# Amino acid ionic liquids as potential candidates for CO2 capture: Combined density functional theory and molecular dynamics simulations

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Amino Acid Ionic Liquids as Potential Candidates for CO₂ Capture:
Combined Density Functional Theory and Molecular Dynamics Simulations

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ABSTRACT

Carbon dioxide is a well-known greenhouse gas that cause global warming. CO₂ capture and sequestration strategy is known promising strategy to reduce the level of CO₂ in the atmosphere. Thus, the usage of Amino Acid Ionic Liquids have gained attention for reversible CO₂ capture. Herein, we use DFT to report the effect of CO₂ chemisorption on tetramethylphosphonium glycinate and tetrabutylphosphonium glycinate ILs. Finally, Molecular Dynamics (MD) simulations were carried out to study the physicochemical properties of ILs in pure form and in the presence of explicit water. Overall, our study confirms the usage of studied ILs to efficiently capture CO₂.

Keywords: Ionic liquids, molecular dynamics simulation, density functional theory, CO₂ capture
INTRODUCTION

One of the major greenhouse gases implicated in global climate change is carbon dioxide (CO₂). Human activities, such as burning of fossil fuels are mainly responsible for increasing the carbon footprint in atmosphere. According to a recent report of Intergovernmental Panel on Climate Change (IPCC) shows that about 79% of the total CO₂ emissions come from fossil fuels and minerals [1] that are being used for power generation and 60% of the total CO₂ emission comes from coal power plants (operated by natural gas and oil) [2]. A very recent report from the International Energy Agency in its annual survey of global carbon levels highlighted that the energy-related emissions increased to 1.4% and that now amounts to 32.5 gigatons in 2017 compared to 17.4 gigatons in 2016. Importantly, the CO₂ emission can impact both the terrestrial and the aquatic life [3]. As a result, various scientific efforts have been made in order to capture carbon dioxide and protect the environment from its hazardous effects. Carbon capture and storage (CCS) seems to be one of the popular technology for capturing CO₂ emissions from power stations and industrial sites and it contains three main techniques: post-combustion process, pre-combustion CCS and oxyfuel. Presently, during post-combustion, methanolamine (MEA) is used for CO₂ capture [4]. However, a major disadvantage of using the aqueous amines is potentially related to its nature causing the corrosion along with the oxidative degradation. The solvent loss due to evaporation further adds to the environmental pollution along with an extra cost for solvent replacement during operation. Hence, these technologies require high energy and are not ecofriendly. On the other hand, metal-based systems have also been used to functionalize CO₂ [5, 6], generating interesting commodities for industry [7, 8]. Take for instance the formation of cyclic carbonates by means of epoxide reagents [9, 10]. However, to go to more environmentally benign
processes [11], apart from either solvent free [12] or halogen free processes [13], organocatalysis is pushing strongly to reproduce the same reactivity with metal-free catalysts [14].

Actually, several methods exist for CO₂ capture that includes the membrane separation, adsorption, and physical and chemical absorption. Further, CO₂ capture using ionic liquids (ILs) have been proposed as potential candidates due to the high solubility of CO₂ in ILs [15-16]. The majority of ILs can be considered as green solvents, due to its ease in recycling them associated with the property of virtually null vapor pressure. The advantages of using ILs lies in the tailorability of the anion or cation that subsequently result in alteration of its function and property [17]. In addition, the low vapor pressure of ILs make it an attractive target for the adsorption of gases. Various types of ILs have been studied till date that includes the conventional ILs, task-specific ILs, and functionalized ILs. In particular, Brennecke et al. studied the CO₂ solubility of the conventional imidazolium-based ionic liquids under high pressures [18]. Next, ILs can be tuned to create task specific ILs (TSILs) such as addition of alkaline –NH₂ group that can be attached to ILs to give zwitterion character [19]. This type of TSILs can help to overcome the limitations of aqueous amine bases ILs. Further, Bao et al. [20] reported the usage of ILs from natural amino acids leading to development of amino acid based ILs (AAILs). A subsequent study by Ohno et al. [21] used 1-ethyl-3-methyl imidazole ([Emim]⁺) as a cation and 20 natural amino acids as anions to synthesize AAILs. Amino acid based ionic liquids possess additional benefits because of their low cost, less environmental impact and biodegradability. Zhang et al. [22] synthesized tetrabutylphosphonium amino acid [P₄444][AA] and observed that at equilibrium, CO₂ absorption capacity was 50 mol% of ILs. A distinct class of tunable basic ILs based on phosphonium based cation for energy-saving and equimolar CO₂ capture was developed by Wang et al. [23] where they observed that [P₆₆₆₁₄][triz] unlike other ILs did not show remarkable increase in viscosity after CO₂ absorption.
Further, Amine-functionalized ILs were developed by Chau et al. [24] where they reported the increase in CO$_2$ absorption efficiency when the amine was added to conventional ILs. Yet another study by Gurkan and Xue [25] clearly pointed out the increased CO$_2$ absorption capacity with the 1:1 (CO$_2$: ILs) mole ratio that could be accomplished by tethering an amine on both the anion and cation of ILs. Cao et al. [26] reported synthesis and computational studies for CO$_2$ capture by amine-functionalized ILs, 1,2-dimethyl-(3-aminoethyl)imidazolium halide ([aEMMIM][X]) and observed 1:1 molar ratio CO$_2$ capture capacity. In addition to experimental studies for studying the adsorption of CO$_2$ on ILS, various computational investigations have also been carried out as highlighted in a very recent review [27]. In particular, Density Functional Theory (DFT) and molecular dynamics (MD) simulations have been checked useful tools in order to investigate the reaction mechanism and to predict physical properties that in turn can be correlated with CO$_2$ adsorption properties [28-32]. It has been observed that functionalized amino acid as an anion and heterocyclic platform that includes phosphonium cation usually possess better CO$_2$ capture tendency along with less increase in viscosity after CO$_2$ absorption [22, 33]. Phosphonium-based ILs are extremely robust and are much more resistant to reaction with bases such as amines than are imidazolium-based ILs [34]. This type of ILs are environmentally benign, and are readily available and used in large scale. Due to their structure and physiochemical properties, these ILs can be tailored for specific functions. In the present study, we aim to investigate the reaction between the anion of ionic liquid with carbon dioxide (capturing CO$_2$) with the usage of two distinct types of cations.

In order to study effect of CO$_2$ absorption on tetramethylphosphonium glycinate [P$_{1111}$][Gly] and tetrabutylphosphonium glycinate [P$_{4444}$][Gly], DFT studies along with the MD simulations have been carried out. We unveiled mechanistic insights, particularly the transition state involved in
CO₂ capture in the gas and in the solvent phase (both implicit and explicit solvent) using SMD solvation model [35-36]. In addition, our main focus is to investigate the pure ILs with two different aliphatic chains on cation and its effect on structural properties and dynamical properties of interest through large-scale MD simulations. In general, the flue gases emitted from power plants comprise a 5-10% of water (~5–10%) [37]. Hence, The ILs was also simulated in the presence of 10% of water to calculate the physical properties. Our current study will help to understand the reaction mechanism that will serve as a guide to design new ionic liquids with improved CO₂ capture capability.

**COMPUTATIONAL DETAILS**

*Quantum Mechanical Calculations.*

All structures, as reported in Chart 1, were modeled using GaussView program and Gaussian09 program was employed to carry out DFT calculations [38]. Optimization of molecules under investigation viz. [P₁₁₁₁], [Gly], [P₄₄₄₄], [P₁₁₁₁][Gly], [P₄₄₄₄][Gly], [P₁₁₁₁][Gly][CO₂] and [P₄₄₄₄][Gly][CO₂] were carried out using M06-2X functional and using the 6-31++G(d,p) basis set. The optimizations were carried out both in gas phase and water solvent using the continuum solvation model SMD as implemented in Gaussian09.

After optimizing these molecules separately, we study the reaction mechanism for CO₂ absorption on [P₁₁₁₁] [Gly] and [P₄₄₄₄][Gly]. In the literature, mechanistic study for CO₂ absorption in amine has already been reported [31]. Based on the proposed reaction, the reaction of CO₂ absorption takes place in two steps, the zwitterionic complex bonds to the free CO₂ followed by the intramolecular proton transfer from the NH₂ chemical group to the closest oxygen atom. In the zwitterionic compound, strong interaction between CO₂ and the N atom of glycinate [Gly]− takes
places to form pre-complex. The proposed mechanism for CO\textsubscript{2} capture using [P\textsubscript{1111}][Gly] is shown in Figure 1.

\begin{center}
\includegraphics[width=\textwidth]{chart.png}
\end{center}

\textbf{Chart 1.} Tetramethyl phosphonium [P\textsubscript{1111}], tetrabutylphosphonium [P\textsubscript{4444}], glycinate [Gly] and (carboxy amino) acetate [GCO] formed after absorption of CO\textsubscript{2}.

\begin{center}
\includegraphics[width=\textwidth]{figure.png}
\end{center}

\textbf{Figure 1.} Proposed mechanism for CO\textsubscript{2} capture on amino acid ionic liquid [P\textsubscript{1111}][Gly].

All geometry optimizations were conducted using M06-2X density functional and the 6-31++G(d,p) basis set [30, 31]. Solvent effects were considered by utilizing the SMD solvation model [36], either with single point energy calculations on the gas phase geometries or directly included in the geometry optimizations, as well. In addition, zero-point energy corrections and thermal corrections were also included that lead to Gibbs free energy values. The nature of the
transition states was confirmed by the corresponding negative vibrational frequency along with Intrinsic Reaction Coordinates (IRC).

**Molecular Dynamics Simulations**

**Force Field.** The force field parameters were generated using the Amber force field [39] for the glycinate, and the modified generalized Amber force field parameters developed by Zhou et al. [40] was used for the parametrization of \([P_{1111}]\) and \([P_{4444}]\) of the ILs. For restrained electrostatic potential (RESP) fitting, standard DFT calculations were carried out with Gaussian09 program [38] utilizing B3LYP and 6-31G(d) basis sets. The Merz–Kollman method using the HF/6-31G(d) level of theory, and a multiconfigurational two-stage RESP fitting was performed in order to generate the electrostatic potential energy surface. Finally, the RESP charge calculations for cations and glycinate were carried out using the Antechamber program. GAFF force field and RESP charges used to model force field in MD simulations in this study are shown in Figure S2.

**Molecular Dynamics.** The initial configurations of the IL mixture were generated by packing 384 pairs of cations and anions using the Packmol program [41]. All the MD simulations reported in this study was carried out using GROMACS 2018 simulation program [42]. After energy minimization, a standard protocol that includes the equilibration simulations were performed for 10ns each using NVT and NPT ensembles. Next, a temperature at 300 K was maintained using the velocity-rescaling thermostat with a coupling time of 5 ps. For all the NPT simulations, and for maintaining a standard pressure to 1 atm, Parrinello–Rahman barostat with a coupling time of 1 ps was used. A time step of 2 fs was used to integrate the equations of motion based on the leapfrog algorithm. Further, the equilibrated system was used for production simulation of 50 ns using NPT ensemble. The electrostatic interactions beyond 1.2 nm were evaluated for by Particle-Mesh-Ewald (PME) method. In order to mimic the bulk behavior, standard Periodic boundary conditions
(PBCs) in all directions were used and the Linear Constraint Solver (LINCS) algorithm was used to constraint the bond lengths.

In addition, effect of 10\% of water was also studied using MD simulation by GROMACS package. All the simulation parameters (algorithm, ensemble, step size etc.) were similar as reported for vacuum simulation. It has been reported that, the CO$_2$/N$_2$ selectivity can be tuned by controlling the free volume (FV) [43] and fractional free volume (FFV) parameters and to further analyze the effect of water on such studied parameters [30]. Hence, all these properties were analyzed using GROMACS tools available in the program. Instead of chemically absorbing the CO$_2$ on to the ILs, we have computed various properties of the ILs (such as prediction of the free volume, diffusion coefficient and density analysis as that are very well known to give an indication if the given IL is able to absorb well the CO$_2$ or not.

**RESULTS AND DISCUSSION**

Experimental studies were conducted to investigate the CO$_2$ absorption by tetrabutylphosphonium hydroxide with different amino acids to synthesize amino acid ionic liquids that include [P$_{4444}$][Gly] ionic liquid molecules [22]. It has been observed that, experimentally tetramethylammonium glycinate [N$_{1111}$][Gly] ILs and its CO$_2$ absorption data are available [28]. However, there are no experimental data available on tetramethylphosphonium glycinate [P$_{1111}$][Gly]. In this study, we investigated the reaction mechanism of CO$_2$ absorption on these phosphonium cation based ILs with glycinate anion using DFT. Further, MD simulations were carried out to calculate various physical properties in order to elucidate how well the CO$_2$ can be physically absorbed on the studied ILs. The chemical structures of the cation ([P$_{1111}$], [P$_{4444}$], and anion ([Gly]), and the products formed after CO$_2$ absorption on [Gly] ([GCO] are shown in Chart 1. The proposed reaction mechanism of CO$_2$ absorption on the [P$_{1111}$] is shown in Figure 1.
activation energy barriers for CO$_2$ absorption on [P$_{1111}$][Gly] in gas phase and using continuum solvation model are shown in Figure 2. First step of the reaction is the formation of intermolecular complexes between glycinate and CO$_2$ [31]. It seems that a strong interaction exists between CO$_2$ and glycinate [44], and this step is extremely fast (kinetically favored) that we could even not locate the transition state for this intermolecular complex formation. Further, linear transits confirmed that this step is barrier less. However, more complex calculations such as the consideration the diffusion coefficient of CO$_2$ in the ILs were avoided that could complicate this step [45]. From the resulting pre-complex moiety, next step of the reaction is the intramolecular proton transfer from the -NH$_2$ moiety to the carboxylate O atom of glycinate. This intramolecular hydrogen transfer is the rate determining step (rds) and verified by a single negative imaginary frequency along reaction coordinates. Even though the energy barrier is high, it should be stated that the previous combination of the cationic moiety, either [P$_{1111}$] or [P$_{4444}$], with the anionic glycine and CO$_2$ requires 11.3 and 9.7 kcal/mol, respectively (see Table S1 in the SI).
Figure 2. Gibbs free energy profile (relative to the Pre-complex in kcal/mol) for absorption of CO$_2$ on [P1111][Gly] optimized in gas phase (and in solvent phase between parentheses); main distances are shown in Å. The transition state has been located both in the presence and absence of an explicit water molecule.
As shown in Figure 2, the transition state (TS) was located with an energy barrier of 3.2 kcal/mol and product was found to be 2.2 kcal/mol below in energy compared to the pre-complex. At the beginning of the reaction, [Gly]− forms a zwitterionic complex with CO2 as shown in Figure 2 (pre-complex). The C-N distance between C of the former CO2 and N of [Gly]− was found to be 1.670 Å. Then at the TS the distance was reduced to 1.537 Å and the final distance for the product was found to be 1.459 Å, thus potentially indicating a strong bond between C of CO2 and N of [Gly]−. To support the evolution of the strength of this C-N bond, we calculated its Mayer Bond Order (MBO) [46]. It changes from 0.655 to 0.964 from the pre-complex to the product.

Figure 2 also shows the key geometrical distances that are changing during the reaction, where the proton plays a fundamental role. Moreover, the reaction appears to be exothermic in both cases. The energy barrier slightly increased from 3.2 to 4.4 kcal/mol after incorporation of the continuum solvation model for the geometry optimizations, and even more from the values in gas phase (2.4 kcal/mol, see Table S1). In solvent phase, the increase in the energy barrier could be due to the hydrophobicity and bulkiness of the cation. The effect of CO2 on only glycinate and in presence of water generally lowers the energy barrier in line with the previous studies [30-31]. As a remark, without the cationic [P1111] the energy barrier becomes null in gas phase (see Table S1), whereas just 3.2 kcal/mol in solvent phase.

Similar calculations were performed for [P4444][Gly] system. It was observed that the reaction takes places again with the formation of a zwitterionic complex, followed by the proton transfer from N to O of carboxylate. Figure 3 shows a potential energy diagram for reaction in presence and absence of solvent. The energy barrier for [P4444][Gly] is ETTS = 2.4 kcal/mol and that of product formation, EP = -3.0 kcal/mol. As shown in Figure 3, the energy barrier for absorption decreases 0.8 kcal/mol in [P4444][Gly] with respect to in [P1111][Gly]. The strength of the amino
acid with CO₂ is stronger than for [P₁₁₁₁][Gly] because it changes from 0.626 to 1.131 from the pre-complex to the product, respectively. To point out that another coordination intermediate was located before the pre-complex, where the C-N distance was close to 3 Å, and consequently with a null MBO, which explains partially why this latter intermediate was thermodynamically unfavored by 4-5 kcal/mol (see SI). However, from Figures 2 and 3, it seems evident that the aliphatic chain that bears the cation does not affect the energy barrier significantly (just 1-2 kcal/mol). On the other hand, in Figures 2 and 3 the TS assisted by an external water molecule was checked to be unfavored by 7.1 and 7.0 kcal/mol for [P₁₁₁₁][Gly] and [P₄₄₄₄][Gly], respectively. The reason is that the favorable effect of the explicit water molecule, shortening the H-transfer, unexpectedly does not compensate here the increase of entropy.
Figure 3. Gibbs free energy profile (relative to the Pre-complex in kcal/mol) for absorption of CO$_2$ on [P$_{4444}$]$^+$(Gly)$^-$. The transition state has been located both in the presence and absence of an explicit water molecule.
Table 1. The value and the band of HOMO and LUMO orbitals for CO$_2$ absorption in [P$_{1111}$][Gly] and [P$_{4444}$][Gly].

<table>
<thead>
<tr>
<th>Complex</th>
<th>[P$_{1111}$][Gly]</th>
<th>[P$_{4444}$][Gly]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HOMO (eV)</td>
<td>LUMO (eV)</td>
</tr>
<tr>
<td>Pre-complex</td>
<td>-0.2955</td>
<td>-0.0216</td>
</tr>
<tr>
<td>TS</td>
<td>-0.3039</td>
<td>-0.0259</td>
</tr>
<tr>
<td>Product</td>
<td>-0.2781</td>
<td>-0.0263</td>
</tr>
</tbody>
</table>

Figure 4. Frontier molecular orbitals (H = HOMO and L = LUMO) of the absorption of CO$_2$ on [P$_{1111}$][Gly], the pre-complex and product, and on [P$_{4444}$][Gly], the pre-complex and product.
Experimentally [P\textsubscript{4444}][Gly] was synthesized and it showed promising CO\textsubscript{2} absorption [22]. However, an increase in viscosity after CO\textsubscript{2} absorption has been observed for this molecule. This is due to the non-polar long chain, which contributes to increase its viscosity in addition to hydrogen bonding of the formed product after absorption. Furthermore, Table 1 shows the highest occupied molecular orbital (HOMO) energy and the lowest unoccupied molecular orbital (LUMO) energy and their gap (\(\Delta\)). HOMO and LUMO energies from the reactant to the product via the transition state do not change significantly, and the plot of the frontier molecular orbitals in Figure 4 unveil that the HOMO orbitals are related to type p contributions of the anionic COO group of the former substrate, whereas the LUMO related to the alkyl chains on the phosphorous atom. However, the gap is small enough to allow electron excitation from HOMO to LUMO. The results reported here are in line with the reported data for [P\textsubscript{4444}][Gly] [47]. According to conceptual DFT analyses [48], the calculation of chemical hardness and electrophilicity in Table 2 from the frontier molecular orbitals, \textit{i.e.} with the Koopmans theorem, leads to the conclusion that the H-transfer does not lead to a big change electronically, but the comparison among both ionic liquids confirms that when dealing with the cationic [P\textsubscript{4444}] moiety instead of the [P\textsubscript{1111}] one, the resulting resting intermediate is harder, and thus more stable according to the chemical hardness. Based on the principle of maximum hardness, the higher the hardness the studied molecule tends to react less. Further, the electrophilicity values are relatively low, with no significant differences between both systems, however with lower values for [P\textsubscript{4444}][Gly]. This confirms that the latter system is less prone to potential nucleophilic attacks. For further confirmation of the latter hypothesis, the noncovalent interactions (NCI) between the glycinate and both cationic moieties were studies by means of NCI plots (see Figure 5), developed by Contreras-Garcia and coworkers [49]. The
successful insights of this technique, to distinguish between similar systems according to H-bonds, are fruitful here. It is plotted the isocontour obtained with a value of 0.5 of the reduced density gradient. And for the interpretation of the results, the interval selected ranged from −0.05 (red and repulsive) to 0.05 (blue and attractive) of the second density Hessian eigenvalue has been utilized for the color scale. The study of the noncovalent interactions between the different regions of both molecular systems unveils more attractive regions for [P_{4444}][Gly]. Although the H-bond between the OH and the N is nearly the same for both systems, the [P_{1111}][Gly] presents less H-bonds among the cationic and the anionic moieties. Actually, the difference is due to its shorter alkyl chains of the cationic phosphines.

Table 2. Chemical Hardness (η) and electrophilicity (ω) for [P_{1111}][Gly] and [P_{4444}][Gly].

<table>
<thead>
<tr>
<th>Complex</th>
<th>[P_{1111}][Gly]</th>
<th></th>
<th>[P_{4444}][Gly]</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>η (eV)</td>
<td>ϵ (eV)</td>
<td>η (eV)</td>
<td>ϵ (eV)</td>
</tr>
<tr>
<td>Pre-complex</td>
<td>0.1369</td>
<td>0.0918</td>
<td>0.1375</td>
<td>0.0893</td>
</tr>
<tr>
<td>TS</td>
<td>0.1390</td>
<td>0.0978</td>
<td>0.1398</td>
<td>0.0933</td>
</tr>
<tr>
<td>Product</td>
<td>0.1259</td>
<td>0.0920</td>
<td>0.1378</td>
<td>0.0881</td>
</tr>
</tbody>
</table>
Figure 5. NCI plots of the absorption of CO$_2$ on [P$_{1111}$][Gly], the pre-complex (a) and product (b), and on [P$_{4444}$][Gly], the pre-complex (c) and product (d). The isosurface represents a value of 0.5 with a color scale for the reduced density gradient from $-0.05$ (red) to $0.05$ (blue).
Further, MD simulations were carried out for 50 ns and the trajectory was analyzed using GROMACS tools available in the GROMACS package. Table 3 shows density, free volume (FV), and fractional free volume (FFV) in vacuum and in water. The density of [P1111][Gly] is decreased in presence of water as it has stronger interaction with glycinate. The density of [P1111][Gly] is high and it has lower free volume. Hence it can be inferred that, [P1111][Gly] may not behave like a liquid and hence not suitable for gas adsorption and this could be reason that in literature phosphonium cation with longer chain were only synthesized and evaluated for CO₂ absorption capacity [22, 50]. The experimental density for [P4444][Gly] was 0.963 g/cm³ and predicted density after MD simulation was 0.993 g/cm³, which corresponds to 3% deviation compared to the experimental density [22]. The density was decreased in presence of 10% of water. The lower density in both the cases is due to stronger interaction between hydrophilic glycinate with water molecules that in turn lower the interaction between cation and glycinate. It can be realized that density is lower in [P4444][Gly] as compared to [P1111][Gly], as density decreases with increase in cation size [50]. The FV and FFV is lower in [P1111][Gly] as compared to [P4444][Gly], since the hydrophobic chain in [P4444] is longer. Higher free volume is responsible for more CO₂/N₂ absorption and lower selectivity.

**Table 3.** Density, FV, and FFV obtained after MD simulation in vacuum and 10% of water. Numbers in the parenthesis represent standard error.

<table>
<thead>
<tr>
<th>Compound</th>
<th>ρ (kg/m³)</th>
<th>FV (%)</th>
<th>FFV (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[P1111][Gly]</td>
<td>1392.24 (23.83)</td>
<td>20.64 (0.15)</td>
<td>0.032 (0.002)</td>
</tr>
</tbody>
</table>
The self-diffusion coefficient for cations, glycinate and water molecule is reported in Table 4. Water displays the highest diffusion coefficient in [P\textsubscript{4444}][Gly] since the system contains higher free volume as compared to [P\textsubscript{1111}][Gly]. Both, [P\textsubscript{1111}][Gly] and [P\textsubscript{4444}][Gly], shows similar diffusion coefficient of ions in vacuum as well in presence of 10% of water.

**Table 4.** Self-Diffusion Coefficients of the Ions in [P\textsubscript{1111}][Gly] and [P\textsubscript{4444}][Gly].

<table>
<thead>
<tr>
<th>Water %</th>
<th>[P\textsubscript{1111}][Gly] (1 x 10\textsuperscript{-7} cm\textsuperscript{2}/s)</th>
<th>[P\textsubscript{4444}][Gly] (1 x 10\textsuperscript{-7} cm\textsuperscript{2}/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.02 (0.01) 0.02 (0.02) -</td>
<td>0.08 (0.02) 0.07 (0.05) -</td>
</tr>
<tr>
<td>10</td>
<td>0.03 (0.01) 0.02 (0.01) 0.03 (0.03)</td>
<td>0.07 (0.04) 0.08 (0.05) 0.32 (0.20)</td>
</tr>
</tbody>
</table>
Figure 6. Plot of coulombic interaction energy a) between \([P_{1111}]\) and glycinate and b) \([P_{4444}]\) and glycinate in gas phase and in explicit 10% of water.

Figure 6a shows the interaction energy between glycinate and \([P_{1111}]\) in two different phases. It is evident that electrostatic interaction decreased between \([P_{1111}]\) and glycinate in presence of water. This is due to the stronger interaction between glycinate and water, which in turn lowers the interaction between \([P_{1111}]\) and glycinate. Figure 6b shows the interaction energy between \([P_{4444}]\) and glycinate that is similar to the one obtained for \([P_{1111}]\) [Gly].
Figure 7. Radial distribution functions (RDFs), and their corresponding coordination numbers, indicating interionic distances and ion-ion coordination in [P$_{1111}$][Gly]. Top left panel shows cation-anion RDFs, middle panel shows cation-cation, and right panel shows anion-anion RDFs. The bottom panel shows corresponding number integrals (n(r)) of the RDFs depicted above. RDFs in gas phase shown with blue color and in presence of 10% of water shown in orange color.

Radial distribution function analysis was carried out using central P atom of cation and C$\alpha$ atom of glycinate, which could give an indication of how the liquid structure of ILs by analyzing distribution of ions around each other and their coordination environments. Figure 7 shows RDFs of cation-anion, cation-cation and anion-anion and their respective coordination number. As it is evident from Figure 7 for cation-anion interaction, there is sharp solvation shell. The first largest peak was observed at 0.53 nm, and the second and third peaks at 0.95 and 1.34 nm, respectively. From Figure 7, it can be seen that cation-anion interaction strength seems to be higher than cation-cation and anion-anion interactions. RDFs for cation-cation interaction shows the first peak at 0.55
nm, the second peak at 0.91 nm and the third at a distance of 1.03 nm. The anion-anion RDFs shows distinct peaks at 0.43, 0.85 and 1.37 nm. It is important to remark that the RDFs in gas phase and in 10% of water differ significantly, and the peak was shifted to lower distances in water, especially for cation-anion interaction.

Figure 8 shows RDFs for [P_{4444}][Gly] in gas phase and in 10% of water. Interestingly, looking at the RDFs as reported in Figure 8, does not show any significant difference in gas phase and in presence of 10% water except for cation-anion interactions. In cation-anion, sharp peak was observed at 0.55 nm, 0.03 nm higher than [P_{1111}][Gly]. The peak at longer distance could be due to the longer alkyl chain in cation, which increases the distance from the anion in [P_{4444}][Gly] as compared to [P_{1111}][Gly]. For cation-cation interaction, RDFs shows a first sharp peak at 0.55 nm, a second peak at 0.72 nm and third broadest peak at 1.01 nm. Analyzing the RDFs for Anion-anion interaction shows the first broadest peak at 0.51 nm, whereas the second and third peaks at 0.89 and 1.44 nm, respectively. In [P_{4444}][Gly] also, cation-anion shows higher g(r) value consequently indicating stronger interaction.
Figure 8. Radial distribution functions (RDFs), and their corresponding coordination numbers, indicating interionic distances and ion-ion coordination in [P4444][Gly]. Top left panel shows cation-anion RDFs, middle panel shows cation-cation, and right panel shows anion-anion RDFs. The bottom panel shows corresponding number integrals (n(r)) of the RDFs depicted above. RDFs in gas phase shown with blue color and in presence of 10% of water shown in orange color.

Table 5 shows the average ion-ion coordination numbers analyzed at the end of corresponding solvation shells in RDFs and their corresponding distances are also shown in parenthesis. It gives an idea about strength of inter-ionic interactions and extent of ion-ion solvation. The higher the value of $n_{C-C}$ and $n_{C-A}$ in [P1111][Gly], the larger is the cation-anion and cation-cation self-interactions. $n_{C-A}$ in [P4444][Gly] shows the highest coordination number, indicating that cation-anion interaction remains higher in gas phase and in presence of water.
Table 5. Average cation (C)-anion (A) ($n_{C-A}$), cation-cation ($n_{C-C}$) and anion-anion ($n_{A-A}$) coordination numbers obtained from the first minima of the RDFs; the corresponding distances are shown in nm within brackets.

<table>
<thead>
<tr>
<th>Ionic Liquids</th>
<th>$n_{C-A}$</th>
<th>$n_{C-C}$</th>
<th>$n_{A-A}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gas phase</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[P$_{1111}$][Gly]</td>
<td>8.4 (0.73)</td>
<td>8.4 (0.75)</td>
<td>3.3 (0.59)</td>
</tr>
<tr>
<td>[P$_{4444}$][Gly]</td>
<td>3.3 (0.71)</td>
<td>0.3 (0.60)</td>
<td>0.2 (0.59)</td>
</tr>
<tr>
<td><strong>10% Water</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[P$_{1111}$][Gly]</td>
<td>8.7 (0.46)</td>
<td>8.1 (0.75)</td>
<td>3.3 (0.59)</td>
</tr>
<tr>
<td>[P$_{4444}$][Gly]</td>
<td>3.3 (0.71)</td>
<td>0.3 (0.60)</td>
<td>0.2 (0.59)</td>
</tr>
</tbody>
</table>

Figure 9. RDFs analysis for intramolecular interaction within glycinate in a) [P$_{1111}$][Gly] and b) [P$_{4444}$][Gly].
Figure 9 shows RDFs analysis for intermolecular and intramolecular bonding within glycinate. It can be seen from Figure 9a that O of the carboxylate has stronger bonding with the other O of the carboxylate. This intramolecular bonding in [P$_{1111}$][Gly] is also seen in [P$_{4444}$][Gly] as shown in Figure 9b. Also it can be seen that N of amine group of glycinate has stronger bonding with O of carboxylate group in glycinate in [P$_{4444}$][Gly] as compared to [P$_{1111}$][Gly]. From N-O peaks, we can infer that amine of glycinate is mainly bonding with carboxylate of other glycinate. Hydrogen bonding interactions were also analyzed. The average number of hydrogen bonds per frame in gas phase for glycinate was 326.78 and 18.97 and in 10% of water was 302.71 and 90.26 for [P$_{1111}$][Gly] [P$_{4444}$][Gly], respectively and not surprisingly, the hydrogen bond of glycinate with water increased considerably in water phase. The results indicate that pure ionic liquids and ionic liquids in presence of small fraction of water show considerable differences. Hence water in flue gas will affect the CO$_2$ absorption capacity, and mainly it will decrease physical CO$_2$ absorption capacity. The main reason for increase in viscosity after CO$_2$ absorption in these phosphonium based ILs is due to increase in hydrophilicity after CO$_2$ chemisorption on glycinate, which leads to stronger hydrogen bonding within GCO moiety. To increase the CO$_2$ absorption capacity, it is recommended that amine group can be added in cation, so that it will act as a dual CO$_2$ absorption sites and also decrease the hydrophobicity of the cation and thereby ILs.

**CONCLUSIONS**

In this paper, we investigated the reaction mechanism of CO$_2$ absorption by an amino-acid ionic liquid. We have unveiled the reaction pathway by DFT calculations. We found that the reaction follows a two-step mechanism, where in the first step CO$_2$ forms zwitterionic pre-complex with
glycinate and subsequently in the second step the intramolecular proton is transferred from NH₂ to the carbonyl oxygen of glycinate. In CO₂ absorption on [P₁₁₁₁][Gly], we found that the activation barrier for proton transfer is 3.2 kcal/mol and 4.4 kcal/mol in gas phase and in solvent respectively. Similarly, for CO₂ absorption on [P₄₄₄₄][Gly] the activation energy was 2.4 kcal/mol and 4.5 kcal/mol in gas phase and in solvent, respectively. The energy barrier increased in solvent environment, as the cation is bulky and hydrophobic. In both cases, the product formation is an exothermic process. Addition of alkyl chain has a crucial role in decreasing the inter-ionic interactions. Importantly, transition state assisted by the inclusion of explicit water molecule was found to be unfavored by 7.1 and 7.0 kcal/mol for [P₁₁₁₁][Gly] and [P₄₄₄₄][Gly], respectively. Even though electronically there are no significant differences, confirmed by conceptual DFT calculations, there is a trend that favors [P₄₄₄₄][Gly], confirmed by NCI plots that demonstrate more H-bonds for this amino acid ionic liquid. To understand the structure of two different [Gly] based ILs with structurally similar cations with different alkyl chain length, we performed MD simulations of the pure ILs. MD simulation analysis show that interaction between cation and anion decreased in presence of water, thereby decreasing diffusion coefficient of cation. Free volume and fractional free volume was found to be higher in [P₄₄₄₄][Gly] as compared to [P₁₁₁₁][Gly]. The resulting lower free volume and higher density in [P₁₁₁₁][Gly] thus will inhibit the absorption of CO₂. Diffusion coefficient analysis shows that 10% of water probably decreased the CO₂ uptake by increasing the viscosity of the compound. Our current study will serve as a potential guide to design new ionic liquids with improved CO₂ capture capability.

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Supporting Information Available: Relative energies (with respect to the pre-complex) of all computed reaction intermediates and transition states, XYZ coordinates and absolute energies (in a.u.) for all computed species with DFT. RESP charges and force field type used in MD.

REFERENCES


