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Molecular Dynamics Study between Amine Solution and Calcium Hydroxide

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Abstract. *Carbon dioxide can be captured by amines and carried into calcium hydroxide to generate calcium carbonate. In this study, molecular dynamics simulations were performed to study the interaction energy and structure between amine solution and calcium hydroxide crystal slab at the molecular level. MDEA was chosen as a representative amine. According to the one-dimensional concentration function, it was found that at a low ratio of MDEA, it was preferentially distributed close to the calcium hydroxide. And as the content in the solution increased, MDEA was gradually distributed equally throughout the aqueous solution. Compared to water, the interaction energy between MDEA and calcium hydroxide is greatly reduced and gradually decreases with increasing amine content. This means that the interaction between the two is reduced, and the reaction is more difficult to occur. In addition, the system of carbon dioxide dissolved in a solution of amine and water was simulated. The distribution of carbonate and bicarbonate was found to be relatively uniform at MDEA ratios of 5% and became irregular above 20%.*

Keywords: *Molecular dynamics (MD) simulation, MDEA, $Ca(OH)_2$.*

1. Introduction

CO_2 is one of the primary greenhouse gases. To avoid further global warming, it is important to reduce these CO_2 emissions. Carbon capture technology is being widely researched and used as one of the methods to deal with CO_2. Among them, using amines to recover and capture carbon dioxide is one of the most important directions.

Recent studies have shown that using $Ca(OH)_2$ as an auxiliary agent in the absorption of CO_2 by amines can convert CO_2 into the mineral product carbonate, thus effectively reducing and reusing the emitted CO_2 (Zhang et al. 2020). Another study (Ji et al. 2022) aimed to gain insight into the interaction between typical amines and alkaline minerals, particularly the effect of amine type on amine regeneration, alkaline metal leaching, and $CaCO_3$ precipitation. The results of a series of studies have shown that the structural properties of amines influence the formation of $CaCO_3$ crystals. Even structural differences in the same type of amine can lead to changes in the composition and purity of the product (Yooa et al. 2020).

However, the current study does not provide a more detailed explanation of the mechanism of these results. We hope that this can be further investigated at the molecular level. Since previous studies (Ahmed et al. 2021) successfully analyzed the CO_2 uptake mechanism through MD simulations, in this study, we chose the molecular dynamics (MD) model hoping to provide valuable insights into the energetic, structural, and dynamic properties at the molecular scale.

In this study, we chose a typical amine, MDEA, and used MD simulations to investigate its

interaction with $Ca(OH)_2$. The system in which MDEA, water, and calcium hydroxide crystals coexist was simulated by MD. The study discussed the effect of the MDEA ratio on $Ca(OH)_2$ in the whole system by analyzing one-dimensional concentration distribution and interaction energy. In addition, the system of coexistence of MDEA, water, carbonate, and bicarbonate when CO_2 was dissolved in an aqueous MDEA solution was simulated, and the effect of the change of MDEA ratio on the system was briefly analyzed for subsequent studies.

2. Model and Method

2.1 Model

2.1.1 Monomer model

A total of five monomer models, MDEA, H_2O, CO_3^{2-} ion, HCO_3^- ion, and Ca^{2+} ion, were used in this paper. In the selection of force fields, the OPLS-AA force field was chosen for the Ca^{2+} ion, and the GAFF force field was used for the other four. Structural optimization is performed by using the steepest descent method, and then the charge of each atom is calculated by using density functional theory (DFT).

2.1.2 $Ca(OH)_2$ crystal model

The pristine calcium hydroxide cell is composed of two calcium hydroxide crystals placed interleaved and then connected with ca-O and O-H bonds. The lattice parameters of the pristine calcium hydroxide cell were a = 7.184Å, b = 6.222Å, c = 4.906Å, and $\alpha = \beta = \gamma = 90°$. The unit cell was then replicated five times on the a (x-axis), five times on the b (y-axis), and twice in the c (z-axis) direction. The final model obtained contains 200 calcium hydroxide molecules. In addition, since the parameters related to calcium hydroxide are not present in the GAFF field force, the parameters of the CLAFF force field (Cygan et al. 2004), as well as the charge, are used here.

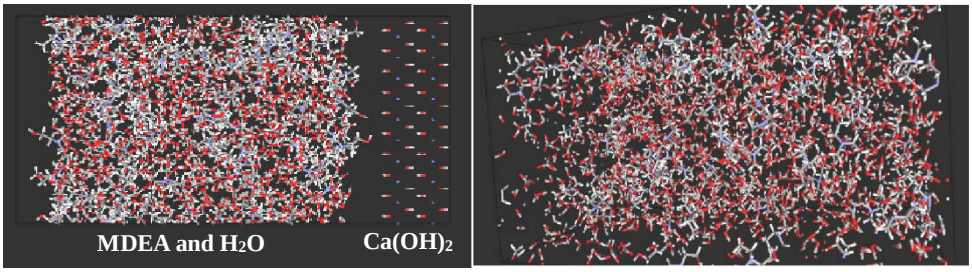

Figure 1. Simulation system: (left) water, amine, and $Ca(OH)_2$ system; (right) *water, amine, CO_3^{2-}, and HCO_3^- system*

2.1.3 Water, amine, and $Ca(OH)_2$ system

Six different systems were simulated with a ratio of 0, 5, 10, 20, 30, and 40% of the number of amine molecules to 1000 water molecules. The water molecules and MDEA molecules were randomly distributed in the systems. The water-amine molecule mixture solution model first relaxed shortly under the NVT ensemble and then under constant temperature and pressure

(NPT ensemble) until the density reached saturation values. During relaxation, the cross-sectional size in the x and y direction was fixed, the same as that of the calcium hydroxide model, to ensure successful merging. These models were then merged with the calcium hydroxide model and again relaxed under NVT and NPT ensembles until they reached an equilibrium state.

2.1.4 Water, amine, CO_3^{2-}, and HCO_3^- system

The pH of the simulated system was set at 10, and the concentration ratio of carbonate to bicarbonate was 9:1. A fixed amount of carbonate and bicarbonate ions in this ratio was added to the six water-amine models obtained in 2.1.3 and randomly distributed in the system. An appropriate amount of calcium ions should also be added to keep the model electrically neutral. The system was similarly relaxed under the NVT ensemble and then under the NPT ensemble until equilibrium.

2.2 Simulation Details

In this study, the simulations were performed using J-OCTA ver.8.0 software. The Nose-Hoover algorithm was chosen for the NVT ensemble, and the Parrinello-Rahman thermostat was used in combination with the Nose-Hoover thermostat for the NPT ensemble. Periodic boundary conditions (PPP) were chosen to eliminate the boundary effects during the simulation. The temperature and pressure were fixed at 300 K and 0.1 MPa for all models with a time step of 1 fs. The data were recorded at 0.1 ps intervals.

3. Result and Discussion

3.1 Water, Amine, and $Ca(OH)_2$ System

3.1.1 Spatial distribution

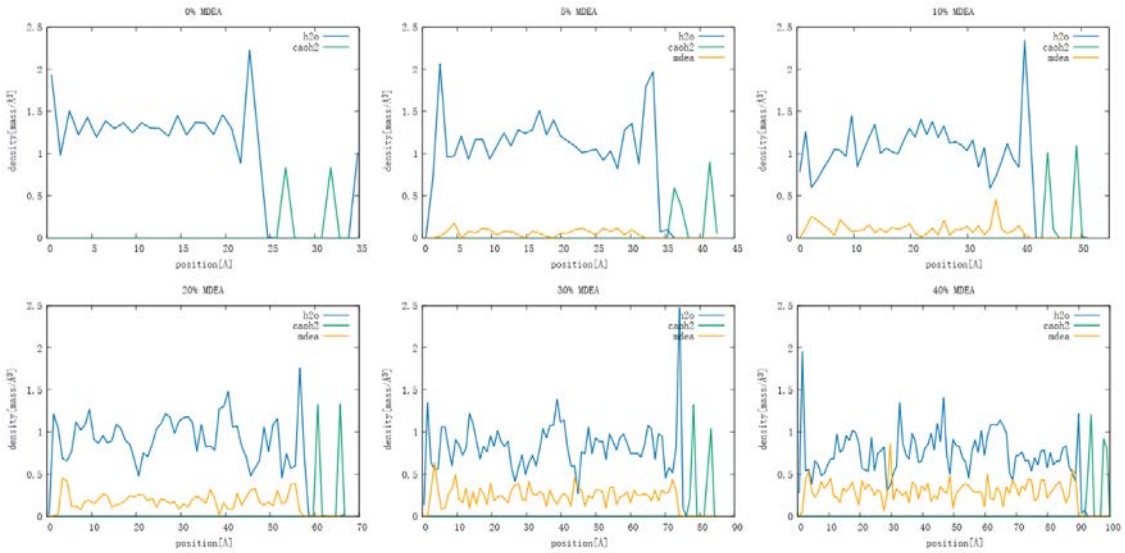

Figure 2. 1D concentration distribution of molecules in the water, amine, and $Ca(OH)_2$ system

1D concentration function in the z-axis direction was analyzed to understand the spatial distribution of MDEA and H_2O at the interface of the $Ca(OH)_2$ slab.

Figure 2 shows the concentration distribution of molecules. It can be noticed that when small amounts of MDEA are added, e.g., 5%, 10%, the MDEA is concentrated at both edges of the solution model, distributed close to the $Ca(OH)_2$. The plot of 10% MDEA has a peak around 36Å, implying that the MDEA clustering is much higher here than at other locations. However, as the MDEA ratio continues to increase, MDEA no longer tends to aggregate around the $Ca(OH)_2$ but begins to distribute evenly throughout the solution gradually.

In the absence of MDEA, the H_2O molecules are slightly denser near the $Ca(OH)_2$ slab and uniformly distributed in other positions. After adding MDEA, the H_2O molecules, which are evenly distributed, also gradually moved closer to $Ca(OH)_2$, resulting in a solution model with large densities at both edges and in the middle.

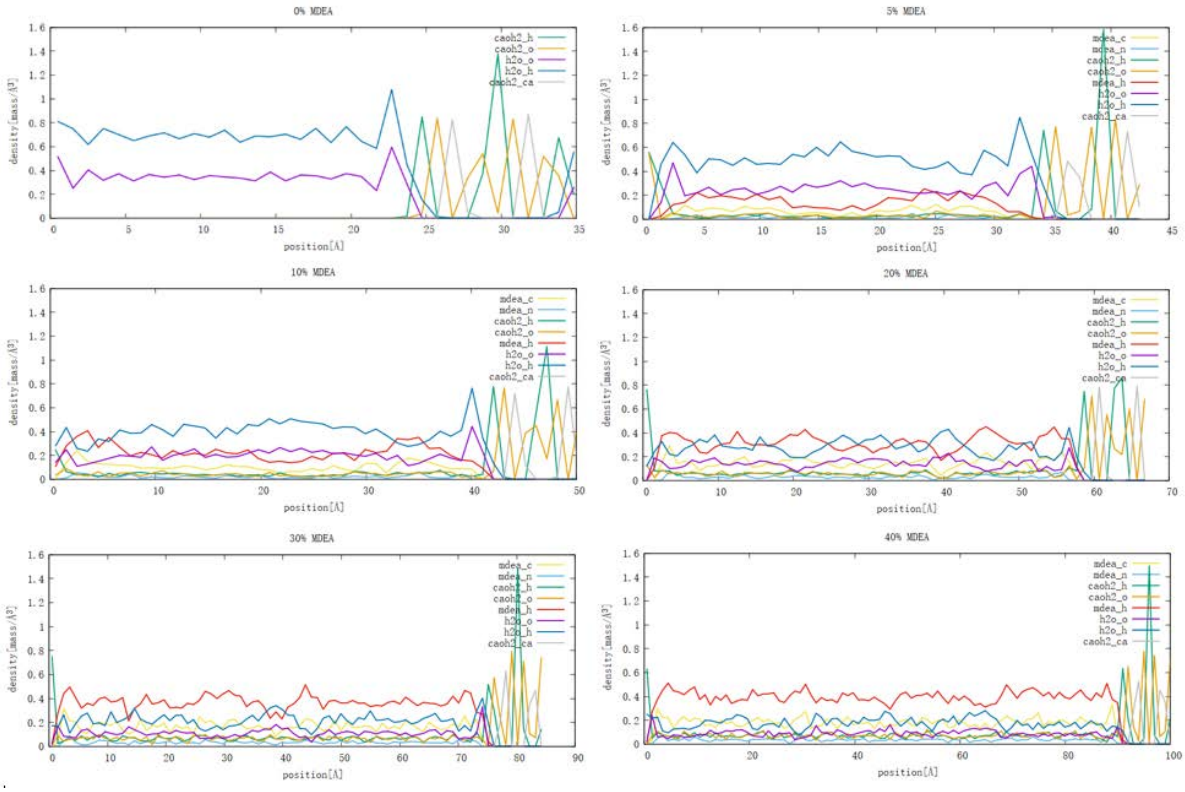

Figure 3. 1D concentration distribution of atoms

Fig. 3 shows the concentration distribution of the atoms in the model. In Fig. 3, the density of the H atoms in MDEA in the z-axis direction gradually increases with the increase of the ratio of amine to water. The density increases greatly when the ratio changes from 5% to 20%, while the maximum density stays around 0.5 mass/Å^3 after the ratio exceeds 20%. The distribution of the H atoms also varies with the increasing ratios, from a concentrated distribution near the calcium hydroxide slab to a gradual average distribution over the solution model, which agrees with the distribution of MDEA. When the ratio of amine to water is 10%, the H atoms in the $Ca(OH)_2$ slab are more evenly distributed, which differs from other ratios.

The maximum density does not exceed 1 mass/Å^3, much smaller than the results at other ratios.

3.1.2 Interaction energy

The interaction energy between the $Ca(OH)_2$ slab and solution was calculated by one-point calculation. Larger absolute values of negative energy (smaller values) indicate stronger interactions. The equation is as follows:

$$E\_int = E\_slab+sol - (E\_slab + E\_sol) \quad (1)$$

Where E_int is the interaction energy, E_slab+sol is the total potential energy obtained from MD, E_slab is the potential energy of calcium hydroxide, and E_sol is the potential energy of the solution.

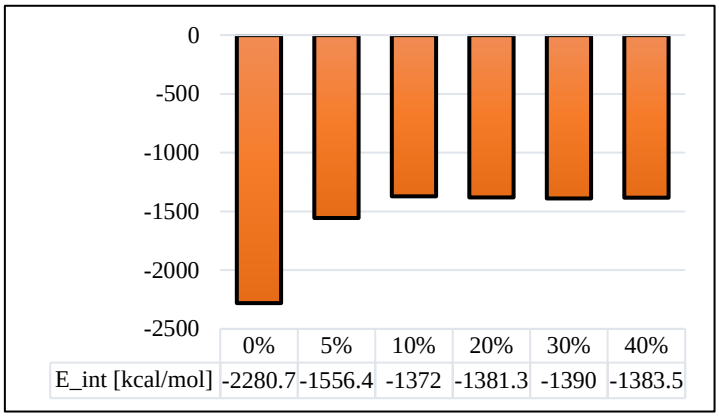

Figure 4. The interaction energy between the MDEA solution and $Ca(OH)_2$ slab

Fig.4 shows that the interaction energy between the MDEA solution and $Ca(OH)_2$ slab is much lower than that between pure water and $Ca(OH)_2$. When the ratio of amine to water is increased from 5% to 10%, the value increases slightly, implying a decrease in the interaction. And when the ratio exceeds 10%, the interaction energy values remain in a stable range. These results indicate that the addition of MDEA molecules decreases the interaction between the solution and the $Ca(OH)_2$ significantly. And when the MDEA exceeds 10%, its interaction with $Ca(OH)_2$ is reduced, making the reaction difficult.

3.2 Water, Amine, CO_3^{2-} and HCO_3^- System

As we can see in Fig.5, in the absence of MDEA addition, bicarbonate ions are concentrated in the first half of the model in an aggregated manner. Carbonate and calcium ions are distributed throughout the solution with high overlap. The difference is that the calcium ions peak at 35 Å, while the carbonate ions are slightly less dense here than in the other parts. H_2O is equally distributed in the system.

After adding 5% MDEA, the distribution of carbonate and calcium ions is more even than before, with both having the highest density peak at the leftmost 5 Å. Bicarbonate ions are not clustered at the front of the model and are slightly more evenly distributed throughout the solution.

When the MDEA ratio is 20% and above, the distribution of all particles becomes irregular,

and the phenomenon becomes more obvious as the MDEA ratio increases.

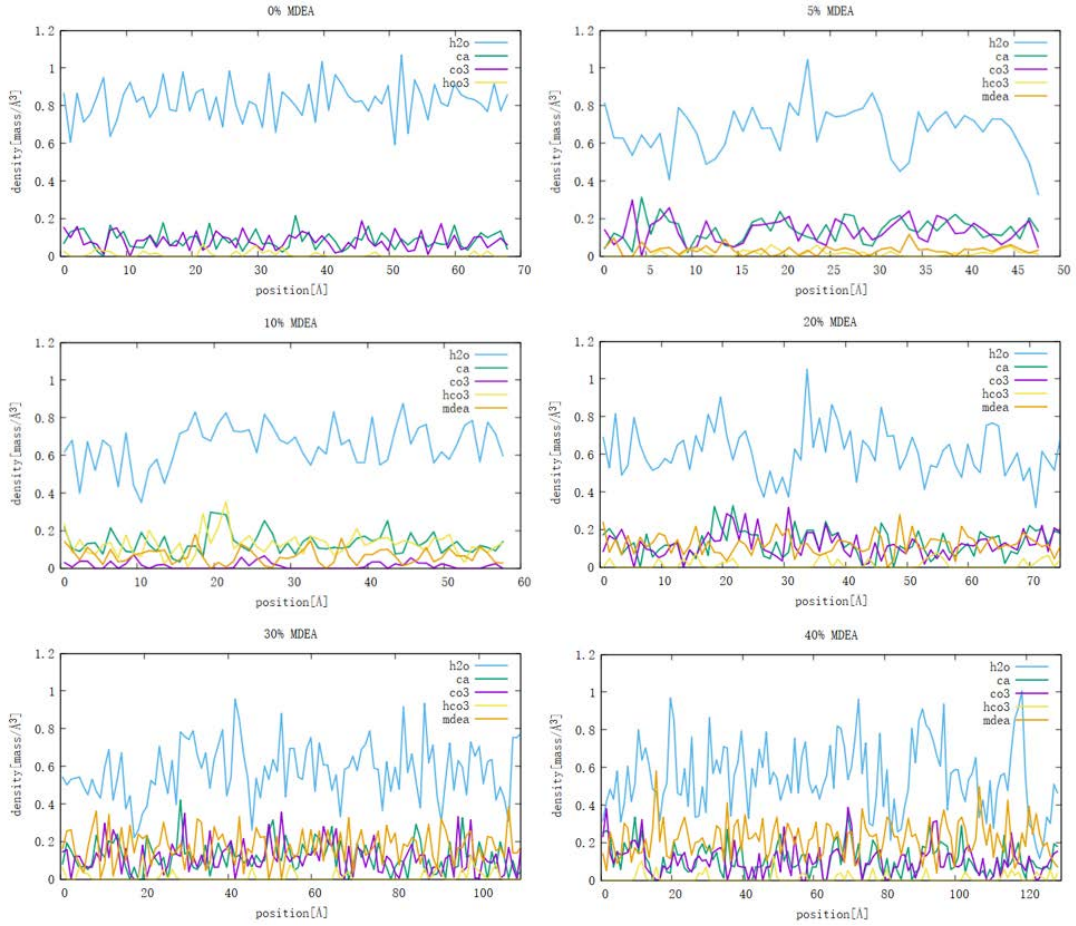

Figure 5. 1D concentration distribution of the water, amine, CO_3^{2-} and HCO_3^- System

4. Conclusion

In this study, the system of MDEA, H_2O, and $Ca(OH)_2$ was simulated with MD, and the relationship between different levels of MDEA and $Ca(OH)_2$ was analyzed at the microscopic level. The distribution of carbonate and bicarbonate in the system when carbon dioxide was dissolved in an aqueous MDEA solution was also analyzed.

The results are as follows:

- When the amount of MDEA in water is low, it preferentially chooses to distribute near calcium hydroxide; when the ratio of MDEA exceeds 10%, MDEA around calcium hydroxide reaches saturation, and MDEA starts to move to other directions in the system until it is uniformly distributed.
- When the ratio of MDEA is 10%, the distribution of H atoms in $Ca(OH)_2$ is more uniform than other ratios. The specific reason needs further study.
- The interaction energy between MDEA and $Ca(OH)_2$ is lower than that between water and $Ca(OH)_2$, and it decreases with the increase of the MDEA ratio.
- Carbonate and bicarbonate are more uniformly distributed when the ratio of MDEA is

5%.

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