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Modeling Temperature Dependency of Amine Basicity Using PCM and SM8T Implicit Solvation Models

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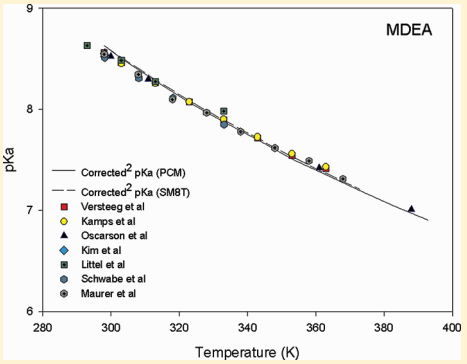
Supporting Information

ABSTRACT: PCM and SM8T continuum solvation models are used to study the temperature dependency of a set of amines in the temperature range 273−393 K using density functional theoretical calculations. Gaseous phase calculations are done using B3LYP and M06 functionals at the 6-311++G(d,p) basis set level. pK_a values calculated computationally are compared with experimental values in the given temperature region using both continuum solvation models. The continuum solvation models predict the temperature trends of pK_a compared to experimental trends very nicely. Accurate pK_a values at 298 K are however required as input to the model. The absolute values of pK_a values are not reproduced well by these continuum solvation models, and a correction term is therefore introduced. A set of 10 amines, which have potential for CO_2 capture, and where also a large experimental data set of temperature dependent pK_a values is available, were studied in this work. The temperature dependency of pK_a values of amines provides a basis for selection for optimum solvents for postcombustion CO_2 capture processes.



INTRODUCTION

Carbon capture and storage (CCS) may play a very important role in controlling anthropogenic CO_2 emissions. The increase in carbon dioxide concentration in the atmosphere seen during the last century is believed to be the main cause of global warming (IPCC, 2007). Significant reduction in CO_2 emissions can be obtained by targeting large point sources such as coal-fired power plants and iron and steel producers. Postcombustion CO_2 capture by absorption is a widely studied technology within CCS. Solvent development in postcombustion CO_2 capture is very important to identify CO_2 absorbent systems that have close to ideal properties with regard to energy use and stability. Amine-based absorption and stripping systems is an established technology and represents a promising option for reliable CO_2 capture.[1] The amines investigated extensively for this application are traditional amines such as monoethanolamine (MEA) and amine blends such as potassium carbonate/piperazine and methyldiethanolamine/piperazine (MDEA/PZ).[2−4]

In the present work, the temperature sensitivity of pK_a values of some potential amines for CO_2 capture is studied, also including piperazine and some of its derivatives. Piperazine (PZ) is a cyclic diamine that has previously been studied in blends with tertiary and sterically hindered amines to improve the CO_2 mass transfer rates.[5] MEA and MDEA are also studied, as these are very important solvents in CCS technology.

The motivation behind this work lies in the fact that the pK_a values of the conjugate acids of amines are important variables to understand their CO_2 reaction rate and absorption capacity. A reliable prediction of these would be of great interest when screening for new promising solvents for CO_2 capture. The amount of protonated and unprotonated forms at a specific pH can be determined with the pK_a value of a molecule. Hence, the equilibrium state of the chemical system can be interpreted.[6] The equilibrium can be shifted toward the acid or the conjugate base side depending upon the extent of solvent interactions with the associated and dissociated forms of the molecule.[7] Papers by Schüürmann et al. discuss the importance of pK_a.[8,9] Calculation of pK_a values using quantum chemical methods provide a good understanding of the structural and environmental factors that influence pK_a values and are essential for interpretation of experimental values in various systems.[10] In the gas phase, these methods can provide reliable results for the acidity of small molecules with equivalent or greater accuracy than that obtained experimentally.[10] For calculating acidities and basicities of isolated molecules in the gas phase, there is quite a large number of well-established theoretical models present. The absolute acidities and basicities well within the experimental error margin of around 8 kJ/mol can be obtained by the use of the best of these methods.[11] However, the situation when acidity or basicity is to be calculated in solution becomes more challenging. In solution, the calculation of free energy of solvation is the main source of error. Supermolecule-style calculations, variants of dielectric continuum theory, and

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cluster-continuum approaches are examples of theoretical models which can deal with this situation. Extensive coverage of the modern solvation models can be found in a recent review by Tomasi et al.[12] Hence, due to the difficulty of calculating solvation energies, the situation is less satisfactory in solution. Moreover, pK_a calculations invariably involve ionic species for which the errors incurred by continuum solvation calculations are considerably larger. Also, continuum methods do not consider direct solute−solvent interactions, for example, hydrogen bonding. Nevertheless, the theoretical calculation of the pK_a of acids and bases in solution continues to gather considerable interest and there have been a number of papers published in this area.[10,13−17] For instance, calculations of Gibbs free energy and pK_a values can be found; see, e.g., Shields,[16,17] Chipman,[19] Yates,[13,14] and Liu.[10]

In conventional acid gas removal plants, the absorber works at 323−333 K and the stripper at 373−393 K, so the pK_a values of amines in the temperature range 273−393 K are of interest and this is the range which is studied in this work.

COMPUTATIONAL DETAILS

Calculations for the gas phase basicity have been carried out using density functional theory (DFT) with B3LYP and M06 functionals at the 6-311++G(d,p) basis set level. Results were compared for two methods, and it was seen that B3LYP and M06 results for gaseous phase protonation energy for studied amines are very close to each other (average difference of approximately 0.004 hartree). The B3LYP functional was chosen for further calculations. The initial set of conformers were generated at the HF/6-31G* level. Potential conformers were then optimized at the B3LYP/6-311++G** level in the gaseous phase. Single point energy calculations on this optimized geometry of the molecule obtained are used to study the solvation effects with the PCM and SM8T solvation models. Thus, the most stable conformer in the gaseous phase calculations is assumed to be the most stable conformer in the solution phase also for the studied amines except MDEA, which is a more flexible molecule. For MDEA, solution phase optimization is carried out using the HF/6-31G* level using the SM8 continuum solvation model in Spartan 08. The equilibrium geometry of the molecule in the ideal gas phase from molecular energy minimization is calculated using Spartan 08. PCM calculations and gaseous phase frequency calculations are done using Gaussian 03 software.[20] These calculations are carried out for the temperature range 273−393 K, using the optimized structure obtained in the previous step. PCM calculations were done using the default settings in Gaussian 03 in the aqueous phase. All calculations were done using density functional theory (DFT) at the B3LYP/6-311++G(d,p)//B3LYP-6-311++G(d,p) level. The implementation of the PCM model[21] can be invoked using the self-consistent reaction field (SCRF) keyword in combination with PCM-specific modifiers. Option read was used to indicate a separate section of options providing calculation parameters for specifying the characteristics of the cavity. The extra options used were RADII = UAHF, which uses the united atom topological model applied on radii optimized for the HF/6-31G (d) level of theory. The calculations done in this work use cavities based on atomic spheres, using the GEPOL algorithm of Nilson et al.[22] GEPOL has been adopted as the default option for PCM calculations in the Gaussian 03 electronic structure program. It gives geometry optimization and energy calculations with better results. Both electrostatic and non-electrostatic (i.e., cavitation, repulsion, and dispersion) terms were included in the calculation of ΔG_{solv} values. SM8T calculations[23] are done in gamessplus for the temperature range 273.15−373 K, using the optimized structure obtained earlier. All SM8T calculations were also done using density functional theory at the B3LYP/6-311++G(d,p)//B3LYP-6-311++G(d,p) level. SM8T is the only continuum solvation model which is documented and parametrized to investigate temperature effects of solvation energy of both neutral and charged molecules.

METHODS

For calculating pK_a values, the first step is to calculate free energies in solution and this calculation of free energies in solution is usually carried out with the help of a thermodynamic cycle in which solution-phase reaction free energies are obtained as the sum of the corresponding gas-phase free energy and the free energy of solvation, which can be written as in eq 1.

$$\Delta G^*_{sol} = \Delta G^*_{gas} + \sum_{i=1}^{N\ \text{products}} n_i \Delta G^*_{solv,i} - \sum_{j=1}^{N\ \text{reactants}} n_j \Delta G^*_{solv,j} \quad (1)$$

Here, * denotes a standard state of 1 mol/L. Assuming ideal gas behavior, a correction corresponding to $\Delta nRT\ln(R^*T)$ must be added to the gas-phase reaction energy which is denoted by ΔG^0_{gas}. This is typically calculated for a standard state of 1 atm. Δn refers to the change in number of species in the reaction, and R and R^* are the gas constant in units of J/(mol K) and L atm/(mol K), respectively.

The main reason for utilizing a thermodynamic cycle is that it allows us to use different levels of theory for gas-phase calculations and solvation calculations. The low levels of theory at which continuum models are typically parametrized and implemented (such as small basis set HF or B3LYP calculations) are not usually sufficiently accurate to reproduce accurate total free energies in solution. Absolute pK_a calculations in the present work are based on the following thermodynamic cycle.

The pK_a of the different amines under study is obtained by using the above thermodynamic cycle. The standard-state free energy change associated with the following reaction, free energy of protonation in solution (ΔG^*_{aq})

$$AH_s^+ \xrightarrow{\Delta G^*_{aq,deprot(AH^+)}} A_s + H_s^+ \quad (2)$$

is related to the aqueous pK_a according to

$$pK_a = \frac{\Delta G^*_{aq}}{RT\ln(10)} \quad (3)$$

where R is the universal gas constant and T is the temperature. Using the thermodynamic cycle shown in Figure 1, ΔG^*_{aq} may be expressed in terms of the aqueous solvation free energies of the acid AH^+ and its conjugate base A

$$\Delta G^*_{aq}(AH^+) = \Delta G^0_{gas}(AH^+) + \Delta G^*_s(A) - \Delta G^*_s(AH^+) + \Delta G^*_s(H^+) + \Delta G^{\circ *} \quad (4)$$

where $\Delta G^*_s(AH^+)$ and $\Delta G^*_s(A)$ are the free energies of solvation of AH^+ and A, respectively, $\Delta G^*_s(H^+)$ is the free

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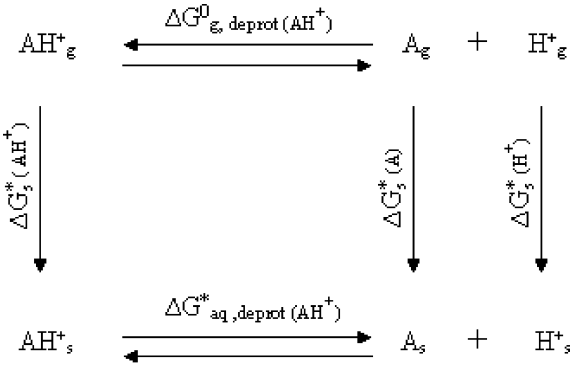

Figure 1. Thermodynamical cycle employed for calculation of pK_a values.

energy of solvation of H^+, $\Delta G^0_{gas}(AH^+)$ is the gas-phase acidity of AH^+, defined by

$$\Delta G^0_{gas} = G^0_{gas}(A) + G^0_{gas}(H^+) - G^0_{gas}(AH^+) \quad (5)$$

and $\Delta G°*$ is the free energy change associated with moving from a standard state that uses a concentration of 1 atm in the gas phase and 1 mol/L in the aqueous phase (denoted by the degree sign) to a standard state that uses a concentration of 1 mol/L in both the gaseous and aqueous phases (denoted by the asterisk). The ideal gas law yields

$$\Delta G°* = -RT\ \ln(24.46) \quad (6)$$

At 298 K, $\Delta G°*$ is 1.89 kcal/mol.

In the above equations, one can also replace H^+ by H_3O^+. For calculating pK_a values, we have used the experimental value for $\Delta G_s^*(H^+)$. Here, the value of the Gibbs free energy of the proton in the gas phase is set to −6.29 kcal/mol using translational entropy calculated according to the well-known Sackur−Tetrode equation.[24] The solution phase free energy used for protons is −263.977 kcal/mol[25] in this work. pK_a values calculted by employing this thermodynamical cycle are compared with available experimental data.[26−57]

The smallest error in the pK_a calculation by this method is contained in the gas-phase free energy calculations. For calculation of ΔG_{gas}, CCSD(T) single-point energy calculations on MP2 or MP4 geometries provide the most accurate results which are within a RMSE of half kcal/mol or better. Highly accurate results can also be obtained by using compound model chemistry methods such as G3, CBS-APNO, and W1. While doing calculations by using DFT methods, it is very important that these methods should be benchmarked against appropriate experimental or ab initio results so that the DFT method of choice is most appropriate for the systems of interest.

For small molecules and with high computational expense, CCSD(T) calculations extrapolated to the complete basis set limit provide gas-phase free energies as accurate as the experiment. A standard deviation of 0.58 kcal/mol was obtained, by employing the CCSD(T)//MP4(SDQ)/aug-cc-pVTZ method,[58−61] and complete basis set limit using the aug-cc-pVTZ and aug-cc-pVQZ basis sets, when compared to a set of data of experimental values of gas-phase deprotonation reactions, which are compiled in the NIST online database.[62,63] At present, CCSD(T) calculations are regarded as the gold standard in ab initio quantum chemistry. Some high levels of theory, such as CBS-QB3[64] and CBS-APNO,[65] also give reliable free energy of protonation in gaseous phase (ΔG_{gas}) values having root-mean-square deviations of 1.1−1.6 kcal/mol, when compared to experimental ΔG_{gas} values compiled in the

Table 1. Amines Studied and Their Experimental pK_a Data at 25 °C

no.	compd	name	type[a]	exp pK_a (25 °C)
1.	piperazine	PZ	s, c	9.81(1),[b] 5.55(2)[b]
2.	morpholine	morpholine	s, c	8.49[c]
3.	piperidine	piperidine	s, c	11.10[d]
4.	1-(2-aminoethyl)-piperazine	AEP	p, s, t, c	9.48(1),[e] 8.45(2)[e]
5.	dimethylethylenediamine	DMEDA	s	10.03[f]
6.	2-methylpiperazine	2-methylPZ	c	9.57[g]
7.	1-methylpiperazine	1-methylPZ	c	9.14[g]
8.	1-ethylpiperazine	1-ethylPZ	c	9.20[g]
9.	*N*-methyldiethanolamine	MDEA	t	8.62[h]
10.	monoethanolamine	MEA	p	9.50[i]

[a]In the type of amines studied, p, s, t, and c stand for primary, secondary, tertiary, and cyclic amines, respectively. [b]Experimental data from Hall et al.[28] [c]Experimental data from Hetzer et al.[34] [d]Experimental data from Perrin et al.[39] [e]Experimental data from Pagano et al.[26] [f]Experimental data from Nasanen et al.[47] [g]Experimental data from Khalili et al.[33] [h]Experimental data from Littel et al.[52] [i]Experimental data from Datta et al.[54]

Table 2. Correction Factors Applied to PCM and SM8T pK_a Results Compared with Experimental pK_a's

	pK_a (298 K)			pK_a (298 K)	
amine	exp	PCM	correction 1^{PCM}	SM8T	correction 1^{SM8T}
PZ	9.81	11.72	1.91	11.06	1.25
morpholine	8.49	8.78	0.29	9.35	0.85
piperidine	11.10	7.11	−3.99	9.22	−1.88
AEP	9.48	12.71	3.23	12.12	2.64
DMEDA	10.03	9.88	−0.15	11.87	1.84
2-methylPZ	9.57	11.36	1.79	10.93	1.36
1-methylPZ	9.14	9.38	0.24	8.73	−0.41
1-ethylPZ	9.20	11.80	2.60	11.70	2.50
MDEA	8.62	9.57	1.05	7.85	−0.67
MEA	9.50	7.51	−1.99	13.20	3.70

Table 3. Error in pK_a Values at 323 K with Correction 1

	pK_a (at 323 K)				
		correction 1 pK_a		error in pK_a	
amine	exp	PCM	SM8T	PCM	SM8T
PZ	9.14[a]	9.03	9.07	0.11	0.07
morpholine	7.95[b]	7.93	7.87	0.02	0.08
piperidine	10.38[c]	10.57	10.44	−0.19	−0.06
AEP	8.77[d]	8.61	8.65	0.16	0.12
2-methylPZ	8.97[e]	8.80	8.83	0.17	0.14
1-methylPZ	8.65[e]	8.52	8.60	0.13	0.05
1-ethylPZ	8.72[e]	8.39	8.41	0.33	0.31
MDEA	8.07[f]	7.99	8.14	0.08	−0.07
MEA	8.813[g]	9.03	8.53	−0.22	0.28

[a]Experimental data from Khalili et al.[33] [b]Experimental data from Hetzer et al.[34] [c]Experimental data from Bates et al.[38] [d]Experimental data from Pagano et al.[26] [e]Experimental data from Khalili et al.[33] [f]Experimental data from Hamborg-Versteeg et al.[48] [g]Experimental data from Bates et al.[55]

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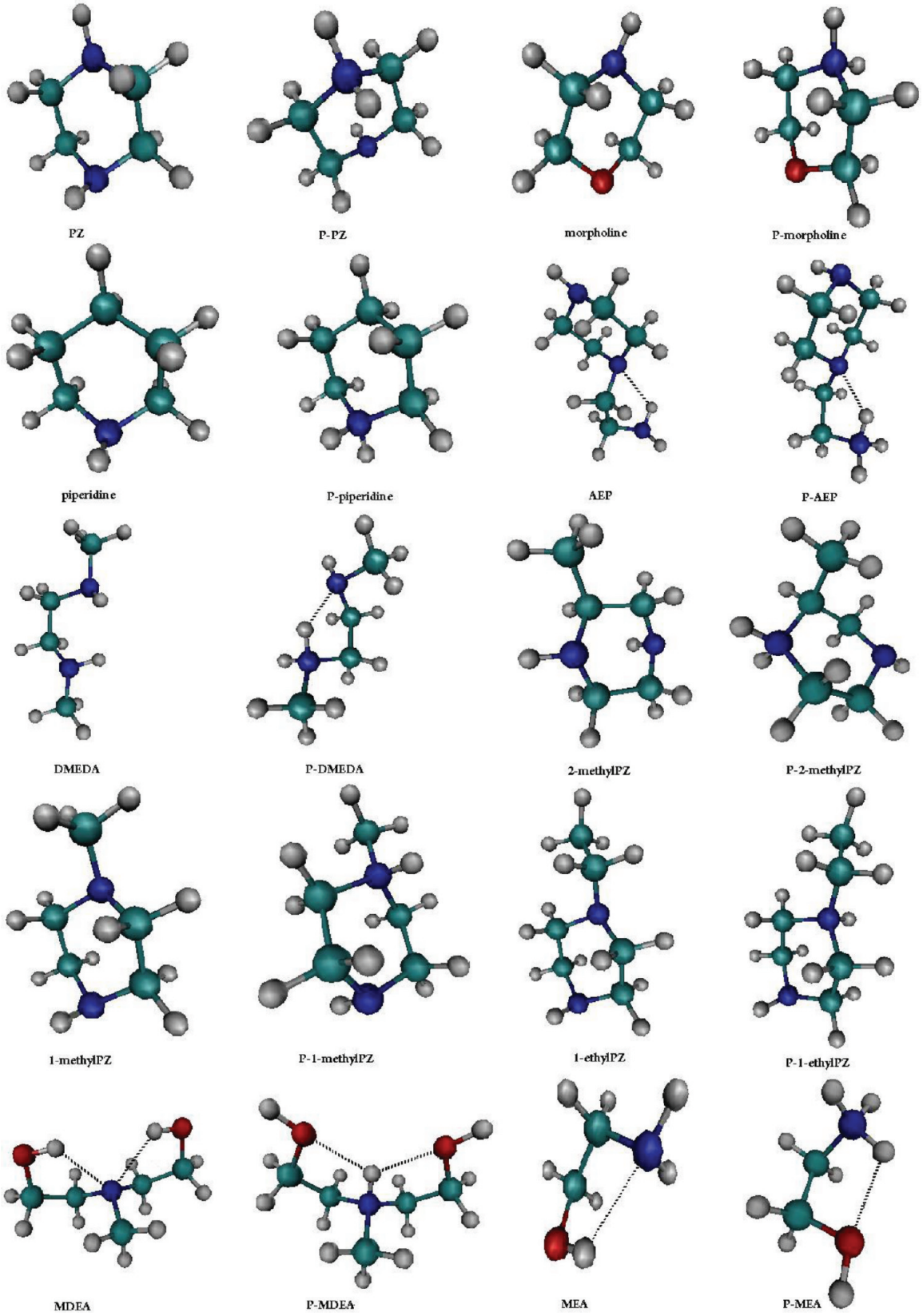

Figure 2. Lowest-energy conformers of neutral and protonated amines in the gaseous phase (the dotted bond shows the hydrogen bond in the molecule).

NIST online database.[62,63] The mean absolute deviations of 1.16, 1.43, 1.06, and 0.95 kcal/mol were achieved by using model chemistries G3,[66] CBS-QB3,[64] CBS-APNO,[65] and W1,[67] respectively. These deviations were confirmed later also for G2, G3, and CBS-APNO geometries, which produced accurate values of ΔG_{gas} for the formation of ion−water clusters on

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comparison with experimental results.[68−72] However, CBS-QB3 produced less accurate results for these clustered ions than the other model chemistries, which was a contradiction to previous publications.

For the calculation of gas-phase free energy calculations, DFT calculations provide a computationally less demanding and similar accuracy pathway. DFT provided very accurate results for PBE1PBE/aug-cc-pVTZ and B3P86/aug-cc-pVTZ[73] basis sets. Many studies have been done to examine the accuracy of B3LYP. Fu et al.[74] studied the ΔG_{gas} values for the change in free ebergy of reaction 2 by using the MP2/6-311++G(d,p) and B3LYP/6-311++G(2df, p) methods, which provided gas-phase acidities, within 2.2 and 2.3 kcal/mol of experimental values. Range et al.[75] also studied that B3LYP with the 6-311++G(3df,2p) basis yields a root-mean square error of 2.5 kcal/mol in ΔG_{gas} for reaction 2, while other high levels of theory, CBS-QB3, G3B3, G3MP2B3, PBE0, and B1B98, produced a root-mean-square error within 1.3 kcal/mol of experimental values. Reaction 2 represents the gas phase dissociation of an acid, which is the top line of the thermodynamical cycle given in Figure 1. Some research also shows that B3LYP produced accurate gas phase free energy calculations on aliphatic amines, diamines, and aminoamines. Bryantsev et al.[76] showed that B3LYP/6-31++G* calculations produced a mean absolute error of 0.78 kcal/mol compared to experimental data of ΔG_{gas} for amines, diamines, and aminoamines without using any computationally expensive levels of theory. The same basis set is used for the DFT calculations in the present work.

To best of our knowledge, the temperature dependency in the PCM model is not documented anywhere for study of temperature effects on solvation free energy and this work is a first attempt to see the temperature sensitivity of PCM solvation free energy calculations. Thus, we suggest an equation that reproduces the model implemented in Gaussian 03. On examining the results obtained from PCM solvation energy for amines and protonated amines, we see that there is no change in the electrostatic and nonelectrostatic components of the solvation free energy, except the cavitation energy term. In other words, we can say that the changes in the solvation free energy term as a function of temperature arise due to the variation in the forces that account for creating the cavity for the solute in the PCM model at different temperatures. This cavitation energy term increases with an increase in temperature, both for amines and protonated amines. We have derived the explicit temperature dependency of the PCM model. This derivation is based on the final results of the free energy of solvation for amines and protonated amines. As in the description of the PCM model, no temperature dependent equations are included, so these equations are derived from the computational results obtained in this study. We believe that the PCM model has these equations integrated while calculating temperature effects. As we have seen that it is only the cavitation energy term which is responsible for temperature sensitivity, the changes of cavitation energy with temperature are given as

$$\mathrm{CavE_T} = \mathrm{CavE_{298}} + (T - 298)\left[\frac{\mathrm{CavE_{298}}}{298}\right] \quad (7)$$

Here, $\mathrm{CavE_T}$ and $\mathrm{CavE_{298}}$ are the cavitation energy terms at any given temperature and at 298 K, respectively. The solvation free energy at any temperature can be obtained by using the following equation:

$$\Delta G_{solv}(T) = \Delta G_{solv}(298) + (T - 298)\left[\frac{\mathrm{CavE}_{298}}{298}\right] \quad (8)$$

The change of cavitation energy of amine and protonated amine with an increase of temperature for piperidine and DMEDA is shown in the Supporting Information.

RESULTS AND DISCUSSION

pK_a values of piperazine, morpholine, piperidine, amino ethyl piperazine (AEP), 2-methylpiperazine, 1-methylpiperazine, 1-ethylpiperazine, dimethylethylenediamine (DMEDA), methyldiethanolamine (MDEA), and 2-aminoethanol (MEA) were determined using the above method. Table 1 summarizes all the amines studied for the present work.

Figure 2 shows the conformers that were identified as the most stable at the B3LYP/6-311++G(d,p) level for the amines in the gaseous state. The selected conformers are drawn from a conformer search at the HF/3-21G(d) level in the gas phase. Some of the most stable conformers identified at that level were also studied at the B3LYP/6-311++G(d,p) level, and it seems likely that these are, in fact, the most stable conformers at this level of theory. It, should, however, be noted that a full study of the conformers at the B3LYP/6-311++G(d,p) level has not been undertaken. The same method was used to identify the conformers of protonated counterparts. It should be noted that, in the present work, we intend to study the temperature dependency of pK_a values, and selection of the conformer is expected to have a minimal effect on the results. Many of the molecules in the present study do also have a limited number of conformers. Thus, a solution phase conformer search is carried out for a more flexible molecule, i.e., MDEA, and its protonated counterpart and the structures of stable conformers are given in Figure 3. More information on conformer selection is given in the Supporting Information.

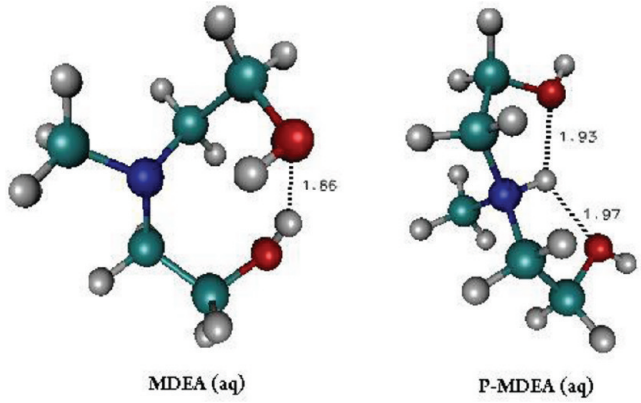

Figure 3. Stable conformers of MDEA and protonated MDEA in solution studied at the HF/6-31G* level using the SM8 continuum solvation model (the dotted lines show the hydrogen bonding in the molecule, and the bond lengths of the hydrogen bonds are also given in angstroms).

The absolute values for pK_a measurements using continuum solvation models are provided in the Supporting Information. As we see from the results, there is a deviation between the absolute values of pK_a of amines calculated from the thermodynamic model, containing gaseous free energy and solvation energies of amine and protonated amine, when

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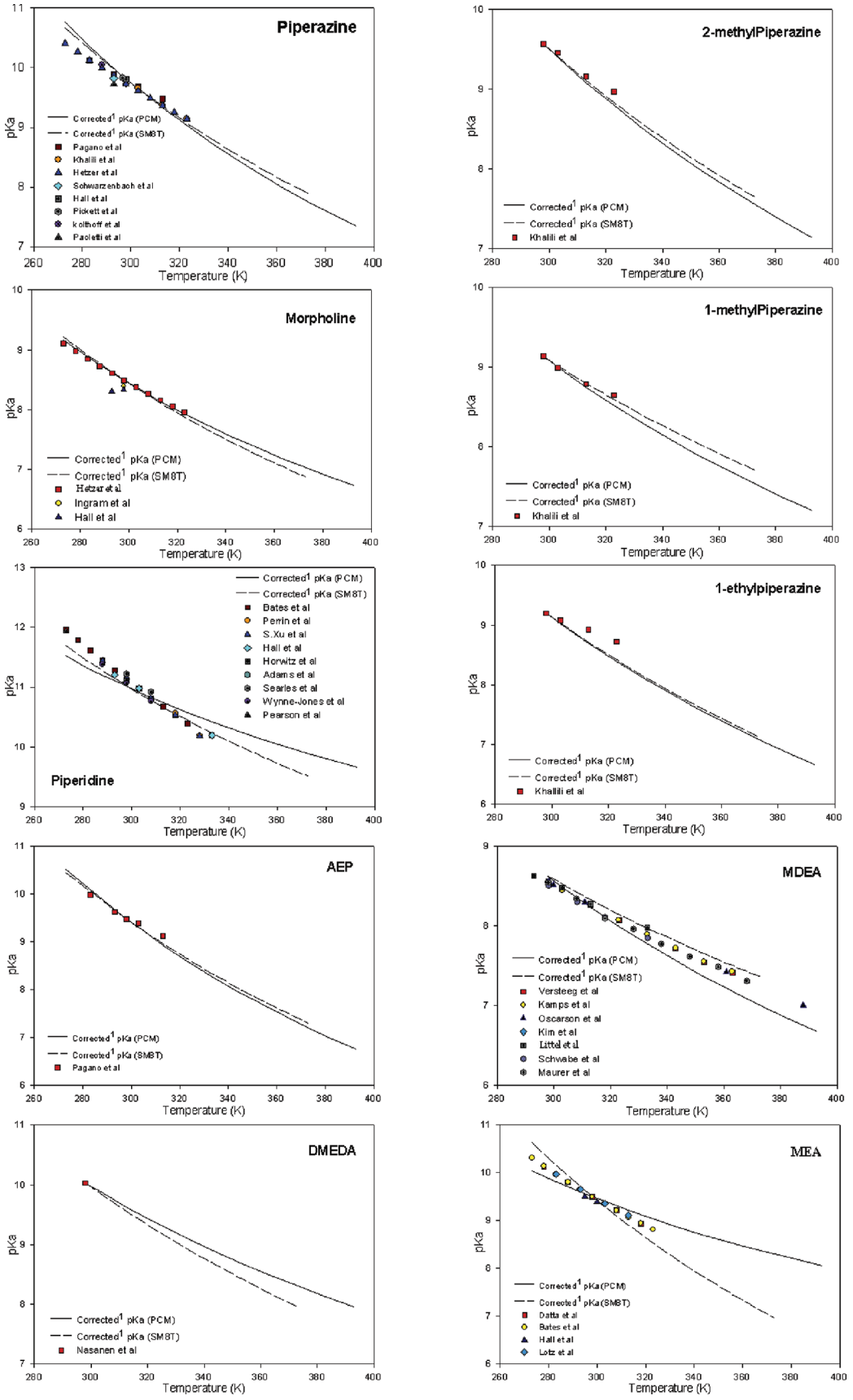

Figure 4. pK_a values (correction 1) of amines from the continuum solvation model and their comparison with available literature data in the 273−393 K temperature range (experimental refs 26−57).

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compared with experimental data. However, in the present work, we focus on the temperature trends of pK_a of these amines. To examine the temperature dependency, we have employed two models. In model 1, the calculated pK_a value is shifted to the experimental value at 298 K for both the PCM and SM8T solvation models, and we call this correction factor 1. pK_a values at all other temperatures were also shifted by the same correction factor.

$$(pK_a)_T = (pK_a)_{calc,T} + \text{correction factor 1} \quad (9)$$

In model 2, instead of shifting the pK_a value itself, the free energy of protonation in solution (ΔG^*_{aq}) is shifted to coincide with the experimental free energy of solution at 298 K. The difference between the experimental free energy of solution at 298 K and the calculated free energy of solution at 298 K is termed correction factor 2.

$$(\Delta G^*_{aq})_T = (\Delta G^*_{aq})_{calc,T} + \text{correction factor 2} \quad (10)$$

Model 1. Of all the amines studied, the PCM model pK_a values were shifted by an average value of 0.48 pK_a units and the SM8T model results were shifted by an average of 0.94 pK_a units. However, this shift does not suggest that the PCM model is behaving better than the SM8T model. In the PCM model, for some amines, the pK_a value is overestimated. In order to get an absolute value, the required correction should be subtracted from the calculated pK_a values at all temperatures. Thus, the numerical value of the size of the correction factor has no relevance to the correctness of the results of a particular model. Table 2 lists the correction factor applied to amines studied in this work, for both the PCM and SM8T model.

All the plots of pK_a values calculated from the PCM and SM8T solvation models, after applying the model 1 correction and their comparison with available literature pK_a data, are presented in graphs for each amine. Figure 4 lists all 10 graphs for the amines studied in the present work.

In Table 3, the corrected pK_a values for both solvation models are compared with experimental values at a temperature of 323 K. Looking at the errors, it can be noted that the errors in pK_a are considerable.

To visualize the changes in the slope of the pK_a curves as a function of temperature for the various amines, a temperature window of 313−323 K has been studied. The results are given in Table 4. It is clear from the results that the change in the absolute value of pK_a with a 10° rise in temperature is very well predicted by both solvation models. For MDEA, the change in pK_a value with 10° increase in temperature is reproduced by the SM8T model.

Table 5. Correction Factor Applied to PCM and SM8T ΔG_{aq} Results Compared with Experimental ΔG_{aq}

	ΔG_{aq} (298 K)			ΔG_{aq} (298 K)	
amine	exp[a]	PCM	correction 2^{PCM}	SM8T	correction 2^{SM8T}
PZ	13.33	15.93	2.60	15.03	1.70
morpholine	11.54	11.94	0.40	12.70	1.16
piperidine	15.11	9.67	−5.45	12.53	−2.59
AEP	12.88	17.27	4.38	16.47	3.59
DMEDA	13.63	13.42	−0.21	16.12	2.49
2-methylPZ	13.00	15.43	2.43	14.85	1.85
1-methylPZ	12.42	12.75	0.33	11.87	−0.55
1-ethylPZ	12.50	16.03	3.53	15.90	3.40
MDEA	11.73	13.00	1.28	10.67	−1.05
MEA	12.91	10.20	−2.71	17.94	5.03

[a]All values are in kcal/mol. Exp ΔG_{aq} are obtained from exp pK_a data in Table 1.

Model 2. As explained earlier, in a second approach, the calculated free energy of protonation in solution at 298 K is shifted to the experimental free energy of solution at 298 K. The difference between these is termed as correction factor 2. This correction is then applied to all free energies of protonation in solution calculations at all the temperatures. The pK_a values for the amines at the various temperatures are then calculated using these corrected free energies of protonation in solution values, using eq 3.

Table 5 lists the experimental free energies of solution and calculated free energies of solution for all the amines studied. The correction factors 2 in the free energy of solution values are also given.

These corrected pK_a values for the temperature range 298−393 K are again plotted against available experimental data. Figure 5 shows all the plots for the corrected pK_a values for all amines. From the figures for the amines, it can be seen that both the PCM and SM8T solvation models are very good in predicting temperature trends of pK_a, and even the experimental results from different literature sources distribute nicely around the predicted results from the computational models.

As can be seen from the graphs, the observed pK_a values are in very good agreement with the experimental data. The

Table 4. Comparison of pK_a Values within a Temperature Window of 313−323 K

	pK_a (correction 1^{PCM})			pK_a (correction 1^{SM8T})		pK_a (exp)		
amine	313 K	323 K	difference of pK_a in temperature window (PCM)	313 K	323 K	313 K	323 K	difference of pK_a in temperature window (exp)
PZ	11.24	10.94	0.30	10.60	10.32	9.48[a]	9.14	0.34
Morpholine	8.43	8.22	0.21	8.96	8.73	8.16[b]	7.96	0.21
Piperidine	6.84	6.67	0.17	8.86	8.64	10.67[c]	10.38	0.29
AEP	12.17	11.84	0.33	11.60	11.29	9.13[d]	8.77	0.36
2-methylPZ	10.87	10.58	0.29	10.47	10.19	9.16[e]	8.97	0.19
1-methylPZ	8.99	8.76	0.23	8.40	8.19	8.79[e]	8.65	0.14
1-ethylPZ	11.29	10.98	0.31	11.21	10.91	8.93[e]	8.72	0.21
MDEA	9.18	8.93	0.24	7.55	7.37	8.26[f]	8.08	0.19
MEA	7.22	7.04	0.18	12.60	12.23	9.0702[g]	8.813	0.26

[a]Experimental data from Pagano et al.[26] [b]Experimental data from Hetzer et al.[34] [c]Experimental data from Bates et al.[38] [d]Experimental data from Pagano et al.[26] [e]Experimental data from Khalili et al.[33] [f]Experimental data from Hamborg-Versteeg et al.[48] [g]Experimental data from Bates et al.[55]

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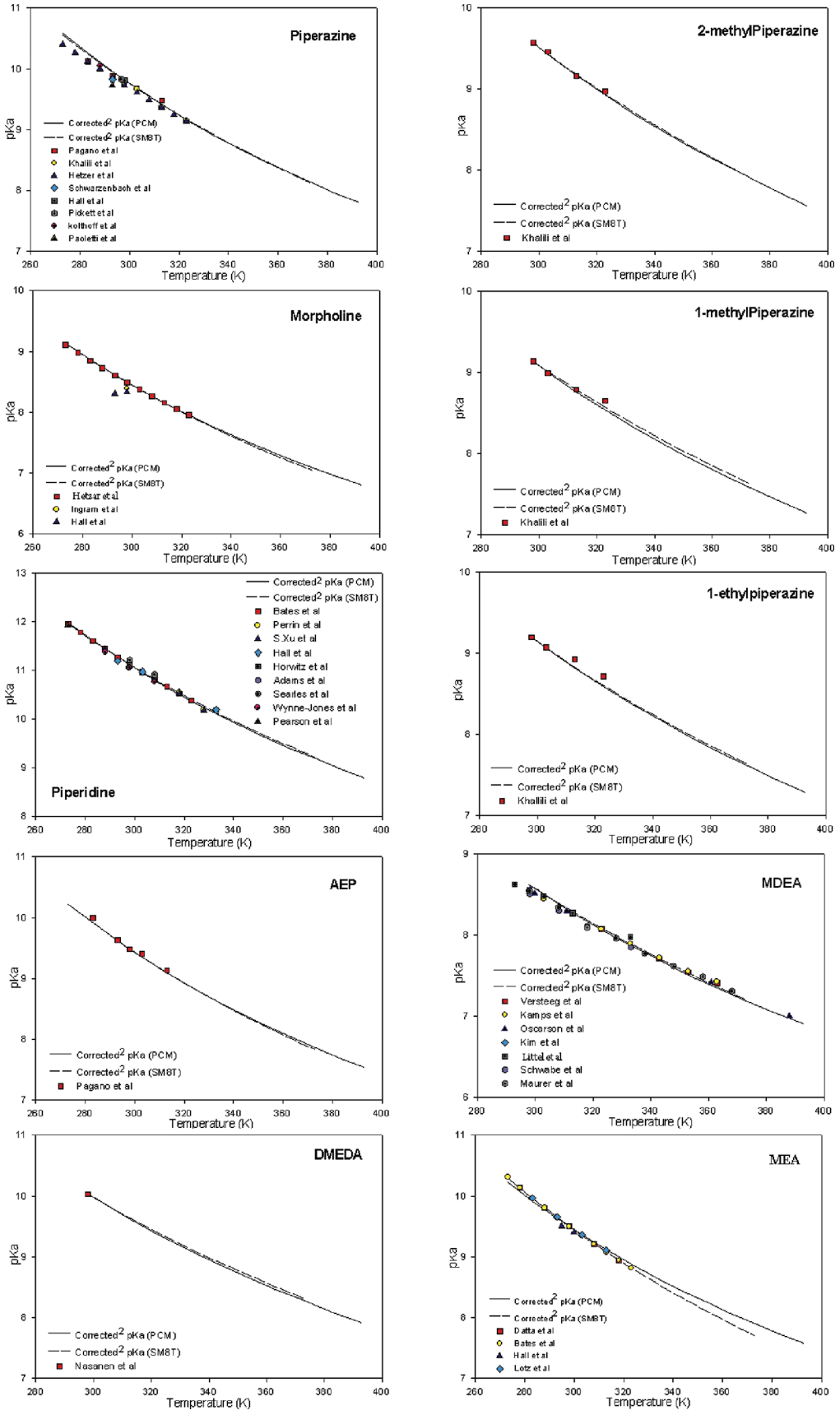

Figure 5. pK_a values (correction 2) of amines from the continuum solvation model and their comparison with available literature data in the 273−393 K temperature range (experimental refs 26−57).

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Table 6. Error in pK_a Values at 323 K with Correction 2

	pK_a (at 323 K)				
		correction 2 pK_a		error in pK_a	
amine	exp	PCM	SM8T	PCM	SM8T
piperazine	9.14	9.17	9.17	0.03	0.03
morpholine	7.95	7.95	7.94	0.00	−0.01
piperidine	10.38	10.37	10.40	−0.01	0.02
AEP	8.77	8.86	8.85	0.09	0.08
2-methylPZ	8.97	8.93	8.94	−0.04	−0.03
1-methylPZ	8.65	8.54	8.57	−0.11	−0.08
1-ethylPZ	8.72	8.59	8.60	−0.13	−0.12
MDEA	8.07	8.07	8.08	0.00	0.01
MEA	8.813	8.88	8.82	0.07	0.00

Table 7. Comparison of Calculated pK_a's with Continuum Solvation Models with Different Experimental Data Sets Available at 333 K for MDEA

data	source	pK_a (at 333 K)
1.	corrected pK_a (PCM)	7.87
2.	corrected pK_a (SM8T)	7.89
3.	Hamborg-Versteeg et al.[48]	7.89
4.	Little et al.[52]	7.98
5.	Schwabe et al.[53]	7.85
6.	Kamps et al.[49]	7.90

corrected pK_a values are compared with experimental data at 323 K, and it can be seen that there is a considerable decrease in deviation from experimental data for model 2 compared to model 1. The calculated pK_a values are now within the range of experimental errors. In Table 6, a comparison of experimental and calculated pK_a values at 323 K is given.

From the results, it can be concluded that the calculated temperature trend for pK_a values calculated with continuum solvation models is within the range of experimental errors. Table 7 shows the deviation of different experimental pK_a values for different data sets. The differences are mainly caused by different sources of experimental data having used different methods for calculating pK_a.

Author: The changes in pK_a values within a temperature window of 313−323 K are calculated also by applying correction factor 2. In this case, even the calculated values for morpholine, piperidine, 1-ethyl piperazine, MDEA, and MEA are seen to be in good agreement with the experimental results (see Table 8).

Thus, it can be observed that continuum solvation models can predict the temperature dependencies of pK_a very accurately and if the pK_a value at 298 K is known the absolute values of the temperature dependent pK_a's can be determined. As it becomes difficult to determine pK_a experimentally at higher temperatures, continuum solvation models give another tool to find pK_a at any temperature for amines. When we shift the calculated free energy of protonation in solution at 298 K to the experimental free energy of protonation in solution, we see that the accuracy of pK_a values at higher temperatures depends approximately 2/3 times on this correction. We have tried to see the effect of various contributions in calculating the free energy of protonation in solution.

From eq 4, it can be seen that gaseous and solution phase free energies are contributing to the overall change in free energy of solution with temperature. We have tried to distinguish the contributions from these various terms by examining the results from employing two gaseous phase calculations (B3LYP and M06 basis set, DFT) and turning off changes in solvation free energies and vica versa. It was observed that solvation free energies have a more important contribution than the gaseous phase free energies in the calculation of the overall temperature dependent free energy of protonation in solution.

Also, obtained temperature dependent pK_a values are compared with pK_a values obtained from the following equation[77]

$$\frac{-\mathrm{d}(\mathrm{pK_a})}{\mathrm{d}T} = \frac{(\mathrm{pK_a} + 0.052\Delta S^0)}{T} \tag{11}$$

In this equation, there are two parameters, pK_a at 298 K and ΔS^0, that need to be determined to calculate the pK_a at any temperature. In the present work, only the pK_a at room temperature is required as experimental input to determine the temperature trends. In comparing the two models, we have found that the present model also yields somewhat better results than those obtained by eq 11. A detailed discussion and comparison of accuracy of pK_a calculation with the empirical model and model 2 are given in the Supporting Information.

CONCLUSIONS

Continuum solvation models together with quantum mechanical calculations of protonation energies are found to be very good computational tools to predict the temperature dependencies of pK_a values of amines. However, accurate absolute values of pK_a at room temperature are very important in order to be able to calculate accurately the absolute temperature variations in pK_a values using continuum solvation models. The

Table 8. Comparison of pK_a Values within a Temperature Window of 313−323 K

	pK_a (correction 2^{PCM})			pK_a (correction 2^{SM8T})			pK_a (exp)		
amine	313 K	323 K	difference of pK_a in temperature window (PCM)	313 K	323 K	difference of pK_a in temperature window (SM8T)	313 K	323 K	difference of pK_a in temperature window (exp)
PZ	9.42	9.17	0.24	9.41	9.17	0.24	9.48	9.14	0.34
morpholine	8.15	7.95	0.20	8.15	7.94	0.21	8.16	7.96	0.21
piperidine	10.66	10.37	0.28	10.67	10.40	0.28	10.67	10.38	0.29
AEP	9.10	8.86	0.24	9.09	8.85	0.24	9.13	8.77	0.36
2-methylPZ	9.17	8.93	0.24	9.18	8.94	0.24	9.16	8.97	0.19
1-methylPZ	8.76	8.54	0.23	8.79	8.57	0.22	8.79	8.65	0.14
1-ethylPZ	8.82	8.59	0.23	8.83	8.60	0.23	8.93	8.72	0.21
MDEA	8.28	8.07	0.22	8.29	8.08	0.21	8.26	8.08	0.19
MEA	9.12	8.88	0.24	9.08	8.82	0.26	9.0702	8.813	0.26

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error bars observed in the computational study are within the range of experimental errors.

■ ASSOCIATED CONTENT

Supporting Information

Calculated pK_a values from the PCM and SM8T solvation models, graphs showing the variation of solvation free energy for protonated amines for both the PCM and SM8T solvation models, discussion on potential confomers of protonated AEP, and comparison of experimental, PCM, and SM8T pK_a data at a temperature range of 273−323 K for morpholine. Gaseous phase protonation energies for DFT/B3LYP/6-311++G(d,p) and DFT/M06/6-311++G(d,p) at 298 K for the amines studied. Solvation energies of both amine and protonated amine calculated by both the PCM and SM8T solvation models at 298 K. Comparison of the B3LYP and M06 basis sets for the results of free energy of solution and pK_a at 298 K for MEA. Comparison of the accuracy of pK_a calculation with the empirical model and model 2 (present model) at 323 K. This material is available free of charge via the Internet at http://pubs.acs.org.

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