

Modeling temperature dependent and absolute carbamate stability constants of amines for CO₂ capture

Mayuri Gupta¹, Hallvard F. Svendsen*

Department of Chemical Engineering, Norwegian University of Science and Technology, 7491 Trondheim, Norway

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ABSTRACT

Thermodynamic properties and carbamate stability constants (K_c) for a dataset of 25 amines and alkanolamines, with desirable post combustion CO₂ capture (PCC) solvent properties, have been studied extensively employing various gaseous phase calculations and solvation models. A comprehensive study of gaseous phase free energy and enthalpy is carried out using density functional methods [B3LYP/6-311++G(d,p)], and composite methods (G3MP2B3, G3MP2, G4MP2 and CBS-QB3). Implicit solvation models (PCM, SM8T and DivCon) and the Explicit Solvation Shell Model (ESS) were used to study solvation free energy of various neutral and ionic species present in the amine-carbamate formation reaction. Temperature dependent carbamate stability constants are calculated for the carbamate formation reaction of amines and alkanolamines to better understand the effect of temperature on temperature swing absorption-desorption PCC processes. The temperature dependency of K_c was compared against available experimental data.

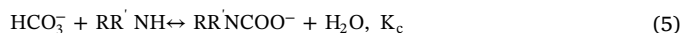
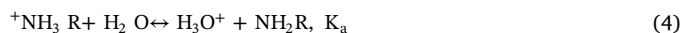
1. Introduction

Significant reduction in the emission of greenhouse gases (e.g. CO₂, CH₄) is required for limiting global temperature rise below 2 °C in coming years. Post combustion CO₂ capture (PCC) based on reactive absorption, is the most mature technology at present for mitigating conceivably catastrophic consequences of climate changes (Stern, 2007; Metz et al., 2005). However, reactive absorption PCC demands high energy for regeneration of the solvent and is relatively costly for large scale deployment. For lowering the energy requirements, developing improved PCC solvents based on better knowledge of underlying thermodynamic properties of the various reactions, is of vital importance.

A solvent carbamate or bicarbonate/carbonate species can be formed in a PCC solvent/CO₂/H₂O system depending upon the type of PCC solvent used (e.g. type of amino group (1°, 2° or 3°), steric hindrance and system conditions). The tendency of PCC solvents to react with CO₂ impacts energy demand of the process. Highly stable solvent carbamate formation in the absorber would require more energy in the desorber for generating a lean solvent. However, a solvent with low carbamate stability may not achieve the required CO₂ capture rate or require a high absorber and more energy for optimum CO₂ capture. However, carbamate formation is associated with high heat of reaction. This is related to high equilibrium temperature sensitivity, which is a

desired attribute of a temperature swing PCC process (Kim and Svendsen, 2011; Svendsen et al., 2011). Equilibrium temperature sensitivity is also governed by activity coefficients, speciation and solvation effects as a function of temperature and impacts the overall potential of the PCC solvent. Formation of bicarbonate/carbonate is less exothermic and demands less energy for regeneration in the desorber. However, the equilibrium temperature sensitivity is lower and overall, the bicarbonate/carbonate formers, like tertiary and sterically hindered amines, alone are less energy efficient than carbamate forming amines for PCC purposes.

The main reactions involved during CO₂ capture with a PCC solvent (mainly amines and alkanolamines) are as follows:



The reaction of CO₂ with water (Eqs. (1) and (2), dissociation of water (Eq. (3)), deprotonation of amine (Eq. (4)) have been studied

* Corresponding author.

E-mail addresses: mayuri.gupta@uhnresearch.ca, mayuri.gupta@utoronto.ca (M. Gupta), hallvard.svendsen@chemeng.ntnu.no (H.F. Svendsen).

¹ Present address: University Health Network, University of Toronto, Toronto, Canada.

extensively earlier (Gupta et al., 2012a, b, 2013a, b, 2016; Aroua et al., 1999; Wang et al., 2010; Harned and Bonner, 1945; Harned and Scholes, 1941; Leung et al., 2007; Pinsent and Roughton, 1951; Pocker and Bjorkquist, 1977). Reaction 5 represents the carbamate formation of the amine and this reaction is much less studied (Gupta et al., 2010; Fernandes et al., 2012; Ermatchkov et al., 2003; Da Silva and Svendsen, 2006).

In this work, a study of carbamate stability constants and their temperature sensitivity, for a dataset of 25 amines, having potential for being PCC solvents, is done using molecular modelling. Recently, we performed a similar study for a dataset of 10 amino acids (Gupta and Svendsen, 2019). The equilibrium constants for the carbamate formation reaction of some amines are available in the literature, but there is a scarcity of experimental data with much variability within the results for the same amine. The carbamate equilibrium constant (K_c) for monoethanolamine (MEA), the most extensively used PCC solvent, was calculated using various experimental techniques, viz. titration with NaOH (Aroua et al., 1999), vapour-liquid-equilibrium (VLE) experiments (Jou et al., 1995; Park et al., 2002), and nuclear magnetic resonance (NMR) studies (Barth et al., 1984; Jakobsen et al., 2005; McCann et al., 2011a). Jensen et al. (1954) published the first results (in early 1950's) for the reaction of alkanolamines with CO_2 using acidimetric titration. They calculated the MEA and diethanolamine (DEA) carbamate formation reaction constant. The carbamate formation of MEA and DEA was also investigated by Aroua et al. (1999) by a NaOH titration method. Park et al. [23] performed VLE experiments to study a few amines and alkanolamines (MEA, DEA and 2-amino-2-methylpropan-1-ol (AMP) (Mehdizadeh et al., 2013a) and their mixtures. ^1H and ^{13}C NMR spectroscopic studies for the calculation of the carbamate stability constant of MEA, methyldiethanolamine (MDEA) and Butylethanolamine (BEA) were carried out by Jakobsen et al. (2005) at 293 K and 313 K. The carbamate stability constants of MEA, 2-amino-1-propanol, propylamine and isobutylamine are calculated using ^1H NMR spectroscopy by McCann et al. (2011a, b) and Austgen et al. (1989, 1991) predicted K_c value for MEA employing the eNRTL activity coefficient model and regressing parameters to CO_2 partial pressure data in their VLE model. Wang (2001) calculated the carbamate stability constant of MEA using ^1H spectra and regression with the Deshmukh and Mather model. Deshmukh and Mather (1981) and Fernandes et al. (2012) studied primary and secondary amine carbamate stability of 19 amines (including MEA, DEA, piperazine (PZ), morpholine (MOR) and ammonia (NH_3)). C (Leung et al., 2007) NMR spectroscopy was also employed to determine K_c of MEA, AMP and DEA by Sartori and Savage (1983). The NMR spectroscopic speciation experiments and VLE measurements are done in literature to study more amines having favorable properties for PCC solvents e.g. MDEA (Bottinger et al., 2008), PZ (Ermatchkov et al., 2003; Bottinger et al., 2008), NH_3 (Mani et al., 2006), diglycolamine and diisopropylamine (Barth et al., 1984), 2-(2-aminoethyl)aminoethanol Jakobsen et al. (2005) and other synthetically prepared, relatively complex amines (Mikkelsen et al., 2010). However, literature data for experimental amine carbamate stability studies are still scarce; but absolutely necessary to identify precisely various factors which effect carbamate chemistry in PCC solvents. Chakraborty et al. and da Silva et al. have done pioneering work involving theoretical studies of amine and alkanolamine carbamate stability constants (Chakraborty et al., 1988; da Silva and Svendsen, 2006). However, selection of optimum PCC solvent requires understanding of various thermodynamic properties and of the underlying reaction species along with their temperature dependency.

In summary, the motivation of the present work is fivefold. 1. Computational calculations of experimentally challenging carbamate stability constants, which provide crucial information for developing PCC solvents. 2. Comparison of solvation free energy calculated using various implicit (SM8T, PCM, DivCon) and explicit solvation shell models, for neutral and ionic species present in amine- CO_2 - H_2O systems. This gives us an opportunity to compare performance of various

solvation models for charged (anionic) amine carbamate species. 3. To present benchmark gaseous phase calculations of thermodynamic properties of amines and alkanolamines using various composite ((G3MP2B3, G3MP2, CBS-QB3, G4MP2), density functional (B3LYP/6-311 + + G(d,p)) and Hartree Fock (HF) methods. This also provided the opportunity to compare the variability within results of various gaseous phase thermodynamic properties and to compare their performance against each other. 4. The temperature dependency of K_c for the studied dataset of amines and alkanolamines presents an opportunity to understand the solvent characteristics for temperature swing PCC processes together with a comparison of the PCM and SM8T continuum solvation models. Moreover, a computational chemistry model can be considered as a valuable tool for calculating temperature effects on K_c of solvents of post combustion CO_2 capture where experimental determination of these constants through NMR spectroscopy or VLE is relatively difficult and challenging. 5. To accelerate PCC solvent development as this is believed to be the dominant CO_2 capture technology through 2030 (Jahandar Lashaki et al., 2019). The data set of 25 amines and alkanolamines studied in the present work have potential for being PCC solvents and our results provide important observations for future solvent development for this technology.

2. Computational details and methods

Gaseous phase optimization calculations were done using Spartan 08 (Shao et al., 2006) computational chemistry software at the B3LYP level of theory using the 6-311 + + G (d, p) basis set. To further ensure absence of any imaginary frequencies in the energy minima, frequency calculations were performed. Thermodynamic properties (free energy and total enthalpies) are calculated using various composite methods (G3MP2B3, G3MP2, G4MP2, CBS-QB3), DFT (B3LYP/6-311 + + G (d,p)), and HF/6-31G*. All calculations were carried out in Gaussian 03 (Frisch et al., 2004), except for G4MP2 thermochemical calculations, which were done in Gaussian 09 (Frisch et al., 2009).

To understand the effect of solvation, various continuum solvation models (PCM (Benedetta, 2012), SM8T (Chamberlin et al., 2008) and Divcon (Wang et al., 2007) were employed. Aqueous phase conformer search and optimization was done using equilibrium calculations in Spartan 08 (solvent model SM8) using option water as a solvent at B3LYP level of theory using 6-311 + + G (d, p) basis set. PCM and SM8T calculations were done using DFT at PCM/B3LYP/6-311 + + G (d, p)//SM8/B3LYP-6-311 + + G (d, p) level and M8T/B3LYP/6-311 + + G(d,p)//SM8/B3LYP-6-311 + + G(d,p) level, respectively. PCM calculations were done in Gaussian 03 using default settings with RADII = UAHF (United Atom Topological Model applied on radii optimized for the HF/6-31 G (d) level of theory), which was activated with Self-Consistent Reaction Field (SCRF) keyword. The free energy of solvation (ΔG_{solv}) included both electrostatic and nonelectrostatic (i.e., cavitation, repulsion, and dispersion) contributions. SM8T calculations were done using DFT at SM8T/B3LYP/6-311 + + G (d, p)//SM8/B3LYP-6-311 + + G (d, p) level in Gamessplus (Higashi et al., 2010) software. Although the SM8T model is not parameterized for ionic molecules, it is anticipated to provide acceptable qualitative results for ions (Chamberlin et al., 2008). Gas phase and aqueous phase temperature dependency of free energy for molecule species involved in the carbamate formation reaction (5) were calculated using PCM and SM8T models employing DFT method at B3LYP/6-311 + + G (d, p) level of theory.

The explicit solvation shell geometries of amine molecules with 5 water molecules were derived from molecular simulations of solute in bulk solvent using the AMBER 12 suite (Case et al., 2012). The obtained ESS clusters were completely optimized using quantum mechanical calculations employing Gaussian 03 software as explained in supporting information and by da Silva et al. (2009) The Poisson-Boltzmann-based model implemented in the DivCon code (Wang et al., 2007) was used for calculation of ESS cluster solvation free energies at AM1 level of

Table 1

The dataset of amines studied in the present work and their corresponding experimental pKa data at 298 K.

S. no.	Amine	Abbreviation	Type ^a	Exp pKa ^b (298 K)
1.	2-Aminoethanol	MEA	p	9.50
2.	3-Amino-1-propanol	3-AP	p	10.0
3.	Ethylenediamine	EDA	p	9.9
4.	Propanamine	PA	p	10.6
5.	2-Methyl-1-propanamine	2-MPA	p	10.5
6.	2-Amino-2-methylpropanol	AMP	p, sh	9.7
7.	2-Amino-2-methyl-1,3-propanediol	AMPD	p, sh	8.8
8.	2-Amino-2-ethyl-1,3-propanediol	AEPD	p, sh	8.8
9.	2-Amino-1-propanol	2-AP	p	9.4
10.	Diethanolamine	DEA	s	9.0
11.	Monomethylethanolamine	MMEA	s	9.8
12.	Morpholine	MOR	s, c	8.33
13.	Piperazine	PZ	s, c	9.83 (1), 5.55 (2)
14.	Piperidine	PIP	s, c	11.10
15.	3-Amino-1-methylaminopropane	MAPA	s, p	9.89
16.	Thiomorpholine	TMOR	s, c	8.7
17.	1-Methylpiperazine	1-methylPZ	c	9.14
18.	4-Piperidinemethanol	4-PIPM	s, c	10.56
19.	4-Piperidineethanol	4-PIPE	s, c	10.62
20.	Aminoethylpiperazine	AEP	p, s, t, c	9.48 (1), 8.45 (2)
21.	Dimethylethylenediamine	DMEDA	s	10.03
22.	2-Methylpiperazine	2-methylPZ	c	9.57
23.	1-Ethylpiperazine	1-ethylPZ	c	9.20
24.	Ammonia	NH3	p	9.24
25.	Diethylenetriamine	DETA	p, s	9.94

^a In the type of amines studied, p, s, t, sh and c stand for primary, secondary, tertiary, sterically hindered and cyclic amines, respectively.

^b Perrin (1965) and Perrin (1965).

theory. The HF/6-31 + G (d) optimized clusters were used to do single point continuum solvation energy calculations. The solvation free

energies for single solutes calculated by DivCon model were also compared against results from other continuum solvation models and the ESS model. A detailed explanation of the quantum mechanical calculations and molecular dynamics simulations, for ESS solvation free energy calculations, are given in supporting information. Further details of ESS cluster configurations and for the thermodynamic cycle employed for calculating ESS solvation free energies, are provided in supporting information. The temperature dependency of PCM and SM8T solvation free energy was calculated as explained in our previous work (Gupta et al., 2013b, a).

3. Results and discussion

The data set of 25 amines and alkanolamines (primary, secondary, tertiary, sterically hindered, cyclic), as given in Table 1, is chosen in the current work for studying various gaseous and solution phase thermodynamic effects on the carbamate formation reaction in amine-CO₂-H₂O systems. The abbreviations used in paper for corresponding amine, type of amine and experimental pKa at 298 K, are given in Table 1. This dataset of amine molecules is shown to be promising and energy efficient solvents for Post Combustion CO₂ Capture (PCC) Processes (da Silva and Svendsen, 2006; Gupta and Svendsen, 2014a; Hamborg and Versteeg, 2009; Heldebrant et al., 2017; Gupta et al., 2014a). A comprehensive study of thermodynamic properties of the carbamate formation reaction of these amines can help in gaining better insight into the understanding of these potential PCC solvents.

The gas phase carbamate formation reaction (reaction 5) free energy and enthalpy, for dataset of amines given in Table 1, was studied in this work using Hartree Fock (HF/6-31 G) (Echenique and Alonso, 2007), density functional methods [B3LYP/ 6-311 + + G (d,p)] (Jones, 2015), and composite methods (G3MP2B3, G3MP2, G4MP2, CBS-QB3) (Curtiss et al., 1998, 2007; Montgomery et al., 1999, 2000). Gas phase free energy and enthalpy of the carbamate formation reaction of amines can be defined as

Table 2

Gas phase carbamate formation reaction free energy of data set of amines studied in this work at 298 K. (All values are in kJ mol⁻¹).

Amine	G3MP2B3	G3MP2	G4MP2	CBS-QB3	DFT(B3LYP/6-311 + + G(d,p))	HF/6-31G
MEA	-17.41	-16.93	-16.24	-17.32	-3.17	-13.48
3-AP	-41.10	-40.66	-39.83	-42.42	-23.77	-9.07
EDA	-12.82	-14.77	-12.18	-14.42	0.45	14.18
PA	-0.67	-0.98	0.06	-1.35	12.12	22.94
2-MPA	-4.28	-5.09	-3.50	-4.95	9.57	22.41
AMP	-25.77	-27.36	-22.73	-26.38	-8.58	-15.48
AMPD	-55.28	-54.84	-52.64	-56.56	-33.85	-15.50
AEPD	-57.63	-56.63	-54.39	-58.58	-35.04	-24.49
2-AP	-33.41	-33.15	-32.46	-35.38	-18.83	-5.34
DEA	-88.88	-85.58	-85.85	-91.06	-66.74	-42.92
MMEA	-42.68	-42.93	-40.35	-44.44	-23.31	-0.74
MOR	-22.94	-23.45	-19.74	-23.02	-5.50	11.53
PZ	-20.20	-20.88	-17.55	-20.59	-0.50	3.44
PIP	-12.96	-13.02	-4.38	-13.12	11.58	23.59
MAPA	-7.34	-8.16	-6.93	-8.03	6.77	7.88
TMOR	-32.77	-33.27	-31.35	-33.88	-11.54	5.57
1-MethylPZ	-18.06	-16.88	-15.18	-18.20	2.53	40.33
4-PIPM	-27.42	-27.61	-25.08	-27.29	-4.84	14.37
4-PIPE	-19.93	-19.81	-18.06	-19.89	-10.32	16.99
AEP	-17.84	-17.02	-16.08	-17.79	1.06	8.52
DMEDA	-8.17	-9.60	-7.83	-9.47	5.74	29.03
2-MethylPZ	-3.84	-5.36	-0.51	-3.62	21.78	33.93
1-EthylPZ	-19.49	-20.32	-16.55	-19.33	0.93	13.10
NH3	29.67	29.33	27.42	28.33	29.56	29.44
DETA	-14.12	-14.15	-13.51	-14.54	2.22	9.71
MAD w.r.t CBS-QB3 (kJ/mol)	0.77	1.01	2.79	0	18.06	30.93
MAD w.r.t CBS-QB3 (kcal/mol)	0.18	0.24	0.67	0	4.32	7.39

Where MAD values presents Mean Absolute Deviation relative to CBS-QB3. The gas phase carbamate formation reaction free energy is calculated using Eq. (7).

Table 3Gas phase carbamate formation enthalpy change of data set of amines studied in this work at 298 K. (All values are in kJ mol⁻¹).

Amine	G3MP2B3	G3MP2	G4MP2	CBS-QB3	DFT(B3LYP/6-311++G(d,p))	HF/6-31G
MEA	-22.92	-22.70	-21.99	-23.11	-9.19	-22.70
3-AP	-49.14	-48.72	-48.32	-50.77	-30.19	-17.46
EDA	-19.39	-19.53	-18.82	-20.79	-3.94	9.33
PA	-6.34	-6.22	-5.99	-6.91	9.19	18.00
2-MPA	-10.31	-10.32	-9.83	-10.87	6.56	17.54
AMP	-35.62	-36.69	-33.90	-37.63	-19.69	-26.10
AMPD	-66.27	-65.23	-63.59	-67.80	-45.95	-26.39
AEPD	-69.37	-68.31	-66.58	-70.32	-45.95	-34.50
2-AP	-41.77	-40.97	-41.07	-43.65	-24.94	-11.82
DEA	-93.33	-92.48	-91.70	-96.13	-72.20	-48.80
MMEA	-49.35	-49.03	-47.33	-51.52	-30.19	-7.19
MOR	-27.21	-28.61	-22.97	-27.73	-6.56	5.94
PZ	-25.44	-26.05	-22.70	-26.23	-3.94	-0.5
PIP	-17.83	-18.61	-15.13	-18.13	1.31	18.01
MAPA	-13.23	-13.64	-12.84	-13.96	1.31	-2.26
TMOR	-37.23	-39.33	-35.87	-39.12	-14.44	-0.25
1-methylPZ	-22.80	-21.54	-19.04	-23.39	-1.31	35.10
4-PIPM	-33.18	-33.76	-30.21	-33.43	-9.19	8.19
4-PIPE	-24.49	-25.34	-20.71	-24.77	-15.76	10.96
AEP	-22.51	-22.43	-21.54	-22.57	-1.31	4.55
DMEDA	-13.73	-14.27	-13.08	-14.43	3.94	22.45
2-MethylPZ	-9.43	-10.11	-6.20	-9.60	17.07	29.68
1-EthylPZ	-24.86	-25.67	-21.83	-25.24	-3.94	7.20
NH3	27.14	26.86	24.90	25.72	26.78	24.33
DETA	-19.16	-19.29	-18.58	-19.50	-1.31	3.58
MAD w.r.t CBS-QB3 (kJ/mol)	0.96	1.07	2.74	0	19.12	30.86
MAD w.r.t CBS-QB3 (kcal/mol)	0.23	0.26	0.66	0	4.57	7.38

Where MAD values presents Mean Absolute Deviation relative to CBS-QB3. The gas phase carbamate formation reaction free energy is calculated using Eq. (7).

$$\text{HCO}_3^- + \text{RR}'\text{NH} \leftrightarrow \text{RR}'\text{NCOO}^- + \text{H}_2\text{O}, \Delta G_{\text{gas}}^0(\text{rxn}) \\ = \Delta G_1^0 \text{ and } \Delta H_{\text{gas}}^0(\text{rxn}) = \Delta H_1^0 \quad (6)$$

$$\Delta G_1^0 = \Delta G_{\text{RR}'\text{NCOO}^-} + \Delta G_{\text{H}_2\text{O}} - \Delta G_{\text{RR}'\text{NH}} - \Delta G_{\text{HCO}_3^-} \quad (7)$$

$$\Delta H_1^0 = \Delta H_{\text{RR}'\text{NCOO}^-} + \Delta H_{\text{H}_2\text{O}} - \Delta H_{\text{RR}'\text{NH}} - \Delta H_{\text{HCO}_3^-} \quad (8)$$

The results for free energy and enthalpy of the carbamate formation reaction at different levels of theory, for the studied dataset of amines and alkanolamines, are given in Tables 2 and 3 respectively.

From the results in Tables 2 and 3 for the gas phase carbamate formation reaction free energy and enthalpy calculations employing various methods, we can see that all composite methods calculate gas phase thermochemical properties of amines within a variability of ~1–2%. In other words, gaseous phase free energy and enthalpy for the carbamate formation reaction can be calculated within generally recognized experimental error bars.

Error bars of ~1.5 kcal/mol are observed for the calculation of gaseous free energy of nitrous acid having an experimental value of 333.7 kcal/mol employing different composite methods, viz. CBS-APNO, CBS-Q, CBS-QB3, and CBS-4, G3MP2, G2, G3, G2MP2, G3B3, G3MP2B3, QCISD(T) (da Silva et al., 2006). However, the average errors observed using DFT and HF levels of theory are 2.72 kcal/mol and 4.66 kcal/mol, respectively. Similar discrepancies within the composite, DFT and HF gaseous phase free energy and enthalpy calculations are observed for the dataset of amines and alkanolamines studied in the present work. Ghahremanpour et al. (2016) observed lower root-mean-square deviations (RMSD) employing CBS-QB3 as compared to other G_n family methods when studying a similar dataset of molecules as in the current work.

The CBS-QB3 method, which is computationally cheaper and more accurate, is concluded to be the best option by comparing various composite methods for studying gaseous phase deprotonation reactions (Pokon et al., 2001). It is evident from the literature that CBS-QB3 gas phase results can be reproduced within an RMSD of ~1.5 kcal/mol (Pokon et al., 2001; Pickard et al., 2006). Our earlier work comprising a study of deprotonation constants for a dataset of amines (Gupta et al.,

2016) and amino acids (Gupta et al., 2013a) also confirmed that lower RMSD values are achieved when employing CBS-QB3. Therefore, gaseous phase free energies and enthalpy values from the CBS-QB3 method were added to the solvation phase free energies from the continuum solvation models and explicit solvation model for calculation of the carbamate stability constants. In order to further ensure accuracy and consistency of CBS-QB3, a comparison with other composite methods (G3MP2B3, G3MP2, and G4MP2) is presented. The results from the comparatively computationally cheaper DFT and HF levels of theory are also presented to provide benchmark calculations of gaseous phase thermodynamic properties for the studied dataset and to understand the variability of the results within the different commonly used methods.

In Tables 2 and 3, mean absolute deviation (MAD) values are calculated w.r.t CBS-QB3 method. The MAD results are given in both kJ/mol and kcal/mol units. From Table 2, it can be seen that gas phase carbamate formation free energy calculated using composite methods are in agreement with the benchmark CBS-QB3 results, with a MAD value of 0.18, 0.24 and 0.67 kcal/mol for G3MP2B3, G3MP2, G4MP2 respectively. These results are very encouraging as the MAD values are low compared to 1–1.5 kcal/mol mostly reported in literature as discussed before. Similar MAD values are observed for composite methods results of gaseous phase carbamate formation enthalpy change data, as shown in Table 3. However, DFT method gives MAD values of 4.32 and 4.57 kcal/mol for the gaseous phase free energy and enthalpy change results. The comprehensive gaseous phase results given in Tables 2 and 3 show composite methods to be more accurate, having less variability of results as compared to DFT and HF methods.

Experimental determination of these thermodynamic properties of the gaseous phase carbamate formation reaction is challenging, and results provided in the current work can be helpful in understanding gaseous phase thermochemistry of these amine solvents.

Fig. 1(a, b) and Fig. 2(a, b) list the optimized gas phase amines and amine carbamate molecules studied in present work at CBS-QB3 level of theory.

The calculation of the free energy of solvation is challenging and entails huge errors, mainly because of the involvement of charged species (amino acid carbamates) for the calculation of the carbamate

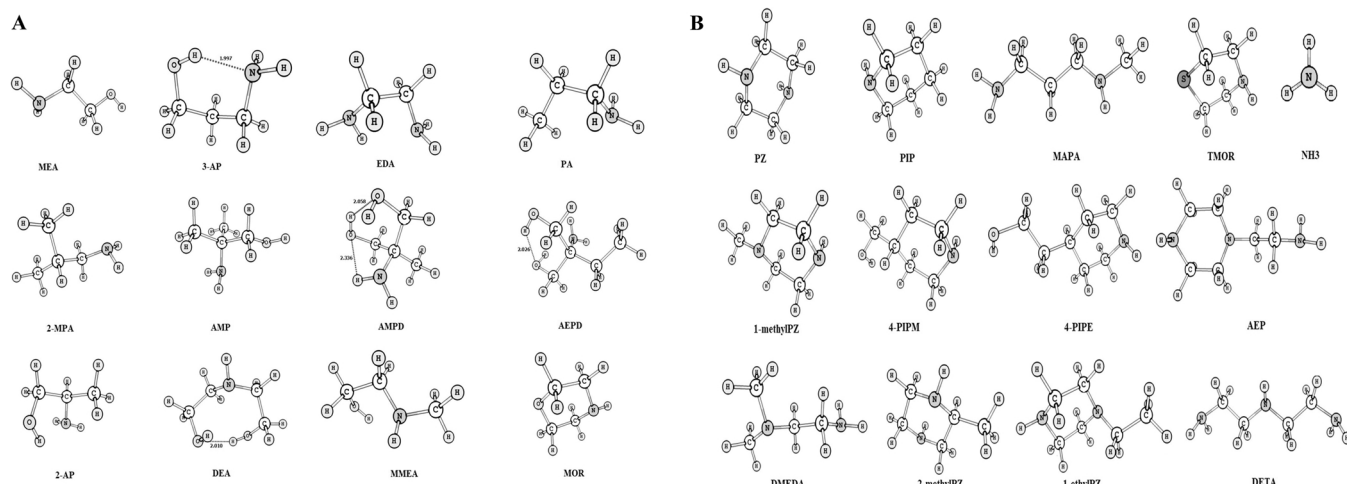


Fig. 1. (a): Optimized gas phase amines studied in present work at CBS-QB3 level of theory. (where Dotted lines show hydrogen bonds, and the bond length of hydrogen bonds is given in angstrom). (b): Optimized gas phase amines studied in present work at CBS-QB3 level of theory.

stability constants for amines. Various implicit, explicit and implicit-explicit solvation models have been used in literature for studying different chemical species, and errors mainly depend upon chemical structure, charge and parametrization of the solvation model employed (Gupta et al., 2013a, c, 2014b; da Silva et al., 2009; Kelly et al., 2006; Mehdizadeh et al., 2013b; Gupta and Svendsen, 2014b; Venkatraman et al., 2016).

In this work, different implicit solvation models, viz. PCM, SM8T and DivCon, and the explicit solvation shell (ESS) model, have been used to compare the solvation free energy of amine (neutral) and the amine carbamate (negatively charged) species using different approaches. Tables 4 and 5 present solvation free energies calculated using the ESS model, which is parametrized for ionic molecules. These tables also list entropies, cluster formation and solvation energies for the dataset of amines and their corresponding carbamates, respectively. The cluster solvation energies are calculated using the Poisson–Boltzmann continuum solvation model. Further details of the ESS solvation free energy calculations are given in supporting information and by da Silva et al. (2009).

In most cases solute-solvent interactions are not represented precisely by a single geometry. To efficiently describe all solute-solvent interactions, 100 different solute-solvent cluster geometries were obtained from molecular dynamics simulations. The resultant ESS

solvation free energies are reported as a linear average of free energies from full ensemble of 100 cluster geometries, which helps in lowering the statistical error. However, out of 100 solute-solvent clusters obtained for each molecule, we observed failed cluster geometry optimizations and vibration frequency calculations for approximately 10–15 clusters. The free energy of failed cluster geometries deviates significantly from the minimum energy cluster geometry. To avoid including results from failed cluster geometries, an energy cutoff of ± 80 kcal/mol from the minimum energy optimized solute-solvent cluster was enforced. The structures of minimum energy clusters of amine and amine carbamate molecules with five explicit water molecules, obtained in the present work, are given in Fig. 3(a, b) and Fig. 4 (a, b), respectively. From Fig. 3 and 4, it can be seen that both amino group (of amines) and alcohol group (of alkanolamines) interact with explicit water molecules to obtain a minimum energy structure. The dotted lines in Fig. 3 and 4 show hydrogen bonds and bond length of hydrogen bonds is given in Angstrom.

The calculated free energy of solvation of the dataset of amines and amine carbamates at 298 K, employing the explicit solvation shell model and continuum solvation models (PCM, SM8T and DivCon), are given in Tables 6 and 7 respectively. From Tables 6 and 7, it can be seen that free energy of solvation of amines and amine carbamates are in the same range but deviate within 5–10 kcal/mol of each other. A similar

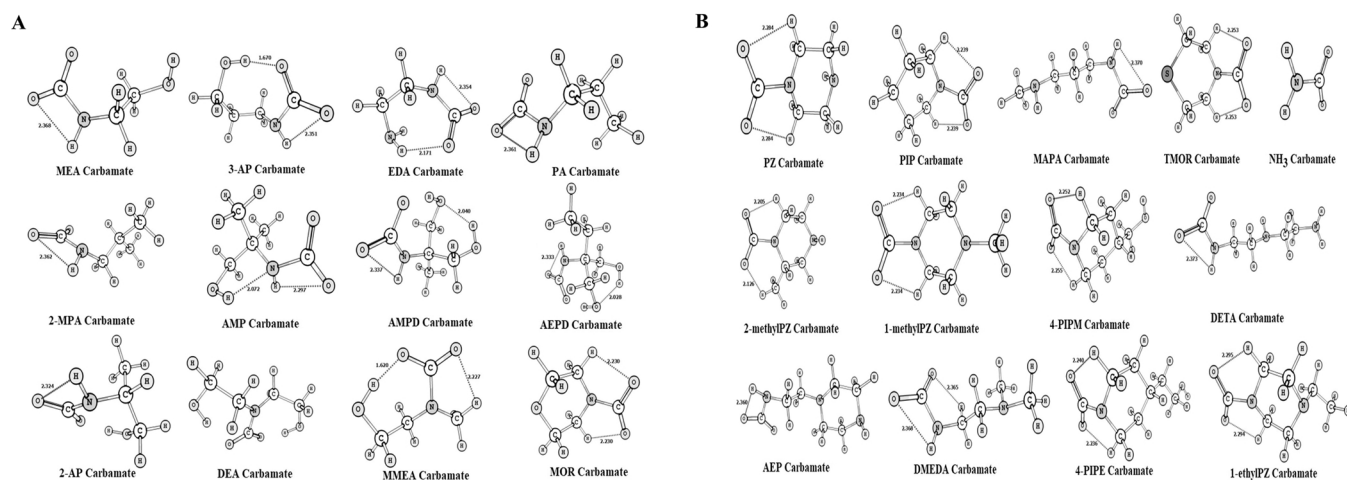


Fig. 2. (a): Optimized gas phase amine carbamate studied in present work at CBS-QB3 level of theory. (where Dotted lines show hydrogen bonds, and the bond length of hydrogen bonds is given in angstrom). (b): Optimized gas phase amine carbamate studied in present work at CBS-QB3 level of theory. (where Dotted lines show hydrogen bonds, and the bond length of hydrogen bonds is given in angstrom).

Table 4

Free energy of solvation of amines calculated by Explicit Solvation Shell Model (ESS). (all values are in kcal/mol).

Amine (Neutral)	ΔG_{solv} (Calcd) ^a	$\Delta E_{\text{cluster}}^*$ ^b	$-\Delta S_{\text{cluster}}^*$ ^c	$\Delta G_{\text{s}}(\text{A}(\text{S})_{\text{n}})^{\text{d}}$	Area ^e
MEA	-3.4	-6.0	9.7	-19.48	215.52
3-AP	0.0	-6.4	10.7	-16.71	225.70
EDA	-2.2	-7.3	10.7	-17.91	212.94
PA	2.4	-6.3	10.9	-14.51	220.46
2-MPA	1.4	-7.3	10.7	-14.34	239.05
AMP	-4.4	-13.3	12.2	-15.72	233.35
AMPD	-3.1	-10.4	12.2	-17.29	234.76
AEPD	-3.3	-9.1	11.4	-18.00	255.48
2-AP	-1.0	-6.9	10.3	-16.74	223.81
DEA	-1.7	-6.0	11.0	-19.05	246.71
MMEA	0.0	-7.3	11.0	-15.93	223.18
MOR	-1.9	-5.5	9.1	-17.84	233.07
PZ	-3.0	-5.4	8.5	-18.43	239.06
PIP	0.3	-8.9	10.3	-13.44	237.24
MAPA	-1.0	-5.3	10.5	-18.63	255.70
TMOR	0.9	-2.1	8.7	-18.10	242.70
1-MethylPZ	-2.2	-7.9	9.8	-16.50	249.49
4-PIPM	-4.8	-8.5	9.4	-17.98	266.00
4-PIPE	-4.0	-7.8	9.8	-18.32	288.30
AEP	-5.6	-5.9	9.0	-21.06	287.24
DMEDA	-1.2	-7.6	10.6	-16.62	251.33
2-MethylPZ	-2.4	-5.3	8.5	-17.85	253.43
1-EthylPZ	-0.9	-6.1	9.6	-16.79	266.08
NH ₃	-4.29	-13.1	11.9	-15.12	232.15
DETA	-5.5	-3.1	9.0	-23.75	272.64

(a) Calculated free energy of solvation; all values shifted by -2.41 kcal/mol to remove systematic error relative to experimental values as in ESS model presented by (da Silva et al., 2009). Estimated sampling standard deviation is 1 kcal/mol. (b) Energy of formation of the cluster at the HF/6-31 + G (d) level, converted from a standard state of 1 atm to 1 mol/L. Thermal corrections to the energy and zero-point energies not included. (c) Temperature (298 K) multiplied by the entropy of formation of the cluster at the HF/6-31 + G (d) level. (d) Free energy of solvation of the cluster calculated with the Poisson–Boltzmann continuum model. (e) Area of clusters calculated with the Poisson–Boltzmann continuum model.

variation in calculated solvation free energy was observed by Kromann et al. (2018) while studying the MNSOL dataset (Marenich et al., 2012), employing various solvation models at different levels of theory (viz. AM1, PM3, PM6, DFTB). They encountered comparatively larger RMSE values for ions. E.g. for anions in their dataset, an RMSE value of 10.1–14.8 kcal/mol was observed. However, the explicit solvation shell model is efficient in capturing solvation effects in comparison to continuum solvation models because of the better description of solute-solvent interactions than in the continuum solvation models. The ESS model is also parametrized for ions. We believe that solvation free energies of amines and amine carbamates calculated using the explicit solvation shell model are more reliable as observed in the literature as well (Gupta et al., 2013a, 2016; Gupta and Svendsen, 2019). Therefore, we have employed ESS free energy of solvation in the further calculations for carbamate stability constants of studied amines.

As discussed earlier, no continuum solvation model has been parameterized to determine solvation free energies of ions. Therefore, based on solvation models presently available in the literature, we are more certain regarding accuracy with calculations using the ESS model. The solution phase reaction free energies for the amine carbamate formation reaction (5), are presented in Table 8. The solution phase free energy of the amine carbamate reaction, according to the ESS model solvation free energy results, for different amines studied in this work shows the following trend

PA > 2-MPA > PZ > PIP > DETA > 2-methylPZ > 1-ethylPZ > MOR > EDA > NH₃ > 1-methylPZ > TMOR > 2-AP > MMEA > AEP > 4-PIPE > MEA > MAPA > 4-PIPM > AMPD > 3-AP > AMP > AEPD > DEA > DMEDA

Table 5

Free energy of solvation of amine carbamate calculated by Explicit Solvation Shell Model (ESS). (all values are in kcal/mol).

Amine carbamate (anion)	ΔG_{solv} (Calcd) ^a	$\Delta E_{\text{cluster}}^*$ ^b	$-\Delta S_{\text{cluster}}^*$ ^c	$\Delta G_{\text{s}}(\text{A}(\text{S})_{\text{n}})^{\text{d}}$	Area ^e
MEA	-72.7	-35.9	10.8	-59.99	232.52
3-AP	-71.3	-36.3	11.4	-58.77	247.4
EDA	-79.2	-39.3	10.3	-62.57	239.05
PA	-78.2	-42.0	10.9	-59.48	242.30
2-MPA	-76.9	-42.1	11.5	-58.62	255.37
AMP	-71.1	-35.7	11.0	-58.67	260.2
AMPD	-70.4	-33.5	10.1	-59.35	268.01
AEPD	-68.8	-32.5	10.6	-59.27	284.11
2-AP	-71.8	-35.6	11.2	-59.86	249.56
DEA	-65.5	-31.3	11.5	-58.11	270.39
MMEA	-70.7	-36.0	11.3	-58.37	245.97
MOR	-76.0	-37.3	10.7	-61.68	255.17
PZ	-78.1	-38.7	10.8	-62.54	256.50
PIP	-74.6	-41.3	11.9	-57.54	254.32
MAPA	-70.1	-32.9	11.7	-61.28	270.35
TMOR	-70.2	-31.8	10.5	-61.25	264.63
1-MethylPZ	-75.4	-37.6	12.4	-62.56	268.94
4-PIPM	-73.5	-28.9	11.3	-68.29	283.95
4-PIPE	-73.4	-29.6	12.2	-68.33	299.08
AEP	-76.2	-34.8	11.6	-65.40	300.82
DMEDA	-50.2	-9.7	11.3	-64.10	271.46
2-MethylPZ	-77.0	-39.2	10.9	-61.00	268.64
1-EthylPZ	-75.1	-39.0	12.3	-60.79	285.61
NH ₃	-77.9	-34.8	11.1	-66.59	194.33
DETA	-80.3	-37.4	11.0	-66.20	287.86

(a) Calculated free energy of solvation; all values shifted by -2.41 kcal/mol to remove systematic error relative to experimental values as in ESS model presented by da Silva et al. (2009). Estimated sampling standard deviation is 1 kcal/mol. (b) Energy of formation of the cluster at the HF/6-31 + G (d) level, converted from a standard state of 1 atm to 1 mol/L. Thermal corrections to the energy and zero-point energies not included. (c) Temperature (298 K) multiplied by the entropy of formation of the cluster at the HF/6-31 + G (d) level. (d) Free energy of solvation of the cluster calculated with the Poisson–Boltzmann continuum model. (e) Area of clusters calculated with the Poisson–Boltzmann continuum model.

Propanamine and 2-methylpropanamine have large negative solution phase energies in comparison to other amines. They are followed by cyclic amines and diamines. AMP, AMPD and AEPD are predicted not to form very stable amine carbamates in the aqueous phase, as observed by Fernandes et al. (2012) and Gifftja et al. (2014) in their ¹H and ¹³C NMR spectroscopy study of carbamate stability constants of amines. The more negative the solution free energy of the carbamate formation reaction represented by reaction 5, the higher is the tendency of carbamate formation in the aqueous phase.

The total reaction free energy and $\ln K_c^{\text{AmCOO}^-}$ values, calculated for the studied dataset of amines and alkanolamines, using different models is summarized in Fig. 6. Carbamate stability constants corresponding to reaction 5 are calculated using the thermodynamic cycle shown in Fig. 5. As explained previously, we believe that the ESS solvation free energies coupled with CBS-QB3 gaseous level calculations would provide reasonably good estimates of the qualitative behavior of the carbamate stability constants of various amines and alkanolamines studied in this work. Therefore, CBS-QB3 gaseous phase free energies and ESS solvation free energies are used, according to the thermodynamic cycle given in Fig. 5, to calculate reaction free energies of carbamate formation reaction in solution phase.

The absolute values calculated using different continuum and explicit solvation shell models are not consistent with each other. As explained previously, neither of the solvation models are parameterized for ionic molecules. Therefore, the results shown in Fig. 7, should be taken as a qualitative indication when working on PCC solvent development. The following trend is obtained for $\ln K_c^{\text{AmCOO}^-}$ for the studied dataset of amine and alkanolamines, with free energies from CBS-QB3

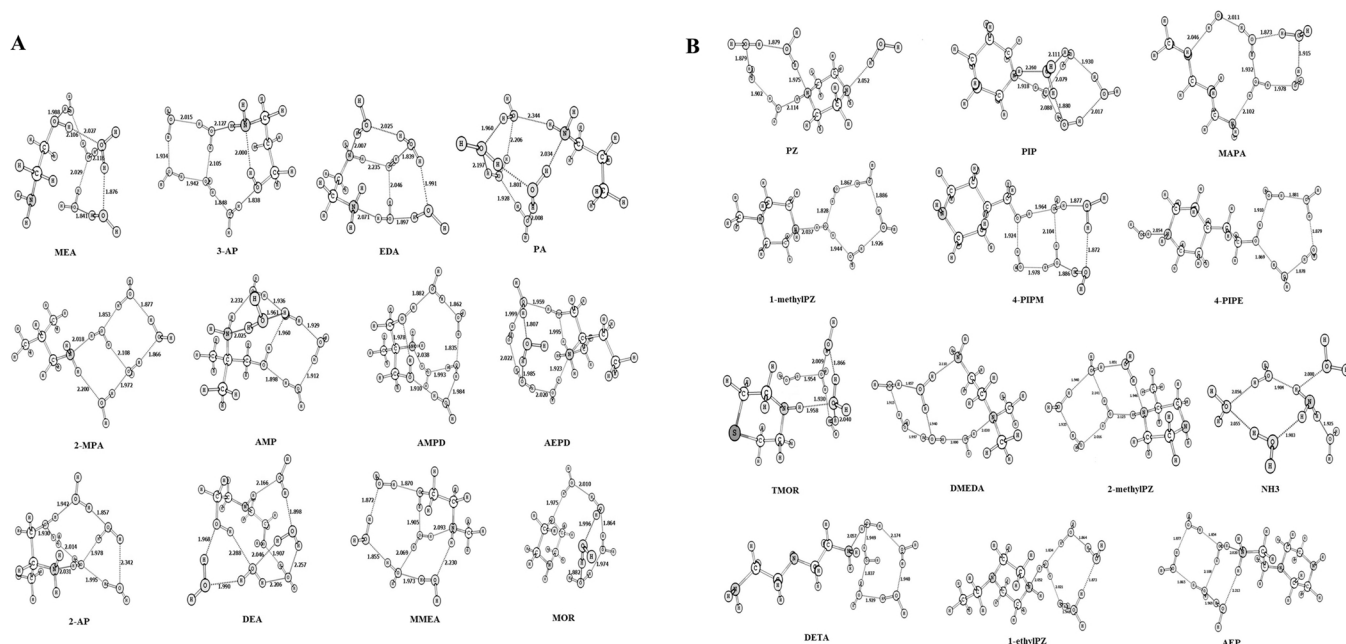


Fig. 3. (a): Optimized most stable ESS clusters of amines obtained in this work. (Dotted lines shows Hydrogen bonds and bond length of Hydrogen bonds is given in Angstrom). b): Optimized most stable ESS clusters of amines obtained in this work. (Dotted lines shows Hydrogen bonds and bond length of Hydrogen bonds is given in Angstrom).

gaseous phase and ESS solvation model.

DEA > MMEA > PA > AMPD > PZ > MOR > 2-MPA > AEPD > 2-AP > TMOR > 1-ethylPZ > DETA > PIP > 1-methylPZ > EDA > 3-AP > 2-methylPZ > 4-PIPM > AEP > 4-PIPE > MEA > AMP > MAPA > NH₃ > DMEDA

In Fig. 7, the results for $\ln K_c$ for the different amines from the ESS model are also plotted separately for a better understanding of the results.

There is scarcity of experimental $\ln K_c^{AmCOO^-}$ values of amines, and the results presented in the current work should be regarded as

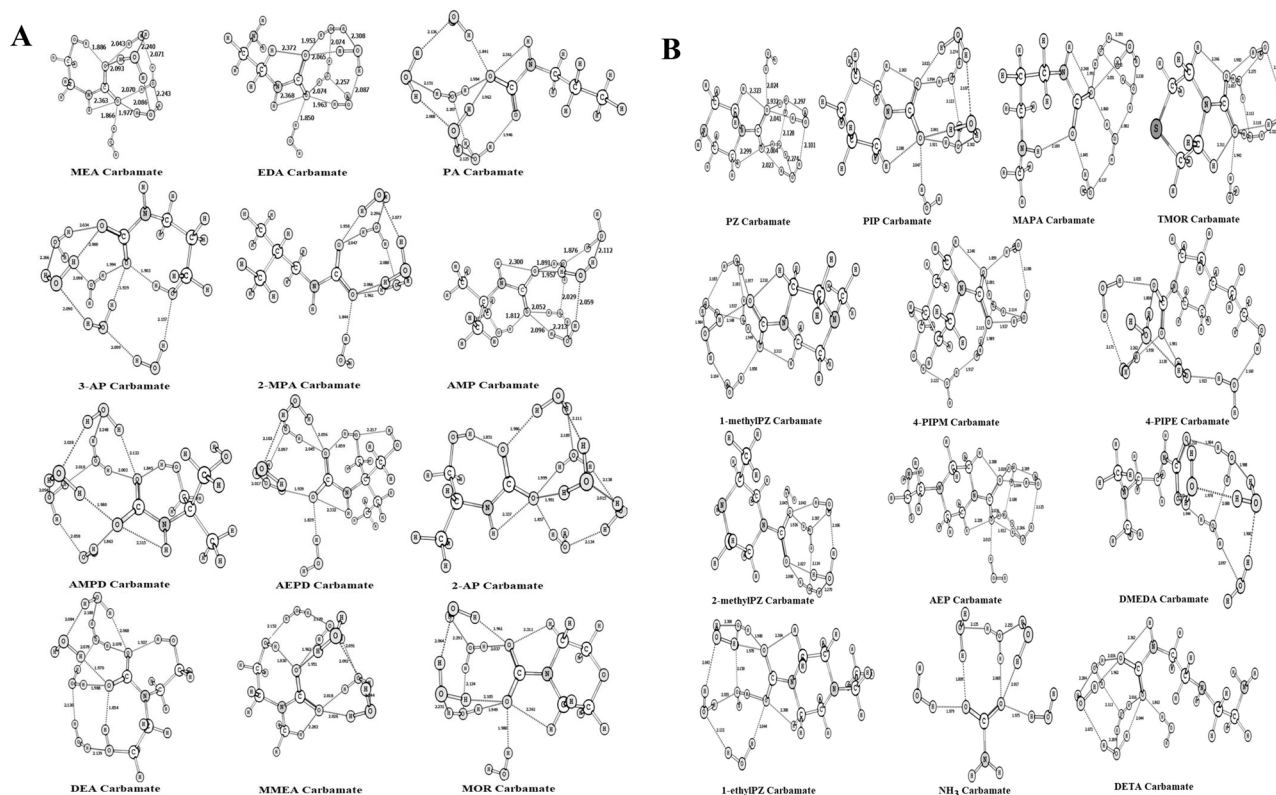


Fig. 4. (a): Optimized most stable ESS clusters of amine carbamate obtained in this work. (Dotted lines shows Hydrogen bonds and bond length of Hydrogen bonds is given in Angstrom). (b): Optimized most stable ESS clusters of amine carbamate obtained in this work. (Dotted lines shows Hydrogen bonds and bond length of Hydrogen bonds is given in Angstrom).

Table 6

Comparison of free energy of solvation of amines calculated by using Explicit Solvation Shell (ESS) Model and Implicit Solvation Models (PCM, SM8T, DivCon). (All values are in kcal/mol).

Amine (Neutral)	ΔG_{solv} (calcd)			
	Explicit solvation shell model ΔG_{solv} (calcd) ^a	Implicit solvation shell models		
		PCM	SM8T	DivCon
MEA	-3.42	-11.65	-9.14	-6.23
3-AP	-4.01	-9.28	-8.19	-4.36
EDA	-5.22	-10.38	-7.82	-6.14
PA	2.38	-4.14	-3.29	-2.09
2-MPA	1.39	-3.03	-2.56	-1.83
AMP	-4.43	-6.64	-6.27	-7.28
AMPD	-3.09	-12.22	-10.01	-6.36
AEPD	-3.34	-10.46	-9.14	-7.35
2-AP	-1.04	-8.67	-7.05	-4.32
DEA	-5.75	-13.43	-11.26	-5.83
MMEA	0.04	-8.44	-6.67	-3.79
MOR	-1.90	-12.67	-9.41	-4.01
PZ	-3.00	-13.06	-10.06	-4.92
PIP	0.34	-6.17	-4.20	-1.27
MAPA	-1.02	-9.74	-7.24	-5.80
TMOR	0.86	-9.37	-5.40	-3.60
1-MethylPZ	-2.25	-10.25	-8.30	-4.17
4-PIPM	-4.79	-11.69	-8.51	-5.26
4-PIPE	-3.98	-11.99	-8.60	-5.16
AEP	-5.65	-13.82	-9.65	-7.50
DMEDA	-1.19	-10.64	-7.57	-4.42
2-MethylPZ	-2.37	-11.29	-8.06	-4.78
1-EthylPZ	-0.91	-9.79	-7.63	-3.45
NH ₃	-4.29	-4.09	-4.61	-3.11
DETA	-5.49	-14.76	-10.48	-9.38

^a Calculated free energy of solvation; all values shifted by -2.41 kcal/mol to remove systematic error relative to experimental values as in ESS model presented by da Silva et al. (2009). Estimated sampling standard deviation is 1 kcal/mol.

qualitative measures of $\ln K_c^{AmCOO^-}$. However, there is a urgent need for experimental data of carbamate stability constants and their corresponding temperature dependency for amine-CO₂-H₂O systems, as this would greatly aid in validating the calculated results of present work and in future development of PCC processes.

As discussed earlier, PCC is a temperature swing process and an optimal PCC solvent would require a trade-off of various properties. A typical PCC process operates in absorption and desorption temperature windows of 313–333 K and 373–393 K respectively. The overall energy requirement for a PCC process depends largely on the temperature sensitivity of the different equilibrium constants viz. pKa and carbamate stability constants. Experimental and computational studies of temperature sensitivity of pKa of numerous PCC solvents are available in literature (Gupta et al., 2013b, a; Hamborg and Versteeg, 2009; Hamborg et al., 2007). However, experimental and computational studies dedicated for calculation of Kc are very few as determination of carbamate stability constants is experimentally challenging. In this work, temperature sensitivity of a dataset of 25 amines and alkanolamines, as given in Table 1, has been studied employing two continuum solvation models (PCM and SM8T) in the temperature window of 273–373 K.

Fig. 7 shows the temperature dependency of the amine carbamate constants ($\ln K_c^{AmCOO^-}$) using PCM and SM8T continuum solvation models for amines and alkanolamines for amines that have more than one available experimental literature result. This includes MEA, DEA, 2-AP and PZ. The temperature dependencies of the free energy of carbamate formation reaction (reaction 5) for amines having available experimental Kc data are calculated as discussed in our previous work and briefly given in the computational details section of this work and in the supporting information (Gupta et al., 2013d). Temperature

Table 7

Comparison of Free Energy of Solvation of amine carbamate calculated by using Explicit Solvation Shell (ESS) Model and Implicit Solvation Models (PCM, SM8T, DivCon). (All values are in kcal/mol).

Amine carbamate (Anion)	ΔG_{solv} (calcd)			
	Explicit solvation shell model ΔG_{solv} (calcd) ^a	Implicit solvation shell models		
		PCM	SM8T	DivCon
MEA	-72.73	-79.78	-83.40	-72.11
3-AP	-71.28	-67.84	-71.02	-70.93
EDA	-79.20	-72.37	-75.52	-75.50
PA	-78.21	-70.95	-75.74	-75.85
2-MPA	-76.93	-68.30	-73.03	-75.52
AMP	-71.08	-71.87	-72.91	-70.11
AMPD	-70.40	-61.39	-68.54	-68.78
AEPD	-68.82	-65.95	-69.59	-67.91
2-AP	-71.85	-67.27	-70.94	-71.68
DEA	-65.53	-63.37	-67.26	-65.46
MMEA	-70.73	-65.22	-69.73	-69.94
MOR	-75.95	-70.00	-72.71	-73.98
PZ	-78.05	-72.24	-74.98	-75.85
PIP	-74.61	-68.47	-72.68	-73.74
MAPA	-70.15	-75.07	-77.83	-72.82
TMOR	-70.17	-66.59	-69.73	-70.29
1-MethylPZ	-75.39	-71.49	-75.13	-74.22
4-PIPM	-73.52	-69.73	-73.90	-73.81
4-PIPE	-73.38	-72.90	-75.49	-74.38
AEP	-76.23	-77.62	-81.13	-78.38
DMEDA	-50.16	-71.46	-74.61	-75.59
2-methylPZ	-77.00	-72.68	-75.62	-74.72
1-ethylPZ	-75.13	-70.91	-74.43	-73.85
NH ₃	-77.89	-76.73	-83.43	-80.77
DETA	-80.26	-79.33	-80.39	-80.15

^a Calculated free energy of solvation; all values shifted by -2.41 kcal/mol to remove systematic error relative to experimental values as in ESS model presented by (da Silva et al., 2009). Estimated sampling standard deviation is 1 kcal/mol.

Table 8

Solution phase reaction free energies for carbamate formation at 298 K. (All values are in kcal mol⁻¹).

Amine	ESS	PCM	SM8T	DivCon
MEA	4.45	5.63	-0.50	7.88
3-AP	6.49	15.20	10.93	7.19
EDA	-0.22	11.77	6.06	4.40
PA	-6.83	6.95	1.31	0.00
2-MPA	-4.56	8.49	3.29	0.07
AMP	7.10	8.53	7.12	10.93
AMPD	6.45	24.59	15.23	11.34
AEPD	8.28	18.27	13.30	13.20
2-AP	2.95	15.16	9.87	6.40
DEA	13.98	23.82	17.75	14.13
MMEA	2.98	16.98	10.69	7.61
MOR	-0.30	16.43	10.47	3.79
PZ	-1.29	14.58	8.83	2.83
PIP	-1.20	11.46	5.28	1.29
MAPA	4.63	8.43	3.17	6.74
TMOR	2.72	16.54	9.42	7.07
1-MethylPZ	0.61	12.52	6.93	3.71
4-PIPM	5.03	15.72	8.37	5.21
4-PIPE	4.35	12.85	6.86	4.54
AEP	3.17	9.95	2.27	2.88
DMEDA	24.78	12.94	6.72	2.59
2-MethylPZ	-0.88	12.37	6.19	3.82
1-EthylPZ	-0.46	12.63	6.96	3.36
NH ₃	0.15	1.12	-5.06	-3.90
DETA	-1.02	9.19	3.85	2.99

sensitivity of amine basicity of a dataset of amines (Gupta et al., 2012a), amino acids (Gupta et al., 2013b) and temperature sensitivity of carbamate formation reaction of MEA was calculated within experimental

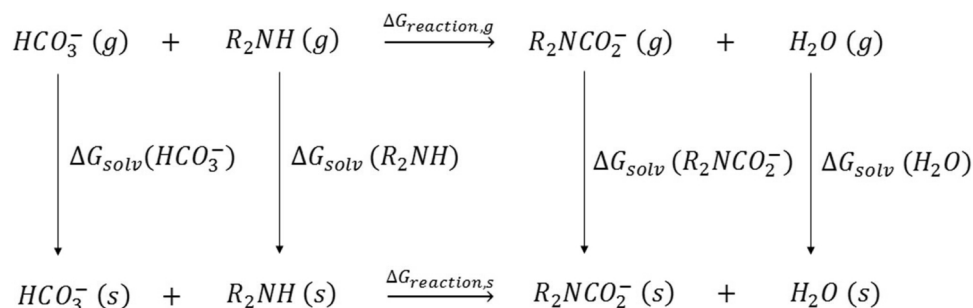


Fig. 5. Thermodynamic cycle employed for calculation of carbamate formation reaction free energy.

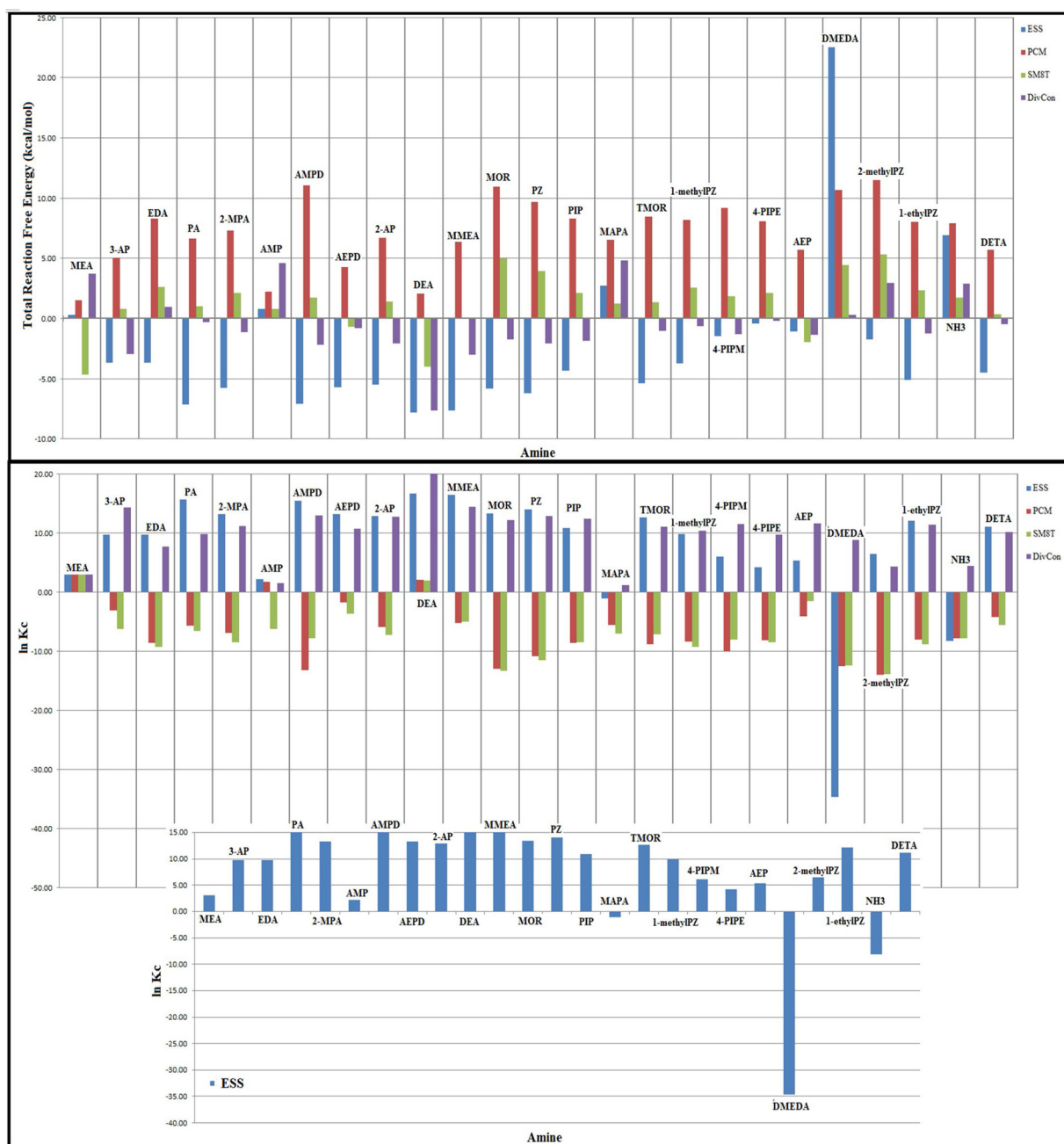


Fig. 6. Total carbamate formation reaction free energy (kcal/mol) and corresponding ln Kc for a data set of amines studied in this work using different solvation models. Ln Kc for different amines calculated from ESS is also shown separately for better understanding of results.

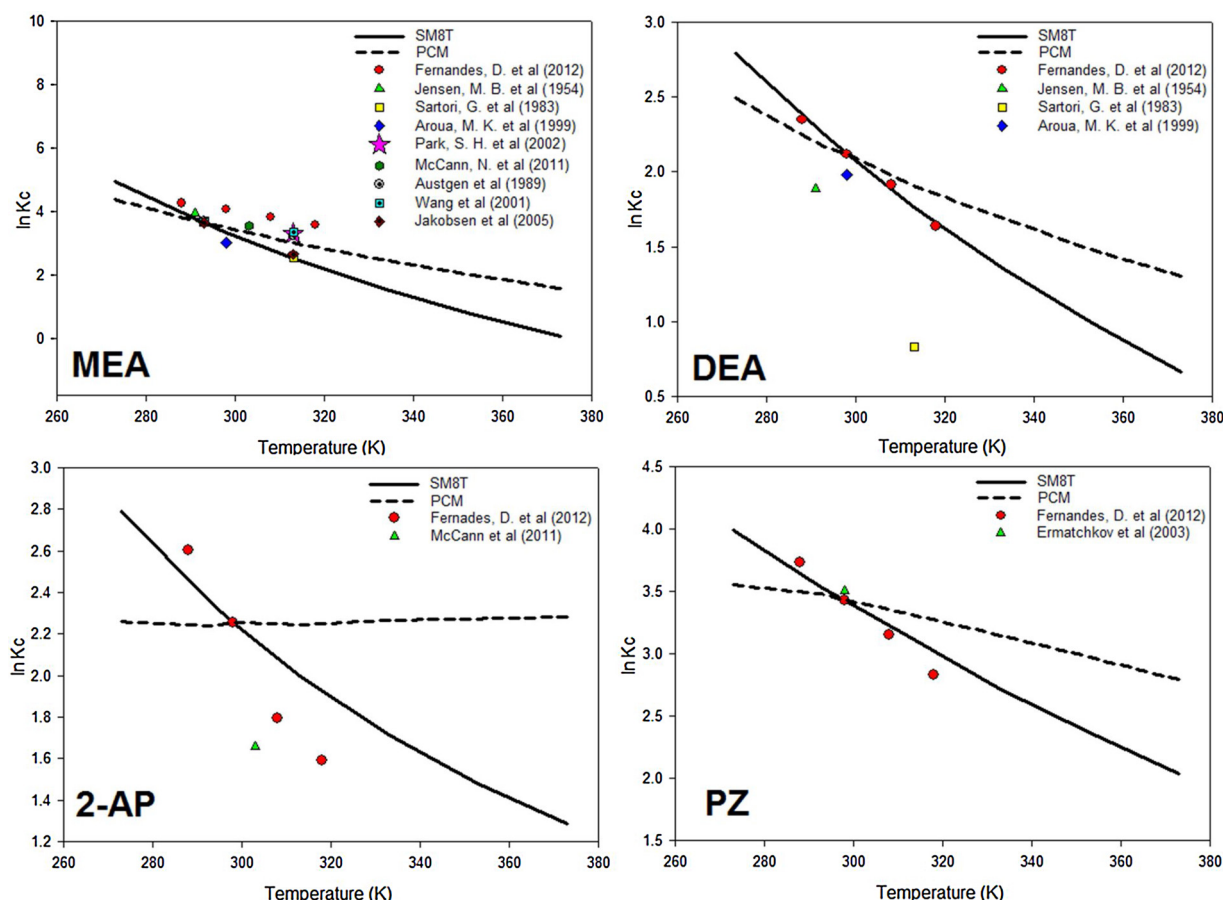


Fig. 7. Temperature dependency of $\ln K_c$ of amines with available experimental data (MEA, DEA, 2-AP and PZ) with PCM and SM8T continuum solvation models. (At room temperature $\ln K_c$ calculated with PCM and SM8T is shifted to corresponding Experimental value).

error bars previously by using the SM8T model (Gupta et al., 2013d). Our recent work involves calculation of temperature sensitivity of the carbamate stability constants of amino acids (Gupta and Svendsen, 2019). The same methodology is implemented for calculating temperature dependency of carbamate formation for amines in this work.

Fig. 7 compares experimental and calculated (using the PCM and SM8T models) temperature sensitivity of $\ln K_c^{AmCOO^-}$ for MEA, DEA, 2-AP and PZ. At 298 K, the calculated free energy of reaction in solution phase for carbamate formation reaction using the DFT method is shifted to experimental free energy of reaction in solution given by Jakobsen et al. (2005) at 293 K (MEA) and by Fernandes et al. (2012) at 298 K (DEA, 2-AP and PZ) according to Model 2 of our recent study (Gupta et al., 2013a, b). Fig. 7 shows that the observed discrepancy within the literature on carbamate stability constants at 298 K, also translates to higher temperatures and a lot of variability within the results is encountered.

The temperature dependency of $\ln K_c^{AmCOO^-}$ for all 4 amines (MEA, DEA, 2-AP and PZ), decreases with an increase in temperature. The results from the SM8T model predict a stronger temperature dependency of $\ln K_c^{AmCOO^-}$ as compared to the PCM model. This correlates nicely with experimental values given by Jakobsen et al. (Shao et al., 2006) and Fernandes et al. (2012) over the 273–373 K temperature window. The more accurate prediction of temperature sensitivity of equilibrium constants employing the SM8T continuum solvation model agrees with our past investigations (Gupta et al., 2013a, b). The amines having high temperature sensitivity of $\ln K_c^{AmCOO^-}$ are desirable for PCC use.

The temperature sensitivity of $\ln K_c^{AmCOO^-}$ for the complete dataset of studied amines in the temperature window 273–373 K, using SM8T model, is presented in Fig. 8. The corresponding temperature

sensitivities employing the PCM model are provided in supporting information. Fig. 8 shows that the temperature sensitivity of $\ln K_c^{AmCOO^-}$ has negative slope for most amines. This is preferable in PCC process. The temperature dependency of $\ln K_c^{AmCOO^-}$ for MEA is also plotted for easy comparison against this benchmark PCC solvent. Ammonia shows relatively high temperature dependency for amine carbamate formation reaction compared to MEA and the rest of the amines. This is consistent with the kinetics study of CO_2 with ammonia conducted by Wang et al. (2011) They found fast reaction rate constants of aq. ammonia with CO_2 and higher cyclic capacity of ammonia compared to MEA and other alkanolamines.

The temperature gradients of $\ln K_c^{AmCOO^-}$ for the studied dataset of amines employing both the PCM and SM8T models, over the temperature window of 273–373, are presented in Fig. 9. The larger temperature gradient of $\ln K_c^{AmCOO^-}$ translates to more economical PCC solvent. The energy demands for stripping CO_2 in the desorber decreases when the partial pressure of CO_2 increases with increase in temperature. The temperature gradients for amines following the results from PCM model, predicts either negative or very small temperature sensitivities. However, the results from the SM8T model shows higher temperature sensitivities compared to PCM model, and is shown to produce more accurate results compared to data from the literature (Gupta et al., 2013a, b). The SM8T model is parametrized for ions, hence we recommend temperature trends predicted by the SM8T model more strongly compared to the PCM model. From Fig. 9 we can see that all studied amines have lower temperature gradient of $\ln K_c^{AmCOO^-}$ than MEA. Ammonia has the highest temperature gradient of $\ln K_c^{AmCOO^-}$, according to the SM8T solvation model results. However, it has very a low $\ln K_c$ as observed from Fig. 6 implying that very little carbamate is formed.

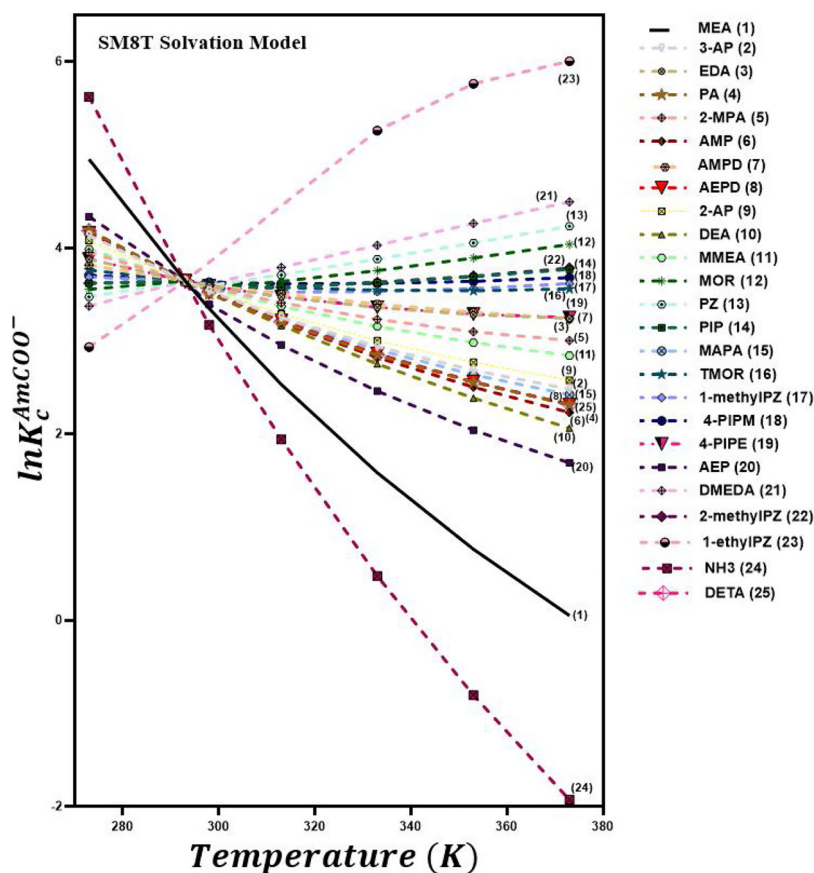


Fig. 8. Temperature dependency of $\ln K_c^{AmCOO^-}$ of amines and alkanolamines calculated using PCM and SM8T continuum solvation models.

In summary, an optimal PCC solvent requires a balanced trade-off between various thermodynamic properties of various equilibrium constants and their temperature dependencies. The results given in Figs. 8 and 9 can be helpful in understanding the qualitative behavior of these amines and their temperature trends.

4. Conclusions

This work presents benchmark gaseous phase and aqueous phase thermodynamic properties of a large dataset of amines and alkanolamines. This will not only help in gaining insights of performance of a potential PCC solvent but also will help advancing fundamental

research in the field of solvation models (implicit, explicit and implicit-explicit) for neutral and ionic molecules. The experimental determination of $\ln K_c^{AmCOO^-}$ is challenging. Absolute and temperature dependent $\ln K_c^{AmCOO^-}$ calculated in this work would help analyze qualitatively different amines and alkanolamines for their potential for CO_2 capture and can guide further development in the field of PCC solvent development. We anticipate that the results presented in this work, would help and motivate experimental determination of absolute and temperature dependent equilibrium constants for the amine- CO_2 - H_2O system in future. Experimental results would not only help in validating our results, but also guide further refinement of theoretical understanding of solvation of ions in aqueous system.

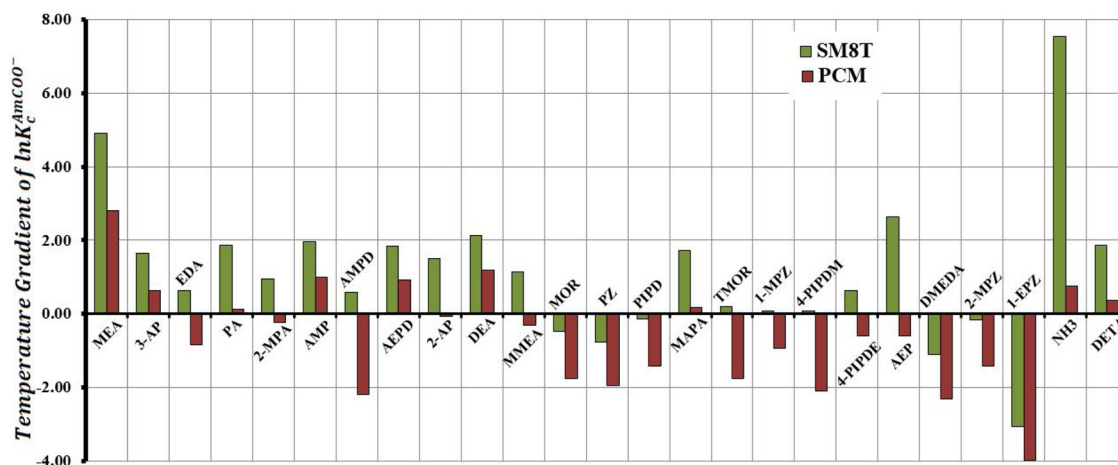


Fig. 9. Temperature gradient of $\ln K_c$ for different amines and alkanolamines over the temperature range of 273–373 w.r.t MEA using SM8T and PCM models. (The results from both models are anchored to Experimental MEA $\ln K_c$ value (Jakobsen et al., 2005) at 293 K for all the amines and MEA.).

Author's statement

This manuscript has not been published and is not under consideration for publication elsewhere.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.ijggc.2020.103061>.

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