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Understanding CO₂ Capture Mechanisms in Aqueous Monoethanolamine via First Principles Simulations

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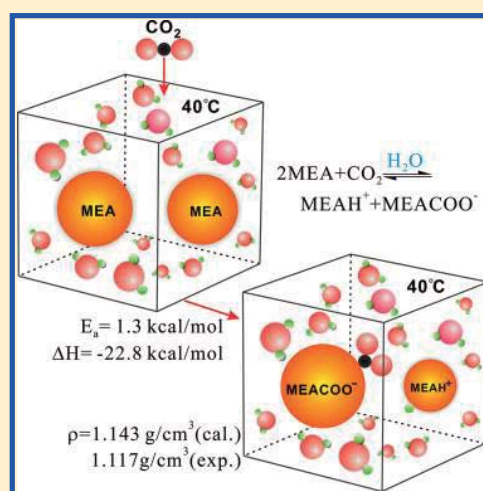
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S Supporting Information

ABSTRACT: CO₂ absorption mechanisms in 30 wt % monoethanolamine aqueous solution were explored at both low and high CO₂ pressures via ab initio molecular dynamics simulations. Detailed reaction processes were analyzed using both implicit and explicit solvent models. The results demonstrate that explicitly including water molecules in the simulation model is critical to achieve quantitative agreement between the calculated heats of absorption and the reported experimental values.

SECTION: Statistical Mechanics, Thermodynamics, Medium Effects



It has been widely accepted that CO₂ release as a result of human activity is responsible for rapid global climate change.¹ Development of energy efficient, cost-effective novel materials and processes for CO₂ capture and subsequent sequestration presents a great technological challenge and has been one of the most active areas of research in recent years.^{2,3} It has been shown that amine-based organic and ionic liquids are capable of chemically interacting with CO₂, among which aqueous monoethanolamine (MEA) has been used in industrial processes to capture CO₂ for many years.⁴ Nevertheless, the associated process costs and high energy consumption have made it difficult to employ these materials and processes at a larger scale to combat global warming caused by greenhouse gases.^{5,6} Unraveling mechanistic details of the capture process is essential for design and development of novel materials with high CO₂ capacity. While a wealth of experimental data on CO₂ complexation with alkanolamines is available, it remains challenging to apply molecular simulation techniques to reproduce heats of reactions for these compounds in accurate agreement with experimental results.^{6,7} Indeed, CO₂ interactions with aqueous alkanolamines or ionic liquids are often described with an implicit model using gas-phase or continuum-based quantum chemical calculations.^{8–11} While these studies provide useful insight into the reaction mechanisms, the reported absorption energies, calculated with a gas-phase or continuum model, range from –6.26 kcal/mol to –17.6 kcal/mol at 0 K,^{11–13} significantly lower

than the experimental value. Furthermore, the solvate/solvent compositions, which critically affect CO₂ absorption mechanisms, are not accounted for.¹¹ In this Letter, we report a first-principles molecular dynamics (MD) simulation study using an explicit model on CO₂ absorption mechanisms in a well-known aqueous phase system with approximately 30 wt % of MEA at 40 °C.¹⁴ To gain further insight into the mechanistic process, we performed static calculations using a continuum model to estimate activation energies of proton transfer and CO₂ complexation reactions. We show that CO₂ absorption-induced proton transfer is the dominant process to prompt CO₂ capture with significant enthalpy of absorption. Quantitative agreement between the calculated and the experimental heats of reaction is achieved.

Low pressure CO₂ capture with 30 wt % MEA aqueous solution is a widely used industrial process. The reported liquid density at 15 °C is 1.01 g/cm³.¹⁴ Recent calorimetric studies reported that CO₂ absorption energy falls into the range between –19 and –24 kcal/mol at 40 °C if the CO₂:MEA ratio is below 1:2.^{6,7} Macroscopic kinetic studies suggest that CO₂ absorption in 30 wt % MEA aqueous solution undergoes a proton transfer process, in which one of the two MEA molecules acts as a

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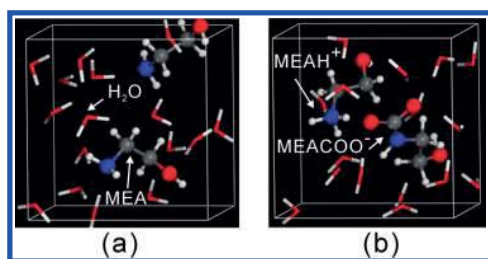


Figure 1. The optimized unit cell of the 30 wt % MEA aqueous solution, (a) before CO₂ adsorption and (b) after CO₂ adsorption. The blue, red, gray, and white colors represent the N, O, C, and H atoms, respectively.

nucleophile for CO₂ and the other serves as a Lewis base.^{15,16} The experimental results clearly indicate that CO₂ interacts strongly with at least two MEA molecules simultaneously at a low pressure. Three important questions thus arise: (1) What is the driving force for CO₂ absorption? (2) What prompts proton transfer? (3) How facile is the CO₂ capture process thermodynamically and kinetically? Here we attempt to use first-principles simulations to address these issues.

The ab initio MD simulation was carried out using periodic density functional theory (DFT) for electronic structure calculations and the nuclear motion was simulated using Newton's equation of motion in a canonical ensemble with Nosé's thermostat¹⁷ at 313 K for 6 ps. The DFT calculations were carried out using the PW91 exchange-correlation functional as implemented in the VASP simulation package. The projector augmented wave (PAW) method was used to describe the electron–core interaction and a planewave basis set was used to describe the valence electrons with a cutoff energy of 430 eV.^{18–20} The Brillouin zone integration was sampled with a $2 \times 2 \times 2$ Monkhorst-Pack k point mesh. To assist understanding of the ab initio MD results and the kinetic process of the absorption, we also employed a COSMO continuum solvation model²¹ using water as the medium by performing a transition state search using the synchronous transit algorithm to estimate the activation barriers. Each of the optimized transition state structures was subsequently verified by normal-mode analysis that yielded only one imaginary frequency. The electronic energy was calculated using DFT with PW91 functional and a DNP basis set as implemented in the DMol³ package.^{22,23}

We first describe our ab initio MD results. A cubic cell containing two MEA molecules and 16 water molecules, roughly representing a 30 wt % MEA aqueous solution, was selected for the simulation. Structural optimization yields a cell parameter of 8.639 Å and a liquid density of 1.057 g/cm³, in reasonable agreement with experimental value of 1.01 g/cm³.^{14,24} The optimized unit cell is shown in Figure 1a, where the MEA molecules are highlighted with a ball and stick model. Our MD simulation results suggest that the two MEA molecules are well separated by water molecules prior to CO₂ absorption and are linked via an extensive H-bonding network. No proton transfer was observed.

For CO₂ capture by MEA, two capacities with the CO₂:MEA ratios of 0.5 and 1 were studied. We first consider the ratio of 0.5, which corresponds to the capacity at low CO₂ pressure. Böttinger and co-workers used online NMR spectroscopy to determine the product distribution of CO₂ in aqueous MEA at various pressures.²⁵ It was found that before the CO₂:MEA ratio reaches 0.5, the concentrations of MEAH⁺ and MEACOO[−] rise up nearly equally, while the MEA molecules are consumed twice as fast. Upon reaching the CO₂:MEA ratio of 0.5, MEA is nearly

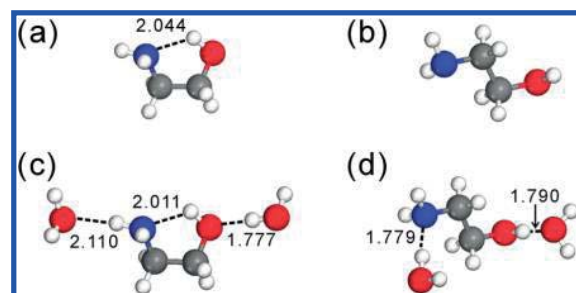
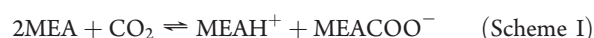


Figure 2. The optimized structures of the MEA molecule: (a) ring configuration, (b) chain configuration, (c) ring configuration with two H₂O molecules, and (d) chain configuration with two H₂O molecules.

disappeared. Therefore, we chose the following scheme for our MD study:



In this scheme, we placed a pair of MEA molecules in the ionized form together with 16 H₂O molecules in a cubic box followed by MD run. The two MEA molecules react with CO₂ concertedly; one acts as a nucleophile for CO₂, and the other serves as a base to accept a proton transferred from the MEA nucleophile. The selected supercell upon equilibration is shown in Figure 1. The calculated liquid density is 1.143 g/cm³, which is slightly higher than the value prior to CO₂ absorption. The volume shrinkage indicates closer molecular packing resulting from the increased Coulomb interactions in the liquid due to the charge separation. Again, the calculated density is in good agreement with the experimental value of 1.117 g/cm³ and consistent with the trend of increased liquid density upon CO₂ uptake.²⁴ The calculated average absorption energy is −22.8 kcal/mol, in excellent agreement with the reported experimental value.^{6,7} The results underscore the importance of the explicit model that includes water molecules in the simulation box with the experimentally utilized water-to-MEA ratio, which could not be accounted for in conventional continuum models.

An interesting issue is how the MEA ion pair ([MEAH⁺][MEACOO[−]]) is formed upon CO₂ absorption, in view of the fact that the ion pair does not exist in the absence of CO₂. Ideally, it would be interesting to observe the ion pair formation from the separated molecules by running long time MD simulations. Unfortunately, computationally, this is prohibitively intensive. Instead, we consider two possible routes that may lead to the formation of the same ion pair to understand the formation mechanisms using the COSMO continuum model with water as the medium with the understanding that the implicit model represents an extremely diluted situation. Two conformations of a single MEA molecule in water continuum, shown in Figure 2a,b, were considered. The ring configuration with intramolecular hydrogen bonding (Figure 2a) was found to be energetically more favorable than the chain structure (Figure 2b) by 3.1 kcal/mol, which is consistent with the calculations by da Silva et al.⁹ However, the higher stability of the ring configuration is likely an artifact since the effects of surrounding water molecules are not explicitly included in the calculations. Indeed, the relative stability of the ring and chain structures is reversed upon explicit inclusion of two water molecules to bind with the two head groups of the MEA molecule. The open chain structure of MEA (Figure 2d) is now more stable than the ring structure (Figure 2c) by 3.0 kcal/mol due to stronger intermolecular hydrogen bonding than the

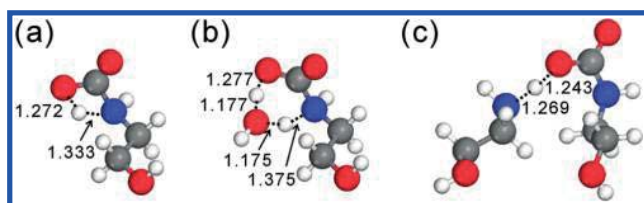


Figure 3. The optimized transition state structures of Route I: (a) the first step without H₂O; (b) the first step with H₂O; (c) the second step.

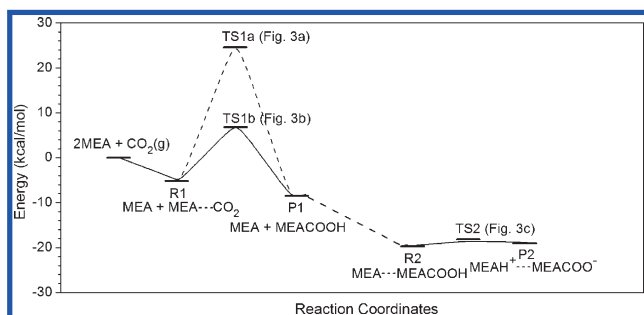


Figure 4. Energy diagram of Route I.

intramolecular hydrogen bonding. Hence, we will use the open chain model to represent the MEA molecule in our calculations. The arbitrariness associated with solvent model selection is an intrinsic problem of the implicit model, which does not explicitly account for the intermolecular hydrogen bonding arising from MEA–water interactions. The results again underscore the importance of the explicit model for unbiased description of MEA structures in aqueous solutions.

There are two possible reaction routes for Scheme I. In the first route, an MEA molecule first reacts with a CO₂ catalyzed by H₂O to form MEACOOH, which subsequently reacts with another MEA to form an ion pair as described below:



In the first step, CO₂ attacks the amine headgroup of a MEA to form MEACOOH. We first consider the possibility of direct transfer of a H atom from amine to CO₂. The optimized transition state structure is shown in Figure 3a. The reaction was found to be kinetically difficult with a high activation barrier of 29.4 kcal/mol due to the long traveling distance for the H atom to migrate from the N atom to the O atom. We then consider the possibility of H transfer explicitly catalyzed by a H₂O molecule. The reaction occurs by exchanging H atoms between H₂O and the amine group facilitated by bridging the CO₂ molecule and the amine group with water, as shown in Figure 3b, which displays the calculated transition state structure. This process is kinetically more favorable than the one without H₂O bridging due to a shorter migration path for the H atom and the strong intermolecular H-bonding. Indeed, the calculated activation barrier of 11.8 kcal/mol is less than half of the value for the direct migration pathway. The reaction is also thermochemically favorable with the calculated reaction energy of −3.5 kcal/mol. In the second step of Route I, the proton of the −COOH group attacks the electron lone pair on the N atom of another MEA to form an ion pair (Figure 3c). The reaction is nearly barrierless (0.9 kcal/mol) and essentially thermo-neutral (0.6 kcal/mol). The facile proton

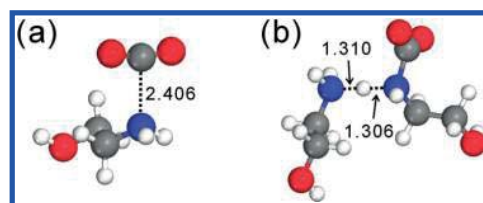


Figure 5. The optimized transition state structures of Route II: (a) the first step; (b) the second step.

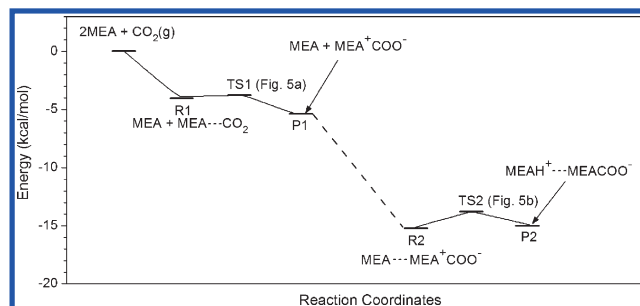
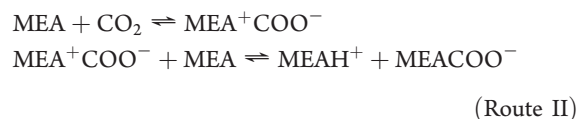


Figure 6. Energy diagram of Route II.

transfer arises from the additional stability provided by the carbamate π -conjugation upon proton transfer from MEACOOH to MEA. The calculated profile of the minimum energy pathway is shown in Figure 4. Here, to facilitate the comparison of energy variation between the two steps, we shifted the energy profile of the first step by including the energy of an additional MEA molecule in the total potential energy. Note that the energy shift from P1 (MEA + MEACOOH) to R2 (MEA...MEACOOH) is purely artificial since the MEA molecule acts as a spectator in the first step with no influence on the reaction. In reality, the reactants are always surrounded by MEA molecules associated with each other including the reactants via H-bonding, which lowers the total potential energy. Here, R2 represents the association between MEA and MEACOOH. The artificial energy shift is again an intrinsic problem of the continuum model since it does not explicitly account for the surrounding molecules. The MEA ion pair formation can also undergo an alternative route via two successive steps shown below:



Here, a MEA molecule reacts with a CO₂ to form a zwitterion structure. Subsequently, the zwitterion transfers a proton to a MEA molecule nearby, giving rise to the formation of the ion pair. The optimized transition state structures are shown in Figure 5, and the calculated minimum energy profile along the reaction pathway is shown in Figure 6. Our results indicate that CO₂ attachment to the amine group of MEA to form the zwitterion intermediate in water is a nearly barrierless process with an activation energy of only 0.1 kcal/mol, releasing approximately −1.5 kcal/mol thermochemical energy. Again, artificial energy shift from P1 (MEA + MEA⁺COO[−]) to R2 (MEA...MEA⁺COO[−]) is observed for the same reason stated above. In the second step, proton transfer from the zwitterion to another MEA is facile with a barrier of 1.4

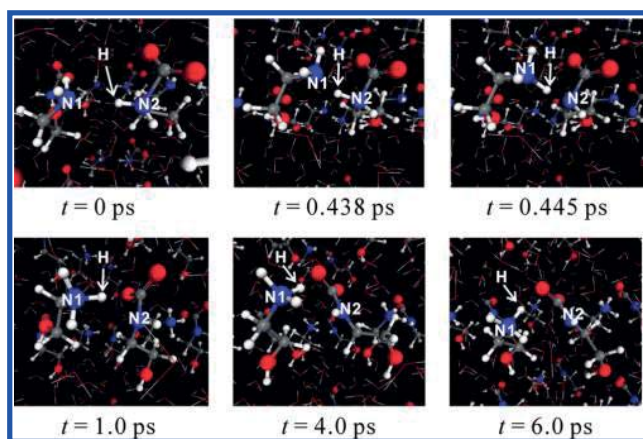


Figure 7. Snapshots of MD trajectory for 30% aqueous MEA+CO₂ at 313 K.

kcal/mol and a modest thermochemical energy of 0.3 kcal/mol. Again, the carbamate π -conjugation upon proton transfer from MEA⁺COO[−] to MEA makes the reaction facile. The results suggest that the potential energy along the designated route is very flat. Of the two reaction routes explored, Route II is energetically more favorable. We therefore conclude that zwitterion formation is a necessary step that leads to the formation of the ion pair. The zwitterion mechanism was first proposed by Danckwerts,²⁶ and the model was subsequently used to explain CO₂ absorption and desorption in aqueous alkanolamine solutions.^{27,28} Recent DFT studies using a polarizable continuum model by Shim et al. also suggested that a zwitterion process is the energetically preferred mechanism for CO₂ absorption in MEA aqueous solution.¹³ Our results are consistent with these experimental and theoretical studies.

To gain further insight into the proton transfer, we performed an *ab initio* MD simulation with a supercell that contains the zwitterion intermediate and a MEA molecule, together with 16 H₂O molecules. It was found that the MEA molecule quickly approaches the zwitterion, prompting a proton transfer from the ammonium zwitterion to the MEA molecule. The proton transfer gives rise to π -conjugation within the resulting −NHCOO[−] group. Figure 7 displays a few snapshots of the simulated MD trajectory. It shows that the two initially separated MEA molecules with one of them forming a zwitterion ($t = 0$ ps) reorient to prepare for proton transfer at $t = 0.438$ ps, which takes place within about 0.5 ps. The associated potential energy profile is shown in Figure 8. While the reorientation is a generally favorable process, the proton transfer requires roughly 1.3 kcal/mol to activate, which is consistent with the calculated activation barrier of 1.4 kcal/mol using the continuum model.

We now proceed to study a higher CO₂ capacity in 30 wt % MEA aqueous solution with the MEA:CO₂ ratio of 1:1, representing the condition at high CO₂ pressures. The online NMR spectroscopic study by Böttinger et al.²⁵ clearly indicates that, as the CO₂:MEA ratio exceeds 0.5, the concentration of HCO₃[−] species rises up rapidly with CO₂ partial pressure, while the MEA molecules are now fully consumed. The increase of MEAH⁺ concentration and the decrease of MEACOO[−] concentration are at approximately the same rate until the CO₂:MEA ratio becomes 1, at which the MEAH⁺ concentration reaches the maximum and the MEACOO[−] concentration vanishes completely. We therefore consider the following reaction scheme for our MD

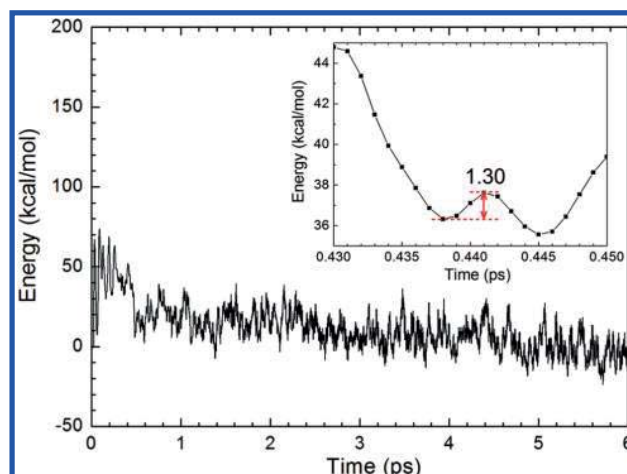


Figure 8. Potential energy profile of proton transfer of the MD simulation for 30% aqueous MEA+CO₂ at 313 K. The inset is the enlarged energy profile from 0.43 to 0.45 ps.

simulation:



Here all MEA molecules act purely as a base. Unlike Scheme I for low-pressure CO₂ absorption, where water does not participate in the reactions, water molecules here react stoichiometrically to capture CO₂ as bicarbonate. Upon MD simulation, the liquid density increases to 1.275 g/cm³, which is substantially higher than the value prior to CO₂ absorption. Again, the underlying reason for the substantial change of liquid density is that strong Coulomb interactions induce much denser molecular packing in the liquid. Our MD simulation yields an average absorption energy of −9.8 kcal/mol per CO₂ molecule, substantially reduced from the values at the lower CO₂ capacity or lower CO₂ partial pressure. While no experimentally measured heat of absorption is available for the CO₂:MEA ratio equal to 1, to the best of our knowledge, the calculated absorption strength is comparable to the experimental data for CO₂ absorption in methyldiethanolamine (MDEA), which undergoes a similar reaction pathway with CO₂ in the presence of water.^{24,27}

In summary, we have performed extensive first-principles MD simulations to unveil the reaction pathways for CO₂ capture in 30 wt % MEA aqueous solution with the CO₂:MEA ratios of 0.5 and 1 at 40 °C. Quantum chemical calculations using the COSMO continuum model were used to assist understanding of the MD results and the kinetic processes. At low CO₂ capacity (i.e., low CO₂ partial pressure), MD simulations were performed for the [MEAH⁺][MEACOO[−]] ion pair surrounded by water molecules. Two reaction routes that lead to the formation of the ion pair were examined. We have identified that the energetically most favorable route is to first form a zwitterion intermediate followed by proton transfer, although another route may also be energetically feasible at the selected temperature. It was found that upon CO₂ attachment to the amine group of a MEA molecule, proton transfer from the zwitterion to a MEA molecule can readily occur, forming a stable carbamate structure with π -conjugation. This is the main driving force for CO₂ absorption. The calculated liquid densities and, in particular, the average absorption energies are in excellent agreement with the reported experimental values. At high CO₂ capacity (i.e., high CO₂ partial pressure), water directly reacts with CO₂, and MEA simply serves

as a base. Substantial increases in liquid densities were found upon CO₂ reaction due to the strong Coulomb interactions in the liquid. Our results demonstrate that the *ab initio* MD method is capable of providing quantitative structural and energetic information for simulations of absorption phenomena in the liquid phase,²⁹ which should pave the way for computational screening of CO₂ absorption in other promising liquid media, including ionic liquids.

■ ASSOCIATED CONTENT

S Supporting Information. The optimized structures of MEAH⁺ and MEACOO[−], the table of relative energies of Route I and Route II, and the equilibrium structure of 2 CO₂ molecules in 30 wt % MEA aqueous solution at 313 K. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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