Theoretical Study of Differential Enthalpy of Absorption of CO2 with MEA and MDEA as a Function of Temperature

4 AUTHORS, INCLUDING:

Mayuri Gupta
Norwegian University of Science and Technol…
13 PUBLICATIONS **54** CITATIONS

Ardi Hartono
Norwegian University of Science and Technol…
43 PUBLICATIONS **552** CITATIONS

Hallvard F. Svendsen
Norwegian University of Science and Technol…
267 PUBLICATIONS **4,963** CITATIONS

# Theoretical Study of Differential Enthalpy of Absorption of CO_2 with MEA and MDEA as a Function of Temperature

Mayuri Gupta,[†] Eirik F. da Silva,[‡] Ardi Hartono,[†] and Hallvard F. Svendsen*,[†]

[†]Department of Chemical Engineering, Norwegian University of Science and Technology, Trondheim, Norway
[‡]Department of Process Technology, SINTEF Materials and Chemistry, Trondheim, Norway

S *Supporting Information*

ABSTRACT: Temperature dependent correlations for enthalpy of deprotonation, carbamate formation, and heat of absorption of the overall reaction between aqueous MEA and MDEA and gaseous CO_2 are calculated on the basis of computational chemistry based ln K values input to the Gibbs–Helmholtz equation. Temperature dependency of reaction equilibrium constants for deprotonation and carbamate formation reactions is calculated with the SM8T continuum solvation model coupled with density functional theoretical calculations at the B3LYP/6-311++G(d,p) level of theory. Calculated reaction equilibrium constants and enthalpies of individual reactions and overall heat of absorption are compared against experimental data in the temperature range 273.15–373 K. Temperature dependent correlations for different reaction equilibrium constants and enthalpies of reactions are given. These correlated results can be used in thermodynamic models such as UNIQUAC and NRTL for better understanding of post-combustion CO_2 capture solvent chemistry.
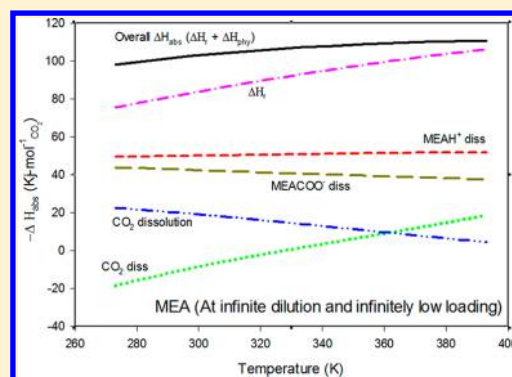
1. INTRODUCTION

Aqueous solutions of alkanolamines are common solvents used for post-combustion capture (PCC) of CO_2 from flue gases. PCC is an important technology to reduce global warming and to help alleviate global climate change.[1] The enthalpy of solution is one of the most important properties required for design of CO_2 removal plants. The steam requirement of the amine regeneration stage in PCC is directly related to the enthalpy of solution. Approximately half of the cost of operating the PCC plant is related to steam costs, so it becomes most crucial to obtain these data as accurately as possible in order to avoid overdesign[2,3] and hence unnecessary costs.

In this work, the computational chemistry continuum solvation model SM8T coupled with quantum mechanical DFT calculations is used to predict the heat of absorption of CO_2 in aqueous MEA and MDEA with the help of the Gibbs–Helmholtz equation. Experimental determination of the enthalpy of absorption has many sources of error and thus contains uncertainty. There are few measurements of the heat of absorption of different amines and alkanolamines by using calorimetric experiments.[4] In addition, experimental determination of the enthalpy of solution of adding CO_2 to alkanolamine solvents has many sources of error. Carson et al.[5] and Merkley et al.[6] have reported uncertainties of ±10 and ±5%, respectively, when calculating enthalpies of solution of CO_2 in 2-aminoethanol (MEA), diethanolamine (DEA), and N-methyldiethanolamine (MDEA). Experimental errors in heat of solution measurements can stem from various sources. The main sources of error are: the uncertainty of the amount of CO_2 added to the calorimeter from the external cylinder due to

temperature changes occurring caused by the large Joule–Thomson effect; the change in the amount of CO_2 in the reactor gas phase; in the determination of heat released by integration of the heat flux curve; in selection of integration limits; and setting in of the baseline.[7,8] A limited range of temperature and pressure and errors in their determinations also contribute to uncertainty observed in experimental enthalpy of solution results. Carson et al.[5] suggested that flow calorimetry can introduce errors like flow rate dependency, low values of enthalpy of solution, and more scatter in the results because of slow kinetics of reaction of CO_2 with some alkanolamines. The computational chemistry methods employed in this work are not computationally expensive (the computational cost of the present calculations is within a couple of hours of 1 PC unit) and provide a very convenient tool to study temperature effects on the heat of absorption of solution.

This work describes equilibrium constants and temperature dependencies of various equilibria involved in CO_2 absorption through computational chemistry tools. Given a thorough understanding of the equilibrium, the associated enthalpy for each reaction is calculated using the Gibbs–Helmholtz equation. Resulting enthalpy results for each equilibrium reaction and the overall heat of solution are then compared with available experimental data for MEA and MDEA. Second, the effect of amine basicity and carbamate stability reaction

Table 1. Coefficients for the Reaction Equilibrium Constants for MEA Used in This Work[a]

$$\ln K = A + \frac{B}{T} + C \ln T + DT + ET^2,$$

$$\Delta H = R(-B + CT + DT^2 + 2ET^3)$$

reaction no.	parameter	A	B	C	D	E	ref
eq 2	K_a^{MEA}	306.3451	−11748.8	−59.3247	0.195428	−0.0001	this work
eq 2	K_a^{MDEA}	−564.988	9154.774	102.7625	−0.28006	0.000142	this work
eq 3	$K_c^{MEACOO^-}$	−69.35	7501.459	8.518298	−0.00015	-2.85×10^{-6}	this work
eq 4	$K_{HCO_3^-}$	2005.822	−50154.6	−368.665	0.953995	−0.00045	Kamps et al.[53]
eq 10	$K_{CO_2}^{Dissolution}$	−468.805	5284.795	95.04081	−0.32395	0.000152	Edwards et al.[54]
eq 7	$K_{Chem}^{MEA\_inf\ dilution}$	328.1224	−4307.81	−54.3276	0.00021	3.46×10^{-5}	this work
eq 8	$K_{Chem}^{MDEA\_inf\ dilution}$	2571.65	−59326.2	−471.587	1.234556	−0.00059	this work
eq 21	$K_{Chem}^{MEA\_30wt\%}$	2051.287	−42213.1	−376.444	0.939854	-4.29×10^{-4}	this work
eq 22	$K_{Chem}^{MDEA\_30wt\%}$	2543.642	−58888.8	−466.756	1.229662	-5.93×10^{-4}	this work

[a] All equilibrium constants in the table are on a mole fraction basis.

enthalpy is investigated. This can be used to understand the potential of alkanolamine solvents in PCC.

2. THERMODYNAMIC FRAMEWORK

2.1. Chemical and Phase Equilibrium. CO_2 absorption in aqueous amine solutions is determined by both physical solubility and the chemical equilibrium for aqueous phase reactions occurring among CO_2, water, and amines. The overall enthalpy of reaction of gaseous CO_2 with aqueous alkanolamines is the sum of the individual enthalpies of reaction in the aqueous phase and the enthalpy of physical absorption of CO_2 from the gas phase.
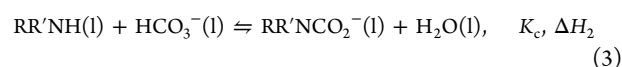
$$\Delta H_{abs} = \Delta H_{Chem} + \Delta H_{Phys}, \quad K_{abs} = K_{Chem} + K_{CO_2}^{Dissolution} \tag{1}$$

2.2. Aqueous-Phase Chemical Equilibrium. CO_2 reacts with alkanolamine solutions to form bicarbonate or carbamate.[9] Chemical absorption of CO_2 in MEA or MDEA solutions involves the following reactions.
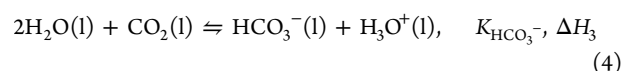
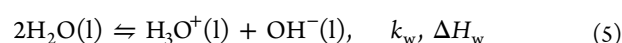Dissociation of protonated alkanolamine:

$$RR'R''NH^+(l) + H_2O(l) \rightleftharpoons RR'R''N(l) + H_3O^+(l), \quad K_a, \Delta H_1 \tag{2}$$
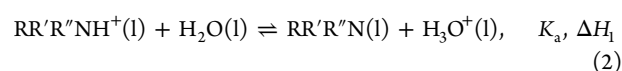
Carbamate formation reaction (for primary and secondary amines):

$$RR'NH(l) + HCO_3^-(l) \rightleftharpoons RR'NCO_2^-(l) + H_2O(l), \quad K_c, \Delta H_2 \tag{3}$$

Dissociation of carbon dioxide:

$$2H_2O(l) + CO_2(l) \rightleftharpoons HCO_3^-(l) + H_3O^+(l), \quad K_{HCO_3^-}, \Delta H_3 \tag{4}$$

Ionization of water:

$$2H_2O(l) \rightleftharpoons H_3O^+(l) + OH^-(l), \quad k_w, \Delta H_w \tag{5}$$

Dissociation of bicarbonate ion:

$$H_2O(l) + HCO_3^-(l) \rightleftharpoons H_3O^+(l) + CO_3^{2-}(l), \quad K_{CO_3^{2-}}, \Delta H_{CO_3^{2-}} \tag{6}$$
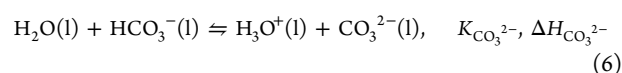
The overall reaction of absorption of CO_2 in MEA (primary amine) can be written as

$$2RNH_2(l) + CO_2(g) \rightleftharpoons RNH_3^+(l) + RNHCOO^-(l),$$
$$K_{Chem}^{MEA\_inf\ dilution}, \Delta H_r^{MEA\_inf\ dilution} \tag{7}$$
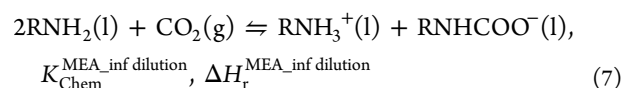
Tertiary amines like MDEA do not form carbamate.[10] In tertiary amines, CO_2 must first react with water to form bicarbonate,[11] and after this, a proton combines with the amine via an acid−base neutralization reaction. The overall reaction occurring in the CO_2−MDEA−H_2O system can be written as

$$RR'R''N(l) + CO_2(g) + H_2O(l) \rightleftharpoons RR'R''NH^+(l)$$
$$+ HCO_3^-(l), \quad K_{Chem}^{MDEA\_inf\ dilution}, \Delta H_r^{MDEA\_inf\ dilution} \tag{8}$$
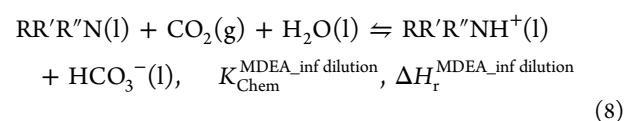
We calculate the equilibrium constants of the reactions from the overall Gibbs free energy given by the following equation

$$\Delta G_r = -RT \ln K \tag{9}$$

where ΔG_r is obtained after adding the gas and solution phase Gibbs free energies of corresponding reactions by using thermodynamic cycles. The thermodynamic cycles used for the various reactions in this work are given in the Supporting Information (Figures S1 and S2). R is the universal gas constant.

2.3. Physical Solubility. Physical solubility is the equilibrium between gaseous CO_2 molecules and CO_2 molecules in the aqueous amine solutions.

$$CO_2(g) \rightleftharpoons CO_2(l), \quad K_{CO_2}^{Dissolution}, \Delta H_{Phys} \tag{10}$$
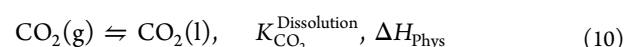
It can be expressed by Henry's law

$$Py_{CO_2}\varphi_{CO_2} = H_{CO_2}x_{CO_2}y_{CO_2}^* \tag{11}$$

where P is the system pressure, y_{CO_2} represents the mole fraction of CO_2 in the vapor phase, and φ_{CO_2} is the CO_2 fugacity coefficient in the vapor phase. H_{CO_2} is the Henry's law constant of CO_2 in the water and amine, x_{CO_2} is the equilibrium CO_2 mole fraction in the liquid phase, and $y_{CO_2}^*$ is the unsymmetric activity coefficient of CO_2 in the mixed solvent of water and amine. The Henry's law constant for CO_2 with water has been extensively studied.[12,13] Carroll et al.[13] collected all the data prior to 1991 and presented a rigorous model for the Henry's constant of CO_2 in water up to 1 MPa and for temperatures from 273 to 433 K. During regression, they considered a molecular system with the activity coefficients of water and CO_2 and the Poynting factor all to be one. In this work, we are using values for Henry's law constant for CO_2 in water from Carroll et al.,[13] as it regresses all available literature data.

9458

dx.doi.org/10.1021/jp404356e | J. Phys. Chem. B 2013, 117, 9457−9468

The overall enthalpy of reaction of CO_2 absorption with alkanolamines can then be expressed as

$$\Delta H_{abs}^{Amine\_inf\ dilution} = \Delta H_r^{Amine\_inf\ dilution} + \Delta H_{Phys},$$

$$K_{abs}^{Amine\_inf\ dilution} = K_{Chem}^{Amine\_inf\ dilution} + K_{CO_2}^{Dissolution} \quad (12)$$

2.4. Temperature Dependency of Free Energy of Solution. The temperature dependencies of the free energy of protonation reactions of MEA and MDEA with CO_2 are calculated as shown in our earlier study.[14] In this method, developed for calculation of pK_a, we shifted the free energy of protonation in solution at 298 K to the experimental free energy of protonation in solution at 298 K (correction factor) according to the following equation:

$$(\Delta G_{aq}^*)_T = (\Delta G_{aq}^*)_{calc,T} + \text{Correction factor} \quad (13)$$

We observed when using this method that the results for amine basicity were within experimental error bars.[14] Temperature dependent gas phase and solution phase free energies of various species of MEA and MDEA in reaction with CO_2 and corresponding correction factors applied are given in the Supporting Information (Tables S1–S4).

2.5. Heat of Absorption. Equilibrium constants at different temperatures can be used accurately to determine temperature dependent enthalpies, entropies, and heat capacities.[15−17] In this work, standard enthalpy changes are calculated from temperature dependent $\ln K$ values based on eq 9 using computational chemistry. These ΔH values can be obtained from equilibrium constant (K) values for different reactions at various temperatures by using the well-known Van't Hoff equation. This equation can be easily derived from the Gibbs−Helmholtz equation.[18]

$$\left(\frac{d \ln K}{dT}\right)_P = \frac{\Delta H}{RT^2} \quad (14)$$

The temperature dependency of the equilibrium constants and the Henry's law constant can be expressed in the form given by Weiland et al.[19] as follows

$$\ln K = A + \frac{B}{T} + C \ln T + DT + ET^2 \quad (15)$$

By differentiating eq 15 w.r.t. T, ΔH can be expressed as follows

$$\Delta H = R(-B + CT + DT^2 + 2ET^3) \quad (16)$$

For calculating ΔH_{Chem}^{MEA}, $\ln K$ for reaction 7 can be written as

$$K_{Chem}^{MEA\_inf\ dilution} = \frac{K_c K_{HCO_3^-}}{K_a^{MEA}},$$

$$\ln K_{Chem}^{MEA\_inf\ dilution} = \ln K_c + \ln K_{HCO_3^-} - \ln K_a^{MEA} \quad (17)$$

Similarly, for calculating ΔH_{Chem}^{MDEA}, $\ln K$ for reaction 8 can be written as

$$K_{Chem}^{MDEA\_inf\ dilution} = \frac{K_{HCO_3^-}}{K_a^{MDEA}},$$

$$\ln K_{Chem}^{MDEA\_inf\ dilution} = \ln K_{HCO_3^-} - \ln K_a^{MDEA} \quad (18)$$

where equilibrium constants for various reactions can be expressed as in eq 19 if the mole fraction based activity of water for simplicity is assumed to be 1 and if H_3O^+ is written as H^+.

$$K_a = \frac{a_{RR'R''N} a_{H^+}}{a_{RR'R''NH^+}}, \qquad K_c = \frac{a_{RR'NCO_2^-}}{a_{RR'NH} a_{HCO_3^-}},$$

$$K_{HCO_3^-} = \frac{a_{HCO_3^-} a_{H^+}}{a_{CO_2}} \quad (19)$$

2.6. Activity Coefficients and Excess Heat of Absorption. Equilibrium constants and enthalpies calculated from eqs 9 and 16, respectively, give values at infinite dilution and at infinitely low loading of CO_2 (the continuum solvation model treats one molecule in a continuum medium of solvent; this condition is referred to as infinitely low loading of CO_2). To compare calculated enthalpy values against available experimental literature, activity coefficients of 30 wt % MEA having infinite dilution as a reference state are added to overall $\ln K$ at infinite dilution.

The equilibrium constants for reactions may be defined in terms of activity coefficients, γ_i, and concentrations, x_i

$$K_{eq} = \prod (\gamma_i x_i)^{\nu_i} \quad (20)$$

The temperature variations of activity coefficients of MEA and MDEA at infinite dilution and for 30 wt % MEA and MDEA are taken from Schmidt et al.[20] Different activity coefficient models and corresponding excess enthalpy contributions were also studied in this work and discussed in the Supporting Information (Tables S6 and S7).

For calculating $\Delta H_r^{MEA\_30wt\%}$, $\ln K$ for reaction 7 can be written as

$$K_{Chem}^{MEA\_30wt\%} = \frac{K_c K_{HCO_3^-}}{K_a^{MEA}} \left(\frac{1}{\left(\frac{\gamma_{MEA}^{30wt\%}}{\gamma_{MEA}^{\infty}}\right)^2} \right),$$

$$\ln K_{Chem}^{MEA\_30wt\%} = \ln K_c + \ln K_{HCO_3^-} - \ln K_a^{MEA}$$

$$- 2 \ln \frac{\gamma_{MEA}^{30wt\%}}{\gamma_{MEA}^{\infty}} \quad (21)$$

Similarly, for calculating $\Delta H_{Chem}^{MDEA\_30wt\%}$, $\ln K$ for reaction 8 can be written as

$$K_{Chem}^{MDEA\_30wt\%} = \frac{K_{HCO_3^-}}{K_a^{MDEA}} \left(\frac{1}{\frac{\gamma_{MDEA}^{30wt\%}}{\gamma_{MDEA}^{\infty}}} \right),$$

$$\ln K_{Chem}^{MDEA\_30wt\%} = \ln K_{HCO_3^-} - \ln K_a^{MDEA} - \ln \frac{\gamma_{MDEA}^{30wt\%}}{\gamma_{MDEA}^{\infty}} \quad (22)$$

The overall enthalpy of reaction of CO_2 absorption with alkanolamines can then be expressed as

$$\Delta H_{abs}^{Amine\_30wt\%} = \Delta H_r^{Amine\_30wt\%} + \Delta H_{Phys},$$

$$K_{abs}^{Amine\_30wt\%} = K_{Chem}^{Amine\_30wt\%} + K_{CO_2}^{Dissolution} \quad (23)$$

2.7. Parameter Fitting. Coefficients for the correlation of reaction equilibrium constants used in this work are given in Table 1. $\ln K$ and enthalpy were calculated by using eqs 15 and 16, as explained in section 2.5.

3. COMPUTATIONAL METHODS

Gas phase calculations and geometry optimizations were carried out using density functional theory (DFT) at the B3LYP/6-311++G(d,p)//B3LYP-6-311++G(d,p) level. Single point energy calculations on the optimized geometry of the molecule obtained are used to study the solvation effects with SM8T solvation models. Conformer search was carried out in both the gaseous and solvent phase. The equilibrium geometry of the molecule in the ideal gas phase from molecular energy minimization was calculated using Spartan 08.[21] Lowest energy conformer structures and conformer search details are given in the Supporting Information (Figure S3). Gaseous phase frequency calculations were done using Gaussian 03 software[22] in the temperature range 273.15−373 K. SM8T calculations[23] were done in Gamessplus[24] for the temperature range 273.15−373 K using the optimized structures obtained earlier. All SM8T calculations were done using density functional theory (DFT) at the SM8T/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 energies of neutral molecules. The SM8T model is not parametrized for ionic molecules, but it is expected to give good qualitative results for ions,[23] and also, in our recent study, we have shown reproducibility of protonation constants using the SM8T solvation energy for amine protonation within experimental error bars.[14]

We have adopted the same approach for calculating the temperature dependency of the carbamate formation reaction (reaction 3) as we have adopted for the protonation reaction. Our model has however not been calibrated for the carbamate formation reaction (due to insufficient experimental data for carbamate stability constants for PCC solvents). There are therefore some uncertainties in the model performance for this reaction. The reaction is however balanced in terms of having species of the same charge on both sides of the equilibrium. We believe that the temperature dependency of such a reaction having charge neutrality of species on each side of the equilibrium is relatively easy to predict from continuum solvation models compared to a complex reaction involving complex species and transfer of neutral species to higher charges.

Thermodynamic cycles used for calculating reaction equilibrium constants for protonation and carbamate formation reactions are given in the Supporting Information (Figures S1 and S2).

4. RESULTS AND DISCUSSION

4.1. Dissociation of Protonated Alkanolamine (Reaction 2).
The MEA and MDEA dissociation constants were calculated using the SM8T continuum solvation model coupled with DFT quantum mechanical calculations of the gas phase. This method is shown to give temperature dependencies of dissociation constants of amines and alkanolamines within experimental error bars, and it takes the experimental value of pK_a at room temperature as input.[14] In Figures 1a and 2a, experimental temperature dependent dissociation constants for MEA[4,25−31] and MDEA,[4,6,17,29,32−36] along with calculated results, are plotted. From these figures, it can be seen that the temperature dependencies of ln K for MEA and MDEA are predicted within experimental error bars from computational chemistry calculations done in this work. As explained in the Computational Methods section, by using these dissociation
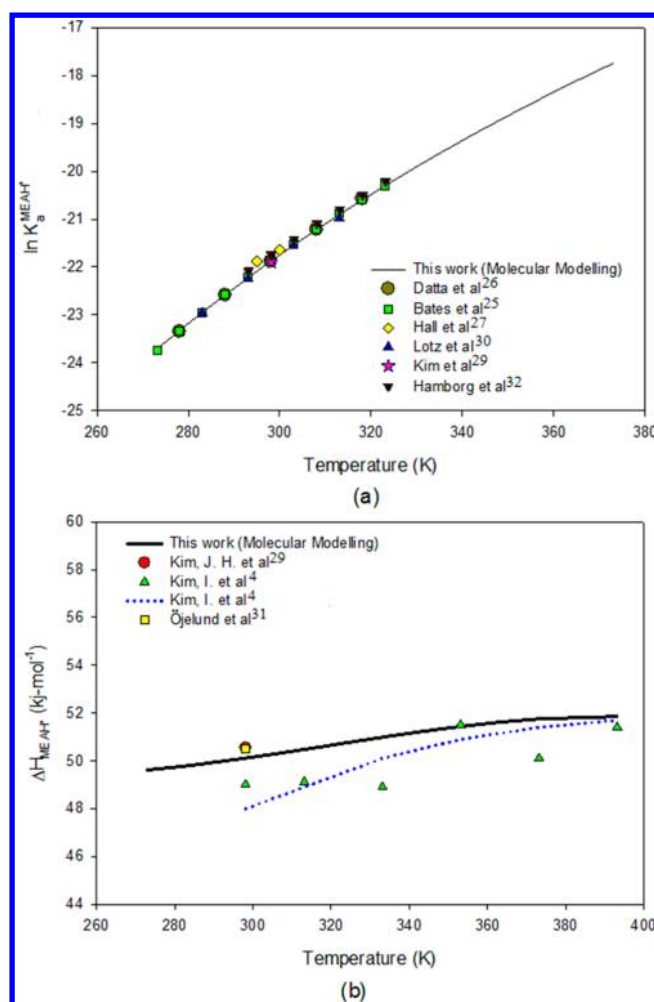

Figure 1. Dissociation constants (a) and enthalpies of deprotonation (b) for MEA as a function of temperature from the SM8T model compared with available literature data.

constants at different temperatures, enthalpies of protonation at different temperatures can be calculated from a differentiation of the Van't Hoff equation (eq 14). The calculated temperature dependent enthalpies for MEA and MDEA are plotted along with experimental data in Figures 1b and 2b.

From Figure 1b, it can be seen that the temperature dependent enthalpy values calculated using computational chemistry in this work are well within experimental uncertainties. The only available experimental measured data for the enthalpy of MEA protonation was found in the work of Kim et al.[29] (1987), Ojelund et al.[31] (1968), and Kim et al.[4] (2011). They all used calorimeter measurements to get the heat of absorption. Kim et al.[4] have explained in their work that their measured values are 2.3% higher than the heats measured by Kim et al.[29] On the other hand, the heat of protonation measured by Ojelund et al.[31] matches exactly with that measured by Kim et al.[29] at 298 K.

From Figure 2b, it can be seen that calculated heats of absorption for MDEA protonation are also within calorimetric heats of protonation determined by Oscarson et al.[37] (1989), Merkley et al.[6] (1987), and Kim et al.[29] (1987). Kim et al.[4] (2011) has explained that enthalpies of protonation of MDEA measured in their work are on average 3% lower than those reported by Oscarson et al.,[37] i.e., slightly outside the experimental uncertainty. They have suggested that this
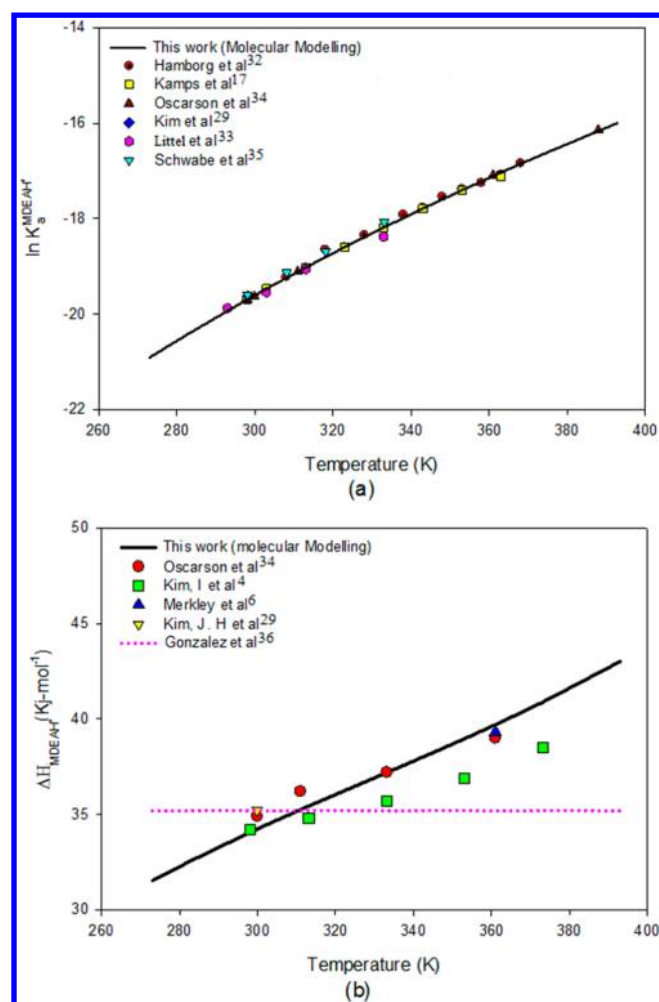
Figure 2. Dissociation constants (a) and enthalpies of deprotonation (b) for MDEA as a function of temperature from the SM8T model compared with available literature data.

difference is probably coming from the difference in the experimental procedure and calculations.

4.2. Carbamate Formation Reaction (Reaction 3). There is a lot of scatter in the literature for the equilibrium constant for MEA carbamate formation (reaction 3), and also, experimental data for this constant is not available for a large number of PCC solvents. The first results reported for reaction of CO_2 with alkanolamines are by Jensen et al.[38] in the early 1950s. They used acidimetric titration, with bromocresol green as an indicator, to calculate the carbamate formation reaction constant for 2-ethanolamine (MEA) and diethanolamine (DEA). They also studied carbamates of propylamines and butyl amines obtained by chemical precipitation methods.[39] ^{13}C NMR spectroscopy was used to study carbamate stability constants of MEA, 2-amino-2-methyl-1-propanol (AMP), and DEA by Sartori and Savage.[40] Aroua et al.[41] studied carbamate formation of MEA and DEA by a NaOH titration method. Vapor–liquid equilibrium (VLE) measurements were performed to study MEA, DEA, AMP, and their mixtures by Park et al.[42] Jakobsen et al.[43] performed ^{1}H and ^{13}C NMR studies on MEA, butylethanolamine (BEA), and MDEA at 293 and 313 K. Recently, McCann et al.[44,45] used ^{1}H NMR spectroscopy to study MEA (also 2-amino-1-propanol, propylamine, and isobutylamine) and to calculate carbamate stability constants. Austgen et al.[46,47] estimated the carbamate stability constant for

MEA as one of the parameters of a VLE model using the eNRTL activity coefficient model. They regressed parameters in their model to CO_2 partial pressure data. Wang et al.[48] used ^{1}H spectra and regression with the Deshmukh and Mather model[49] to obtain the carbamate stability constant of MEA. Very recently, Fernandes et al.[50] have used ^{1}H NMR to study the carbamate stability of MEA and other important solvents for PCC. Special care has to be taken regarding standard state conditions, concentration of the amine, and the method involved before comparing data from various literature sources. In this work, data from each literature source were shifted to infinite dilution conditions and compared with computational chemistry results obtained. The ionization constant for MEA carbamate is plotted as a function of temperature in Figure 3a along with available literature data.
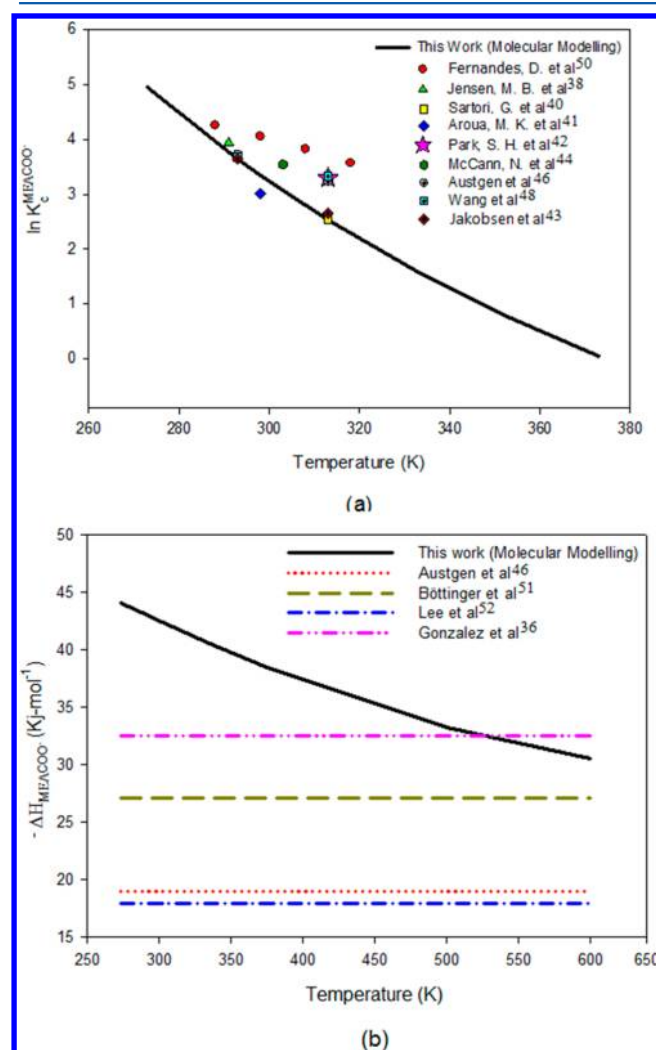
Figure 3. $\ln K_c^{MEACOO^-}$ (a) and ΔH_{MEACOO^-} (b) for MEA carbamate formation as a function of temperature.

$$RR'NH(l) + HCO_3^-(l) \leftrightharpoons RR'NCO_2^-(l) + H_2O(l)$$
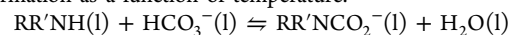
From this figure, we can see that not only data for $\ln K_{MEACOO^-}$ at 298 K are scattered on the basis of different literature sources, but also its temperature dependency is uncertain. A computational chemistry model can be considered as a valuable tool for calculating temperature effects on K_{carb} of

solvents of post-combustion CO_2 capture where experimental determination of these constants through NMR spectroscopy or VLE is relatively difficult and challenging. The computational chemistry values for $\ln K_c$ are anchored to the experimental value of 3.642 for $\ln K_{MEACOO^-}$ at 293 K given by Poplsteinova et al.[43] Poplsteinova et al.[43] agree with Austgen et al.,[46] Wang et al.,[48] and Sartori et al.[40] at 293 K but do not agree with Austgen et al.[46] and Wang et al.[48] at 313 K. The carbamate stability constant of MEA calculated by computational chemistry agrees with NMR spectroscopy data of Sartori et al.[40] and Poplsteinova et al.[43] at 313 K.

MDEA, being a tertiary alkanolamine, does not form carbamate.[10]

No experimental data was found in the literature for the enthalpy of MEA carbamate formation. Application of the Gibbs−Helmholtz equation (eq 14) to $\ln K$ correlations given by the work of Austgen et al.[46] (1989), Böttinger et al.[51] (2008), Lee et al.[52] (1996), and Gonzalez et al.[36] (1998) results in a constant value of the enthalpy for this reaction, as shown in Figure 3b. In the present work, from molecular modeling studies, we found a temperature dependent enthalpy for this reaction and we found that with an increase in temperature the reaction becomes less exothermic.
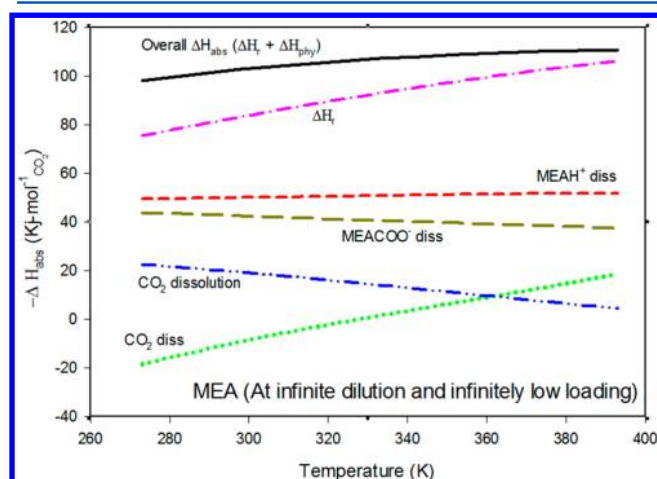
4.3. Overall Differential Heat of Absorption of CO_2 with MEA and MDEA (Infinite Dilution Solution) as a Function of Temperature at Infinite Loading of CO_2. In order to calculate the overall heat of absorption, equilibrium constants ($\ln K$) and enthalpy values for all reactions involved must be known. For MEA, reactions 2−4 are added to give the overall absorption reaction of CO_2 in aqueous MEA. The enthalpies of reactions 4 and 5 were calculated from the SM8T model as explained above. Reaction 4 (dissociation of carbon dioxide) is well-defined in the literature, and $\ln K$ for this reaction was taken from Kamps et al.[53] and the corresponding enthalpy calculated from the differential form of the Van't Hoff equation. This reaction is believed to take place in the liquid phase. Hence, in order to calculate the overall enthalpy, physical absorption of CO_2 must also be added according to eq 10. The Henry's law constant for CO_2 dissolution was taken from Edwards et al.[54]

Heats of reaction for each of the individual reactions taking place between MEA and CO_2 in the temperature range 273.15−373 K at infinite dilution are plotted in Figure 4. Heat of reaction in the liquid phase is denoted by ΔH_r, and overall heat of reaction is denoted by overall ΔH_{abs}.
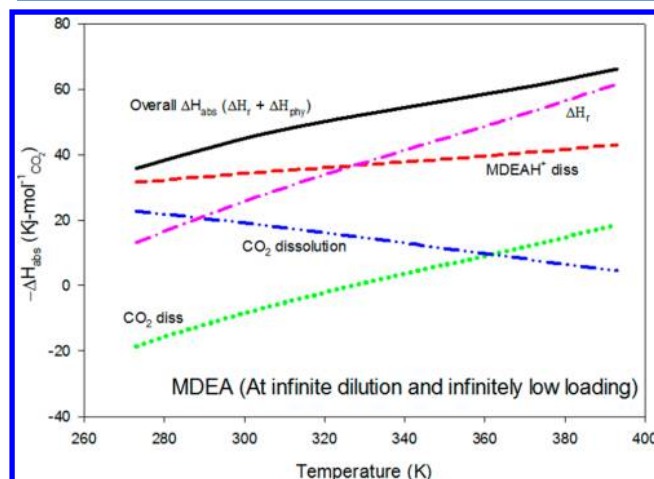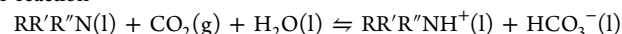

Figure 4. Overall differential heat of absorption of CO_2 with MEA for reaction

$$2RNH_2(l) + CO_2(g) \rightleftharpoons RNN_3^+(l) + RNHCOO^-(l)$$

and heats of each of the individual reactions as a function of temperature at infinite dilution and infinitely low loading of CO_2.

Figure 5. Overall differential heat of absorption of CO_2 with MDEA for reaction

$$RR'R''N(l) + CO_2(g) + H_2O(l) \rightleftharpoons RR'R''NH^+(l) + HCO_3^-(l)$$

and heats of each of the individual reactions as a function of temperature at infinite dilution and infinitely low loading of CO_2.

Table 2. Temperature Dependent ln K Values of Various Reactions Involved in the MEA−CO$_2$−H$_2$O System[a]

temp (K)	$\ln K_a^{MEA}$	$\ln K_c^{MEACOO^-}$	$\ln K_{HCO_3^-}$	$\ln K_{Chem}^{MEA\_inf\ dilution}$	$2\ln(\gamma_{MEA}^{30wt\%}/\gamma_{MEA}^\infty)$	$\ln K_{Chem}^{MEA\_30wt\%}$	$\ln K_{CO_2}^{Dissolution}$
273	−23.72	5.66	−19.14	10.23	0.58	9.65	6.61
283	−22.95	4.97	−18.89	9.03	0.45	8.59	6.95
298	−21.88	4.05	−18.63	7.30	0.28	7.01	7.39
303	−21.54	3.77	−18.58	6.73	0.24	6.50	7.51
313	−20.91	3.24	−18.51	5.64	0.15	5.49	7.74
323	−20.30	2.74	−18.47	4.57	0.08	4.49	7.94
333	−19.73	2.29	−18.47	3.55	0.02	3.53	8.10
343	−19.20	1.86	−18.51	2.55	−0.04	2.59	8.24
353	−18.69	1.46	−18.56	1.59	−0.08	1.67	8.36
363	−18.20	1.09	−18.64	0.65	−0.13	0.78	8.46
373	−17.74	0.75	−18.74	−0.25	−0.16	−0.09	8.53
393	−16.89	0.12	−19.00	−1.98	−0.22	−1.76	8.63

[a]$\ln K_{Chem}^{MEA\_inf\ dilution} = \ln K_c^{MEACOO^-} + \ln K_{HCO_3^-} - \ln K_a^{MEA}$. $\ln K_{Chem}^{MEA\_30wt\%} = \ln K_{Chem}^{MEA\_inf\ dilution} - 2\ln(\gamma_{MEA}^{30wt\%}/\gamma_{MEA}^\infty)$.

Table 3. Temperature Dependent Enthalpy Values of Various Reactions Involved in the MEA−CO$_2$−H$_2$O System^a

temp (K)	ΔH_1	ΔH_2	ΔH_3	ΔH_{Phys}	$\Delta H_r^{\text{MEA\_inf dilution}}$	$\Delta H_{\text{abs}}^{\text{MEA\_inf dilution}}$	ΔH_{Excess}	$\Delta H_r^{\text{MEA\_30wt\%}}$	$\Delta H_{\text{abs}}^{\text{MEA\_30wt\%}}$
273	49.62	−44.09	18.48	−22.62	−75.65	−98.27	−9.13	−66.10	−88.72
283	49.79	−43.50	14.51	−21.43	−78.82	−100.24	−8.31	−70.47	−91.90
298	50.11	−42.63	9.12	−19.43	−83.39	−102.83	−7.23	−76.39	−95.82
303	50.23	−42.34	7.45	−18.73	−84.86	−103.59	−6.91	−78.21	−96.94
313	50.48	−41.78	4.27	−17.25	−87.73	−104.98	−6.33	−81.66	−98.91
323	50.73	−41.22	1.27	−15.71	−90.49	−106.20	−5.80	−84.88	−100.59
333	50.99	−40.67	−1.60	−14.13	−93.14	−107.26	−5.34	−87.92	−102.05
343	51.23	−40.14	−4.38	−12.51	−95.67	−108.18	−4.92	−90.82	−103.33
353	51.44	−39.61	−7.13	−10.88	−98.08	−108.96	−4.55	−93.63	−104.50
363	51.62	−39.09	−9.88	−9.24	−100.37	−109.61	−4.21	−96.38	−105.62
373	51.76	−38.59	−12.68	−7.62	−102.53	−110.15	−3.90	−99.12	−106.74
393	51.86	−37.61	−18.61	−4.48	−106.471	−110.946	−3.33	−104.74	−109.22

^{a}ΔH_1, ΔH_2, ΔH_3, and ΔH_{phys} correspond to the enthalpy of deprotonation of MEA, carbamate formation reaction of MEA, dissociation of carbon dioxide, and physical solubility of CO$_2$ represented by eqs 4, 5, 6, and 2, respectively, in the manuscript. $\Delta H_r^{\text{MEA\_inf dilution}}$ is calculated by correlating ln $K_{\text{Chem}}^{\text{MEA\_inf dilution}}$ values from the Gibbs−Helmholtz equation. $\Delta H_{\text{abs}}^{\text{MEA\_inf dilution}} = \Delta H_r^{\text{MEA\_inf dilution}} + \Delta H_{\text{phys}}$. ΔH_{Excess} is calculated by correlating $2 \ln(\gamma_{\text{MEA}}^{30wt\%}/\gamma_{\text{MEA}}^{\infty})$ values from the Gibbs−Helmholtz equation. $\Delta H_r^{\text{MEA\_30wt\%}}$ is calculated by correlating ln $K_{\text{Chem}}^{\text{MEA\_30wt\%}}$ values from the Gibbs−Helmholtz equation. $\Delta H_{\text{abs}}^{\text{MEA\_30wt\%}} = \Delta H_r^{\text{MEA\_30wt\%}} + \Delta H_{\text{phys}}$.

Table 4. Temperature Dependent ln K Values of Various Reactions Involved in the MDEA−CO$_2$−H$_2$O System^a

temp (K)	ln K_a^{MDEA}	ln $K_a^{\text{HCO}_3^-}$	ln $K_{\text{Chem}}^{\text{MDEA\_inf dilution}}$	$\ln(\gamma_{\text{MDEA}}^{30wt\%}/\gamma_{\text{MDEA}}^{\infty})$	ln $K_{\text{Chem}}^{\text{MEA\_30wt\%}}$	ln $K_{\text{CO}_2}^{\text{Dissolution}}$
273	−20.91	−19.14	1.76	0.58	1.18	6.61
283	−20.41	−18.89	1.52	0.51	1.01	6.95
298	−19.70	−18.63	1.06	0.41	0.66	7.39
303	−19.47	−18.58	0.89	0.37	0.52	7.51
313	−19.03	−18.51	0.52	0.31	0.21	7.74
323	−18.60	−18.47	0.13	0.24	−0.11	7.94
333	−18.19	−18.47	−0.29	0.18	−0.46	8.10
343	−17.79	−18.51	−0.71	0.12	−0.83	8.24
353	−17.41	−18.56	−1.15	0.06	−1.21	8.36
363	−17.04	−18.64	−1.60	0.00	−1.60	8.46
373	−16.68	−18.74	−2.06	−0.05	−2.01	8.53
393	−15.99	−19.00	−3.00	−0.16	−2.84	8.63

^{a}ln $K_{\text{Chem}}^{\text{MDEA\_inf dilution}} = \ln K_{\text{HCO}_3^-} - \ln K_a^{\text{MDEA}}$. ln $K_{\text{Chem}}^{\text{MDEA\_30wt\%}} = \ln K_{\text{Chem}}^{\text{MDEA\_inf dilution}} - \ln(\gamma_{\text{MDEA}}^{30wt\%}/\gamma_{\text{MDEA}}^{\infty})$.

Table 5. Temperature Dependent Enthalpy Values of Various Reactions Involved in MDEA−CO$_2$−H$_2$O System^a

temp (K)	ΔH_1	ΔH_3	ΔH_{Phys}	$\Delta H_r^{\text{MDEA\_inf dilution}}$	$\Delta H_{\text{abs}}^{\text{MDEA\_inf dilution}}$	ΔH_{Excess}	$\Delta H_r^{\text{MDEA\_30wt\%}}$	$\Delta H_{\text{abs}}^{\text{MDEA\_30wt\%}}$
273	31.52	18.48	−22.62	−13.04	−35.61	−7.54	−8.49	−31.11
283	32.58	14.51	−21.43	−18.07	−39.50	−7.83	−13.32	−34.75
298	34.05	9.12	−19.43	−24.94	−44.38	−8.24	−19.89	−39.32
303	34.52	7.45	−18.73	−27.07	−45.80	−8.37	−21.92	−40.65
313	35.42	4.27	−17.25	−31.15	−48.40	−8.62	−25.82	−43.07
323	36.31	1.27	−15.71	−35.03	−50.74	−8.87	−29.52	−45.23
333	37.18	−1.60	−14.13	−38.78	−52.90	−9.10	−33.09	−47.22
343	38.06	−4.38	−12.51	−42.44	−54.95	−9.32	−36.58	−49.09
353	38.95	−7.13	−10.88	−46.08	−56.97	−9.53	−40.06	−50.94
363	39.88	−9.88	−9.24	−49.76	−59.02	−9.73	−43.58	−52.82
373	40.86	−12.68	−7.62	−53.54	−61.17	−9.92	−47.21	−54.83
393	43.01	−18.61	−4.48	61.6253	66.1007	−10.28	−55.00	−59.48

^{a}ΔH_1, ΔH_3, and ΔH_{Phys} correspond to the enthalpy of deprotonation of MDEA, dissociation of carbon dioxide, and physical solubility of CO$_2$ represented by eqs 4, 6, and 2, respectively, in the manuscript. $\Delta H_r^{\text{MDEA\_inf dilution}}$ is calculated by correlating ln $K_{\text{Chem}}^{\text{MDEA\_inf dilution}}$ values from the Gibbs−Helmholtz equation. $\Delta H_{\text{abs}}^{\text{MDEA\_inf dilution}} = \Delta H_r^{\text{MDEA\_inf dilution}} + \Delta H_{\text{Phys}}$. ΔH_{Excess} is calculated by correlating $2 \ln(\gamma_{\text{MDEA}}^{30wt\%}/\gamma_{\text{MDEA}}^{\infty})$ values from the Gibbs−Helmholtz equation. $\Delta H_r^{\text{MDEA\_30wt\%}}$ is calculated by correlating ln $K_{\text{Chem}}^{\text{MDEA\_30wt\%}}$ values from the Gibbs−Helmholtz equation. $\Delta H_{\text{abs}}^{\text{MDEA\_30wt\%}} = \Delta H_r^{\text{MDEA\_30wt\%}} + \Delta H_{\text{Phys}}$.

The heat of reaction for each of the individual reactions and the overall heat of absorption for the MDEA−CO$_2$−H$_2$O system in the temperature range 273.15−373 K are given in Figure 5 at infinite dilution. As discussed earlier, MDEA does not form carbamate, so the deprotonation reaction (reaction 2) and bicarbonate formation reaction (reaction 4) are the most important reactions in this system. Enthalpy values for reaction 4 (dissociation of carbon dioxide) are
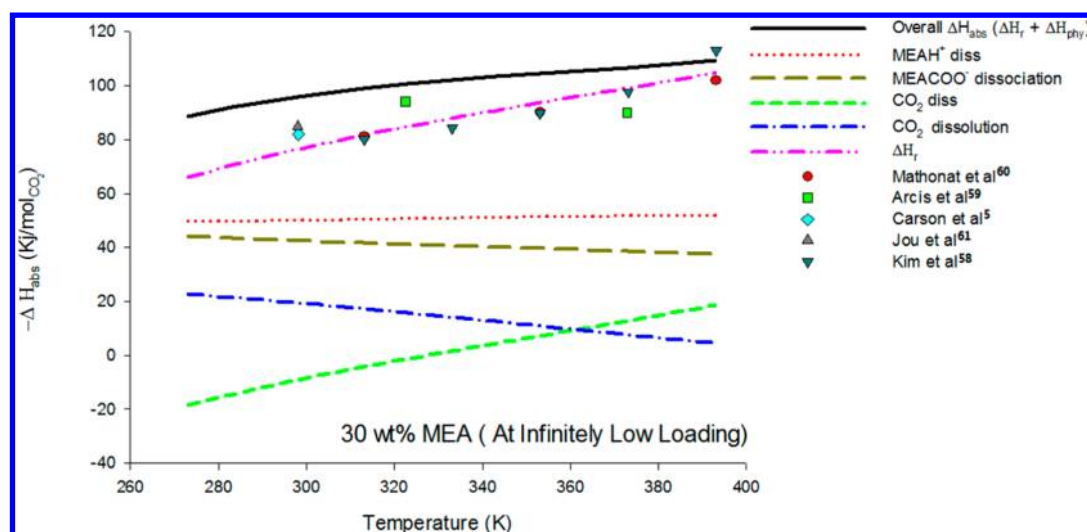
Figure 6. Calculated and experimental overall differential heat of absorption of CO_2 with 30 wt % MEA for reaction

$$2RNH_2(l) + CO_2(g) \rightleftharpoons RNH_3^+(l) + RNHCOO^-(l)$$

and heats of each of the individual reactions as a function of temperature at infinitely low loading of CO_2.

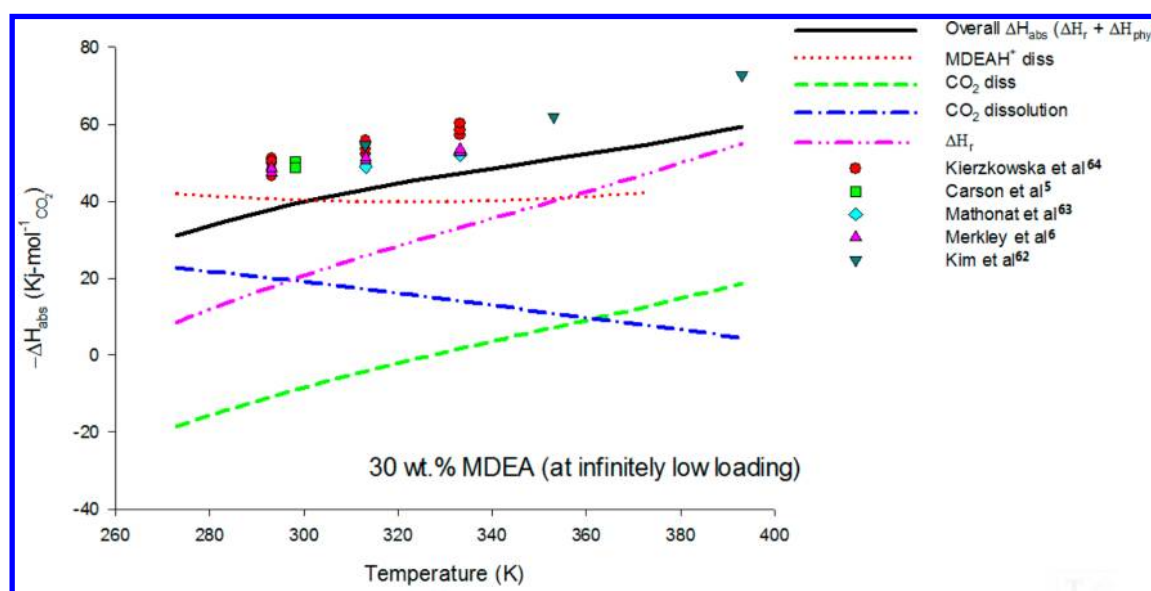**Figure 7.** Calculated and experimental overall differential heat of absorption of CO_2 with 30 wt % MDEA for reaction

$$RR'R''N(l) + CO_2(g) + H_2O(l) \rightleftharpoons RR'R''NH^+(l) + HCO_3^-(l)$$

and heats of each of the individual reactions as a function of temperature at infinitely low loading of CO_2.

taken from differentiating the ionization constant for this reaction from Kamps et al.[53] as in the case of MEA. For physical absorption of CO_2, ln K data were taken from Edwards et al.[54]

4.4. Comparison of Heat of Absorption of CO_2 with MEA and MDEA from Molecular Modeling and Literature Values. To compare calculated enthalpies against experimental data for 30 wt % MEA, we have added activity coefficients of MEA at 30 wt % with infinite dilution as a reference state. Activity coefficients for MEA at infinite dilution and for 30 wt % MEA were taken from Schmidt et al.[20] as explained in the Computational Methods section. ln K and excess enthalpy calculations for MEA and MDEA based on this

activity coefficient model as explained in section 2.6 are given in Tables 2–5, respectively.

$\gamma_{\text{alkanolamine}}^{\text{30wt\%}}$ values obtained are sensitive to the model used for calculating activity coefficients. To conduct a sensitivity test, we have compared MEA and MDEA excess enthalpy and activity coefficient at infinite dilution obtained from Schmidt et al.,[20] Austgen et al.,[55] Chang et al.,[56] and Posey et al.[57] at 298.15 K. These results are given in the Supporting Information (Table S6). The values for γ^∞ and H_{Excess}^∞ calculated from these models vary significantly from each other, which would result in variation in absolute value of $\Delta H_{\text{abs}}^{\text{alkanolamine\_30wt\%}}$ and its temperature dependency. The excess term for enthalpy corresponding to the 30 wt % MEA activity coefficients is given in Table 3. To conduct a
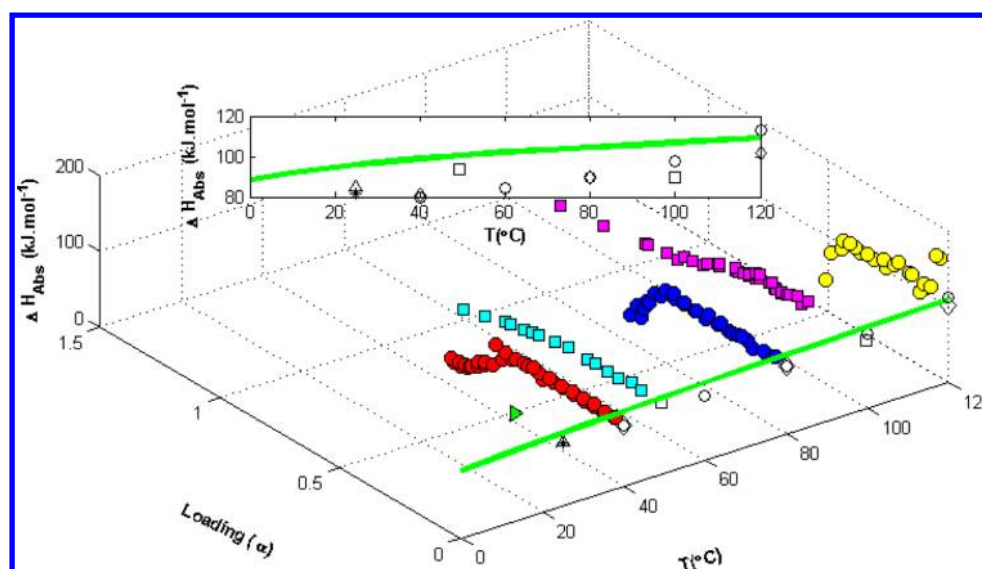
Figure 8. Comparison of experimental and calculated overall heat of absorption of CO_2 in 30 wt % MEA as a function of loading and temperature. Green line, molecular modeling (at infinite dilution); red circles, 40 °C; blue circles, 80 °C; yellow circles, 120 °C (ref 58); cyan squares, 49.5 °C; magenta squares, 99.9 °C (ref 59); green triangle, 25 °C (ref 52). Unfilled symbols represent enthalpy values at infinite dilution as a function of temperature (○, ref 58; □, ref 59; ◇, ref 60; ∗, ref 5; △, ref 61).
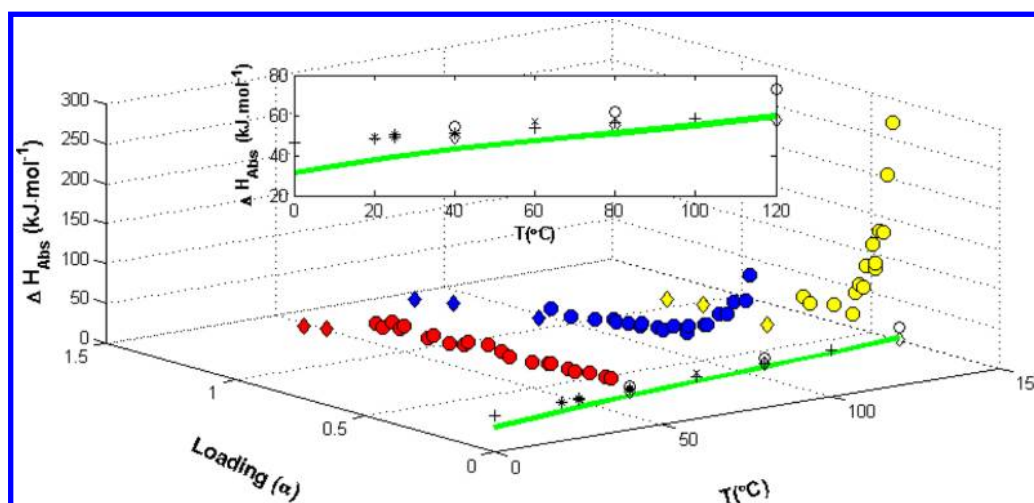

Figure 9. Comparison of experimental and calculated overall heat of absorption of CO_2 in 30 wt % MDEA as a function of loading and temperature. Green line, molecular modeling (at infinte dilution); red circles, 40 °C; blue circles, 80 °C; yellow circles, 120 °C (ref 62); red diamonds, 40 °C; blue diamonds, 80 °C; yellow diamonds, 120 °C (ref 63). Unfilled symbols represent enthalpy values at infinite dilution as a function of temperature (○, ref 62; ◇, ref 63; ∗, ref 5; +, ref 6; ×, ref 64).

sensitivity test for different models, a comparison of γ_{MEA}^{∞}, $\gamma_{MEA}^{30wt\%}$, H_{Excess}, and $\Delta H_{abs}^{MEA\_30wt\%}$ for MEA calculated from Austgen et al., Schmidt et al., and Chang et al. as a function of temperature is given in the Supporting Information (Table S7). Thus, calculation of $\Delta H_{abs}^{alkanolamine\_30wt\%}$ from enthalpy values at infinite dilution calculated from computational chemistry is sensitive for the thermodynamic model used for obtaining temperature dependent γ_{MEA}^{∞} and $\gamma_{MEA}^{30wt\%}$. Figures 6 and 7 show a comparison between calculated and experimental results for MEA and MDEA, respectively.

From Figures 6 and 7, we can see that, although enthalpy values calculated for 30 wt % MEA and MDEA deviate somewhat from values reported in the literature, one has to keep in mind that experimental values for enthalpy are also scattered and there are many sources of errors in their calculations (±10%). Also, as explained above, activity

coefficient models give different values for γ_{MEA}^{∞} and $\gamma_{MEA}^{30wt\%}$, which would also result in deviation of overall $\Delta H_{abs}^{alkanolamine\_30wt\%}$. Both computational chemistry and experimental data, however, show that the enthalpy of absorption of CO_2 in alkanolamines is temperature dependent.

Computational chemistry enthalpy values calculated in this work are at conditions of infinitely low loading of CO_2. From the literature, we have seen that the enthalpy of solution varies significantly with changes in loading. Figures 8 and 9 present comparisons of calculated and experimental overall heat of absorption of CO_2 in 30 wt % MEA as a function of loading and temperature. In Figures 9 and 11, the increase in the experimental value of enthalpy of absorption at very low loading is mainly because of the presence of other reactions occurring simultaneously in the solution.
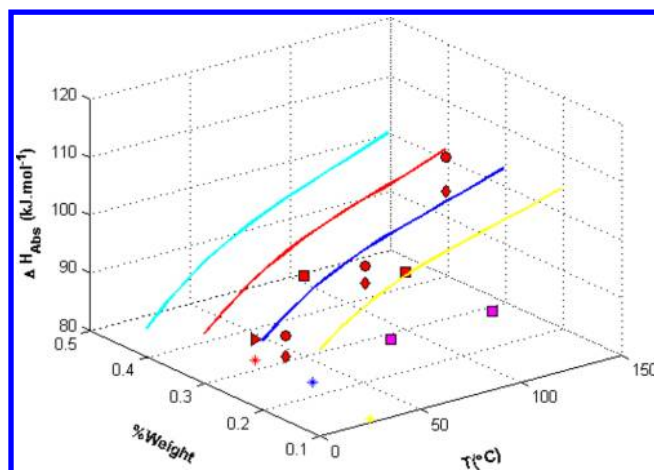
Figure 10. Comparison of experimental and calculated overall heat of absorption of CO_2 in MEA as a function of wt % of MEA and temperature. Solid lines, molecular modeling; ○, ref 58; □, ref 59; ◇, ref 60; ∗ ref 5; ▷, ref 52. Different wt % values of MEA are given by different colors (yellow, 10 wt % MEA; blue, 20 wt % MEA; red, 30 wt % MEA; cyan, 40 wt % MEA).
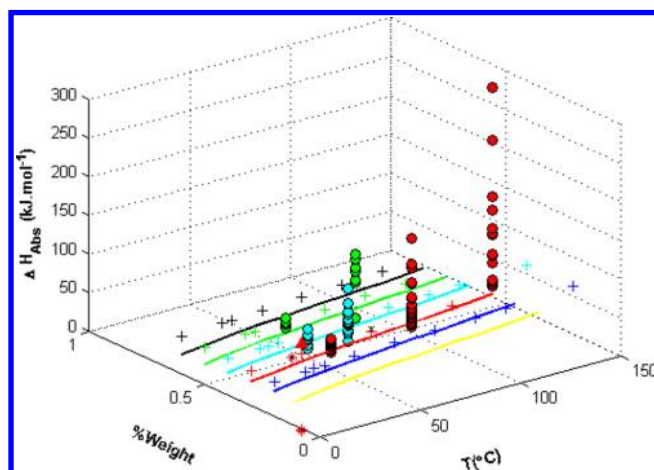

Figure 11. Comparison of experimental and calculated overall heat of absorption of CO_2 in MDEA as a function of wt % of MDEA and temperature. Solid lines, molecular modeling; ○, ref 62; ∗, ref 5; △, ref 61; +, ref 6; ✕, ref 64. Different wt % values of MDEA are given by different colors (yellow, 10 wt % MDEA; blue, 20 wt % MDEA; red, 30 wt % MDEA; cyan, 40 wt % MDEA; green, 50 wt % MDEA; black, 60 wt % MDEA).

The changes in enthalpy of solution as a function of wt % of MEA and MDEA and temperature are given in Figures 10 and 11. We have found that the enthalpy of solution changes with increasing concentration of alkanolamine, but these changes are not very significant.

5. CONCLUSIONS

Results from determining the temperature dependency of the enthalpy of absorption of CO_2 in MEA and MDEA show that computational chemistry provides a good tool for screening solvents for PCC where experimental data for enthalpy values are scattered or missing. The main finding of this work is that from the fundamental Gibbs−Helmholtz equation it is shown that the enthalpy of absorption of CO_2 in alkanolamine solutions is temperature dependent. It has to be emphasized that accurate temperature dependencies for the deprotonation

and carbamate formation constants are needed as input to derive the temperature dependent enthalpy of overall reaction of CO_2 with solvent in the absorption process. Computational chemistry is a powerful tool to provide such temperature dependencies for the various equilibrium constants for amines and alkanolamines[14] where experimental determination is difficult, such as the carbamate and deprotonation constants at high temperatures. Also, calculated overall temperature dependent enthalpy at infinite dilution from molecular modeling studies can provide good insight for the potential of various solvents in PCC. Methods and correlations given in this work can be used in future fitting models to predict the absorption of CO_2 into other amines and alkanolamines important for CO_2 capture processes.

■ ASSOCIATED CONTENT

ⓢ Supporting Information
Thermodynamic cycles employed for calculating the free energy of deprotonation of MEA and MDEA and the free energy of carbamate formation reaction of MEA. Most stable conformers of MEA, protonated MEA, MEA carbamate, MDEA, and protonated MDEA. Temperature dependent gas phase free energy and solvation energies of MEA, protonated MEA, MEA carbamate, MDEA, and protonated MDEA. Temperature dependent gas phase free energy and solvation energies of H_2O and HCO_3^- used in calculation of the free energy of reaction of carbamate formation of MEA. Correction factors applied to free energy of protonation in solution of MEA and MDEA at 298 K. Temperature dependent experimental ln $K_c^{MEACOO^-}$ values from different literature sources. Comparison of temperature dependency calculated as a result of anchoring to two different literature data at 298 K, viz., Jakobsen et al. (2005) and Fernandes et al. (2012). ln $K_c^{MEACOO^-}$ for MEA carbamate formation as a function of temperature. By shifting the ln K_c value at 298 K to Fernandes et al (2012). Comparison of MEA and MDEA excess enthalpy and activity coefficient at infinite dilution obtained from Schmidt et al., Austgen et al., Chang et al., and Posey et al. at 298.15 K. Comparison of γ_{MEA}^∞, $\gamma_{MEA}^{30wt\%}$, H_{Excess}, and $\Delta H_{abs}^{MEA\_30wt\%}$ of MEA calculated from Austgen et al., Schmidt et al., and Chang et al. as a function of temperature. Details of calculations for equilibrium constants. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: hallvard.svendsen@chemeng.ntnu.no. Phone: +47 73594100. Fax: +47 73594080.

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Zhang, Y.; Chen, H.; Chen, C. C.; Plaza, J. M.; Dugas, R.; Rochelle, G. T. Rate-Based Process Modeling Study of CO_2 Capture with Aqueous Monoethanolamine Solution. *Ind. Eng. Chem. Res.* **2009**, 48, 9233−9246.
(2) Jassim, M. S.; Rochelle, G. T. Innovative Absorber/Stripper Configurations for CO_2 Capture by Aqueous Monoethanolamine. *Ind. Eng. Chem. Res.* **2006**, 45, 2465−2472.

(3) Oyenekan, B. A.; Rochelle, G. T. Energy Performance of Stripper Configurations for CO_2 Capture by Aqueous Amines. *Ind. Eng. Chem. Res.* **2006**, *45*, 2457−2464.

(4) Kim, I.; Jens, C. M.; Grimstvedt, A.; Svendsen, H. F. Thermodynamics of Protonation of Amines in Aqueous Solutions at Elevated Temperatures. *J. Chem. Thermodyn.* **2011**, *43*, 1754−1762.

(5) Carson, J. K.; Marsh, K. N.; Mather, A. E. Enthalpy of Solution of Carbon Dioxide in (Water + Monoethanolamine, or Diethanolamine, or N-Methyldiethanolamine) and (Water + Monoethanolamine + N-Methyldiethanolamine) at T = 298.15 K. *J. Chem. Thermodyn.* **2000**, *32*, 1285−1296.

(6) Merkley, K. E.; Christensen, J. J.; Izatt, R. M. Enthalpies of Absorption of Carbon-Dioxide in Aqueous Methyldiethanolamine Solutions. *Thermochim. Acta* **1987**, *121*, 437−446.

(7) Kim, I. Heat of Reaction and VLE of Post Combustion CO_2 Absorbents. Ph.D. Thesis, Norwegian University of Science and Technology, 2009.

(8) Carson, J. K. M.E. Thesis, University of Canterbury, New Zealand, 1998.

(9) Versteeg, G. F.; Van Dijck, L. A. J.; Van Swaaij, W. P. M. On the Kinetics between CO_2 and Alkanolamines Both in Aqueous and Non-Aqueous Solutions. An Overview. *Chem. Eng. Commun.* **1996**, *144*, 113−158.

(10) Kohl, A. L.; Nielsen, R. B. *Gas Purification*, 5th ed.; Gulf Publishing Company: Houston, TX, 1997.

(11) Donaldson, T. L.; Nguyen, Y. N. Carbon-Dioxide Reaction-Kinetics and Transport in Aqueous Amine Membranes. *Ind. Eng. Chem. Fundam.* **1980**, *19*, 260−266.

(12) Yan, Y. Z.; Chen, C. C. Thermodynamic Modeling of CO_2 Solubility in Aqueous Solutions of NaCl and Na2SO4. *J. Supercrit. Fluids* **2010**, *55*, 623−634.

(13) Carroll, J. J. What Is Henry Law. *Chem. Eng. Prog.* **1991**, *87*, 48−52.

(14) Gupta, M.; da Silva, E. F.; Svendsen, H. F. Modeling Temperature Dependency of Amine Basicity Using PCM and SM8T Implicit Solvation Models. *J. Phys. Chem. B* **2012**, *116*, 1865−1875.

(15) Hepler, L. G. Correct Calculation of Deltah0, Delta-Cp0, and Deltav0 from Temperature and Pressure Dependences of Equilibrium-Constants - the Importance of Thermal-Expansion and Compressibility of the Solvent. *Thermochim. Acta* **1981**, *50*, 69−72.

(16) Guggenheim, E. A. Thermodynamics of an Activated Complex. *Trans. Faraday Soc.* **1937**, *33*, 607−614.

(17) Kamps, A. P. S.; Maurer, G. Dissociation Constant of N-Methyldiethanolamine in Aqueous Solution at Temperatures from 278 to 368 K. *J. Chem. Eng. Data* **1996**, *41*, 1505−1513.

(18) Denbigh, K. G. *The Principles of Chemical Equilibrium*, 4th ed; Cambridge University Press: Cambridge, U.K., 1984.

(19) Weiland, R. H.; Chakravarty, T.; Mather, A. E. Solubility of Carbon-Dioxide and Hydrogen-Sulfide in Aqueous Alkanolamines. *Ind. Eng. Chem. Res.* **1993**, *32*, 1419−1430.

(20) Schmidt, K. A. G.; Maham, Y.; Mather, A. E. Use of the NRTL Equation for Simultaneous Correlation of Vapour-Liquid Equilibria and Excess Enthalpy. *J. Therm. Anal. Calorim.* **2007**, *89*, 61−72.

(21) *Spartan'08*; Wavefunction, Inc.: Irvine, CA.

(22) Frisch, M. J.; et al. *Gaussian 03*, revision D.02; Gaussian, Inc.: Wallingford, CT, 2004.

(23) Chamberlin, A. C.; Cramer, C. J.; Truhlar, D. G. Extension of a Temperature-Dependent Aqueous Solvation Model to Compounds Containing Nitrogen, Fluorine, Chlorine, Bromine, and Sulfur. *J. Phys. Chem. B* **2008**, *112*, 3024−3039.

(24) Chamberlin, A. C.; Kelly, C. P.; Pu, J.; Thompson, D. J.; Xidos, J. D.; Li, J.; Zhu, T.; Hawkins, G. D.; Chuang, Y.-Y.; Fast, P. L.; Lynch, B. J.; Liotard, D. A.; Rinaldi, D.; Gao, J.; Cramer, C. J.; Truhlar, D. G. *GAMESSPLUS, 4.8*; University of Minnesota: Minneapolis, MN, 2007 (software can be obtained from: http://comp.chem.umn.edu/gamessplus).

(25) Bates, R. G.; Pinching, G. D. *J. Res. Natl. Bur. Stand. (U. S.)* **1951**, *46*, 349−352.

(26) Datta, S. P.; Grzybowski, A. K. Acid Dissociation Constants of Ammonium Group in 2-Aminoethanol, 2-Aminoethyl Phosphate, and 2-Aminoethyl Sulphate. *J. Chem. Soc.* **1962**, 3068.

(27) Hall, N. F.; Sprinkle, M. R. Relations between the Structure and Strength of Certain Organic Bases in Aqueous Solution. *J. Am. Chem. Soc.* **1932**, *54*, 3469−3485.

(28) Hamborg, E. S.; Versteeg, G. F. Dissociation Constants and Thermodynamic Properties of Amines and Alkanolamines from (293 to 353) K. *J. Chem. Eng. Data* **2009**, *54*, 1318−1328.

(29) Kim, J. H.; Dobrogowska, C.; Hepler, L. G. Thermodynamics of Ionization of Aqueous Alkanolamines. *Can. J. Chem.* **1987**, *65*, 1726−1728.

(30) Lotz, J. R.; Block, B. P.; Fernelius, W. C. A Thermodynamic Study of Some Coordination Compounds of Metal Ions with Amines Containing Oxygen. *J. Phys. Chem.* **1959**, *63*, 541−544.

(31) Ojelund, G.; Wadso, I. Heats of Ionization of Some Alkylammonium and Hydroxy Alkylammonium Compounds. *Acta Chem. Scand.* **1968**, *22*, 2691.

(32) Hamborg, E. S.; Niederer, J. P. M.; Versteeg, G. F. Dissociation Constants and Thermodynamic Properties of Amino Acids Used in CO2 Absorption from (293 to 353) K. *J. Chem. Eng. Data* **2007**, *52*, 2491−2502.

(33) Littel, R. J.; Bos, M.; Knoop, G. J. Dissociation-Constants of Some Alkanolamines at 293-K, 303-K, 318-K, and 333-K. *J. Chem. Eng. Data* **1990**, *35*, 276−277.

(34) Oscarson, J. L.; Vandam, R. H.; Christensen, J. J.; Izatt, R. M. Enthalpies of Absorption of Hydrogen-Sulfide in Aqueous Diethanol-amine Solutions. *Thermochim. Acta* **1989**, *154*, 89−95.

(35) Schwabe, K.; Graichen, W.; Spiethoff, D. Physikalisch-chemische Untersuchungen an Alkanolaminen. *Z. Phys. Chem. (Munich)* **1959**, *20*, 68−82.

(36) Gonzalez, E. B.; Sanchez, F. G.; Garduza, O. H.; Rueda, E. B. Thermodynamics of Vapour−Liquid Equilibria in Aqueous Solutions of Acid Gas−Alkanolamine. *Rev. Mex. Fis.* **1998**, *44*, 250−267.

(37) Oscarson, J. L.; Wu, G.; Faux, P. W.; Izatt, R. M.; Christensen, J. J. Thermodynamics of Protonation of Alkanolamines in Aqueous-Solution to 325-Degrees-C. *Thermochim. Acta* **1989**, *154*, 119−127.

(38) Jensen, M. B.; Jorgensen, E.; Faurholt, C. Reactions between Carbon Dioxide and Amino Alcohols. 1. Monoethanolamine and Diethanolamine. *Acta Chem. Scand.* **1954**, *8*, 1137−1140.

(39) Jensen, A.; Jensen, M. B.; Faurholt, C. Studies on Carbamates 0.10. The Carbamates of Di-Normal-Propylamine and Di-Iso-Propyl-amine. *Acta Chem. Scand.* **1954**, *8*, 1129−1136.

(40) Sartori, G.; Savage, D. W. Sterically Hindered Amines for Co2 Removal from Gases. *Ind. Eng. Chem. Fundam.* **1983**, *22*, 239−249.

(41) Aroua, M. K.; Benamor, A.; Haji-Sulaiman, M. Z. Equilibrium Constant for Carbamate Formation from Monoethanolamine and Its Relationship with Temperature. *J. Chem. Eng. Data* **1999**, *44*, 887−891.

(42) Park, S. H.; Lee, K. B.; Hyun, J. C.; Kim, S. H. Correlation and Prediction of the Solubility of Carbon Dioxide in Aqueous Alkanolamine and Mixed Alkanolamine Solutions. *Ind. Eng. Chem. Res.* **2002**, *41*, 1658−1665.

(43) Jakobsen, J. P.; Krane, J.; Svendsen, H. F. Liquid-Phase Composition Determination in CO2-H2O-Alkanolamine Systems: An NMR Study. *Ind. Eng. Chem. Res.* **2005**, *44*, 9894−9903.

(44) McCann, N.; Maeder, M.; Hasse, H. A Calorimetric Study of Carbamate Formation. *J. Chem. Thermodyn.* **2011**, *43*, 664−669.

(45) McCann, N.; Duong, P.; Fernandes, D.; Maeder, M. A Systematic Investigation of Carbamate Stability Constants by H-1 NMR. *Int. J. Greenhouse Gas Control* **2011**, *5*, 396−400.

(46) Austgen, D. M.; Rochelle, G. T.; Peng, X.; Chen, C. C. Model of Vapor Liquid Equilibria for Aqueous Acid Gas Alkanolamine Systems Using the Electrolyte Nrtl Equation. *Ind. Eng. Chem. Res.* **1989**, *28*, 1060−1073.

(47) Austgen, D. M.; Rochelle, G. T.; Chen, C. C. Model of Vapor-Liquid-Equilibria for Aqueous Acid Gas-Alkanolamine Systems 0.2. Representation of H2s and Co2 Solubility in Aqueous Mdea and Co2

Solubility in Aqueous Mixtures of Mdea with Mea or Dea. *Ind. Eng. Chem. Res.* **1991**, *30*, 543−555.

(48) Wang, D. Equilibrium Constant Study for Carbamate Fomation in Alkanolamine Solutions from NMR Measurements. Master Thesis, University of Canterbury, Christchurch, New Zealand, 2001.

(49) Deshmukh, R. D.; Mather, A. E. A Mathematical-Model for Equilibrium Solubility of Hydrogen-Sulfide and Carbon-Dioxide in Aqueous Alkanolamine Solutions. *Chem. Eng. Sci.* **1981**, *36*, 355−362.

(50) Fernandes, D.; Conway, W.; Burns, R.; Lawrance, G.; Maeder, M.; Puxty, G. Investigations of Primary and Secondary Amine Carbamate Stability by H-1 NMR Spectroscopy for Post Combustion Capture of Carbon Dioxide. *J. Chem. Thermodyn.* **2012**, *54*, 183−191.

(51) Böttinger, W.; Maiwald, M.; Hasse, H. Online NMR Spectroscopic Study of Species Distribution in MEA−H2O−CO2 and DEA−H2O−CO2. *Fluid Phase Equilib.* **2008**, *263*, 131−143.

(52) Lee, L. L. *Thermodynamic Models for Natural Gas Sweetening Fluids*. Report on GPI/GPA Project 5091-260-2288; Univerisity of Oklahoma: Norman, OK, 1996; p 216.

(53) Kamps, A. P. S.; Balaban, A.; Jodecke, M.; Kuranov, G.; Smirnova, N. A.; Maurer, G. Solubility of Single Gases Carbon Dioxide and Hydrogen Sulfide in Aqueous Solutions of N-Methyldiethanolamine at Temperatures from 313 to 393 K and Pressures up to 7.6 MPa: New Experimental Data and Model Extension. *Ind. Eng. Chem. Res.* **2001**, *40*, 696−706.

(54) Edwards, T. J.; Maurer, G.; Newman, J.; Prausnitz, J. M. Vapor-Liquid-Equilibria in Multicomponent Aqueous-Solutions of Volatile Weak Electrolytes. *AIChE J.* **1978**, *24*, 966−976.

(55) Austgen, D. M., Jr. A Model of Vapor-Liquid Equilibria for Acid Gas-Alkanolamine-Water Systems. Ph.D. Dissertation, The University of Texas at Austin, 1989.

(56) Chang, H. T.; Posey, M.; Rochelle, G. T. Thermodynamics of Alkanolamine Water Solutions from Freezing-Point Measurements. *Ind. Eng. Chem. Res.* **1993**, *32*, 2324−2335.

(57) Posey., M. L. Thermodynamic Model for Acid Gas Loaded Aqueous Alkanolamine Solutions. Ph.D. Dissertation, The University of Texas at Austin, 1996.

(58) Kim, I.; Svendsen, H. F. Heat of Absorption of Carbon Dioxide (CO2) in Monoethanolamine (MEA) and 2-(Aminoethyl)-ethanolamine (AEEA) Solutions. *Ind. Eng. Chem. Res.* **2007**, *46*, 5803−5809.

(59) Arcis, H.; Ballerat-Busserolles, K.; Rodier, L.; Coxam, J. Y. Enthalpy of Solution of Carbon Dioxide in Aqueous Solutions of Monoethanolamine at Temperatures of 322.5 and 372.9 K and Pressures up to 5 MPa. *J. Chem. Eng. Data* **2011**, *56*, 3351−3362.

(60) Mathonat, C.; Majer, V.; Mather, A. E.; Grolier, J. P. E. Use of Flow Calorimetry for Determining Enthalpies of Absorption and the Solubility of CO2 in Aqueous Monoethanolamine Solutions. *Ind. Eng. Chem. Res.* **1998**, *37*, 4136−4141.

(61) Jou, F. Y.; Otto, F. D.; Mather, A. E. Vapor-Liquid-Equilibrium of Carbon-Dioxide in Aqueous Mixtures of Monoethanolamine and Methyldiethanolamine. *Ind. Eng. Chem. Res.* **1994**, *33*, 2002−2005.

(62) Kim, I.; Svendsen, H. F. Comparative Study of the Heats of Absorption of Post-Combustion CO2 Absorbents. *Int. J. Greenhouse Gas Control* **2011**, *5*, 390−395.

(63) Mathonat, C.; Majer, V.; Mather, A. E.; Grolier, J. P. E. Enthalpies of Absorption and Solubility of CO2 in Aqueous Solutions of Methyldiethanolamine. *Fluid Phase Equilib.* **1997**, *140*, 171−182.

(64) Kierzkowska, P. H.; Zarzycki, R. Calorimetric Measurements of CO2 Absorption into Aqueous N-Methyldiethanolamine Solutions. *Chem. Pap.* **2002**, *56* (4), 219−227.