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A computational investigation on the structural features of alkanolamine solvents for CO_2 capture process from power plant flue gas

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ABSTRACT

The present study aimed at investigating the chemical properties of the solvents playing the key role in CO_2 absorption process from the exhaust stream of power plants or other industrial sources. For this purpose, energy computations were performed using a DFT-based quantum chemistry method at B3LYP/6-311++G(d,p) level of theory. Furthermore, the solvent effect was taken into account by means of a dielectric constant in SMD continuum model at HF/6-31G(d) level of theory. With this approach, the relative stability of carbamate ion versus bicarbonate ion as the main products of CO_2 absorption into the aqueous alkanolamine solvents was evaluated and the results were discussed in terms of various factors such as types of alkanolamine, carbon chain length in alkanolamine and steric hindrance. This study revealed that increasing both carbon chain length and steric hindrance leads to a decrease in carbamate stability. Moreover, DEA as a secondary alkanolamine demonstrated a lower carbamate stability.

Keywords: CO_2 absorption; Alkanolamine; Carbamate stability; Density Functional Theory

INTRODUCTION

Tetrahedrane According to Intergovernmental Panel on Climate Change (IPCC) report the major cause of global warming is carbon dioxide (CO_2) emissions from fossil fuel combustion, cement production, and land use changes such as deforestation [1]. One approach for reducing these emissions is carbon capture and storage (CCS) method. According to this concept, CO_2 is captured from large industrial sources, such as power plants, and injected into underground geologic formations. The most promising technology for carbon capture is absorption with alkanolamine solvents [2-5]. Alkanolamines are chemical solvents containing both amine and alcohol functional groups. Among these solvents, monoethanolamine (MEA) has been the most widely used solvent for several decades [6-8]. However, there are some challenges associated with using MEA as a solvent for CO_2 capture from exhaust gases including large energy consumption, instability, and high level of corrosion. Therefore, carbon capture using conventional solvents is not cost effective and finding a suitable alternative is essential for designing more economical technologies.

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In the chemical absorption of CO_2 in aqueous amine based systems, the CO_2 is bound as either, carbamate or bicarbonate:

Reaction of carbamate formation:

$$2R_1R_2NH + CO_2 \longrightarrow R_1R_2NHCO_2^- + R_1R_2NH_2^+ \quad (1)$$

Reaction of bicarbonate formation:

$$R_1R_2NH + CO_2 + H_2O \longrightarrow R_1R_2NH^+ + HCO_3^- \quad (2)$$

Primary and secondary amines react with CO_2 via both paths. Whereas, tertiary amines and some sterically hindered amines are unable to form carbamate ion and merely react to form reaction bicarbonate ion [9].The reaction of carbamate formation has the advantage of fast kinetic over the reaction of bicarbonate formation. However, it has low CO_2 absorption capacity and high regeneration energy. Therefore, understanding of equilibrium constants of the two mentioned reactions can be useful to design new amine based solvents.

A number of various studies have focused on the same issue up to now. For instance, McCann et al. [10] have recently used ^{1}HNMR spectroscopy to study carbamate formation in monoethanolamine, 2-amino-1-propanol, propylamine and isobutylamine. Their studies reveal that both steric hindrance and the acid dissociation constant of the parent amine have a significant effect on the stability of the resulting carbamates. Furthermore, Singh et al. [11] studied the structural effects of various amine-based absorbents on the initial CO_2 absorption rate and capacities. Their results showed that an increase in chain length between the amine and different functional groups in the absorbent structure, results in a decrease in the absorption rate whereas the absorption capacity increased in most absorbents.

Carbamate stability constants have also been studied through molecular approach and by using ab Initio methods by da Silva et al. [12].They concluded that ‘trends in carbamate stability apparently cannot be explained, in terms of any single molecular characteristic’. However, we believe that further studies are inevitable to explore all the structural effects influencing carbamate formation. Hence, introducing systematic changes in the molecular structure of alkanolamines, we have investigated some important factors which influence carbamate stability including amine type, carbon chain length and steric hindrance effect. For this purpose, we have employed a combination of density functional theory (DFT) and SMD continuum solvation model. Studied alkanolamines are listed in Table 1.

Table 1. Molecules studied in this work

No.	Amine	Abbreviation name
1	monoethanolamine	MEA
2	diethanolamine	DEA
3	triethanolamine	TEA
4	3-amino-1-propanol	MPA
5	4-Amino-1-butanol	MBA
6	2-amino-1-propanol	AP
7	2-amino-2-methylpropanol	AMP

COMPUTATIONAL METHODS

All electronic structure calculations were performed using Gaussian 09 suit of programs [13]. Gas phase conformer search was carried out using semi-empirical PM3 method and the most stable conformers were used for calculations. The gas phase calculations were carried out using Becke’s three-parameter functional [14] and the correlation function of Lee, Yang, and Parr (B3LYP) [15] with a 6-311++G(d,p) basis set within DFT method. Our previous studies on amines have revealed that this computational level produces reasonable results [16, 17]. The calculations in the solution phase were performed exploiting the latest implicit solvation model called SMD. This model was developed by Marenich et al. [18] to predict solvation free energies of neutral and ionic solutes in solutions. The parametrization results of this solvation model using the IEF-PCM protocol and the HF/6-31G(d) method shows the least mean unsigned error in comparison with experimental data [18]. Hence in this work, this method was selected to calculate the free energy of solvation process. Furthermore, water was used as the solvent with a dielectric constant (ε) equal to 78.35.

To compute the stability constant of carbamate, an alternative equilibrium for eq. 1 was employed:

$$HCO_3^- + R_1R_2NH \longrightarrow R_1R_2NCO_2^- + H_2O \quad (3)$$

$$K_{a,carb} = \frac{a_{R_1R_2NCO_2^-}}{a_{R_1R_2NH}\, a_{HCO_3^-}} \quad (4)$$

where $K_{a,carb}$ is the equilibrium constant of eq. 3. Also, *a* represents the activity of species and the activity of water is assumed to be 1.

Similarly, the equilibrium constant of bicarbonate formation reaction (eq. 2) can be written as follows:

$$K_{a,\mathrm{bicarb}} = \frac{a_{HCO_3^-}\, a_{R_1R_2NH^+}}{a_{R_1R_2NH}} \quad (5)$$

To calculate the equilibrium constants, we used the following thermodynamic cycle following Liptak [19].

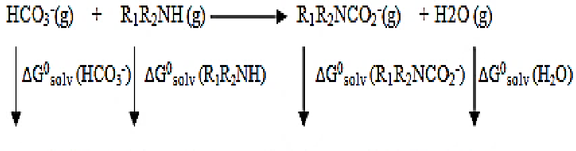


Fig. 1. Thermodynamic cycle used in the calculation of K_a.

Accordingly the reaction standard free energy in the solution (ΔG^0_s) can be divided into two contributions

$$\Delta G_s^0 = \Delta G_g^0 + \Delta\Delta G_{solv}^0 \quad (6)$$

where ΔG^0_g is

$$\Delta G_g^0 = G_g^0(R_1R_2NCO_2^-) + G_g^0(H_2O) - G_g^0(R_1R_2NH) - G_g^0(\mathrm{HCO_3^-}) \quad (7)$$

and $\Delta\Delta G^0_{solv}$is

$$\Delta\Delta G_{solv}^0 = \Delta G_{solv}^0(R_1R_2NCO_2^-) + \Delta G_{solv}^0(H_2O) - \Delta G_{solv}^0(R_1R_2NH) - \Delta G_{solv}^0(HCO_3^-) \quad (8)$$

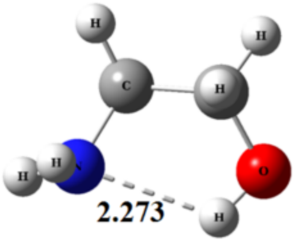
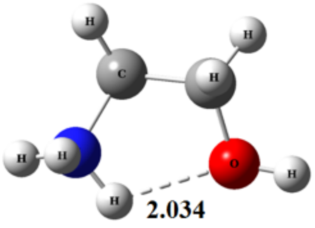
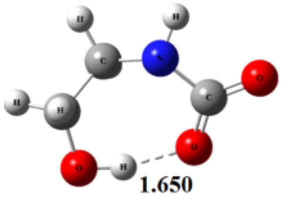
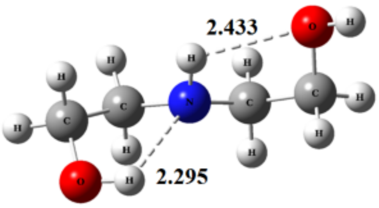
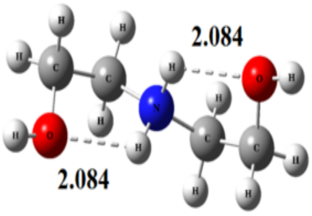
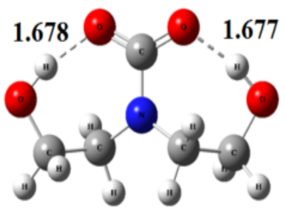
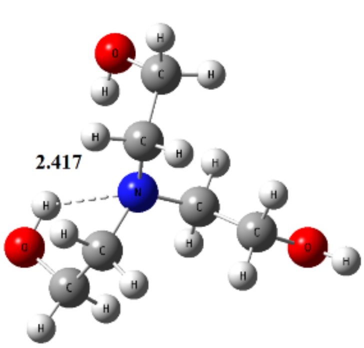
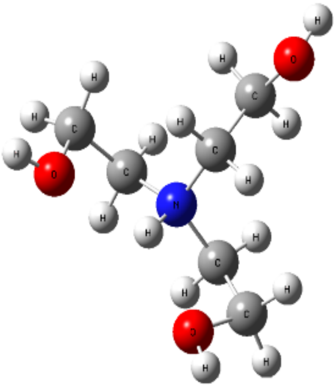
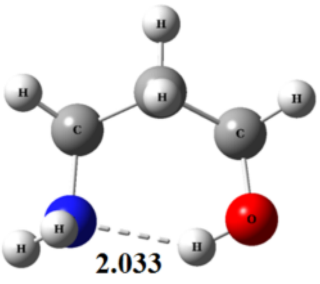
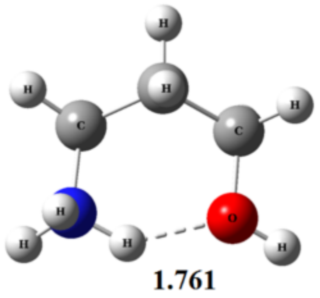
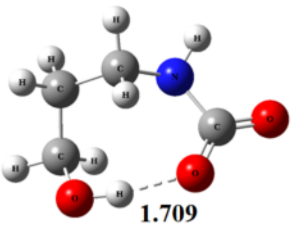
The standard free energies in the gas phase were obtained using harmonic vibrational frequency calculation by assuming ideal gas and rigid rotor approximation. Furthermore, the standard solvation free energies of the involved species were obtained by using SMD solvation model as mentioned before. Since proton contains no electrons, its free energy cannot be obtained using quantum calculations. Hence, using the equation of thermodynamics (eq. 9) and the Sackur-Tetrode equation [20] the value of -6.28 kcal/mol for $G^0_{gas}(H^+)$ at 298K was achieved.

$$G_{gas}^0(H^+) = {}^5\!/_2\, RT - TS^0 \quad (9)$$

Also, the experimental value of -265.9 kcal/mol was applied for $\Delta G^0_{solv}(H^+)$ on which general consensus has been recently achieved [21].

RESULTS AND DISCUSSION

The Neutral and protonated amines as well as carbamate ions are flexible molecules and have several conformations in the gas and solution phase. Hence, we conducted a detailed conformational search to find the lowest-energy conformers. The results indicated that in all cases, the conformers with intramolecular hydrogen bond are the most stable. We found intramolecular hydrogen bonds HN...HO, HO...HNH_2^+ and COO^-...HO respectively for neutral amines, protonated amines and carbamate ions as it can be seen in Fig. 2. For all involved species we reoptimized structures in the solution phase according to the Bryantsev's study [22] which showed that ‘geometry optimization in the solution is essential for systems possessing intramolecular hydrogen bonds’.

Amine	Neutral	Protonated	Carbamate
MEA			
DEA			
TEA			
MPA			

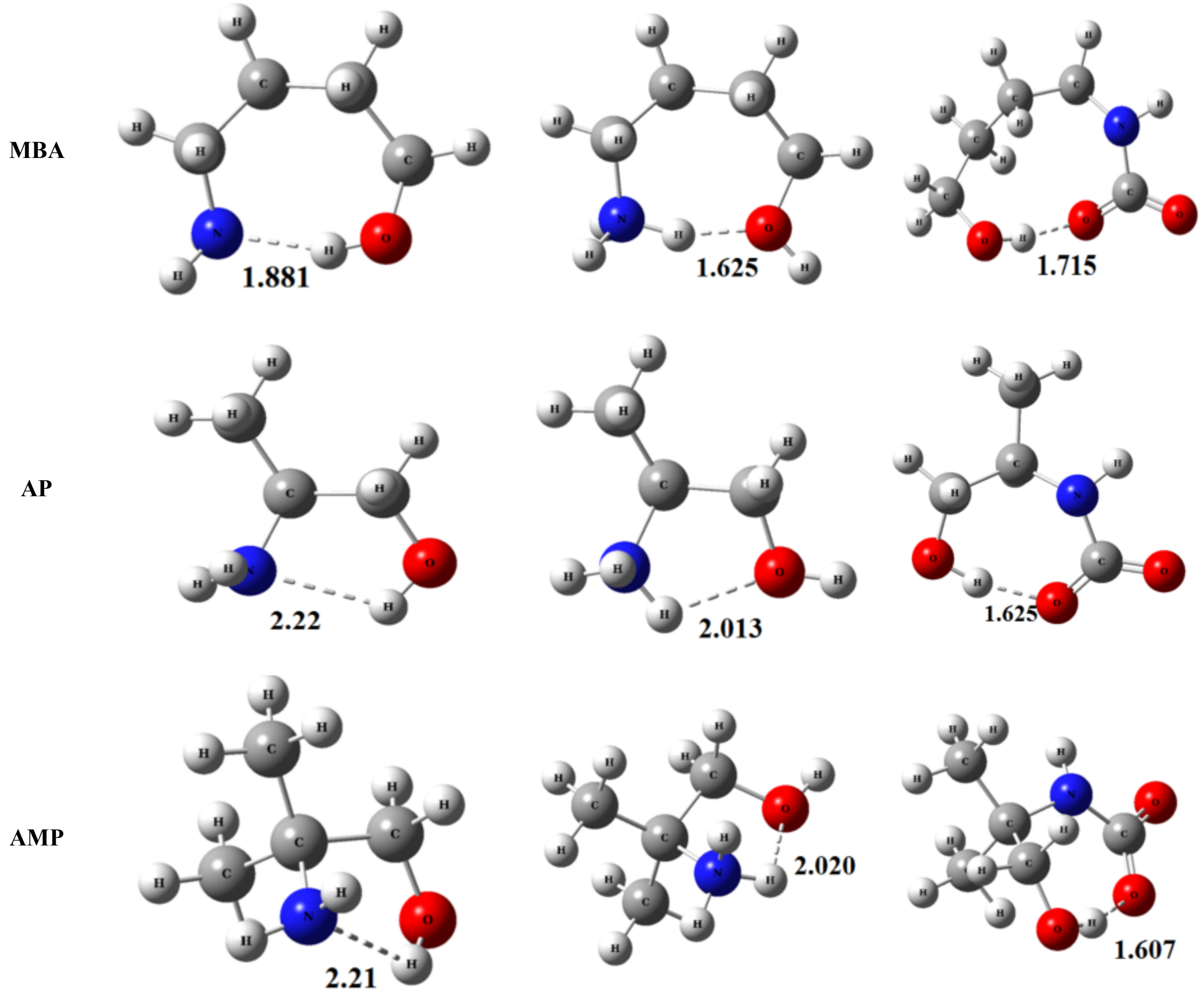


Fig. 2. The most stable conformers of neutral amines, protonated amines and carbamate ions in the gas phase calculated at B3LYP/6-311++g(d,p) level. Intramolecular hydrogen bondings are identified by dotted lines. The lengths are given in angstroms.

Different types of alkanolamines

In order to examine the absorption characteristics of different types of alkanolamines, we selected MEA, DEA and TEA which are prototypes of primary, secondary and tertiary alkanolamines respectively. We have summarized the standard free energy changes in the gas-phase (ΔG^0_g) and solvation free energies ($\Delta\Delta G^0_{solv}$) in Table 2. Also, the standard free energy changes in the solution phase (ΔG^0_s) which were obtained using a combination of gas phase energies and solvation energies according to the eq.6 are given in Table 3. The results show that the solution free energy of carbamate reaction reduces (without considering sign) from MEA to DEA while the solution free energy of bicarbonate increases in mentioned amines. Since, the standard free energy change of reaction directly relates to the stability constant of reaction, hence it can be noted that carbamate stability significantly decreases from MEA to DEA. This finding can be ascribed to the solvation effects. A comparison of solvation energies of these amines shows that the carbamate group in DEA molecule was less solvated than MEA whereas neutral DEA was completely solvated. In fact, the bulky group in DEA structure makes the carbamate group less accessible to the solvent.

In case of TEA, which is a tertiary alkanolamine without attached hydrogen to amine group, carbamate formation was not observed.

Table 2. Gas phase reaction free energies calculated at B3LYP/6-311++G(d,p) level of theory and solvation free energies of neutral amines (B), protonated ions (BH^+) and carbamate ions ($BCOO^-$) calculated at SMD/IEF-PCM/HF/6-31g(d) level of theory (energies in kcal/mol)

No.	Amine	$\Delta G^0_{g,carbamate}$	$\Delta G^0_{g,bicarbonate}$	ΔG^0_{solv}		
				B	BH^+	$BCOO^-$
1	MEA	-5.743	132.51	-9.01	-74.26	-77.00
2	DEA	13.61	120.71	-14.58	-68.94	-71.05
3	TEA	No carbamate	7.75	-20.15	-64.39	No carbamate

Table 3. Calculated free energies of carbamate and bicarbonate formation reaction in the solution phase upon using combination of B3LYP/6-311++G(d,p) and SMD/IEF-PCM/HF/6-31g(d) level of theory (energies in kcal/mol)

No.	Amine	$\Delta G^0_{aq,carbamate}$	$\Delta G^0_{aq,bicarbonate}$
1	MEA	-4.01	-3.49
2	DEA	-0.36	-4.40
3	TEA	No carbamate	2.11

The variation of carbon chain length

Variation of carbon chain length between hydroxyl and amine group from n=2 to n=4 gives MEA, MPA, and MBA molecules. The calculated carbamate and bicarbonate reaction free energies for the listed amines are given in Tables 4 and 6 and Fig. 3.

Table 4. Calculated free energies of carbamate and bicarbonate formation reaction in the gas phase upon using the B3LYP/6-311++G(d,p) level of theory and solvation free energies of neutral amines (B), protonated ions (BH^+) and carbamate ions ($BCOO^-$) calculated at SMD/IEF-PCM/HF/6-31g(d) level of theory (energies in kcal/mol)

No.	Amine	$\Delta G^0_{g,carbamate}$	$\Delta G^0_{g,bicarbonate}$	ΔG^0_{solv}		
				B	BH^+	$BCOO^-$
1	MEA	-5.743	132.51	-9.01	-74.26	-77.00
2	MPA	-5.674	125.208	-9.20	-66.72	-77.08
3	MBA	0.3106	121.763	-9.71	-63.74	-79.95

Table 5. Calculated free energies of carbamate and bicarbonate formation reaction in the solution phase upon using combination of B3LYP/6-311++G(d,p) and SMD/IEF-PCM/HF/6-31g(d) level of theory (energies in kcal/mol)

No.	Amine	$\Delta G^0_{aq,carbamate}$	$\Delta G^0_{aq,bicarbonate}$
1	MEA	-4.01	-3.49
2	MPA	-3.83	-3.06
3	MBA	-0.21	-3.02

The results show that as carbon chain length increases from n=2 to n=4, the magnitude of $\Delta G^0_{aq,carbamate}$ significantly decreases. In addition, the ratio of the resulting carbamate to bicarbonate also decreases. Therefore increasing carbon chain length between hydroxyl and amine group leads to decreased carbamate stability. It can be explained by reducing electron withdrawing effect of hydroxyl group by increasing carbon chain length.

Substitution of methyl group on α position

In this section, primary alkanolamines, AP and AMP were selected to compare their performance with MEA as a benchmark molecule in CO_2 absorption process. AP has a –CH3 group on α carbon to the amine nitrogen and addition of a second –CH3 group to α carbon gives AMP molecule. The results of computations of ΔG^0_g, $\Delta\Delta G^0_{solv}$ and ΔG^0_s are summarized in Table 7 and 8. As it can be observed in Table 8, the carbamate reaction energy (without considering the sign) decreases in this sequence: MEA →AP→AMP. On the other hand, the bicarbonate reaction energy increases from MEA to AMP. So that in case of AMP, the ratio of carbamate/bicarbonate is very low (ΔGcar/ΔGbicar≈0.2). In fact, substitution of methyl group(s) at α carbon to the amine group initiates the interaction between the methyl and COO^- group in carbamate and consequently imposes a steric hindrance effect. As a result, with increasing steric hindrance, the carbamate stability decreases. These findings are in agreement with literature. Sartori and Savage [23] found $\log K_{carb} = 1.10$ and <-1, respectively for MEA and AMP by ^{13}C NMR spectroscopy and concluded that the steric interactions are responsible for the lower carbamate stability. In addition, decreased carbamate formation can be attributed to the electronic effects of methyl substitution at α carbon as Chakraborty et al. do [25]. Based on semi-empirical MNDO calculations, they remarked that "upon methyl substitution at α carbon atom the interactions of the methyl group orbitals with the nitrogen lone-pair orbital lead to subtle but significant changes in the donor properties of the amino species".

Table 7. Calculated free energies of carbamate and bicarbonate formation reaction in the gas phase upon using the B3LYP/6-311++G(d,p) level of theory and solvation free energies of neutral amines (B), protonated ions (BH^+) and carbamate ions ($BCOO^-$) calculated at SMD/IEF-PCM/HF/6-31g(d) level of theory (energies in kcal/mol)

No.	Amine	$\Delta G^0_{g,carbamate}$	$\Delta G^0_{g,bicarbonate}$	ΔG^0_{solv}		
				B	BH^+	$BCOO^-$
1	MEA	-5.743	132.51	-9.01	-74.26	-77.00
2	AP	-4.96	129.285	-8.75	-71.09	-76.75
3	AMP	-3.83	126.851	-7.98	-68.53	-79.94

Table 8. Calculated free energies of carbamate and bicarbonate formation reaction in the solution phase upon using combination of B3LYP/6-311++G(d,p) and SMD/IEF-PCM/HF/6-31g(d) level of theory (energies in kcal/mol)

No.	Amine	$\Delta G^0_{aq,carbamate}$	$\Delta G^0_{aq,bicarbonate}$
1	MEA	-4.01	-3.49
2	AP	-3.24	-3.8
3	AMP	-1.07	-4.45

CONCLUSIONS

Using a computational approach, the performance of a variety of aqueous alkanolamines in CO_2 absorption process has been evaluated and compared with MEA as a conventional solvent. In this regard, some important factors that affect the products ratio of CO_2 absorption (carbamate to bicarbonate) were investigated. For this purpose the standard free energy changes of both reactions were computed employing B3LYP/6-311++G(d,p) method in conjunction with a continuum solvation model (SMD//HF/6-31G(d)). The results revealed that the carbamate stability decreases from primary to secondary alkanolamines so that tertiary alkanolamines do not form carbamate ion. Also, it was found that the increase in carbon chain length due to the reduction in the electron withdrawing effect and substitution methyl group in α position because of the steric hindrance leads to a decrease in carbamate stability. Hence, by making changes in the structure of alkanolamine molecules, we can modify the properties of these solvents and therefore improve the CO_2 capture process.

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