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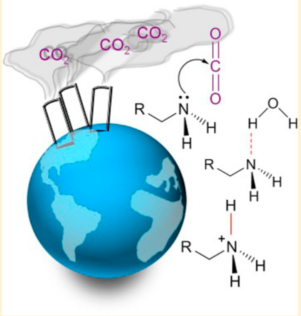
^{13}C and ^{15}N NMR Characterization of Amine Reactivity and Solvent Effects in CO_2 Capture

Cristina Perinu,[†] Bjørnar Arstad,[‡] Aud. M. Bouzga,[‡] and Klaus-J. Jens*,[†]

[†]Faculty of Technology, Telemark University College, Kjølnes Ring 56, 3901 Porsgrunn, Norway
[‡]SINTEF Materials and Chemistry, Forskningsveien 1, 0314 Oslo, Norway

S Supporting Information

ABSTRACT: Factors influencing the reactivity of selected amine absorbents for carbon dioxide (CO_2) capture, in terms of the tendency to form amine carbamate, have been studied. Four linear primary alkanolamines at varying chain lengths (MEA, 3A1P, 4A1B, and 5A1P), two primary amines with different substituents in the *β*-position to the nitrogen (1A2P and ISOB), a secondary alkanolamine (DEA), and a sterically hindered primary amine (AMP) were investigated. The relationship between the ^{15}N NMR data of aqueous amines and their ability to form carbamate, as determined at equilibrium by quantitative ^{13}C NMR experiments, was analyzed, taking into account structural−chemical properties. For all the amines, the ^{15}N chemical shifts fairly reflected the observed reactivity for carbamate formation. In addition to being a useful tool for the investigation of amine reactivity, ^{15}N NMR data clearly provided evidence of the importance of solvent effects for the understanding of chemical dynamics in CO_2 capture by aqueous amine absorbents.



1. INTRODUCTION

Acid gas (e.g., CO_2, H_2S) scrubbing by chemical absorption into aqueous alkanolamine solutions is widely practiced in the gas industry and may become the first deployed technology for postcombustion carbon capture (PCC) for global warming abatement.[1] The most widely used solvent for these purposes is aqueous monoethanolamine (MEA), the benchmark absorbent, which is known for its high reactivity and favorable reaction kinetics toward CO_2, although degradation and unfavorable thermodynamics reduce its potential for being the ideal PCC absorbent for energy industry applications.[2]

In gas processing, physical dissolution of CO_2 into the water phase takes place before the reaction of CO_2 with an amine. Primary and secondary amines react directly with CO_2 to form amine carbamate (in thermodynamic equilibrium with carbamic acid for aqueous-phase reactions) (reaction 1).[3] In contrast, tertiary amines and some so-called sterically hindered amines act as bases accepting a proton from the carbonic acid (a product of CO_2 with water) and/or possibly as catalysts in the CO_2 hydration (reaction 2).[4]

$$2R_1R_2NH + CO_2 \leftrightarrows R_1R_2NCOO^- + R_1R_2NH_2^+ \qquad (1)$$

$$R_1R_2R_3N + CO_2 + H_2O \leftrightarrows HCO_3^- + R_1R_2R_3NH^+ \qquad (2)$$

Reaction 2 is more efficient than reaction 1 in terms of CO_2 absorption capacity, but reactions of primary and secondary amines with CO_2 (reaction 1) show the fastest reaction kinetics. However, during the CO_2 desorption/amine regeneration step, the energy demand for the reverse of reaction 1 is higher than reaction 2 due to the stability of the carbamates.[4,5] Therefore, the CO_2 absorption capacity of an amine−CO_2−H_2O system is related to the ability of an amine to form carbamate, which depends on chemical-structural properties of the amine and reaction and process conditions; and this is the reason why the carbamate formation step is considered to be a distinguishing factor between the amines.[6] Identification of the factors influencing the tendency of an amine to form carbamate is therefore important for improving the CO_2 absorption processes.

Several structure−activity relationship studies have discussed the influence of electronic and steric effects, together with chemical properties of amines in the reaction with CO_2 in order to obtain information on governing factors for solvent performances. Recently, Yamada et al. investigated the CO_2 absorption capacity of secondary alkanolamines with varied alkyl and alcohol chain lengths by combining computational data and ^{13}C NMR experiments.[7] As the distance between the hydroxyl (−OH) and amino (−NH) functional groups increased within the amine structure, the amount of carbamate formed at equilibrium was decreased, and CO_2 absorption capacity was increased. In contrast, varied alkyl chain length did not have a significant effect. The sensitivity to the alcohol chain length was attributed to intramolecular hydrogen bonds between −OH and −NH in neutral alkanolamines, −OH and $-NH_2^+$ in protonated alkanolamines, −OH and $-NCOO^-$ in carbamate anions. However, the role played by intermolecular hydrogen bonds was neither clear nor excluded.[7] Puxty et al. published a systematic screening study of the CO_2 absorption capacity of 76 structurally diverse amines, and seven of them

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were identified for outstanding activity.[8] These seven amines had some common structural features, such as the hydroxyl group located two or three carbons distant from the amino functionality, but the role played by this structural characteristic was unclear.[8] Furthermore, with respect to the amine basicity, some Brønsted correlations relating rate and equilibrium constants for the carbamate formation to protonation contants of amines have been reported in the literature.[6,9] Hamborg et al. described the base strength of the alkanolamines to be dependent on the dielectric constants and temperature of the solvent.[10] However, no clear trend between the CO_2 absorption capacity of the amines and the corresponding basicity was identified.[8,11]

In view of the fact that water is the predominant component in amine solvents for CO_2 scrubbing, only a few reports have considered the properties of water (e.g., high polarity and extensive hydrogen bonding ability) in these reactions. Han et al. reported that water could be considered as a spectator in the reaction between amine and CO_2;[12] in contrast Arstad et al. showed in a computational study that water molecules can act as catalysts for the C—N bonding in the formation of carbamic acid (the corresponding acid to the carbamates)[13] and da Silva has taken into account solvation in terms of stabilizing effect depending on structural accessibility.[14] However, the influence of the water solvent has never been considered in terms of the availability of the nitrogen's lone pair of electrons to interact with water, although reactivity and CO_2 absorption capacity of the amines could be influenced greatly.

In order to provide further insight into amine solvents as absorbents for CO_2 capture, we have applied ^{13}C and ^{15}N NMR to characterize the amine reactivity, in terms of tendency to form amine carbamate. The background is that, during carbamate formation, the amino nitrogen is acting as a nucleophile (Lewis base) donating an electron pair to an electrophile (Lewis acid), such as CO_2 and/or HCO_3^-, and the ability of a nucleophile to attack an electrophile depends not only on chemical structural properties of the molecules but also on medium effects. Increased electron density on the nitrogen raises the energy of the electron pair and makes it more reactive, which is the reason why the reactivity is thus strongly influenced by the availability of the electron lone pair of the N nucleus, making parameters describing the local electronic properties on the N atoms important for understanding these reactions. A technique that has been considered a useful tool to assess the electron density on the amino nitrogen atom and to study solvent interactions is ^{15}N NMR spectroscopy, since it can provide information about the lone pair availability of nitrogen and the factors influencing the electron density on this nucleus, directly through the measured chemical shift values.[15] Indeed, ^{15}N chemical shift values not only depend on the electronic chemical environment defined by the molecular structure but, as compared to ^{1}H and ^{13}C NMR, are also much more sensitive to medium effects (e.g., concentration, temperature, and solvent) and, in general, to inter- and intramolecular interactions of the amino nitrogen with other functional groups.[15]

Little focus has been given on ^{15}N NMR within the field of PCC, with the exception of Yoon et al., who reported a ^{15}N NMR study discussing the electronic effects of substituents in sterically hindered amines on CO_2 absorption capacity. However, factors other than amine molecular structure (like, e.g., hydrogen bonds and solvent effects) were not considered.[16]

In the current study, we have measured the amount of carbamate formed at equilibrium in reactions of different amines with bicarbonate (HCO_3^-), by means of quantitative ^{13}C NMR experiments, and compared these values to ^{15}N NMR data and structural-chemical properties of the selected amines.

We have examined linear primary alkanolamines with carbon chains of varying length from two (2-amino-1-ethanol, termed MEA or ethanolamine) to five methylenes (5-amino-1-pentanol, 5A1P) between the hydroxyl and amino nitrogen functional groups. Two other primary amines, 1-amino-2-propanol (1A2P) and isobutylamine (ISOB), featuring the same carbon chain length but a different substituent at the position β to the nitrogen, were also analyzed to understand the effect of the hydroxyl function on the amine structure. Furthermore, 2,2′-iminodiethanol (also termed diethanolamine, DEA) and 2-methyl-2-amino-1-propanol (AMP), a secondary and a sterically hindered amine, respectively, were included in the investigation to scrutinize overall structure−activity relationships (Figure 1).

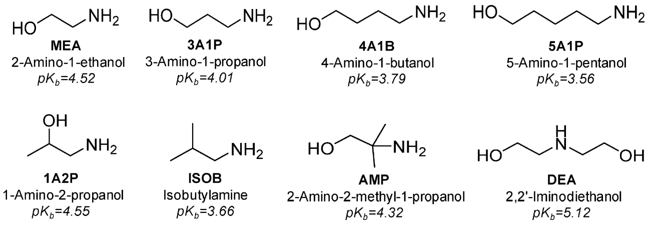

Figure 1. Amines investigated in this study.

This approach allowed us to identify overall factors influencing the tendency of the selected amines to form carbamate. In particular, ^{15}N NMR spectroscopy was a useful tool to investigate the amine reactivity toward formation of amine carbamate, as determined by ^{13}C NMR spectroscopy, and to examine the role played by the solvent (e.g., water).

2. EXPERIMENTAL SECTION

2.1. Sample Preparation. The following chemicals were used in the present study: 2-Amino-1-ethanol (EMSURE) and sodium hydrogen carbonate (sodium bicarbonate) from Merck, 3-amino-1-propanol (99%), 4-amino-1-butanol (98%), 5-amino-1-pentanol (95%), isobutylamine (99%), (R/S)-1-amino-2-propanol (98%), 2,2′-iminodiethanol (≥98%), 2-amino-2-methyl-1-propanol (≥99%), ethanolamine hydrochloride (≥99%), and hydrochloric acid (37%) from Sigma-Aldrich. They were utilized without any further purification.

Amines were weighed and solutions (2M) were prepared with distilled and degassed water. The concentrations were calculated by measuring the density with a pycnometer (5.554 cm^3). The same procedure was used for preparation of water (H_2O)/dimethoxyethane (DME) (1:1) (2 M) amine solutions (MEA and AMP) and for the aqueous protonated amines (amineH^+) and the 1:1 ratio amine/amineH^+ (2 M) solutions (MEA and 3A1P). In the first case, a weighted amount of amine was dissolved in H_2O−DME, previously mixed at 1:1 ratio; in the second case, commercially available protonated MEA was used, whereas protonated 3-amino-1-propanol was obtained by adding equimolar amounts of hydrochloric acid (HCl) into the amine solution. A 600 μL sample of the above solutions or of

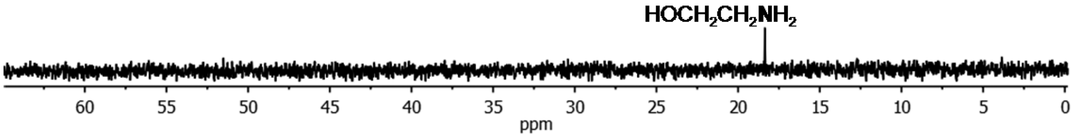

Figure 2. ^{15}N NMR spectrum of aqueous MEA solution (2 M) at 298.15 K. The nitrogen is shown in bold in the formula.

Table 1. ^{15}N Chemical Shift Values of the Amines Solutions Investigated in This Study

amines	^{15}N chemical shift (ppm)				
	amines (2M) in H_2O	pure amines	amines (2 M) in H_2O/DME 1:1	amine/amineH^+ 1:1 (2M) in H_2O	amineH^+ (2M) in H_2O
1A2P	17.74	17.29			
MEA	18.38	16.84	18.05	24.34	29.01
3A1P	24.26	22.89		29.42	33.66
4A1B	25.39	24.06			
5A1P[a]	25.34				
ISOB	22.15	18.70			
DEA[a]	29.58				
AMP[a]	48.75		48.44		

[a]Solid at STP conditions.

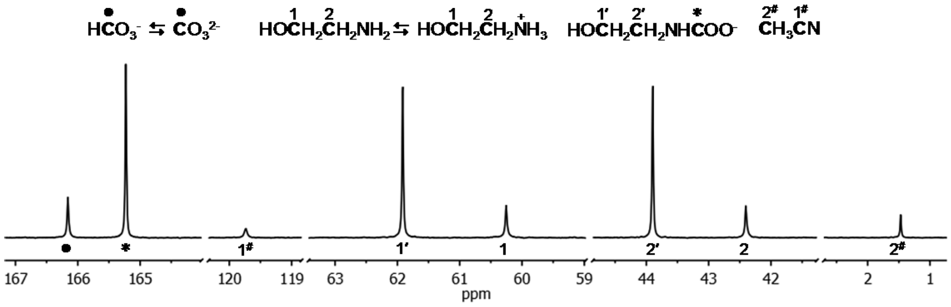

Figure 3. ^{13}C NMR spectrum and assignments for MEA/$NaHCO_3$ 1:1 ratio reaction mixture at the equilibrium. The observed carbons are given in bold in the formulas; CH_3CN is the reference.

the neat amines (directly withdrawn from the bottle) was inserted in the NMR tube for ^{15}N NMR measurements.

The synthesis of amine carbamate was carried out by reacting the aqueous amine solutions (2 M) with sodium bicarbonate at 1:1 molar ratio (reaction 3). The mixtures were stirred for more than 24 h at 298.15 K to achieve equilibrium and after 48 h quantitative ^{13}C NMR experiments were performed.

$$RNH_2 + HCO_3^- \leftrightarrows RNHCOO^- + H_2O \quad (3)$$

2.2. NMR Experiments. ^{13}C and ^{15}N NMR experiments were performed at 9.4 T on a Bruker Avance III 400 MHz spectrometer using a BBFO Plus double resonance probe head at 298.15 K; the spectra were processed using MestreNova software v 7.1.1.

2.2.1. Qualitative ^{15}N NMR Experiments. Qualitative ^{15}N NMR experiments were carried out on the amine solutions at the same concentration (2 M) and at constant temperature (298.15 K) in order to eliminate the corresponding influences on the chemical shifts. At the same temperature, ^{15}N NMR experiments were also performed on the neat amines. For all amines, the experiments were run with the inverse gated decoupling method, pulse angle of 90° (14 μs pulse width) and a pre-scan delay of 250 μs (optimized to reduce probe ringing). The choice of the recycle delay was based on the need of observing a signal at short experimental time. Therefore, for all amine solutions, a recycle delay of 10 s and scans up to 4352 were set, except for 2 M 5A1P solution which required a recycle delay of 50 s and 512 scans. In order to record the ^{15}N NMR chemical shift values, the referencing via direct measurements of the absolute frequency of the field/frequency lock signal was used.[17] A capillary containing deuterated benzene was inserted in the NMR tube for locking and referencing and, in a separate NMR tube, pure formamide (δ = 113.3 ppm) was used to validate the ppm values.[17] This method was applied to replace medium effects on the shielding of the reference standard in such solutions and reduce the acquisition time. Indeed, the relatively low amount of standard reference that would be added into the NMR tubes, combined with the low isotopic abundance of ^{15}N (0.37%), would result in long acquisition time. Each aqueous amine solution (2M) was prepared twice for ^{15}N NMR measurements, and the uncertainty in the chemical shift values was estimated to be in the range of ±0.01−0.03 ppm.

A typical ^{15}N NMR spectrum is reported in Figure 2, whereas the ^{15}N chemical shift values of all the amine solutions are reported in Table 1. ^{15}N NMR spectra of all the aqueous amines solutions at 2 M can be found in the Supporting Information (SI).

2.2.2. Quantitative ^{13}C NMR Experiments. Quantitative ^{13}C NMR experiments were performed on the equilibrated reaction mixtures (aqueous solutions after carbamate formation). Acetonitrile (CH_3CN) and deuterated water (D_2O), inserted in a sealed capillary, were used as standard reference and lock solvents, respectively.[18] After the measurements of the longitudinal relaxation time constant (T_1) of the ^{13}C nuclei of the species in the MEA reaction mixture and of the standard in the capillary, the following parameters were used: recycle delay of 120 s (corresponding to 6 times the longest T_1), pulse angle of 90° (8.9 μs pulse width) and 512 scans.[18]

A typical ^{13}C NMR spectrum of the carbons containing species, observed and quantified at the equilibrium, is reported in Figure 3. ^{13}C NMR spectra, including assignments, for all the amines in the reaction mixtures are documented in the SI. The assignment of each signal to the corresponding carbon was performed by means of 2D NMR experiments.

To calculate the area integrals, the ^{13}C NMR spectra were fitted and the area of each peak was related to that of the C-2$^{\#}$ of the CH_3CN standard. The area of the signal corresponding to the C-* carbon of the amine carbamate and that corresponding to the C-1$^{\#}$ carbon of the standard were not taken into account for the calculation of the concentrations of the species in solutions because their T_1 values are longer than the longest T_1 (20 s) which was used for setting the recycle delay. Since the concentration of the amine carbamate species could be determined by using carbons other than carbonyl and the area of each carbon could be related to one of the signals from the standard (i.e., C-2$^{\#}$), the recycle delay was set to be 6 times 20s. The longest T_1 value was that of the methyl carbon of the standard, and this allowed us to apply the same recycle delay to all the reaction mixtures under study, avoiding T_1 measurements of ^{13}C nuclei in each of them.[18]

The fast exchanging proton species (neutral/protonated amines and carbonate/bicarbonate) appear with a common peak in the ^{13}C NMR spectra and only the sum of their concentration can be obtained. Various methods could be utilized to estimate the contribution of each of these species but this was not necessary for the present work.

The analyses of the quantitative ^{13}C NMR spectra for the different amines were consistent with a decrease of the amount of carbonate species (HCO_3^-/CO_3^{2-}) at increasing amount of carbamate in solution (SI). Furthermore, in the reaction mixtures of the amines with lower pK_b (stronger bases), the carbons corresponding to HCO_3^-/CO_3^{2-} species were resonating at a higher chemical shift value which corresponds to an higher ratio of CO_3^{2-} (carbonate) to HCO_3^- (bicarbonate)[19](SI). However, since the aim of the present work is the study of the amine reactivity toward carbamate formation, we will focus the discussion of the ^{13}C NMR results on the carbamate species only.

The amount of carbamate in the equilibrated reaction mixtures was expressed in percentage with respect to the sum of the concentrations of all the species detected in the ^{13}C NMR spectra, as shown in eq 4:

$$\%\text{carbamate} = ([\text{RNHCOO}^-]\cdot 100) \times ([\text{RNHCOO}^-] + [\text{RNH}_2/\text{RNH}_3^+] + [\text{HCO}_3^-/\text{CO}_3^{2-}])^{-1} \quad (4)$$

The error in the calculation of the % of carbamate was estimated to be ±0.76 percentage points which corresponded to the standard deviation between the % of carbamate obtained from three equilibrium experiments performed on MEA.

3. RESULTS AND DISCUSSION

The effect of molecular structure on base strength for the current amines is related to inductive effects operating through single bonds. Indeed, the hydroxyl function exerts an electron-withdrawing inductive effect through bonds, whereas the alkyl groups induce an electron-donating effect.[11a,20] As the distance between the hydroxyl and nitrogen functions increases, the electron-withdrawing effect weakens, leaving the amino nitrogen surrounded by greater electron density and thereby strengthening the basicity (Figure 1). Brønsted and Lewis bases are both synonyms of nucleophiles but, for the Brønsted bases, the proton is the only possible electrophile, which is the reason why they are considered to be a subcategory of the more encompassing Lewis bases.[20]

In Figure 4, the pK_b of each amine[21] (SI for the background) is plotted against the amount of carbamate (in % as calculated by eq 4).

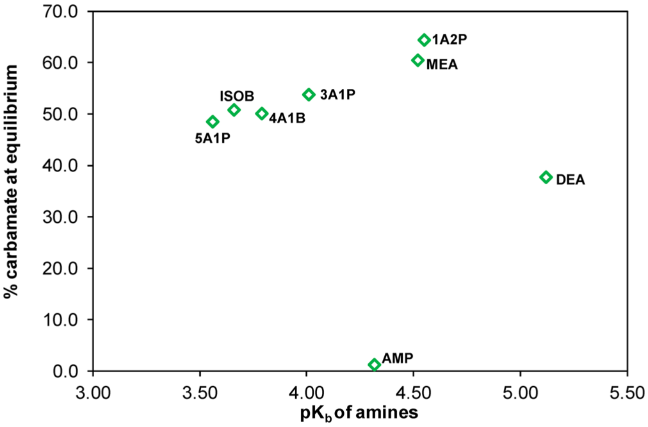

Figure 4. Amine basicity (pK_b, 293.15 K)[21] as a function of the percentage (%) of carbamate at equilibrium.

For linear primary amines, the amount of carbamate at equilibrium decreased with increasing basicity (lower pK_b, stronger bases). However, DEA and AMP did not fit into any apparent correlation in this plot.

The carbamate forming reaction is the reaction of an amine (Lewis base) with the electrophilic center (Lewis acid) of the HCO_3^- anion. The data presented in Figure 4 shows a discrepancy between the basicity, a function of the molecule's chemical structure, and the reactivity to form carbamate. Indeed, the weaker bases, MEA and 1A2P, with the hydroxyl function in the β position with respect to the nitrogen, would be expected to have lower electron density on the nitrogen and, consequently, relatively lower tendency to react, but we observed the opposite.

The basicity and expected electron density on the nitrogen of DEA and AMP also did not reflect the predicted tendency to form carbamate, but this behavior might be attributed to the substitution effects and steric hindrance which reduce the ability of the nitrogen to interact with the electrophilic center of the HCO_3^- anion. Similar findings have been reported by Conway et al., who have related the protonation constants of various amines with the kinetic and equilibrium constants for the reaction of amine and CO_2(aq) to carbamic acid/carbamate.[6,9b] For the linear amines, a quite linear relationship was observed and the deviation from that trend was attributed to steric hindrance and substitution effects. However, ammonia, which does not have any steric hindrance, also showed a deviation; this was tentatively explained as being due to different solvation properties.[6]

However, pK_b is a measure of proton accepting power of a Brønsted base (e.g., the amine) in water. The above situation indicates that not all underlying factors influencing the reactivity of amine to form carbamate may be reflected when setting up a relationship, as shown in Figure 4.

The ^{15}N NMR chemical shift is a measure for the relative electron density present on a N nucleus in respect to molecular structure and medium effects. In Figure 5, the ^{15}N chemical shift values of the amines at 2 M concentration (before bicarbonate is added) are reported as a function of the % of carbamate found at equilibrium (after the reaction of the amines with bicarbonate).

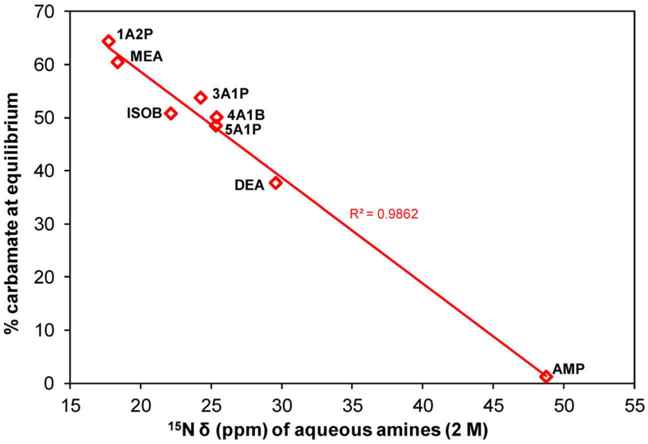

Figure 5. ^{15}N chemical shift (δ) of amines (2 M, 298.15 K) as a function of the percentage (%) of carbamate formed in reaction mixtures. Note that no bicarbonate was added when the ^{15}N measurements were done.

Figure 5 shows a fairly good linear trend for all the data in contrast to Figure 4. It appears that as the electron density increased on the nitrogen (reflected in decreasing ppm values), the amount of carbamate formed at equilibrium (after bicarbonate addition) increased.

There was a clear linear relationship between the ability of MEA, DEA, and AMP to form carbamate and their ^{15}N chemical shift values, a trend that was consistent with their chemical structures. Indeed, the lower electron density on the nitrogen of DEA as compared to MEA can be attributed to the presence of two hydroxyl groups in the β-position relative to the nitrogen, as compared to MEA's one hydroxyl group. Even though AMP has two methyl groups located α to the nitrogen, the electron density on the nitrogen is relatively low in comparison to the other amines. Chakraborty et al. showed that the interaction between the nitrogen lone pair and the methyl group orbitals can lead to significant changes in the donor properties of the amino species, resulting from a higher and more delocalized HOMO (Highest Occupied Molecular Orbital) which leads to a lower charge on the donor nitrogen site.[22]

For the unhindered primary amines (1A2P, MEA, 3A1P, 4A1B, 5A1P, and ISOB), the ^{15}N chemical shift trend and, consequently, the electron density on the nitrogen do not appear to reflect their structure. With shorter distances between the −OH and the $-NH_2$ functional groups (decreased basicity), the ^{15}N nuclei should be more deshielded but, in the case of these primary amines, the opposite is observed: the ^{15}N nuclei of the weaker bases, such as MEA and 1A2P, have an increased electron density (lower ppm values), resulting in an increased relative availability of the unshared electrons on the nitrogen to attack an electrophile (the carbon of bicarbonate in this study).

Other factors that could influence the ^{15}N chemical shifts, such that at increasing basicity there are shifts to higher ppm values (lower electron density), can be attributed to the interactions of the nitrogen lone-pair with hydrogen of donor groups, such as the water solvent and hydroxyl groups in other amine molecules or in its own molecule.[15a]

Water is a protic solvent characterized by a relatively strong polarity, as evidenced by the dielectric constant (ε = 78.4) and the molecular dipolar moment (μ= 1.8). Moreover, it plays an important role as hydrogen bond donor, since it exhibits a hydrogen bond donor acidity (α = 1.17) higher than a hydrogen bond acceptor basicity (β = 0.47).[23] The hydrogen of water can form hydrogen bonds with the unshared electron pair on nitrogen and the degree of this interaction depends on the degree of the lone pair delocalization. Hydrogen bonds to a protic solvent should strengthen with increasing basicity and the transition between intermolecular effects and chemical reactions may not be clear.[24] This is particularly true for proton exchange reactions, such as amine protonation ($RNH_2 + H_2O \leftrightarrows RNH_3^+ + OH^-$). It is impossible to distinguish in the NMR spectra the species exchanging a proton with water because the proton transfer is faster than the NMR time scale at 298.15 K and, as expected, only a single ^{15}N NMR signal is observed for both the solvated protonated and solvated free amine group in the amine molecules. Hence, at the same concentration and temperature, the ^{15}N nucleus of the aqueous amines at increased base strength will resonate at higher chemical shift values (which depend on the relative amount of the solvated free and solvated protonated amines) due to the interactions of the water hydrogen with the amino nitrogen, in terms of hydrogen bonds and/or protonation. An experimental confirmation of this expected ^{15}N chemical shift trend is given by further ^{15}N NMR experiments performed on MEA and 3A1P. Specifically, the chemical shift values of the ^{15}N nuclei of the amines, the fully protonated amines (amineH^+) and the amine/amineH^+ (1:1) mixture in aqueous solutions at the same concentration (2M) and temperature (298.15 K) were recorded and compared (Table 1). The increased ^{15}N ppm values at increased protonation (i.e., MEA 18.38 ppm, MEA/MEAH^+ 24.34 ppm, MEAH^+ 29.01 ppm and 3A1P 24.26 ppm, 3A1P/3A1PH^+ 29.42 ppm, 3A1PH^+ 33.66 ppm) are consistent with the expected increase of the chemical shifts with increasing interactions of the lone pair electrons of the amino nitrogen with water.

The hydroxyl functionality on the structure of the amine molecules also has an effect on the ^{15}N chemical shifts in terms of inter- and intramolecular hydrogen bonds. The latter were computed by Yamada et al., who combined ^{13}C NMR data and computations to investigate secondary alkanolamines with varied alkyl and alcohol chain length.[7] Their analyses indicated the likeliness of intramolecular H-bonds in alkanolamines if allowed by the amine's structure, i.e., if the molecular structure is such that the −OH group can be aligned toward the N's electron lone pair.

In our experiments, the first evidence of such possible interactions was observed for the ISOB molecule which lacks the −OH functional group. At 2 M concentration, the nitrogen resonated at a chemical shift value lower (higher electron density) than the other primary amines of comparable basicity and reactivity (i.e., 4A1B and 5A1P which have an −OH group in the structure). Similarly, further evidence of such inter- and intramolecular bonding effects was given by the ^{15}N NMR experiments performed on pure amines without any water dilution (Table 1).

As expected, in neat preparations, the nitrogen atom of each molecule resonates at a chemical shift lower than the corresponding aqueous amines at 2 M concentration because of the lack of water interactions. However, the stronger pure bases would be expected to have ^{15}N chemical shift values lower than the weaker pure ones. But, a trend similar to the diluted aqueous amines was observed, suggesting the presence of similar interactions which involve $-OH$ and $-NH_2$ functional groups of the amine structure. Comparisons of the chemical shift differences ($\Delta\delta$) between the pure and diluted amines indicated that the linear primary alkanolamines show similar $\Delta\delta$s (for MEA it is 1.54 ppm, for 3A1P it is 1.37 ppm, and for 4A1B it is 1.33 ppm), whereas for 1A2P, the value is 0.45 ppm and for ISOB, 3.45 ppm. The smaller $\Delta\delta$ for 1A2P as compared to the other molecules can probably be attributed to the particular position of the hydroxyl group. Compared to the linear primary alkanolamines, 1A2P could be more restricted to movements (more rigid) so that the chemical shifts are similar either with or without water. For ISOB, the large $\Delta\delta$ observed may be ascribed to the lack of inter- and intramolecular hydrogen bondings of the nitrogen atom to the hydroxyl group on the amine.

Our ^{15}N NMR data for linear primary alkanolamines would suggest that both solvent interactions and inter/intra molecular hydrogen bonds between functional groups on the amine structure could influence the carbamate formation reaction, but the molecular structure of the alkylamine ISOB provided insight into the main component affecting the reactivity of the studied unhindered primary amines. ISOB has a base strength and reactivity similar to 4A1B and 5A1P, but differs by the absence of hydrogen bonds between the nitrogen free electron pair and the hydroxyl function on the structure. Therefore, the main factor influencing the reactivity of these primary unhindered amines can be considered to be the interaction of the nitrogen electron lone-pair with water. The stronger the base, the more interactions with water occur, leading to a more solvation (which also involves the protonated amines) and, consequently, to the need of desolvation before nucleophilic attack for carbamate formation.[25]

Moreover, the hydroxyl function in the β-position to the nitrogen atom of the current unhindered primary amines (MEA and 1A2P) showed to increase the amine reactivity due to the electron-withdrawal property which reduced the basicity and, consequently, led to a relative weaker solvation. In the case of DEA and AMP, substitution effects and steric hindrance should also be considered. The structures of DEA and AMP differ from the other studied amines, but intra- and intermolecular H-bond networks cannot be excluded.

To further investigate the role played by the solvent on the availability of the lone pair electrons on the nitrogen atom, we performed ^{15}N NMR experiments on MEA and AMP in solvent blends containing both polar-protic and -aprotic components. Specifically, MEA and AMP solutions at 2 M concentration were prepared in water (H_2O)/dimethoxyethane (DME) at 1:1 ratio and the ^{15}N chemical shift values were compared to those obtained for the same amines in 100% water (Table 1). DME has a dielectric constant ($\varepsilon = 7.2$) lower than that of water ($\varepsilon = 78.4$) and the chemical shift values of the amines in DME-H_2O solvent are lower than in water alone. Thus, the electron density on the nitrogen is increased because the tendency of the amines to be protonated in this solvent is reduced (the dissociation constants will be different). This finding is in accordance with the reported decrease in amine base strength with decreasing solvent dielectric constants.[10]

Carbamate formation in amine-H_2O−DME mixtures was not studied because sodium bicarbonate is unsoluble in such solutions. Moreover, further attempts with other solvents were not carried out, as such investigations were beyond the scope of the current work. However, since the ^{15}N chemical shifts reflect the tendency to form carbamate, it may be assumed that the equilibrium for the carbamate formation in H_2O/DME would be shifted toward higher amounts of carbamate than that observed in 100% water.

Our findings that the tendency for carbamate formation is well described by the ^{15}N chemical shift values for these different molecules advances the understanding of the chemistry involved in aqueous amine solutions. Specifically, the solvent effect has been identified to be an additional factor influencing the reactivity of the amines.

4. CONCLUSIONS

In this study, ^{13}C and ^{15}N NMR spectroscopy was used to investigate the relationship between the chemical properties of amines and their tendency to form amine carbamates. For all the amines under study, the ^{15}N chemical shift values reflected the observed reactivity for forming carbamates very well.

Brønsted and Lewis bases are both synonyms of nucleophiles but, for the Brønsted bases, the proton is the only possible electrophile. The pK_b is indeed a measure of the proton accepting strength of a Brønsted base (e.g., the amine) in water. The ^{15}N NMR chemical shift is a measure of the relative electron density present on the N atom in respect to molecular structure and medium effects. In the current study, ^{15}N NMR chemical shift data are able to fit all our carbamate formation data (reaction of an amine Lewis base, the nucleophile, with the Lewis acid center, the electrophile, of the HCO_3^-) into a linear relationship, in contrast to a pK_b based relationship.

We demonstrated that the amount of amine carbamate formed by MEA and related unhindered primary amines decreased at increasing basicity due to the water solvent effect, which influenced the reactivity of the amine group. Under equivalent reaction conditions, the stronger unhindered bases were shown to have less availability of the N lone pair electrons to attack an electrophilic carbon for carbamate formation. This was attributed to their higher tendency to interact with the solvent. Such solvent effects have thus far been underestimated in the field of chemical absorption of CO_2. Concerning DEA and AMP, substitution and steric hindrance make their structures to some degree quite different from the other amines. However, their reactivity was well reflected by the ^{15}N NMR chemical shifts, and was therefore dependent on the availability of lone pair electrons on this nucleus, but the main factors influencing this have not been identified in this study.

In the field of chemical absorption of CO_2 by amine absorbents, these findings represent a step toward understanding the underlying dynamics of reactivity and, based on ^{15}N chemical shift values, allow us to estimate the amine activity.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

pK_b background of the amines, ^{15}N- and ^{13}C- NMR spectra, and a graph on the ^{13}C NMR spectra analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Tel.: +47-35575193; fax: +47-35575001; e-mail: Klaus.J.Jens@hit.no.

Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

MEA, 2-amino-1-ethanol or ethanolamine; 3A1P, 3-amino-1-propanol; 4A1B, 4-amino-1-butanol; 5A1P, 5-amino-1-pentanol; ISOB, isobutylamine; 1A2P, 1-amino-2-propanol; DEA, 2,2′-iminodiethanol or diethanolamine; AMP, 2-amino-2-methyl-1-propanol; DME, dimethoxyethane; STP conditions, Standard Temperature Pressure conditions; HCO_3^-, bicarbonate; CO_3^{2-}, carbonate; CO_2, carbon dioxide; CH_3CN, acetonitrile; AmineH$^+$, protonated amine; H_2O, water; NMR, Nuclear Magnetic Resonance; —OH, hydroxyl functional group; —NH_2, amino functional group in primary amines; —NH, amino functional group in secondary amines; —$NCOO^-$, amino functional group in amine carbamates; %, percent; δ, chemical shift; $\Delta\delta$, chemical shift differences; T_1, longitudinal relaxation time constant; s, seconds; h, hour; μs, microseconds; K, Kelvin (unit of temperature); ppm, parts per million

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