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Title: Reaction mechanisms of aqueous monoethanolamine with carbon dioxide: a combined quantum chemical and molecular dynamics study

Molecular mechanisms underlying the reaction of aqueous MEA with CO₂ are examined using *ab initio* and classical molecular dynamics simulations combined with static quantum chemical calculations, with special attention to the influence of solvent structure and dynamics. This work highlights the critical role of H₂O molecules, particularly their availability and arrangement around zwitterionic intermediates, in the progression of competing CO₂ capture and solvent regeneration processes. This improved understanding can contribute to developing more comprehensive kinetic models for use in modeling and optimizing the CO₂ capture process.
Reaction mechanisms of aqueous monoethanolamine with carbon dioxide: a combined quantum chemical and molecular dynamics study†

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Aqueous monoethanolamine (MEA) has been extensively studied as a solvent for CO2 capture, yet the underlying reaction mechanisms are still not fully understood. Combined ab initio and classical molecular dynamics simulations were performed to revisit and identify key elementary reactions and intermediates in 25–30 wt% aqueous MEA with CO2, by explicitly taking into account the structural and dynamic effects. Using static quantum chemical calculations, we also analyzed in more detail the fundamental interactions involved in the MEA–CO2 reaction. We find that both the CO2 capture by MEA and solvent regeneration follow a zwitterion-mediated two-step mechanism; from the zwitterionic intermediate, the relative probability between deprotonation (carbamate formation) and CO2 removal (MEA regeneration) tends to be determined largely by the interaction between the zwitterion and neighboring H2O molecules. In addition, our calculations clearly demonstrate that proton transfer in the MEA–CO2–H2O solution primarily occurs through H-bonded water bridges, and thus the availability and arrangement of H2O molecules also directly impacts the protonation and/or deprotonation of MEA and its derivatives. This improved understanding should contribute to developing more comprehensive kinetic models for use in modeling and optimizing the CO2 capture process. Moreover, this work highlights the importance of a detailed atomic-level description of the solution structure and dynamics in order to better understand molecular mechanisms underlying the reaction of CO2 with aqueous amines.

I. Introduction

The ever-increasing rate of carbon dioxide (CO2) emissions, mainly as a result of growing fossil fuel consumption, has become a widespread concern.1 At present, aqueous alkanolamine solvents are the predominantly used method to remove CO2 from flue gas and natural gas.2−6 Particularly, monoethanolamine (MEA) has been the most extensively studied for decades and is commonly used as the benchmark solvent.2,4,6 However, scaling up of the aqueous MEA system for commercial-scale applications tends to be impeded by MEA degradation, corrosion problems, and moreover the high parasitic energy consumption during solvent regeneration.5,4,7 Several experimental and modeling studies have been undertaken to better understand the CO2 capture process with aqueous MEA, but some fundamental aspects of the MEA–CO2 reaction in an aqueous solution, particularly the role of water molecules, still remain uncertain despite its importance in designing more efficient MEA-based solvents and processes.

It has been thought that two MEA molecules react with one CO2 molecule to form carbamate and protonated MEA, perhaps via a single-step termolecular (direct) or two-step zwitterion mechanism. The two-step process involves the formation of a zwitterion as an intermediate which undergoes deprotonation by another MEA to form carbamate and protonated MEA.8,9 The single-step mechanism assumes that amine, CO2, and base molecules form a loosely-bound complex, rather than a zwitterion, which breaks up to form the products.10 Although recently the zwitterion mechanism is commonly adopted to explain the MEA–CO2 reaction, some fundamental aspects of the MEA–CO2 interaction in aqueous solution remain uncertain.11–20

Atomic-level characterization of the complex reaction-diffusion behavior in aqueous solutions appears to be very challenging,
in part because of the limited capabilities of common instrumentation. A complementary computational effort has been made in studying the fundamental issues related to CO₂ capture and solvent regeneration. The reaction of CO₂ with aqueous amines has often been studied using an implicit solvent approach based on (static) quantum mechanical (QM) calculations. The implicit QM model may provide useful insight into the reaction paths and energetics and the relative stability of reaction intermediates. However, there are several less studied aspects like the microstructure of the solvent that may have a critical influence on the MEA–CO₂ reaction. Very recently, ab initio molecular dynamics (AIMD) has been applied to identify the likely events and the reaction intermediates involved in the CO₂ capture by MEA. This method possibly better accounts for the solution structure and dynamics and their effects on the progress of the reaction, but is limited to small systems. While a quantitative understanding of the CO₂ capture mechanisms is still lacking, the solvent regeneration process that may be the most energy intensive and least understood seems to be forgotten in most of the previous computational studies reported in the literature thus far. In addition, there are relatively few studies investigating how MEA and intermediates behave in bulk solution, and little understanding of how they may affect the ability of CO₂ to be captured or the solvent to be regenerated.

In this work, we investigate molecular mechanisms underlying the CO₂ capture by aqueous MEA and the solvent regeneration using combined QM and force field calculations. Using AIMD, we first identify the likely elementary reaction steps and intermediates taking into account the structural and dynamics effects in the MEA–CO₂–H₂O solution. We then use a static quantum chemical approach at the B3LYP/6-311++G level of theory to explain the events observed from AIMD in terms of the reaction energetics and the relative stability of intermediates. Thereafter we use classical molecular dynamics (CMD) to analyze the availability and arrangement of H₂O molecules around amine species, particularly intermediate zwitterions, and discuss its impact on the progress of the MEA–CO₂ reaction. We believe that this effort will help us to better understand the fundamental mechanisms for CO₂ capture and solvent regeneration, which will in turn assist in identifying the factors that could lead to the development of improved solvents.

II. Computational methods

A. Quantum mechanical calculation

We performed AIMD simulations within the Born–Oppenheimer (BO) approximation. The potential energy surfaces for AIMD were generated using density functional theory (DFT) within Perdew–Burke–Ernzerhof generalized gradient approximation (GGA-PBE), as implemented in the Vienna Ab initio Simulation Package (VASP). The projector augmented wave (PAW) method with a planewave basis set was employed to describe the interaction between the core and valence electrons. An energy cutoff of 400 eV was applied for planewave expansion of the electronic eigenfunctions. Only the gamma point was sampled for Brillouin zone integration.

B. Classical molecular dynamics simulation

CMD simulations were performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) program. We used a modified AMBER force field for MEA and its derivatives with the SPC/E water model, and obtained the atomic charges for MEA–CO₂ zwitterion, carbamate, and protonated MEA from QM calculations at the B3LYP/6-311++G level of theory; the force field parameters employed are available in ESI. All the bonds involving H atoms were constrained using the SHAKE algorithm. Spherical cutoffs of 10 Å and 12 Å were used for the Lennard-Jones and Coulomb interactions, respectively. Electrostatic interactions beyond the cutoff were calculated using the Ewald summation method. Simulations were run in the NVT ensemble with the temperature controlled by a Nosé–Hoover thermostat with a 100 fs damping parameter. Each simulated system was first annealed at 1000 K and then quenched to 323 K, followed by another anneal and quench cycle. Production runs were carried out for 0.7 ns with a timestep of 1 fs.

III. Results and discussion

A. Elementary reaction steps identified using AIMD

We first attempted to identify the possible elementary steps involved in the reaction of CO₂ with aqueous MEA. The aqueous MEA–CO₂ system has a large number of degrees of freedom and the static approach is often inadequate to accurately describe the complex solution structure and dynamics. AIMD simulations may help identify the likely events and the reaction intermediates; this approach has been proven to be a reliable option for the study of CO₂ absorption and proton transfer in aqueous amine solutions.

As presented in Fig. 1, we have identified four likely elementary reaction steps for CO₂ capture:

(a) CO₂ binding with the N of MEA to form the zwitterionic adduct [MEA + CO₂ → MEA·COO⁻].

(b) Deprotonation by H₂O from the zwitterion to form the carbamate and the solvated proton [MEA·COO⁻ + H₂O → MEACOO⁻ + H₂O⁺].

(c) Abstraction of the solvated proton by another MEA molecule to form the protonated MEA [MEA + H₂O⁺ + MEACOO⁻ → MEAH⁺ + H₂O + MEACOO⁻].

(d) Protonation of the O site of carbamate to form the carbamic acid [MEACOO⁻ + H₂O⁺ → MEACOOH + H₂O]; it is
found that the proton is subsequently transferred through a water bridge to nearby MEA to form MEAH⁺.

Looking at reaction (a), the polarized CO₂ in water adopts a bent configuration from its linear shape due to reordering of molecular orbitals (that causes increased charge separation between the C and O atoms, i.e., C becomes slightly more positive). The O–C–O bond angle decreases below 140° while the CO₂ approaches MEA to form a zwitterionic adduct (MEA⁺COO⁻). In the zwitterion, the interaction between C (of CO₂) and N (in MEA) seems to be weak as the C–N distance varies between 1.43 Å and 2.11 Å.

Our AIMD simulations were performed using a cubic box of side length 9.278 Å with periodic conditions; each simulation box consists of 2MEA, 1CO₂, and 20H₂O molecules, corresponding to ≈25 wt% aqueous MEA solution. The calculated density of 1.095 g cm⁻³ is in reasonable agreement with experiments.³⁶ We first relaxed the initial structure of system using CMD simulations, and then carried out AIMD simulations at 400 K to examine the reaction of CO₂ with MEA. Here, the relatively high temperature of 400 K was used to speed up the reaction so as to identify possible elementary reactions involved during the limited simulation time span (~100 ps). As discussed in the following sections, the elementary reactions identified are mainly governed by the arrangement and configuration of the involved species with no significant barriers, rather than the relative heights of activation barriers among possible events. Hence, raising the temperature would be an appropriate way of accelerating the reaction dynamics as it may not significantly alter the ratios of the
low-barrier rate constants; nonetheless, to minimize any potential temperature-induced biases, we ran several independent simulations by varying the initial distributions of constituent molecules. The same simulation conditions were employed for the cases (b)–(d).

In reaction (b), the N-bound proton is transferred to the water network through a close-by H$_2$O molecule; the deprotonation strengthens the C–N bond in the resulting MEACOO$^-$ . Our AIMD simulation shows that the deprotonation and the subsequent proton hopping happen rapidly. This suggests that the barrier for the deprotonation process would be insignificant if the local water arrangement allows the strong interaction between the acidic H (in MEA$'$COO$^-$) and O (in H$_2$O) atoms; indeed, our static QM calculations show that the deprotonation barrier can be less than 0.1 eV, depending on the water arrangement (vide infra). These results show the zwitterionic adduct to be the intermediate for the formation of stable carbamate, as also suggested by previous studies.$^{8,9}$

The solvated proton is found to undergo rapid migration following the Grothuss-like mechanism$^{37}$ until it is abstracted by an available basic site such as N in MEA (or MEACOO$^-$) or O in MEACOO$^-$ . As shown in Fig. 1(c), the proton binds to the N of MEA giving rise to an ion-pair [MEA$^+$/MEACOO$^-$/C0]. This is consistent with previous nuclear magnetic resonance (NMR) studies that show MEACOO$^-$ and MEAH$^+$ to be the major products of CO$_2$ capture in aqueous MEA.$^{38}$

Our AIMD simulations also show that a proton preferentially binds to the O of MEACOO$^-$, rather than the N site, forming carbamic acid, as illustrated in Fig. 1(d); this is because the O site is more easily accessible by neighboring H$_2$O molecules, as discussed in Section C. We also find that the proton in MEACOOH tends to be easily released and is eventually abstracted by MEA (if available) to form MEAH$^+$, implying that MEACOOH is another important intermediate, rather than a product.

Fig. 1(e) and (f) show the AIMD snapshots for CO$_2$ removal from MEACOO$^-$ (MEA regeneration). The simulation was run at 1000 K in order to accelerate the solution dynamics and thus the reaction; the high-temperature AIMD would not significantly bias the reaction, as reasoned earlier. Here, 2MEACOO$^-$ molecules, 20H$_2$O molecules, and 3 protons were placed in a cubic box of side length 9.364 Å. We observe the protonation of the N in MEACOOH forms an unstable protonated species followed by deprotonation from the O site to form a relatively more stable MEA$'$COO$^-$ ([e]). Then, as shown in Fig. 1(f), the alkanolamine chain is seen to reconfigure to the ring form, which allows the intramolecular H-bonding interaction between acidic H (in NH$_2$) and O (in OH), facilitating CO$_2$ removal. These results highlight how the competition between the intramolecular and intermolecular H-bonding interactions, as determined by the local water arrangement around NH$_2$, affects the MEA$'$COO$^-$ configuration and in turn the relative probability between CO$_2$ desorption and deprotonation.

We also estimated the reaction energy of CO$_2$ ($\Delta E_{\text{rxn}}$) in 30 wt% aqueous MEA by comparing the total energies of the reacted ($E_R$) and unreacted ($E_U$) systems from AIMD simulations (see Fig. S1, ESI†), i.e., $\Delta E_{\text{rxn}} = E_R - E_U$. Here, the reacted and unreacted systems consist of [1MEACOO$^-$, 1MEA$^+$, 16H$_2$O] and [2MEA, 1CO$_2$, 16H$_2$O], respectively; all simulation boxes were cubic with side lengths of 8.77 Å and periodic boundary conditions. Our calculations predict $\Delta E_{\text{rxn}}$ to be $-73.33 \pm 27.02$ kJ mol$^{-1}$ CO$_2$, although the sizes of the simulation systems are fairly small, the predicted $\Delta E_{\text{rxn}}$ is in reasonable agreement with the experimentally estimated value of $-89 \pm 4$ kJ mol$^{-1}$ CO$_2$ in 30 wt% MEA.$^{39}$

**B. Static QM analysis of fundamental MEA–CO$_2$ interactions**

In this section, we attempted to address the following fundamental questions raised from the AIMD simulations using static QM calculations.

- What is the driving force for the CO$_2$ capture by MEA?
- How does the CO$_2$ binding affect the deprotonation from MEA$'$COO$^-$?
- How does the arrangement of H$_2$O molecules affect the protonation/deprotonation and CO$_2$ capture/removal processes?

We analyzed the geometric and electronic structures of MEA and its derivatives and calculated the activation energy barriers for specific protonation/deprotonation reaction steps at the B3LYP/6-311++G level of theory.

The interaction of CO$_2$ and MEA represents a classical donor–acceptor interaction, wherein, CO$_2$ is the Lewis acid and MEA is the Lewis base. The anti-bonding (empty) orbital of CO$_2$ accepts electrons from the lone pair of N in MEA; the non-bonding molecular orbital is calculated to display about 26.84% s character and 73.16% p character in an aqueous system.

As shown in Fig. 2, in the QM study, we mostly considered open chain-like geometry for the considered amine species with two additional H$_2$O molecules; the explicit H$_2$O molecules were placed to form hydrogen bonds with the NH$_2$ and OH functional groups of the amines. When the N and O atoms are exposed to nearby H$_2$O molecules and form intermolecular H-bonding, the MEA and its derivatives are likely to adopt an open chain configuration to maximize the intermolecular H-bonding interactions. Note that, in contrast to this, if the water arrangement does not allow intermolecular H-bonding, the alkanolamine molecules attain stability by adopting a ring-like form which facilitates the intramolecular H-bonding interaction between N (or H) in NH$_2$ and H (or O) in OH.

In the MEA–CO$_2$ zwitterion (MEA$'$COO$^-$), the distance between C (of CO$_2$) and N (of MEA) is predicted to be 1.608 Å with a C–N vibrational frequency of 692.71 cm$^{-1}$. Note that the calculated vibrational frequency is somewhat perturbed by neighboring bonds, but the information is useful in understanding the nature of C–N interaction; in this case, the C–N bond is much weaker than a single C–N bond that typically shows a frequency greater than 1100 cm$^{-1}$. Once the C–N interaction is established, the N–H interaction is weakened with a concurrent depopulation of $\Pi_{\text{NH}}$ bonding orbitals that may facilitate deprotonation (MEA$'$COO$^-$ $\rightarrow$ MEACOO$^-$ + H$^+$).$^{10}$

Considering a simplistic picture, wherein the $\Pi_{\text{NH}}$ orbital is obtained by a constructive combination of the H 1s and N 2p orbitals, our QM calculation predicts the gross population of the $\Pi_{\text{NH}}$ orbital to reduce to 2.839 in MEA$'$COO$^-$ (from the 2.957 in MEA). In addition, natural bond order analysis was carried out using single points calculations with STO-3G basis set after the geometric optimization with B3LYP/6-311++G.
We obtained the following orbital coefficients and hybridizations for the two N–H bonding orbitals in MEA and MEA’COO⁻:

**MEA:**
- (1) 0.7715 N sp³.06 + 0.6363 H s and
- (2) 0.7718 N sp³.05 + 0.6359 H s

**MEA’COO⁻**:
- (1) 0.7895 N sp³.06 + 0.6138 H s and
- (2) 0.8090 N sp².74 + 0.5858 H s

In MEA, the coefficients corresponding to (1) and (2) are almost identical. Note that the slight difference in values results from the different orientation of H atoms (in NH₂) with respect to the OH group and the intermolecular H-bonding between N (of MEA) and H of (H₂O). On the other hand, in MEA’COO⁻, the N contribution in (2) is higher than (1) by 3.13%, indicating that the N–H(2) bond is more N-like and the acidic H may undergo relatively easy deprotonation.

MEA’COO⁻ is also reported to react with OH⁻ (or H₂O) and form bicarbonate (HCO₃⁻), but carbamide (MEACOOH) and carbamic acid (MEACOOH) may be more likely to form,¹⁷ as also shown earlier in our AIMD simulations [Fig. 2(d) and (e)]. The C–N distance of 1.39 Å in MEACOO⁻ is similar to 1.36 Å in MEACOOH, however a lower C–N vibrational frequency of 1280 cm⁻¹ (compared to 1578 cm⁻¹) in MEACOOH suggests that MEACOO⁻ yields a greater single bond like character; the predicted frequency value shows excellent agreement with the experimental value of 1322 cm⁻¹ (ref. 39). Another important product is protonated MEA (MEA²⁺) [Fig. 2(b)]. After deprotonation from MEA’COO⁻, the proton hopping through water bridges can facilitate proton abstraction by another MEA molecule.

Next, we estimated the relative binding strengths of proton and CO₂ in MEA’COO⁻ using the following formulas.

\[
  E_b(H^+) = E_M + E_{H^+} - E_{H^+/M}
\]

\[
  E_b(CO_2) = E_M + E_{CO_2} - E_{CO_2/M}
\]

where \(E_{H^+/M}\) and \(E_{CO_2/M}\) represent the total energies of the protonated and CO₂ bound species, respectively, \(E_M\) is for the species before proton/CO₂ binding, and \(E_{H^+}\) and \(E_{CO_2}\) are the energies of solvated proton and gas-phase CO₂, respectively. Here, \(E_{H^+}\) was calculated considering the difference in energies between a system with pure H₂O (5 molecules) and a system with one H₂O⁺ molecule and 4 water molecules; to verify the proton solvation energy, we also considered a system with H₂O⁺ cluster formation and the energy turned out to be similar. \(E_{H^+}\) is predicted to be 279 kcal mol⁻¹, very close to the experimental value of 270 kcal mol⁻¹.¹⁴

Predicted \(E_b(H^+)/E_b(CO_2)\) values are found to be sensitive to the H-bonding interactions in the system, as shown in Fig. 3. When considering a continuum implicit solvent model with no explicit H₂O molecule, for the open-chain configuration [[a]], \(E_b(CO_2)\) is predicted to be 0.38 eV while \(E_b(H^+)\) is significantly lower with a value of 0.19 eV; on the other hand, in the ring form [[b]], predicted \(E_b(CO_2)\) and \(E_b(H^+)\) values are 0.49 eV and 0.36 eV, respectively. The significant differences in \(E_b\) between the ring and open-chain configurations may stem from the additional intramolecular H-bonding interaction between H(1) (in NH₂) and O (in OH) in the ring form, as shown in Fig. 3(b); the resulting weakening of the N–H(1) bond in turn strengthens the N–H(2) and N–C (of CO₂) bindings.

As summarized in Fig. 4, for various configurations (see ESI†), we also calculated and compared the proton binding strengths at N in MEA (denoted as \(E_M\)) and N in MEACOO⁻ (N_C). The lower \(E_b(H^+)\) at the N_C site relative to the \(E_M\) site suggests the relative ease of deprotonation from MEA’COO⁻. In addition, we find that the deprotonation barrier can be insignificant provided the proton is linked to a well-connected water network; as shown in Fig. S3 (ESI†), our value of 0.08 eV is much smaller than 0.26–0.35 eV as recently reported by Guido et al.¹⁸ most likely due to different water arrangements around the amine species considered. We also consider direct proton transfer from MEA’COO⁻ to a nearby MEA, which turns out to be very facile with a negligible barrier provided they are in the...
right orientation (see Fig. S4, ESI†); however, solvation of MEA’COO\(^-\) is more likely in the 30 wt% MEA solution.

To better understand the key role played by neighboring H\(_2\)O molecules in facilitating proton transfer, we calculated the activation barriers for the proton transfer from one abstraction site to another mediated by one and two H\(_2\)O molecules, as displayed in Fig. 5. For the proton transfer from the N to the O atom in MEA’COO\(^-\), the activation barrier is substantially reduced from 0.67 eV to 0.40 eV as the process is mediated by two H\(_2\)O molecules [(b)], compared to the case with one H\(_2\)O molecule [(a)]. This result clearly demonstrates that the local arrangement of H\(_2\)O molecules may play a critical role in determining the protonation/deprotonation processes, although the simple model systems considered may not represent the complex reaction dynamics in the aqueous MEA–CO\(_2\) system. This warrants more systematic investigations regarding the influence of local water arrangement around amine species on the reaction of CO\(_2\) with aqueous amines; in the following section, we will attempt to touch on this issue rather briefly.

C. Effect of solvation environment in reaction progression studied using CMD

As seen from the above AIMD simulations, proton transfer may mainly occur through water bridges in the aqueous solvent. It is therefore expected that the arrangement of H\(_2\)O molecules around the basic N and O atoms, in addition to the proton binding energies at the base sites, will be an important factor in determining which sites are preferentially protonated.

The spatial arrangement of H\(_2\)O molecules around each protonation or deprotonation site was evaluated by calculating radial distribution functions (RDF) for selected pairs of atoms. Here, we considered N in MEA (denoted as N\(_M\)), N in MEACOO\(^-\) (N\(_C\)), and O of the CO\(_2\) moiety in MEACOO\(^-\) (O\(_C\)), and their
pairwise interactions with H in H$_2$O (H$_W$) to assess the protonation processes. Similarly, to understand the deprotonation reactions, we also looked at the pairwise interactions between acid H in MEAH$^+$ (H$_{N,PM}$) or MEA$^+$COO$^-$ (H$_{N,ZI}$) and O in H$_2$O (O$_W$).

In this work, two systems of different composition were taken into account to examine how the pairwise interactions will vary with the progress of the CO$_2$ capture by MEA. System 1 consists of 182MEA and 1517H$_2$O molecules in a $40 \times 40 \times 40$ Å$^3$ simulation box with periodic boundary conditions, corresponding to approximately 30 wt% aqueous MEA. System 2 contains 10MEA, 86MEAH$^+$, 86MEACOO$^-$, and 1517H$_2$O molecules in the same simulation box size, assuming that the aqueous MEA solution captures CO$_2$ to nearly 50% absorption capacity. In both systems, 10 additional MEA$^+$COO$^-$ intermediates were added; the model systems may not represent all possible composition variations during actual processing, but should be sufficient for understanding the influence of composition on the local arrangement of H$_2$O molecules around MEA and its derivatives.

Fig. 6 shows the RDF profiles for the H$_W$–N$_M$, H$_W$–N$_C$, and H$_W$–O$_C$ pairs in System 2 based on the CMD results at 323 K. The inset compares the g(H$_W$–N$_M$) between System 1 and System 2. g(r) was averaged from trajectories generated every 2 ps according to the following equation where $n(r, r + dr)$ is the number of atoms in a spherical shell of radius r (from the reference atom) and thickness of dr and $\rho$ is the bulk number density.

$$g(r) = \frac{n(r, r + dr)}{4\pi r^2 \rho dr}$$

All RDFs exhibit a distinct peak at a distance around 2 Å, due to the H-bonding interaction with the nearest H$_2$O neighbors, approaching 1 as the distance increases due to a lack of long-range ordering, as typically seen in liquid. The first peak intensity for the H$_W$–O$_C$ pair is predicted to be 2.79, and drops to 0.68 and 0.31, respectively, for the H$_W$–N$_M$ and H$_W$–N$_C$ pairs; note also that the first peak position increases from 1.74 Å to 1.86 Å and 1.98 Å. Although there is no experimental data available for the MEA–H$_2$O–CO$_2$ system, the MEA–H$_2$O interaction qualitatively agrees with other CMD simulations, and the SPC/E model of water has been shown to predict reliably the structure of pure water.

The higher intensity and closer position of the first peak of g(H$_W$–O$_C$) suggests that the terminal O$_C$ atoms are more likely to form H bonds with neighboring H$_2$O molecules, compared to the N$_C$ and N$_M$ atoms, and thus kinetically they can more easily abstract H$^+$ from the protonated water network. The significant reduction in the first peak intensity of g(H$_W$–N$_C$), in comparison to g(H$_W$–N$_M$), is primarily due to the bound COO$^-$ attracting H$_2$O molecules that would otherwise be interacting with N$_C$. As shown in the inset of Fig. 6, we also find that there is no significant change between System 1 and System 2 for g(H$_W$–N$_M$), suggesting that the interaction of N$_M$ with neighboring H$_2$O molecules is not strongly affected by varying amine composition at different stages of the CO$_2$ absorption process.

Fig. 7 shows the RDFs for the atom pairs of O$_W$–H$_{N,PM}$, O$_W$–H$_{N,ZI}$, and O$_W$–H$_{N,M}$ in System 2; here, H$_{N,M}$ indicates an H atom in the NH$_2$ functional group of MEA, which is included for comparison. The first peak intensities for the O$_W$–H$_{N,PM}$, O$_W$–H$_{N,ZI}$, and O$_W$–H$_{N,M}$ cases are estimated to be 1.27, 1.08, and 0.62, respectively; the peak positions correspondingly increase from 1.86 Å to 1.98 Å and 2.22 Å. According to the RDF analysis, the H$_N$ atoms of both MEAH$^+$ and MEA$^+$COO$^-$ are likely to more strongly interact with neighboring H$_2$O.
molecules compared to the MEA case, which is not surprising considering the more positively charged H_{N,PM} and H_{N,ZI} than the H_{N,M}. This result also suggests that deprotonation of MEAH^+ may be more kinetically favorable than that of MEA’COO^-, albeit insignificant; note that H_{N,PM} is freely exposed to surrounding H_2O molecules while H_{N,ZI} is somewhat shielded by COO^-. However, considering the substantially smaller E_{b}(H^+) at N_C compared to N_A (as shown in Fig. 4), we can expect that deprotonation from MEA’COO^- will be more facile than the MEAH^+ case.

From the inset of Fig. 7 which compares g(O_W-H_{N,ZI}) in System 1 and System 2, we can see a noticeable decrease in the first peak intensity from 1.33 (System 1) to 1.08 (System 2). This suggests that, as the reaction of MEA with CO_2 proceeds and thus more MEAH^+ and MEACOO^- are generated, the charged products tend to attract H_2O molecules, which in turn suppresses the H-bonding interaction between the H_{N,ZI} and O_W atoms. As a consequence, the likelihood of MEA’COO^- deprotonation to the H-bonded water network decreases.

As the H-bonding interaction with surrounding H_2O molecules dwindles, MEA’COO^- tends to be stabilized by forming an intramolecular hydrogen bond between H_{N,ZI} and O_{H,ZI} (of the OH group). The increased intramolecular H-bonding interaction suppresses deprotonation while enhancing CO_2 removal from MEA’COO^-, thereby facilitating MEA regeneration. Our study highlights the importance of the availability and arrangement of H_2O molecules, particularly around the zwitterionic intermediate, in the progression of competing CO_2 capture and MEA regeneration processes.

IV. Summary

We examined molecular mechanisms underlying the reaction of aqueous MEA with CO_2 using a combination of quantum mechanical and classical force field calculations, with particular attention to the structural and dynamics effects in the MEA-CO_2-H_2O solution. First, DFT-based AIMD was employed to identify key elementary reactions and intermediates. The simulation results clearly demonstrate that MEA reacts with CO_2 to form a zwitterionic intermediate. The zwitterion is found to undergo deprotonation predominantly by a close-by H_2O molecule in 25 wt% aqueous MEA considered. The solvated proton undergoes rapid migration following the Grothuss-like mechanism until abstracted by MEA (or carbamate) to form protonated MEA (or carbamic acid); the proton in carbamic acid tends to be easily released and is eventually abstracted by MEA (if available). We also found that carbamate may revert to the zwitterionic state by grabbing a proton. More interestingly, CO_2 tends to be released from the zwitterion, rather than deprotonation, if the acidic H (in NH_3) forms an intramolecular H-bond with O (in OH) instead of interacting with nearby H_2O molecules. Our AIMD results suggest that the competing intramolecular and intermolecular H-bonding interactions, as determined by the availability and arrangement of H_2O molecules around the zwitterion, directly impact the relative probability between CO_2 removal (MEA regeneration) and deprotonation (carbamate formation).

Next, we performed static quantum chemical calculations at the B3LYP/6-311++G level of theory to analyze in more detail the fundamental interactions involved in the MEA-CO_2 reaction. Our analysis of vibration frequencies and gross orbital populations unequivocally demonstrates that CO_2 is bound to MEA by forming a relatively weak C-N bond (compared to a C-N single bond); the CO_2 binding causes a significant weakening of the N-H interaction, which may in turn facilitate deprotonation from the zwitterionic intermediate. The CO_3 and proton binding energies in the zwitterion tend to be lower when it is in the open-chain relative to the ring configuration; in addition, the proton binding strengths at the different basic sites of MEA and carbamate are found to be sensitive to their configurations (which are mainly determined by the competing intramolecular and intermolecular H-bonding interactions). Our calculation also shows that the energy barriers for proton transfer can be significantly altered by the local arrangement of H_2O molecules.

Finally, we evaluated the spatial arrangement of H_2O molecules around MEA and its derivatives by calculating pairwise RDFs using CMD simulations. In particular, we looked at the pairwise interactions of H(O) in H_2O with basic N/O (acidic H) in MEA or carbamate (protonated MEA or zwitterion) to assess the protonation (deprotonation) processes, assuming that proton transfer primarily occurs through water bridges in the aqueous solvent as seen from our AIMD simulations. The results clearly show that the RDFs vary significantly for the different sites considered. For instance, the O of carbamate is more likely to be H-bonded with H_2O, and thus is more kinetically favored for protonation than the N of MEA (or carbamate), consistent with the trend observed in AIMD. We also found that the acidic H of zwitterion interacts less with the O of H_2O, as the reaction progresses and more charged products (such as protonated MEA and carbamate) are present; this may in turn lead to an increase in the intramolecular H-bonding interaction, thereby expectably suppressing deprotonation while enhancing CO_2 removal from the zwitterion. This study highlights the critical role of H_2O molecules, particularly their availability and arrangement around zwitterions, in the progression of competing CO_2 capture and MEA regeneration processes. This also suggests that an explicit description of the solution structure and dynamics on the atomic level would be crucial for elucidating the underlying mechanisms of CO_2 reaction with aqueous amines.

Acknowledgements

This work was supported by the Korea CCS R&D Center (KCRC) grant (No. 2014M1A8A1049270) funded by the Korea government (Ministry of Science, ICT & Future Planning) and the R.A. Welch Foundation (No. F-1535). We would also like to thank the Texas Advanced Computing Center for use of the Stampede supercomputing system (OCI-1134872). Helpful discussions with Gary T. Rochelle and Hoon Sik Kim are also greatly acknowledged.
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