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Investigation of Ideal Reaction Conditions for Optimal CO_2 Absorption using Amino Acid Salt Solutions
Category: Chemistry
Research Plan

a. **RATIONALE:**

The world currently faces the pressing issue of global warming and increased greenhouse emissions. Carbon dioxide (CO_2) is the most common one given its prominence in the atmosphere, especially due to the combustion of fossil fuels for transportation and electricity.[1] In 2018, the International Energy Agency reported that global CO_2 emissions increased by 1.7%, and CO_2 emissions from combustion were directly at fault for over 0.3°C of each 1°C increase in global average annual surface temperatures.[2]

To reduce emissions, researchers have focused on post-combustion capture, the most commonly used technique of carbon capture and storage technology.[1] The government recognizes it as responsible for absorbing 80-90% of CO_2 emissions from fossil fuel-fired power plants.[3] Other methods of carbon capture and storage would require additional steps to be implemented into current power plants, whereas post-combustion capture does not, so it is the most practical and economical approach to reduce CO_2 emissions into the atmosphere.[4]

Scientists search for the best method to absorb CO_2 within post-combustion capture. Through both experimental and computational procedures, researchers have determined that amine solutions, often derived from ammonia, are effective at absorbing CO_2.[4] Unfortunately, they work poorly at high temperatures and often produce toxic byproducts that harm the environment.[3,5] An ideal CO_2 absorbent would be efficient at high temperatures, and it would have low volatility, little oxidative degradation, high CO_2 capture capacity, and low activation energy. In addition, the substance would be environmentally friendly.[4] Since amine solutions

lack some of these characteristics, scientists are attempting to find a replacement. With a low volatility, ensuring that less solvent would be lost to the atmosphere upon desorption, and a heightened resistance to oxygen degradation, amino acid salt solutions (AAS) are attractive prospects for CO_2 capture.[1,6] Even better, AAS are naturally occurring.[1] The AAS possess some ideal properties, but researchers hope to show that the remaining ones exist.

While experiments have been done on AAS, computational chemistry has recently been utilized to investigate them. Computational chemists simulate computer models that apply thermodynamics and quantum mechanisms to understand chemical reactions and molecules. Often, Monte Carlo (MC) simulations are run, which employ random moves of the particles, including translations and rotations, to create snapshots of the reaction.[4] Within MC, the reaction ensemble Monte Carlo method (RxMC) informs about the equilibrium state of chemically reacting systems, including solutions at extreme conditions.[7–9] The RxMC is favored because the reaction mechanism can be unknown, useful in this scenario since there is ambiguity regarding the stages of amino acid and CO_2 reactions. The input for the RxMC includes the structure, connectivity, partial charges, and forces on and between molecules.[7] The output states the equilibrium concentrations of molecules and the average properties of the system.[9] By using MC, researchers can more quickly test theories regarding CO_2 and amino acid reactions, like the effects of extreme conditions, with greater efficiency and lower costs than if done experimentally.[7] Using predictions from computational chemistry, researchers hope to identify a way to reduce global warming more quickly and accurately, with a focus on implementation in power plants and laboratories.

b. **RESEARCH QUESTION (S), HYPOTHESIS (ES), ENGINEERING GOAL (S), EXPECTED OUTCOMES:**

The goal of this research is to use computer simulations of single amino acid solutions to investigate how temperature, CO_2 loading, and the amino acid concentration in water can affect CO_2 absorption. It will examine amino acid solutions rather than AAS, but the properties of amino acids that are deduced can be applied to the reaction between AAS and CO_2. This is because the amine group of the amino acid rather than the cation of the ion interacts with CO_2. With the study, the RASPA program will be implemented to run RxMC simulations. Prior research that considered temperature primarily viewed amines in a laboratory setting, testing only up to approximately 308 K.[10,11] Moreover, as aforementioned, amine solutions are inefficient at high temperatures, but this study hopes to show that AAS are more effective. Furthermore, the research will examine the capacity of the amino acids to absorb CO_2 with variable loadings of the molecule. A CO_2 loading refers to the ratio of moles of CO_2 compared to moles of the amino acid within the reaction.[12] Finally, the research will determine how the concentration of the amino acid can impact the ability of the solution to reduce CO_2 emissions. The study hopes to see decreases in the equilibrium concentrations of CO_2.

By assessing how each amino acid interacts with CO_2 at various reaction conditions, the research hopes to identify the optimal conditions for maximum CO_2 absorption. More importantly, scientists could more easily understand which solutions should be implemented in power plants or other fuel-consuming institutions.

c.

- **Procedures:** The RxMC simulations will be executed using the RASPA 2.0 software. To run it, the MobaXterm terminal, Personal Edition version 10.8, will be implemented. This software can be downloaded on either a Windows or Mac machine.

This study will be examining computer versions of several molecules, including the active, protonated, and carbamate forms of the following amino acids: glycine, lysine, alanine, proline, and glutamate. In addition, H_2O (water), CO_2, H_3O (hydronium) and bicarbonate are involved. These five amino acids serve as a strong representative sample of all amino acids. Glycine is the smallest amino acid, with only H for its functional group, lysine is basic, proline has a secondary amine because of the ring structure it has, alanine has a methyl functional group, and glutamate is acidic. In order to run the program, pre-defined files that explain the molecular structure, connectivity, interactions, and partial charge on the molecules are implemented. The molecular definition files specify structure and connectivity, or bonding. Force field files discuss interactions, and the pseudo-atom files explain the partial charges of each atom in the molecules.

Before creating code, first determine what values of amino acid concentration, temperature, and CO_2 loading will be tested. The concentration will be investigated at 0.3 wt %, 0.6 wt %, and 0.9 wt %. The unit of measurement is weight percentage in decimal form (wt %), indicating the fraction of the total mass that the amino acids will comprise. Calculations will also be made for a 0.5 wt % concentration, but this will not be in the concentration domain. Instead, at 0.5 wt %, there are at least ten amino acid molecules for every amino acid, which simplifies the division and rounding when calculating the number of CO_2 molecules. The constants for the concentration trials will be 298.15 K (room temperature) and a CO_2 loading of 50%. Temperature will be tested from 298.15 K to 348.15 K at 10 degree Kelvin increments. During the temperature trials, concentration will remain at 0.5 wt % and the CO_2 loading will be 50%. Finally, CO_2 loading will be examined at 25%, 50%, 75%, 100%, and 125%. The concentration will be 0.5 wt % with a temperature of 298.15 K when CO_2 loading is examined.

For each test, the number of H_2O molecules, amino acid molecules, and CO_2 molecules must be found. To find the number of amino acid molecules for particular concentrations, first fix the H_2O molecules at a particular number. This study will use 100 H_2O molecules for every simulation. Next, the molar mass of H_2O and the amino acid in the calculation will be determined. Solve for the number of amino acid molecules at a particular concentration using

$$Amino\ Acid\ Concentration\ (wt\%) = \frac{X_m\ (\frac{M_x}{N_A})}{X_m\ (\frac{M_x}{N_A}) + Y_m\ (\frac{M_x}{N_A})} \quad (1)$$

where N_A is Avogadro's number at 6.022 x 10^{23} molecules per mole, X_m is the number of amino acid molecules, M_x is the molar mass of the amino acid molecule in grams, Y_m is the number of water molecules, and M_y is the molar mass of a water molecule in grams.

After calculating X_m, it will be rounded to the nearest whole number since the reaction cannot use a fraction of a molecule. The CO_2 loading in the concentration trials will be fixed at 50%, so divide the unrounded X_m by two, and then round to the nearest whole number to determine the number of CO_2 molecules.

For the CO_2 loading trials, use the unrounded X_m from a 0.5 wt % concentration. Solve for the number of CO_2 molecules using

$$CO_2\ Loading\ (\%) = \frac{Z_m}{X_m}\ x\ 100 \quad (2)$$

where Z_m represents number of CO_2 molecules. Using the rounding rule, Z_m will be made into a whole number. The molecules used in the temperature trials will be those at a concentration of 0.5 wt % and a CO_2 loading of 50%, so calculate accordingly. All of the calculated initial values will be compiled into a table to help identify which numbers need to be adjusted for each task.

The initial values will be entered into the pre-defined simulation input files. The files will contain a field for initial concentrations of each molecule, so these will be modified to match the

calculated values. To alter temperature, the researcher will change the value listed at the ExternalTemperature method.

To represent the system, the RxMC method creates a box. At the method BoxLengths, this box dimensions should be set to 25 by 25 by 25, unless there are over 100 molecules of any substance. If this is the case, the box dimensions should be increased by five on each side. Prior to the beginning of the job, molecules are randomly inserted into the to ensure that there is enough space for all without any overlap. In some cases, this process fails, but the job continues to run. To avoid this issue, check the simulation folder once the job begins to ensure that output folders have been created. If they have not, cancel the job, increase the box dimensions by five units on each side, and then re-submit the simulation.

The RxMC method should be coded to complete 1,000 initialization cycles and 20,000 production cycles. The initialization runs generate a suitable mixture of the molecules, which helps determine the equilibrium properties of the solution once the production runs begin. Next, the production runs begin, where the RxMC method examines three particular reactions between CO_2 and an amino acid. The equations below show glycine. $Glycine_a$ is the active form, $glycine_p$ is the protonated version, and $glycine_c$ is the carbamate form. Hydronium molecules, though not shown, are added to both sides in order to balance charges since they act similarly to protons. The goal of the reactions is to reduce CO_2 with amino acids, which convert it carbamate and bicarbonate. This can occur directly as indicated by Equation 3, showing carbamate formation, and Equation 5, demonstrating base-catalyzed bicarbonate formation. However, depending on the stability of the carbamate, Equation 2 indicates how carbamate can hydrolyze to create bicarbonate and the active form of the amino acid.

$$CO_2 + 2\ glycine_a^{-1} \leftrightarrow\ glycine_p +\ glycine_c^{-2} \tag{3}$$

$$H_2O + glycine_c^{-2} \leftrightarrow glycine_a^{-1} + HCO_3^{-1} \quad (4)$$

$$CO_2 + H_2O + glycine_a^{-1} \leftrightarrow HCO_3^{-1} + glycine_p \quad (5)$$

These reactions are represented in the RASPA code, as during the production runs, the RxMC randomly selects a reaction and a forward or reverse direction during each cycle. The simulation then randomly removes either reactants or products and inserts the opposite molecules into the system to test whether the reactions satisfy thermodynamic properties.[7] If the so-called acceptance algorithm is fulfilled, the RxMC continues running it, eventually finding the equilibrium concentrations and properties of the system. If the algorithm fails, it re-randomizes the reaction. Finally, the simulation returns histogram values of the equilibrium concentrations, which should be recorded for later analysis.

- **Risk and Safety:** Because this study only requires a computer, the only risk is extensive screen time. To evade headaches and fatigue, avoid working for too many consecutive hours. Short, frequent breaks can reduce the negative impacts of the computer screen.
- **Data Analysis:** Using the initial and equilibrium concentrations, calculate the mole fraction of the molecules of the initial and equilibrium states. The mole fraction allows a scientist to see what part of a solution a molecule comprises, which allows the various solutions to be easily compared. The most important molecules in the reaction are the active and carbamate forms of the amino acid, bicarbonate, and CO_2, so the mole fractions will only be calculated for them. On the other hand, the protonated amino acid, H_2O, and H_3O serve to create and balance the solution. To calculate the initial mole fraction (I_{mf}), sum all of the reactant molecules together, and then use the following formula

$$I_{mf} = \frac{M_i}{T_i} \quad (6)$$

where M_i is the number of molecules of a substance in the initial state and T_i is total number of initial molecules. To find the equilibrium mole fraction (E_{mf}), plug into the equation

$$E_{mf} = \frac{M_e}{T_e} \tag{7}$$

where M_e is the number of molecules of a substance in the equilibrium state and T_e is total number of equilibrium molecules.

The mole fractions will be compiled into a table, and they will allow the researcher to compare reactions and identify ones that reduce the presence of CO_2 in the solution at the largest degrees. The study will then calculate the mole difference between the E_{mf} and I_{mf} through subtraction. By doing this, the research will be able to isolate the reaction mixtures that generate the greatest differences in CO_2. This will be computed for each amino acid separately, but all of the differences will then be viewed in one data set. Excel will be used to create visual representations of the results. Ultimately, through this analysis, the research hopes to be able to identify the reaction most effective at absorbing CO_2.

d. **BIBLIOGRAPHY:**

(1) Zhang, Z.; Li, Y.; Zhang, W.; Wang, J.; Soltanian, M. R.; Olabi, A. G. Effectiveness of Amino Acid Salt Solutions in Capturing CO2: A Review. *Renew. Sustain. Energy Rev.* **2018**. https://doi.org/10.1016/j.rser.2018.09.019.

(2) IEA. *Global Energy and CO2 Status Report*; 2018.

(3) Wei, S. C. C.; Puxty, G.; Feron, P. Amino Acid Salts for CO2capture at Flue Gas Temperatures. In *Energy Procedia*; 2013. https://doi.org/10.1016/j.egypro.2013.05.134.

(4) Yang, X.; Rees, R. J.; Conway, W.; Puxty, G.; Yang, Q.; Winkler, D. A. Computational Modeling and Simulation of CO 2 Capture by Aqueous Amines. *Chemical Reviews*. 2017. https://doi.org/10.1021/acs.chemrev.6b00662.

(5) Lerche, B. M. *CO2 Capture from Flue Gas Using Amino Acid Salt Solutions : Ph. D. Thesis*; DTU Chemical Engineering, Department of Chemical and Biochemical Engineering, 2012.

(6) Guo, D.; Thee, H.; Tan, C. Y.; Chen, J.; Fei, W.; Kentish, S.; Stevens, G. W.; Da Silva, G. Amino Acids as Carbon Capture Solvents: Chemical Kinetics and Mechanism of the Glycine + CO2 Reaction. *Energy and Fuels* **2013**. https://doi.org/10.1021/ef400413r.

(7) Turner, C. H.; Brennan, J. K.; Lisal, M.; Smith, W. R.; Karl Johnson, J.; Gubbins, K. E. Simulation of Chemical Reaction Equilibria by the Reaction Ensemble Monte Carlo

Method: A Review. *Mol. Simul.* **2008**. https://doi.org/10.1080/08927020801986564.
(8) Dubbeldam, D.; Calero, S.; Ellis, D. E.; Snurr, R. Q. RASPA: Molecular Simulation Software for Adsorption and Diffusion in Flexible Nanoporous Materials. *Mol. Simul.* **2016**. https://doi.org/10.1080/08927022.2015.1010082.
(9) Dubbeldam, D.; Torres-Knoop, A.; Walton, K. S. On the Inner Workings of Monte Carlo Codes. *Mol. Simul.* **2013**. https://doi.org/10.1080/08927022.2013.819102.
(10) Simons, K.; Brilman, W.; Mengers, H.; Nijmeijer, K.; Wessling, M. Kinetics of CO2 Absorption in Aqueous Sarcosine Salt Solutions: Influence of Concentration, Temperature, and CO2 Loading. *Ind. Eng. Chem. Res.* **2010**. https://doi.org/10.1021/ie100241y.
(11) Littel, R. J.; Versteeg, G. F.; Van Swaaij, W. P. M. Kinetics of CO2 with Primary and Secondary Amines in Aqueous Solutions-I. Zwitterion Deprotonation Kinetics for DEA and DIPA in Aqueous Blends of Alkanolamines. *Chem. Eng. Sci.* **1992**. https://doi.org/10.1016/0009-2509(92)80319-8.
(12) Kim, Y. E.; Lim, J. A.; Jeong, S. K.; Yoon, Y. Il; Bae, S. T.; Nam, S. C. Comparison of Carbon Dioxide Absorption in Aqueous MEA, DEA, TEA, and AMP Solutions. *Bull. Korean Chem. Soc.* **2013**. https://doi.org/10.5012/bkcs.2013.34.3.783.

1. **Human participants research:** Not applicable
2. **Vertebrate animal research:** Not applicable
3. **Potentially hazardous biological agents research:** Not applicable
4. **Hazardous chemicals, activities & devices:** Not applicable

NO ADDENDUMS EXIST