LLNL-JRNL-434075

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June 4, 2010

Chemical Physics Letters

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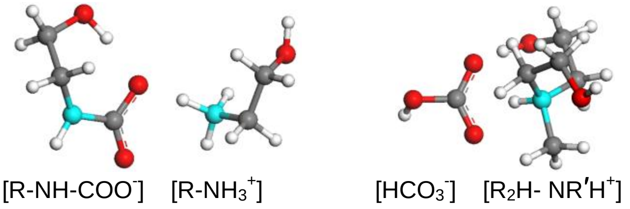
Of the various proposed post-combustion methods of carbon capture from large emission sources the most practical and economically viable method appears to be amine scrubbing, i.e., dissolution into aqueous solutions of amines.(1) The most widely studied amines in this regard, especially for small-scale applications, are primary amines like monoethanolamine (MEA) and tertiary amines like methyl-diethanolamine (MDEA). Such amines can be represented by the general chemical formula R-NR′-R″. For MEA: R = C_2H_4OH (ethanol), R′ = R″ = H; while for MDEA: R = R″ = C_2H_4OH, R′ = CH_3. The chemistry of CO_2 dissolution in these basic amines, including some knowledge of solubility and vapor-liquid equilibrium have been known for some time,(2)-(6) while more recently physical properties like density and viscosity as a function of CO_2 loading and temperature have been measured and fitted with correlation functions.(7),(8) Such knowledge, though important at engineering scale applications, requires significant experimental measurements and/or parameter development. For a cost-effective exploration of any new system, e.g., piperazines and modified amines,(9) as necessitated by larger-scale industrial applications, it is important to adopt faster, cheaper, and chemically aware strategies like atomistic modeling. Insights from such models can be used to optimize solubility and other solvent properties,(10) or in designing catalyst systems to speed up the CO_2 absorption and solvent regeneration processes.



(a) (b)

Figure 1. DFT-optimized Ion Pair structures formed by CO_2 absorption in: (a) MEA and (b) MDEA; R = C_2H_4OH; R′ = CH_3. Anions: MEA-carbamate $[R\text{-}NH\text{-}COO^-]$, bicarbonate $[HCO_3^-]$; Cations: protonated amines *p*-MEA $[R\text{-}NH_3^+]$, *p*-MDEA $[R_2H\text{-}NR'H^+]$. *Color scheme*: C (grey), N (blue), O (red), H (white).

In this communication we report our first set of results from atomistic modeling on MEA and MDEA, focusing on two types of properties associated with CO_2 chemisorption: (i) Gibb's free energy changes, and (ii) ion association and density changes. We employ both Density Functional Theory (DFT) based Quantum Chemical methods, and classical molecular dynamics (MD) simulations in realistic solvent environments. In addition to demonstrating quantitative accuracy, the results provide interesting insights into the nature of ions, hydration shells, volume changes upon CO_2 chemisorption, and the basic differences between primary and tertiary amines.

Before describing the simulation methods and results, we need to recognize that there are three ways in which CO_2 can potentially dissolve into an aqueous amine solution: (i) physical dissolution; (ii) chemical dissolution as carbamate ions; and (iii) chemical dissolution as bicarbonate ions. The present work is not about vapor-liquid equilibrium, but rather concerns determining the thermodynamically stable form of adsorbed CO_2. To this end our intention was to compute the Gibb's free energy change (ΔG) when a physically adsorbed CO_2 goes into one of the ionic forms, i.e., carbamate or bicarbonate. It is to be noted that in tertiary amines carbamates cannot form, while for primary (and secondary) amines both ionic forms are a possibility. Thus we studied the following three reactions:

$$CO_2 + 2\ MEA = MEA\text{-carbamate} + p\text{-}MEA\ ; \qquad (R1)$$

$$CO_2 + MEA + H_2O = \text{bicarbonate} + p\text{-}MEA\ ; \qquad (R2)$$

$$CO_2 + MDEA + H_2O = \text{bicarbonate} + p\text{-}MDEA\ , \qquad (R3)$$

where the CO_2 on the left-hand-side of each reaction is in the physisorbed form in the solution, and the "*p*-" prefix indicates a protonated amine, i.e, an ammonium center (Fig. 1). In order to calculate the ΔG of the above reactions, we used DFT to structurally optimize the ion pairs (IP) created upon carbamate and bicarbonate formation in MEA (with the carbamate-IP shown in Fig. 1(a)), and bicarbonate formation in MDEA (Fig. 1(b)). We employed all-electron DFT through the code Turbomole,(11) with the Becke-Perdew exchange-correlation functional and TZVP basis set as used previously.(12) An implicit, yet realistic representation of the solvent environment was carried out through the COSMO-RS methodology,(12),(13) which allows computation of many thermodynamic quantities, including Gibb's free energy.

Table 1 lists the computed ΔG of the three reactions of interest:

Reaction	Amine/water ratio	CO_2 loading*	ΔG (kcal/mol)
R1	0 wt% MEA	0.0	-17.9
	30 wt% MEA	0.0	-16.4
	30 wt% MEA	0.5	-16.8
R2	0 wt% MEA	0.0	-13.5
	30 wt% MEA	0.0	-11.9
	30 wt% MEA	0.5	-12.4
R3	0 wt% MDEA	0.0	-15.2
	45 wt% MDEA	0.0	-12.8
	45 wt% MDEA	0.5	-13.0

**Expressed as mole fraction of amine, with 0.0 indicating infinite dilution.*

Important results to note from Table 1 are: (1) all reactions in the *solution phase* are highly exothermic (i.e., $\Delta G < 0$), implying complete adsorption in the carbamate or bicarbonate forms at room temperature; for the same calculations in non-polar solvents like benzene (or vacuum) we obtain *positive* values of ΔG, consistent with poor solubility; (2) the presence of amine lowers the magnitude of ΔG, although by a small amount, while it increases slightly as a function of CO_2 loading; (3) carbamate formation in MEA (R1) is energetically more favorable than bicarbonate formation (R2). However, the magnitude of ΔG in R_2 is *more than half* of that in R_1. Since carbamate formation involves 2 amine molecules while bicarbonate involves only 1, the above fact implies that up to about 0.5 CO_2 loading carbamate should be the primary species, while above 0.5 loading the bicarbonate fraction should increase monotonically, with bicarbonate being the only anionic species at a CO_2 loading of 1. Such a picture is indeed consistent with the results of more elaborate chemical engineering models.(5)

We should add that all calculations in Table 1 were performed assuming charge-neutral *ion-pairs* (IP) rather than individual dissociated ions as products. To check whether such an assumption is realistic, we performed classical MD simulations on two systems, i.e., a 30 wt% MEA solution and a 45 wt% MDEA solution, each represented by 3D periodic cubic supercells of 50 amine and 400 water molecules. The inter-atomic interactions were represented by a state-of-the-art class II forcefield COMPASS,(14) specifically parameterized for condensed-phase systems like liquids. We carried out 100 ps simulations in the *NPT* ensemble under ambient conditions employing the Anderson thermostat and barostat,(15) which preserves the cell shape during volume change.

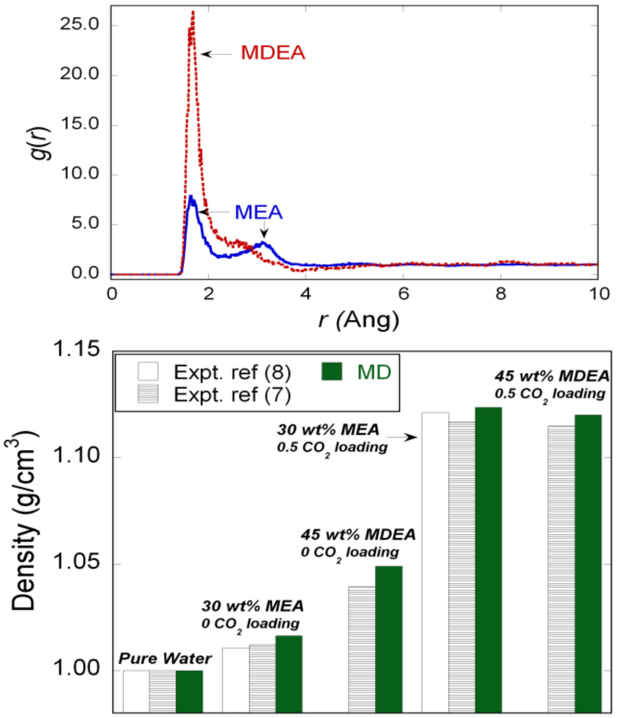


Figure 2. (top) MD-averaged radial distribution function $g(r)$ between a cationic H bonded to N and an anionic O in the COO^- group. Sharp peaks indicate strong ionic association. (bottom) Effect of CO_2 capture on the density of various aqueous amine systems -- molecular dynamics (MD) results compared with available experimental data.(7),(8)

Our MD analysis focused on two quantities of interest: (1) the nature of ionic association, and (2) volume and density changes upon CO_2 loading. Fig. 2(top) plots the radial distribution function $g(r)$ (averaged over the whole simulation) between an amine H on the cation and a carbamate (or bicarbonate) O on the anion. The sharp peak structures indicate strong association between all IP in the simulation cell during the entire simulation, as also becomes apparent by watching the animation of MD trajectory (see supplementary material). Fig. 2 (bottom) summarizes the MD results on density changes upon 0.5 CO_2 loading in both the MEA and the MDEA systems. In accordance with the ΔG results discussed above, we assumed IP involving only carbamate species in MEA and only bicarbonate species in MDEA. We note that the experimental density increases by roughly 10.7% and 7.3% in MEA and MDEA respectively, with each CO_2 molecule adding a net volume of only 2.8 and 9.0 Å^3 respectively. The simulation results are in good agreement with the experimental density values.(7),(8) More specifically, it correctly predicts the higher density increase in MEA as compared to MDEA. Such density changes are pivotal to the design of novel capture approaches under consideration within our group.

Finally, we note that the higher density increase in MEA is somewhat counterintuitive because smaller bicarbonate ions in MDEA are expected to have a tighter solvation shell.(7) However, given that the MD simulations reveal strongly associated IP, such arguments in terms of individual ions can be misleading. To gain more insight, we analyzed the molar volumes of solvated shells of isolated amine molecules and the corresponding IP (see Fig. 3 for the solvated structure of MEA-IP). Such analysis, which corresponds to low CO_2 loading levels, yields a volume increase of ~ 13 and 25 Å^3 per chemisorbed CO_2 in MEA and MDEA respectively, consistent with a higher density increase in MEA.

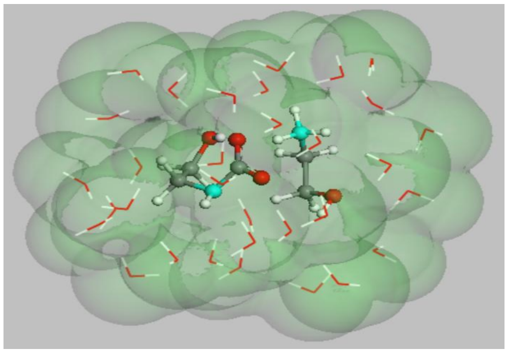


Figure 3. A solvation shell of 32 water molecules around an isolated MEA-IP along with the solvent-accessible isosurface. For visual clarity, the MEA ions are shown in ball and stick while the water molecules are in stick representation. *Color scheme*: same as in Fig. 1.

In summary, atomistic simulations through DFT-based solvation models and classical MD were used to obtain a number of important results for CO_2 absorption chemistry in primary and tertiary amines, including the relative fraction of ion species, nature of ionic association, and density and volume changes as a function of CO_2 loading. All simulation results are in excellent agreement with available experimental data, thus validating the accuracy and power of such computational methods in predicting properties of new solvent systems and capture designs.

Acknowledgement. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

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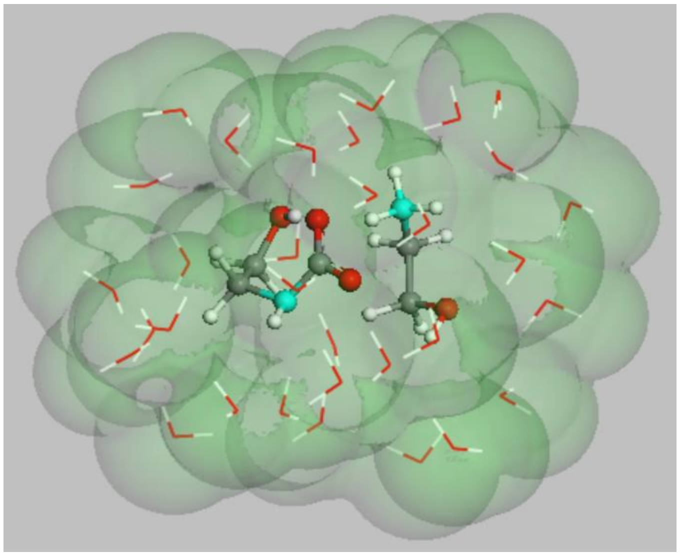

With the aim of exploring new amine-based chemistry for CO_2 capture applications at large industrial scale, we performed atomistic modeling of CO_2 chemisorption in aqueous solutions of primary and tertiary amines. DFT-based quantum chemical solvation models and classical molecular dynamics in explicit solvent environments were shown to yield a number of important results, including the relative fraction of ion species (carbamate and bicarbonate), nature of ionic association, and density and volume changes as a function of CO_2 loading. Simulation results are in excellent agreement with available experimental data, thus validating the accuracy and power of such computational methods in predicting properties of new solvent systems and capture designs.