Understanding Carbamate Formation Reaction Thermochemistry of Amino Acids as Solvent for Post Combustion CO_2 Capture

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ABSTRACT

Carbamate stability constant for a dataset of 10 amino acids, having potential for being post combustion CO_2 capture (PCC) solvents, has been calculated using various implicit and explicit solvation shell models (ESS). The current work also includes an extensive study of gas phase free energy and enthalpy for the amino acid carbamate formation reaction with Hartree Fock (HF), density functional methods (B3LYP/6-311++G(d,p)) and composite methods (G3MP2B3, G3MP2, CBS-QB3, G4MP2). Ideal PCC solvent properties require finding a profitable tradeoff between various thermodynamic and system optimization parameters. Benchmark gaseous phase and solution phase thermodynamic properties given in the present work can help in making informed decisions when choosing promising PCC solvents. The temperature dependency of the carbamate stability constant of amino acids is predicted using PCM and SM8T implicit solvation models. PCC is a temperature swing absorption-desorption process and high temperature sensitivity of the $ln\ K_c^{AmCOO^-}$ value is of vital importance in attaining cost efficient processes.

1. INTRODUCTION

Post combustion CO_2 capture (PCC) based on reactive absorption is the most developed technology available today for reducing emissions of greenhouse gases and for avoiding potentially disastrous effects of anthropogenically induced climate changes.[1-2] The new IPCC report[3] emphasizes that CO_2 emissions mitigation must be implemented rapidly if the 1.5°C global temperature rise target is to be fulfilled. CO_2 removal by absorption combined with underground storage is the only deployment-ready technology available at the moment. One drawback of reactive absorption PCC is the significant energy demand required for regeneration of the solvent. To lower this energy demand, development of improved solvent mixtures based on a good understanding of the chemistry involved, is needed. Present work explores the potential of amino acids for being PCC solvents by understanding the underlying reaction chemistry of amino acids with CO_2.

Amino acids are naturally occurring and mostly environmental friendly green chemicals and have many advantages over conventional PCC solvents e.g. monoethanolamine (MEA), diethanolamine (DEA) etc.[4-7] The most commonly suggested amino acid solvent systems, neutralized with potassium hydroxide, are ionic systems and hence nonvolatile. This gives them an environmental advantage while working at low pressure and intermediate (60-70°C) temperature PCC plant conditions.[8] Amino acids are more stable towards oxidative degradation[9-10] than most amines, have viscosities similar to water[11-12] and high surface tension.[13-14] This makes them suitable for practical PCC processes in absorbers and also for so-called membrane contactors. Other advantages of amino acids include: high loading capacity,[6, 10, 15-16] fast reaction kinetics compared to MEA[4, 17-18] and a potential for low heat of regeneration in the stripper because of high equilibrium temperature sensitivity.[19] One of the distinct features of some amino

acids as PCC solvents is the formation of solid precipitates after absorption of CO_2. This can further increase CO_2 loading and reduce energy requirement[15, 20-21]. Ahn et. al.[22] have studied the corrosion properties of glycine and Taurine in PCC processes and have found less corrosion in case of Taurine compared to MEA. Amino acids can also be neutralized with an amine.[21,23] These amine amino acid salt solutions (AAAS) of glycine, alanine and sarcosine performed better than MEA at similar concentration levels in studies for their potential of CO_2 capture.[21] In their study of AAAS, sarcosine was found to perform best, but further room for enhancement of solvent properties to make PCC process more efficient were shown.[24] Amino acids such as glycine,[25-27] arginine,[25, 28] sarcosine,[25, 27] proline,[25, 27] histidine,[25] alanine;[25] have also been used as a promoters in various PCC processes.

The aqueous neutralized amino acid solvent system reacts with CO_2 either to form bicarbonate/carbonate in an acid–base reaction, or to form carbamate. Reactions involving dissociation of carbon dioxide (eq. 1, 2) and ionization of water (eq. 3) have been studied extensively in the literature.[29-34] However, the overall absorption rate of CO_2 in amino acids has very little dependency on these reaction rate constants and therefore knowledge of the forward reaction rate constants for reactions given in equation 4 and 5 becomes very important in order to understand the chemistry of a potential PCC solvent.

$$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+, \quad K_{a1} \tag{1}$$

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+, \quad K_{a2} \tag{2}$$

$$H_2O \leftrightarrow OH^- + H^+, \quad K_W \tag{3}$$

$$^+NH_3CHRCOO^- + H_2O \leftrightarrow H_3O^+ + NH_2CHRCOO^-, \quad K_{amino\ acid} \tag{4}$$

$$HCO_3^- + {}^-OOCRHCNH_2 \leftrightarrow {}^-OOCRHCNHCOO^- + H_2O, \quad K_c \tag{5}$$

The understanding of the reactions involving dissociation of protonated amino acid (eq. 4) and the carbamate formation reaction of amino acids (eq. 5) is crucial for getting insights into the reaction chemistry of the solvent. The deprotonation reaction for amino acids has been studied in the literature both computationally and experimentally.[35-36] In the present work, the carbamate stability constant, Kc (eq. 5) and its temperature dependency for a set of amino acids is predicted by using molecular modeling. We are not aware of any experimental determination of carbamate stability constants of amino acids because of it being an experimentally challenging domain. However, in the literature, Kc values for a few amines are available. The carbamate equilibrium constant of monoethanolamine (MEA) was calculated by various methods in the literature, e.g. by titration against NaOH,[37] by performing vapour–liquid-equilibrium (VLE) experiments,[38-39] and from nuclear magnetic resonance spectroscopic (NMR).[40-43] Sartori and Savage[44] calculated Kc values for MEA, 2- amino-2-methyl-1-propanol (AMP) and diethanolamine (DEA) by doing

C^{13} NMR spectroscopy experiments. NMR speciation studies and vapour liquid equilibrium (VLE) experiments were done to calculate carbamate stability constants for other amines such as MDEA,[45] piperazine,[45-46] ammonia,[47] diglycolamine and diisopropylamine,[40] 2-(2-aminoethyl)aminoethanol[41] and some more complex synthetically prepared amines.[48] However, in spite of the availability of a huge amount of literature data for PCC solvents, data for the carbamate stability constants is still scarce and we are to date not aware of any available data for amino acid Kc values. Nevertheless, carbamate stability constants are absolutely crucial to analyze thoroughly various factors which affect carbamate formation reaction chemistry in PCC solvents. Chakraborty et al. and da Silva et al.[49-50] are pioneer studies on theoretical investigations of amine carbamate stability constants.

PCC solvents having a very strong or a very weak tendency to bind with CO_2 may not be attractive choices as solvents. Solvents with low heat of reaction may not achieve high loadings and may have low equilibrium temperature sensitivity, whereas high heats of reaction may increase the energy demand in the desorber for reversing the carbamate formation reaction. On the other hand, high heat of reaction may indicate good equilibrium temperature sensitivity.[19] Variation in heat of reaction is mainly due to class of amine, primary, secondary or tertiary, see Kim et. al.,**[51]** but variations within each class exist. In addition to heat of reaction, solvation effects, influencing the component activity coefficients, play an important role in the equilibrium temperature sensitivity. In other words, the potential of a promising PCC solvent structure can, to a great extent, be determined by understanding the equilibrium constants governing the formation of different species involved. The choice of a potential solvent for PCC will then involve tradeoffs between various solvent thermochemical properties.

To summarize, we have studied carbamate stability constants and their temperature dependency in the present work because of three main underlying motivations. First, experimental carbamate stability constants of amino acids are not available, and as these are highly charged species (anionic, dianionic and trianionic), this provided us with a possibility of comparing the performance of various continuum solvation models with the explicit solvation shell model used in the present work. Second, to provide a comparison and comprehensive overview of variability within results of gaseous phase thermodynamic properties employing various composite methods (G3MP2B3, G3MP2, CBS-QB3, G4MP2), density functional (B3LYP/6-311++G(d,p)) and Hartree Fock (HF) methods. Third, the present work includes benchmark calculations of gaseous and solvent phase calculations for thermodynamic properties for promising PCC solvents. Hopefully, this can accelerate further development in the PCC area.

2. COMPUTATIONAL DETAILS AND METHODS

In this work, we have used Gaussian –n theories (G3MP2B3, G3MP2, G4MP2), complete basis set method (CBS-QB3), density functional theories (DFT) at B3LYP/6-311++G (d,p) level and HF/6-31G* gaseous phase calculations for amino acids and amino acid carbamates. Gas phase conformer search calculations and geometry optimizations were performed using HF/6-31G* and B3LYP/6-311++G (d,p) in Spartan 08.[52] Frequency calculations were performed for optimized structure obtained for confirming the absence of any imaginary frequency in the minima. The Gaussian 03 suite of quantum chemical program[53] was used for gaseous phase total enthalpies and free energy calculations using DFT, HF, CBS-QB3 and Gaussian –n theories. One exception is G4MP2, which was carried out in Gaussian 09.[54] Gas phase free energy and enthalpy of the

carbamate formation reaction of amino acids, not having any side chain carboxyl group, were calculated by using equations 6-8 as represented below

$$HCO_3^- + {}^-OOCRHCNH_2 \leftrightarrow {}^-OOCRHCNHCOO^- + H_2O, \quad \Delta G^0_{gas}(rxn) = \Delta G^0_1 and\ \Delta H^0_{gas}(rxn) = \Delta H^0_1 \tag{6}$$

$$\Delta G^0_1 = \Delta G_{{}^-OOCRHCNHCOO^-} + \Delta G_{H_2O} - \Delta G_{{}^-OOCRHCNH_2} - \Delta G_{HCO_3^-} \tag{7}$$

$$\Delta H^0_1 = \Delta H_{{}^-OOCRHCNHCOO^-} + \Delta H_{H_2O} - \Delta H_{{}^-OOCRHCNH_2} - \Delta H_{HCO_3^-} \tag{8}$$

Gas phase free energy and enthalpy of the carbamate formation reaction of amino acids having side chain acidic group (Glutamic acid and Aspartic acid in the present study) were calculated by using equations 9-11 given below

$$HCO_3^- + ({}^-OOC)_2RHCNH_2 \leftrightarrow ({}^-OOC)_2RHCNHCOO^- + H_2O, \quad \Delta G^0_{gas}(rxn) = \Delta G^0_2 and\ \Delta H^0_{gas}(rxn) = \Delta H^0_2 \tag{9}$$

$$\Delta G^0_2 = \Delta G_{({}^-OOC)_2RHCNHCOO^-} + \Delta G_{H_2O} - \Delta G_{({}^-OOC)_2RHCNH_2} - \Delta G_{HCO_3^-} \tag{10}$$

$$\Delta H^0_2 = \Delta H_{{}^-OOCRHCNHCOO^-} + \Delta H_{H_2O} - \Delta H_{({}^-OOC)_2RHCNH_2} - \Delta H_{HCO_3^-} \tag{11}$$

The solvent effects were studied using various continuum solvation models viz. PCM,[55] SM8T[56] and DivCon.[57] Solution phase conformer search and geometry optimization were carried out using equilibrium calculations in solvent model SM8 in Spartan 08 at HF/6-31G* and B3LYP-6-311++G (d, p) level. PCM and SM8T solvent phase calculations were carried out using Density Functional Theory (DFT) at PCM/B3LYP/6-311++G (d, p)//SM8/B3LYP-6-311++G (d, p) level and SM8T/B3LYP/6-311++G (d, p)//SM8/B3LYP-6-311++G (d, p) level respectively. PCM calculations were performed using default settings in the Gaussian 03 electronic structure program using Self-Consistent Reaction Field (SCRF) keyword and extra options read. The cavities based on atomic spheres, the GEPOL algorithm of Silla et al.[58] and RADII = UAHF, which uses the United Atom Topological Model applied on radii optimized for the HF/6-31G (d) level of theory are used. The SMx solvation models are a series of semi empirical models for computation of solvation free energy. The SM8T calculations were carried out using Gamessplus,[59] which also includes temperature dependency of the solvation free energy. It should be noted that none of the continuum solvation model is parameterized for ionic molecules such as amino acid carbamate in the present study. Continuum solvation models represent the solvent as a dielectric continuum and lacks the capability of capturing proton transfer or solute-solvent interactions such as intermolecular hydrogen bonding.[60]

In order to accurately account for such explicit solute solvent interactions, the explicit solvation shell (ESS) model introduced by da Silva et. al.[61] was used to calculate the solvation free energies of amino acid and amino acid carbamate studied in the present work. Molecular simulations of the solute molecule in bulk solvent were done to obtain solvation shell geometries of the cluster molecules for calculation of solvation free energies using ESS. We refer to da Silva et al.[61] for details regarding optimization of extracted clusters using quantum mechanical calculations and

calculations of cluster solvation free energies using Poisson-Boltzmann-based model in the DivCon code.[57] The results for solvation free energy of single solutes using DivCon model are retained in the current work for comparison with solvation energies obtained using other models. Gaussian 03 software was used to carry out all quantum mechanical calculations and all simulations were done using Sander from the AMBER 12 suite.[62] Supporting information contains a summary of the Poisson-Boltzmann model and details of the MD simulations. The complete description of ESS calculations can be found in da Silva et al.[61] and Gupta et al.[63] Using various continuous solvation models and ESS enabled us to compare solvation free energies obtained from various solvation models in the present work.

The thermodynamic cycle employed for calculation of solvation free energies in the present work using cluster-continuum models is given in Fig. 1. Many research groups report various thermodynamic cycles for computation of hydration free energy in the literature.[64-73] The one used in present work is discussed in detail by da Silva et al. and Bryantsev et al.[61, 74]

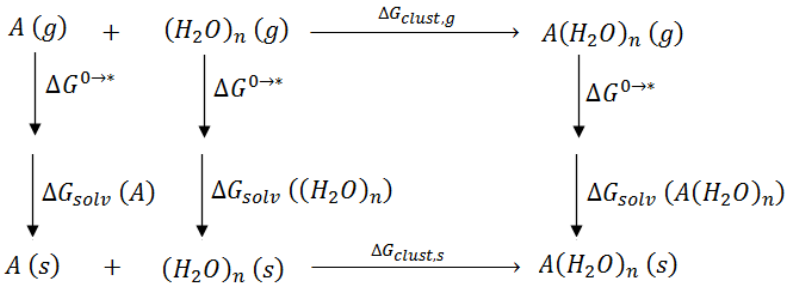

Fig 1: Thermodynamic Cycle for Computing Solvation Free Energies with the Explicit Solvation Shell Model.

The gas phase reaction between A (solute) and a water molecule cluster, ($(\mathbf{H_2O})_\mathbf{n}$), is shown by the upper leg of the thermodynamic cycle as given below

$$A(g) + (H_2O)_n(g) \xrightarrow{\Delta G_{clust,g}} A(H_2O)_n(g) \quad (12)$$

Using this thermodynamic cycle, the solvation free energy, $\Delta G^*_{solv}(A)$, of the solute was calculated by equation 13.

$$\Delta G^*_{solv}(A) = \Delta G^*_{clust,g}(A(H_2O)_n) + \Delta G^*_{solv}(A(H_2O)_n) - \Delta G^*_{solv}((H_2O)_n) - \Delta G^{0\to*} - \Delta G^{*\to l} \quad (13)$$

$\Delta G^*_{solv}(A)$ is determined by summing up the free energy of the gas phase solute-water cluster ($\Delta G^*_{clust,g}(A(H_2O)_n)$) formation having 'n' explicit H_2O molecules, the difference between the solvation free energies of the solute–water cluster ($\Delta G^*_{solv}(A(H_2O)_n)$) and the water cluster, $\Delta G^*_{solv}((H_2O)_n)$. Gas phase concentrations and the water cluster concentration were adjusted by standard state corrections ($\Delta G^{0\to*} = RTln(24.46)$) from 1 mol per 24.46 L to 1 M and from 1 M to 55.34/n M[75-76] ($\Delta G^{*\to l} = RT\ln([H_2O]/n)$) respectively. The gaseous phase standard state correction ($\Delta G^{0\to*}$) is 1.89 kcal mol^{-1} at 298K. This thermodynamic cycle was employed to study the solvation of a large series of cations and anions with clusters having five explicit water molecules and motivation for using five explicit H_2O molecules is discussed.[61] In the current work, we carried out our study using 5 explicit water molecules as well, mainly due to three considerations. First, by canceling out various common errors emerging from gaseous phase calculations, entropy calculations and solvation free energy becomes easier by having a consistent number of explicit water molecules compared to adding a different number of explicit water molecules for different molecules. Second, the dataset of amino acids chosen in the current

work contains small organic molecules which can be reasonably solvated using 5 explicit water molecules. Third, keeping the computational costs of the calculations within modest limits is also important. Finally, the results shown in the study by da Silva et al.[61] are promising enough to continue the present work using the same number of explicit water molecules. It should be noted, however, that there is a lot of discussion on the subject of number of explicit water molecules to be included to accurately describe solute-solvent interactions. Bryantsev et. al.[74] claimed that an approach of adding explicit H_2O molecules until the computed hydration free energies converge could be more reliable compared to methods based on size and polarization of ionic molecules. On the other hand, this approach is computationally costly and would likely not help in complete elimination of errors arising due to variations in gaseous and solvation phase calculations within one studied data set of molecules.

The carbamate stability constants (Kc) for amino acids without any acidic or basic side groups and for amino acids having a side chain acidic group correspond to reactions 9 and 10 respectively, represented by

$$HCO_3^- + {}^-OOCRHCNH_2 \leftrightarrow {}^-OOCRHCNHCOO^- + H_2O \qquad (14)$$

$$HCO_3^- + ({}^-OOC)_2RHCNH_2 \leftrightarrow ({}^-OOC)_2RHCNHCOO^- + H_2O \qquad (15)$$

For amino acids having a side chain acidic group, the carbamate formation occurs on the amino acid dianion because amino acids with an acidic side chain go through double deprotonation before the amino group is available for forming carbamate species. In the present study, we have

two amino acids which have a side chain carboxyl group (glutamic acid and aspartic acid). Carbamate stability constants corresponding to reaction 9 were calculated using the thermodynamic cycle shown in Figure 2 below.

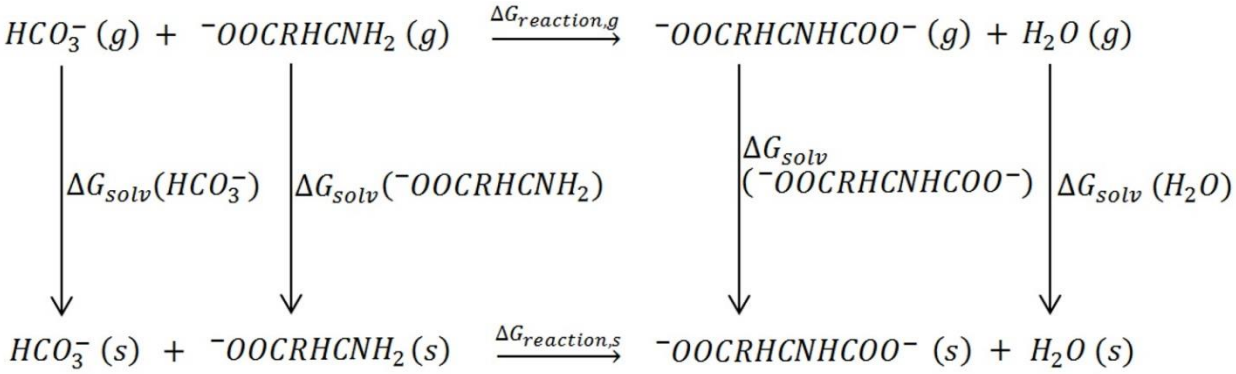

Fig 2: Thermodynamic cycle employed for calculation of carbamate stability constants for amino acids corresponding to reaction 9.

For glutamic acid and aspartic acid, amino acid and amino acid carbamate were replaced with their corresponding ionic species in the above thermodynamic cycle, as presented in reaction 10. We are not aware of any experimental study on carbamate stability constants of amino acids.[77] Determination of carbamate stability constants of amino acids using NMR or VLE methods pose experimental challenges, and these systems have not yet been studied in great detail. However, computational chemistry tools can be useful to obtain qualitative measures of the binding of CO_2 with different amino acid molecules. Gas phase calculations can be highly precise dependent on level of theory and method employed. Gaussian –n theories have been shown to calculate gaseous phase properties within experimental error bars. For solvation energies, continuum solvation models provide computationally inexpensive calculations. However, one has to be cautious about

the results as these models (PCM, SM8T and DivCon in the present study) are not parameterized for ionic species and amino acid and amino acid carbamate molecules involved in the present study are highly charged molecules (anions, dianions and trianions). The explicit solvation shell model used in this work appears to be a reasonably good approach for calculating solvation free energies of ionic species. This is the reason why solvation energies calculated with the ESS model were used for the final calculations of the carbamate stability constants. However, a full comparison of solvation free energies calculated from the different continuum solvation models (PCM, SM8T, DivCon) and ESS is also provided in this work.

3. RESULTS AND DISCUSSION

Table 1 presents the set of amino acids selected for this study together with their corresponding experimental pKa_1, pKa_2 and pKa_3 values at 298 K. The proposed amino acids have been shown in the literature to have desirable properties for being potential solvents for post combustion CO_2 capture processes.[78] This motivated us to perform a comprehensive study of gaseous and aqueous phase thermodynamic properties of these molecules which could help in understanding the underlying chemistry making these potentially good PCC solvents and thereby ease the search for new potent solvents.

Table 1 Studied set of amino acids including experimental pKa_1, pKa_2 and pKa_3 values at 298 K.

No.	Amino Acid	Abbreviation	Type*	Exp pKa** (298 K)		
				pKa_1	pKa_2	pKa_3
1.	Glycine	Gly	α, A	2.35[a]	9.77[b]	
2.	β-alanine	β-ala	β, A	3.55[c]	10.33[a]	
3.	Taurine	Tau	α	1.5[d]	9.06[a]	
4.	Sarcosine	Sar	A	2.21[e]	10.21[a]	
5.	Methionine	Meth	α, B	2.13[f]	9.3[a]	
6.	Proline	Pro	α, A	1.95[g]	10.76[a]	
7.	6-aminohexanoicacid	6-AHA	α	4.37[h]	10.80[h]	
8.	Phenylalanine	Phe-ala	α, B	2.2[i]	9.31[i]	
9.	Glutamic acid	Glu	α, A	2.19[j]	10.1[j]	4.45[j]
10.	Aspartic acid	Asp	α, A	1.99[h]	10.002[h]	3.9[h]

*A: Non-essential amino acid; B: Essential amino acid; **Experimental data from: a: King et al.[79] b:Hamborg et al.[35] c:May et al.[80] d: Andrews et al.[81] e: Datta et al.[82] f: Pelletier et al.[83] g: Smith et al.[84] h: Smith et al.[85] i: Anderson et al.[86] j: Nagai et al.[87]

Table 2 and 3 compares the Gn family,[88-89] CBS-QB3,[90-91] DFT[92] and HF[93] methods for calculation of gas phase Gibb's free energy and enthalpy change of the carbamate formation reaction for the studied set of amino acids. The results presented in Table 2 and 3 for gas phase free energy and enthalpy from the various composite methods show that the methods agree fairly well with each other and that the variation is within expected experimental error bars.

Table 2 Gibb's free energy of the amino acid carbamate formation reaction for the set of amino acids given in Table 1, using G3MP2B3, G3MP2, G4MP2, CBS-QB3, DFT and HF level of theories, at 298 K. (All values are in kJ mol^{-1})

Amino Acid	G3MP2B3	G3MP2	G4MP2	CBS-QB3	DFT(B3LYP/6-311++G(d,p))	HF/6-31G*
Gly	271.02	271.31	271.26	269.92	279.82	279.85
β-ala	241.82	243.37	241.55	244.00	242.16	254.45
Tau	212.94	212.18	213.34	212.65	220.39	224.38
Sar	241.61	276.81	280.74	278.51	291.95	303.85
Meth	242.35	238.74	244.93	241.00	258.04	261.95
Pro	269.80	281.72	281.49	281.17	300.69	311.97
6-AHA	153.87	152.76	154.83	154.02	164.10	166.48
Phe-ala	244.02	245.15	244.47	249.48	263.82	267.24
Glu	487.34	486.59	486.53	485.35	495.15	495.97
Asp	543.28	544.29	541.07	542.33	548.94	554.46

*The gas phase carbamate formation reaction free energy is calculated using eq. 7 and 10.

Table 3 Enthalpy of amino acid carbamate formation reaction for a data set of amino acids given in Table 1, using G3MP2B3, G3MP2, G4MP2, CBS-QB3, DFT and HF level of theories, at 298 K. (All values are in kJ mol-1)

Amino Acid	G3MP2B3	G3MP2	G4MP2	CBS-QB3	DFT	HF/6-31G*
Gly	266.64	265.67	266.56	265.51	275.68	278.74
β-ala	243.18	243.21	242.77	244.31	239.86	254.01
Tau	209.12	208.16	209.58	208.67	217.36	219.97
Sar	236.40	271.71	274.67	271.98	286.77	298.38
Meth	231.57	229.02	234.11	230.36	249.00	256.25
Pro	258.05	277.71	279.59	278.73	296.94	307.02
6-AHA	149.87	148.66	150.37	149.59	168.20	161.76
Phe-ala	239.27	239.40	239.87	254.43	255.96	260.92
Glu	480.13	479.07	480.17	478.67	490.17	489.19
Asp	540.74	539.62	539.47	540.12	547.94	549.45

*The gas phase carbamate formation reaction enthalpy is calculated using eq. 8 and 11.

Ghahremanpour *et. al.*[94] have found that CBS-QB3 gives similar or lower root mean square deviation (RMSD) compared to the Gn family of composite methods for similar compounds as reported in the current study. In the current work, as given in Table 2 and 3, we have also observed that calculated gas phase thermochemical properties of amino acids, for various Gn theories and CBS-QB3 levels of theory, lie within expected limits of experimental error bars of ~1-2%. Results from DFT calculations are also in the same range as the results calculated by using various composite methods. However, Hartree Fock theory was not able to produce results in a similar experimental error bar range of around 2%. This can be attributed to the lack of electron correlation considerations in its basic parametrization. Da silva *et. al.*[95] found similar error bars of around 1.5 kcal/mol compared to the experimental value of 333.7 kcal/mol, for calculation of gas phase free energy of nitrous acid, using various composite methods viz. G3MP2, G2, G3, G2MP2, G3B3, G3MP2B3, QCISD(T), CBS-4, CBS-Q, CBS-QB3, and CBS-APNO. They observed an average error of 2.72 kcal/mol and 4.66 kcal/mol for density functional theory at B3LYP and HF level of theory respectively. This is consistent with corresponding errors seen in the current gas phase calculations.

Gas phase free energy of reaction can be reproduced within a RMSD of approximately 1.5 kcal/mol using high level methods such as CBS-QB3.[96-97] This is the method chosen for the final calculations of the carbamate stability constants in the current work. From our earlier work on pKa calculations for a dataset of amino acids[63] and amines[60], we have seen that employing CBS-QB3 gaseous phase results for pKa calculations yielded lower RMSD values. error. For ensuring accuracy of CBS-QB3, results are compared against other composite methods (G3MP2B3, G3MP2, G4MP2). Computationally less expensive DFT and HF results are also compared against composite methods to ensure comparison of gaseous phase results over full range of commonly

employed methods and the variability of results within different methods. Optimized amino acid and amino acid carbamate structures at CBS-QB3 level of theory are given in Fig. 3.

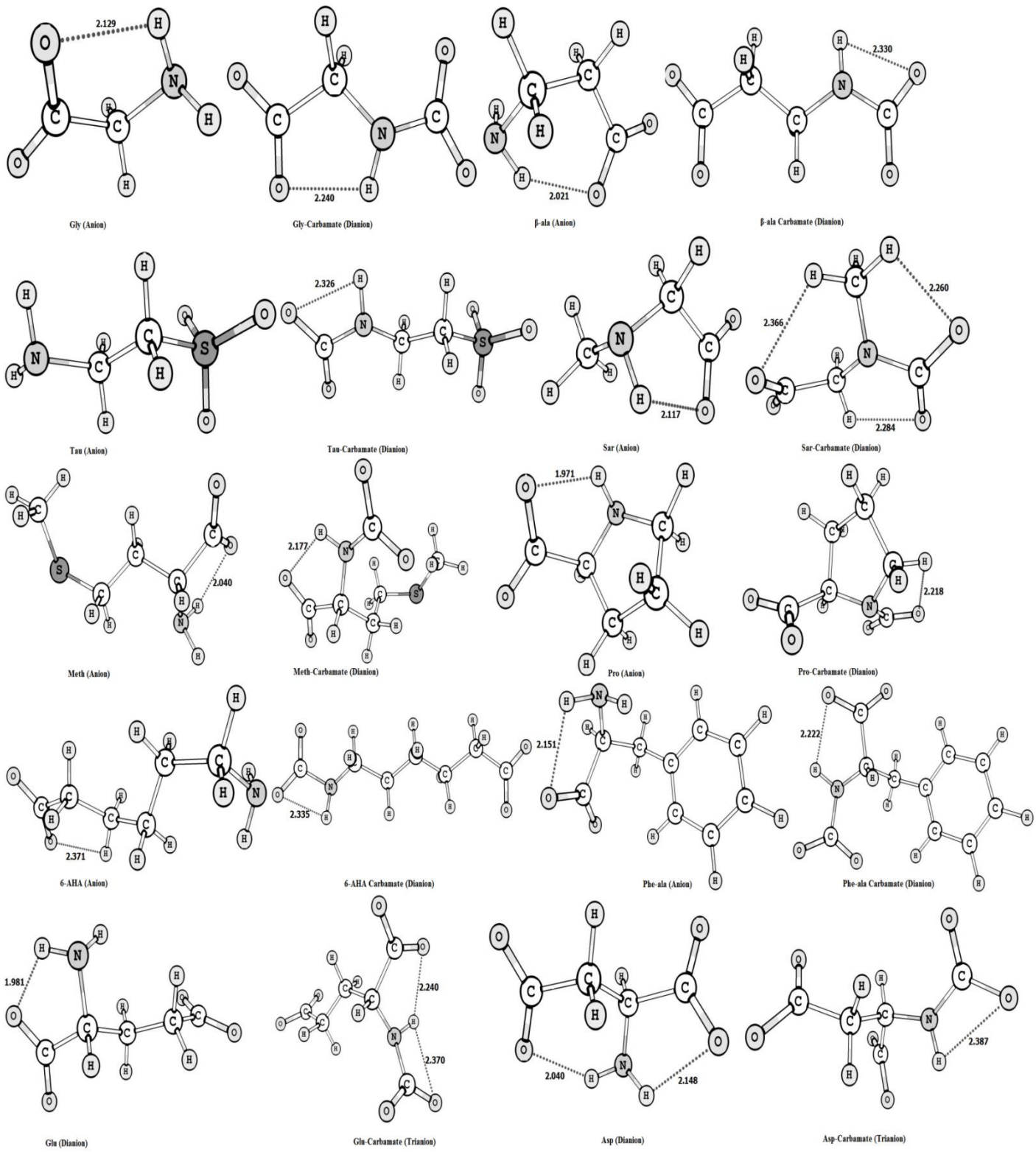

Fig 3: Optimized gas phase form of amino acids and amino acid carbamate studied in present work at CBS-QB3 level of theory.

Experimental data for gas phase free energy and enthalpy are not available for carbamate formation reactions. We assume that such data are unlikely to be available in the near future, given the demanding nature of experimental work necessary and the stability and complexities of the reaction solutions of the various amino acid-CO_2-water systems in PCC processes. This further signifies the importance and need for the presented studies for gas phase thermochemical properties in the current work.

Calculation of free energy of solvation for amino acids and amino acid carbamates is the largest contributor to the error or uncertainty in the carbamate stability constant calculation. This is still a challenging domain in computational chemistry and largely depends upon the type of solvation model, viz. implicit, explicit or implicit-explicit method, and level of theory employed.[60-61, 63, 98] In the current work, the solvation free energies for amino acids and amino acid carbamates were calculated using various implicit solvation models, viz. PCM, SM8T and DivCon, and the explicit solvation shell model (ESS) in order to have a thorough comparison of solvation free energies calculated by using different approaches.

The results of free energy of solvation for amino acids and amino acid carbamates studied in the present work, calculated using the explicit solvation shell model, are given in Table 4. Table 4 also lists corresponding cluster formation energies, entropies and cluster solvation energies for the studied molecules using the ESS model. The Poisson-Boltzmann continuum solvation model was used to calculate the cluster solvation energies given in Table 4. A detailed explanation of the ESS solvation free energy calculations and various corrections applied to obtain the final results in the present study can be found in da Silva et al[61] and in the supporting information to the present work.

Table 4 Free energy of solvation for the selected amino acids and amino acid carbamates calculated by the Explicit Solvation Shell Model (ESS). (All values are in Kcal/mol).

AminoAcid Species (Charge)	ΔG_{solv} (Calcd)[a]	$\Delta E^*_{cluster}$ [b]	$-T\Delta S^*_{cluster}$ [c]	$\Delta G_s(A(S)_n)$ [d]	Area[e]
Amino Acid					
Gly (-1)	-74.22	-32.03	10.09	-64.65	214.11
β-ala (-1)	-69.13	-30.80	12.14	-62.82	227.27
Tau (-1)	-71.46	-27.81	11.00	-67.02	241.32
Sar (-1)	-73.32	-35.79	10.56	-60.45	229.44
Meth (-1)	-67.56	-29.46	11.04	-61.51	282.03
Pro (-1)	-70.18	-34.77	11.57	-59.34	246.71
6-AHA (-1)	-72.59	-28.45	11.92	-68.41	283.15
Phe-ala (-1)	-68.90	-32.79	11.86	-60.33	292.83
Glu (-2)	-201.19	-54.15	12.29	-171.69	274.04
Asp (-2)	-207.75	-56.41	12.83	-176.53	252.43
Amino Acid Carbamate					
Gly (-2)	-216.1	-62.89	11.6	-177.14	238.91
β-ala (-2)	-205.1	-54.77	11.4	-174.10	263.83
Tau (-2)	-197.9	-49.54	11.3	-172.08	275.27
Sar (-2)	-215.7	-64.24	12.2	-176.00	252.57
Meth (-2)	-201.7	-54.72	11.6	-170.96	308.53
Pro (-2)	-216.4	-63.86	13.4	-178.33	268.76
6-AHA (-2)	-185.7	-48.77	11.8	-161.06	321.84
Phe-ala(-2)	-204.9	-59.27	11.7	-169.71	321.56
Glu (-3)	-393.88	-76.89	12.9	-342.27	303.18
Asp (-3)	-414.46	-87.06	14.0	-353.76	278.37

(a) Calculated free energy of solvation; all values shifted by -2.41 kcal/mol to remove systematic error relative to experimental values as in ESS model presented by da Silva et al[61]. Estimated sampling standard deviation is 1 kcal/mol. (b) Energy of formation of the cluster at the HF/6-31+G (d) level, converted from a standard state of 1 atm to 1 mol/L. Thermal corrections to the energy and zero-point energies not included. (c) Temperature (298 K) multiplied by the entropy of formation of the cluster at the HF/6-31+G (d) level. (d) Free energy of solvation of the cluster calculated with the Poisson-Boltzmann continuum model. (e) Area of clusters calculated with the Poisson-Boltzmann continuum model.

We believe that it is difficult for a single solute-solvent geometry to represent all possible interactions. Therefore, hundred different solute-solvent cluster geometries were extracted by using molecular dynamics simulations. Out of 100 explicit solvent-solute configurations submitted for calculations, we encountered roughly 10-15 failed cluster geometry optimizations and vibration frequency calculations for each molecule. This is similar to what was observed by da Silva et al.[61] in their work. Observed breakdown of solute or solvent molecule geometry could be a result of imperfect initial cluster configuration geometry obtained from the molecular dynamics simulations. An energy deviation of ±80 Kcal/mol, from the minimum energy solute-solvent cluster geometry obtained, was assigned as cut off for ensuring removal of failed geometries and to keep only stable cluster geometries. The most stable solute solvent cluster geometries obtained in the current work are presented in Figure 4 and 5 for amino acids and amino acid carbamates respectively. From Figure 4 and 5, it can be seen that the explicit solvent molecules interact with most of the solute generating a complete solvation shell for the amino acids Gly, β-ala, Glu and Asp and for nearly all the optimized amino acid carbamate clusters. However, for other amino acids, an explicit solvation shell is not perfectly created as solvent molecules are clustered near hydrophilic groups in the amino acids, exposing hydrophobic groups in the solute molecule.

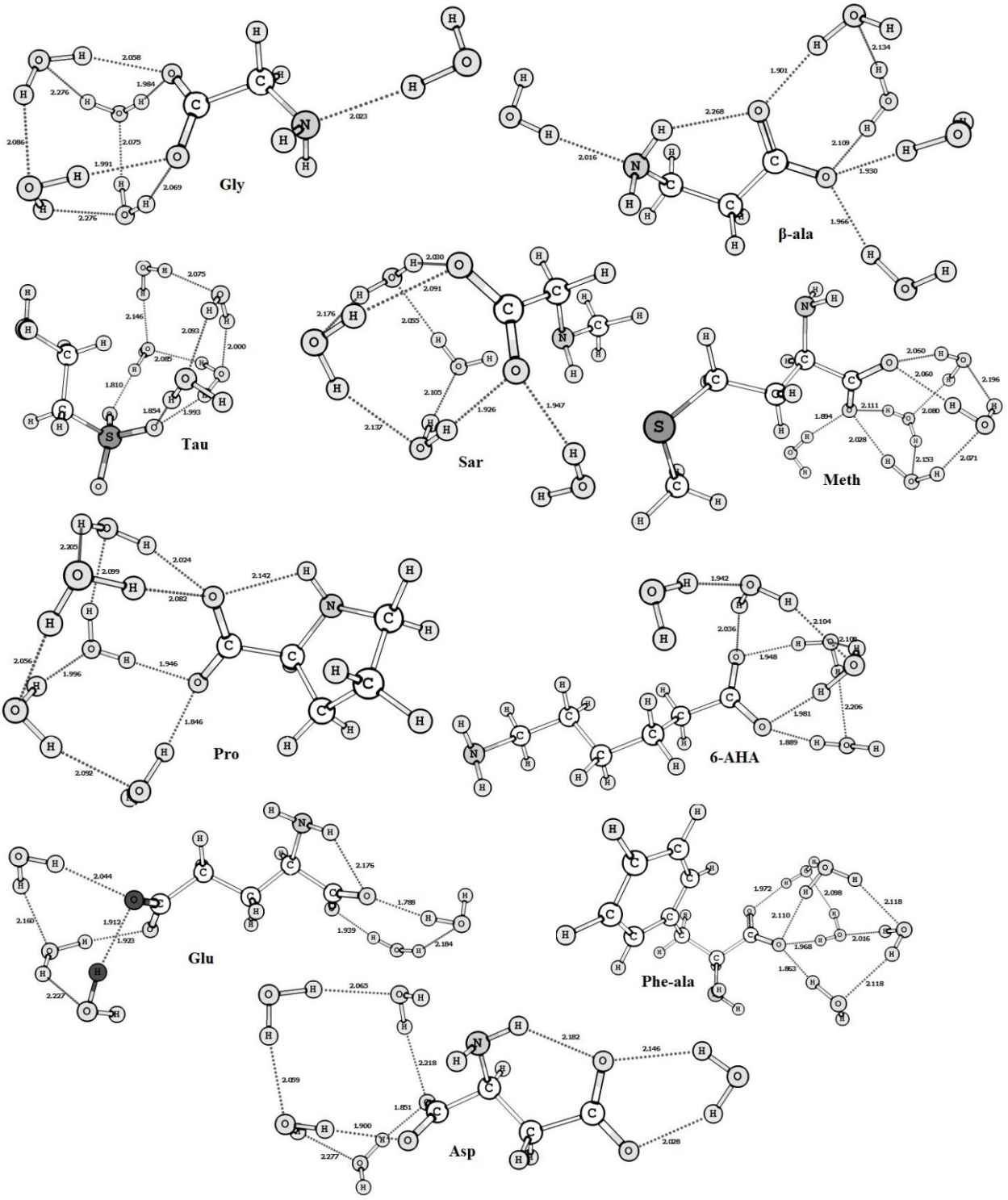

Fig 4: Optimized clusters of amino acids studied in this work. (Dotted lines show Hydrogen bonds and bond lengths of Hydrogen bonds are given in Angstrom).

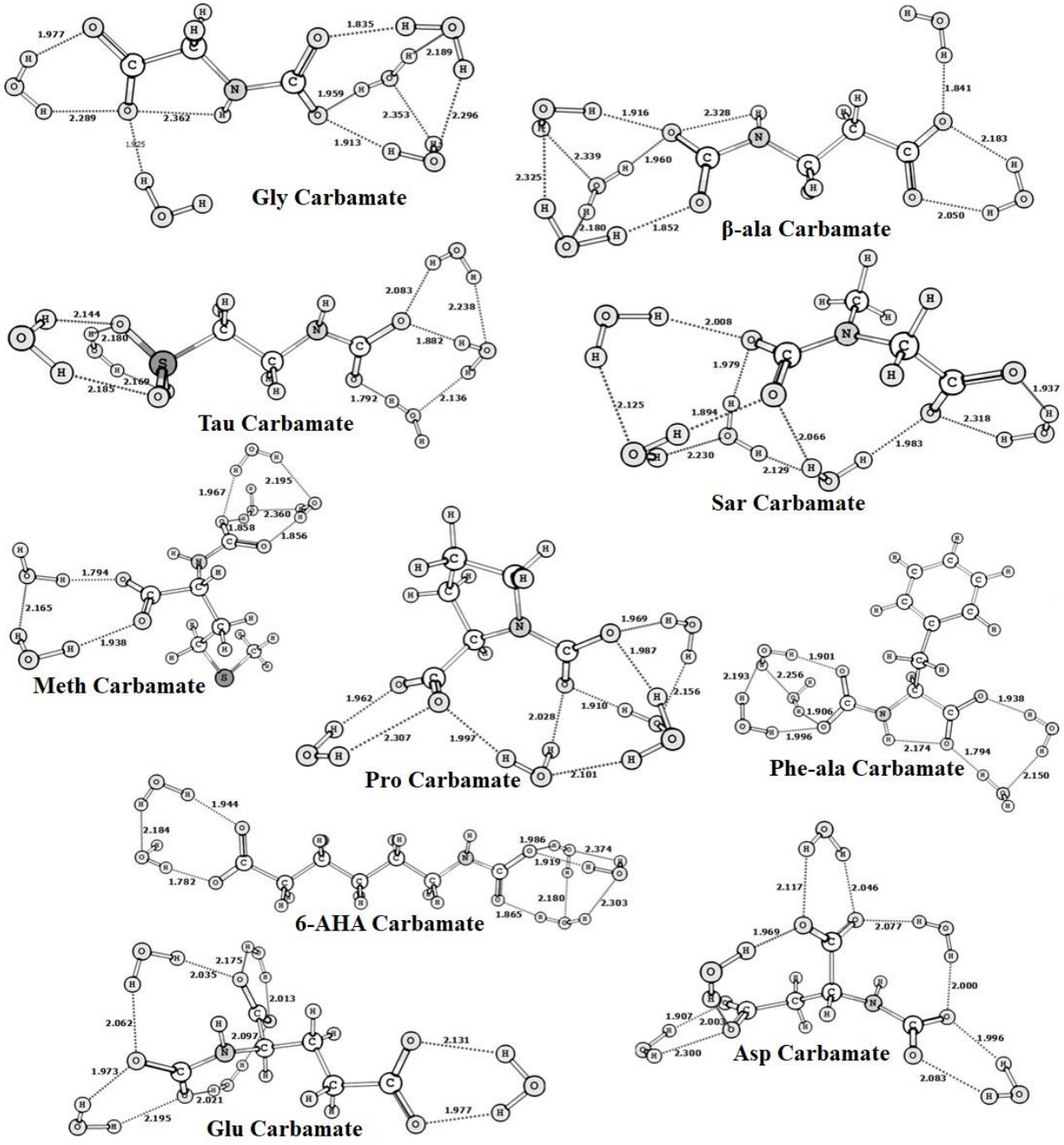

Fig 5: Optimized clusters of amino acid carbamate studied in this work. (Dotted lines show Hydrogen bonds and bond lengths of Hydro-gen bonds are given in Angstrom)

The free energies of solvation for the amino acids and corresponding carbamate counterparts, calculated using the explicit solvation shell model and various implicit solvation shell models (PCM, SM8T and DivCon), are given in Table 5.

Table 5 Comparison of Free Energy of Solvation for the selected amino acids and amino acid carbamates calculated using the Explicit Solvation Shell (ESS) Model and the Implicit Solvation Models (PCM, SM8T, DivCon). (All values are in Kcal/mol).

Amino Acid Species (Charge)	ΔG_{solv} (calcd)			
	Explicit Solvation Shell Model	Implicit Solvation Shell Models		
	ΔG_{solv} (Calcd)[a]	PCM	SM8T	DivCon
Amino Acid				
Gly (-1)	-74.22	-71.30	-73.63	-74.26
β-ala (-1)	-69.13	-73.04	-74.93	-72.53
Tau (-1)	-71.46	-68.54	-78.33	-74.27
Sar (-1)	-73.32	-70.27	-73.505	-72.73
Meth (-1)	-67.56	-63.80	-65.17	-69.66
Pro (-1)	-70.18	-69.63	-72.25	-71.19
6-AHA (-1)	-72.59	-75.46	-76.77	-74.67
Phe-ala (-1)	-68.90	-64.67	-65.76	-70.2
Glu (-2)	-201.19	-190.63	-198.47	-200.75
Asp (-2)	-207.75	-203.27	-215.80	-210.16
Amino Acid Carbamate				
Gly (-2)	-216.11	-205.10	-217.70	-215.17
β-ala (-2)	-205.08	-198.60	-208.79	-204.98
Tau (-2)	-197.91	-188.68	-208.68	-199.94
Sar (-2)	-215.73	-200.89	-213.92	-214.64
Meth (-2)	-201.74	-192.01	-203.99	-203.31
Pro (-2)	-216.43	-202.28	-216.27	-215.69
6-AHA (-2)	-185.71	-181.93	-189.32	-184.94
Phe-ala(-2)	-204.87	-190.34	-202.30	-204.15
Glu (-3)	-393.88	-373.25	-395.11	-393.85
Asp (-3)	-414.46	-390.99	-417.23	-413.64

(a) Calculated free energy of solvation; all values shifted by -2.41 kcal/mol to remove systematic error relative to experimental values as in ESS model presented by da Silva et al.[61] Estimated sampling standard deviation is 1 kcal/mol.

From Table 5, it can be seen that solvation free energies calculated by the different models are in the same range. Results from ESS, SM8T and DivCon model vary within ±5 Kcal/mol for most of the molecules. For the amino acid carbamate species, however, we believe that the ESS results are more reliable than the continuum solvation model results because of the better description of the solute-solvent interactions in the explicit solvation shell model compared to the continuum solvation models. In our previous study[63], pKa of dataset of amino acids employed in current work, is shown to give lower errors utilising ESS solvation energies combined with CBS-QB3 gaseous phase free energies. No computational model has been parameterized for the highly charged amino acid carbamate anions studied in this work as there are no experimental solvation energy data available for such molecules. The reason is that it is difficult to experimentally study molecules having high charge. Moreover, any experimental solvation free energy of ions will inherit around 10 kcal/mol of uncertainty present in the solvation free energy of the proton upon which it depends. This can be calculated as shown in equation 16 below.[98-101] $\Delta G_{solv}^{*,conv}(ion)$ represents the conventional solvation free energy of the ion and in principle this can be calculated from experiments. The absolute free energy of solvation, $\Delta G_{solv}^{*}(ion)$, however, depends also upon $\Delta G_{solv}^{*}(H^+)$. q represents the net charge of the ion.

$$\Delta G_{solv}^{*}(ion) = \Delta G_{solv}^{*,conv}(ion) + q\Delta G_{solv}^{*}(H^+) \quad (16)$$

Noyes et al.[100] and Marcus et al.[99] used $\Delta G_{solv}(H^+)$ equal to −262.4 kcal/mol and −254.3 kcal/mol respectively for the determination of the experimental free energy of solvation of ions. Merz and co-workers employed the Marcus et al.[89] data set for calculating the free energy of solvation of

ions,[102-104] whereas the data set developed by Noyes et al.[90] was used for derivation of ion-water potential parameters of metal cations.[105] Reif et al.[106] proposed a value of −264.8 kcal/mol for $\Delta G_{solv}(H^+)$ for the recalibration of interaction parameters of charged amino acid side chains to develop the GROMOS 54A8 force field. For development of the Minnesota solvation database[107] and the universal solvation model (SMD),[108] a $\Delta G_{solv}(H^+)$ value of 265.9 kcal/mol was used. This value was predicted by Tissandier et. al.[109] and is believed to be the best estimate for $\Delta G_{solv}(H^+)$ in the literature at present.[76] This discrepancy in $\Delta G_{solv}(H^+)$ demands careful evaluation of the experimental free energy of solvation of ions, amino acids and amino acid carbamates (once these value become available in literature), before comparing these to computationally predicted values as presented in this work. Among the computational chemistry based methods available today for calculation of solvation free energies, we have most confidence in the free energy of solvation results for ions calculated with the explicit solvation shell model approach and these values are used for calculation of the final Kc values as discussed before.

Solution phase reaction free energies for carbamate formation are given in Table 6. By looking at the results, Proline seems to have a large solution phase energy in comparison to the other amino acids with no side chain group. It is followed by Sarcosine, Glycine, Methionine and Phenyl-alanine. The more negative the solution free energy of the carbamate formation reaction is, represented by reaction 14 and 15, the stronger is the tendency of that amino acid to capture CO_2 in aqueous solution. From the results presented in Table 6, Proline has a promising solution phase free energy for being a potential CO_2 capture solvent. Glutamic acid and Aspartic acid have high solution phase free energies. However, it is essential to be careful while weighing their potential for being CO_2 capture solvent as they have high molecular weight and hydrocarbon groups, which make them less efficient in CO_2 binding. Also, the higher solubility of proline in water as compared

to glutamic acid and aspartic acid, can result in higher CO_2 loading per unit liquid volume, possibly leading to lower regeneration cost as the total solvent volume required for CO_2 capture can decrease, which depends on the cyclic capacity of the solvent. In the literature as well, proline[4, 17, 110] and sarcosine[4, 111-112] are shown to be promising solvents in various experimental kinetics studies of amino acids because of having high reaction rate constant. Shen et. al.[113] studied a potassium prolinate (ProK)/ethanol solution as CO_2 absorbent system and found that this system shows fast absorption rate with proline carbamate, bicarbonate and ethyl carbonate salts being the main species as studied by NMR and XRD analysis.

Table 6 Solution phase reaction free energies for carbamate formation at 298 K. (All values are in kcal mol^{-1})

Amino Acid	ESS	PCM	SM8T	DivCon
Gly	-68.13	-60.04	-70.32	-67.15
β-ala	-62.20	-51.80	-60.10	-58.69
Tau	-52.69	-46.38	-56.60	-51.91
Sar	-68.65	-56.86	-66.66	-68.15
Meth	-60.42	-54.45	-65.06	-59.89
Pro	-72.50	-58.89	-70.26	-70.74
6-AHA	-39.37	-32.71	-38.79	-36.51
Phe-ala	-62.22	-51.91	-62.79	-60.19
Glu	-118.93	-108.86	-122.88	-119.34
Asp	-132.95	-113.96	-127.67	-129.72

Figure 6 summarizes the results from the different models for total reaction free energy for carbamate formation. Absolute values from different solvation models are not consistent with each other because, as explained earlier, none of the models are parameterized for highly charged ionic

species. Hence, the results presented in Figure 6, should be regarded as a qualitative test for the different amino acids as well as of the performance of the various solvation models for charged species. We believe that the solvation free energies from the ESS model combined with CBS-QB3 gas level calculations can provide reasonably good estimates for the carbamate stability constants of amino acids studied in this work. In Figure 6, results for ln Kc for the different amino acids from the ESS model are also plotted separately for a better visibility of the results. The results for the total reaction free energies calculated by adding the solvation free energies from ESS and gaseous phase energy from the CBS-QB3 method, suggest the following trend for ln Kc for the amino acids studied in the present work.

Proline > β-alanine > Phenyl-alanine > Glycine > Aspartic acid > Glutamic acid > Methionine > 6-aminohexanoic acid > sarcosine > Taurine

However different trends would be obtained following free energy of solvation calculations from different continuum solvation models.

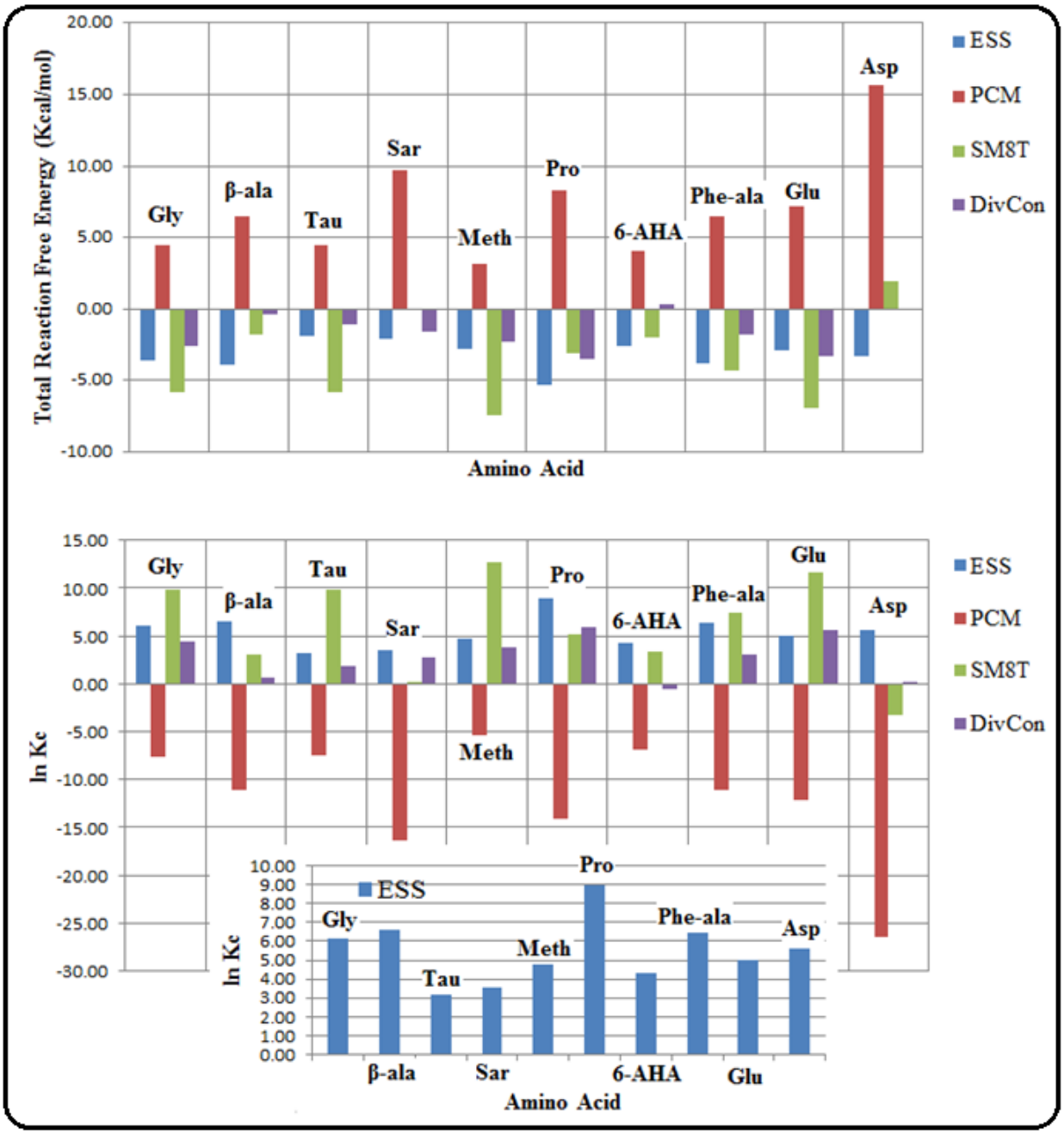

Fig 6: Total carbamate formation reaction free energy (kcal/mol) and corresponding ln Kc for a data set of amino acids studied in this work using different solvation models. Ln Kc for different amino acids is also shown for ESS separately for better understanding of results.

Since there are no experimental results available for amino acid carbamate formation, the results presented in this work can be useful in better understanding the potential of amino acids as CO_2 capture solvents. However, the results provided in this work, should be regarded as qualitative measures of Kc, and we strongly encourage the need for experimental data for such systems as this would also help in validating results presented.

Finding a promising solvent for PCC processes, having temperature swing, entails tradeoffs between various properties. The temperature sensitivity of the various equilibrium constants plays a vital role in determining the overall energy cost of a solvent. There is a lot of experimental[35, 114] and computational[36, 115] research reported in the literature on the temperature sensitivity of pKa of various PCC solvents. This has proven to be of high importance in understanding the overall performance of an absorbent system. In the current study, the temperature dependency of amino acid carbamate constants in a temperature range of 273-373 K has been studied using PCM and SM8T solvation models. This temperature range was chosen as absorption and desorption take place at around 40-60^{0}C and 100-120^{0}C respectively, in commonly used PCC processes. Understanding the temperature sensitivity of various solvents in this temperature region can give significant insight about the performance of the absorbent system. Fig. 7 shows a comparison between experimental and calculated (using the PCM and SM8T models) temperature sensitivity of the carbamate stability constant for MEA. For PCM and SM8T models, calculated ΔG_{solv} is shifted to experimental ΔG_{solv} given by Jakobsen et. al.[41] at 293 K. From Fig. 7, we see that the uncertainty in the experimental ln Kc values is not only limited to values at 298 K but has also been translated to its temperature sensitivity. However, the temperature sensitivity in $ln\ K_c^{AmCOO^-}$ calculated by using the SM8T model correlates nicely with experimental values given by Jakobsen et al.[41] and Sartori et al.[44] over a temperature window of 293-313 K, and gives us

confidence in the predictive capabilities of the SM8T model for $ln\ K_c^{AmCOO^-}$ over the studied temperature range in the current work. Calculated (PCM and SM8T) $ln\ K_c^{AmCOO^-}$ values at 293 K have been anchored to experimental $ln\ K_c^{AmCOO^-}$ value of Jakobsen et. al.[41] ($ln\ K_c^{AmCOO^-}$ = 3.64 at 293K) as explained in our previous work.[36, 115] Experimental $ln\ K_c^{AmCOO^-}$ value at only one other temperature ($ln\ K_c^{AmCOO^-}$ = 2.645 at 313 K) is given by Jakobsen et. al.[41], and to understand accuracy of predicted temperature dependency from PCM and SM8T models, the calculated $ln\ K_c^{AmCOO^-}$ (at 313K) is compared against this value. The root mean square error (RMSE) of SM8T predicted lnKc (2.53) and PCM predicted $ln\ K_c^{AmCOO^-}$ (3.00) at 313K, is 0.11 and 0.36 respectively. These findings agree with our previously reported study of temperature dependency of pKa of amino acids[36] and amines[115] using SM8T and PCM solvation models, where we had shown similar higher accuracy for SM8T solvation model for predicting temperature dependency. SM8T is parametrized for ions and may predict better solvation free energies for ionic species as encountered in present work.

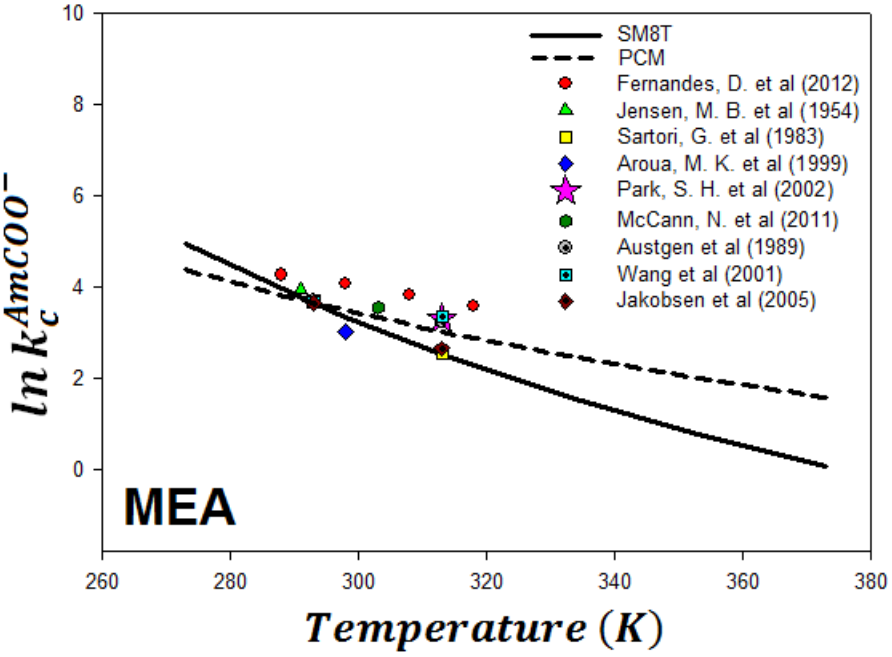

Fig 7: ln $K_c^{MEACOO^-}$ for MEA carbamate formation reaction [$RR'NH(l) + HCO_3^-(l) \leftrightarrows RR'NCO_2^-(l) + H_2O(l)$] as a function of temperature.

The temperature sensitivity of the carbamate stability constant for the selected set of amino acids was studied using both the SM8T and PCM models. Results from the SM8T model are presented in Fig. 8 and results from the PCM model are given in supporting information. From Fig. 8, we can see that $ln\ K_c^{AmCOO^-}$ for all studied amino acids decreases with increasing temperature, as also observed for MEA. At 293 K, the calculated $ln\ K_c^{AmCOO^-}$ was shifted to the experimental carbamate stability constant[41] for MEA ($ln\ K_c^{MEACOO^-}$) for easy comparison of the temperature sensitivity of $ln\ K_c^{AmCOO^-}$ over the studied temperature range.

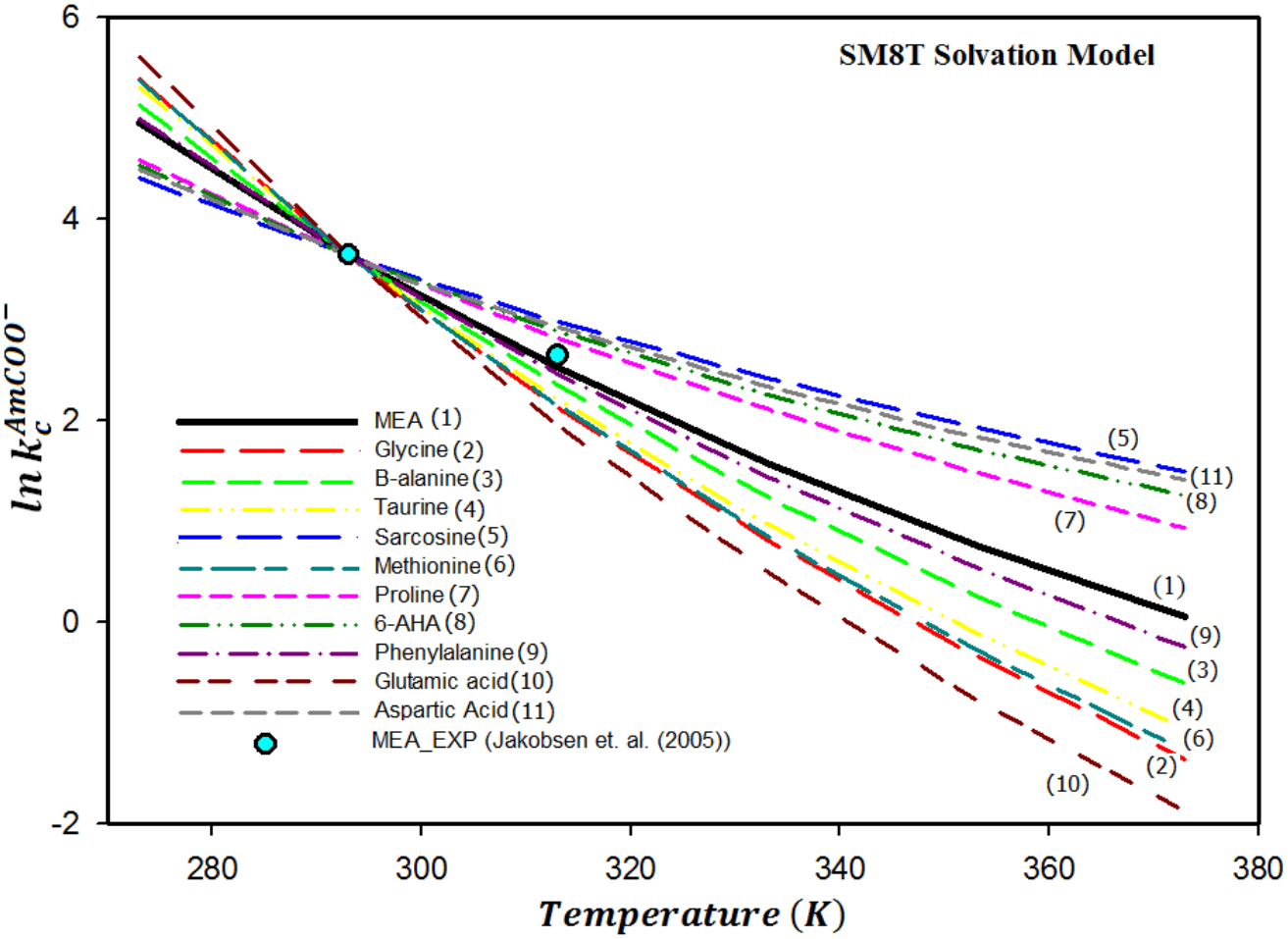

Fig 8: Temperature dependency of amino acid carbamate stability constant [$ln\ K_c^{AmCOO^-}$] with SM8T continuum solvation model. (At 293 K calculated amino acid carbamate stability constant is shifted to the experimental MEA ln Kc value (Jakobsen et. al. 2005)).

Fig. 9 shows the temperature gradient of $ln\ K_c^{AmCOO^-}$ over the temperature window of 273-373 predicted by both the SM8T and PCM models. High temperature gradient for $ln\ K_c^{AmCOO^-}$ value for a temperature dependent PCC solvent ensures less energy intensive desorption for that solvent as the partial pressure of CO_2 will increase more rapidly with temperature. Hence, the higher the

temperature gradient of $ln\ K_c^{AmCOO^-}$, the better are the chances for it being a promising PCC solvent. From Fig. 9, it can be seen that PCM model predicts negative temperature sensitivity for some amino acids and it predicts generally very low sensitivities, including MEA. PCM model is thus not efficient in capturing temperature sensitivity of amino acid carbamate stability constants. From the results on carbamate stability constant temperature gradient using the SM8T model in Fig. 9, we can see that most of the amino acids in the studied data set have a greater or similar temperature gradient of the $ln\ K_c^{AmCOO^-}$ value than MEA (except Proline, 6-AHA, Aspartic Acid and Sarcosine, as clearly visible from Fig. 8). The SM8T model, as mentioned earlier, is parametrized for ionic molecules and efficient in predicting temperature gradients of amino acid carbamates.

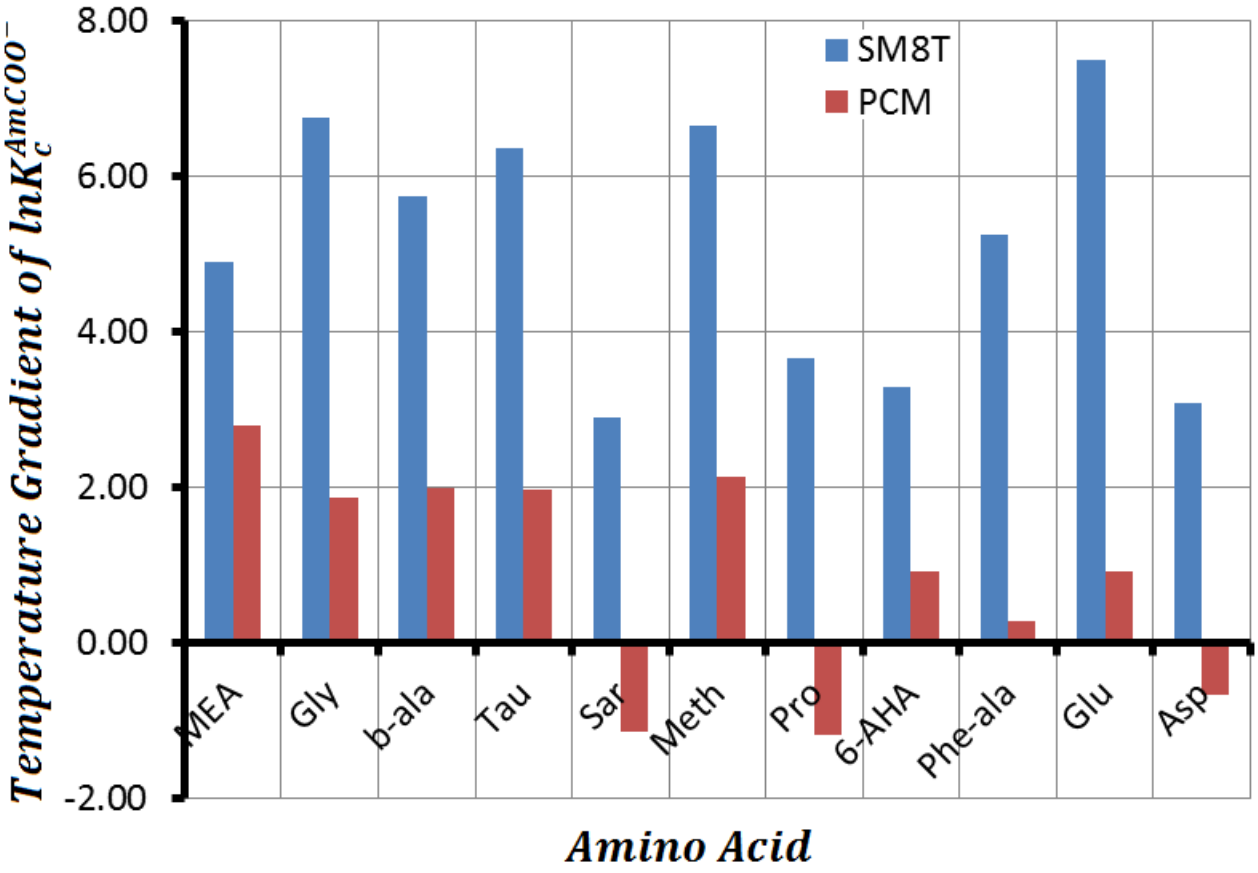

Fig 9: Temperature gradient of ln Kc for different amino acids over the temperature range of 273-373 w.r.t MEA using SM8T and PCM models. (The results from both models are anchored to Experimental MEA ln Kc value (Jakobsen et. al. 2005) at 293 K for all the amino acids and MEA.)

From Fig. 9, we can see that proline has a lower temperature sensitivity than MEA, but has the highest ln Kc value as shown in Fig. 6. As earlier discussed, finding an optimal solvent for CO_2 capture requires an optimal balance of various properties of the solvent. For proline, high ln Kc value indicates high affinity of proline for CO_2, i.e relatively stable proline carbamate, and still it possesses almost similar temperature sensitivity as MEA. This means that even a stable proline

carbamate will have lower regeneration energy requirements, and can boost energy efficiency. The high temperature sensitivity trend observed for glutamic acid is promising, but as previously discussed it may have lower cyclic capacity on liquid volume basis (due to its high molecular weight and low solubility in water).

To sum up, an ideal PCC solvent should have an optimal value for both ln Kc, temperature sensitivity and other properties as most of these properties depend upon each other. We believe that gaseous and aqueous thermodynamic studies provided in present work, can help further development and understanding of amino acids as promising PCC solvents.

4. CONCLUSIONS

The ln Kc data presented in this work would help to screen different amino acid molecules for being potential PCC solvents and on the other hand this work provides a comparison of solvation free energies calculated from various continuum solvation models and explicit solvation models and benchmark gaseous phase thermochemical properties for studied set of amino acids and amino acid carbamate. Calculated solvation free energy values for amino acids and amino acid carbamates can serve as helping tool for more advancement in the field despite having lack of experimental results available at present. From current study, proline and sarcosine seems to be having fairly large reaction free energy for carbamate formation reaction, whereas Glycine and methionine shows very promising temperature gradient for $ln\, K_c^{AmCOO^-}$ value. So, having thermochemical properties of a set of amino acids can help in choosing an absorbent system which could help in retaining profitable trade off of maximum properties and result in cost effective PCC solvent.

ASSOCIATED CONTENT

Supporting Information: Molecular geometries for various amino acids species (anion (amino acid)), di-Anion (amino acid carbamate, amino acids having side chain carboxylic group) and tri-Anion (amino acid carbamate from amino acids having side chain carboxylic group)) (x, y, z Cartesian Coordinates in Å). Constant terms utilized in calculations for ESS model. Underlying data for Table 4, energy of solute and cluster in gas phase, thermal corrections to the energy and entropy of solute and cluster. Gaseous Phase Gibb's free energy and enthalpy of studied set of amino acids and amino acid carbamates, using G3MP2B3, G3MP2, G4MP2, CBS-QB3, DFT and HF level of theories, at 298 K. Temperature dependency of amino acid carbamate constant with PCM and SM8T continuum solvation models. Simulation Details. Explanation of QM/PB Continuum Solvent Model. Full citation for References used in manuscript. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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TOC Graphic

Understanding Carbamate Formation Reaction Thermochemistry of Amino Acids as Solvent for Post Combustion CO_2 Capture

Mayuri Gupta, and Hallvard F. Svendsen