Wettability of Supercritical CO₂–Brine–Mineral: The Effects of Ion Type and Salinity

Cong Chen,^{*,†} Zhuang Chai,[‡] Weijun Shen,[‡] Weizhong Li,[†] and Yongchen Song[†]

[†]Key Laboratory of Ocean Energy Utilization and Energy Conservation of Ministry of Education, Dalian University of Technology, Dalian 116024, P. R. China

[‡]Key Laboratory for Mechanics in Fluid Solid Coupling Systems, Institute of Mechanics, Chinese Academy of Sciences, Beijing 100190, P. R. China

Supporting Information

ABSTRACT: Deep saline aquifers are considered as perfect storage sites to sequester CO₂. Interfacial tensions (IFTs) and contact angles (CAs) are key parameters in the heat and mass transfer processes for CO₂/brine/mineral systems in porous media. In the present study, a molecular dynamics simulation method was used to investigate the effects of brine salinity and ion type on wettability of CO₂/brine/mineral systems at 20 MPa and 318.15 K. Four common brines were selected as NaCl, KCl, CaCl₂, and MgCl₂. Interfacial tensions, water contact angles, and hydrogen bond structure and dynamics have been analyzed. The effects of brine salinity and ion type on water contact angles were found to be very complicated. For MgCl₂ and NaCl solutions, the contact angle increases with salinity. For CaCl₂ and KCl solutions, contact angle first increases and then remains constant with salinity. The product of IFT(CO₂–brine) and the cosine of CA was found to be constant for all brine solutions studied. In the context of large uncertainty of experimentally measured contact angles, this finding is very useful to predict contact angles using interfacial tension data. Due to the fact that IFT(CO₂–brine) × cos(CA) is usually related with capillary pressure and residual trapping capacity, this finding is also very helpful to predict these parameters at different brine conditions. More work is required to study the effects of pressure, temperature, and solid surface structure on this relationship.

1. INTRODUCTION

CO₂ capture and storage (CCS) is a potential technique to significantly reduce CO₂ emissions to the atmosphere from industrial processes. Geological sequestration is a CCS technique, and possible storage locations include oil or gas reservoirs, coal seams and deep saline aquifers. Deep saline aquifers are regarded as the most promising option for long-term safe sequestration of CO₂.¹

There are various knowledge gaps related to aquifer storage of CO₂ which need addressing before widespread commercial implementation. Heat and mass transfer during movement of injected CO₂ through permeable pore networks determines CO₂ distribution and stability within reservoirs; these are related to CO₂ sequestration safety and efficiency. Under reservoir conditions, the heat and mass transfer process is controlled by interfacial tension (IFT) and wettability of CO₂–reservoir brine–mineral systems.² Wettability is usually evaluated by contact angles (CAs). The contact angle can be related to interfacial tension through the equation

$$\gamma_{\text{brine-mineral}} + \cos(\theta_{\text{water}})\gamma_{\text{brine-CO}_2} = \gamma_{\text{CO}_2\text{-mineral}} \quad (1)$$

or

$$\gamma_{\text{CO}_2\text{-mineral}} + \cos(\theta_{\text{CO}_2})\gamma_{\text{brine-CO}_2} = \gamma_{\text{brine-mineral}} \quad (2)$$

where $\gamma_{\text{brine-CO}_2}$, $\gamma_{\text{brine-mineral}}$, and $\gamma_{\text{CO}_2\text{-mineral}}$ are respectively, interfacial tension between brine and CO₂, interfacial tension between brine and mineral, and interfacial tension between CO₂ and mineral. θ_{water} and θ_{CO_2} are contact angles for brine droplets and CO₂ bubbles as shown in Figure 1. Equations 1

and 2 are identical as $\theta_{\text{water}} + \theta_{\text{CO}_2} = \pi$, and contact angle is usually defined based on the water (brine) droplet using eq 1.

Only one of the interfacial tensions can be measured directly from experiments, namely IFT between CO₂ and brine. It has been recognized that the presence of salts can significantly increase the interfacial tension between brine and CO₂.^{3–10} The increment caused by salinity is a function of pressure and temperature,^{3,7} and it has been shown to linearly increase with salinity in experiments^{7–9} and molecular dynamics simulations.¹¹ The slope of the linear relationship between IFT and salinity was found to change with the valence of cations.⁶ At an identical salinity, the IFT increment for CaCl₂ brine was found to be at least twice that for NaCl brine. Further studies showed that IFT increments were additive when brine was composed of various salts.⁷

Wettability of CO₂/water/mineral systems has been extensively studied.^{12,13} The effects of pressure, temperature, and mineral surface compositions have been investigated and discussed.^{14–16} In this study, we focus on the effect of brine salinity and ion type on wettability. Most research on wettability of CO₂/brine/mineral systems was based on NaCl brine, and CA was found to increase as NaCl concentration increases.^{17–20} Although NaCl is dominant under real storage conditions, the brine of reservoirs is a mixture of different salts containing Na⁺, K⁺, Ca²⁺, Mg²⁺, etc. Water contact angles for CaCl₂ brine were found to be larger than that of pure

Received: March 23, 2017

Revised: June 13, 2017

Published: June 19, 2017

Figure 1. Chart of the relationship between contact angle and interfacial tension for a brine droplet (left) and CO₂ bubble (right).

Figure 2. Sample simulation box constructed for interfacial tension prediction. Water molecules, ions, and CO₂ molecules are drawn in lines, VDW, and CPK formats, respectively. A brine box is sandwiched by two CO₂ boxes to construct two CO₂–brine interfaces.

Figure 3. Simulation boxes constructed for contact angle predictions. The structure of the silica plate is shown in an enlarged picture. A unit cell of alpha-cristobalite was used to create the silica plate on the [202] plane with an area density of SiOH groups of 4.7/nm².

water.^{12,21,22} Compared with NaCl, at same brine salinity, CA for CaCl₂ was predicted to be larger on quartz surfaces.^{12,22} At 10 MPa and 318 K, for NaCl aqueous solutions, water contact angle increased from 21° to 25° when salinity increased from 0 to 3 M. For CaCl₂ aqueous solutions, water contact angle increased 6° within the same salinity range.¹² However, an investigation regarding water salinity effect on coal wettability found that CaCl₂ increased the contact angle values compared to pure water, but its effect was slightly lower than that for NaCl.²¹ When brine salinity equals 20 g/L, water contact angles on coal were 85° and 81° for NaCl and CaCl₂ brine, respectively, at ambient pressure, and as pressure increases, the effect of cation type became negligible.²¹ The possible reason for this disagreement may be that the solid surface used in these studies was different. The trend of contact angle changing with salinity was shown to be different for NaCl and CaCl₂.¹² The effects of Mg²⁺ on CA was found to be stronger than that of Ca²⁺ and Na⁺.²² As far as we know, the effect of K⁺ on CA for CO₂/water/mineral systems has not been investigated.

Compared with interfacial tensions, the effects of brine on wettability are not well-understood. Under real sequestration conditions, reservoir brine is a mixture of different salts, so the effect of each salt must be fully understood to better predict the wetting behavior of the salts mixture. Although the concentrations of other salts may be lower compared with NaCl at normal conditions, the increase of salt concentrations occurs during the migration process (such as salt precipitation).²³ There are large uncertainties for experimental contact angles of CO₂/brine/mineral systems, and several possible factors causing the uncertainty have been proposed: surface contamination has been regarded as one of the main factors.^{24,25} One of the advantages of molecular dynamics (MD) simulation is to avoid any possible contamination which may be difficult to control in experiments. MD simulation has been proven to be a good tool to predict contact angles.^{16,26} In the present study, MD simulations have been performed to predict brine contact angles with different ion types and salinities. To better understand the mechanism by which ions affect contact angles, interfacial tensions between CO₂ and

brine as well as hydrogen bonds between water and surface silanol groups have also been investigated. The hydrogen bond's characteristics were used to evaluate the water–solid interaction.¹⁶

2. METHODS

2.1. Simulation Boxes. Based on compositions of reservoir brines, four common cations Na^+ , K^+ , Ca^{2+} , and Mg^{2+} and one anion Cl^- were selected to construct brine solutions with different salinities. Three concentrations for monovalent ions were chosen namely 1, 3, and 6 M. The concentrations for divalent ions were 0.33, 1, and 2 M relative to the same ionic strength with monovalent ions. Silica is selected as a model mineral due to its abundance in nature.

Interfacial Tension. A water box and a CO_2 box were cut from equilibrated boxes obtained in former simulations. The dimensions in y and z directions were kept the same for water and CO_2 boxes. Different number of ions were added into the water box at random positions to construct brine solutions with different salinities. Then the CO_2 box was replicated to sandwich the water box in the x direction. One sample simulation box constructed for interfacial tension prediction is illustrated in Figure 2. The simulation boxes constructed using this method have two CO_2 –brine interfaces and have been applied by several other authors.^{11,27}

Contact Angle. Two CO_2 boxes, one silica plate, and a half-cylindrical water droplet were constructed. At first, the silica plate was sandwiched by the two CO_2 boxes. Then, the water droplet was placed on the top surface of the silica plate. The CO_2 molecules with same coordinates as the water molecules were removed. By using this method, two three-phase contact lines were formed to eliminate the line tension caused by spherical drop method.²⁸ A simulation box for contact angle prediction is illustrated in Figure 3.

2.2. Force Fields. A force field is extremely important in molecular dynamics simulations as it determines the accuracy of interaction energies. The potential energies of CO_2 molecules were calculated by a fully flexible force field²⁹ which was modified based on a semiflexible EPM2 model.³⁰ Potential energies of water, silica, and ions were calculated using a flexible force field which has been optimized for interfacial properties.³¹ The interaction parameters between unlike atoms were calculated using the Lorentz–Berthelot combining rules. These force fields have been successfully applied to predict contact angles of CO_2 /water/silica systems.¹⁴ These force fields were further validated by comparing predicted and experimentally measured water/brine– CO_2 interfacial tensions (section 3.1).

2.3. Molecular Dynamics Simulation. A free parallel molecular dynamics simulation package NAMD was used to perform all simulations.³² In three dimensions, periodic boundary conditions were applied. For nonbonded Lennard-Jones (LJ) interaction energy calculation, the neighborhood method was used to search atom pairs and the truncation technique was applied to reduce computation complexity. A cutoff of 13.5 Å was selected. To calculate Coulombic interaction energy, the same cutoff value was used to split into long-range and short-range Coulombic interactions. A particle mesh Ewald (PME) method³³ using a cubic PME interpolation order with a direct sum tolerance of 10^{-6} was applied to calculate long-range Coulombic interaction. The PME grid spacing was set to 1.0 Å. Nonbonded LJ interaction and short-range Coulombic interaction energies were calculated at each time step. The long-range Coulombic interaction energy was computed every two time steps. The difference of computation frequency was processed by a multiple time steps integration technique r-RESPA.³⁴ Atoms in minerals except those in hydroxyl groups were fixed during simulations using the SHAKE algorithm.³⁵ NPT ensembles were applied, and the temperature was held at 318.15 K by a Langevin dynamics method with a damping coefficient of 5/ps. The pressure was fixed at 20 MPa using the Langevin piston Nose–Hoover method which is a combination of the Nose–Hoover constant pressure method³⁶ with piston fluctuation control implemented using Langevin dynamics.³⁷ A time step of 1 fs was used and all molecular dynamics simulations were performed 15

ns where the first 12 ns was run to equilibrate and the last 3 ns was for data analysis.

2.4. Hydrogen Bonds. For silica–brine interaction, hydrogen bonds can only be formed between water molecule and hydroxyl group. An illustration of a hydrogen bond configuration is shown in Figure 4. By forming a hydrogen bond, the H atom, donor atom, and

Figure 4. Hydrogen bond formed between one water molecule and one hydroxyl group on silica surface. O_d and O_a are donor and acceptor atoms, respectively.

acceptor atom construct a triangle. Lengths $\text{H}\cdots\text{O}_a$ and $\text{O}_a\cdots\text{O}_d$ as well as angles HO_dO_a and O_dHO_a are usually selected to define a hydrogen bond by geometrical criteria.³⁸ In this study, length $\text{H}\cdots\text{O}_a$ and angle HO_dO_a were chosen. A hydrogen bond was recognized when length $\text{H}\cdots\text{O}_a$ and angle HO_dO_a were smaller than their thresholds. The threshold of length $\text{H}\cdots\text{O}_a$ was determined from the radial distribution functions for O–H atom pairs. The cutoff of angle HO_dO_a was selected to 30° as used in other studies.³⁹

The silica–brine interaction was evaluated by the mean number of hydrogen bonds per squared nanometer on the silica surface and hydrogen bond lifetimes. The mean number of hydrogen bonds per squared nanometer is calculated by

$$n_{\text{HB}} = \frac{1}{N} \sum_{i=1}^{i=N} (N_{\text{donor}}^i + N_{\text{acceptor}}^i) \times 4.7 \quad (3)$$

where N is the number of hydroxyl groups, N_{donor}^i and N_{acceptor}^i are numbers of hydrogen bonds for the i th hydroxyl group as donor and acceptor, respectively.

The hydrogen bond lifetime τ_{HB} is computed by the continuous autocorrelation function $S_{\text{HB}}(t)$:⁴⁰

$$\tau_{\text{HB}} = \int_0^\infty S_{\text{HB}}(t) dt \quad (4)$$

$$S_{\text{HB}}(t) = \frac{\langle n_{ij}(t) \cdot n_{ij}(0) \rangle}{\langle n_{ij}(0)^2 \rangle} \quad (5)$$

where $n_{ij}(0)$ equals 1 when atoms i and j are hydrogen bonded at time 0; otherwise, $n_{ij}(0) = 0$. $n_{ij}(t) = 1$ when atoms i and j are hydrogen bonded at time 0 and the hydrogen bond holds until time t without breaking; otherwise, $n_{ij}(t) = 0$.

2.5. Interfacial Tension and Contact Angle Measurement. Interfacial tensions can be predicted using the three principal components of the stress tensor:^{11,27,41}

$$\gamma = \frac{1}{2} [p_{xx} - 0.5(p_{yy} + p_{zz})] L_x \quad (6)$$

where p_{xx} is pressure in the direction normal to the CO_2 –brine interface, p_{yy} and p_{zz} are pressures in directions parallel to the interface and L_x is the simulation box length in the direction normal to the interface. A total of 1000 trajectory files were generated and interfacial tensions obtained were split into 10 blocks to predict average and standard deviations.

As half cylindrical water droplets were used, due to symmetry, the final shapes of water droplets can be determined in the xz plane. A total of 3000 trajectory files were generated, and six blocks were used. For each block, water density profiles were calculated from the trajectory and the triple phase contact point, water– CO_2 contact line (WCCL), silica–water contact line (SWCL), and silica– CO_2 contact

line (SCCL) were then determined from the density profile. Contact angles were obtained by directly measuring the angle formed between WCCL and SWCL.

3. RESULTS AND DISCUSSION

3.1. Validation of Force Fields. Water–CO₂ interfacial tensions at 323 K were predicted as a function of pressure, and the results are summarized in Figure 5 for comparison with

Figure 5. Comparison of water–CO₂ interfacial tensions predicted by molecular dynamics simulation with experimental measurements (Exp1⁴³ and Exp2⁴²) at 323 K.

experimental data. The experimental CO₂–water interfacial tensions selected have been identified as high quality based on three criteria: temperature near the CO₂–water interface, density difference between CO₂ and water, and equilibration time.²⁷ The two experimental data sets selected are both obtained using a pendant drop method.^{42,43} The predicted interfacial tensions agree well with experimental results; this proves that the force fields of water and CO₂ molecules selected are good to predict interfacial properties.

To validate the force field of ions, three additional simulations were performed. The CO₂–MgCl₂ interfacial tension at 20 MPa and 343.15 K with a salinity of 5 M was

predicted to be 38.5 ± 3.7 mN/m agreeing well with the experimental value of 39.3 mN/m.⁴⁴ The tension of the CO₂–5 M CaCl₂ interface at 20 MPa and 343.15 K was calculated to be 41.9 ± 3.5 mN/m, and the experimental result is 47.2 mN/m.⁴⁴ A 4.95 M brine solution containing NaCl and KCl (mole ratio: 0.864/0.136) at 20 MPa and 323.15 K was also predicted. The molecular dynamics simulation result is 39.4 ± 3.3 mN/m and agrees excellently with the experimental result (38 mN/m⁸).

3.2. Hydrogen Bonding Analysis. Radial Distribution Functions. Radial distribution functions for atom pairs related with hydrogen bonds between silica and water were calculated. Two types of hydrogen bonds can be formed between the hydroxyl group and water molecules: O_s–H_w and H_s–O_w, where O_s and O_w are O atoms in hydroxyl group and water; H_s and H_w are H atoms in hydroxyl and water. Radial distribution functions for atom pairs O_s–H_w and H_s–O_w are illustrated in Figure 6. The results are similar for different brine solutions and only results of CaCl₂ solutions are shown. Well hydration structure can be found for both atom pairs similar to other studies related with hydroxyl group–water interaction.^{45,46} Salinity affects the peak values slightly, however, the peak positions do not change with salinity. The peak positions of first minima are around 0.24 nm, and it was selected as the cutoff of length H_s–O_a for potential hydrogen bonds.

Hydrogen Bond Structure and Dynamics. The hydrogen bond structure has been analyzed. The mean numbers of hydrogen bonds per squared nanometer were calculated, and the results are summarized in Table 1. The continuous autocorrelation functions were calculated using eq 5, and the effect of ion type is rather small. So, only the results for MgCl₂ solutions are shown in Figure 7. Autocorrelation functions decay quickly with time and reach about 0 after 4 ps. By integrating the autocorrelation functions, hydrogen bond lifetimes were calculated using eq 4 and summarized in Table 1. It can be seen that the hydrogen bond lifetimes vary slightly with ion type and salinity; however, considering the standard errors, the effect is negligible. The mean numbers of hydrogen bonds for CaCl₂, NaCl, and MgCl₂ brines do not change with salinity and vary between 7.33 and 7.71/nm². For KCl, the situation is a little different. As KCl molality increases from 1 to 3 M, the mean number of hydrogen bonds per squared

Figure 6. Radial distribution functions $g(r)$ as a function of distance r for atom pairs O_s–H_w (left) and H_s–O_w (right) with different CaCl₂ molalities.

Table 1. Mean Numbers of Hydrogen Bonds per Squared Nanometer (n_{HB}) and Lifetimes for Hydrogen Bonds between Silica and Water in Different Solutions (τ_{HB} , ps)^a

	n_{HB}	τ_{HB}		n_{HB}	τ_{HB}
0 M	7.57(0.09)	0.46(0.06)			
	CO ₂ –CaCl ₂			CO ₂ –MgCl ₂	
0.33 M	7.61(0.14)	0.48(0.07)	0.33 M	7.71(0.14)	0.51(0.05)
1 M	7.47(0.24)	0.49(0.09)	1 M	7.52(0.19)	0.53(0.10)
2 M	7.47(0.24)	0.49(0.08)	2 M	7.47(0.05)	0.52(0.06)
	CO ₂ –NaCl			CO ₂ –KCl	
1 M	7.52(0.14)	0.46(0.04)	1 M	7.52(0.14)	0.50(0.06)
3 M	7.38(0.19)	0.50(0.03)	3 M	7.10(0.19)	0.46(0.03)
6 M	7.33(0.14)	0.44(0.05)	6 M	6.11(0.09)	0.45(0.09)

^aThe standard deviations are shown in parentheses.

Figure 7. Continuous autocorrelation functions for hydrogen bonds between silica–MgCl₂ solutions.

nanometer decreases about 0.42. Further increase of salinity to 6 M leads to a 1.0 reduction.

3.3. Interfacial Tensions and Contact Angles. The equilibration of CO₂ and brine is important for interfacial tension prediction. Density profiles for water and CO₂ were calculated and are illustrated in Figure 8 as well as a snapshot of equilibrated simulation box. Snapshot and density profiles show good equilibration of simulation boxes. Pressure tensor was calculated and used to predict IFT following eq 6. IFT data is summarized in Table 2. Density profiles for water droplet were calculated to predict contact angles. Snapshots of equilibrated simulation boxes for KCl brine are shown in Figure 9. All CA data are shown in Table 2.

3.4. Discussion. Trends of Water Contact Angles. A clear increase of interfacial tensions has been found when salt is added into water which agrees well with results in literature.^{3–10} For all systems studied, contact angles of brine solutions are larger than the value of pure water as expected.^{12,17–22} Compared with NaCl, at same brine salinity, contact angles for CaCl₂ are larger as predicted by other researchers.^{12,22}

Figure 8. Density profiles along direction normal to CO₂–brine interfaces for simulation box with a salinity of 0.33 M MgCl₂. The final configuration of the simulation box is also shown.

Table 2. Interfacial Tension (IFT, mN/m) and Contact Angle (CA, deg) Values for Different Simulation Boxes^a

	IFT	CA		IFT	CA
0 M	30.9(3.1)	22.4(5.4)			
	CO ₂ –CaCl ₂			CO ₂ –MgCl ₂	
0.33 M	33.4(2.6)	31.0(1.9)	0.33 M	33.2(3.5)	24.4(3.5)
1 M	33.5(3.4)	41.1(5.5)	1 M	31.2(3.7)	35.1(2.8)
2 M	42.3(4.7)	39.3(4.9)	2 M	40.8(5.5)	43.7(5.9)
	CO ₂ –NaCl			CO ₂ –KCl	
1 M	32.6(2.2)	30.8(5.4)	1 M	34.9(3.1)	27.6(3.1)
3 M	36.4(3.9)	42.4(4.3)	3 M	35.2(2.9)	36.1(2.9)
6 M	40.4(5.4)	47.5(3.9)	6 M	38.0(5.7)	35.7(5.9)

^aThe standard deviations are shown in parentheses. **Figure 9.** Snapshots of equilibrated simulation boxes for KCl brine.

It seems that contact angles in brine solutions depend on not only valence but also ion type. For MgCl₂ and NaCl solutions, CA increases with salinity. However, for CaCl₂ and KCl solutions, CA first increases and then keeps constant with salinity. The trends of contact angle varying with salinity for NaCl and CaCl₂ solutions have also been found in our former experimental study of static contact angles on quartz surface.¹² At the same brine salinity (1 M), the order of effect on water contact angle is Ca²⁺ > Mg²⁺ > Na⁺ > K⁺, showing that divalent ions have a strong effect on water contact angles than monovalent ions which agrees well with published data.^{12,22} Water contact angle increases about 10.3° for 1 M CaCl₂ solution relative to 1 M NaCl solution. For 1 M MgCl₂ solution, CA only increases 4.3°. However, the effect of ion type on water contact angle varies with brine salinity. For divalent ions, at smaller salinities (0.33 and 1 M), CAs of CaCl₂ solutions are larger than the value of MgCl₂ solutions. However, at larger salinity (2 M), the water contact angle of MgCl₂ solution becomes larger than that of CaCl₂ solution. The situation for monovalent ions is quite different. For all brine salinities investigated (1–6 M), Na⁺ shows a stronger effect on water contact angles than K⁺.

The effects of ionic strength on water contact angles can also be investigated. When ionic strength is 1 M (divalent ions 0.33 M, monovalent ions 1 M), water contact angles in brine solutions follow the order as Na⁺ ≈ Ca²⁺ > K⁺ ≈ Mg²⁺. As ionic strength increases to 3 M, the same order follows. However,

when ionic strength increases to 6 M, the order changes to Na⁺ > Mg²⁺ > Ca²⁺ > K⁺.

The effect of ions on water contact angles for CO₂/brine/mineral surface seems very complicated which depends on ion type, valence and salinity. It is hard to find a general trend for all ion types. It is hard to explain the trends of water contact angles with brine using the definition of CA in eq 1: the predicted water contact angles are all between 20° and 50°; the values of cos(CA) are in the range of 0.64 and 0.94; as a result, the variation of water contact angles becomes negligible in the form of cosine compared with changes of three interfacial tensions.

Trends of IFT(CO₂–brine) × cos(CA). In fact, the cosine of contact angle is much more useful than contact angle itself in fluid flow,⁴⁷ capillary pressure, and residual trapping.⁴⁸ The cosine of contact angle was multiplied by interfacial tension and the results for all brine solutions are averaged. Surprisingly, the values of IFT(CO₂–brine) × cos(CA) are 28.7 ± 2.3 mN/m which are identical for all brine solutions within estimated errors.

From eq 1, it can be concluded that the difference between γ_{CO₂–mineral} and γ_{brine–mineral} is not affected by brine salinity and ion type. For CO₂/brine/mineral systems, if only salinity and ion type change, the interfacial tension between CO₂ and mineral does not vary. So, the effect of brine salinity and ion type on interfacial tension between brine and mineral is negligible. An equation of state approach has been applied to predict IFT between solid and liquid. For coal, the predicted solid–liquid interfacial tensions for DI water and NaCl brine are very close (20 and 22 mN/m, respectively, for DI water and NaCl brine).²¹ The interaction between mineral and brine can be evaluated using hydrogen bonds between hydroxyl groups and water.¹⁶ From Table 1, the mean number of hydrogen bonds per nm² mineral surface varies a little with brine salinity and ion type. Although for KCl solution, the number decreases from 7.52 to 6.11, the effect on brine–mineral interaction seems to be negligible as only ~1 hydrogen bond for each squared nanometer. Hydrogen bonds lifetime varies a little between 0.44 and 0.53 which is also negligible considering the estimated deviations. This shows that the hydrogen bond strength between a hydroxyl group and water does not change with brine salinity and ion type.

Brine salinity and ion type affect brine–CO₂ interfacial tension and contact angle for CO₂/brine/mineral systems. According to the analysis above, the variations of IFT(CO₂–brine) and cos(CA) seem to counteract with each other. A change of water contact angle is mainly caused by the variation of interfacial tension between brine and CO₂. This finding is very useful for predicting contact angles in the context of large uncertainty of experimentally obtained contact angles.²⁴ The interfacial tensions between gas and liquid are easy to measure. Using this relationship found in the present study, water contact angles can be easily predicted using IFT(CO₂–brine) data. Due to the fact that IFT(CO₂–brine) × cos(CA) is usually related with capillary pressure and residual trapping capacity,⁴⁸ our finding is also very helpful to predict these parameters at different brine conditions. However, it should be noted that this relationship between IFT(CO₂–brine) and CA may be different when pressure, temperature, and/or mineral surface composition change. More work is required to evaluate the effects of pressure, temperature, and mineral surface structure on mineral–brine interactions as well as the IFT(CO₂–brine) × cos(CA) relationship.

4. CONCLUSION

Molecular dynamics simulations have been performed to investigate the effects of brine salinity and ion type on wettability of CO₂/brine/mineral systems. Water contact angles were calculated. Hydrogen bonds structure and dynamics were also analyzed as well as interfacial tensions to better understand the factors affecting water contact angles. The interaction parameters were validated by comparing predicted CO₂–brine interfacial tension with experimental data in the literature and good agreement was obtained.

The effects of brine salinity and ion type on water contact angles are very complicated. For MgCl₂ and NaCl solutions, CA increases with salinity. For CaCl₂ and KCl solutions, CA first increases and then remains constant with salinity. The values of IFT(CO₂–brine) × cos(CA) are found to be identical for all brine solutions within estimated errors. This implies that the effects of brine salinity and ion type on mineral–brine interfacial tensions are negligible which has been proven by hydrogen bonding structure and dynamics analysis. The relationship found between IFT(CO₂–brine) and cos(CA) is very useful to predict contact angles using IFT(CO₂–brine) data as well as predicting capillary pressure and residual trapping capacity. Further study is required to consider the effects of pressure, temperature, solid surface, etc.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.energyfuels.7b00840.

Details of potential energy parameters. Figure S1: atom types of a water molecule. Figure S2: atom types of a CO₂ molecule. Figure S3: types of ions. Figure S4: atom types of silica. Table S1: atom partial charges and Lj energy parameters. Table S2: interaction parameters for bond stretching and angle bending (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: congchen@dlut.edu.cn. Telephone: 86-411-84708774.

ORCID

Cong Chen: 0000-0001-5035-1026

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the National Natural Science Foundation of China (51206016 and 51676027), Natural Science Foundation of Liaoning Province (201602147), and Fundamental Research Funds for the Central Universities (DUT17LAB03).

■ REFERENCES

- (1) Vilarrasa, V.; Carrera, J. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112*, 5938–5943.
- (2) Tokunaga, T. K.; Wan, J. M. In *Geochemistry of Geologic CO₂ Sequestration*; DePaolo, D. J., Cole, D. R., Navrotsky, A., Bourg, I. C., Eds.; Mineralogical Soc Amer: Chantilly, 2013; Vol. 77, pp 481–503.
- (3) Liu, Y.; Li, H. A.; Okuno, R. *Ind. Eng. Chem. Res.* **2016**, *55*, 12358–12375.
- (4) Liu, Y.; Mutailipu, M.; Jiang, L.; Zhao, J.; Song, Y.; Chen, L. *Environ. Prog. Sustainable Energy* **2015**, *34*, 1756–1762.

- (5) Bachu, S.; Bennion, D. B. *J. Chem. Eng. Data* **2009**, *54*, 765–775.
- (6) Aggelopoulos, C. A.; Robin, M.; Perfetti, E.; Vizika, O. *Adv. Water Resour.* **2010**, *33*, 691–697.
- (7) Aggelopoulos, C. A.; Robin, M.; Vizika, O. *Adv. Water Resour.* **2011**, *34*, 505–511.
- (8) Li, X.; Boek, E.; Maitland, G. C.; Trusler, J. P. M. *J. Chem. Eng. Data* **2012**, *57*, 1078–1088.
- (9) Chalabaud, C.; Robin, M.; Lombard, J. M.; Bertin, H.; Egermann, P. *Oil Gas Sci. Technol.* **2010**, *65*, 541–555.
- (10) Lun, Z.; Fan, H.; Wang, H.; Luo, M.; Pan, W.; Wang, R. *Energy Fuels* **2012**, *26*, 3958–3962.
- (11) Zhao, L.; Ji, J.; Tao, L.; Lin, S. *Langmuir* **2016**, *32*, 9188–9196.
- (12) Chen, C.; Wan, J.; Li, W.; Song, Y. *Int. J. Greenhouse Gas Control* **2015**, *42*, 655–665.
- (13) Iglauder, S.; Pentland, C. H.; Busch, A. *Water Resour. Res.* **2015**, *51*, 729–774.
- (14) Chen, C.; Dong, B.; Zhang, N.; Li, W.; Song, Y. *Energy Fuels* **2016**, *30*, 5027–5034.
- (15) Zhang, L.; Kim, Y.; Jung, H.; Wan, J.; Jun, Y.-S. *Environ. Sci. Technol. Lett.* **2016**, *3*, 92.
- (16) Chen, C.; Zhang, N.; Li, W.; Song, Y. *Environ. Sci. Technol.* **2015**, *49*, 14680–14687.
- (17) Jung, J.-W.; Wan, J. *Energy Fuels* **2012**, *26*, 6053–6059.
- (18) Li, X.; Fan, X. *Int. J. Greenhouse Gas Control* **2015**, *36*, 106–113.
- (19) Arif, M.; Al-Yaseri, A. Z.; Barifcani, A.; Lebedev, M.; Iglauder, S. *J. Colloid Interface Sci.* **2016**, *462*, 208–215.
- (20) Ameri, A.; Kaveh, N. S.; Rudolph, E. S. J.; Wolf, K. H.; Farajzadeh, R.; Bruining, J. *Energy Fuels* **2013**, *27*, 1015–1025.
- (21) Ibrahim, A. F.; Nasr-El-Din, H. A. *Energy Fuels* **2016**, *30*, 7532–7542.
- (22) Al-Yaseri, A. Z.; Lebedev, M.; Barifcani, A.; Iglauder, S. *J. Chem. Thermodyn.* **2016**, *93*, 416–423.
- (23) Miri, R.; Hellevang, H. *Int. J. Greenhouse Gas Control* **2016**, *51*, 136–147.
- (24) Wan, J. M.; Kim, Y.; Tokunaga, T. K. *Int. J. Greenhouse Gas Control* **2014**, *31*, 128–137.
- (25) Iglauder, S.; Salamah, A.; Sarmadivaleh, M.; Liu, K. Y.; Phan, C. *Int. J. Greenhouse Gas Control* **2014**, *22*, 325–328.
- (26) Javanbakht, G.; Sedghi, M.; Welch, W.; Goual, L. *Langmuir* **2015**, *31*, 5812–5819.
- (27) Nielsen, L. C.; Bourg, I. C.; Sposito, G. *Geochim. Cosmochim. Acta* **2012**, *81*, 28–38.
- (28) Tenney, C. M.; Cygan, R. T. *Environ. Sci. Technol.* **2014**, *48*, 2035–2042.
- (29) Vlcek, L.; Chialvo, A. A.; Cole, D. R. *J. Phys. Chem. B* **2011**, *115*, 8775–8784.
- (30) Harris, J. G.; Yung, K. H. *J. Phys. Chem.* **1995**, *99*, 12021–12024.
- (31) Emami, F. S.; Puddu, V.; Berry, R. J.; Varshney, V.; Patwardhan, S. V.; Perry, C. C.; Heinz, H. *Chem. Mater.* **2014**, *26*, 2647–2658.
- (32) Phillips, J. C.; Braun, R.; Wang, W.; Gumbart, J.; Tajkhorshid, E.; Villa, E.; Chipot, C.; Skeel, R. D.; Kale, L.; Schulten, K. *J. Comput. Chem.* **2005**, *26*, 1781–1802.
- (33) Darden, T.; York, D.; Pedersen, L. *J. Chem. Phys.* **1993**, *98*, 10089.
- (34) Procacci, P.; Marchi, M. *J. Chem. Phys.* **1996**, *104*, 3003.
- (35) Ryckaert, J. P. *Mol. Phys.* **1985**, *55*, 549–556.
- (36) Martyna, G. J.; Tobias, D. J.; Klein, M. L. *J. Chem. Phys.* **1994**, *101*, 4177–4189.
- (37) Feller, S. E.; Zhang, Y.; Pastor, R. W.; Brooks, B. R. *J. Chem. Phys.* **1995**, *103*, 4613–4621.
- (38) Zhang, N.; Shen, Z.; Chen, C.; He, G.; Hao, C. *J. Mol. Liq.* **2015**, *203*, 90–97.
- (39) Chen, C.; Li, W. Z.; Song, Y. C.; Yang, J. *J. Mol. Liq.* **2009**, *146*, 23–28.
- (40) Elola, M. D.; Ladanyi, B. M. *J. Chem. Phys.* **2006**, *125*, 184506.
- (41) Hamm, L. M.; Bourg, I. C.; Wallace, A. F.; Rotenberg, B. In *Geochemistry of Geologic CO₂ Sequestration*; DePaolo, D. J., Cole, D. R., Navrotsky, A., Bourg, I. C., Eds.; Mineralogical Soc Amer: Chantilly, 2013; Vol. 77, pp 189–228.

- (42) Kvamme, B.; Kuznetsova, T.; Hebach, A.; Oberhof, A.; Lunde, E. *Comput. Mater. Sci.* **2007**, *38*, 506–513.
- (43) Chiquet, P.; Daridon, J.-L.; Broseta, D.; Thibaud, S. *Energy Convers. Manage.* **2007**, *48*, 736–744.
- (44) Li, X.; Boek, E. S.; Maitland, G. C.; Trusler, J. P. M. *J. Chem. Eng. Data* **2012**, *57*, 1369–1375.
- (45) Kroutil, O.; Chval, Z.; Skelton, A. A.; Predota, M. *J. Phys. Chem. C* **2015**, *119*, 9274–9286.
- (46) Ho, T. A.; Argyris, D.; Papavassiliou, D. V.; Striolo, A.; Lee, L. L.; Cole, D. R. *Mol. Simul.* **2011**, *37*, 172–195.
- (47) Briant, A. J.; Yeomans, J. M. *Phys. Rev. E* **2004**, *69*, 031603.
- (48) Chalbaud, C.; Robin, M.; Lombard, J.-M.; Martin, F.; Egermann, P.; Bertin, H. *Adv. Water Resour.* **2009**, *32*, 98–109.