are the 3 diagonal components of the pressure tensor. Since our simulation box contains two interfaces, a multiplication factor of 1/2 is needed in the above equation. Our simulation cells are $36 \times 36 \text{ \AA}$ in the directions parallel to the interface. The simulation box length L_z is at least about $100 \text{ \AA}$, which is sufficiently large to ensure that the bulk phase properties are observed in both fluid phases and that the IFT is independent of the system size.^{17,35}

In our simulations, the TIP4P/2005 water model is preferred over the simple point charge (SPC) water model because the former model has been shown to provide a relatively better estimate of water surface tension.^{17,36} Note also that by replacing

the TIP4P/2005 water model with the flexible F3C water model,²⁸ poor results were obtained for the simulated IFT of the carbon dioxide-methane-water system.¹⁷

3 Theoretical details

3.1 Bulk properties

The cubic-plus-association (CPA)^{37,38} equation of state (EoS) with Soave-Redlich-Kwong cubic term and the van der Waals one-fluid mixing rules is applied to compute bulk properties such as solubility. The association term in CPA EoS takes into account the specific site-site interaction between molecules. Water was modeled with the 4C association scheme.³⁹ In addition, carbon dioxide is assumed to be able to cross-associate with water (solvation).⁴⁰ The values of the CPA parameters from the literature³⁹⁻⁴² are listed in Tables S1 and S2.

The presence of salt in the system was modeled by adding an electrostatic term^{43,44} to the fugacity coefficient term of nonelectrolyte components:

$$\ln \phi_i = \ln \phi_i^{EoS} + \ln \gamma_i^{EL}, \quad (2)$$

where ϕ_i^{EoS} is the fugacity coefficient of component i evaluated by the CPA EoS and γ_i^{EL} is the Debye-Hückel activity coefficient. The electrostatic term is given as

$$\ln \gamma_i^{EL} = \frac{2Ah_{is}M_m}{B^3}f(BI^{1/2}), \quad (3)$$

where the parameters A and B, and the function f is obtained from Aasberg-Petersen et al.⁴³ Each interaction coefficient between the salt and the nonelectrolyte component h_{is} taken from the literature^{16,25,44} is listed in Table S3. In addition, the interaction coefficient between methane and CaCl₂ has been optimized by using experimental data of methane solubility.⁹

3.2 Density gradient theory

The Helmholtz free energy functional of the system with a planar interface of area a is given by^{45,46}

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

where f_0 is the Helmholtz free energy density of the homogeneous fluid at local composition $n(z)$. F also contains a corrective term which is function of the local density gradients (dn_i/dz is the density gradient of component i). The cross influence parameter⁴⁷⁻⁴⁹

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

where β_{ij} is the binary interaction coefficient and c_{ii} is the influence parameter of component i . The values of pure component influence parameters from the literature are listed in Table S4.

After minimization of the Helmholtz free energy, the equilibrium density profiles across the interface satisfy the following Euler-Lagrange equations:

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

where $\mu_i^0 \equiv (\frac{\partial f_0}{\partial n_i})_{T,V,n_j}$, μ_i is the chemical potential of component i and N_c is the number of components. The above set of equations are reduced to a finite domain by applying 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} are the densities of the coexisting bulk phases and l is the thickness of the interface. The bulk properties were evaluated using the CPA EoS as mentioned above. The thickness l is initially assumed to be 5 Å and then gradually increased until the convergence is reached for the IFT value.^{45,46} A linear density profile was used as an initial guess. The non-linear equations were discretized by a finite difference method

and solved by Newton-Raphson iteration. 500 equidistant grid points were used. Once the density profiles are known, the interfacial tension can be determined as

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

4 Results and discussion

4.1 Carbon dioxide–methane–water system

Before presenting the results of the CaCl_2 case, we discuss the recent progress in the experimental and simulation studies of the carbon dioxide–methane–water system under geological conditions. In addition, theoretical modeling is used to attain a better understanding of the behavior of this system. Fig. 1 displays the IFT of the carbon dioxide–methane–water system obtained using the density gradient theory (smooth lines) at 348 K. Also shown in Fig. 1 are the experimental¹⁸ (closed symbols) and the MD simulation¹⁷ (open symbols) results. Our theory is in good agreement with both experiment and simulation results. For example, the absolute average deviation between experimental and calculated IFT values is about 6%. This shows that the DGT approach with the bulk phase properties estimated using the CPA EoS can well describe, for example, the general decrease in the interfacial tension with increasing pressure, and the increase in the IFT of the CO_2 –water system in the presence of methane. The values of the adjustable binary interaction coefficient β_{ij} used for the theoretical calculations are given in Table 1. Note that to maintain the stability of the interface, the values of β_{ij} are typically in the range between 0 and 1.^{47–49}

The atomic density profiles can be readily obtained from both molecular simulations and theory. For example, Fig. 2 shows the density profiles of methane, CO_2 , and water in the carbon dioxide–methane–water system at 16 MPa and 348 K. The results are given for mole fraction of CO_2 in the carbon dioxide- or methane-rich phases, $x_{\text{CO}_2} \approx 0.6$. We see that the theoretical predictions of density profiles closely follows the results obtained from the molecular simulations. Our DGT approach can well describe

the familiar tanh shape of the water density profiles and the preferential adsorption of carbon dioxide over methane at the interface. The preferential adsorption of carbon dioxide over methane reflects the higher affinity of water for carbon dioxide. Similar behavior was also observed by Míguez et al.³¹

The estimates of species mole fractions in the carbon dioxide–methane–water system may be essential to improve injection approaches during geological carbon dioxide storage and gas production.^{2,4,6,11–13} Fig. 3 shows bulk mole fractions in the carbon dioxide–methane–water system at 9 MPa and 323 K, as calculated using the CPA EoS (smooth lines). Also shown in Fig. 3 are the experimental^{11–13} (closed symbols) and the MD simulation¹⁷ (open symbols) results. We see that our theoretical calculations are in good quantitative agreement with the experimental results. Also, EoS models such as the mixed-solvent electrolyte, STOMP-COMP, and the statistical associating fluid theory for variable range Mie potentials (SAFT γ –Mie) accurately predict water solubilities in the carbon dioxide–methane–water system.¹¹ Of these models, improvement could be afforded to the SAFT γ –Mie model in fluids with greater methane content. Note that the simulated¹⁷ and experimental mole fractions of water differ by a factor of up to 2. The simulation results may be improved by use of, e.g., polarizable models.⁵⁰

4.2 Carbon dioxide–methane–brine system

First we will discuss cases of $x_{\text{CO}_2} = 0$ (methane–brine system) and $x_{\text{CO}_2} = 1$ (carbon dioxide–brine system). The IFT values of the methane–brine (CaCl_2) system as obtained from the MD simulations are shown in Fig. 4. These IFT values at selected pressures are replotted as functions of temperature and salt concentration (molality) in Figs. S1 and S2, respectively. Here the changes in the IFT are similar to those obtained for the corresponding methane–NaCl brine system.¹⁷ Notably, the slope of IFT vs salt concentration decreases with increasing temperature from about 3.0 to 1.5 mN/(m mol kg^{−1}), almost independent of pressure (see Fig. S2). For system with NaCl, a slope of about 2.2 mN/(m mol kg^{−1}) was reported¹⁷ at these conditions. The

higher slope of the system with CaCl_2 may be due to the stronger hydration of Ca^{2+} ions and their stronger repulsion from the interface as compared to Na^+ (see below).

Density profiles may provide further insight into the understanding of the behavior of the IFT. For example, Fig. 5 displays the density profiles in the methane–brine ($1.8 \text{ mol kg}^{-1} \text{ CaCl}_2$) system estimated from molecular simulations at 16 MPa and 373 K. Overall, the density distributions are similar to those obtained previously.¹⁷ We obtained the familiar tanh shape of the water density profiles in both cases with and without NaCl .¹⁷ However, our simulations show a local enrichment of water in the system with CaCl_2 . Similar behavior of water is reported for KCl -water system by Peng and Firouzi⁵¹ This may be explained by the higher ionic strength enhanced desorption of ions in the interfacial region. Also, we see the local enrichment of methane at the interface. The methane density in the H_2O -rich phase decreases with salt concentration consistent with experiments.⁹ Notably, this density is relatively low for system with CaCl_2 . For example, densities of methane in salt-free,¹⁷ NaCl ,¹⁷ and CaCl_2 (see inset of Fig. 5) systems are about 1.3 , 0.8 , and $0.6 \times 10^{-3} \text{ g/cm}^3$, respectively.

The IFT values of the carbon dioxide–brine (CaCl_2) system as obtained from simulations (open symbols) are shown in Fig. 6. The experimental results (solid symbols) by Aggelopoulos et al.²¹ are also shown in Fig. 6. Similar experimental results were also obtained by other researchers.²³ We find a good qualitative agreement between simulation results and experimental data. These IFT values at selected pressures are replotted as functions of temperature and salt concentration in Figs. S3 and S4, respectively. Here the changes in the IFT are similar to those obtained for the corresponding carbon dioxide– NaCl brine system.¹⁷ It is interesting to note that the nonmonotonic behavior of the IFT with temperature is more pronounced for the case of CaCl_2 system (see, e.g., Fig. S3). Also, the slope of IFT vs salt concentration decreases with increasing temperature from about 2.5 to $2.0 \text{ mN}/(\text{mol kg}^{-1})$, almost independent of pressure (see Fig. S4). For system with NaCl , a slope of about $2.0 \text{ mN}/(\text{mol kg}^{-1})$ was reported¹⁷ at these conditions. The higher slope of the system with CaCl_2 has also been reported in previous simulation studies.²⁸

Fig. 7 displays the density profiles in the carbon dioxide–brine ($1.8 \text{ mol kg}^{-1} \text{ CaCl}_2$) system estimated from molecular simulations at 16 MPa and 373 K. Overall, the density distributions of water and ions are similar to those mentioned above. We also find the local enrichment of carbon dioxide at the interface, as observed previously.¹⁷ The carbon dioxide density in the H_2O -rich phase decreases with salt concentration consistent with experiments.¹⁰ Notably, this density is relatively low for system with CaCl_2 . For example, densities of carbon dioxide in salt-free,¹⁷ NaCl ,¹⁷ and CaCl_2 (see inset of Fig. 7) systems are about 3.5 , 1.8 , and $1.3 \times 10^{-2} \text{ g/cm}^3$, respectively.

Fig. 8 displays the IFT of the carbon dioxide–methane–brine ($1.8 \text{ mol kg}^{-1} \text{ CaCl}_2$) system as obtained from MD studies at 348 and 398 K. These IFT values at selected pressures are replotted as a function of x_{CO_2} in Fig. S5. We find a general decrease in the IFT with increasing temperature or increasing pressure in all investigated cases as expected. We also find that the slopes of IFT vs x_{CO_2} plots are almost independent of the salt molality or ion type. As with the previous cases¹⁷ and depending on the pressure, slopes of IFT vs x_{CO_2} plots change from about -12 to -19 mN/m at 348 K and -9 to -16 mN/m at 398 K (see Fig. S5). Here, system with CaCl_2 generally shows higher IFT than the corresponding NaCl system,¹⁷ as in the methane–brine and carbon dioxide–brine cases.

Fig. 9 displays the density profiles in the carbon dioxide–methane–brine ($1.8 \text{ mol kg}^{-1} \text{ CaCl}_2$) system estimated from molecular simulations at 16 MPa and 348 K. The results are given for $x_{\text{CO}_2} \approx 0.6$. Also, Figs. S6-S10 show these density profiles at other conditions. The density profiles are similar as in the methane–brine and carbon dioxide–brine systems mentioned above. As in our previous studies,¹⁷ density profiles show a preferential adsorption of carbon dioxide over methane. We also see that the local accumulation of water at the interface decreases with increasing temperature. This may be due to the fact that ion hydration increases as the temperature decreases,⁵² resulting in stronger repulsion of ions from the interface. This may be also the reason that, the slopes of the plots of IFT vs CaCl_2 concentration are dependent on temperature.

The simulation results of IFT may also be interpreted by means of the surface excess.³⁵ The IFT and surface excess can be related using the Gibbs adsorption equation:

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

where μ_i is the chemical potential of component i . This equation, for example, indicates that increasing the chemical potential of a component with a positive surface excess would reduce the IFT. The following expression was employed for the calculation of surface excess of each component i with respect to water:⁵³

$$\Gamma_{i,H_2O} = -\alpha_i \int_{-\infty}^{+\infty} \Delta C(z) dz, \quad (10)$$

with

$$\Delta C(z) = \frac{n_{H_2O}(z) - n_{H_2O}^{II}}{\alpha_{H_2O}} - \frac{n_i(z) - n_i^{II}}{\alpha_i}, \quad (11)$$

where

$$\alpha_i = \frac{n_i^{II} - n_i^I}{n_i^{II} - n_i^I + n_{H_2O}^{II} - n_{H_2O}^I}, \quad (12)$$

and

$$\alpha_{H_2O} = \frac{n_{H_2O}^{II} - n_{H_2O}^I}{n_i^{II} - n_i^I + n_{H_2O}^{II} - n_{H_2O}^I}. \quad (13)$$

Here, I denotes the methane or carbon dioxide-rich phase, and II the water-rich phase. The surface excesses of methane and carbon dioxide show a non-monotonic relationship with pressure (see Figs. S11-S12). The higher surface excess of gas in the low pressure range indicates a steeper decline of the IFT. There is a moderate increase in the IFT at relatively high pressures and the minimum in the IFT may be at the transition point between the positive and negative relative adsorption of gas molecules.^{16,48} We see that this transition point shifts toward higher pressures in the presence of salt. Our results also indicate a negative surface excess for the ions which can explain the increase in the IFT with increasing chemical potential of ions.

Fig. 10 displays species mole fractions in the carbon dioxide–methane–brine (1.8 mol kg⁻¹ CaCl₂) system at 348 K from both simulations (symbols) and theory (lines).

Also, Fig. S13 shows these mole fractions at 398 K. We see that our simulations are in good qualitative agreement with the theoretical results. We checked that the solubility data for the brine systems with $x_{\text{CO}_2} = 0$ and $x_{\text{CO}_2} = 1$ predicted by theory are in very good agreement with the experimental results^{9,10}(not shown). This shows that the CPA EoS along with the electrostatic term from the Debye-Hückel activity model can well describe the effect of salt on solubilities. A better agreement is obtained for y_{CH_4} and y_{CO_2} . Note that the simulated and calculated mole fractions of water differ by a factor of up to 2. As in the carbon dioxide–methane–water case mentioned above, this difference may be due to the force field model used in the simulations. In the future, we plan to study the effects of, e.g., cross-interaction parameters and polarizable models⁵⁰ on the interfacial properties of carbon dioxide-methane-brine system. It is important to note that equations of state rooted in statistical mechanics such as the SAFT also provides accurate predictions for methane⁵⁴ and CO₂ solubilities in brines.^{54–56}

4.3 Conclusions

In this study, we investigated carbon dioxide–methane–water and carbon dioxide–methane–brine systems under geological conditions by using molecular dynamics simulations and theoretical analysis. The density gradient theory has been combined with the CPA EoS to model the interfacial properties of the carbon dioxide–methane–water system. The IFT values for the carbon dioxide–methane–water system estimated by the DGT method using a binary interaction coefficient (Table 1) are in good agreement with experimental data. Notably the local accumulations of methane and carbon dioxide at the interface, and the preferential adsorption of carbon dioxide over methane predicted by the DGT method are consistent with simulation results. Importantly, the solubility data for the carbon dioxide–methane–water system calculated using the CPA EoS are in very good agreement with experimental results.

Simulations of carbon dioxide–methane–brine system indicate that for a given salt concentration the IFT of the NaCl case¹⁷ is typically lower than that of the CaCl₂ case. This may be explained by the higher ionic strength enhanced desorption of ions in the

interfacial region. No change in the shape of the simulated ionic profiles is observed with valency. However, we found evidence for water enrichment (Fig. 9) at the interface in the case with CaCl_2 . The solubility data for the carbon dioxide–methane–brine system calculated using the CPA EoS along with the modified Debye-Hückel electrostatic term which takes into account the effect of salt are consistent with simulations. The treatment of salt effects within the DGT framework is challenging that, for example, the initial model²⁵ is not able to predict the local enrichment of water. Further studies are needed to understand the properties of mixed and other brine systems in the presence of carbon dioxide and methane.

Acknowledgments

The research reported in this publication is partly based upon work supported by the King Abdullah University of Science and Technology (KAUST) Office of Sponsored Research (OSR) under Award No. 2993. Y. Y. and A. K. N. N. gratefully acknowledge computational facilities provided at KAUST.

Supporting Information

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

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Table 1: DGT binary interaction coefficient (β_{ij}) for pairs among CH₄, CO₂, and H₂O.

Pair	β_{ij}
CH ₄ -H ₂ O ^a	0.39
CO ₂ -H ₂ O ^b	0.27
CH ₄ -CO ₂	0.04

^aKashefi et al.¹⁶ ^bPereira et al.²⁵

Figure 1: Interfacial tension as a function of pressure for the carbon dioxide–methane–water system at 348 K. The lines represent the DGT results. Also shown are the experimental¹⁸ (solid symbols) and the MD simulation¹⁷ (open symbols) results.

Figure 2: Atomic density profiles for the carbon dioxide–methane–water system ($x_{\text{CO}_2} \approx 0.6$) at 16 MPa and 348 K. The blue color represents the DGT results. Also shown are the MD simulation¹⁷ (black) results. The solid, dashed, and dotted lines denote water, carbon dioxide, and methane, respectively. The inset shows the same set of data in linear-log scale.

Figure 3: Species mole fractions in the carbon dioxide–methane–water system at 9 MPa and 323 K. The lines represent the DGT results. Also shown are the experimental^{11–13} (solid symbols) and the MD simulation¹⁷ (open symbols) results.

Figure 4: Simulated interfacial tension as a function of pressure for the methane–brine (CaCl₂) system with salt concentrations of (a) 0.9 mol kg⁻¹ and (b) 1.8 mol kg⁻¹. Error bars are smaller than the symbols.

Figure 5: Atomic density profiles for the methane–brine (1.8 mol kg⁻¹ CaCl₂) system at 16 MPa and 373 K. The MD simulation results are shown as solid, dashed, dotted, and dot-dashed lines for water, methane, Ca²⁺, and Cl⁻, respectively.

Figure 6: Interfacial tension as a function of pressure for the carbon dioxide–brine (CaCl₂) system with salt concentrations of (a) 0.9 mol kg⁻¹, (b) 1.8 mol kg⁻¹, and (c) 2.7 mol kg⁻¹. The MD simulation results are shown as open symbols. Error bars are smaller than the symbols. Also shown are the experimental data of Aggelopoulos et al.²¹ as solid symbols.

Figure 7: Atomic density profiles for the carbon dioxide–brine (1.8 mol kg⁻¹ CaCl₂) system at 16 MPa and 373 K. The MD simulation results are shown as solid, dashed, dotted, and dot-dashed lines for water, carbon dioxide, Ca²⁺, and Cl⁻, respectively.

Figure 8: Simulated interfacial tension for the carbon dioxide–methane–brine (1.8 mol kg⁻¹ CaCl₂) system. Error bars are smaller than the symbols.

Figure 9: Atomic density profiles for the carbon dioxide–methane–brine ($1.8 \text{ mol kg}^{-1} \text{ CaCl}_2$) system at 16 MPa and 348 K. The results are given for $x_{\text{CO}_2} \approx 0.6$. The MD simulation results are shown as thick solid, dashed, dotted, dot-dashed, and thin solid lines for water, carbon dioxide, methane, Ca^{2+} , and Cl^- , respectively.

Figure 10: Mole fractions of (a) methane, (b) carbon dioxide, and (c) water in the carbon dioxide–methane–brine ($1.8 \text{ mol kg}^{-1} \text{ CaCl}_2$) system at 348 K. The symbols represent results from the MD simulations, and the estimates obtained by combining the CPA EoS with the modified Debye–Hückel electrostatic term are shown as lines.

TOC Graphic

Effect of Ion Valency on the Properties of Carbon Dioxide-Methane-Brine System

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KEYWORDS. Carbon dioxide-methane-brine system, interfacial tension, molecular dynamics simulations, density gradient theory.