Investigations of Primary and Secondary Amine Carbamate Stability by $^1$H-NMR Spectroscopy for Post Combustion Capture of Carbon Dioxide

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ABSTRACT
Carbamate formation is one of the major chemical reactions that can occur in solution in the capture of CO$_2$ by amine-based solvents, and their formation makes a significant enthalpy contribution to the absorption-desorption of CO$_2$ that occurs in the absorber/stripper columns of the PCC process. Consequently, the formation of carbamates of selected series of primary and secondary amines over the temperature range 288-318 K has been investigated by equilibrium $^1$H nmr studies, and the stability constants ($K_9$) for the equilibrium:

$$\text{RNH}_2 + \text{HCO}_3^- \rightleftharpoons K_9 \text{RNHCOO}^- + \text{H}_2\text{O}$$

are reported. van’t Hoff analyses have resulted in standard molar enthalpies, $\Delta H_m^o$, and entropies, $\Delta S_m^o$, of amine-carbamate formation. A $\Delta H_m^o-\Delta S_m^o$ plot generates a linear correlation for amine-carbamate formation (providing a mean standard molar free energy, $\Delta G_m^o$, for carbamate formation of about -7 kJ/mol), and this relationship helps provide a guide to the selection of an amine(s) solvent for CO$_2$ capture, in terms of enthalpy considerations. A linear $\Delta H_m^o-\Delta S_m^o$ plot also occurs for carbamate protonation.
The formation of the carbamates has been correlated with systematic changes in composition and structure, and steric effects have been identified by comparing molecular geometries obtained using density functional B3LYP/6-311++G(d,p) calculations. Trends in steric effects have been identified in the series of compounds monoethanolamine (MEA), 1-amino-2-propanol, 2-amino-1-propanol (AP) and 2-amino-2-methyl-1-propanol (AMP). In the case of 2-piperidinemethanol, 2-piperidineethanol and 3-piperidinemethanol, strong intramolecular hydrogen bonding is shown to be the likely cause for lack of carbamate formation, and in the ring systems of pyrrolidine, morpholine, piperidine and thiomorpholine trends in carbamate formation (as given by $K_0$) have been correlated with the internal ring angle at the amine nitrogen, as well as the planarity of the environment around the nitrogen atom.
1. Introduction

The great bulk of scientific evidence points to the fact that continued and growing greenhouse gas emissions, notably CO$_2$, are threatening climate patterns. Power generation, particularly from fossil fuels, accounts for approximately 25% of global CO$_2$ emissions, and these are set to rise dramatically over the next 25 years [1]. A wide range of options are being investigated to reduce greenhouse gas emissions [2], and post-combustion capture of CO$_2$ (PCC) followed by, for example, storage in underground formations, has the potential to reduce these emissions. This technology can be retrofitted to existing power plants, or integrated into new plants.

Carbon dioxide capture using aqueous amines is a well established technology which has been used to separate CO$_2$ from H$_2$ or CH$_4$, and is currently used in ammonia production and in natural gas processing [3]. Chemical absorption using aqueous amines involves two independent steps. Firstly, CO$_2$ absorption occurs at relatively low temperatures in the absorber column and, secondly, because the reaction is reversible, CO$_2$ desorption is able to occur at high temperatures in the stripper column. The regenerated amine solution is then circulated back to the absorber column and the process repeated [4].

Applying this technology to chemical absorption/desorption processes in PCC faces new challenges, particularly in regard to added energy consumption and hence cost. The majority of this energy is required for regeneration of the amine; that is, releasing CO$_2$ from the amine-solvent solution. The absorption enthalpy itself is directly important for the process as it partially determines the temperature profile in the absorber and the energy that must be input for desorption and amine regeneration. The enthalpy of CO$_2$ absorption/desorption consists of both physical and chemical contributions. From the viewpoint of the chemical reactions that occur in solution, an understanding of the chemistry of the reactions of CO$_2$ with amines is therefore crucial to the development of new amine-based solvents that have the potential to reduce energy costs, compared to current solvents.

In the PCC process, CO$_2$ reacts with an aqueous amine solution via two different pathways: formation of carbamic acid and its subsequent deprotonation to
carbamate, equation (1), or a simple acid-base reaction, formation of carbonic acid followed by deprotonation, equation (2).

\[ 2\text{RNH}_2 + \text{CO}_2 \xrightarrow{K} \text{RNHCOO}^- + \text{RNH}_3^+ \]  
(1)

\[ \text{RNH}_2 + \text{H}_2\text{O} + \text{CO}_2 \xrightarrow{} \text{HCO}_3^- + \text{RNH}_3^+ \]  
(2)

In equation (1) carbamates are the amides formed upon reactions between amines and carbonic acid. Depending upon its acidity, the carbamic acid may give up a proton to a second amine molecule to form a carbamate, resulting in an overall amine:CO\textsubscript{2} stoichiometry of 2:1 [5]. Both primary and secondary amines can follow this pathway, and under the conditions commonly found in PCC, the product is primarily the amine-carbamate. The second pathway that contributes to CO\textsubscript{2} absorption, equation (2), is CO\textsubscript{2} hydration to form bicarbonate, HCO\textsubscript{3}-. In this pathway an amine simply acts as a proton-accepting base, and possibly a catalyst, for the hydration of CO\textsubscript{2} [6,7]. The overall stoichiometry for this pathway is 1:1, so in terms of capacity it is more efficient for CO\textsubscript{2} absorption than the pathway given in equation (1). For tertiary (and some sterically-hindered) amines this is the only pathway that contributes to absorption of CO\textsubscript{2}. While both pathways have advantages and limitations, equation (1) is more favourable for its faster kinetics than equation (2) [5], and as such a thorough understanding of the factors that influence the formation of amine-carbamates is essential for the development of any new amine system.

Carbamate stability constants (\(K_9\); see below for complete definition of all stability constants relevant to this study) of simple amines, as defined in equation (3):

\[ \text{RNH}_2 + \text{HCO}_3^- \xrightarrow{K} \text{RNHCOO}^- + \text{H}_2\text{O} \]  
(3)

as well as amino acids, were reported as long ago as the 1950s. Studies included the carbamates of the propyl- and butyl-amines, and were obtained by chemical precipitation methods [8-10]. Other studies included the prototypical PCC alkanolamine, monoethanolamine (MEA), as well as diethanolamine (DEA) [11]. More recently, Sartori and Savage [12] studied the carbamates of MEA, 2-amino-2-methyl-1-propanol (AMP) and DEA by \textsuperscript{13}C nmr spectroscopy. Aroua et al. studied carbamate formation of MEA and DEA from 298 to 328 K, using a NaOH titration method [13,14], and Jou et al. [15] and Park et al. [16] studied MEA (as well as DEA, AMP and their mixtures) using vapour-liquid equilibrium (VLE) measurements from
273 to 423 K. $^{13}$C nmr spectroscopy was also used by Barth et al. [17] and Poplsteinova-Jakobsen et al. [18] to study MEA (as well as diglycolamine, diisopropanolamine, butylethanolamine and methyl diethanolamine) over the temperature range 293 to 363 K, while more recently McCann et al. used $^1$H nmr spectroscopy to study MEA (as well as 2-amino-1-propanol, propylamine and isobutylamine) at 303 K [19]. Isothermal titration calorimetry has also been used to study the formation of the carbamates of MEA, DEA and NH$_3$ at 298 K [20]. Other studies on DEA have included that by Böttinger et al., who used a combined $^{13}$C nmr and VLE approach to study carbamate formation from 293 to 333 K [21].

In this study we examine the formation of carbamates of series of primary and secondary acyclic and cyclic aliphatic alkanolamines/amines using $^1$H nmr studies, and report the temperature dependence of the carbamate formation constants. From these studies the standard molar enthalpies, $\Delta H_m^o$, and molar entropies, $\Delta S_m^o$ of carbamate formation are evaluated. The series of alkanolamines/amines were chosen to cover a range of related geometries, differing by, for example, substitution of –OH or –CH$_3$ groups at selected locations, thereby giving variations in electronic and stereochemical effects, and also cyclic structures with variations in ring heteroatom substitution and external pendant groups in the case of piperidine. Trends in the formation of carbamates are examined and, where possible, carbamate formation is correlated with stereochemical factors, ring strain, and electronic factors obtained from density functional B3LYP/6-311++G(d,p) calculations. This study provides a comprehensive report of enthalpy and entropy changes in solution for the reactions of carbonate species with series of amines that have been selected to demonstrate systematic changes in their structures.

2. Experimental

2.1 Materials

The primary amines monoethanolamine (MEA), 2-amino-1-propanol (AP), 2-amino-2-methyl-1-propanol (AMP), 2-amino-2-methyl-1,3-propanediol (AMPD), 2-amino-1,3-propanediol (BIS or serinol) and 2-amino-2-hydroxymethyl-1,3-propanediol (TRIS); and the secondary/cyclic amines diethanolamine (DEA), piperidine (PIP), morpholine (MORP), thiomorpholine (TMORP), piprazine (PIPZ), 1-
methylpiperazine (1-MPIPZ), pyrrolidine (PYRR), 2-piperidinemethanol (2-PIPDM), 2-piperidineethanol (2-PIPDE), 3-piperidinemethanol (3-PIPDM), 4-piperidinemethanol (4-PIPDM), 4-piperidineethanol (4-PIPDE) were obtained from Sigma-Aldrich with a purity of 95-99.8%, except for 2-PIPDE, which was 90%, and were used without any further purification. Sodium carbonate was purchased from Sigma-Aldrich. Hydrochloric acid was obtained from Ajax Finechem. The concentration of the acid was determined by titration with Na$_2$CO$_3$ using an automated titration apparatus under a nitrogen atmosphere. All solutions were stored in a glove bag under a nitrogen atmosphere.

2.2 $^1$H nmr titrations

For each alkanolamine/amine a stock solution of 0.040 M amine and 0.080 M Na$_2$CO$_3$ was prepared using ultra-high purity Milli-Q water, which had been boiled to remove CO$_2$ gas. Samples were prepared in a series of 5 mm-diameter nmr tubes, each containing a sealed glass capillary containing TSP (3-(trimethylsilyl)propionic acid-$d_4$, sodium salt) as the reference in D$_2$O, with the latter as the locking agent. The tubes were filled with 1.5 mL of stock solution, and different volumes of standardised 2.0 M HCl, in increments of 10 $\mu$L, were added to each series of tubes. The nmr tubes (over ¾ full of solution) were capped and sealed with “Parafilm” to ensure that no CO$_2$ was lost, although it should be appreciated that at higher acidities some CO$_2$ must escape from solution into the gas phase above the liquid. All samples were thermostatted for 24 hours or until complete equilibrium had been established. Only solutions with final pH values greater than 6 were used in the data analysis, as the potential for losing CO$_2$ at lower pH values cannot be discounted, despite the precautions taken to seal the tubes.

The $^1$H nmr spectra of the amine/Na$_2$CO$_3$/HCl solutions were measured on a Bruker Avance DPX-300 operating at a frequency of 300.13 MHz. An example of a series of spectra in the case of MEA is given in the Supporting Information, Figure S1. The relative integrals of the $^1$H nmr peaks were used to quantitatively investigate the formation of amine-carbamate species, as these are a direct measure of the hydrogen-containing species in solution. Thus the concentrations of initial and product species could be directly evaluated as the HCl was varied, taking into account
dilution. Separate signals for amine-carbamate and amine-carbamic acid cannot be individually resolved, but give rise to changes in chemical shift as the pH changes. Similar circumstances pertain to the amine and protonated amine species, which give rise to a single signal.

For the alkanolamines/amines that did not form carbamates, no changes in the composition of the solutions were observed, except that the chemical shifts for the alkanolamine/amine shifted as the pH was lowered. Again this is attributable to protonation of the amine. The limits of detection of the amine-carbamates were of the order of < ~0.5% of the major peaks of the amines/protonated amines in the $^1$H nmr spectra. This is based on the observation of the $^{13}$C satellites associated with, for example, the methyl resonances, $i.e.$ from $^1$J($^{13}$C,$^1$H) coupling (where the $^{13}$C natural abundance is 1.1%).

2.3 Data Analysis

We have recently developed a general reaction scheme that includes all interactions of an amine with CO$_2$ and all carbonate species in aqueous solution (note that $K_n$ represents an equilibrium constant) [22]. This is shown in the scheme below, which has been adapted to include the reactions of CO$_2$ with water to give HCO$_3^-$ and H$^+$ ($K_{CO2}$), and of CO$_2$ plus amine to give carbamate and H$^+$ ($K_{10}$).
In the data analysis the equations involving CO$_2$, equations (4) to (7), water, equation (8), and the equations involving the amine, equations (9) and (10), in addition to equation (3) above, that were used to fit the concentration data obtained from the $^1$H nmr integrated intensities were:

\[
\begin{align*}
\text{CO}_2{}^{\text{(aq)}} + \text{H}_2\text{O} & \overset{K_1}{\rightleftharpoons} \text{H}_2\text{CO}_3 \\
\text{CO}_2{}^{\text{(aq)}} + \text{OH}^- & \overset{K_2}{\rightleftharpoons} \text{HCO}_3^- \\
\text{CO}_3^{2-} + \text{H}^+ & \overset{K_3}{\rightleftharpoons} \text{HCO}_3^- \\
\text{HCO}_3^- + \text{H}^+ & \overset{K_4}{\rightleftharpoons} \text{H}_2\text{CO}_3 \\
\text{OH}^- + \text{H}^+ & \overset{K_5}{\rightleftharpoons} \text{H}_2\text{O} \\
\text{RNH}_2 + \text{H}^+ & \overset{K_6}{\rightleftharpoons} \text{RNH}_3^+ \\
\text{RNHCOO}^- + \text{H}^+ & \overset{K_6}{\rightleftharpoons} \text{RNHCOOH}
\end{align*}
\]

The data on the reactions of CO$_2$ and the $K_6$ data at all four temperatures were obtained from references [23,24] and fixed during analysis. The pathway ($K_9$) given by equation (3) is much easier to study experimentally, as opposed to $K_{10}$, and hence it is easier to evaluate an equilibrium constant for this reaction (note that equation (3) has been the dominant reaction pathway used in the literature for which carbamate stability constants have been reported, and is often designated as $K_{\text{carb}}$ [8-21]). By microscopic reversibility, it is possible to calculate values for $K_{10}$, equation (11), by the expression $K_{10} = K_9 \cdot K_{\text{CO}_2}$, with data for $K_{\text{CO}_2}$ obtained from reference [25].

\[
\begin{align*}
\text{RNH}_2 + \text{CO}_2 & \overset{K_{10}}{\rightleftharpoons} \text{RNHCOO}^- + \text{H}^+
\end{align*}
\]

For the calculations of the concentrations of amine and amine-carbamate only well separated peak signals were used to obtain peak integrals. All data analysis was performed in ReactLab-Equilibrium [26] and in-house software written in Matlab. The analysis of the equilibrium concentration data showed good agreement between the experimental and the calculated values. An example of the experimental data and fitted curves for the MEA/CO$_3^{2-}$/HCl system at the four different temperatures is
shown in Figure 1. The markers represent experimental values based on $^1$H nmr integrated intensities and the lines represent calculated values based on the fitted model for the four different temperatures. Titrations with the other alkanolamine/amines showed similar results, although the spectra were more complex from the increased complexity of their molecular structures. Nevertheless, individual peaks attributable to both amine and the amine-carbamate (and their protonated forms) could be identified in all measurements, and the peak positions over the course of the titration showed similar trends to those of MEA when carbamate formation occurred.

Activity coefficient corrections were applied to all charged species. While not perfect, the corrections applied are certainly superior to the alternative of ignoring them altogether. Estimates for the activity coefficients were based on the simple Debye-Hückel equation, as given in equation (12).

$$\log_{10} \gamma_i = \frac{-Az_i^2 \sqrt{\mu}}{1+\sqrt{\mu}}$$

In this equation $\mu$ is the ionic strength of the solution, $\gamma_i$ is the activity coefficient of species $i$, $z_i$ the charge on the $i$th component, while the parameter $A$ is defined by the dielectric constant of the solvent and the temperature [27,28]. Nonlinear least-squares fitting of the equilibrium constants was based on standard Newton-Gauss-Levenberg/Marquardt algorithms which also deliver error estimates for the fitted parameters [29,30]. From the data analysis $\log_{10} K_9$ (i.e. carbamate formation), equation (3), and $\log_{10} K_8$ (protonation of the carbamate anion) were obtained at 288, 298, 308 and 318 K.

The standard molar enthalpy change $\Delta H_m^\circ$ and the standard molar entropy change $\Delta S_m^\circ$ were calculated using a van’t Hoff plot of $\ln K$ against $1/T$, equation (13). The molar free energy change ($\Delta G_m^\circ$) under standard state conditions was calculated from $\Delta H_m^\circ$ and $\Delta S_m^\circ$ using equation (14).

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$
2.4 Density functional theory calculations

Quantum chemical calculations were performed using Spartan ’04 or ’06 (Wavefunction Inc., Irvine, CA, USA). Calculations used, unless otherwise indicated, the B3LYP density functional method, with a 6-311++G(d,p) basis set. For each molecule, all possible geometries were explored using the molecular mechanics conformer search module, and the geometry with the lowest strain energy was submitted for equilibrium geometry calculations. In several cases it was found that the second lowest strain energy configuration produced a more stable geometry. This occurred for AP and DEA.

The charge on an atom is not a quantum chemical observable, and there is no unique way of assigning electronic charge to an atom in a molecule [31-33]. In the present study we have employed electrostatic charges, rather than Mulliken or natural charges. The Mulliken charge approach has well-known shortcomings and is, moreover, sensitive to basis set size [31-33]. While electrostatic and natural charges are much less sensitive to basis set size and both have advantages and disadvantages [32,33], it was found in initial studies that the electrostatic charges offered a wider range of charge values and better differentiation between the calculated charges for very similar compounds than did natural charges. For this reason electrostatic charges were preferred. The electrostatic charge on the nitrogen atom of the amine group, $Q(N)_{\text{ES}}$, and also the oxygen atoms of the anionic carbamates, were obtained from the output available in Spartan. Note that for AP and DEA averaged values for the charge metrics were used based on the two lowest optimised geometries, which differed by $< R T (2.48 \text{ kJ/mol})$.

3. Results and discussion

In the present study selected series of related alkanolamines/amines have been examined, covering primary and secondary alkanolamines and cyclic secondary amines. Not all amines/alkanolamines formed carbamates, and reasons for this are analysed below. For those species that formed carbamates, the $\log_{10} K_0$ values at 298 K, as well as the derived $\Delta H^\circ_m$ and $\Delta S^\circ_m$ data are given in Table 1. Full $\log_{10} K_0$ temperature data (288-318 K), including comparison with available literature data, and $\Delta G^\circ_m$ values are available in the Supporting data, Table S1. Also included in
Table 1 are values of $\log_{10} K_{10}$, equation (11), which is an important reaction regarding CO$_2$ absorption by amine-based solvents in PCC applications. The $\log_{10} K_{10}$ values range from -3.6 to -5.6, as $\log_{10} K_9$ is dominated by $\log_{10} K_{\text{CO}_2}$. Carbamate protonation gives the corresponding carbamic acid, full $\log_{10} K_8$ data and the standard molar enthalpies, $\Delta H_m^\circ(\text{carbH})$, standard molar entropies, $\Delta S_m^\circ(\text{carbH})$ and standard molar free energies of carbamate protonation, $\Delta G_m^\circ(\text{carbH})$, are given in the Supporting data, Table S2.

Few values of $\log_{10} K_9$ for amine-carbamate formation have been reported, and fewer values for the standard enthalpy of carbamate formation, $\Delta H_m^\circ$. Most studies have concentrated on MEA and closely related compounds. Our value for $\log_{10} K_9 = 1.76(2)$ at 298 K is consistent with previously reported data (Table S1). However, there is a considerable spread in the reported value for $\Delta H_m^\circ$. Values vary from -13(2) to -33(2) kJ/mol [13,15-17], and a recent value for $\Delta H_m^\circ$ based on isothermal titration calorimetry of -29.7(1) kJ/mol, together with an accompanying $\Delta S_m^\circ$ of -69.0(7) J/mol/K, has been recently reported [20]. Our values for $\Delta H_m^\circ$ and $\Delta S_m^\circ$ are -18(1) kJ/mol and -25(3) J/mol/K, respectively. The former is intermediate within the reported data range for $\Delta H_m^\circ$, but lower than the calorimetrically-determined value, while $\Delta S_m^\circ$ is also lower than the reported value [20]. Smaller variations in $\log_{10} K_9$ and $\Delta H_m^\circ$ appear for DEA. Our $\log_{10} K_9$ value is in good agreement with the reported data (Table S1), but again there is considerable variation in $\Delta H_m^\circ$. Values ranges from -12.4 to -34.1 kJ/mol [14,17,21], with a calorimetrically-determined value of -23.7(9) kJ/mol, and a $\Delta S_m^\circ$ of -63(4) J/mol/K [20]. Our values of -18(1) kJ/mol and -44(4) J/mol/K for $\Delta H_m^\circ$ and $\Delta S_m^\circ$, respectively, are slightly lower than those reported in the recent calorimetric study.

3.1 Correlations of $\log_{10} K_9$ with electronic and structural properties; $\Delta H$-$\Delta S$ plots

The thermodynamic data listed in Table 1 for the carbamate-forming alkanolamines/amines can be analysed using a $\Delta H_m^\circ$–$\Delta S_m^\circ$ plot, as shown in Figure 2. Enthalpy and entropy values derived from $\log_{10} K_9$ data for ammonium carbamate formation using a van’t Hoff plot are also included [34] (although the original data does not include ionic strength corrections). This plot sheds light on the structural trends for carbamate formation. The $R^2$ value (linear correlation coefficient) is 0.955,
which effectively results from the relatively similar $\Delta G_m^o$ values and hence values of log$_{10} K_9$ for carbamate formation, which has a mean value of 1.27 with a standard deviation of 0.56. The greatest value for log$_{10} K_9$ occurs for PYRR, with a value of 2.69 at 298 K. The $\Delta H_m^o$–$\Delta S_m^o$ correlation works because $\Delta G_m^o$ must be < 0 kJ/mol, and for reversible carbamate formation must not be too negative, say > -18 kJ/mol (these boundaries have been added to Figure 2). All ($\Delta H_m^o$, $\Delta S_m^o$) points are therefore restricted to a corridor close to the line-of-best fit in Figure 2, which must result in a high $R^2$ value. The plot therefore has predictive value, if $\Delta H_m^o$ or $\Delta S_m^o$ can be independently estimated either empirically, such as through comparisons with a library of related compounds, or based on theoretical calculations.

There are several trends in $\Delta H_m^o$ and $\Delta S_m^o$ that can be identified for amines that lead to carbamate formation:

(a) As $\Delta H_m^o$ becomes more exothermic (i.e. negative), $\Delta S_m^o$ also becomes more negative, thereby generating more order in the system. This is a consequence of the relatively constant $\Delta G_m^o$ for carbamate formation. As carbamate formation in equation (3) involves ionic species, it is not surprising that $\Delta S_m^o$ is generally quite negative, as there will be a large amount of solvent reorganisation and ordering (i.e. electrostriction) of the solvent molecules associated with formation of the negatively-charged HCO$_3^-$ and amine-carbamate species. Indeed, solvent reorganisation should dominate $\Delta S_m^o$ in reactions involving ionic species.

(b) In the series NH$_2$CO$_2^-$ → MEA-carbamate → AP-carbamate, $\Delta H_m^o$ becomes more exothermic, suggesting a trend with increasing size of the aliphatic organic group. Indeed, for 4-PIPDM and 4-PIPDE, $\Delta H_m^o$ increases with increasing length of the pendant side chain. The large negative value of $\Delta S_m^o$ for 4-PIPDE is likely related to the highly-fluctuational –CH$_2$CH$_2$OH group and interactions with solvent molecules through hydrogen bonding, thereby generating order, while the smaller –CH$_2$OH group is less fluctuational and generates a less negative $\Delta S_m^o$ value.

(c) In the case of the cyclic PYRR and PIPD systems, $\Delta H_m^o$ becomes more exothermic on decreasing the ring size, and this is consistent with a greater release of ring strain in PYRR (as discussed below) by a change in conformation and accompanying solvent reorganisation.
For 1-MPIPZ and PIPD, more positive values of $\Delta S_m^\circ$ presumably result from considerable conformational change produced in their ring structures, and reorientation of the $-\text{CH}_3$ substituent in 1-MPIPZ, on carbamate formation, thereby increasing the solvent ordering within both systems.

For the series of compounds investigated, several amines/alkanolamines did not form carbamates, and reasons for this are discussed below.

### 3.2 Primary alkanolamines

Of the six alkanolamines studied, MEA, AP, AMP, BIS, AMPD and TRIS, only MEA and AP formed carbamates. Examination of the electrostatic charge for the amine group nitrogen atom, $Q(N)_{\text{ES}}$, (Supporting data, Table S3), shows that all calculated charges are more negative than those of the secondary amines examined, and specifically DEA, which has the lowest negative charge on nitrogen of any amine that forms a carbamate. Thus all of the primary alkanolamines are relatively strong bases. This is also indicated by their $\log_{10} K_b$ values for amine protonation, which vary from 8.10 to 9.67 at 298 K (Supporting data, Table S3) [24]. It also indicates that the lack of carbamate formation for AMP, BIS, AMPD and TRIS is most likely to be stereochemical in origin, rather than from a lack of basicity. Based on semi-empirical MNDO calculations, Chakraborty et al. argued that the nitrogen in AMP, relative to MEA, is softer, with a smaller HOMO-LUMO (highest occupied molecular orbital-lowest unoccupied molecular orbital) energy gap and a higher (more positive) energy for the HOMO (both effectively a measure of atom hardness) [35]. On the basis of these electronic effects, they concluded that carbamate formation was less likely in AMP. However, examination of the HOMO-LUMO gap and HOMO energy data in Table S3 for the six structurally-related alkanolamines, a wider range of species than used by Chakraborty et al., shows no trends that correlate with carbamate formation.

In the sequence MEA $\rightarrow$ AP $\rightarrow$ AMP, which involves successive replacement of a hydrogen on the carbon $\alpha$ to the amine group by a $-\text{CH}_3$ group, $Q(N)_{\text{ES}}$ becomes progressively more negative. The increasing negative charge is expected as the $-\text{CH}_3$ group is a good electron donor. Electron donation is only slightly reduced by replacing a hydrogen on a $-\text{CH}_3$ group by an $-\text{OH}$, as found in BIS relative to AP and
TRIS relative to AMP, such that the expected increase in negative charge on nitrogen is not as great in both cases. This is not surprising, given the highly electronegative nature of oxygen. Addition of a –CH$_3$ group at the carbon $\alpha$ to the amine group in BIS, to give AMPD, results in an increasing negative charge on nitrogen, as expected.

While MEA forms a carbamate, $\log_{10} K_9$ decreases in AP, which has a –CH$_3$ group on the carbon $\alpha$ to the amine nitrogen. Addition of a second –CH$_3$ group to the $\alpha$ carbon gives AMP, which does not form a carbamate. The trend is observed despite $Q(N)_{ES}$ becoming progressively more negative in the sequence MEA $\rightarrow$ AP $\rightarrow$ AMP, and suggests a stereochemical effect from the –CH$_3$ group. Likewise, BIS, AMPD and TRIS all have more negative charges on nitrogen than does MEA, yet they do not form carbamates. These species have –CH$_2$OH and –CH$_3$ groups located at the $\alpha$ carbon, and the stereochemical effect of the former is apparently greater than that of the latter (which is demonstrated by the fact that BIS does not form a carbamate, yet AP does), so that it is not surprising that these species do not form carbamates. Note that placement of a –CH$_3$ group on the carbon $\beta$ to the nitrogen atom, to give 1-amino-2-propanol (1-A-2-P), does result in carbamate formation [36]. Thus there is little stereochemical effect from the –CH$_3$ group further away from the amine nitrogen atom.

The reduced stability of a carbamate with one or more –CH$_3$ groups on the $\alpha$ carbon is caused by the close approach of the oxygen atoms of the –COO$^-$ group to the hydrogen atoms of one or more close –CH$_3$ groups. This introduces a significant stereochemical strain in the molecule. da Silva and Svendsen compared the equilibrium geometries of the carbamates of MEA and AMP using B3LYP/6-311++G(d,p) calculations [37]. These calculations have been repeated in the present study, with almost identical results, and supplemented with equivalent calculations on the carbamates of AP and 1-A-2-P. The relevant data appear in Table 2. The N–C–C(OH) angle decreases from 114.55° (114.53° [37]) in MEA-carbamate to 111.40° (111.38° [37]) in AMP-carbamate as a result of the presence of the two –CH$_3$ groups on the carbon $\alpha$ to the amine nitrogen atom. This indicates that the nitrogen atom, along with the carbamate functionality, is forced away from a –CH$_3$ on the $\alpha$ carbon. The analogous values for AP-carbamate and 1-A-2-P-carbamate are 113.06° and
114.63°, respectively, the former intermediate between those of MEA- and AMP-carbamates, as expected, as it has only one close –CH$_3$ group compared to two in AMP-carbamate, while the angle in 1-A-2-P-carbamate is similar to that in MEA-carbamate, showing that there is almost no effect from a –CH$_3$ group on the β-carbon. A consequence of a smaller N–C–C(OH) angle is that the intramolecular (OC)$_2$O···H(O) bond becomes shorter, but also that the (O$_2$)C–N–C angle increases (Table 2). The O–C–C, (H···)O–C–N and H–O–C bond angles are almost constant (differences of only 1.50, 1.21 and 0.68°, respectively, between the MEA- and AMP-carbamates). The steric effect is also demonstrated by the progressively decreasing intramolecular hydrogen bond length, with (OC)$_2$O···H(O) distances similar for the carbamates of MEA and 1-A-2-P, and decreasing from MEA-carbamate by 0.020 Å for AP-carbamate and a further 0.022 Å in the case of AMP-carbamate.

An interesting comparison can also be made with carbamates of the butylamines [10]. The analogous data is given in Table 2. In this case the N–C–C angles decrease from 116.5° in isobutylamine-carbamate to 109.67° (note, average of three angles!) in t-butyramine-carbamate, as log$_{10} K_9$ progressively decreases. This is the same trend as found for the alkanolamine-carbamates. The (O$_2$)C–N–C angle is constant except for t-butyramine-carbamate when it increases significantly, while the closest non-bonding (C)O···H(C) distance, other than that to the amine hydrogen, is fairly constant in the four carbamate structures. Interestingly, t-butyramine forms a carbamate, yet it has three –CH$_3$ groups on the carbon α to the –NH$_2$ group. The formation of a carbamate in this case appears to be linked to a the longer N–C(O$_2$) bond in all of the butylamine-carbamate structures compared to the alkanolamine-carbamates, thereby reducing steric strain from the –CH$_3$ group(s) (Table 2). This highlights the differences between the alkanolamines and amines in carbamate formation.

### 3.3 Secondary amines; cyclic amines

DEA, PIPD, 4-PIPDM, 4-PIPDE, PIPZ, 1-MPIPZ, MORP, TMORP and PYRR all form carbamates. No carbamate formation was observed for 2-PIPDM, 2-PIPDE or 3-PIPDM. For all species the nitrogen charge varies from -0.44 to -0.67 e$^-$ (Supporting data, Table S3) with the least negative charge found in DEA, which
forms a carbamate. The fact that there are two –CH$_2$– groups bound to nitrogen might suggest that a stereochemical problem could reduce carbamate stability. However, the log$_{10} K_9$ values of PIPD (cyclic) and DEA (acyclic) are not that much less than that of MEA, so that having two –CH$_2$– groups bound to the nitrogen in a secondary amine does not cause a significant stereochemical problem, such that carbamate formation does not occur. DEA has the freedom to rotate both of its –CH$_2$CH$_2$OH arms around nitrogen, unlike the ring systems, and also has a slightly lower log$_{10} K_9$ value than does PIPD. This, therefore, suggests some minor steric influence.

All of the cyclic amines have more negative nitrogen charges than does DEA, and also have higher log$_{10} K_6$ (amine protonation) values [24], which indicates that lack of carbamate formation for 2-PIPDM, 2-PIPDE and 3-PIPDM must be stereochemical rather than electronic in nature, or occurs for another reason. Steric hindrance cannot occur in 3-PIPDM, as the –CH$_2$OH group is too far away from the secondary amine nitrogen atom, while 2-PIPDM and 2-PIPDE both mimic DEA, which does form a carbamate. The relative energies of the potential carbamates of 2-PIPDM and 3-PIPDM, and 2-PIPDE were actually 34.1 and 40.1, and 42.8 kJ/mol, respectively, more stable than their analogous (and isodesmic-like [38]) 4-PIPDM- and 4-PIPDE-carbamates, (thermal and zero point energies are likely to be almost identical in these species, and were not included in the above calculations). The increase in stability is caused by the presence of intramolecular hydrogen bonding, which is not possible in 4-PIPDM and 4-PIPDE. All 2- and 3-substituted amines should therefore form carbamates based on electronic (i.e. their $Q(N)_{ES}$ values) and stereochemical considerations. No clear trend was observed in the HOMO-LUMO gap, or in the energy of the HOMO itself for these species (Supporting data, Table S3). Thus it is suggested that 2-PIPDM, 2-PIPDE and 3-PIPDM do not form carbamates because the parent amines all have strong intramolecular hydrogen bonds. Thus B3LYP/6-311++G(d,p) calculations give intramolecular N···H(O) distances for 2-PIPDM, 2-PIPDE, and 3-PIPDM of 2.316, 2.021 and 2.035, respectively, for their equilibrium geometries. It is assumed that these interactions are strong enough in aqueous solution to prevent carbamate formation, despite competition from hydrogen bonding to the solvent water molecules. While the calculated equilibrium geometries have N···H(O) intramolecular hydrogen bonds, alternative structures with (H)O···H(N) intramolecular hydrogen bonds may also be drawn. However, for 2-PIPDM, 2-PIPDE
and 3-PIPDM these are 19.0, 24.2 and 19.5 kJ/mol, respectively, less stable than the structures with N···H(O) bonds (B3LYP/6-311G* calculations).

In the absence of steric effects or strong intramolecular hydrogen bonding, it would be expected that formation of a carbamate would depend on the basicity of the amine nitrogen atom, and hence be related to the electronic charge on the nitrogen atom. However, for those species that do form carbanates, there was no overall correlation of log$_{10}$ $K_9$ with $Q(N)_{ES}$, even when taking a selected subset of data, such as the cyclic amines. Moreover, there was no strong correlation with the log$_{10}$ $K_6$ of the amine/alkanolamine, or just for the cyclic amines. Attempted correlation with the HOMO-LUMO energy gap, or the energy of the HOMO, was also unsuccessful. This is not surprising as the make-up of the HOMO and LUMO are complex in these systems, involving contributions from several different types of atoms.

Within the ring systems steric strain will have a major effect on the basicity of the nitrogen atom. In cyclic systems basicity depends on the size of the ring and the nature of the heteroatoms (e.g. cyclic amines vs. cyclic phosphines) [39]. For the present group of amines, there are rings of different sizes, different types of substituents, and some with multiple as well as different heteroatoms. It is thus not surprising that trends are hard to discern given the limited range of species examined. However, some measure of ring strain at the secondary nitrogen can be gained from the magnitude of the internal C–N–C ring angle (based on B3LYP/6-311++G(d,p) calculations). When the neutral amines are arranged in decreasing order of log$_{10}$ $K_9$ (together with their calculated C–N–C angles) as follows:

PYRR (105.26°) > PIPZ (111.79°) > 4-PIPDM (112.32°) ~ 4-PIPDE (112.13°) > PIPD (112.62°) ~ MORP (111.06°) > 1-MPIPZ (111.31°) > TMORP (114.18°)

the C–N–C angle correlates inversely with log$_{10}$ $K_9$. The smallest angle is found in the 5-membered ring PYRR, which has the highest log$_{10}$ $K_9$, while the largest angle is found in the 6-membered ring of TMORP, which has the lowest log$_{10}$ $K_9$. The remaining amines can be grouped together (with an average C–N–C angle = 111.87°), and have log$_{10}$ $K_9$ values that are similar and intermediate between those of PYRR and TMORP. The calculated C–N–H angles vary accordingly, 112.75° for PYRR, an
average of 110.63° for the intermediate six cyclic systems, and 110.04° for TMORP. Thus the sum of the bond angles around nitrogen increases from 330.76° in PYRR to 334.26° in TMORP. This indicates that the nitrogen environment becomes more planar, so that the lone pair on nitrogen assumes more p character from PYRR to TMORP, making it a weaker base towards an acid and consistent with the trend in log_{10} K_9. However, the lack of absolute correlation of log_{10} K_9 with the C–N–C angle suggests that several other factors play a role. For example, the least negative charges are found on the two amines with the lowest log_{10} K_9 values, 1-MPIPZ and TMORP, while the other cyclic amines all have similar values of Q(N)_{ES}. Electronic charge is, therefore, one such factor.

On formation of a carbamate, the internal ring C–N–C angle increases relative to that in the parent amine, and the nitrogen becomes close to coplanar with the surrounding three carbon atoms. In the X-ray crystal structures of the PIPD-carbamate and MORP-carbamate anions, the internal C–N–C angles are 114.44 (±0.12) and 115.1 (±0.5)°, respectively [40,41]. If the nitrogen and three carbon atoms were rigorously coplanar, the (O_2)C–N–C1–C5 dihedral angle would be 180° (the numbers following the carbon atoms are their positions around the piperidine ring). The experimental values for PIPD-carbamate and MORP-carbamate are 163.4 and 165.2°, respectively, showing that the nitrogen is slightly displaced from the plane of the surrounding three carbon atoms. Similar (and more extensive) data comes from B3LYP/6-311++G(d,p) calculations. In the carbamates of PYRR, PIPD, MORP and TMORP, the calculated C–N–C angles are 108.36, 113.97, 112.39, and 114.97°, respectively, all greater than those in the free amines. Thus one consequence on formation of carbamates is the increase in internal C–N–C angle, as the environment around nitrogen becomes more planar (i.e. bonding tends towards sp^2 hybridization, with the nitrogen lone pair having higher p character). The change in C–N–C angle from the neutral amine to amine-carbamate is PYRR (+3.10°) > PIPD (+1.35°) > MORP (+1.33°) > TMORP (+0.79°). The significant change for PYRR (thereby decreasing ring strain and the nitrogen approaching sp^3 hybridization in the carbamate) is consistent with the high value of log_{10} K_9, while the low value for TMORP is consistent with the observation that the internal ring angle does not change greatly on carbamate formation (and actually moves further away from sp^3 hybridization towards sp^2 (+p) hybridization). For PYRR, the C–N–C angle is able to
increase in the carbamate because the 4 CH$_2$ groups in the ring twist, so that they become staggered with respect to each other (giving a gauche conformation). Thus the ring C–C–C–C dihedral angle in PYRR increases from 1.42° in the free amine to 24.33° in the carbamate.

3.4 Alkanolamine/amine carbamic acids

A further result of the fitting procedures of the $^1$H nmr data was the determination of the protonation constants, log$_{10}$ $K_8$, for the alkanolamine/amine carbamates. These are difficult to obtain accurately, as at lower pH values CO$_2$ is lost from solution. Consequently, in the present study only $^1$H nmr signal intensity data at pH > 6 was used in the analysis, as noted above. Few data are available for comparison, and of the present library of amines, only values for MEA and AP have been reported. The log$_{10}$ $K_8$ for MEA has been reported as 7.49(2) at 303 K [19] and 7.93(7) at 298 K [20], while that of AP is 8.0(2) at 303 K [19]. The present values are slightly lower than these values, and this may be related to the amount of CO$_2$ in solution at the low pH values required to obtain data at significant concentrations of the protonated carbamates in solution.

In the present work, attempts to correlate log$_{10}$ $K_8$ with the calculated electrostatic charges on the oxygen atoms, $Q$(O)$_{ES}$, of the carbamate anions were unsuccessful. This is not surprising given the range of structures studied, despite the site of protonation being somewhat removed from the rest of the carbamate anion. Again there are no correlations with the HOMO-LUMO energy gap or the energy of the HOMO itself for the carbamate anions.

The thermodynamic data for protonation of the carbamate anions (Supporting data, Table S2) also can be analysed using a $\Delta H_m^o$($\text{carbH}$)–$\Delta S_m^o$($\text{carbH}$) plot. This is shown in Figure 3. For this relationship $R^2 = 0.967$. However, such a correlation is not surprising for protonation of the carbamate anions, as a similar correlation exists for protonation of the aliphatic carboxylate anions from C3 to C6 ($R^2 = 0.969$; see also Supporting data, Figure S3) [42,43]. Both correlations result from similar $\Delta G_m^o$ values for protonation within each of the series, but different (mean) values between series (carbamates: $\Delta G_m^o = -43.1$ kJ/mol; carboxylates -27.6 kJ/mol). In the present
case, changes in composition and basicity of the parent amines appear to have little effect on the carbamate protonation constants. This is not surprising as the site of protonation is far removed both spatially and electronically from the rest of the molecule.

3.5 Implications of the $\Delta H_m^o-\Delta S_m^o$ plot for carbamate formation and protonation to CO$_2$ absorption/desorption in PCC applications

Recently, McCann et al. developed a model for the prediction of CO$_2$ capacity and associated enthalpy changes in amine-based solvents during absorption/desorption of CO$_2$ [44]. For MEA, assuming a typical flue gas composition with a CO$_2$ pressure of 12 kPa, a 30 wt % MEA solution, and absorption and desorption temperatures of 40 and 100°C, respectively, the total enthalpy for CO$_2$ desorption at 40°C was shown to be ~83 kJ/mol. Of this, ~50 kJ/mol is associated with deprotonation of MEA (together with a minor contribution involving ionisation of H$_2$O). This contribution was found to be more important than the formation of gaseous CO$_2$ from CO$_2$(aq) and H$_2$CO$_3$ (~21 kJ/mol), or from the decomposition of MEA-carbamate (~12 kJ/mol). It is apparent that of the chemical reactions that occur in solution, the contribution from protonation/deprotonation of the amine to the overall enthalpy change is highly significant. When carbamate formation occurs, a significant, although smaller, contribution to the enthalpy change also occurs.

The overall equilibrium constant for the reaction of CO$_2$ with amine (in a 1:2 ratio), as given by equation (1), is:

$$K_c = \frac{[\text{RNHCOO}^-][\text{RNH}_3^+]}{[\text{CO}_2][\text{RNH}_2^2]^-}$$ (15)

This can be related to the equilibrium constants for equation (3) ($K_9$), equation (5) ($K_2$), and equation (9) ($K_6$) by the expression $K_c = (K_9).(K_2).(K_6)$. The $\Delta H_m^o$ and $\Delta S_m^o$ values follow accordingly, with data on the CO$_2$-HCO$_3^-$ system and amine protonation coming from references [23-25]. Thus provided data on carbamate formation ($K_9$) and amine protonation ($K_6$) are known, thermodynamic data for equation (1) can be calculated, effectively defining all amine-based enthalpy changes in solution in PCC applications.
Previously, we have provided correlations of the enthalpy of protonation of an alkanolamine/amine with structure, leading to suggestions for the best amine(s) to employ in PCC applications, based on this criterion [24]. Amine protonation/deprotonation provides the major contribution to the enthalpy changes that occur in solution, and a more exothermic $\Delta H_m^o$ for protonation may be regarded as important as it results in a greater difference in $\log_{10} K_6$ between the absorber and stripper and hence to an increased energy efficiency for the process. On carbamate formation, the type of correlations found in Figures 2 and 3 can also provide information on enthalpy contributions, in this case for amine-carbamate formation and carbamate protonation. While there is as yet only a limited range of data available to provide structural and thermodynamic insights, some interpretation has been provided above. In order to decide on the best amine(s) for PCC applications these structure-enthalpy relationships need to be considered, along with consideration of the amine protonation/deprotonation reactions that occur in solution.

4. Conclusions

The formation of selected series of amine-carbamates have been investigated using $^1$H nmr studies at four different temperatures ranging from 288-318 K. Many of these values have been obtained for the first time. van’t Hoff analyses have resulted in standard molar enthalpies and entropies for carbamate formation, and trends for related species have been discussed. A $\Delta H_m^o - \Delta S_m^o$ plot shows a linear relationship which provides a guide to the selection of an amine for PCC purposes based on carbamate formation. A $\Delta H_m^o$(carbH)–$\Delta S_m^o$(carbH) plot for carbamate protonation also produces a linear correlation.

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Supporting Data Available

TABLES S1-S3. Temperature dependence (288-318 K) of $\log_{10} K_9$, and values of $\Delta H_m^o$, $\Delta S_m^o$ and $\Delta G_m^o$, including literature data and references (S1); Temperature
dependence (288-318 K) of log $K_8$, and values of $\Delta H_m^o$(carbH), $\Delta S_m^o$(carbH) and $\Delta G_m^o$(carbH) (S2); All $Q(N)_{ES}$ data, log$_{10}$ $K_6$ values for amines, HOMO-LUMO energy gaps and HOMO energies of alkanolamines/amines (S3).

Figures S1-S2. $^1$H nmr spectroscopic titration of 0.040 M MEA/0.080 M Na$_2$CO$_3$ solution with 2.0 M HCl (S1); Plot of $\Delta H_m^o–\Delta S_m^o$ for the protonation of aliphatic carboxylate anions (C3-C7) (S2).

### References


TABLE 1. Log\(_{10}\) \(K_9\) (carbamte formation) log\(_{10}\) \(K_{10}\), log\(_{10}\) \(K_8\) (carbamate protonation) (all at 298 K) and the \(\Delta H_m^\circ\) and \(\Delta S_m^\circ\) for carbamate formation, and the \(\Delta H_m^\circ\)(carbH) and \(\Delta S_m^\circ\)(carbH) for carbamate protonation. (Standard deviations in last figure in parentheses.)

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<th>Amine</th>
<th>(\log_{10} K_9)</th>
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<th>(\Delta S_m^\circ) /J/mol/K</th>
<th>(\log_{10} K_{10})</th>
<th>(\log_{10} K_8)</th>
<th>(\Delta H_m^\circ) (carbH) /kJ/mol</th>
<th>(\Delta S_m^\circ) (carbH) /J/mol/K</th>
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TABLE 2. Log_{10} K_9, and the geometrically important distances and angles for the carbamates of MEA, 1-amino-2-propanol (1-A-2-P), AP, AMP and the isomeric forms of the butylamines (B3LYP/6-311(++)G(d,p) calculations).

| Alkanolamine-carbamates | Parent amine | log $K_9$ 298 K; $\mu = 0$ M N–C–C angles (°) (O_2)C-N-C angle (°) d[O⋯H] (Å) d[(O_2)C–N] (Å) |
|-------------------------|--------------|----------------------------------|-----------------|-----------------|-----------------|
| MEA                     | 1.76         | 114.55 b, 121.56, 1.648, 1.443    |                 |                 |                 |
| 1-A-2-P Carbamate formed | 114.63 b     | 121.42, 1.635, 1.442             |                 |                 |                 |
| AP                      | 0.98         | 113.06 b, 113.86, 124.01, 1.628, 1.444 |                 |                 |                 |
| AMP No carbamate formed | 111.40 b, 111.04 b, 106.04, 112.32 av. 109.92 | 125.51, 1.606, 1.445 |                 |                 |

| Amine-carbamates | Parent amine | log $K_9$ 291 K c | N–C–C angles (°) (O_2)C-N-C angle (°) d[(C)O⋯H(C)] (Å) d[(O_2)C–N] (Å) |
|------------------|--------------|------------------|-----------------|-----------------|-----------------|
| isobutyl         | 1.99         | 116.50           | 120.14, 2.492, 1.457 |                 |
| n-butyl          | 1.79         | 116.11           | 120.07, 2.483, 1.458 |                 |
| sec-butyl        | 1.31         | 111.04, 112.90 av. 111.97 | 120.15, 2.313, 1.464 |                 |
| t-butyl          | 0.86         | 107.01, 109.67, 112.34 av. 109.67 | 123.79, 2.332, 1.461 |                 |

a Reference [36].  
b N-C-C(OH) angle.  
c Reference [10].
Figure 1. Equilibrium concentration profiles for the titration of MEA/Na$_2$CO$_3$ (0.040 M/0.080 M with 2.0 M HCl at 288, 298, 308 and 318 K. The decreasing concentrations (empty markers) are the MEA species (protonated/deprotonated) and the increasing concentrations (filled markers) correspond to the MEA-carbamate species (protonated/deprotonated).
Figure 2. $\Delta H_m^o$–$\Delta S_m^o$ plot for formation of amine-carbamates. Legend: 1, PIPD; 2, 1-MPIPZ; 3, NH$_3$; 4: MEA; 5: MORP; 6, TMORP; 7, DEA; 8, PIPZ; 9, 4-PIPDM; 10, AP; 11, PYRR; 12, 4-PIPDE. The red-dotted lines represent $(\Delta H_m^o, \Delta S_m^o)$ values for $\Delta G_m^o$ values of 0 (top) and -18 (bottom) kJ/mol.
Figure 3. $\Delta H_m^\circ$ (carbH)–$\Delta S_m^\circ$ (carbH) plot for the protonation of amine-carbamate anions. Legend: 1, PIPZ; 2, 1-MIPZ; 3, NH$_3$; 4, AP; 5: TMORP; 6: MORP; 7, PYRR; 8, 4-PIPDE; 9, PIPD; 10, MEA; 11, DEA; 12, 4-PIPDM.