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## Molecular Dynamics Simulations of the CO<sub>2</sub>-Water-Silica Interfacial Systems

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### Abstract

CO<sub>2</sub> injection and migration in porous media are dependent of interfacial tension (IFT), wettability, capillarity and mass transfer. The interfacial property at high pressure and high temperature (HPHT) condition and various water salinities must be investigated for application of CO<sub>2</sub> sequestration in deep saline aquifer. Molecular Dynamics (MD) simulation can deal with multi-components system, such as brine (water)/CO<sub>2</sub> interface, and easily control pressure, temperature and ratio of ions. In addition, most of experiments have employed the pendant droplet method to determine the interfacial tension based on a general Laplace-Young equation. This method requires a very accurate density measurement *in situ*, which is, however, not so easy to be instrumented. Consequently, the reported data are controversial and some of them are problematic. MD calculations can avoid this type of problem encountered by experimental measurement, as it uses a different way to determine the IFT. In our study, IFT for brine/CO<sub>2</sub> system and wettability for water/CO<sub>2</sub>/Silica were calculated using MD. We have discussed how pressure, temperature and water salinity have an influence on IFT and wettability. At first, IFT sharply decreases with pressure below the critical pressure (i.e. in the presence of gaseous CO<sub>2</sub>), while IFT stays constant with pressure at high pressure when CO<sub>2</sub> density is constant (i.e. in the presence of liquid or supercritical CO<sub>2</sub>). Secondly, IFT decreases with temperature at high pressure, while IFT is less affected by temperature at low pressure however a maximum is discernible. At last, water salinity builds IFT up with no strong relation to pressure. Contact angle calculations showed that wettability for water/CO<sub>2</sub>/hydrophilic Silica is independent of pressure change and water contact angle is about 20°.

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## 1. Introduction

CO<sub>2</sub> sequestration in deep saline aquifer has received widespread attention as one of the most effective ways to reduce man-made Green House Gas [1]. Injected CO<sub>2</sub> invades into pore space of reservoir sand rock, replacing brine. This brine and CO<sub>2</sub> transportation mechanism in porous media depends on interfacial interactions which contains interfacial tension (IFT), wettability, capillarity, and mass transfer [2, 3]. In this study, we focused on IFT and wettability because these two fundamental interfacial properties control the brine and CO<sub>2</sub> transportation mechanism in reservoir rock. To evaluate the wettability of three phase system, water/CO<sub>2</sub>/rock, some recent experiments [4-6] have been performed for measuring the contact angle. Some experimental measurements of IFT of brine (water)/CO<sub>2</sub> were also performed at several temperatures and pressures [7-11], but still scarcely done at HPHT condition and with various salt concentrations systematically and simulation studies have been even fewer [12].

Pendant drop method has been generally used as IFT measurement based on following equation [8],

$$\frac{d\phi}{ds} = 2k_{\text{apex}} - \left(\frac{z\Delta\rho g}{\gamma}\right) - \left(\frac{\sin\phi}{x}\right) \quad (1)$$

where  $\phi$  is the angle between the tangent at any point P on the profile of the drop and the horizontal axis,  $s$  is the respective arc length from the apex of the drop to the point P,  $k_{\text{apex}}$  is the curvature at the drop's apex,  $z$  is the height of point P from the horizontal axis,  $x$  is the distance of point P from the vertical axis,  $\Delta\rho$  is the density difference between each phase of brine and CO<sub>2</sub>, and  $g$  is the local gravitational acceleration. According to the second term in right side of equation (1), the density difference ( $\Delta\rho$ ) has large influence on  $\gamma$ . However, there are two obstacles to get accurate  $\gamma$  values due to  $\Delta\rho$ . (i) At first,  $\Delta\rho$  becomes too small in high pressure and low temperature [8]. In fact, assuming densities of the pure compounds at  $T = 298$  K, CO<sub>2</sub> density become close to water density above 43.7MPa [13]. That is why, at that condition it is difficult to obtain  $\gamma$  in the experimental method. (ii) The second problem is that a measurement of in-situ densities of saturated fluids seems to be difficult, because of the experimental setting. In such binary systems consisted of water and CO<sub>2</sub>, CO<sub>2</sub> diffuses into water phase and water into CO<sub>2</sub> phase. However due to the difficulty of measurement of in-situ density, the pure compound densities are often substituted [7]. This approximation causes underestimation of IFT when used under conditions not far enough from the density inversion (i.e.  $\rho_{\text{water}} \sim \rho_{\text{CO}_2}$ ) [9]. In fact, the reported experimental data are still controversial on the temperature-dependence of the IFT between brine (water) and CO<sub>2</sub> [7-11].

In our study, Molecular Dynamics (MD) simulation was performed to calculate IFT values  $\gamma$  and contact angle in water/CO<sub>2</sub>/hydrophilic Silica system and analyse these molecular interface structures. MD is very useful for calculating properties of multi-components. Furthermore, this computational method has advantages in calculating IFT: In MD simulation, the IFT value can be calculated by equation (2) mentioned below, which does not contain  $\Delta\rho$ . Thus, we could avoid these technical matters included in experiments. We show the IFT calculation results at pressures of 10 and 25 MPa and temperatures of 297 to 398 K, salt concentrations of 0 to 4.8 mol/l.

## 2. Method

### 2.1. The potentials

Molecular dynamics (MD) simulations were computed using GROMACS program package. The temperature was controlled by Nose-Hoover thermostat [14, 15]. The Particle Mesh Ewald summation

was used for the electrostatic interactions [16, 17], and a cutoff of 14Å was used for the van der Waals interactions. A 1.0fs time step was used, and the coordinates were output every 1.0ps. The potential model of water is described by the standard SPC/E model [18], the extended simple point charge model. It has been improved experimentally by Berendsen et al and its design is quite simple and well stands for material properties of water at standard temperature and pressure. EPM2 model [19] is used in order to describe the potential of CO<sub>2</sub>. For describing the rigid models, CO<sub>2</sub> and H<sub>2</sub>O, we have used the LINCS algorithm that resets bonds to their correct lengths after an unconstrained update [20]. The cations (Na<sup>+</sup>) and the anions (Cl<sup>-</sup>) are modelled by using Compatible ions model [21]. For hydrophilic Silica, CLAYFF force field was employed [22].

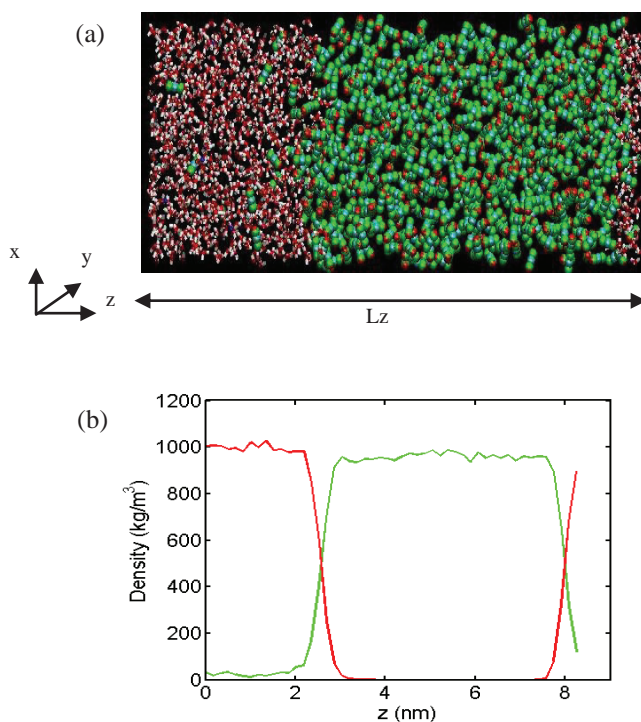


Figure 1. (a) The snapshot of a brine (left) - CO<sub>2</sub> (right) system at 296 K and 25 MPa. The salt concentration is 0.3M. The periodic boundary condition is applied in all directions. (b) Density profiles of water (red) and CO<sub>2</sub> (green) at 296 K and 25 MPa. They are gotten by time averaging for 0.1ns in equilibrium state.

## 2.2. Interfacial tension

All MD simulations for the water (brine)/CO<sub>2</sub> system was performed in a NPT ensemble. The simulated brine – CO<sub>2</sub> interface is shown in Fig 1. Interfacial tension ( $\gamma$ ) is defined as an integral of pressure difference between average of x and y direction and z, which is normal to the interface. In simulations, time rolling average needs to be taken to get appropriate values. In this study, the results of 4ns calculation in equilibrium state were used to obtain the interfacial tension.  $\gamma$  is given by following equation [23-25],

$$\gamma = \frac{1}{2} \int_0^{L_z} [P_{zz} - \frac{1}{2}(P_{xx} + P_{yy})] dz \quad (2)$$

where  $L_z$  is the length of the simulation cell vertical to the interface and  $P_{xx}$ ,  $P_{yy}$  and  $P_{zz}$  are the three diagonal components of pressure tensors along the x, y and z directions, respectively.

### 2.3. Wettability

The MD simulation for calculating the contact angle was performed in NVT ensemble at 296 K. The size of water/CO<sub>2</sub>/hydrophilic Silica system is 3.438 nm × 14.888 nm × 6.63778 nm. We calculated the density profiles of water and CO<sub>2</sub> by averaging the system for the last 2ns in whole calculation time since it is difficult to evaluate the contact angle from snapshot only. Fig.2 shows the snapshot of water/CO<sub>2</sub>/hydrophilic Silica system and density profile. In this system, directly calculation of the CO<sub>2</sub> pressure is difficult. So CO<sub>2</sub> pressure was calculated from CO<sub>2</sub> bulk density by using the well-known equation of states of CO<sub>2</sub> [13]. In this work, we regard that the CO<sub>2</sub> in the regime, where the density of CO<sub>2</sub> is constant, is bulk. We chose points whose densities are “bulk density” and determined the interface between CO<sub>2</sub> and water by curve fitting with the least squares method. After that, we got the contact angle for averaging of at top and bottom surface.

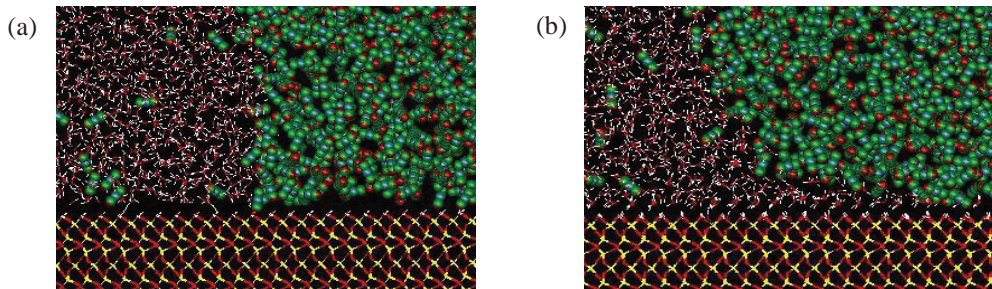


Figure 2. (a) Water (left)/CO<sub>2</sub> (right)/Silica (bottom) system before calculation (b) After calculation.

## 3. Results

### 3.1. Interfacial tension for brine/CO<sub>2</sub> system

The calculated IFT values in brine/CO<sub>2</sub> binary system at different temperature and salinity are shown in Fig.3. In the result at 296K, pressure dependence of IFT is clearly understood. That is, IFT sharply decreases with pressure in the presence of gaseous CO<sub>2</sub>, while IFT became constant with pressure at high pressure when CO<sub>2</sub> density was constant. This trend can be seen in almost all experimental results [7-11]. As shown in Fig.4, water salinity built IFT up regardless of temperature and pressure, which also has good agreement with the experimental data [9, 11].

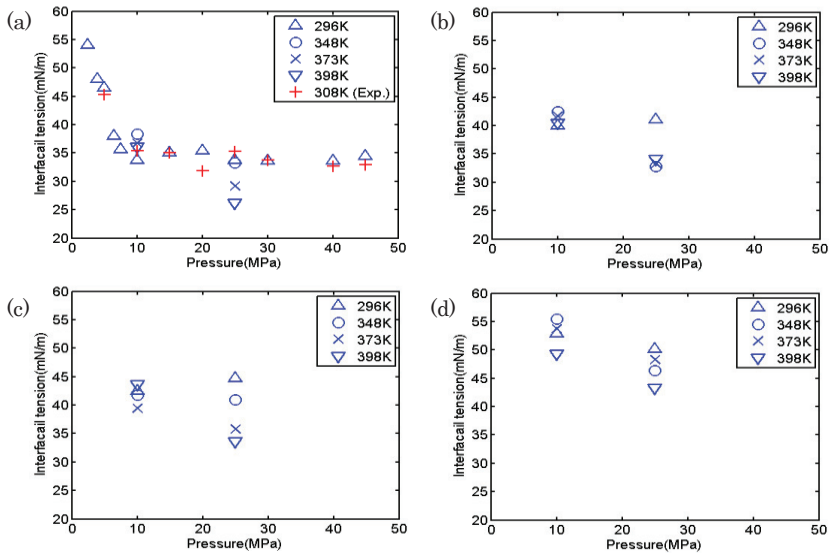


Figure 3. Calculated IFT vs pressure at different isotherms for water salinities of (a) pure water (experimental data refer to P. Chiquet et al. (2007)) (b) 1.2 mol/l (c) 2.4 mol/l (d) 4.8 mol/l.

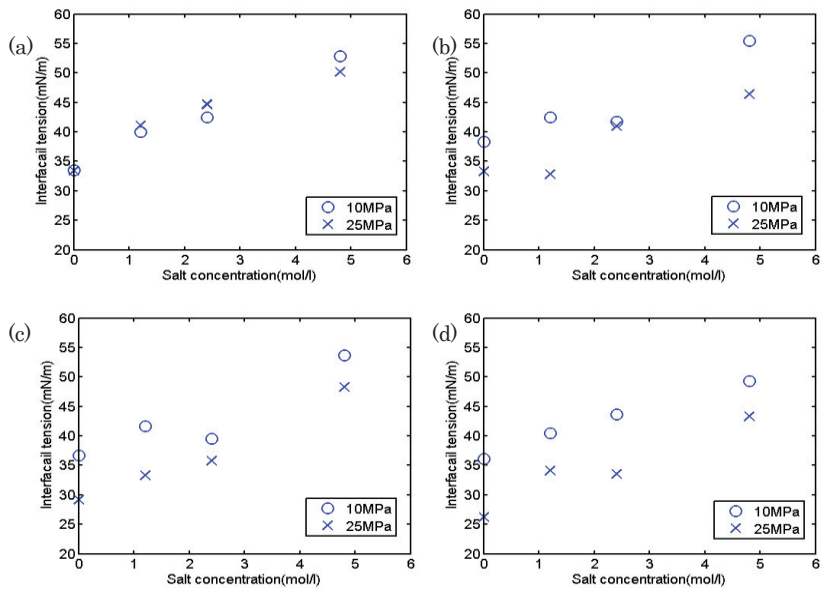


Figure 4. Calculated IFT vs water salinities at different pressures for isotherms of (a) 296 K (b) 348 K (c) 373 K (d) 398 K.

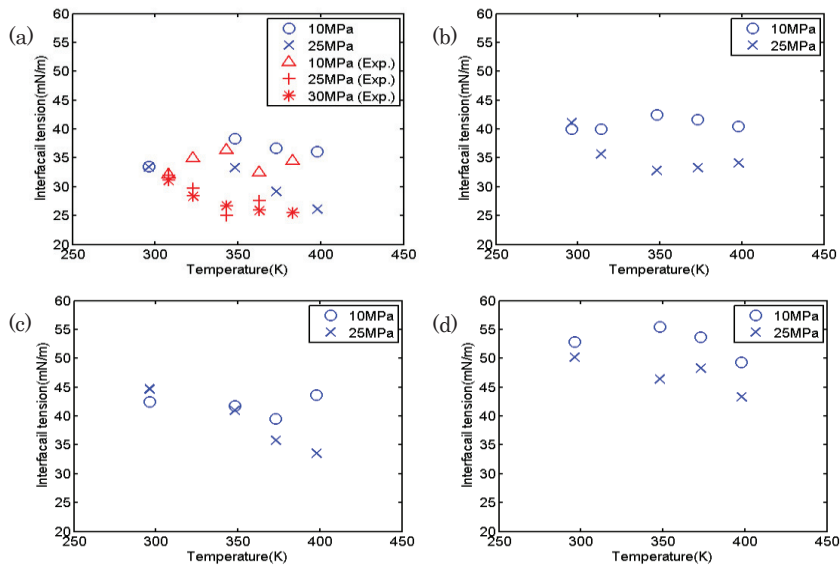


Figure 5. Calculated IFT vs temperature at different pressures for water salinities of (a) pure water (experimental data refer to P. Chiquet et al. (2007)) (b) 1.2 mol/l (c) 2.4 mol/l (d) 4.8 mol/l.

Fig.5 shows that IFT decreases with temperature at high pressure, and a local maximum of IFT was observed at 348 K and 10 MPa. This IFT decrease at high pressure range was also observed in the experiment of Chiquet et al [9], where they paid particular attention to obtain accurate density measurements. Our simulation could certainly avoid this problem and reproduce experimental IFT values well.

The surface tension of water (i.e. water-air interfacial tension) is especially high compared to other liquid such as hydrocarbon liquids due to the contributions of hydrogen bonding [26, 27]. The surface tension of liquid water decreases faster than the other liquid with temperature increase due to the weakening the hydrogen bonding. On the other hand, the solubility of  $\text{CO}_2$  increases with temperature decrease [11]. As an extreme example, the  $\text{CO}_2$ -water interface transforms into the  $\text{CO}_2$ -hydrate at temperature below  $\sim 278$  K, where a significant decrease of the IFT is anticipated [10]. So it seems natural that we observed a maximum IFT as function of temperature at certain pressure and salt concentration window. The agreement between calculate data and experiments supports this statement of IFT maximum.

### 3.2. Wettability for water/ $\text{CO}_2$ /hydrophilic Silica system

The calculated contact angles of water are listed on Table.1. Water molecules preferentially accumulate on hydrophilic surface against  $\text{CO}_2$  molecules and gotten contact angles became so small. The results show the contact angle is almost constant at different pressures for water/ $\text{CO}_2$ /hydrophilic Silica system, which is corresponding to experimental values [5]. Interestingly, a different behavior was observed for hydrophobic surface where the contact angle increases with pressure [28]. Furthermore, it is shown that a small increase of salinity only modify the contact angle marginally. Therefore, we only anticipate a significant difference only at very high salt concentration [6].

Table 1. Contact angle of water/CO<sub>2</sub>/hydrophilic Silica at different pressures.

Contact angle	7.8MPa	13.9MPa	28.8MPa
Water/CO <sub>2</sub> /hydrophilic Silica system (296K)	19° (±1° )	20° (±5° )	17° (±4° )

#### 4. Conclusions

The IFT calculations for water/CO<sub>2</sub> system using MD were performed at various P-T conditions, and different salt concentrations. The results of analysis are written in following bulleted list,

- 1- IFT sharply decreases with pressure when CO<sub>2</sub> density is sensitive to pressure change (namely, for vapor phase) and at high pressure stays constant.
- 2- IFT is directly proportional to water salinity at any P-T conditions.
- 3- At 25 MPa, IFT decreases with temperature increase. On the other hand, at 10MPa, a local maximum of IFT can be observed at around 348 K. In this way, we succeeded in reproduction of the reliable experimental results.
- 4- On hydrophilic silica surface, water molecules are attracted by hydroxyl group and we observed small water contact angle independent of pressure.

According to these results, it is important to perform various measurements at different P-T conditions and at different water salinity in order to apply interfacial property to analysis of the brine/CO<sub>2</sub> transportation or other interfacial phenomena. It is remarkable that one should pay careful attention to the way of measurement of interfacial property.



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