

13C and 15N NMR characterization of amine reactivity and solvent effects in CO2 capture

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Dette er siste forfatterversjon av artikkelen før publisering i tidsskriftet

Journal of Physical Chemistry, 2014, 118(34), 10167-10174

Forlaget versjon er tilgjengelig [her](#)

doi: [10.1021/jp503421x](https://doi.org/10.1021/jp503421x)

Tidsskriftets forlag, *ACS Publications*, tillater at siste forfatterversjon legges i åpent publiseringsarkiv ved den institusjon forfatteren tilhører

¹³C and ¹⁵N NMR Characterization of Amine Reactivity and Solvent Effects in CO₂ Capture

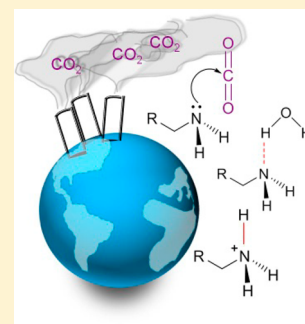
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S Supporting Information

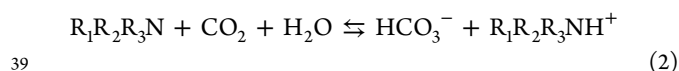
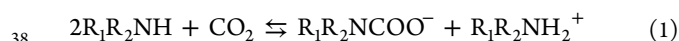
ABSTRACT: Factors influencing the reactivity of selected amine absorbents for carbon dioxide (CO₂) capture, in terms of the tendency to form amine carbamate, have been studied. Four linear primary alkanolamines at varying chain lengths (MEA, 3A1P, 4A1B, and 5A1P), two primary amines with different substituents 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 ¹⁵N NMR data of aqueous amines and their ability to form carbamate, as determined at equilibrium by quantitative ¹³C NMR experiments, was analyzed, taking into account structural–chemical properties. For all the amines, the ¹⁵N chemical shifts fairly reflected the observed reactivity for carbamate formation. In addition to being a useful tool for the investigation of amine reactivity, ¹⁵N NMR data clearly provided evidence of the importance of solvent effects for the understanding of chemical dynamics in CO₂ capture by aqueous amine absorbents.



1. INTRODUCTION

Acid gas (e.g., CO₂, H₂S) 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 CO₂, 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 CO₂ into the water phase takes place before the reaction of CO₂ with an amine. Primary and secondary amines react directly with CO₂ 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 CO₂ with water) and/or possibly as catalysts in the CO₂ hydration (reaction 2).⁴



Reaction 2 is more efficient than reaction 1 in terms of CO₂ absorption capacity, but reactions of primary and secondary amines with CO₂ (reaction 1) show the fastest reaction kinetics. However, during the CO₂ 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 CO₂ absorption capacity of an amine–CO₂–H₂O 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 CO₂ 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 CO₂ in order to obtain information on governing factors for solvent performances. Recently, Yamada et al. investigated the CO₂ absorption capacity of secondary alkanolamines with varied alkyl and alcohol chain lengths by combining computational data and ¹³C 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 CO₂ 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 –NH₂⁺ 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 CO₂ absorption capacity of 76 structurally diverse amines, and seven of them

Received: April 7, 2014

Revised: July 10, 2014

75 were identified for outstanding activity.⁸ These seven amines
 76 had some common structural features, such as the hydroxyl
 77 group located two or three carbons distant from the amino
 78 functionality, but the role played by this structural characteristic
 79 was unclear.⁸ Furthermore, with respect to the amine basicity,
 80 some Brønsted correlations relating rate and equilibrium
 81 constants for the carbamate formation and protonation
 82 constants of amines have been reported in the literature.^{6,9}
 83 Hamborg et al. described the base strength of the alkanol-
 84 amines to be dependent on the dielectric constants and
 85 temperature of the solvent.¹⁰ However, no clear trend between
 86 the CO₂ absorption capacity of the amines and the
 87 corresponding basicity was identified.^{8,11}

88 In view of the fact that water is the predominant component
 89 in amine solvents for CO₂ scrubbing, only a few reports have
 90 considered the properties of water (e.g., high polarity and
 91 extensive hydrogen bonding ability) in these reactions. Han et
 92 al. reported that water could be considered as a spectator in the
 93 reaction between amine and CO₂;¹² in contrast Arstad et al.
 94 showed in a computational study that water molecules can act
 95 as catalysts for the C—N bonding in the formation of carbamic
 96 acid (the corresponding acid to the carbamates)¹³ and da Silva
 97 has taken into account solvation in terms of stabilizing effect
 98 depending on structural accessibility.¹⁴ However, the influence
 99 of the water solvent has never been considered in terms of the
 100 availability of the nitrogen's lone pair of electrons to interact
 101 with water, although reactivity and CO₂ absorption capacity of
 102 the amines could be influenced greatly.

103 In order to provide further insight into amine solvents as
 104 absorbents for CO₂ capture, we have applied ¹³C and ¹⁵N NMR
 105 to characterize the amine reactivity, in terms of tendency to
 106 form amine carbamate. The background is that, during
 107 carbamate formation, the amino nitrogen is acting as a
 108 nucleophile (Lewis base) donating an electron pair to an
 109 electrophile (Lewis acid), such as CO₂ and/or HCO₃⁻, and the
 110 ability of a nucleophile to attack an electrophile depends not
 111 only on chemical structural properties of the molecules but also
 112 on medium effects. Increased electron density on the nitrogen
 113 raises the energy of the electron pair and makes it more
 114 reactive, which is the reason why the reactivity is thus strongly
 115 influenced by the availability of the electron lone pair of the N
 116 nucleus, making parameters describing the local electronic
 117 properties on the N atoms important for understanding these
 118 reactions. A technique that has been considered a useful tool to
 119 assess the electron density on the amino nitrogen atom and to
 120 study solvent interactions is ¹⁵N NMR spectroscopy, since it
 121 can provide information about the lone pair availability of
 122 nitrogen and the factors influencing the electron density on this
 123 nucleus, directly through the measured chemical shift values.¹⁵
 124 Indeed, ¹⁵N chemical shift values not only depend on the
 125 electronic chemical environment defined by the molecular
 126 structure but, as compared to ¹H and ¹³C NMR, are also much
 127 more sensitive to medium effects (e.g., concentration, temper-
 128 ature, and solvent) and, in general, to inter- and intramolecular
 129 interactions of the amino nitrogen with other functional
 130 groups.¹⁵

131 Little focus has been given on ¹⁵N NMR within the field of
 132 PCC, with the exception of Yoon et al., who reported a ¹⁵N
 133 NMR study discussing the electronic effects of substituents in
 134 sterically hindered amines on CO₂ absorption capacity.
 135 However, factors other than amine molecular structure (like,
 136 e.g., hydrogen bonds and solvent effects) were not consid-
 137 ered.¹⁶

In the current study, we have measured the amount of ¹³C
 carbamate formed at equilibrium in reactions of different
 amines with bicarbonate (HCO₃⁻), by means of quantitative
¹³C NMR experiments, and compared these values to ¹⁵N
 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).

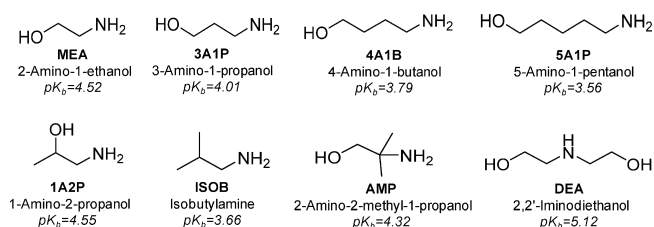


Figure 1. Amines investigated in this study.

This approach allowed us to identify overall factors
 influencing the tendency of the selected amines to form
 carbamate. In particular, ¹⁵N NMR spectroscopy was a useful
 tool to investigate the amine reactivity toward formation of
 amine carbamate, as determined by ¹³C 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 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 hydro-
 chloric 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
 cm³). The same procedure was used for preparation of water
 (H₂O)/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 H₂O–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

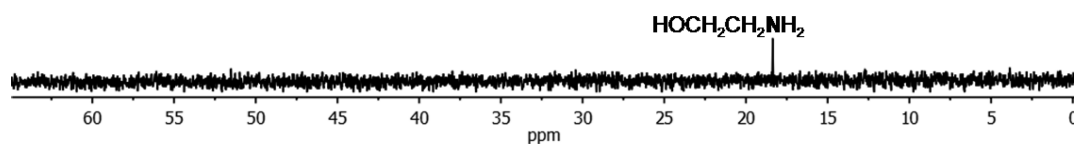


Figure 2. ^{15}N NMR spectrum of aqueous MEA solution (2 M) at 298.15 K. The nitrogen is shown in bold in the formula.

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 $\text{H}_2\text{O}/\text{DME}$ 1:1 | amine/amine H^+ 1:1 (2M) in H_2O | amine H^+ (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 | | |

^aSolid at STP conditions.

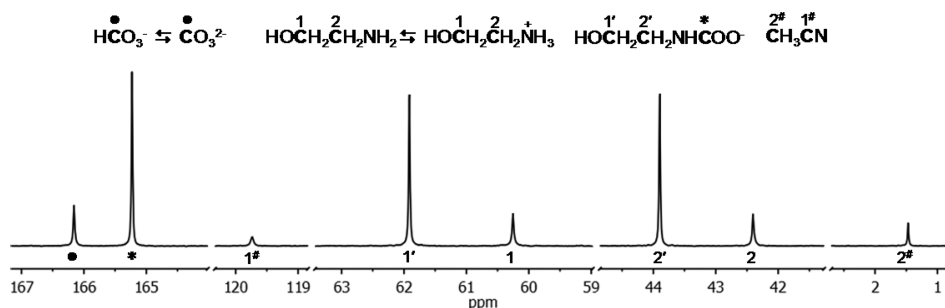


Figure 3. ^{13}C NMR spectrum and assignments for MEA/ NaHCO_3 1:1 ratio reaction mixture at the equilibrium. The observed carbons are given in bold in the formulas; CH_3CN is the reference.

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

188 The synthesis of amine carbamate was carried out by reacting
189 the aqueous amine solutions (2 M) with sodium bicarbonate at
190 1:1 molar ratio (reaction 3). The mixtures were stirred for more
191 than 24 h at 298.15 K to achieve equilibrium and after 48 h
192 quantitative ^{13}C NMR experiments were performed.



194 **2.2. NMR Experiments.** ^{13}C and ^{15}N NMR experiments
195 were performed at 9.4 T on a Bruker Avance III 400 MHz
196 spectrometer using a BBFO Plus double resonance probe head
197 at 298.15 K; the spectra were processed using MestreNova
198 software v 7.1.1.

199 **2.2.1. Qualitative ^{15}N NMR Experiments.** Qualitative ^{15}N
200 NMR experiments were carried out on the amine solutions at
201 the same concentration (2 M) and at constant temperature
202 (298.15 K) in order to eliminate the corresponding influences
203 on the chemical shifts. At the same temperature, ^{15}N NMR
204 experiments were also performed on the neat amines. For all
205 amines, the experiments were run with the inverse gated
206 decoupling method, pulse angle of 90° (14 μs pulse width) and
207 a prescan delay of 250 μs (optimized to reduce probe ringing).
208 The choice of the recycle delay was based on the need of
209 observing a signal at short experimental time. Therefore, for all
210 amine solutions, a recycle delay of 10 s and scans up to 4352
211 were set, except for 2 M 5A1P solution which required a recycle
212 delay of 50 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 ($\delta = 113.3$ 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
amine 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

241 in the capillary, the following parameters were used: recycle
242 delay of 120 s (corresponding to 6 times the longest T_1), pulse
243 angle of 90° ($8.9 \mu\text{s}$ pulse width) and 512 scans.¹⁸

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

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

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

272 The analyses of the quantitative ^{13}C NMR spectra for the
273 different amines were consistent with a decrease of the amount
274 of carbonate species ($\text{HCO}_3^-/\text{CO}_3^{2-}$) at increasing amount of
275 carbamate in solution (SI). Furthermore, in the reaction
276 mixtures of the amines with lower $\text{p}K_b$ (stronger bases), the
277 carbons corresponding to $\text{HCO}_3^-/\text{CO}_3^{2-}$ species were
278 resonating at a higher chemical shift value which corresponds
279 to an higher ratio of CO_3^{2-} (carbonate) to HCO_3^-
280 (bicarbonate)¹⁹(SI). However, since the aim of the present
281 work is the study of the amine reactivity toward carbamate
282 formation, we will focus the discussion of the ^{13}C NMR results
283 on the carbamate species only.

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

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

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

3. RESULTS AND DISCUSSION

293 The effect of molecular structure on base strength for the
294 current amines is related to inductive effects operating through
295 single bonds. Indeed, the hydroxyl function exerts an electron-
296 withdrawing inductive effect through bonds, whereas the alkyl
297 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 nitro-
gen 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 $\text{p}K_b$ of each amine²¹ (SI for the background)
is plotted against the amount of carbamate (in % as calculated
by eq 4).

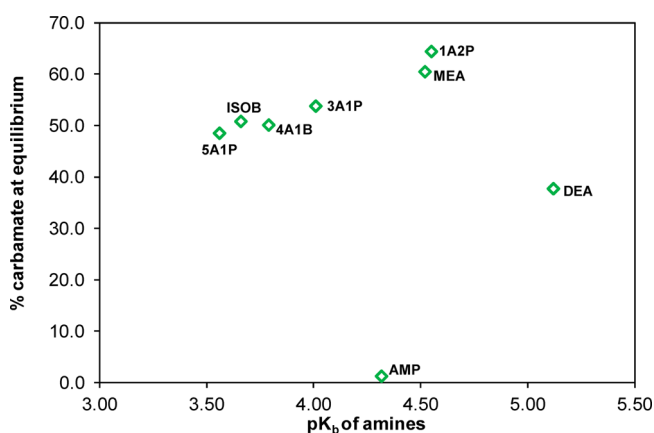


Figure 4. Amine basicity ($\text{p}K_b$, 293.15 K)²¹ as a function of the percentage (%) of carbamate at equilibrium.

For linear primary amines, the amount of carbamate at
equilibrium decreased with increasing basicity (lower $\text{p}K_b$,
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 $\text{CO}_2(\text{aq})$ 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, $\text{p}K_b$ 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

341 reactivity of amine to form carbamate may be reflected when
 342 setting up a relationship, as shown in Figure 4.
 343 The ^{15}N NMR chemical shift is a measure for the relative
 344 electron density present on a N nucleus in respect to molecular
 345 structure and medium effects. In Figure 5, the ^{15}N chemical

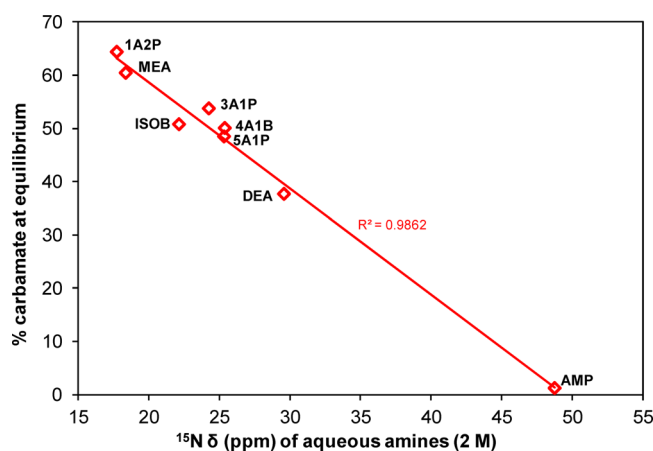


Figure 5. ^{15}N chemical shift (δ) of amines (2 M, 298.15 K) as a function of the percentage (%) of carbamate formed in reaction mixtures. Note that no bicarbonate was added when the ^{15}N measurements were done.

346 shift values of the amines at 2 M concentration (before
 347 bicarbonate is added) are reported as a function of the % of
 348 carbamate found at equilibrium (after the reaction of the
 349 amines with bicarbonate).

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

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

371 For the unhindered primary amines (1A2P, MEA, 3A1P,
 372 4A1B, 5A1P, and ISOB), the ^{15}N chemical shift trend and,
 373 consequently, the electron density on the nitrogen do not
 374 appear to reflect their structure. With shorter distances between
 375 the $-\text{OH}$ and the $-\text{NH}_2$ functional groups (decreased
 376 basicity), the ^{15}N nuclei should be more deshielded but, in
 377 the case of these primary amines, the opposite is observed: the
 378 ^{15}N nuclei of the weaker bases, such as MEA and 1A2P, have an
 379 increased electron density (lower ppm values), resulting in an
 380 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 ($\epsilon = 78.4$) and
 the molecular dipolar moment ($\mu = 1.8$). Moreover, it plays an
 important role as hydrogen bond donor, since it exhibits a
 hydrogen bond donor acidity ($\alpha = 1.17$) higher than a
 hydrogen bond acceptor basicity ($\beta = 0.47$).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 ($\text{RNH}_2 + \text{H}_2\text{O}$
 $\rightleftharpoons \text{RNH}_3^+ + \text{OH}^-$). 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 con-
 firmation 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 $-\text{OH}$ 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 $-\text{OH}$ 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 $-\text{OH}$ 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 protic groups ($-\text{OH}$, $-\text{NH}_2$) in 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 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 ($\epsilon = 7.2$) lower than that of water ($\epsilon = 78.4$) 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 insoluble 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 $\text{p}K_{\text{b}}$ 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 for 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 $\text{p}K_{\text{b}}$ 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, i.e., with the hydrogen of water. 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.

564 ■ ASSOCIATED CONTENT

565 ■ Supporting Information

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

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573 Notes

574 The authors declare no competing financial interest.

575 ■ ACKNOWLEDGMENTS

576 Financial assistance, a scholarship (to C.P.) provided by the
577 Research Council of Norway (CLIMIT grant nr. 199890), and
578 support from the SINTEF NMR lab, including staff are
579 gratefully acknowledged.

580 ■ ABBREVIATIONS

581 MEA, 2-amino-1-ethanol or ethanolamine; 3A1P, 3-amino-1-
582 propanol; 4A1B, 4-amino-1-butanol; 5A1P, 5-amino-1-penta-
583 nol; ISOB, isobutylamine; 1A2P, 1-amino-2-propanol; DEA,
584 2,2'-iminodiethanol or diethanolamine; AMP, 2-amino-2-
585 methyl-1-propanol; DME, dimethoxyethane; STP conditions,
586 Standard Temperature Pressure conditions; HCO_3^- , bicarbon-
587 ate; CO_3^{2-} , carbonate; CO_2 , carbon dioxide; CH_3CN ,
588 acetonitrile; AmineH^+ , protonated amine; H_2O , water; NMR,
589 Nuclear Magnetic Resonance; $-\text{OH}$, hydroxyl functional
590 group; $-\text{NH}_2$, amino functional group in primary amines;
591 $-\text{NH}$, amino functional group in secondary amines; $-\text{NCOO}^-$,
592 amino functional group in amine carbamates; %,
593 percent; δ , chemical shift; $\Delta\delta$, chemical shift differences; T_1 ,
594 longitudinal relaxation time constant; s, seconds; μs , micro-
595 seconds; K, Kelvin (unit of temperature); ppm, parts per
596 million

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