

Thermodynamics of CO₂ reaction with methylamine in aqueous solution: A computational study

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ABSTRACT

Separation and capture of carbon dioxide from the flue gas of power plants in order to reduce environmental damages has always been of interest to researchers. In this study, aqueous solution of methylamine was used as an absorbent for CO₂ capture. In order to study this reaction, Density Functional Theory (DFT) was employed at the level of B3LYP/6-311++G(d,p) by using the conductor-like polarizable continuum model (CPCM). Two possible reaction products were studied: carbamate ion and bicarbonate ion. The estimation of the thermodynamic parameters indicated that the reaction of bicarbonate ion forming is not thermodynamically feasible at room temperature. However, the reaction of carbamate ion formation is exothermic ($\Delta H = -12.4 \text{ kcal mol}^{-1}$) and exergonic ($\Delta G = -1.48 \text{ kcal mol}^{-1}$). Also, various atomic radii were employed to build up the solute cavity within CPCM model and the effects of the solute cavity on the thermodynamic properties of the reaction were studied.

Keywords: CO₂ absorption; Amines; Density Functional Theory; Solvation model

INTRODUCTION

The emission of carbon dioxide (CO₂), which is one of the major greenhouse gases, has raised great concerns about global warming. CO₂ is produced in large quantities in industry, for instance, by the combustion of coal, coke, and natural gas, in the fermentation of carbohydrate materials and sugars, in the manufacture of cement, lime, and etc. Therefore, CO₂ removal and separation from gaseous stream either in combustion units as flue gas or in the natural gas treatment plants is important. In this regard there are a variety

of technologies available for capturing CO₂ [1]. One of the most common technologies used for capturing the carbon dioxide is absorption-desorption process within which different kinds of chemical solvents are used. Among all known solvents, amine-based absorbents are the most mature and are the focus of most research studies [2-5]. While this is a proven technology, efforts are ongoing to improve it in order to make it a more attractive technology for large scale use to reduce CO₂ emissions. Finding solvents

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with better properties is one approach to improving the technology.

In this regard there are a number of different studies in the computational chemistry used to improve the understanding of the chemistry of CO₂ absorption in amine systems [6-8]. For instance, da silva [9] conducted a study on the mechanism of carbamate formation from CO₂ and monoethanolamine, a primary alkanolamine, by scanning the potential energy curve at the HF/3-21G (d) level. Xie et al. [10] studied the influence of various substituent groups on the heats of substituted amines with CO₂ using ab initio calculations at the MP2/aug-cc-pVDZ level. Iida et al. [11] investigated the proton transfer step in CO₂ capture by amines using a hybrid method of electronic structure theory and statistical mechanics.

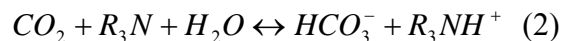
In the present work, the computational chemistry was performed on the reaction between CO₂ and methylamine in aqueous solution to estimate thermodynamic parameters of the reactions. These parameters (the Gibbs free energy change of reaction and heat of reaction) are important variables for designing appropriate amines to enhance the CO₂ removal process. For example, since this process is an absorption-regeneration one, the lower the heats of the reaction, the lower energy is required to regenerate solvent and hence the operational costs reduce.

In general the reaction of CO₂ with amine may result in the production of carbamate ion or bicarbonate ion. The following reaction shows the formation of carbamate ion (where RNH₂ can be any primary or secondary amine component.)



Amine can also directly react with CO₂ and water to form a bicarbonate ion

(HCO₃⁻), as shown in reaction 2 (where R₃N can be any amine.)



COMPUTATIONAL DETAILS

In this work the calculations containing the geometry optimizations and harmonic vibrational frequencies of the reactants and products were performed using Gaussian 09 suit of programs [12] at the B3LYP/6-311++G (d,p) level. In the first step we obtained the equilibrium geometry of the reactants and products in the ideal gas phase from molecular energy minimization. Gas phase conformer search was carried out using semi-empirical PM3 method and the most stable conformers were used for calculations.

Solute-solvent interactions can have dramatic effects on molecular energies, structures, and properties. Such effects can be computed very effectively in the framework of continuum solvation models. Accordingly, the implicit solvent effects were accounted for by using the conductor-like polarizable continuum model (CPCM) [13, 14] with the dielectric constant of water (ε) equal to 78.39. Hence a SCRf (Self Consistent reaction Field) geometry optimization was performed on the reactants and products beginning at the optimized gas phase structures. Firstly, the UAHF radii were used in the construction of the solute cavity for calculations. Afterwards, in order to investigate the effect of cavity definition, UFF, UAHF, UAKS, UA0, UFF, Bondi, and Pauling atomic radii were also used within CPCM model in computing energies and the other properties.

In order to evaluate the thermodynamic parameters of the reactions, frequency calculations were carried out. The enthalpy for each species was calculated using the following equation:

$$H = E_{SCF} + H_{Corr} \quad (3)$$

where E_{SCF} is the total energy from the quantum mechanical calculation, H_{corr} is a correction term given by

$$H_{Corr} = E_{Corr} + k_B T \quad (4)$$

where E_{corr} is the internal energy including the translational, rotational, and vibrational energies as well as zero point energy (ZPE), k_B is the Boltzmann constant and T is the absolute temperature in Kelvin.

The enthalpy change of the reaction can be obtained as follow:

$$\Delta H_r(298K) = \sum (E_{SCF} + H_{corr})_{products} - \sum (E_{SCF} + H_{corr})_{reactants} \quad (5)$$

Gibbs free energy of each compound was also calculated by using the following equation:

$$G = E_{SCF} + G_{corr} \quad (6)$$

G_{corr} is a correction term given by

$$G_{corr} = E_{corr} + k_B T - TS \quad (7)$$

where S is the entropy. The Gibbs free energy change of the reaction (ΔG) can be obtained in the same way as the enthalpy change (ΔH).

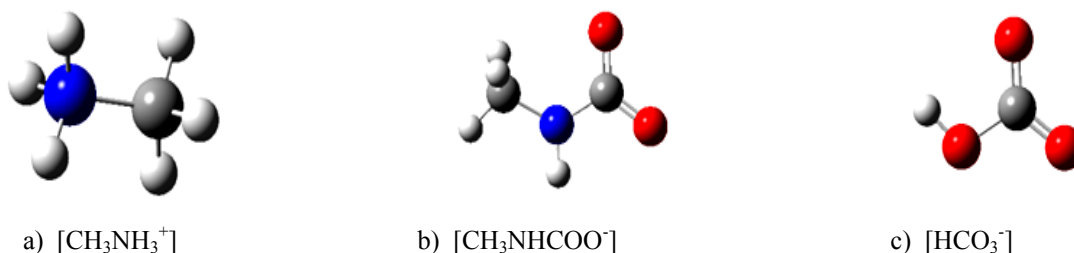
RESULTS AND DISCUSSION

The reaction of methylamine with CO_2 was studied in an aqueous solution. The solvent

can affect the equilibrium constant of the reaction by differential stabilization of the reactant or product. Therefore, the implicit solvent effects for the reaction of methylamine with CO_2 were studied through exploiting the conductor-like polarizable continuum model (CPCM). This method was initially devised by Tomasi and co-workers [15-17]. In the continuum models the solvent is described by a dielectric medium and a cavity is defined inside this dielectric medium. This cavity is formulated to insert the molecule in the solvent phase. In these models, outside the cavity of solute, the solvent distribution is kept constant by reproducing the density of the solvent.

The optimized structures of ions formed by CO_2 absorption in methylamine solution in the presence of implicit solvent have been displayed in Fig. 1.

This work has focused on two possible reactions in the methylamine- CO_2 - H_2O system: carbamate ion, having a 2:1 amine: CO_2 reaction stoichiometry, and bicarbonate ion, having a 1:1 stoichiometry. In Table 1, the computed thermodynamic parameters of both reactions at 298 K have been shown. A comparison of the results indicates that the reaction of CO_2 with methylamine via forming bicarbonate ion is not possible ($\Delta G > 0$). However, the reaction of carbamate ion forming is moderately exergonic ($\Delta G = -1.48 \text{ kcal mol}^{-1}$), suggesting satisfactory absorption of CO_2 molecules in order to form the carbamate ion.



a) $[\text{CH}_3\text{NH}_3^+]$

b) $[\text{CH}_3\text{NHCOO}^-]$

c) $[\text{HCO}_3^-]$

Fig. 1. The optimized structure of a) methyl ammonium, b) carbamate ion and c) bicarbonate ion.

To run a comparison, different atomic radii were used for computing thermodynamic properties of the carbamate ion forming reaction (reaction 1). Atomic radii are used to define the solute cavity in continuum-based methods. The definition of the cavity is one of the most important factors in determining the accuracy of the continuum solvation model [18]. By default, Gaussian builds up the cavity using the UFF radii, which places a sphere around each solute atom, with the radii scaled by a factor of 1.1. There are also three United Atom (UA) models available. UAHF atom radii uses the United Atom Topological Model applied on radii optimized for the HF/6-31G(d) level of theory, UA0 radii uses the United Atom Topological Model applied on atomic radii of the UFF force field for heavy atoms and UAKS radii uses the United Atom Topological Model applied on radii optimized for the PBE1PBE/6-31G(d) level of theory. Also Pauling uses the Pauling atomic radii and Bondi uses the Bondi atomic radii (uses explicit hydrogens). The results of the calculations

have been displayed in Table 2. By running the same calculations in gas phase (vacuum), positive values of ΔH and ΔG were obtained as was expected. UA0, UFF, Pauling and bondi models could not accurately predict thermodynamic parameters. The results of UAHF and UAKS models are similar and are consistent with the experimental data obtained for similar amines [19, 20]. It should be added that in this work, the association of ions was neglected in all calculations. Finally, the calculated absolute values of thermodynamic functions as well as thermal corrections have been presented in Tables 3-9 as supporting information.

CONCLUSION

In this paper, the reaction of methylamine with CO_2 in the aqueous solution was studied by employing an implicit solvent method based on the density functional theory (DFT) at the B3LYP/6-311++G(d,p) level. For this purpose, the two following reactions were investigated:

Table 1. The thermodynamic functions of the studied reactions upon using the B3LYP/6-311++G(d,p) level of theory with UAHF radii within the CPCM model

Reaction	$\Delta H/ \text{kcal mol}^{-1}$	$\Delta G/ \text{kcal mol}^{-1}$	$\Delta S/ \text{kcal K}^{-1}\text{mol}^{-1}$
1) $\text{CO}_2 + 2\text{CH}_3\text{NH}_2 \leftrightarrow \text{CH}_3\text{NHCO}_2^- + \text{CH}_3\text{NH}_3^+$	-12.4	-1.48	-0.037
2) $\text{CO}_2 + \text{CH}_3\text{NH}_2 + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{CH}_3\text{NH}_3^+$	-8.57	1.64	-0.034

Table 2. Thermodynamic parameters of the reaction of carbamate forming upon using the B3LYP/6-311++G(d,p) level of theory with UAHF, UFF, UA0, UAKS, Bondi, Pauling radii within the CPCM model

Model	$\Delta H/ \text{kcal mol}^{-1}$	$\Delta G/ \text{kcal mol}^{-1}$	$\Delta S/ \text{kcal K}^{-1}\text{mol}^{-1}$
UAHF	-12.35	-1.48	-0.03647
UAKS	-12.26	-1.39	-0.03646
UA0	7.59	18.61	-0.03659
UFF	10.29	21.20	-0.03695
Bondi	-4.45	6.02	-0.03509
Pauling	-6.16	4.34	-0.03521

carbamate ion, having a 2:1 amine: CO₂ reaction stoichiometry, and bicarbonate, having a 1:1 stoichiometry. The heats of the reactions and Gibbs free energy change for both reactions were calculated. The results indicated that the formation of bicarbonate ion is not possible. Furthermore the reaction of methylamine with CO₂ through carbamate ion forming is exothermic and exergonic at room

temperature. Finally, the different atomic radii in the construction of solute cavity were used and the effects of the definition of the solute cavity in computing thermodynamic properties were investigated. It was found that UAHF and UAKS models can fairly predict the thermodynamic parameters of the studied reactions that are consistent with the experimental data.

Table 3. The absolute values of thermodynamic functions and thermal corrections for the reaction of carbamate ion forming upon using the B3LYP/6-311++G(d,p) level of theory with UAHF radii within the CPCM model

Species	E(a.u.)	H(a.u.)	G(a.u.)	E _{corr} (a.u.)	H _{corr} (a.u.)	G _{corr} (a.u.)	S (cal K ⁻¹ mol ⁻¹)
CH ₃ NH ₂	-95.908193	-95.842465	-95.869807	0.06478	0.06573	0.03839	57.55
CO ₂	-188.651088	-188.635975	-188.660242	0.01417	0.01511	-0.00915	51.08
CH ₃ NH ₃ ⁺	-96.377629	-96.297488	-96.324051	0.07920	0.08015	0.05358	55.91
CH ₃ NHCOO ⁻	-284.112718	-284.043104	-284.078164	0.06867	0.06961	0.03455	73.79

Table 4. The absolute values of thermodynamic functions and thermal corrections for the reaction of bicarbonate ion forming upon using the B3LYP/6-311++G(d,p) level of theory with UAHF radii within the CPCM model

Species	E(a.u.)	H(a.u.)	G(a.u.)	E _{corr} (a.u.)	H _{corr} (a.u.)	G _{corr} (a.u.)	S (cal K ⁻¹ mol ⁻¹)
H ₂ O	-76.477149	-76.454029	-76.475505	0.022176	0.023120	0.001644	45.20
CO ₂	-188.651088	-188.635975	-188.660242	0.014169	0.015113	-0.009154	51.07
CH ₃ NH ₂	-95.908193	-95.842465	-95.869807	0.064784	0.065729	0.038386	57.55
HCO ₃ ⁻	-264.677107	-264.648645	-264.678883	0.027518	0.028462	-0.001776	63.64
CH ₃ NH ₃ ⁺	-96.377628	-96.297488	-96.324051	0.079203	0.069614	0.053584	55.91

Table 5. The absolute values of thermodynamic functions and thermal corrections for the reaction of carbamate ion forming upon using the B3LYP/6-311++G(d,p) level of theory with UAKS radii within the CPCM model

Species	E(a.u.)	H(a.u.)	G(a.u.)	E _{corr} (a.u.)	H _{corr} (a.u.)	G _{corr} (a.u.)	S (cal K ⁻¹ mol ⁻¹)
CH ₃ NH ₂	-95.908193	-95.842465	-95.869807	0.064784	0.065729	0.038386	57.55
CO ₂	-188.65109	-188.636132	-188.66040	0.01417	0.01511	-0.00915	51.08
CH ₃ NH ₃ ⁺	-96.377629	-96.297502	-96.324072	0.07920	0.08015	0.05358	55.92
CH ₃ NHCOO ⁻	-284.11271	-284.043104	-284.078164	0.06867	0.06961	0.03455	73.79

Table 6. The absolute values of thermodynamic functions and thermal corrections for the reaction of carbamate ion forming upon using the B3LYP/6-311++G(d,p) level of theory with UFF radii within the CPCM model

Species	E(a.u.)	H(a.u.)	G(a.u.)	E _{corr} (a.u.)	H _{corr} (a.u.)	G _{corr} (a.u.)	S (cal K ⁻¹ mol ⁻¹)
CH ₃ NH ₂	-95.898754	-95.830625	-95.857945	0.067185	0.068129	0.040810	57.50
CO ₂	-188.649792	-188.634653	-188.658920	0.014195	0.015140	-0.009128	51.08
CH ₃ NH ₃ ⁺	-96.353699	-96.269702	-96.296193	0.083053	0.083998	0.057507	55.76
CH ₃ NHCOO ⁻	-284.086442	-284.014105	-284.048962	0.071393	0.072337	0.037480	73.36

Table 7. The absolute values of thermodynamic functions and thermal corrections for the reaction of carbamate forming upon using the B3LYP/6-311++G(d,p) level of theory with UA0 radii within the CPCM model

Species	E(a.u.)	H(a.u.)	G(a.u.)	E _{corr} (a.u.)	H _{corr} (a.u.)	G _{corr} (a.u.)	S (cal K ⁻¹ mol ⁻¹)
CH ₃ NH ₂	-95.89826008	-95.830297	-95.857619	0.067019	0.067963	0.040642	57.50
CO ₂	-188.6497948	-188.634655	-188.658923	0.014195	0.015139	-0.009128	51.08
CH ₃ NH ₃ ⁺	-96.34797015	-96.265073	-96.291617	0.081953	0.082897	0.056353	55.87
CH ₃ NHCOO ⁻	-284.0860429	-284.013782	-284.048766	0.071317	0.072261	0.037277	73.63

Table 8. The absolute values of thermodynamic functions and thermal corrections for the reaction of carbamate forming upon using the B3LYP/6-311++G(d,p) level of theory with Pauling radii within the CPCM model

Species	E(a.u.)	H(a.u.)	G(a.u.)	E _{corr} (a.u.)	H _{corr} (a.u.)	G _{corr} (a.u.)	S (cal K ⁻¹ mol ⁻¹)
CH ₃ NH ₂	-95.902473	-95.834396	-95.86173	0.067133	0.068077	0.040748	57.52
CO ₂	-188.655177	-188.640121	-188.66439	0.014112	0.015056	-0.009216	51.09
CH ₃ NH ₃ ⁺	-96.371508	-96.287349	-96.31485	0.083215	0.084159	0.056661	57.88
CH ₃ NHCOO ⁻	-284.103771	-284.031377	-284.06608	0.071450	0.072394	0.037692	73.04

Table 9. The absolute values of thermodynamic functions and thermal corrections for the reaction of carbamate forming upon using the B3LYP/6-311++G(d,p) level of theory with Bondi radii within the CPCM model

Species	E(a.u.)	H(a.u.)	G(a.u.)	E _{corr} (a.u.)	H _{corr} (a.u.)	G _{corr} (a.u.)	S (cal K ⁻¹ mol ⁻¹)
CH ₃ NH ₂	-95.902049	-95.834003	-95.861328	0.067102	0.068046	0.040721	57.51
CO ₂	-188.651867	-188.636775	-188.661045	0.014112	0.015056	-0.009216	51.08
CH ₃ NH ₃ ⁺	-96.369462	-96.285524	-96.313025	0.082994	0.083938	0.056437	57.88
CH ₃ NHCOO ⁻	-284.098681	-284.026342	-284.061086	0.071396	0.072340	0.037595	73.13

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