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# Modeling biomimetic absorbent compounds for capturing carbon dioxide

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## ABSTRACT

Carbon capture and storage is a critical component of negative emission technologies for achieving economy-wide carbon neutrality to mitigate climate change and limit global temperature increase. Removal of $CO_2$ can be undertaken after the standard pollution controls. Yet, the separation of $CO_2$ from flue gas via $CO_2$ capture processes is challenging because a high volume of gas must be treated, the $CO_2$ is dilute, the flue gas is at atmospheric pressure, trace impurities can degrade capture media, and the captured $CO_2$ must be compressed. We present a computational study of a novel family of biomimetic materials for such carbon capture processes based on the Crassulacean Acid Metabolism. Phosphoenolpyruvate serves as a template for designing similar molecules for use as $CO_2$ solvents with designed thermochemical properties.

## 1. Introduction

Carbon capture and storage (CCS) is considered a critical component of negative emission technologies (NETs) for achieving economy-wide carbon neutrality to mitigate climate change and limit global temperature increase [1]. Burning fuels (e.g., coal, methane, oil, and biomass) by combustion produces a flue gas containing a mixture of gaseous (primarily $N_2$, $CO_2$, and $H_2O$) and particulate matter (PM) components as byproducts. Removal of $CO_2$ can be undertaken after the standard pollution controls. Yet, the separation of $CO_2$ from flue gas via $CO_2$ capture processes is challenging because a high volume of gas must be treated, the $CO_2$ is dilute, the flue gas is at atmospheric pressure, trace impurities can degrade capture media, and the captured $CO_2$ must be compressed.

In principle, the gas separation technologies which are currently used in the chemical industry, such as absorption in chemical solvents, can be adapted for post-combustion capture (PCC) of $CO_2$. A 30wt% aqueous solution of monoethanolamine (MEA) is considered the benchmark solvent for regenerative chemical absorption-based PCC. The process relies on aqueous phase chemistry between an organic base (amines) and acid gas ($CO_2$), and is by far the most heavily studied, technologically mature, and economically viable approach [2].

A major drawback of amine-based systems is that they are energy intensive and thus significantly increase operational costs. The benchmark for new and emerging technologies in terms of cost, energy penalty, $CO_2$ capture efficiency, and physicochemical properties is MEA. $CO_2$-loaded MEA solutions are also corrosive to process infrastructure and degrade rapidly.

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Inevitably, some of these will be lost to the atmosphere where they react to form toxic compounds. In addition, amines contain nitrogen so require nitrogen fixation to manufacture, which is very energy intensive, countering the whole point of carbon capture. MEA also requires high solvent circulation rates, which leads to large equipment sizes and high energy consumption, making the technology capital and operating expenditures unacceptably high. There is a need for cost-effective alternative solvents to reduce the energy penalty and costs of $CO_2$ capture with absorbents for wide-scale commercial deployment of PCC-based CCS technologies [3].

The present disclosure is predicated on the discovery that bioinspired carbon capture compounds can replace amines in CCS processes and systems. The present inventors built upon a regenerative chemical absorption carbon capture system utilized by a unique group of plants that have adapted to arid climates using a process called Crassulacean Acid Metabolism (CAM) where, to conserve water, the plants uptake $CO_2$ by opening their stoma at night, rather than the day, and then immediately react it with another compound, phosphoenolpyruvate (PEP), to store the $CO_2$ overnight [4]. The reaction is reversed in the morning when the sun rises, releasing the $CO_2$ to participate in photosynthesis. For the present disclosure, PEP serves as a template for designing similar molecules for use as $CO_2$ solvents with thermochemical properties that address one or more of the drawbacks of MEA, facilitating CCS technologies, including in PCC absorber-stripper systems. As PEP itself might not be the ideal chemical compound we are also testing a few variants where simple side groups are added.

## 2. Computational Methods

ReaxFF is a reactive force field that allows bond formation and dissociation and therefore can model chemical reactions which most other force fields cannot do. The total system energy is comprised of bonded energies which depend on bond order as well as non-bonded energies. [5,6]. Bond orders (BO) are continous functions of interatomic distances. At infinite distances they are zero and they increase with decreasing sepration, they are used to mimick the chemical bond orders. Van der Waals and Coulomb interactions are also included for all atom pairs, where a shielding term avoids close range non-bonded interactions. Additionally polarization effects are considered [7,8].

The ReaxFF force field ff.P/N/C/O/H/Na [9] was used as starting point for our optimization. Water parameters were unchanged from Ref. [10]. Other parameters were re-parametrized see Ref [11]. The resulting force field describes the relevant reactions and thermodynamics very well. Detailed simulation conditions are shown in Table 1.

Table 1: Simulation Parameters

| Weight% PEP | #PEP (neutral) | #PEP ions | # Water |
|---|---|---|---|
| 31.93 | 92 | 408 | 9940 |
| 39.49 | 113 | 387 | 7145 |
| 45.83 | 129 | 371 | 5612 |
| 48.23 | 137 | 363 | 5005 |
| 49.49 | 141 | 359 | 4759 |
| 50.41 | 144 | 356 | 4587 |
| 51.76 | 148 | 352 | 4346 |
| 52.77 | 150 | 350 | 4173 |
| 54.62 | 156 | 344 | 3874 |
| 56.64 | 162 | 338 | 3569 |
| 58.81 | 168 | 332 | 3266 |
| 59.99 | 172 | 328 | 3110 |

All MD simulations were performed in LAMMPS [12]. 24 PEPs were randomly distributed in 520 waters to create a 30wt% PEP solution. PEPs and bicabonates started neutral for initial equilibration. Added Counter ions ensure charge neutrality. Pressure fluctuations converted some carbonic acids to $CO_2$, so in order to have enough bicarbonates to react with PEP, 36 bicarbonates were used. The initial box contained 520 $H_2O$, 24 neutral PEP, 36 carbonic acid, 108 $H_3O^+$ and 108 $OH^-$, and was first equilibrated in the canonical (NVT) ensemble for 20 ps at 300 K, and subsequently in the isothermal-isobaric (NpT) ensemble for another 25 ps at 300 K and 1 atm. Temperature was maintained using a Nosé-Hoover thermostat with a damping parameter of 25 fs, and pressure was maintained using a Nosé-Hoover barostat with a damping parameter of 250 fs. Then 6 PEP were transformed to $PEP^{3-}$, protons were removed from 9 carbonic acid to create 9 bicarbonate, together with 27 $OH^-$, and the system was equilibrated in NPpT for 10 ps. This deletion and equilibration process was repeated 4 times. Then the resulting system was simulated with full reactions allowed for 2 ns in NPT at 300 K and 1 atm. Time steps of 0.25 fs were used for all the NVT and NpT runs.

## 3. Results and discussion

### *Enthalpy of Mixing*

First the enthalpies of mixing were determined. For that one simply compares the enthalpies of the mixed

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system with the weighted (by their mole fractions x) unmixed enthalpies which are direct simulation outputs.

$$\Delta H = H_{mix} - x_1 H_1 - x_2 H_2 \qquad (1)$$

A solubility curve for aqueous PEP solutions was generated and demonstrates the expected features. As PEP is charged and polar, it has an energy minimum at a high concentration of about 50 wt% in water, which corresponds to a mole fraction of about 10%. This puts it slightly below the commonly used MEA concentration of 11%. The wide energy minimum is indicative of good solubility over a range of conditions.

*Solution Structure*

With increasing PEP concentration no significant local structural changes were observed in the radial distribution functions (RDF) of water around PEP (cf. Figure 1). The first peak in the RDF increases with PEP conncentration. This can be explained as higher concentrations contain fewer waters; thus, increasing fractions of the total water participates in PEP hydration shells and indicating a slightly better solubility of PEP with decreasing water. The lack of any significant change in RDF implies that the structure of the hydration shells is independent of concentration and correspondingly the solvation mechanism is unchanged. No indications of structural transition or unmixing were observed.

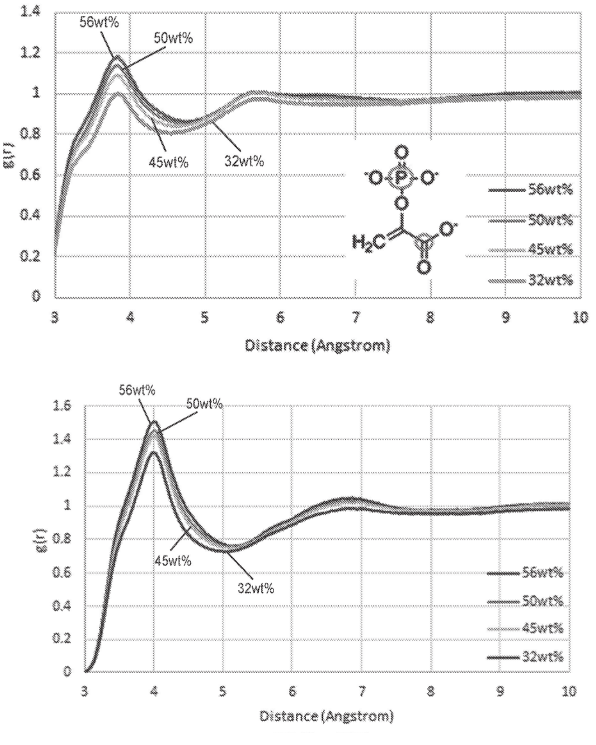

Fig 1: Radial Distribution Functions of water around the carbon (Top) and phosphorous (Bottom) atoms of PEP.

*Viscosity*

Figure 2 shows viscosity as a function of %wt. aqueous PEP concentration determined using the Green-Kubo relation.

$$\eta = \frac{V}{k_B T}\int_0^\infty \langle P_{xy}(0)P_{xy}(t)\rangle dt \qquad (2)$$

The values obtained were about 50% below the experimentally expected value where available. This is not unusual for simulations of this type [13]. The value obtained for pure water was 0.342 millipascal-second (mPa·s), whereas its expected value is around 0.79. Simulations of a 30% wt. aqueous MEA solution were also performed to compare relative numbers and was found to have a value of 0.647 mPa*s. found to have a value of 0.647 mPa*s (marked as x in Figure 2), against a literature value of 1.536 mPa*s [14].

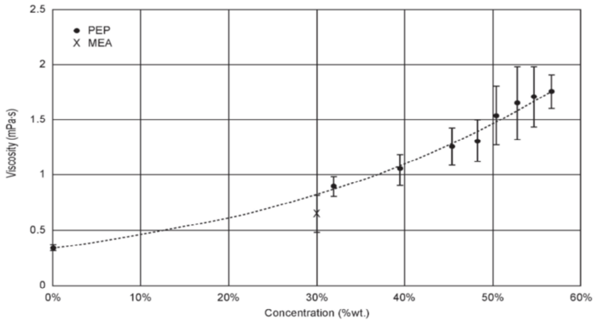

Fig 2: Viscosity of Water PEP mixtures as a function of concentratrion. The 30% water MEA mixture (marked as x) is added for comparison.

*Diffusion Coefficient*

The mean square displacement over time was used to calculate the diffusion coefficient of PEP over a range of concentrations.

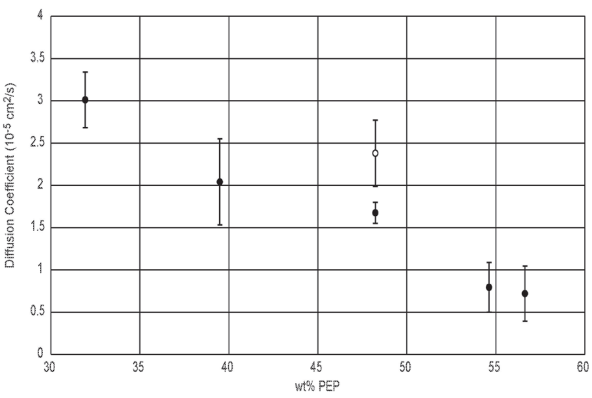

Fig. 3: Diffusion coefficient as a function of the PEP concentration ranging from 30 to 60 % by weight.

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Fig. 3 shows the diffusion coefficient as a function of the PEP concentration ranging from 30 to 60 % weight. At 48 wt% PEP, bicarbonate was determined to have a diffusion coefficient of 2.381 ± $0.392\times10^{-5}$ $cm^2/s$, roughly a third of its literature value for pure water.

Bicarbonate transport was also determined in the simulations. The bicarbonate concentration was calculated according to:

$$[HCO_3^-]=(K_{c1}\,H\_(CO_2)\;p(CO_2))/([H^+]) \qquad (3)$$

Values for constants were taken from the literature [15]. The equilibrium constant $K_{c1}$ had a value of $2.5 \times 10^{-4}$, and the Henry's law constant for $CO_2$ is approximately 0.034 mol/L atm at neutral pH value. The mole fraction of $CO_2$ was 0.205 based on the assumption that all oxygen in the air had been converted to $CO_2$ in the combustion process [2].

### *Free Energy of PEP Variants*

PEP appears to be a suitable replacement for MEA in PCC based on its above computed properties in aqueous solution. However, variations on the PEP structure obtained by removing or adding functional groups were tested if they might be even better PCC solvent alternatives. An assessment of exemplary PEP variants is given here. Fig. 4 displays the free energy diagram of PEP based on solubility. Subsequent analyses of PEP variants are judged solely on the merit of their free energy diagrams compared to that of the original. For the variant to have any advantage over the original PEP molecule, they should have lower energy of dilution in water. For the sake of simplicity, the 3 lowest points were the only points compared across all variants since they represent the energy minimum. The first PEP variant ($C_2H_5O_6P$) eliminates the terminal double bonded carbon. Its free energy diagram in comparison with that of PEP demonstrates that it has higher energy of dilution. These simulations do not suggest this variant to be a better replacement to PEP. Substituting one of the hydrogen atoms bound to carbon atom $C_2$ with a hydroxyl group also results in higher free energy. Again, this suggests the variant shows no improvements over PEP, although the difference between the curves is small. Replacing a hydrogen atom on $C_2$ with a carboxylic acid group (O=C-OH) instead of hydroxyl group increases the energy of dilution even more than the previous two variants. It is not immediately clear why the addition of a carboxylic group increases the dilution energy, but without being bound by theory, it may involve steric hindrances to the hydration shell. A possible explanation is that the carboxylic group aids the dissociation of the first proton but makes it more difficult for the second proton to dissociate due to electrostatic attraction to the nearby carboxylate anion. For the fourth PEP variant ($C_2H_3O_7P$), the hydrogen atom attached to $C_2$ is substituted with a double bonded oxygen (oxy-group). The energy of dilution is this case is lower than the original PEP molecule. These results demonstrate that the aqueous solution properties of PEP can be improved by changing the functional groups in the nonreacting parts of the molecule. The PEP variant $C_3H_5O_7P$ has a carbon atom bonded to a hydroxyl group (C-OH) which substitutes the hydrogen on the $C_2$ atom. Like the previous variant but to a lesser extent, the minimum in the energy of dilution is lower than that found in original PEP. Again, this demonstrates the ability to optimize the properties of PEP by modifying the chemical structure of the nonreacting regions.

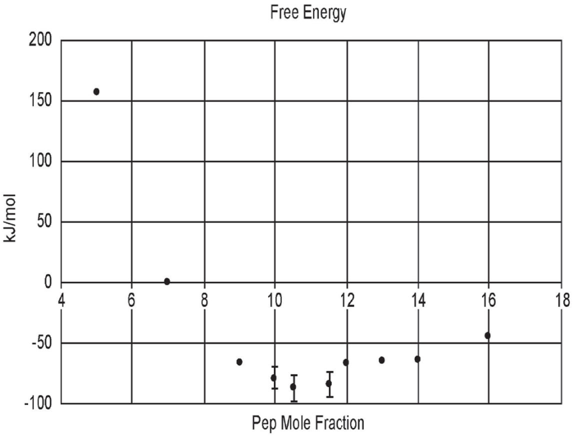

Fig. 4: Free energy/chemical potential of PEP as a function of mole fraction

The chemical potential-concentration curve shows that the expected solubility of PEP at 20 °C is about 9.8 mol%. This is slightly lower than the 11 mol% of the standard MEA solution. However, the stoichiometric ratio of MEA to $CO_2$ during absorption is 2:1 as shown below while that of the PEP-$CO_2$ reaction is 1:1. Therefore, the absorption capacity of the PEP solvent for $CO_2$ is almost doubled compared to most primary and secondary amines, which all follow the same general reaction stoichiometric ratio shown below:

$$CO_2 + NHR_2 + NR_3 \leftrightarrow NR_2CO_2^- + NR_3H^+ \qquad (4)$$

where $NR_3$ can be any primary, secondary or tertiary amine and NHR_2 is either a primary or secondary amine. Higher temperatures present in absorber systems may further improve the solubility of PEP, especially given the curve is very shallow up to 55 wt% (11 mol%).

The viscosity of the PEP solution in the 45 to 55 wt% (about 10 mol%) range was estimated to be roughly triple that of the standard MEA solution, with a real viscosity of about 3 mPa*s. Based on the viscosity alone, a rough calculation shows that the same pipe infrastructure would require about 6% more power to pump PEP solution than MEA solution. Fortunately, the amount of power required to pump MEA is a negligibly small part of the PCC energy cost.

Hydration shells, viscosity, and self-diffusion coefficient trends for PEP showed no notable behavior change over the examined range of concentrations. It is therefore unlikely that any sort of relevant phase or structure change is taking place.

In total, the observations made here show the promise of alternative PCC solvents based on phosphoenol compounds to increase the desired solvent properties relative to benchmark amines such as MEA.

## 4. Conclusion

We modeled PEP and some variants of it to compare with the standard MEA solution for carbon capture. The model was able to correctly predict vacuum properties of the molecules and reaction related to our target carbon capture chemistries, as well as solution properties. The developed model also correctly predicted the target reactions during MD simulations, where bicarbonates react with PEPs in solution to form the intermediate species and then dissociate into the carboxyphosphate and enolate form of pyruvate. We also observed that if the PEP reacts with its neighboring bicarbonate, the partial charge of its P tends to be lowered and is negatively correlated with its coordination number. Thus, we have developed a model which can determine the impact of local structure on reactions necessary to perform carbon capture using PEP. This will enable selection of optimal reaction conditions and design of new PEP variants that are more reactive with bicarbonate, more stable after reaction, and possibly more energy-efficient.

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