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NMR-Based Carbamate Decomposition Constants of Linear Primary Alkanolamines for CO2 Capture

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S Supporting Information

ABSTRACT: The amine carbamate related equilibrium ($RNHCOO^- + H_2O \leftrightarrows RNH_2 + HCO_3^-$) has been investigated with ^{13}C NMR (Nuclear Magnetic Resonance) spectroscopy for a series of linear primary alkanolamines, and the apparent carbamate decomposition equilibrium constants have been estimated. A quantitative NMR method for the calculation of the concentration of the species formed in solution has been provided, including the assessment of each of the fast exchanging proton species (whose nuclei resonate at the same chemical shifts in the NMR spectra). For this purpose, NMR-based calibration curves were utilized and an alternative method was applied for validation. The overall results showed that the amount of carbamate found at the equilibrium decreased as the length of the carbon chain increased, while the corresponding apparent carbamate decomposition equilibrium constants featured the same order of magnitude (10^{-2}).

1. INTRODUCTION

Aqueous alkanolamine solutions are currently of interest as solvents for post combustion carbon capture technology. The absorption of CO_2 into aqueous amine solvents involves several parallel reactions, and, among them, the direct reaction between CO_2 and unhindered primary and/or secondary amines in water is critical (carbamate formation, reaction 1). Carbamate formation is indeed characterized by favorable kinetics, but at the same time it results in low CO_2 absorption capacity due to an overall amine:CO_2 stoichiometry of 2:1, and also due to the high energy demand for the regeneration step leading to a reduction of the efficiency of the overall CO_2 capture process.[1]

$$2RNH_2 + CO_2 \leftrightarrows RNHCOO^- + RNH_3^+ \tag{1}$$

CO_2 absorption capacity, along with kinetic and thermodynamics aspects, is dependent on the amine structure, but the establishment of a relationship between them is complicated by many factors that are dynamically interrelated to each other, e.g., structural–chemical properties of the molecules and reaction and process conditions.

In order to advance the rational development of novel solvents, systematic investigations of amines featuring proper structural–chemical properties under specific reaction conditions is required to understand the complex chemistry underlying the CO_2 capture process. Reliable estimates of the liquid phase composition are necessary to propose reaction mechanisms and for the development of thermodynamic models.[2] Knowledge of the carbamate-related equilibrium constants is required to optimize the absorption processes and to establish a linear energy relationship between molecules. However, these types of studies are hampered by the difficulty of monitoring the ongoing reactions in such multi-equilibrium aqueous systems.

Among common analytical tools, NMR spectroscopy is widely used to study chemical reactions since direct measure-ments of specific nuclei of the species in solution can be performed.[3] In particular, NMR provides qualitative and quantitative information about reaction products, including those not available as pure standards (e.g., amine carbamate) and/or unknown degradation reaction products. NMR spectroscopy is therefore considered well suited for the study of aqueous amine absorbents, and, despite the lengthy measurements, ^{13}C NMR spectroscopy is commonly preferred when information is required on all species formed during the CO_2 absorption/desorption steps in both single and blended amine systems.[3] For instance, Barzagli et al. applied ^{13}C NMR spectroscopy to investigate quantitatively and qualitatively the main reactions occurring during the uptake and release of CO_2 in several aqueous alkanolamine systems.[4] Or one more, using ^{13}C NMR technique, Yang et al. have published a systematic study of primary and secondary alkanolamines and diamines to establish a structure–activity relationship on the basis of what type of species and the amounts that were formed after CO_2 absorption and desorption.[5] However, only a few NMR-based papers have dealt with the estimation of the carbamate-related equilibrium constants, which also require assessment of each of the fast exchanging proton species.[3] Indeed, amines and protonated amines, as well as HCO_3^- (bicarbonate) and CO_3^{2-} (carbonate), have nuclei that resonate at the same chemical shift (expressed in ppm) in the NMR spectra and the ppm values depend on the relative amounts of the two species. To quantify each of these species, various methods could be utilized, including NMR-based calibration experiments.[3]

In this work, ^{13}C NMR experiments have been performed to quantify all of the species in solution (including each of the fast exchanging proton species) after carbamate formation in a
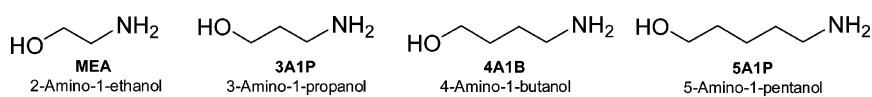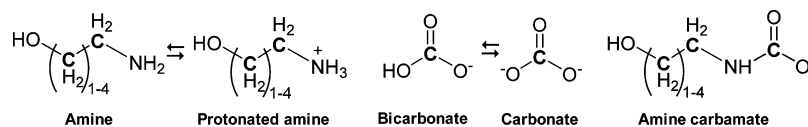
Figure 1. Amines investigated in this study.

Figure 2. Chemical structure of the main species at equilibrium. The nuclei of the atoms observable in the ^{13}C NMR spectra are in bold.
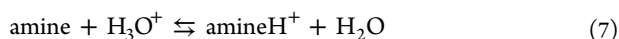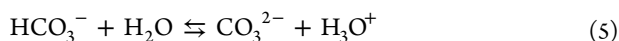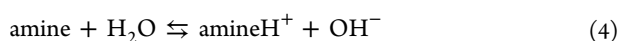
series of linear primary alkanolamines with varying numbers of methylene carbons between the hydroxyl (-OH) and amino (-NH$_2$) functional groups (Figure 1). The aim was to provide a NMR method to calculate the apparent equilibrium constants for the step of carbamate decomposition (reaction 2), whose ideal values will later be calculated and used to fit the parameters for the establishment of a linear free-energy relationship between the molecules and/or develop thermodynamic models.

$$RNHCOO^- + H_2O \leftrightarrows RNH_2 + HCO_3^- \qquad (2)$$
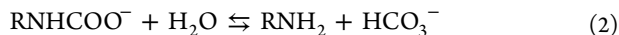
Moreover, based on the speciation analyses and equilibrium constants obtained in this work and on the data available in the literature on CO$_2$ absorption/desorption capacity of the same or similar amines, an evaluation of the most suitable alkanolamine for CO$_2$ capture among those in the present study has been provided.

2. CHEMICAL REACTIONS

To focus on the step of carbamate formation/decomposition, aqueous amine solutions were allowed to react with sodium bicarbonate (NaHCO$_3$) until equilibrium was achieved. In these systems, the following reactions were expected to occur:

$$2H_2O \leftrightarrows H_3O^+ + OH^- \qquad (3)$$

$$amine + H_2O \leftrightarrows amineH^+ + OH^- \qquad (4)$$

$$HCO_3^- + H_2O \leftrightarrows CO_3^{2-} + H_3O^+ \qquad (5)$$

$$amine + HCO_3^- \leftrightarrows amineCOO^- + H_2O \qquad (6)$$

$$amine + H_3O^+ \leftrightarrows amineH^+ + H_2O \qquad (7)$$

Usually, reaction 4 is neglected, but here it was considered because the carbamate formation was also influenced by amine basicity, which was the driving force to move reaction 4 toward the protonated amine at the expense of the carbamate compound.[6]

Based on reactions 3−7, the species at equilibrium that we expected to observe and quantify by ^{13}C NMR spectroscopy after the carbamate formation reaction are reported in Figure 2.

3. EXPERIMENTAL SECTION

3.1. Materials. The following chemicals from the indicated sources were used in the present study: ethanolamine (≥99.5%), sodium hydrogen carbonate (≥99.7%), and sodium carbonate (≥99.9%) from Merck; ethanolamine hydrochloride (≥99%), 3-amino-1-propanol (99%), 4-amino-1-butanol (98%), 5-amino-1-pentanol (95%), and hydrochloric acid

(37%) from Sigma-Aldrich. All chemicals were utilized without any further purification.

3.2. Equilibrium Experiments. A weighed amount of NaHCO$_3$ was added to a flask containing a weighed amount of aqueous amine solutions (2 M), corresponding to bicarbonate−amine molar ratios of 0.5, 0.75, and 1.0. The flask with the reaction mixture was placed in an oil bath and stirred at 298.15 K for more than 24 h, and ^{13}C NMR experiments were acquired after 48 h. Two equilibrium experiments were performed for each bicarbonate−amine ratio and each amine (a total of six carbamate formation reactions for each amine).

3.3. Quantitative ^{13}C NMR Experiments. NMR experiments were performed on a Bruker Avance III spectrometer (9.4 T, 400 MHz) using a BBFO Plus double resonance probehead at 298.15 K. The spectra were processed using MestreNova software v 7.1.1. For the determination of the concentrations of the species formed in the equilibrated reaction mixtures, quantitative ^{13}C NMR experiments were performed by setting appropriate acquisition and processing parameters to obtain reliable area integrals.[3] Acetonitrile (CH$_3$CN) and deuterated water (D$_2$O) were chosen as external reference standard and "lock" solvents, respectively, and were inserted in a sealed capillary. The ^{13}C NMR spectra were acquired with the inverse gated decoupling acquisition sequence, using a recycle delay time of 120 s (corresponding to 6 times the longest ^{13}C spin−lattice relaxation time, T_1), 512 scans, and a pulse width of 8.9 μs (90° pulse angle). In order to set the recycle delay, T_1 values of the ^{13}C nuclei of the species in the MEA reaction mixture and of the reference standard solvent in the capillary have previously been measured by using the inversion−recovery method.[7] The longest T_1 was estimated to be of ca. 13 s for the carbons of HCO$_3^-$/CO$_3^{2-}$ and of ca. 23 s for the carboxyl carbon of ethanolamine carbamate (MEACOO$^-$), while the methyl carbon of the reference standard CH$_3$CN had a T_1 value of ca. 20 s. The T_1 for the carbon of the -CN function of the standard was not measured because the magnetization recovery to its equilibrium was not reached at the experimental conditions set for the T_1 measurements, suggesting T_1 values longer than the other ^{13}C nuclei in the current solutions.

In the field of amine−CO$_2$−H$_2$O systems, T_1 values ranging from ca. 4−30 s have been documented for both the carbons of HCO$_3^-$/CO$_3^{2-}$ and the carboxyl function of amineCOO$^-$.[3,8] In particular, for the specific carboxyl carbon of MEACOO$^-$, T_1 values from ca. 8.9[8d] to 30 s[8e] have been given in the literature.

The reason for different T_1 values for the same nucleus in the same species (e.g., carboxyl carbon of MEACOO$^-$) in different works, relies on the fact that, e.g., the chemical environment (e.g., pH, dissolved oxygen, and viscosity), temperature, magnetic field, and mobility influence T_1 values.[7]

In our experiments, considering that the amount of amine carbamate can be quantified by taking into account the carbons bound to hydrogen (i.e., CH, CH_2, and CH_3), which have relaxation times shorter than carboxyl functions,[4a] the T_1 of 20 s (corresponding to the methyl carbon of the standard) was chosen as a reference value to set the recycle delay. Therefore, since T_1 measurements are quite time-consuming and the relaxation time of each nucleus can vary in different amine systems, the use of a standard solvent having nuclei with a T_1 value higher than those of typical carbons in amine−CO_2−H_2O systems allowed us to apply the same acquisition method to several solutions. Moreover, acetonitrile has ^{13}C chemical shifts (1.47 and 119.68 ppm)[9] far from those typical for the current amine systems, and hence overlapping of signals were avoided.

After acquisition, the ^{13}C NMR spectra were processed by proper signal phasing and baseline correction to reduce integration errors; a line broadening factor of 1.5 Hz was applied to enhance the signal-to-noise ratio. The exact relative area integrals were defined by fitting the spectra with a pure Lorentzian function which was also useful to extract the overlapping peaks, if any were present. The area of each peak was related to that of the methyl carbon of the standard (CH_3CN) in the capillary at a known concentration. The ^{13}C NMR spectra for all of the reaction mixtures are reported in the Supporting Information (Figures S3−S6). The assignment of each signal to the corresponding carbon was performed by means of 2D NMR experiments.

3.4. Calibration Experiments. *3.4.1. Calibration of the Concentration of the Standard in the Capillary.* Quantitative analyses usually require a reference compound for calculating the concentration of the species in solution. For NMR measurements, inserting the reference standard and the lock solvent in a sealed capillary has the advantage of avoiding any sort of interference with the loaded solution in the NMR tube. In addition, it can be reused for quantitative analyses of a variety of samples, so that the calculated concentrations of the species in solution are relative to a fixed concentration of reference compound.[10] The main disadvantage of this method is represented by the reduced sensitivity of NMR signals due to less unit volume of sample in the radio frequency coil region. Moreover, the concentration of the reference-compound solution placed in the capillary cannot be directly used for quantification, but a calibration is needed.

In this work, a sealed capillary, filled with a solution of CH_3CN/D_2O (1 M), was inserted in the NMR tube containing a standard solution at known concentration. Specifically, quantitative ^{13}C NMR experiments were performed on standard MEA solutions at different concentrations and the CH_3CN concentration in the capillary was calculated by relating its area peak to those of MEA. The concentration of the standard in the capillary was determined to be 0.172 ± 0.002 mol/L for the quantitative analyses of loaded samples.

3.4.2. Calibration Curves for Splitting HCO_3^-/CO_3^{2-} and Amine/AmineH$^+$. Standard aqueous solutions of free amine and protonated amine, as well as of $NaHCO_3$ and Na_2CO_3, were prepared and mixed in different appropriate ratios. Protonated ethanolamine, carbonate, and bicarbonate were commercially available, while hydrochloric acid was used to protonate the other amines. Qualitative ^{13}C NMR experiments were acquired, and the chemical shift values, relative to the ^{13}C chemical shift of the methyl group of the acetonitrile in D_2O (inserted in the capillary), were noted. Moreover, to test if any change in chemical shift could be observed at different

concentrations and pH values, some further ^{13}C NMR experiments were performed on $NaHCO_3$, Na_2CO_3, and $NaHCO_3/Na_2CO_3$ (1:1 ratio) solutions at concentrations ranging from 0.1 to 1 M and on MEA, MEAH$^+$, and MEA/MEAH$^+$ (1:1 ratio) solutions at concentrations ranging from 0.5 to 2 M (Tables S1 and S2 in the Supporting Information). The carbonate solutions showed a $\pm$ 0.1 ppm shift of the corresponding carbon signal, whereas no relevant shifts were observed for the MEA carbons. Subsequently, the ppm values of the nuclei of each standard solution were plotted against the species ratios because the chemical shifts of the carbons of the fast exchanging proton species depended on the chemical environment defined by the nuclei of the atoms and could be directly correlated to their ratios (which change as a function of the equilibria and pH in solution, not directly influencing the chemical shift values). In Figures 3 and 4, the calibration curves for the carbonates and amine species are shown (see also Tables S3−S7 in the Supporting Information).
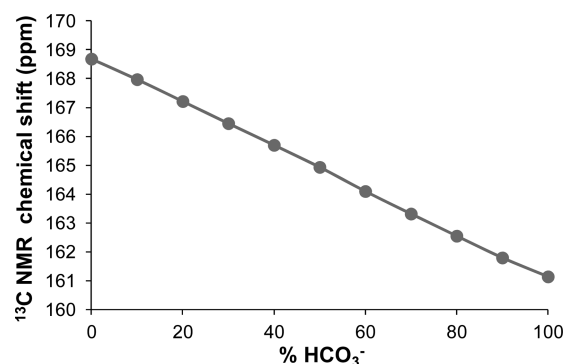
Figure 3. ^{13}C NMR chemical shifts recorded from standard solutions of carbonates at increasing percentage (%) of HCO_3^-.

The carbonate species, having 168.7 and 161.1 ppm as limiting shifts for 100% CO_3^{2-} and 100% HCO_3^-, respectively, moved toward lower ppm values at increasing HCO_3^- concentrations. These values were in good agreement with those already reported in the literature,[11] such as for instance 168.5 and 160.7 ppm in Shi et al.[12] Also for the amines, the chemical shift values changed as a function of the degree of protonation or rather on the amine/amineH$^+$ ratio. It has been typically observed that the nuclei (i.e., H_α and C_β) located at a site separated by two covalent bonds from the site of protonation (i.e., N) showed a ppm shift larger than other nuclei.[2a,13] The same behavior has been observed for the current amines (Table 1) and, for this reason, only the C_β was used as reference for the calculation of the free and molecular forms of the fast exchanging proton amine species in the solutions under study.

4. RESULTS AND DISCUSSION

4.1. Quantification of Fast Exchanging Proton Species and Validation. The ^{13}C chemical shift values of the signals corresponding to HCO_3^-/CO_3^{2-} and to the C_β of amine/amineH$^+$ in the reaction mixture at equilibrium were noted (see Table S8 in the Supporting Information). By using the calibration curves, the percentage of each species composing the peak was obtained and the relative amount (expressed in mol/L), with respect to the total concentration of HCO_3^-/CO_3^{2-} and/or of amine/amineH$^+$, was calculated.
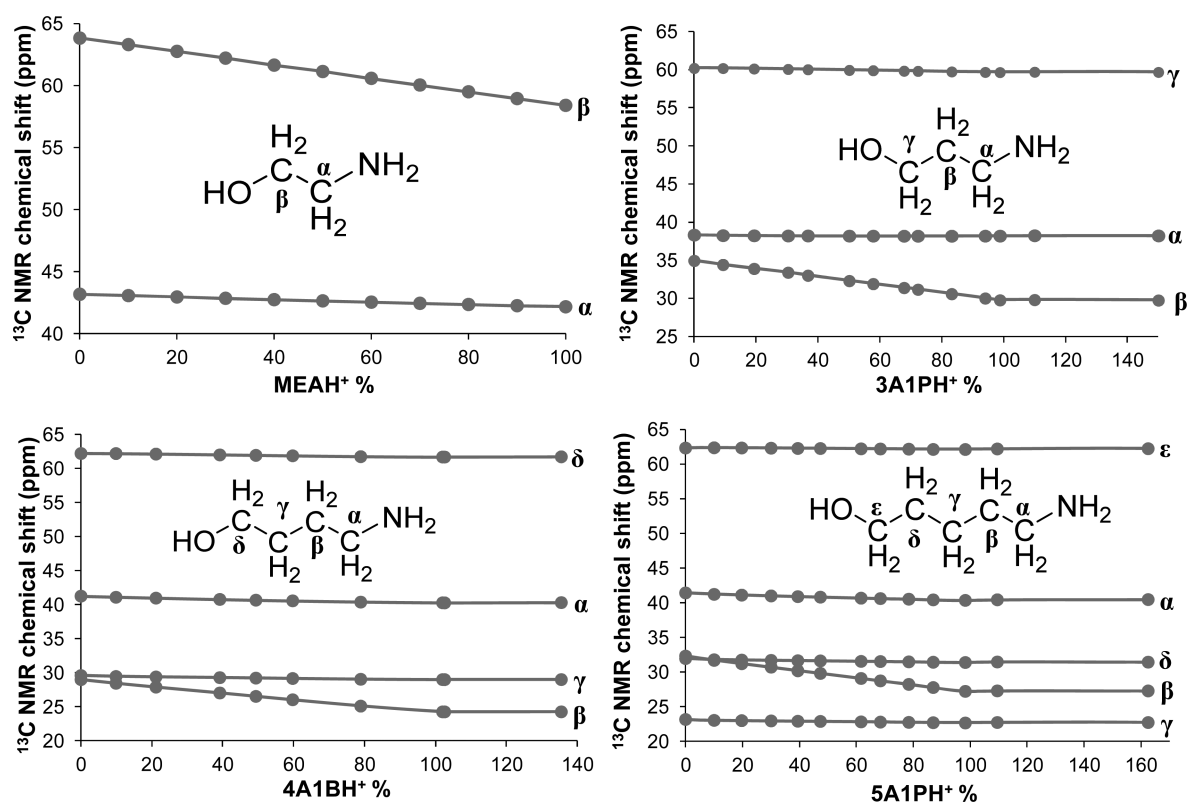
Figure 4. ^{13}C NMR chemical shifts recorded from amine standard solutions at increasing amine protonation. Each carbon is represented by α, β, γ, δ, and ε, as indicated in the structural formulas.

Table 1. Maximum ^{13}C Protonation Shift Observed in the Calibration Curves[a]

amine	^{13}C shift (Δppm)				
	C_α	C_β	C_γ	C_δ	C_ε
MEA	1.0	5.4			
3A1P	0.2	5.2	0.5		
4A1B	1.0	4.7	0.6	0.5	
5A1P	1.1	5.1	0.5	0.6	0.2

[a]Each carbon is represented by α, β, γ, δ, and ε, as indicated in the structural formulas in Figure 4.

In order to confirm the data obtained with calibrations, an alternative method was also used. In 1998, Holmes et al. performed ^{13}C NMR analyses on ammonia−CO_2−H_2O systems and the concentrations of carbonate, bicarbonate, and carbamate were calculated by combining the carbon balance with NMR data.[8c] Later, this NMR-based method was applied not only to loaded ammonia systems[14] but also to alkanolamine−CO_2−H_2O solutions for assessing the relative amount of bicarbonate and carbonate resonating with a common ^{13}C signal in the NMR spectra.[15] In our study, this approach has been utilized to validate the calibration curves performed for HCO_3^-/CO_3^{2-} species and, in addition, we have extended it to amine/amineH$^+$. Thus, the formulas proposed by Holmes et al. have been revisited as follows:

$$[AH] = \frac{A_{ppm} - S}{(A_{ppm} - AH_{ppm})(1 + R)}[X]$$
(8)

$$[A] = \frac{S - AH_{ppm}}{(A_{ppm} - AH_{ppm})(1 + R)}[X]$$
(9)

$$R = \frac{AMCOO^-_{area}}{(A + AH)_{area}}$$
(10)

AH represented the protonated form of the species, i.e., HCO_3^- or amineH$^+$; A represented the corresponding base, i.e., CO_3^{2-} or amine; A_{ppm} and AH_{ppm} were the chemical shift limit values corresponding to 100% of the corresponding species (for the amines, the chemical shift limit values of the C_β were used for calculations); S was the chemical shift of the amine/amineH$^+$ (C_β) or carbonate/bicarbonate signal observed in the ^{13}C NMR spectra of the equilibrated reaction mixture; R was the ratio between the areas of the signals corresponding to amine carbamate (AMCOO$^-$) and carbonate or amine species ($A + AH$); X corresponded to the initial concentration of NaHCO$_3$ (since no CO_2 was used in this study) for the estimation of the amount of HCO_3^- and CO_3^{2-} and to the initial concentration of amine for the calculation of the amount of free and protonated amines.

The calculated relative amounts of HCO_3^- and CO_3^{2-}, as well as of amine and amineH$^+$, were expressed in percent (%) with respect to the total HCO_3^-/CO_3^{2-} and amine/amineH$^+$, respectively, and compared to the corresponding percentage obtained by using the calibration curves.

It is evident that the results presented in Figures 5 and 6 obtained with both approaches were in good agreement. In particular, the difference in the estimation of the relative amounts of carbonate and bicarbonate was 0−1%, while it was 0−4% for amine and amineH$^+$ (see also Tables S9 and S10 in the Supporting Information).

4.2. Error Analyses and Calculation of the Apparent K_{hyd}. There are several sources of errors associated with the plotted data. In order to assess the reproducibility of our NMR
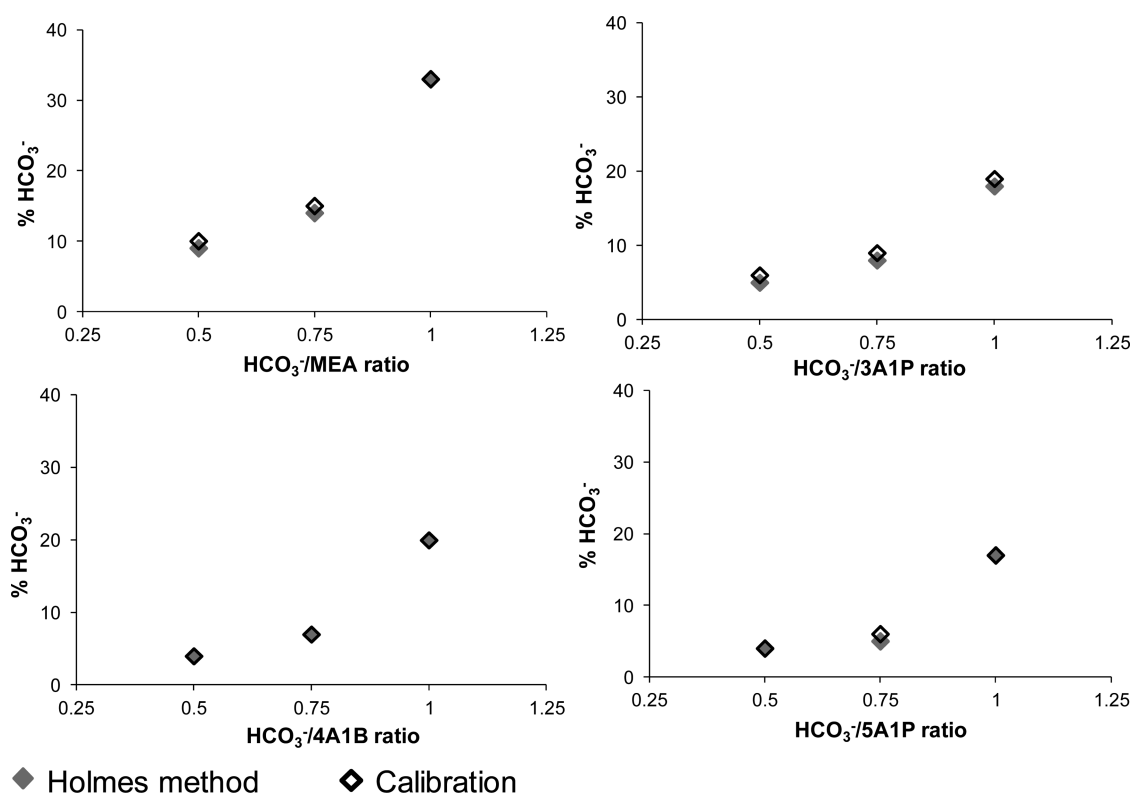
Figure 5. Comparison of HCO_3^- percent (%), with respect to the total HCO_3^-/CO_3^{2-} amount, calculated by means of calibration curves and the Holmes method for one reaction mixture of each HCO_3^-/amine ratio.
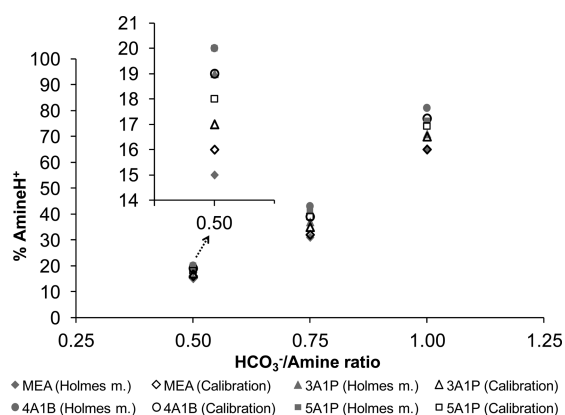
Figure 6. Comparison of amineH$^+$ percent (%), with respect to the total amine/amineH$^+$ amount, calculated by means of calibration curves and the Holmes method for one reaction mixture of each HCO_3^-/amine ratio.

experiments, two parallel ^{13}C NMR measurements of the same sample (HCO_3^-/MEA, 0.5 ratio) placed in two different NMR tubes were performed and the percentage difference (eq 11) was calculated.

$$\% \text{ difference} = \frac{|E_1 - E_2|}{\frac{1}{2}(E_1 + E_2)} \times 100 \tag{11}$$

The percentage difference between the two measurements (represented by E_1 and E_2 in formula 11) ranged from 0.3 to 3.7% (it is higher for the lowest relative area calculated for HCO_3^-/CO_3^{2-}). The ppm shifts of the corresponding signals in two ^{13}C NMR spectra were negligible, being in the range of 0.000−0.006 ppm.

In order to assess the error from processing of the spectra, the ^{13}C NMR spectrum of a reaction mixture obtained at 0.5 HCO_3^-/MEA ratio was phased and fitted five times. The standard deviations between the different relative area integrals ranged from 3.24×10^{-4} to 1.03×10^{-2}, whereas between the corresponding concentrations they ranged from 5.58×10^{-5} to 1.08×10^{-3}.

For the equation of carbamate hydrolysis (reaction 2 or the reverse of reaction 6), the apparent carbamate decomposition constant can be calculated by using the concentrations of amine, bicarbonate, and amine carbamate (eq 12) (Table S11 in the Supporting Information). To obtain the ideal equilibrium constants, the activity coefficient factors might be measured experimentally or calculated. In this NMR-based study, the activity coefficient factors have not been calculated and only the apparent carbamate decomposition constants for the four amines have been reported.

$$K_{\text{hyd}} = \frac{[RNH_2][HCO_3^-]}{[RNHCOO^-]} \tag{12}$$

K_{hyd} was estimated for each equilibrium experiment performed (six in total for each amine, twice at each HCO_3^-/amine ratio of 0.5, 0.75, and 1.0). For calculation of the uncertainty in the K_{hyd} (ΔK_{hyd}) we have applied the general error propagation formula 13:[16]

$$\Delta q = \sqrt{\left(\frac{\partial q}{\partial x_1}\Delta x_1\right)^2 + \dots + \left(\frac{\partial q}{\partial x_n}\Delta x_n\right)^2} \tag{13}$$

where q is a function of x_i, $i = 1, n$. The uncertainty in q is Δq, and each measurement of $x_1, x_2, \dots, x_n$ has an uncertainty denoted by $\Delta x_1, \Delta x_2, \dots, \Delta x_n$. Our expression for evaluation of

E

Table 2. NMR-Based Carbamate Decomposition Constants, K_{hyd} (mol/L), at 298.15 K for MEA and Related Linear Primary Alkanolamines

HCO$_3^-$/amine ratio[a]	K_{hyd} ($\pm\Delta K_{hyd}$)			
	MEA	3A1P	4A1B	5A1P
0.50	2.03×10^{-2} ($\pm 4.23 \times 10^{-4}$)	3.13×10^{-2} ($\pm 6.50 \times 10^{-4}$)	1.60×10^{-2} ($\pm 3.32 \times 10^{-4}$)	1.62×10^{-2} ($\pm 3.36 \times 10^{-4}$)
0.75	1.76×10^{-2} ($\pm 3.66 \times 10^{-4}$)	1.68×10^{-2} ($\pm 3.49 \times 10^{-4}$)	1.51×10^{-2} ($\pm 3.14 \times 10^{-4}$)	1.41×10^{-2} ($\pm 2.93 \times 10^{-4}$)
1.00	1.82×10^{-2} ($\pm 3.78 \times 10^{-4}$)	1.27×10^{-2} ($\pm 2.65 \times 10^{-4}$)	1.45×10^{-2} ($\pm 3.01 \times 10^{-4}$)	1.49×10^{-2} ($\pm 3.10 \times 10^{-4}$)

[a]The uncertainty in the HCO$_3^-$/amine ratios is estimated to be in the range of 0.8–1.4%.

the uncertainty in K_{hyd} is shown below in eq 14. The calculation was carried out as reported in eq 15. The average values for K_{hyd}, calculated at the same HCO$_3^-$/amine ratio (performed twice), were estimated as shown in eq 16.

$$\Delta K_{hyd} = \left[\left(\frac{\partial K_{hyd}}{\partial[\text{RNH}_2]} \Delta[\text{RNH}_2] \right)^2 + \left(\frac{\partial K_{hyd}}{\partial[\text{HCO}_3^-]} \Delta[\text{HCO}_3^-] \right)^2 \right.$$
$$\left. + \left(\frac{\partial K_{hyd}}{\partial[\text{RNHCOO}^-]} \Delta[\text{RNHCOO}^-] \right)^2 \right]^{1/2} \tag{14}$$

$$\Delta K_{hyd} = \left[\left(\frac{[\text{HCO}_3^-]}{[\text{RNHCOO}^-]} \Delta[\text{RNH}_2] \right)^2 + \left(\frac{[\text{RNH}_2]}{[\text{RNHCOO}^-]} \Delta[\text{HCO}_3^-] \right)^2 \right.$$
$$\left. + \left(-\frac{[\text{RNH}_2][\text{HCO}_3^-]\Delta[\text{RNHCOO}^-]}{[\text{RNHCOO}^-]^2} \right)^2 \right]^{1/2} \tag{15}$$

$$K_{hyd} = \frac{K_{hyd1} + K_{hyd2}}{2} \left(\pm \frac{\Delta K_{hyd1} + \Delta K_{hyd2}}{2} \right) \tag{16}$$

In Table 2, the K_{hyd} values and the corresponding uncertainties (ΔK_{hyd}) are reported for each amine. The K_{hyd} uncertainty ranged from 2.65×10^{-4} to 6.50×10^{-4}, being higher for the reaction mixture at the HCO$_3^-$/3A1P ratio of 0.5 where the ^{13}C NMR signal corresponding to HCO$_3^-$/CO$_3^{2-}$ species was broadened (see Figure S4 in the Supporting Information).

The influence of ionic strength, especially of Na$^+$ coming from NaHCO$_3$, will be reflected through the activity coefficients and is expected to change the actual value of the equilibrium constants but not the order of magnitude.[17] For instance, Aroua et al. reported both apparent and ideal K_{hyd} in the MEA−NaHCO$_3$−H$_2$O system.[17c] Similar to us, they used NaHCO$_3$, instead of CO$_2$, to investigate the carbamate-related equilibrium and the order of magnitude of the apparent carbamate hydrolysis constants was equal to the ideal ones. In their study, to investigate the effect of ionic strength on the apparent carbamate-related constants, various amounts of sodium perchlorate (NaClO$_4$) were added to the solutions and, only in most of these MEA−NaHCO$_3$−H$_2$O−NaClO$_4$ systems, a change of the order of magnitude of the apparent equilibrium constants with respect to the ideal ones was found.[17c]

The K_{hyd} values estimated for MEA at 298.15 K in this study were compared to those found in the literature at the same temperature, whereas those for 3A1P, 4A1B, and 5A1P have not been reported before. The comparison showed that the order of magnitude of MEA carbamate decomposition constants determined in this study were in good agreement with the activity-based values reported in other studies, such as in Fernandes et al. (1.74×10^{-2} mol/L),[1a] and Aroua et al. (4.8×10^{-2} mol/L in their study, and 3.0×10^{-2} mol/L and $1.3 \times$

10^{-2} mol/L obtained from literature).[17c] Recently, we have reported a study[18] where speciations for DEA (diethanolamine, a secondary alkanolamine) after carbamate formation were obtained at 298.15 K by Raman spectroscopy and compared to those calculated by quantitative ^{13}C NMR spectroscopy, using the current NMR method. Estimation of the apparent K_{hyd} of DEA from the NMR-based concentrations gave values ranging from 1.56×10^{-1} to 1.73×10^{-1} mol/L, in line with the activity-based ones already reported in literature at the same temperature (1.20×10^{-1} mol/L in Fernandes et al.[1a] and 1.40×10^{-1} mol/L in Aroua et al.[17b]). These data proved once more the reliability of the NMR method reported in this study.

The four alkanolamines investigated in this study, having as a common feature a primary amino function connected to a linear carbon-containing structure, showed carbamate decomposition constants within the same order of magnitude (10^{-2}), but a trend between the apparent K_{hyd} values and the structural−chemical properties of each molecule could not be established so far. Yamada et al. expected that the carbamate stability constant of 5A1P was less than MEA because of different effects of intramolecular hydrogen bonds between -NH$_2$ and -OH functional groups.[8a] The carbamate yield for 30 wt % MEA[2a] was indeed observed to be higher than those for 30 wt % 5A1P. Also in our study we observed that the tendency to form amine carbamate decreased as the length of the carbon chain increased, showing the same trend at different HCO$_3^-$/amine ratios (Figure 7). Likewise, in a recent study on
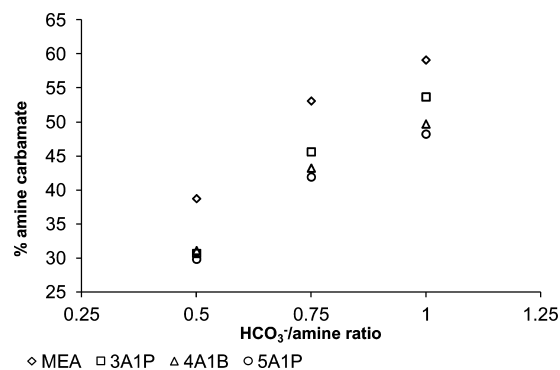
Figure 7. Percent (%) of amine carbamate, with respect to the total reaction mixture content at equilibrium, formed in amine solutions at different HCO$_3^-$/amine ratios. Note that each percent in the graph corresponds to the average percent of carbamate calculated from the reaction mixtures at the same HCO$_3^-$/amine ratio (performed twice).

secondary alkanolamines, it has been reported that, in the ^{13}C NMR spectra, the relative peak areas of the nuclei belonging to the amine carbamates decreased as the length of the carbon chain between the amino moiety and the hydroxyl function increased.[19]

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A recent ^{15}N NMR investigation into several amine absorbents gave experimental evidence of the factors that influenced the carbamate formation from the linear primary alkanolamines at increasing carbon chain length. The hydroxyl function played a role in defining the basicity of the molecules, which increased with increasing distance between -OH and -NH$_2$ (from pK_b = 4.52 of MEA to pK_b = 3.56 of 5A1P),[20] and the amount of carbamate decreased as basicity increased due to the solvent effect (i.e., water) which was higher for the stronger bases.[6]

The same molecules have also been analyzed by other authors, looking at the overall CO$_2$ absorption and desorption capacity.[5] In particular, the chain length alone made no strong impact on the CO$_2$ absorption and desorption, and, in our investigation, it appeared that the amines had similar features as the apparent carbamate decomposition constants were similar. However, considering that the amount of carbamate at the equilibrium differed, it could be speculated that 5A1P could be more suitable than MEA for CO$_2$ removal since it had the tendency to form less carbamate and it would be expected to demand less energy for the step of carbamate hydrolysis. However, it is worth noting that pure 5A1P is more expensive than MEA.

5. CONCLUSION

In this study, the apparent equilibrium constants for the step of carbamate decomposition (K_{hyd}) are reported for ethanolamine and related linear primary alkanolamines (3-amino-1-propanol, 4-amino-1-butanol , and 5-amino-1-pentanol). The concentrations of the species formed in solution after carbamate formation have been calculated by means of quantitative ^{13}C NMR spectroscopy, whereas the contribution of each of the fast exchanging proton species, appearing as a common signal in the NMR spectra, was assessed by NMR-based calibration curves. The latter were validated by using the approach followed by Holmes et al.,[8c] which for the first time has been extended to amine/amineH$^+$ species in the current study. Between the two approaches, a maximum of 4% difference in the estimation of the relative amount of the fast exchanging proton species was observed.

For the four linear primary alkanolamine systems, the amount of carbamate found at the equilibrium decreased with increasing carbon chain length, while the corresponding apparent K_{hyd} featured the same order of magnitude (10^{-2}). The uncertainties in the estimation of the K_{hyd} were reasonable, in the range of 2.65×10^{-4} to 6.50×10^{-4}. Moreover, there was good agreement with the values already reported in the literature for ethanolamine at the same temperature, whereas the carbamate-related equilibrium constants for 3-amino-1-propanol, 4-amino-1-butanol, and 5-amino-1-pentanol have not been reported before. Further studies will be necessary to obtain the ideal carbamate-related equilibrium constants which could be used as fitting parameters for the establishment of the free-energy relationship between the molecules and/or development of thermodynamic models for the optimization of absorption processes.

ASSOCIATED CONTENT

S Supporting Information

Figures showing amines investigated, species observed in ^{13}C NMR spectra, and ^{13}C NMR spectra of the equilibrated reaction mixtures and tables listing chemical shifts of the species in solutions for calibration experiments and in equilibrated reaction mixture, data on validation of the calibration curves, and concentrations of the species in equilibrated reaction mixtures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

NOMENCLATURE

3A1P = 3-amino-1-propanol
4A1B = 4-amino-1-butanol
5A1P = 5-amino-1-pentanol
amineH$^+$ = protonated amine
amineCOO$^-$ = amine carbamate
CH$_3$CN = acetonitrile
CO$_2$ = carbon dioxide
D$_2$O = deuterated water
HCO$_3^-$ = bicarbonate or sodium hydrogen carbonate
CO$_3^{2-}$ = carbonate
H$_2$O = water
h = hours
MEA = ethanolamine or 2-amino-1-ethanol
MEACOO$^-$ = ethanolamine carbamate
MEAH$^+$ = protonated ethanolamine
mol/L = moles per liter (M, molarity)
-NH$_2$ = amino functional group
NMR = nuclear magnetic resonance
-OH = hydroxyl functional group
ppm = parts per million
s = seconds
T_1 = spin−lattice relaxation time constant

Greek Letters:

$\alpha, \beta, \gamma, \delta, \varepsilon$ = each letter represents a carbon position as designated in Figure 4
Δ = designates change in parameter or uncertainty

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