

Protonation Constants and Thermodynamic Properties of Amines for Post Combustion Capture of CO₂

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ABSTRACT

The leading process for the post combustion capture (PCC) of CO₂ from coal-fired power stations and hence reduction in greenhouse gases involves capture by aqueous amine solutions. Of the reactions that occur in solution, which include CO₂ hydration, deprotonation of carbonic acid, amine protonation and carbamate formation, the protonation of the amine in the absorber and its subsequent deprotonation in the stripper involve the greatest enthalpy changes. In this study, protonation constants (reported as log₁₀ K_{prot}) of selected series of primary, secondary and tertiary alkanolamines/amines over the temperature range 288-318 K are reported. Selected series studied involve primary, secondary and tertiary mono-, di- and tri-alkanolamines, secondary amines including heterocyclic species, and both –CH₂OH and –CH₂CH₂OH substituted piperidines. van't Hoff analyses have resulted in the standard molar enthalpies, $\Delta H_{\text{m}}^{\circ}$, and molar entropies, $\Delta S_{\text{m}}^{\circ}$, of protonation. Trends in $\Delta H_{\text{m}}^{\circ}$ are correlated with systematic changes in composition and structure of the

selected series of amines/alkanolamines, while $\Delta H_m^\circ - \Delta S_m^\circ$ plots generated linear correlations for the mono-, di-, and tri-alkanolamines, the $-\text{CH}_2\text{OH}$ and $-\text{CH}_2\text{CH}_2\text{OH}$ substituted piperidines, and the alkylamines. These relationships provide a guide to the selection of an amine(s) solvent for CO_2 capture, based on a greater difference in $\log_{10} K_{\text{prot}}$ between the absorber and stripper temperatures.

Keywords:

Post combustion capture of CO_2

Amine protonation constants

Standard molar enthalpy of protonation

Standard molar entropy of protonation

CO_2 absorption

1. Introduction

Aqueous solutions of alkanolamines/amines are used for the removal of acid gases, such as CO₂ and H₂S, from a range of gas streams [1]. Potentially, such solutions can be used for post-combustion capture (PCC) processes involving CO₂, which is of importance in the reduction of CO₂ discharge to the atmosphere from the flue gases of coal-fired power plants [2]. The acid-base properties of the amines play an important role in their application in acid gas removal, while their investigation contributes to our understanding of the relationships between molecular structure, the chemical-physical properties of individual atoms or groups of atoms within the molecules, and ultimately reaction rates for PCC applications.

In the PCC of CO₂, the protonation constant of the amine plays an important role in the absorption/desorption-cooling/heating cycle of the process. In the absorber, the acid gas is chemically absorbed by the basic solvent solution, which is generally an amine. At an elevated temperature in the desorber, the base strength of the absorbent is reduced and the acid gas is released. The basicity of the amine is a key factor for the reaction rate and absorption capacity of the solvent in this process [3]. However, a major problem with the PCC of CO₂ for power generation using aqueous amines is the high energy cost of the process, which is associated with the energy required for solvent regeneration, that is, the release of the CO₂ from the solvent at elevated temperatures.

The energy requirement for the cyclic cooling/heating process is strongly dependent on the enthalpy of protonation of the amine, and thus on the protonation constant (K_{prot}). The temperature dependence of the protonation constant provides a measure of the reaction enthalpy that accompanies the change of the base strength of the absorbent with temperature. This is evident from the studies of McCann *et al.* [3], who developed a model for the prediction of CO₂ capacity and associated enthalpy changes in amine-based solvents during absorption/desorption of CO₂. For the prototypical PCC amine species monoethanolamine (MEA), assuming a typical flue gas composition with a CO₂ pressure of 12 kPa, a 30 wt % MEA solution, and absorption and desorption temperatures of 313 and 373 K, respectively, the enthalpy for CO₂ desorption at 313 K was shown to be ~83 kJ/mol. Of this, some 50 kJ/mol is

associated with deprotonation of MEA. In terms of enthalpy changes, this contribution is more important than the formation of gaseous CO_2 from $\text{CO}_{2(\text{aq})}$ and H_2CO_3 (~21 kJ/mol), or the decomposition of MEA-carbamate (~12 kJ/mol). While the heat capacity of the solution was not included in the above study, it is apparent that of the chemical reactions that occur in solution, the contribution of amine protonation/deprotonation to the enthalpy change is highly significant, and consequently to the energy required for solvent regeneration. In cases where carbamate formation does not occur, such as for sterically-hindered and tertiary alkanolamines/amines, the enthalpy contribution from the protonation/deprotonation of an amine is even more important. Furthermore, a more exothermic ΔH° is regarded as important to enthalpy changes in solution, as it results in a greater difference in $\log_{10} K_{\text{prot}}$ between the absorber and stripper and hence to an increased energy efficiency for the process and hence reduced energy costs. Thus knowledge of the temperature dependence of the $\log_{10} K_{\text{prot}}$ values for protonation, as well as the accompanying ΔH_m° and ΔS_m° values, is important in the selection of an amine (or amines) for PCC applications.

The protonation constants of many alkanolamines/amines are available in the literature under standard state conditions (see, for example, [4]); however, the temperature dependence of many constants is often not reported. For many obscure and less common species, potentially relevant to PCC by providing trends in, for example, K_{prot} as well as the enthalpy of protonation as the structure is varied, this data is unknown. In the present study, potentiometric titrations have been employed for the determination of $\log_{10} K_{\text{prot}}$ values, including their temperature dependence from 288-318 K, for structurally related series of acyclic, cyclic and substituted cyclic alkanolamines/amines. Thus data on all of these alkanolamines/amines have been obtained under the same conditions, thereby allowing accurate comparisons of trends in the $\log_{10} K_{\text{prot}}$ values and derived data as their structures are varied. The species include primary, secondary and tertiary mono-, di- and tri-alkanolamines, which involve increasing numbers of added $-\text{OH}$ groups, along with $-\text{CH}_3$ for $-\text{H}$ substitutions at the α -carbon for primary alkanolamines; secondary cyclic amines with varying heteroatoms (*i.e.* piperidine, piperazine, *N*-methylpiperazine, morpholine and thiomorpholine); and the sequences of $-\text{CH}_2\text{OH}$ and $-\text{CH}_2\text{CH}_2\text{OH}$ substituted

piperidines. van't Hoff analyses have yielded the ΔH_m° and ΔS_m° values. This has allowed trends in $\log_{10} K_{\text{prot}}$, and both ΔH_m° and ΔS_m° , upon systematic changes in structure to be identified (*e.g.* increasing numbers of $-\text{OH}$ groups in alkanolamines), and provide a guide the selection of the best amines for PCC applications based on enthalpy changes for protonation/deprotonation in solution.

2. Experimental

2.1 Materials

Millipore Milli-Q water was used for solution makeup and potentiometric titrations. Monoethanolamine (MEA), 2-amino-1-propanol (AP), 2-amino-2-methyl-1-propanol (AMP), 2-amino-2-methyl-1,3-propandiol (AMPD), 2-amino-1,3-propandiol (BIS or serinol), 2-amino-2-hydroxymethyl-1,3-propandiol (TRIS), diethanolamine (DEA), morpholine (MORP), thiomorpholine (TMORP), piperazine (PIPZ), 1-methylpiperazine (MPIPZ), piperidine (PIPD), 2-piperidinemethanol (2-PIPDM), 3-piperidinemethanol (3-PIPDM), 4-piperidinemethanol (4-PIPDM), 4-piperidineethanol (4-PIPDE), triethanolamine (TEA), *N*-methyldiethanolamine (*N*-MDEA) and *N,N*-dimethylethanolamine (*N,N*-DMEA), all ≥ 95 -99% purity, except for 2-piperidineethanol (2-PIPDE) which was 90%, were purchased from Sigma-Aldrich. All species were subjected to ^1H nmr spectroscopy to check on their purity prior to use, with little or no evidence of impurities observed. Sodium hydroxide was obtained from Merck, and potassium hydrogen phthalate (used for the standardisation of NaOH) and hydrochloric acid from Ajax Chemicals.

2.2. Potentiometric titrations

Potentiometric titrations were performed using a 665 Metrohm dosimat automated burette system, with a jacketed titration vessel that was connected to a Melcor liquid chiller (Model MRC300DH2-HT-DV) that was used to control temperature. A Metrohm combined micro-pH glass electrode (Model 6.0234.100) was used for the titrations, interfaced with a National Instruments NI-DAQ 7 board amplifying and translating the electrode signal, which was recorded in mV. The mV signal was used directly in the analysis of the titration data and transformed into pH using our software [5]. At each temperature the electrode was calibrated for

concentration (*i.e.* $\text{pH} = -\log_{10} [\text{H}^+]$) by titrating hydrochloric acid of known concentration with standardised NaOH solution. The principle is based on GLEE (glass electrode evaluation), a new computer program for glass electrode calibration [6]. The $\text{p}K_w$ values for the different temperatures were taken from reference [4].

For each set of titrations on an amine, a known mass of amine was initially acidified by addition of standardised HCl (0.015 M) in a ratio of 1:1.5 amine:HCl (diamines, 1:3). This gave an acidified solution of amine of 0.010 M, which was accurately known. From this acid solution 10.00 mL was transferred to the thermostatted titration vessel and back titrated with standardised NaOH (0.10 M) to high pH. The titrations were repeated a minimum of three times to ensure reproducibility. The titrations were performed at 288, 298, 308 and 318 K (± 0.1 K). Nitrogen was bubbled through the acidified solutions for 10 minutes prior to beginning the titrations and subsequently passed above the solutions during the actual titrations to ensure exclusion of CO_2 .

The alkanolamines/amines protonate as described in equation (1), while for the diamines piperazine and 1-methylpiperazine there are two protonation steps, equations (1) and (2) (note, $K_{\text{prot1}} = K_{\text{prot}}$ for amines that have only one protonation step):



Rather than maintaining approximately constant ionic strength using excess inert salts in the titrations, activity coefficients were applied to all charged species. This results straightway in thermodynamically correct protonation constants at zero ionic strength. Activity coefficient corrections were calculated from the Debye-Hückel equation (3):

$$\log_{10} \gamma_i = \frac{-Az_i^2 \sqrt{\mu}}{1 + \sqrt{\mu}} \quad (3)$$

In this equation, the activity coefficient γ_i is a function of the ionic strength μ , the charge z_i of the *i*th component, and the parameter *A*, which is defined by the dielectric constant of the solvent and the temperature [7,8].

In the procedure employed, $\log_{10} K_{\text{prot}}$ values (for the diamines $\log_{10} K_{\text{prot1}}$ and $\log_{10} K_{\text{prot2}}$) were determined at the four temperatures. Fitting of the titration data was achieved using in-house software written in Matlab. The standard state molar enthalpy and entropy changes ($\Delta H_{\text{m}}^{\circ}$ and $\Delta S_{\text{m}}^{\circ}$) of the protonation(s) of each amine were calculated using a van't Hoff plot of $\ln K_{\text{prot}}$ against $1/T$, equation (4).

$$\ln K = -\frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R} \quad (4)$$

The molar standard state free energy ($\Delta G_{\text{m}}^{\circ}$) was calculated from $\Delta H_{\text{m}}^{\circ}$ and $\Delta S_{\text{m}}^{\circ}$ by:

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \quad (5)$$

2.3 Density functional theory calculations

Quantum chemical calculations were performed using Spartan '04 (Wavefunction Inc., Irvine, CA, USA). Calculations used the B3LYP method, with a 6-311G* basis set. For each species (neutral or protonated), the molecular mechanics conformer search module was used to explore all possible geometries, and those two or three conformers with the lowest strain energies were submitted for equilibrium geometry calculations. The standard criteria for convergence in Spartan '04 were employed.

3. Results and Discussion

3.1. Protonation constants of alkanolamines/amines

The alkanolamines/amines investigated in this work are given in Table 1, along with the $\log_{10} K_{\text{prot}}$ values at 298 K and their $\Delta H_{\text{m}}^{\circ}$ and $\Delta S_{\text{m}}^{\circ}$ values. Representations of the structures can be found in the Supplementary data, Figure S1, along with full $\log_{10} K_{\text{prot}}$ temperature data (288, 298, 308 and 318 K) in Tables S1-S4. Data on several species are reported here for the first time: these include AP, BIS, 2-PIPDM, 3-PIPDM, 4-PIPDM, 4-PIPDM, TMORP, *N*-MPIPZ and *N,N*-DMEA. For those amines where literature data was available, this data has been included in the Supplementary data (Tables S1-S4). We have reported $\log_{10} K_{\text{prot}}$ values in our study (equivalent to $\text{p}K_{\text{a}}$ values for the protonated species) as used in the NIST database [4].

Our ΔH_m° , ΔS_m° and ΔG_m° data (Supplementary data, Tables S1-S4) are given for the protonation reaction(s), as has the literature data.

A plot of $\log_{10} K_{\text{prot}}$ vs $1/T$ for the prototypical PCC amine MEA is linear, and is shown in Figure 1. Generally good agreement of $\log K_{\text{prot}}$ with the literature data is found [9-13]. In the study by Hamborg and Versteeg [9], the slope of the plot is slightly greater than that found here, which is reflected in the value of ΔH_m° . This is most likely an effect of the solution ionic strength at which the studies were performed, and which were adjusted by different approaches to zero ionic strength. As $\log_{10} K_{\text{prot}}$ increases with ionic strength a greater error/difference may be expected with literature studies depending on how the ionic strength effect is handled. For other alkanolamines and amines, where the $\log_{10} K_{\text{prot}}$ data is available, good agreement with the literature data (Tables S1 to S4) was obtained for TRIS, AMP, AMPD, DEA, PIPD, PIPZ, MORP and TEA. The error associated with the individual protonation constants in most cases is very small ($<1.5\%$ in $\log_{10} K_{\text{prot}}$ over all temperatures). Data for 1-MPIPZ and *N*-MDEA were only a little higher ($<1.9\%$), while 2-PIPDE showed the greatest difference to our data (differences in $\log_{10} K_{\text{prot}}$ of 2 to 5%). The small differences may be the result of how the ionic strength has been handled in the different studies. In the present study, over the temperature range examined, the trend in $\log_{10} K_{\text{prot}}$ vs $1/T$ for each alkanolamine/amine was always linear, with most linear correlation coefficients $R^2 > 0.994$, with a minimum in the case of 1-MPIPZ of 0.976.

Examination of the ΔH_m° values indicates that they are all significantly exothermic. The protonation reactions are thus enthalpically driven. Moreover, as the proton has no steric requirements because of its small size, on addition to the amine nitrogen any trends in ΔH_m° should reflect electronic influences from variations in the attached groups, although changes in solvent reorganisation must play a significant role. Of all species studied, ammonia has the most exothermic ΔH_m° and the lowest absolute value of ΔS_m° . The latter is a consequence of the highly solvated environment that ammonia experiences in solution, with considerable hydrogen bonding in both its neutral and protonated forms. Thus both NH_3 and NH_4^+ are not dissimilar to H_2O and H_3O^+ in terms of size and the arrangement of the hydrogen bonding environment, and thus little change in entropy is expected upon protonation.

Notwithstanding the relatively select range of data, several trends in the ΔH_m° values are evident. Thus replacement of $-H$ by $-CH_3$ on the carbon α to the NH_2 group of a primary alkanolamine leads to a more exothermic ΔH_m° . This is shown by AP and AMP relative to MEA, and AMPD relative to BIS. This is attributable to the presence of more electron donating $-CH_3$ groups, which increases the basicity of the nitrogen atom. A similar increase in the exothermic ΔH_m° value occurs for 1-amino-2-propanol, where the $-CH_3$ group is now attached to the β carbon ($\Delta H_m^\circ = -50.4$ kJ/mol, and $\log_{10} K_{\text{prot}} = 9.46$, 298 K, $\mu = 0$ M [4]). The presence of more hydrophobic $-CH_3$ groups apparently decreases ΔS_m° in the substituted species relative to MEA.

Successive replacement of $-H$ by $-CH_2CH_2OH$ around the amine nitrogen, to give the sequence of primary, secondary and tertiary amines $MEA \rightarrow DEA \rightarrow TEA$, leads to a progressively less exothermic ΔH_m° , which might be associated with the presence of increasing numbers of more electron-withdrawing groups, thereby reducing the basicity of the nitrogen atom. However, similar trends in ΔH_m° are observed in the alkylamines RNH_2 , R_2NH and R_3N ($R = Et, Pr$), which do not have any $-OH$ groups in their structures (Et: $\Delta H_m^\circ = -57.1, -53.1$ and -43.1 kJ/mol, respectively; Pr: $\Delta H_m^\circ = -57.6, -54.8$ and -43.9 kJ/mol, respectively, 298 K, $\mu = 0$ M [4]). In both of these alkyl-substituted sequences it is the secondary amine that has the highest $\log_{10} K_{\text{prot}}$ (Et: $\log_{10} K_{\text{prot}} = 10.67, 11.00, 10.72$, respectively; Pr: $\log_{10} K_{\text{prot}} = 10.57, 10.92, 10.66$, respectively, 298 K, $\mu = 0$ M [4]). This stems from the well-known effects of hydrogen bonding in aqueous solution versus electronic (*i.e.* inductive) effects that are opposed, leading to the secondary amine having the highest $\log_{10} K_{\text{prot}}$, although when examined in detail the reasons for this have been found to be complex [14,15]. Trends in ΔS_m° for the alkylamines have been comprehensively discussed in the literature [16-18]. In the present series of alkanolamines, inductive effects (with the presence of the electron withdrawing $-OH$ on the $-CH_2CH_2OH$ groups) and increasing solvation effects (from the $-OH$ groups) on sequential replacement vary in a regular manner from $MEA \rightarrow DEA \rightarrow TEA$. This leads to the observed trends in $\log_{10} K_{\text{prot}}$ and ΔH_m° . Thus even though there are increasing numbers of the hydrophobic $-CH_2-$ groups being introduced, it is apparent that the

presence of multiple –OH groups have an overriding effect on ΔH_m° . In contrast, the effects on ΔS_m° from these two factors presumably cancel, leading to an almost constant value. Thus while decreases in entropy are expected from the increasing numbers of hydrophobic groups, this must be counterbalanced by the decrease in order in the hydrogen bonding environment of the solvent by the increasingly large solute species, despite the greater involvement of the –OH groups in hydrogen bonding. For the tertiary amines, the successive replacement of a –CH₃ group by a –CH₂CH₂OH at the amine nitrogen to give the sequence (*N,N*-DMEA) → *N*-MDEA → TRIS does not give rise to trends in ΔH_m° or ΔS_m° .

In contrast to the clear trend found for the MEA-DEA-TEA series, successive replacement of –H or –CH₃ by –CH₂OH at the carbon α to the nitrogen of a primary amine does not provide an obvious trend in ΔH_m° or ΔS_m° . This is demonstrated by the sequences MEA → BIS → TRIS and AMP → AMPD → TRIS. Presumably solvent reorganisation that results from changes in hydrogen bonding is complex in these two series.

In the sequence of substituted piperidines 2-PIPDM → 3-PIPDM → 4-PIPDM, ΔH_m° becomes progressively less exothermic as substitution occurs at a site further removed from the nitrogen location, likely because of changes to the intramolecular hydrogen bonding following protonation of the amine nitrogen, combined with changes in solvation [19]. Concomitantly, ΔS_m° becomes more positive along this sequence. Note that B3LYP/6-311G* calculations show that for the equilibrium geometries of 2-PIPDM, 2-PIPDE and 3-PIPDM, there are fairly strong intramolecular hydrogen bonds, with (H)N \cdots H(O) distances of 2.234, 1.996 and 2.011 Å, respectively, while for the protonated species there are now intramolecular hydrogen bonds of the type (N⁺)H \cdots O, with bond lengths of 2.095, 1.811 and 1.843 Å, respectively. Neutral 4-PIPDM and 4-PIPDE or their protonated species cannot form these intramolecular hydrogen bonds. Thus significant changes in the intramolecular hydrogen bonds occur on protonation for 2-PIPDM, 2-PIPDE and 3-PIPDM. Notably, da Silva and Svendsen have shown that intramolecular hydrogen bonds have a major effect in determining the $\log_{10} K_{\text{prot}}$ values of the alkanolamines [20], which in turn must affect the ΔH_m° and ΔS_m° values. The same trend for ΔH_m° (and ΔS_m°) is

observed for 2-PIPDE \rightarrow 4-PIPDE, although the chain length here may play a role, as the difference in ΔH_m° is not as great.

3.2. $\Delta H_m^\circ - \Delta S_m^\circ$ plot and implications for the selection of an amine for PCC applications

The data in Table 1 can be analysed using a $\Delta H_m^\circ - \Delta S_m^\circ$ plot. Linear relationships in $\Delta H - \Delta S$ plots are common in solution chemistry [21], and are found for the enthalpies and entropies of solution of series of non-polar or weakly polar atoms or molecules in non-interacting solvents (the so-called Barclay-Butler rule) [22], in the ionisation of aliphatic carboxylic acids from C3 to C6 and also amino acids [17,18], and for the enthalpies (ΔH^\ddagger) and entropies (ΔS^\ddagger) of activation in kinetic studies. In the present equilibrium studies, a plot of ΔH_m° against ΔS_m° for the alkanolamines listed in Table 1 (plus 1-amino-2-propanol, monopropanolamine and *N*-methylethanolamine, Supplementary data, Table S5) generate linear correlations for the primary, secondary and tertiary mono-, di- and tri-alkanolamines, and the substituted piperidines [$R^2 = 0.952, 0.995, 1.000$ (only two species!) and 0.996 , respectively]. These are shown in Figure 2. The data for 11 alkylamines (RNH_2 , R_2NH and R_3N , where $\text{R} = \text{Me}, \text{Et}$ and Pr , plus isopropylamine and *t*-butylamine; Supplementary data, Table S5) have also been included ($R^2 = 0.954$). Four sequences, with the exclusion of the substituted piperidines, are approximately parallel. The trends for all five series indicate that those species that exhibit a lower positive ΔS_m° have a more exothermic ΔH_m° , and vice versa. Thus increasing entropy, caused by more internal degrees of freedom and increasing solvent reorganisation, leads to less exothermic ΔH_m° values. The correlations intersect the ΔH axis at -62.1 (alkylamines), -56.9 (monoalkanolamines), -50.8 (dialkanolamines), and -46.4 kJ/mol (trialkanolamines), with the substituted piperidines at -56.5 kJ/mol. (These values are, of course, approximate ΔG_m° values for each of the five groups, which are almost constant within each sequence.) Thus any addition of $-\text{OH}$ to a structure causes a change of $\sim +5$ kJ/mol (at constant ΔS), leading to a more positive ΔH_m° , and hence to a less efficient heat difference between the absorber and stripper in PCC applications. Consequently, ΔH_m° is more exothermic as follows (for a constant ΔS value):

- (1) alkylamines $>$ NH_3 $>$ monoalkanolamines $>$ dialkanolamines $>$ trialkanolamines.

Moreover, for each of the three alkanolamine sequences (excluding the substituted piperidines), ΔH_m° generally is more exothermic according to the sequence:

(2) primary > secondary > tertiary species.

From Figure 2 it is apparent that increasing the length of the *n*-alkyl chain leads to progressively more exothermic ΔH_m° values. Data on increasing *n*-alkyl chain length (C4, C5 and C6) has been included in the Supplementary data, Table S5, but Figure 2 has been limited to C3 chains. For the alkylamines, the effect of increasing chain length on ΔH_m° has been discussed in the literature [16,17]. The trends observed in Figure 2 will help guide the selection of suitable amine-based compounds for PCC applications. The maximum exothermic value for ΔH_m° for the types of compounds studied is ~ -62 kJ/mol, which is close to the value for *t*-butylamine. Provided that a more negative ΔH_m° for protonation of the amine group is regarded as important to heat changes (this results in a greater difference in $\log_{10} K_{\text{prot}}$ between absorber and stripper), it is apparent that the best amine is based around a primary amine, $\text{H}_2\text{N}-\text{CR}_1\text{R}_2\text{R}_3$, with a rigid structure. The R groups may involve steric hindrance, depending on whether or not carbamate formation is considered desirable (this leads to faster kinetics of CO_2 adsorption, but to a lower absorption uptake per mole of amine than for an amine that does not generate a carbamate). The introduction of at least one $-\text{OH}$ (to reduce volatility and increase solubility through hydrogen bonding with the water solvent) would be advantageous. As regards rigidity of the R groups, increasing (alkyl) chain length may be important, but an alternative would be to use one or more rigid groups, such as a substituted phenyl or heterocyclic aromatic ring, with a substituent on the ring that may form hydrogen bonds with water (for example, a sulfonate, $-\text{SO}_3^-$, which would also require a counter cation such as Na^+ , or a nitro group, $-\text{NO}_2$). Aliphatic bicyclo[2.2.2]octane compounds (with, for example, external amine groups) are another possibility, although these may be too flunctional and thus have unappealing entropy contributions.

The five sequences of alkanolamines appear to obey an equation of the form $\Delta H_m^\circ = k\Delta S_m^\circ + \text{constant}$, where the slope *k* has the dimension of temperature, and is formally known as the isoequilibrium temperature, T_{iso} (for enthalpies and entropies of activation it is the analogous isokinetic temperature) [21]. However, it has been

shown that a ΔH – ΔS plot does not provide an appropriate way to establish if a T_{iso} exists for a series of compounds [23-25]. The best way to demonstrate if a series of compounds is linked by an isoequilibrium temperature is to plot, in the present case, $\log_{10} K_{\text{prot}}$ against $1/T$ for each compound [23-25]. Linear relationships will intersect at a common value of $1/T$ if the compounds are part of a series with the same T_{iso} value. No common value of T_{iso} was observed for any sequence (except for the substituted piperidines, see below), and it is concluded that none of these sequences of compounds form connected series, but that the compounds in each sequence are only linked by similar $\log_{10} K_{\text{prot}}$ (and hence $\Delta G_{\text{m}}^{\circ}$) values. This is not surprising as there are considerable variations in structure for each sequence, involving primary and/or secondary and tertiary amines. For the trialkanolamines the $\log_{10} K_{\text{prot}}$ vs $1/T$ data for TRIS and TEA intersect, but as there are only two members in this group, more examples should be investigated. In contrast, the five substituted piperidines (3-piperidineethanol is not commercially available) form a series with a T_{iso} of 252 ± 2 K, as shown in Figure 3. This is not surprising as all have highly similar structures, with just the $-\text{CH}_2\text{OH}$ and $-\text{CH}_2\text{CH}_2\text{OH}$ pendent arms located at different substitution sites around the piperidine ring.

4. Conclusions

The temperature dependence of the protonation constants (K_{prot}) of selected series of primary, secondary and tertiary amines relevant to PCC applications have been determined, leading to evaluation of their molar enthalpies and entropies of protonation by van't Hoff analyses. Many of these values have been determined here for the first time. Trends in the $\Delta H_{\text{m}}^{\circ}$ and $\Delta S_{\text{m}}^{\circ}$ values have been discussed, and a $\Delta H_{\text{m}}^{\circ}$ – $\Delta S_{\text{m}}^{\circ}$ plot has established guidelines for the selection of an amine (or amines) best suited for PCC of CO_2 involving amine-based aqueous solutions. This is based on greater differences in $\log_{10} K_{\text{prot}}$ between the absorber and stripper for the amine species, which will lead to a more energy efficient process.

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Supplementary data

Tables S1-S5. Temperature dependence (288-318 K) of $\log_{10} K_{\text{prot}}$, and values of $\Delta H_{\text{m}}^{\circ}$, $\Delta S_{\text{m}}^{\circ}$ and $\Delta G_{\text{m}}^{\circ}$, including literature data and references (S1-S4); Literature $\Delta H_{\text{m}}^{\circ}$ and $\Delta S_{\text{m}}^{\circ}$ data, and $\log_{10} K_{\text{prot}}$ values for selected alkylamines and alkanolamines (S5)

Figure S1. Structures of all alkanolamines/amines (S1).

Supplementary data associated with this article can be found, in the online version, at doi: (address to be added as appropriate).

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TABLE 1. $\log_{10} K_{\text{prot}}$, and $\Delta H_{\text{m}}^{\circ}$ and $\Delta S_{\text{m}}^{\circ}$ values for primary, secondary, tertiary alkanolamines/amines, and ammonia. (Standard deviations in all values are given in parentheses.)

Amine	$\log_{10} K_{\text{prot}}$ (298 K; $\mu = 0 \text{ M}$)	$\Delta H_{\text{m}}^{\circ}$ /(kJ/mol)	$\Delta S_{\text{m}}^{\circ}$ /(J/mol/K)
Primary amines			
2-aminoethanol (monoethanolamine) (MEA)	9.44(1)	-41(2)	42(5)
2-amino-1,3-propanediol (serinol) (BIS)	8.81(2)	-37.8(1)	41(4)
2-amino-2-hydroxymethyl-1,3-propanediol (TRIS)	8.10(1)	-45.4(1)	3(3)
2-amino-1-propanol (AP)	9.52(1)	-47(1)	25(2)
2-amino-2-methyl-1-propanol (AMP)	9.67(1)	-46.6(3)	29(1)
2-amino-2-methyl-1,3-propanediol (AMPD)	8.84(1)	-47.2(9)	11(3)
Secondary and cyclic amines			
2,2'-iminodiethanol (diethanolamine) (DEA)	8.86(1)	-37.5(7)	43(2)
piperidine (PIPD)	11.14(2)	-40(3)	80(8)
2-piperidinylmethanol (2-PIPDM)	10.11(1)	-46(2)	38(8)
3-piperidinylmethanol (3-PIPDM)	10.35(2)	-40.3(2)	63(1)
4-piperidinylmethanol (4-PIPDM)	10.56(3)	-34(2)	86(6)
2-piperidinyethanol (2-PIPDE)	10.48(2)	-37(2)	78(5)
4-piperidinyethanol (4-PIPDE)	10.62(3)	-35(2)	85(8)
piperazine (PIPZ) 1	9.77(2)	-36(1)	66(1)
2	5.60(2)	-33.6(1)	-5(1)
1-methylpiperazine (MPIPZ) 1	9.31(1)	-37(4)	53(13)
2	5.12(1)	-41(2)	41(4)
morpholine (MORP)	8.49(1)	-38.4(4)	34(1)
thiomorpholine (TMORP)	8.70(1)	-42(1)	27(3)
Tertiary amines			
2,2',2''-nitrilotriethanol (triethanolamine)	7.82(1)	-32(1)	43(1)

(TEA)			
bis(2-hydroxyethyl)methylamine methyldiethanolamine) (<i>N</i> - <i>N</i> -MDEA)	8.65(1)	-36(1)	45(4)
2-(dimethylamino)ethanol dimethylethanolamine) (<i>N,N</i> - <i>N,N</i> -DMEA)	9.23(2)	-34(1)	65(2)
Ammonia			
NH ₃	9.237(3)	-53.7(7)	-4(2)

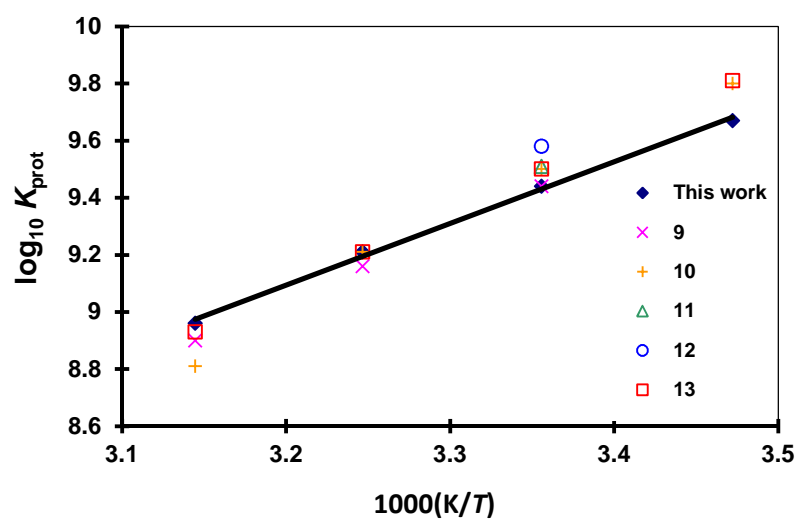


FIGURE 1. Plot of $\log_{10} K_{\text{prot}}$ vs $1/T$ for the protonation of MEA.

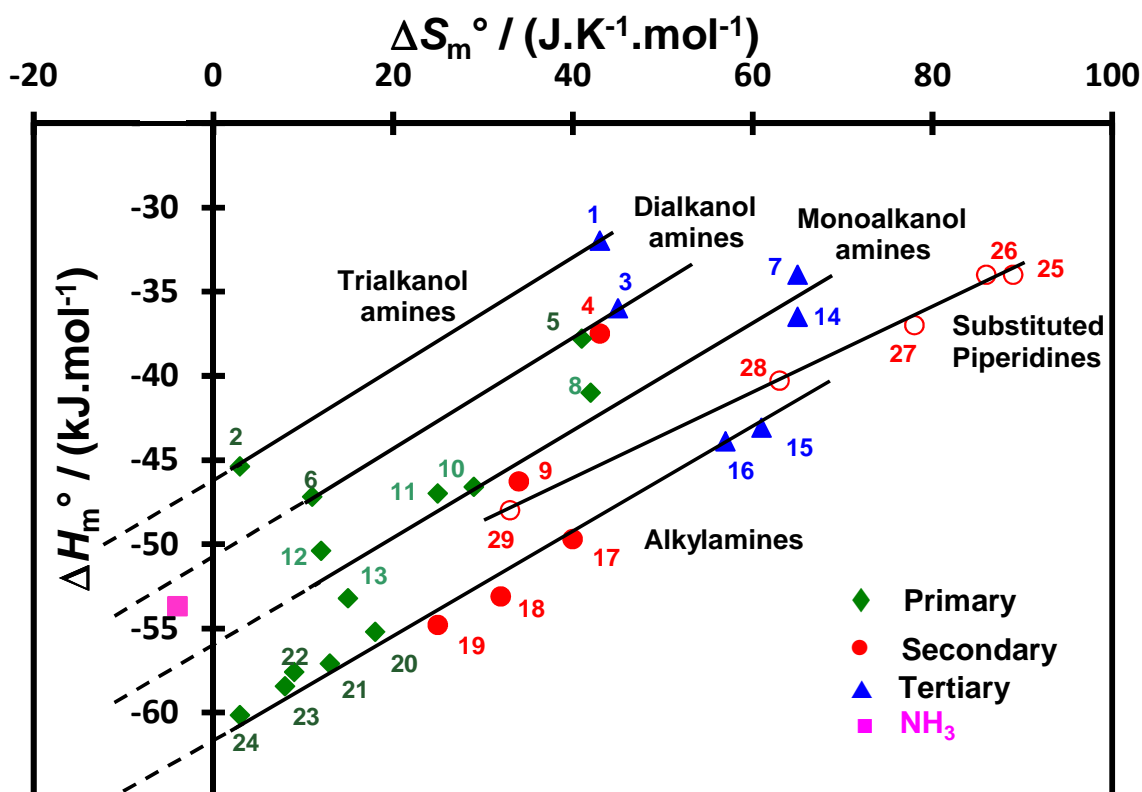


FIGURE 2. $\Delta H_m^0 - \Delta S_m^0$ plot for the alkylamines, the mono-, di- and tri-alkanolamines, and the $-\text{CH}_2\text{OH}$ and $-\text{CH}_2\text{CH}_2\text{OH}$ substituted piperidines. Legend: 1: TEA, 2: TRIS, 3: *N*-MDEA, 4: DEA, 5: BIS, 6: AMPD, 7: *N,N*-DMEA, 8: MEA, 9: *N*-methylethanolamine, 10: AMP, 11: AP, 12: monopropylamine, 13: 1-amino-2-propanol, 14: Me_3N , 15: Et_3N , 16: Pr_3N , 17: $(\text{Me})_2\text{NH}$, 18: $(\text{Et})_2\text{NH}$, 19: $(\text{Pr})_2\text{NH}$, 20: MeNH_2 , 21: EtNH_2 , 22: PrNH_2 , 23: isopropylamine, 24: *t*-butylamine, 25: 4-PIPDM, 26: 4-PIPDE, 27: 2-PIPDE, 28: 3-PIPDM, 29: 2-PIPDM.

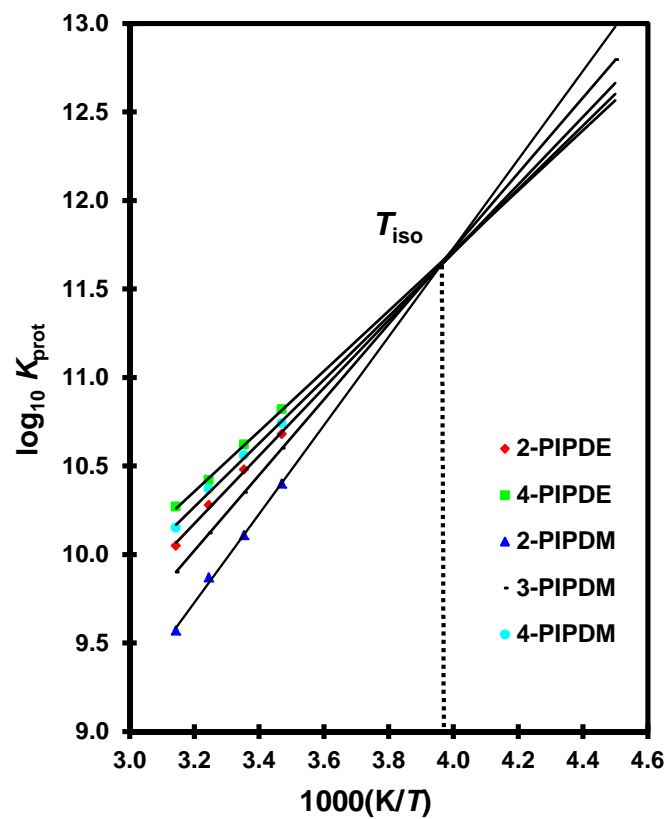


FIGURE 3. Equilibrium constants ($\log_{10} K_{\text{prot}}$) as a function of the inverse temperature for the substituted piperidines.

Supplementary data

Protonation constants and thermodynamic properties of amines for post combustion capture of CO₂

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TABLE S1. Temperature dependence (288-318 K) of $\log_{10} K_{\text{prot}}$, and values of $\Delta H_{\text{m}}^{\circ}$, $\Delta S_{\text{m}}^{\circ}$ and $\Delta G_{\text{m}}^{\circ}$ for primary amines, including literature data.

TABLE S2. Temperature dependence (288-318 K) of $\log_{10} K_{\text{prot}}$, and values of $\Delta H_{\text{m}}^{\circ}$, $\Delta S_{\text{m}}^{\circ}$ and $\Delta G_{\text{m}}^{\circ}$ for secondary and cyclic amines, including literature data.

TABLE S3. Temperature dependence (288-318 K) of $\log_{10} K_{\text{prot}}$, and values of $\Delta H_{\text{m}}^{\circ}$, $\Delta S_{\text{m}}^{\circ}$ and $\Delta G_{\text{m}}^{\circ}$ for tertiary amines, including literature data.

TABLE S4. Temperature dependence (288-318 K) of $\log_{10} K_{\text{prot}}$, and values of $\Delta H_{\text{m}}^{\circ}$, $\Delta S_{\text{m}}^{\circ}$ and $\Delta G_{\text{m}}^{\circ}$ for ammonia, including literature data (includes literature references for Tables S1 to S4).

TABLE S5. Standard molar enthalpy ($\Delta H_{\text{m}}^{\circ}$) and entropy ($\Delta S_{\text{m}}^{\circ}$) data, and $\log_{10} K_{\text{prot}}$ values (298 K) for selected amines and alkanolamines.

Figure S1. Structures of the primary, secondary and tertiary amines investigated in this study.

TABLE S1. Temperature dependence (288-318 K) of $\log_{10} K_{\text{prot}}$, and values of $\Delta H_{\text{m}}^{\circ}$, $\Delta S_{\text{m}}^{\circ}$ and $\Delta G_{\text{m}}^{\circ}$ for primary amines, including literature data. (Standard deviations in all values are given in parentheses.)

Amine	288 K	298 K	308 K	318 K	$\Delta H_{\text{m}}^{\circ}$ /(kJ.mol ⁻¹)	$\Delta S_{\text{m}}^{\circ}$ /(J.K ⁻¹ . mol ⁻¹)	$\Delta G_{\text{m}}^{\circ}$ /(kJ.mol ⁻¹)	Reference
MEA	9.67(1)	9.44(1)	9.21(4)	8.96(3)	-41(2)	42(5)	-53(2)	This work
		9.44	9.16	8.90	-48.6			[1]
	9.80	9.50	9.21	8.81	-50.5			[2]
		9.51						[3]
		9.58						[4]
	9.81	9.50	9.21	8.93	-50.89			[5]
BIS	9.01(1)	8.81(2)	8.57(1)	8.38(4)	-37.8(1)	41(4)	-50(1)	This work
TRIS	8.39(1)	8.10(1)	7.85(1)	7.62(1)	-45.4(1)	3(3)	-46(1)	This work
	8.36	8.08	7.80	7.55	-47.58			[6]
	8.36	8.07	7.80	7.55	-47.78			[7]
AP	9.82(2)	9.52(1)	9.25(1)	9.02(1)	-47(1)	25(2)	-54(2)	This work
AMP	9.96(1)	9.67(1)	9.41(1)	9.16(1)	-46.6(3)	29(1)	-55(1)	This work
	10.04	9.64	9.40	9.13				[8]
		9.69			-53.99			[9]
AMPD	9.15(1)	8.84(1)	8.58(1)	8.28(1)	-47.2(9)	11(3)	-50(3)	This work
	9.10	8.80	8.52	8.26	-49.85		-50.24	[10]

TABLE S2. Temperature dependence (288-318 K) of $\log_{10} K_{\text{prot}}$, and values of $\Delta H_{\text{m}}^{\circ}$, $\Delta S_{\text{m}}^{\circ}$ and $\Delta G_{\text{m}}^{\circ}$ for secondary and cyclic amines, including literature data. (Standard deviations in all values are given in parentheses.)

Amine	288 K	298 K	308 K	318 K	$\Delta H_{\text{m}}^{\circ}$ /(kJ.mol ⁻¹)	$\Delta S_{\text{m}}^{\circ}$ /(J.K ⁻¹ . mol ⁻¹)	$\Delta G_{\text{m}}^{\circ}$ /(kJ.mol ⁻¹)	Reference
DEA	9.09(1) 9.13	8.86(1) 8.88	8.66(1) 8.63	8.44(1) 8.41	-37.5(7) -42.4	43(2)	-50(1)	This work [11]
PIPD	11.33(2) 11.44 11.44	11.14(2) 11.16 11.12 11.12	10.91(2) 10.81 10.82	10.65(2) 10.53 10.53	-40(3) -52.3 -53.4	80(8) 33.9	-63(4)	This work [12] [13] [14]
2-PIPDE	10.68(1) 10.47	10.48(2) 10.14	10.28(2) 9.82	10.05(2) 9.52	-37(2) -53.8	78(5)	-60(1)	This work [8]
4-PIPDE	10.87(2)	10.62(3)	10.41(3)	10.27(4)	-35(2)	85(8)	-60(2)	This work
2-PPDM	10.37(1)	10.11(1)	9.87(1)	9.57(1)	-46(2)	38(8)	-57(2)	This work
3-PIPDM	10.60(2)	10.35(2)	10.12(2)	9.90(2)	-40.3(2)	63(1)	-59(1)	This work
4-PIPDM	10.74(3)	10.56(3)	10.37(3)	10.15(2)	-34(2)	86(6)	-59(3)	This work
MORP	8.721(1) 8.72	8.49(1) 8.49 8.49	8.263(4) 8.27	8.067(3) 8.06	-38.4(4) -39	34(1) 31.7	-48(2)	This work [15] [13]
TMORP	8.97(1)	8.70(1)	8.46(1)	8.26(1)	-42(1)	27(3)	-50(3)	This work
PIPZ	9.98(2)	9.77(2)	9.56(1)	9.37(1)	-36(1)	66(1)	-55(3)	This work
1	9.97 9.99	9.72 9.73 9.77	9.47 9.48	9.24 9.25 9.25	-42.8 -42.9 -35.6	42 42	-55.45 -55.55 -55.89	[1] [13] [16]
2	5.82(1) 5.60 5.52	5.60(2) 5.41 5.33 5.76	5.42(1) 5.22 5.16 5.56	5.24(1) 5.05 4.98	-33.6(1) -32.3 -31.1 -31.8	-5(1) -5 -2	-32(1) -30.87 -32.95	This work [1] [13] [16]
1-MPZ	9.49(2)	9.31(1) 9.14	9.13(2)	8.84(1)	-37(4) -29.9	53(13)	-52(3)	This work [17]
2	5.35(2)	5.12(1) 4.63	4.91(2)	4.63(1)	-41(2) -34	41(4)	-28(4)	This work [17]

TABLE S3. Temperature dependence (288-318 K) of $\log_{10} K_{\text{prot}}$, and values of $\Delta H_{\text{m}}^{\circ}$, $\Delta S_{\text{m}}^{\circ}$ and $\Delta G_{\text{m}}^{\circ}$ for tertiary amines, including literature data. (Standard deviations in all values are given in parentheses.)

Amine	288 K	298 K	308 K	318 K	$\Delta H_{\text{m}}^{\circ}$ /(kJ.mol ⁻¹)	$\Delta S_{\text{m}}^{\circ}$ /(J.K ⁻¹ . mol ⁻¹)	$\Delta G_{\text{m}}^{\circ}$ /(kJ.mol ⁻¹)	Reference
TEA	8.01(1)	7.82(1)	7.63(1)	7.46(1)	-32(1)	43(1)	-44(3)	This work
	7.91	7.72	7.54	7.37	-31.3		-44.07	[1]
	7.96	7.76	7.57	7.39	-33.5		-44.31	[18]
		7.77			-34		-44.31	[3]
	7.94	7.81	7.59	7.44	-29.7			[19]
N-MDEA	8.84(1)	8.65(1)	8.45(1)	8.23(2)	-36(1)	45(4)	-49(2)	This work
		8.56	8.36	8.17	-34.9		-48.87	[20]
		8.51	8.31	8.11	-35.7		-48.59	[21]
N,N-DMEA	9.42(2)	9.23(2)	9.04(1)	8.86(1)	-34(1)	65(2)	-53(3)	This work

TABLE S4. Temperature dependence (288-318 K) of $\log_{10} K_{\text{prot}}$, and values of $\Delta H_{\text{m}}^{\circ}$, $\Delta S_{\text{m}}^{\circ}$ and $\Delta G_{\text{m}}^{\circ}$ for ammonia, including literature data (includes literature references for Tables S1 to S4). (Standard deviations in all values are given in parentheses.)

Amine	288 K	298 K	308 K	318 K	$\Delta H_{\text{m}}^{\circ}$ /(kJ.mol ⁻¹)	$\Delta S_{\text{m}}^{\circ}$ /(J.K ⁻¹ . mol ⁻¹)	$\Delta G_{\text{m}}^{\circ}$ /(kJ.mol ⁻¹)	Reference
NH ₃	9.551(3)	9.237(3) 9.244(5)	8.931(3)	8.631(3)	-53.7(7) -52.00	-4(2) 2	-52(2)	This work [22]

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TABLE S5. Standard molar enthalpy (ΔH_m°) and entropy (ΔS_m°) data, and $\log_{10} K_{\text{prot}}$ values (298 K) for selected amines and alkanolamines.

Species	Standard molar enthalpy $\Delta H_m^\circ/(\text{kJ}\cdot\text{mol}^{-1})$	Standard molar entropy $\Delta S_m^\circ/(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$	$\log_{10} K_{\text{prot}}$ (298 K, $\mu = 0$ M)
(CH ₃)NH ₂	-55.2	18	10.632
(CH ₃) ₂ NH	-49.7	40	10.774
(CH ₃) ₃ N	-36.5	65	9.799
(C ₂ H ₅)NH ₂	-57.11	13	10.673
(C ₂ H ₅) ₂ NH	-53.13	32	11.00
(C ₂ H ₅) ₃ N	-43.13	61	10.715
(<i>n</i> -C ₃ H ₇)NH ₂	-57.57	9	10.566
(<i>n</i> -C ₃ H ₇) ₂ NH	-54.81	25	10.92
(<i>n</i> -C ₃ H ₇) ₃ N	-43.9	57	10.66
(<i>n</i> -C ₄ H ₉)NH ₂	-58.28	8	10.64
(<i>n</i> -C ₄ H ₉) ₂ NH	-57.15	24	11.25
(<i>n</i> -C ₅ H ₁₁)NH ₂	-58.49	7	10.597
(<i>n</i> -C ₆ H ₁₃)NH ₂	-58.65	7	10.63
isopropylamine	-58.45	8	10.67
<i>t</i> -butylamine	-60.16	3	10.685
1-amino-2-propanol	-50.37	12	9.464
monopropanolamine	-53.22	15	10.088
<i>N</i> -MEA	-46.27	34	9.88

^a Data taken from NIST Standard Reference Database 46 Version 6.0, NIST Critically Selected Stability Constants of Metal Complexes, A.E. Martell and R.M. Smith, 2001, NIST Standard Reference Data, Gaithersberg, MD, 20899, USA.

Figure S1. Structures of the primary, secondary and tertiary amines investigated in this study.

Primary Amines		Secondary amines		Tertiary amines	
MEA		DEA		TEA	
AP		PIPD		MDEA	
AMP		MORP		N,N-DMEA	
AMPD		TMORP			
BIS (serinol)		PIPZ			
TRIS		MPIPZ			
		2-PIPDE			
		4-PIPDE			
		2-PIPDM			
		3-PIPDM			
		4-PIPDM			