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ARTICLE

DFT Study on Thermodynamic Parameters of CO_2 Absorption into Aqueous Solution of Aliphatic Amines

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Using density functional theory (DFT), the thermodynamic parameters of the CO_2 absorption into the aqueous solution of the aliphatic amines including some alkylamines, alkanolamines, diamines and a type of aminoamide were calculated. The geometry optimization and the calculation of vibrational frequencies in the gas phase were performed at the B3LYP/6-311++G(d,p) level of theory. Moreover, the standard solvation free energies of the studied species were computed upon the solution phase optimized geometries through the latest continuum solvation model (SMD/IEF-PCM) at the HF/6-31G(d) level of theory. With this approach, two important properties of the CO_2 absorption into the aqueous solutions of the studied amines were evaluated: the acid dissociation constant (pK_a) of the parent amines and the standard enthalpy change ($\Delta H^{\ominus}_{\text{abs}}$) related to the CO_2 absorption process. A roughly linear relationship was observed between pK_a and $\Delta H^{\ominus}_{\text{abs}}$. This finding suggests that a raise in the basicity of an amine leads to an increase in the heat released in CO_2 absorption and consequently in the required energy for the regeneration of amine.

Key words: Density functional theory, Amine, CO_2 absorption, Heat of absorption, SMD solvation model

I. INTRODUCTION

Carbon capture is a technology to reduce the unfavorable environmental impacts of CO_2 emission by separating CO_2 from the exhaust gas streams released in power plants or industrial processes. To date, using amine solvents is considered the most advanced technology in CO_2 removal and, hence, has attracted a great deal of research in this regard [1−3]. As an exothermic reaction, the absorption-regeneration process of CO_2 capture by amine requires certain quantities of energy for amine regeneration. Hence, the more exothermic the reaction, the more energy is required for the regeneration which leads to an increase in operation costs. Therefore, one of the main challenges in CO_2 removal process is to reduce the required regeneration energy by option for an economical solvent with low heat of absorption. However, monoethanolamine (MEA) which has been conventionally used as a solvent for several decades [4−6] entails a number of disadvantages including large energy consumption, instability and high level of corrosion. These drawbacks have been calling for efforts to improve the existing systems or introduce an efficient alternative. Some instances of such efforts include utilizing a mixture of amines [7, 8], sterically hindered amines [9, 10], and/or amines with multiple amino groups [11, 12].

The following equilibriums show the two main reactions that occur in the amine-CO_2-H_2O system [13]:

$$CO_2 + 2RNH_2 \rightleftharpoons RNHCO_2{}^- + RNH_3{}^+ \qquad (1)$$

$$CO_2 + R_3N + H_2O \rightleftharpoons HCO_3{}^- + R_3NH^+ \qquad (2)$$

In reaction (1), which results in the formation of carbamate ion, only primary and secondary amines can take part. Tertiary amines, having no hydrogen atom attached to amine nitrogen, and steric hindrance amines can merely form bicarbonate ion (reaction (2)). Although, the two above reactions have different mechanisms, by amine acting as Lewis base in the former and as a simple base in the latter, in both processes the basicity of amine plays an important role in the heat of reaction.

Experimental evaluation of enthalpy change regarding the reaction of CO_2 with aqueous solution of amines has been the subject of several studies. For instance, the heat of absorption for 30wt% monoethanolamine (MEA) and 2-(2-aminoethyl)aminoethanol (AEEA) solutions was measured as a function of CO_2 loading [14]. In another study, McCann *et al.* [15] determined the enthalpy change of CO_2 absorption into alkanolamines including MEA, diethanolamine

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(DEA), methyldiethanolamine (MDEA), and 2-amino-2-methyl-1-propanol (AMP). Finally, different diamines and polyamines were examined using calorimetry [16].

Nonetheless, it can be argued that in parallel with experimental studies, computational chemistry can be employed as a fast and at the same time powerful method to predict the molecular structures and chemical properties of species and to investigate their relationship. Also, it offers a great deal of implications in designing new systems with improved properties [17−21]. In this work, by employing computational chemistry, we explored the reaction of amines with CO$_2$ and focused on the thermodynamic properties of this reaction, including enthalpy changes and the acid dissociation constant. Furthermore, an attempt was made to explore the relationship between the basicity of the parent amine and the heat of the CO$_2$ absorption process. In a similar study, Xie *et al.* [20] investigated the influence of various substituent groups on the heat of the reaction between substituted MEA and CO$_2$ utilizing an *ab initio* calculation. In this work we went further by taking into consideration of a diverse set of amines with different functional groups whose pK_a values range from 6 to 11. The examined amines include alkylamines (propylamine, butylamine, isobutylamine and trifluoromethylethanamine), alkanolamines (monoethanolamine and diethanolamine), diamines (ethanediamine, 1,3-propanediamine, 1,4-butanediamine and dimethylethanediamine) and aminoamide (aminoacetamide). The corresponding calculations were performed based on the density functional theory (DFT) in both gas phase and solution phase in which the solvent effect was computed by a continuum solvation model.

II. COMPUTATIONAL DETAILS

All computations were performed using Gaussian 09 suit of programs [22]. As the first step, a detailed conformational analysis was carried out using a semiempirical method (PM3) and the most stable conformers of the reactants and products were selected as initial structures for geometry optimizations. Nonlocal hybrid three-parameter B3LYP density functional method [23, 24] with a 6-311++G(d,p) basis set was employed for geometry optimizations and corresponding vibrational frequency calculations. Earlier theoretical studies on amines and systems involving hydrogen bonds have revealed that this computational level produces reasonable results [19, 20, 25−27].

To compute the pK_a of the studied amines, the direct method was employed following Liptak [28]. Accordingly, the acid dissociation of a protonated amine can be represented by the following equilibrium:

$$\mathrm{BH}^+_{(\mathrm{aq})}\xrightarrow{K_\mathrm{a}}\mathrm{B}_{(\mathrm{aq})}+\mathrm{H}^+_{(\mathrm{aq})} \tag{3}$$

$$K_\mathrm{a}=\frac{a_\mathrm{B}a_{\mathrm{H}^+}}{a_{\mathrm{BH}^+}} \tag{4}$$

$$\mathrm{p}K_\mathrm{a}=-\log K_\mathrm{a} \tag{5}$$

where B represents an amine molecule and K_a is the acid dissociation constant. The pK_a can be calculated from the standard free energy change related to the acid dissociation reaction (3) in the solution.

$$\mathrm{p}K_\mathrm{a}=\frac{\Delta G^\ominus_\mathrm{aq}}{2.303RT} \tag{6}$$

where $\Delta G^\ominus_\mathrm{aq}$ is calculated from summation of the standard free energy change of the reaction in the gas phase ($\Delta G^\ominus_\mathrm{gas}$) and the standard free energy of solvation ($\Delta G^\ominus_\mathrm{solv}$) as follows:

$$\Delta G^\ominus_\mathrm{aq}=\Delta G^\ominus_\mathrm{gas}+\Delta G^\ominus_\mathrm{solv}(\mathrm{B})+\Delta G^\ominus_\mathrm{solv}(\mathrm{H}^+)-\Delta G^\ominus_\mathrm{solv}(\mathrm{BH}^+) \tag{7}$$

$$\Delta G^\ominus_\mathrm{gas}=G^\ominus_\mathrm{gas}(\mathrm{B})+G^\ominus_\mathrm{gas}(\mathrm{H}^+)-G^\ominus_\mathrm{gas}(\mathrm{BH}^+) \tag{8}$$

The Gibbs free energy in the gas phase was obtained for the involved species using harmonic vibrational frequency calculation by assuming ideal gas and rigid rotor approximation. The value of −6.28 kcal/mol for $G^\ominus_\mathrm{gas}(\mathrm{H}^+)$ was applied, which was obtained through the following equation at 298 K where the entropy S is given from Sackur-Tetrode equation.

$$G^\ominus_\mathrm{gas}(\mathrm{H}^+)=\frac{5}{2}RT-TS^\ominus \tag{9}$$

Furthermore, the correction term $RT\ln(RT/P)$ equal to 1.894 kcal/mol was added to $\Delta G^\ominus_\mathrm{gas}$ to convert the standard state of 1 atm in the gas phase to the standard state of 1 mol/L in the solution phase. To calculate $\Delta G^\ominus_\mathrm{solv}$, the implicit solvation model called SMD was exploited. SMD was developed by Marenich *et al.* [29] based on a self-consistent reaction field treatment of bulk electrostatics that involves an integration of the nonhomogeneous Poisson equation and on a cavity dispersion-solvent-structure protocol for the nonelectrostatic contribution to the free energy of solvation. According to a recent comment [30], to obtain accurate solution-phase free energy, the same level of theory at which the continuum solvation model was parameterized should be applied. The SMD model has been parameterized using six electronic structure methods among which the HF/6-31G(d) method yields the least mean unsigned error (0.37 kcal/mol) in the values of solvation free energies of neutral aliphatic amines and a few errors (3.1 kcal/mol on average) for ions that have H, C, N, O atoms [29]. Hence this method was selected to calculate the free energy of solvation process. For this purpose, a self-consistence reaction field (SCRF) calculation was performed on optimized structures in the solution phase and water was used as the solvent with a dielectric constant ε equal to 78.35. The

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TABLE I Calculated gas phase basicities of amines upon using the B3LYP/6-311++G(d,p) method along with the experimental data.

Amine	pK_a	Gas phase basicity/(kcal/mol)	
		Calc.	Expt. [33]
Propylamine	10.54 [34]	211.79	211.26
Butylamine	10.60 [34]	212.64	212.10
Isobutylamine	10.48 [35]	213.08	212.91
2,2,2-Trifluoro-N-methylethanamine	6.05 [36]	201.3	204.11
Monoethanolamine	9.50 [34]	214.58[a], 212.57[b]	214.34
Diethanolamine	8.95 [37]	224.37	219.89
1,2-Ethanediamine	9.92 [34]	219.17	218.10
1,3-Propanediamine	10.55 [34]	226.58	224.66
1,4-Butanediamine	10.80 [34]	230.47	228.08
N,N'-dimethyl-1,2-ethanediamine	10.30 [37]	224.8	226.31
2-Aminoacetamide	7.95 [37]	209.72	211.08

[a] Data for tGg′ conformer.

[b] Data for gGg′ conformer.

solvation free energy in SMD is calculated through the following equation [30]:

$$\Delta G^{\ominus}_{\text{solv}} = E^{\ominus}_{\text{aq}} + G^{\ominus}_{\text{nes}} - E^{\ominus}_{\text{gas}} \tag{10}$$

where $E^{\ominus}_{\text{aq}}$ and $E^{\ominus}_{\text{gas}}$ are the respective standard electronic energies of the solute in the presence and absence of the solvent field and $G^{\ominus}_{\text{nes}}$ is the sum of the non-electrostatic contributions to the solvation free energy such as cavitation, dispersion, and repulsion interactions. For the standard solvation free energy of H$^+$, $\Delta G^{\ominus}_{\text{solv}}(\text{H}^+)$, the experimental value of -265.9 kcal/mol, on which general consensus has been recently achieved, was applied [31].

Moreover, the standard enthalpy change of the reaction in the solution phase was calculated by summing up the standard enthalpy change in the gas phase and solvation energy similar to what was used for obtaining the standard free energy of the solution phase.

III. RESULTS AND DISCUSSION

As a key step in calculations, the search for the most stable conformers of the reactants and products in the gas phase indicated that for most considered species (except alkylamines and butyldiamine) the lowest-energy conformers are those which involve the formation of intramolecular hydrogen bonds. Optimized structures of these species are illustrated in Fig.1 along with the corresponding intramolecular hydrogen bond lengths. As it can be seen, due to the formation of intramolecular hydrogen bonds, the gauche conformer is a preferable conformer in the gas phase. However, in the case of butyldiamine, in contrast with other diamines, it was found that the *trans* conformer has a lower energy than the *gauche* does in the gas phase. This may be due to angle strain resulting from the formation of the seven-membered ring in the *gauche* conformer. In the case of MEA, as a primary alkanolamine, the gGg′ conformer has proved to be the most stable in the gas phase and tGg′ the most populated conformer according to da Silva's study [32]. Both of these conformers are depicted in Fig.1. The calculations were performed respective of the both conformers. The results of these calculations are discussed in the following. For DEA, as a secondary alkanolamine which has several conformers for neutral and protonated forms, the most stable conformer proved to be the one which forms two intramolecular hydrogen bonds.

Furthermore, the considered structures were reoptimized in the solution phase based on Bryantsev's findings that geometry optimization in the solution was essential for systems possessing intramolecular hydrogen bonds [27]. Accordingly, the solution phase conformers of the studied neutral and protonated amines as well as carbamate ions are identified and presented in Table S1 of the supplementary material.

The calculated gas phase basicities are listed in Table I. The gas phase basicity is defined as Gibbs free energy change associated with the protonation reaction [33]. The Gas phase basicities of the studied alkylamines and diamines showed an increase with longer alkyl chain and substitution of hydrogen atoms with methyl groups in consistence with experimental data. In the case of aminoacetamide, a significant decrease in basicity was observed due to the existence of electron withdrawing carbonyl group. For MEA with tGg′ conformer the results obtained were more consistent with experiments in comparison with its other conformer. As it can be seen in Table I the value of the gas basicity of tGg′ conformer is approximately similar to its experimental value, while the other conformer has a difference

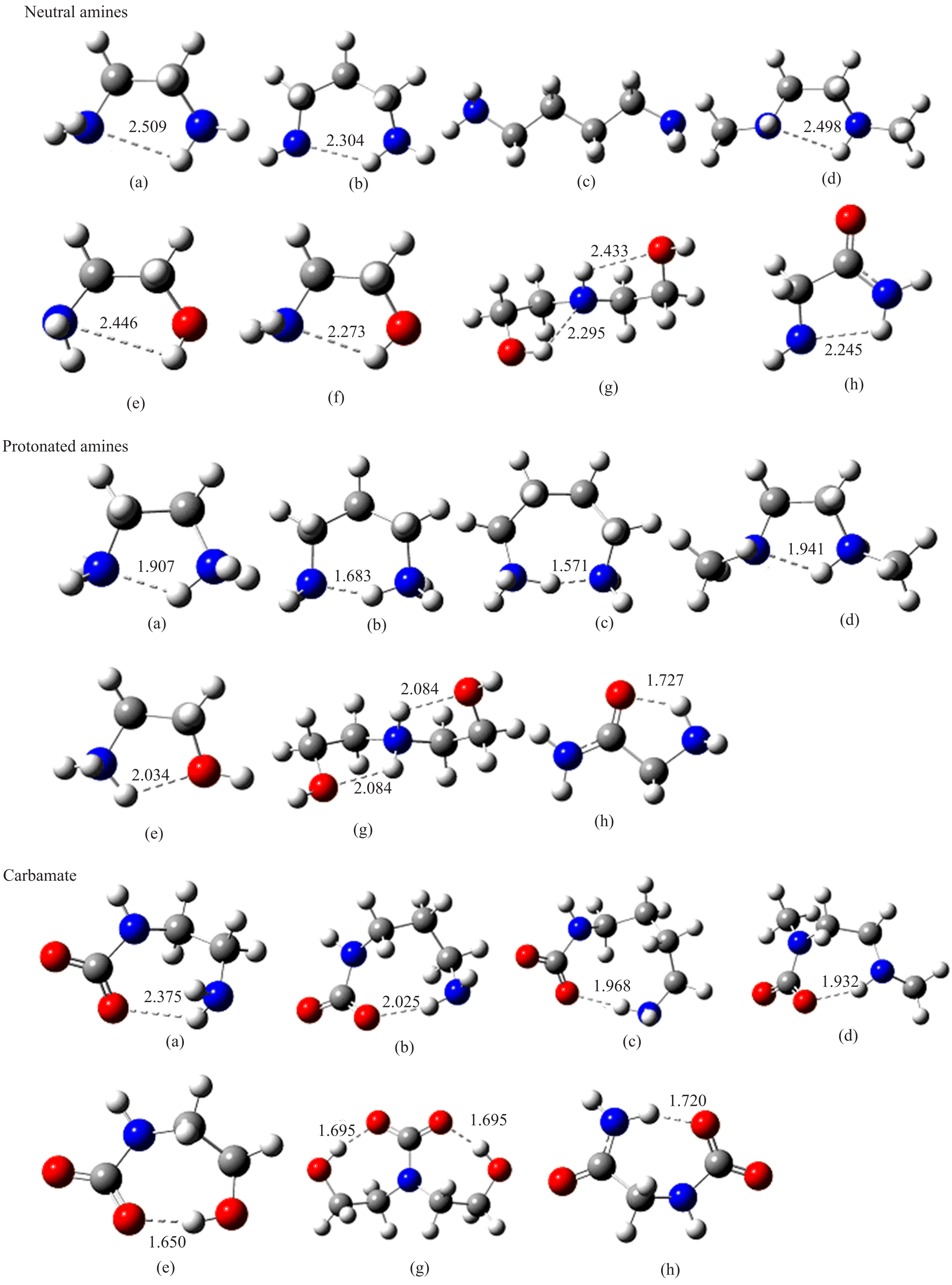

FIG. 1 The most stable conformers of neutral amines, protonated amines and carbamate ions in the gas phase for (a) ethandiamine, (b) 1,3-propandiamine, (c) 1,4-butandiamine, (d) dimethylethandiamine, (e) monoethanolamine (tGg conformer), (f) monoethanolamine (gGg′ conformer), (g) diethanolamine, and (h) aminoacetamide calculated at B3LYP/6-311++G(d,p) level. Intramolecular hydrogen bonds are identified by dotted lines. The lengths are given in Å.

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TABLE II Solvation free energies of neutral and protonated amines and carbamate ions and enthalpies of the studied reactions using the B3LYP/6-311++G(d,p) in combination with SMD/IEF-PCM/HF/6-31G(d) level of theory.

Amine	Solvation free energy/(kcal/mol)			Enthalpy of absorption/(kcal/mol)	
	B	BH^+	$BCO_2{}^-$	Reaction (1)[a]	Reaction (2)[b]
Propylamine	−4.25	−70.00	−82.72	−19.13	−12.63
Butylamine	−4.05	−69.20	−81.52	−18.86	−12.84
Isobutylamine	−3.55	−68.70	−81.32	−19.63	−13.31
2,2,2-Trifluoro-N-methylethanamine	−4.78	−73.59	−72.07	−9.56	−5.30
Monoethanolamine	−12.46	−74.26	−77.00	−16.67	−11.83
Diethanolamine	−14.58	−68.94	−71.05	−16.77	−14.07
1,2-Ethandiamine	−10.59	−68.53	−84.10	−17.62	−12.80
1,3-Propandiamine	−10.49	−61.86	−82.62	−19.34	−13.93
1,4-Butandiamine	−9.98	−58.57	−81.06	−19.66	−16.36
N,N'-Dimethyl-1,2-ethanediamine	−9.15	−62.84	−84.48	−20.80	−14.05
2-Aminoacetamide	−15.02	−79.52	−77.83	−12.52	−9.71

[a] Carbamate formation.

[b] Bicarbonate formation.

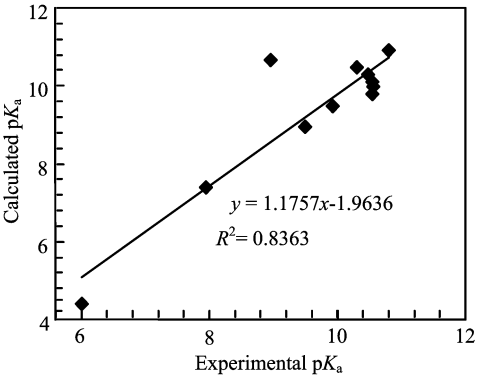

FIG. 2 Plot of the calculated pK_a values of studied amines versus experimental values.

of rough 2 kcal/mol. The data in Table I demonstrate a fairly good agreement for most amines except DEA which shows the maximum deviation (4.48 kcal/mol) from experimental values. This discrepancy might be due to the existence of two hydrogen bonding in the DEA structure.

Table II summarizes the standard solvation free energies ($\Delta G^{\ominus}_{\text{solv}}$) of the species. These values are obtained using SMD solvation model as the recommended option for computing $\Delta G^{\ominus}_{\text{solv}}$ in Gaussian 09 package. Consequently, pK_a values were calculated using the method described above.

In Fig.2, the calculated pK_a values are plotted against the experimental values. As it can be seen, there is a roughly linear relationship between the experimental and calculated values with a correlation coefficient (R^2) of 0.8363. Furthermore, the slope of the regression line is close to the theoretical value of 1 according to the following equation:

$$\mathrm{p}K_a(\text{calc.}) = c_1 \mathrm{p}K_a(\text{expt.}) + c_2 \qquad (11)$$

However, some differences can be observed between the experimental values of pK_a and the calculated results. These deviations originate from two main sources of error. The first error which is in the calculation of $\Delta G^{\ominus}_{\text{g}}$ has been already discussed. The second error concerns the accuracy of the calculations for $\Delta G^{\ominus}_{\text{solv}}$ of species especially the ions and it may be attributed to the uncertainty in the description of the solvent-solute interactions and the estimation of hydrogen bonding strength by continuum solvation model.

Finally, the enthalpy changes of the reactions of carbamate and bicarbonate formation are shown in Table II. Although, both mentioned reactions are exothermic, the magnitudes of $\Delta H^{\ominus}_{\text{abs}}$ in the reactions leading to bicarbonate formation are lower. This implies that carbamate formation is more favorable than bicarbonate formation as long as energy is concerned. The calculated value of MEA is comparable with the value measured by Kim and Svendsen of −19.1 kcal/mol [14] and the value reported by Xie *et al.* equal to −17.3 kcal/mol [20].

In order to find the relationship between basicity and heat of absorption, the values of $\Delta H^{\ominus}_{\text{abs}}$ of the reactions as a function of pK_a are plotted in Fig.3. Experimental pK_a values showed a good correlation with the values of reaction enthalpy for carbamate formation with R^2=0.9428. A fairly good correlation also exists between the enthalpies of reaction and pK_a values calculated by SMD (R^2=0.8723). In the case of bicarbonate reaction, a similar linear relationship is observable, however, with a lower correlation coefficient (Fig.4). Deviations from the linear correlation may be attributed to the uncertainties in the calculations using implicit sol-

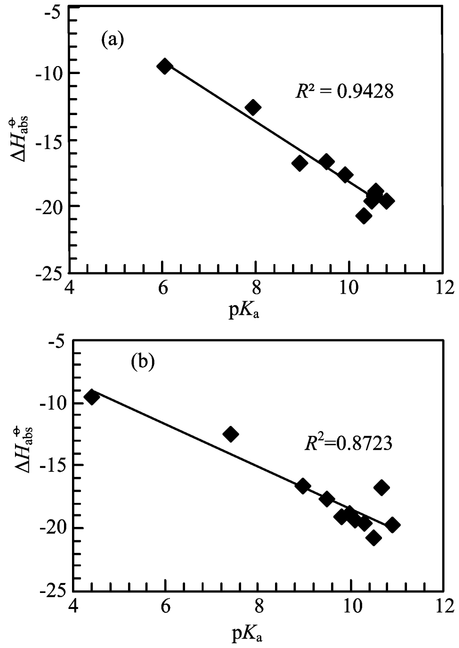

FIG. 3 Heats of absorption for carbamate forming versus (a) experimental pK_a and (b) calculated pK_a.

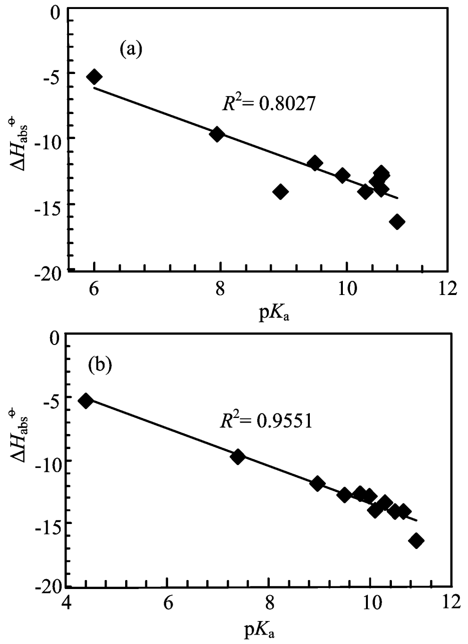

FIG. 4 Heats of absorption for bicarbonate forming versus (a) experimental pK_a and (b) calculated pK_a.

vation model as mentioned before. Moreover, it should be noted that the association of ions and the possibility of forming byproducts were neglected in all of the enthalpy calculations. Anyhow, a linear relationship can be observed between the basicity and enthalpy of reactions in all cases. This suggests that higher values of amine basicity produce more heat in the reaction with CO_2.

It can be argued that the enthalpy change of the reaction is one of the most important properties of amine-based systems due to the fact that the required energy for the regeneration of the solvent directly depends on the amount of the emitted enthalpy of absorption. Hence, the results in this work are hopefully useful for selecting new solvents with less heat of reaction to improve the absorption process.

IV. CONCLUSION

Theoretical calculations of the thermodynamic parameters of the reaction between CO_2 and a diverse series of amines were performed using a combination of density functional theory and the latest continuum solvation model called SMD. The calculated values of pK_a of amines showed a good agreement with experimental data except a few cases. Observed discrepancies between the calculated pK_a and the experimental data were attributed to the calculation of the gas phase basicity and uncertainties in calculating the solvation free energy of the species, especially the ions through implicit solvation model. The enthalpies of the absorption process were also calculated. The results revealed that an increase in the pK_a of amine leads to a linear increase in the enthalpy change of the reaction and consequently an increase in the regeneration energy. Therefore, by adjusting the basicity of amine, new solvents may be designed with lower amounts of absorption heat.

Supplementary material: Cartesian coordinates and energies (Hartrees) for the most stable conformers of the studied neutral and protonated aliphatic diamines, alkanolamines, and aminoamide as well as relevant carbamate ions in the solution phase obtained at B3LYP/6-311++G(d,p) in combination with SMD/IEF-PCM/HF/6-31G(d) level of theory are available.

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