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Application of ^{15}N-NMR spectroscopy to analysis of amine based CO_2 capture solvents

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Abstract

^{15}N NMR spectroscopy is a useful tool for amine reactivity characterization since it can provide information about the availability of the lone pair of electrons on nitrogen through the measured chemical shift values, which depend on molecular structure and medium effects. Although the amino nitrogen is the focal nucleus of the carbon dioxide-amine reaction, ^{15}N NMR measurements have so far received little attention in the field of amine-based chemical absorption of carbon dioxide. In this study, from one hand, through ^{15}N NMR chemical shifts measurements, the effect of solvent on the electron density of the nitrogen of 2-methyl-2-amino-1-propanol (AMP) in solvent blends was investigated; from the other hand, ^{15}N NMR chemical shifts of aqueous primary non-hindered and hindered alkyl amines were related to the corresponding carbamate forming and carbamate stability equilibrium constants as well as carbamate forming kinetic constants, showing linear relationships. Such correlations could be useful for predictive estimation of carbamate-related equilibrium and kinetic constants.

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Keywords: ^{15}N NMR; amines; carbon dioxide; reactivity; carbamate-related constants.

1. Introduction

In spite of intensive global carbon dioxide (CO_2) capture research and development initiatives, the well known CO_2 gas-liquid absorption process is expected to be the technology of choice for early large scale deployment of post combustion carbon capture (PCC) [1, 2]. The main current challenge is to develop more cost effective and

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superior performing amine solvents. Molecular structure property understanding of solvents is crucial in this respect. Reaction of CO_2 with primary or secondary aqueous amine solutions can be described by equations (1) to (4) [3].

$$CO_2 + H_2O \leftrightarrows H_2CO_3 \leftrightarrows [H]^+[HCO_3]^- \quad (1)$$
$$CO_2 + [R_1R_2NH_2]^+[OH]^- \leftrightarrows [R_1R_2NH_2]^+[HCO_3]^- ; (R_2= R, H) \quad (2)$$
$$CO_2 + 2R_1R_2NH \leftrightarrows [R_1R_2NCO_2H + R_1R_2NH] \leftrightarrows [R_1R_2NCO_2]^- [R_1R_2NH_2]^+; (R_2= R, H) \quad (3)$$
$$[R_1R_2NCO_2]^- [R_1R_2NH_2]^+ + H_2O \leftrightarrows R_1R_2NH + [R_1R_2NH_2]^+[HCO_3]^- ; (R_2= R, H) \quad (4)$$

In general, carbamate formation reaction (3) is the fast reaction, defining the CO_2 capacity of the aqueous amine solvent to be 0.5 mol CO_2 per mol of amine. Reactions (1), (2) and (4) are less important under these circumstances. However, carbamate hydrolysis reaction (4) is important for steric hindered amines for which CO_2 capacities larger than 0.5 can be achieved [4]. Understanding reactions (3) and (4) is important background for identification of improved aqueous amine solvents.

The equilibrium constant and the kinetic constant for carbamic acid formation (first step in reaction (3)) have been rationalized for some amines to be a function of amine protonation constant. Deviation from this Brønsted relationship has been proposed to be due to steric effects (e.g. steric hindered amines); for ammonia (NH_3), solvation effects have been thought to be the reason for deviation from this relationship [5].

NMR spectroscopy is a non-invasive analytical technique which allows direct measurement of specific nuclei of the species in solution and it is hence a good method for gaining chemical insight into PCC solvent systems [6]. In spite of numerous valuable results obtained by use of ^{1}H- and ^{13}C-NMR spectroscopic experiments on PCC solvents, direct measurement of the amino atom, the focal nucleus of the CO_2-amine reaction, has so far received little attention [7, 8]. ^{15}N-NMR, a well known spectroscopic method, is a powerful tool for assessment of nitrogen (N) containing molecular reactivity [9, 10], including insight into the solvent effects on the carbamate formation reaction [7]. Indeed, due to the presence of a lone pair of electrons on the nitrogen, the relative electron density on the N atom depends not only on the electronic environment as defined by the molecular structure but, as compared to ^{1}H and ^{13}C, it is also more sensitive to medium effects (e.g. solvent, concentration and temperature) and, in general, to inter- and intra-molecular effects. The changes in electron density are reflected trough the chemical shifts variations [11, 12].

The carbamate formation reaction is a nucleophilic addition reaction: the N atom is acting as nucleophile (Lewis base) which donates the lone pair electrons to the electrophilic centre (carbon, C) of the CO_2 (Lewis acid), forming a new bond and, consequently, a new species (i.e. amine carbamic acid/carbamate). Estimation of the relative electron density on the nitrogen atom by means of ^{15}N NMR spectroscopy appears to be a useful method to characterize the reactivity of the amines, both in terms of reaction equilibrium [7] and of reaction kinetics [13].

We here report application examples of ^{15}N-NMR spectroscopy for PCC solvent understanding.

Qualitative ^{15}N-NMR experiments have been performed at 298.15 K on primary amines (2 M). From one hand, the effect of solvents, other than water, on the ^{15}N chemical environment of a primary steric hindered amine, 2-amino-2-methyl-1-propanol (AMP), has been investigated in order to achieve insights into the relative availability of the lone pair of electrons on the nitrogen to react with CO_2. On the other hand, the ^{15}N chemical shift values of aqueous primary alkylamines (before CO_2 loading) have been related to corresponding carbamate-related constants available in literature [14]. It can be shown that there is a linear relationship between the ^{15}N chemical shift values, the equilibrium constants, i.e. log K_c for reaction (3) and log K_{hyd} for reaction (4), and the kinetic constants, i.e. log k for reaction (3), of the amines under study.

2. Experimental Section

All the amines were purchased from Sigma Aldrich (assay: ≥ 99%) and used as received. In a typical sample preparation, weighed amount of amine and water (deionised and degassed) were mixed and the concentrations (2.00 ± 0.04 M) were calculated by measuring the density with a pycnometer. The same procedure was used for preparation of AMP solutions in solvent blends. The samples were then transferred to a NMR tube for ^{15}N NMR measurements.

^{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. The

experiments were carried out on amine solutions at the same concentration (2M) and at the same temperature (298.15 K) to avoid corresponding effects on the chemical shift values. The uncertainty in the chemical shit values was estimated to be in the range of ±0.01-0.03 ppm. The used method is fully described in the ^{15}N NMR study by Perinu et al.[7].

3. Results and Discussion

The ^{15}N NMR chemical shift is a measure for the relative electron density present on the N nucleus which is depending on molecular structure and medium effects. Increased electron density on the nitrogen corresponds to an increased energy of the lone pair electrons, making the amino function more reactive.

Recently, ^{15}N NMR spectroscopy has been applied to investigation of the carbamate formation reactions of selected aqueous amine absorbents belonging to different classes (primary, secondary and steric hindered amines). In that study, the ^{15}N NMR chemical shifts fairly reflected the observed amount of carbamate formed at equilibrium, resulting in a linear relationship. Moreover, analysis of ^{15}N NMR data for non-hindered primary amines clearly provided evidence of the effect of solvent on the carbamate formation reaction [7]. It was demonstrated that at equilibrium the amount of carbamate formed from non-hindered primary amines decreased at increasing basicity due to the higher tendency of the stronger bases to interact with water which reduced the availability of the lone pair electrons on the nitrogen for the carbamate formation reaction [7].

In Figure 1, ^{15}N chemical shifts (expressed in part per million, ppm) observed for AMP in different solvent blends are reported. Considering that the ^{15}N chemical shift reflects the availability of lone pair electrons of the nitrogen atom to react [7], it would be expected that the equilibrium for carbamate formation could be influenced by changing the type of solvent.

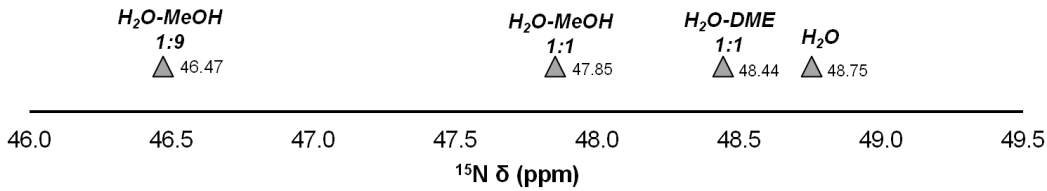


Figure 1. ^{15}N NMR chemical shifts measured at 298.15 K on AMP (2 M) in solvent blends (DME: 1,2-Dimethoxyethane; H_2O: Water; MeOH: Methanol).

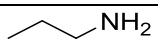
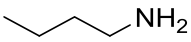
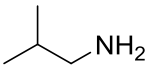
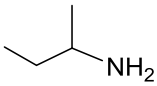
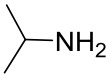
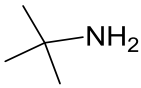
Table 1 shows the carbamate-related constants of sterically hindered and non-hindered primary alkyl amines for reaction (3) and (4), the pK_b values and the ^{15}N NMR chemical shift values of the respective aqueous amine solutions (2 M, before CO_2 loading).

Since both reactions (3) and (4) are Lewis acid-base reactions, as expected, reaction equilibrium constants can be related to the relative electron density on the nitrogen nucleus of the respective amine, similar to our above mentioned study [7].

In Figure 2, the ^{15}N NMR chemical shifts of the primary alkyl amines (before CO_2 loading) are plotted versus the equilibrium constants for a) the carbamate formation reaction (K_c, reaction 3) and b) the carbamate stability or hydrolysis reaction (K_{hyd}, reaction 4), taken from literature [14] (Table 1). Linear relationships are observed.

Decreasing ppm value of the ^{15}N NMR chemical shift corresponds to increased relative electron density on the N nucleus. Figure 2a shows that the carbamate formation equilibrium constant increases at increased electron density on the N nucleus (lower ppm values). On the contrary, Figure 2b shows that carbamate hydrolysis constant increases for those amines which have the tendency to form less carbamate and are characterized by a lower relative electron density on the N (high ppm values). It is worth noting that both non-hindered and hindered amines lie on the same line in both correlations plotted in Figure 2.

Table 1. Names, structures, carbamate-related equilibrium constants (Log K_c and Log K_{hyd}), kinetic constants of carbamate formation (Log k), base dissociation constants (pK_b) and measured ^{15}N chemical shift (δ, expressed in ppm) values of aqueous primary alkyl amines (2 M, before CO_2 loading).

Amine name and abbreviation	Structure	$LogK_c$ (291.15 K) [14]	$LogK_{hyd}$ (291.15 K) [14]	Log k (291.15 K) [14]	pK_b^* (298.15K) [5, 15, 16]	^{15}N δ (ppm) (298.15 K)
Propylamine (NH_2Pr)		6.18	-1.89	5.20	3.43	25.23
Butylamine (NH_2Bu)		6.04	-1.80	5.30	3.36	25.40
Isobutylamine (NH_2iBu)		6.11	-2.00	5.20	3.52	22.15
Sec-Butylamine (NH_2sBu)		5.58	-1.31	4.85	3.44	42.44
Isopropylamine (NH_2iPr)		5.56	-1.20	4.83	3.33	46.81
Tert-Butylamine (NH_2tBu)		5.04	-0.85	4.28	3.32	60.87

* $pK_b = pK_{w(298.15\,K)} - pK_a$ that is $pK_b = 14.00 - pK_a$

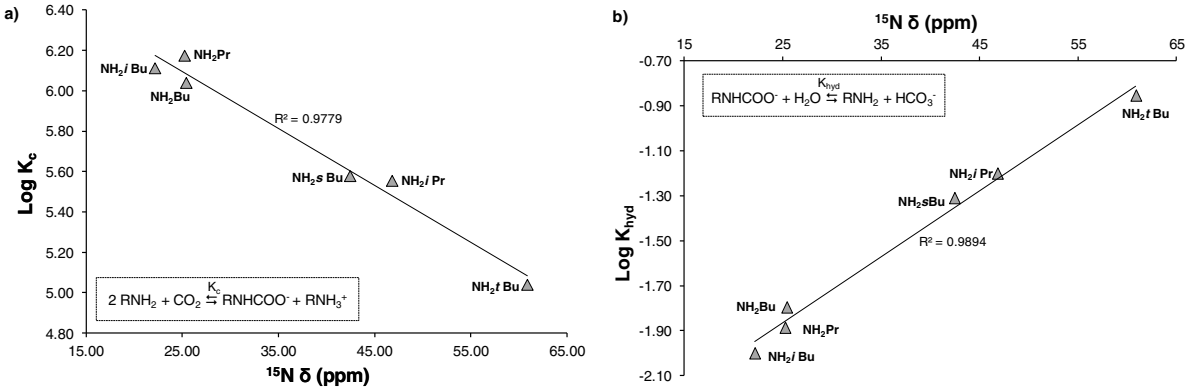


Figure 2. ^{15}N NMR chemical shifts (δ) values of aqueous primary non-hindered and hindered alkyl amines (2 M, before CO_2 loading) as a function of the corresponding a) carbamate forming equilibrium constants (Log K_c) and b) carbamate stability equilibrium constants (Log K_{hyd}).

However, when plotting the carbamate formation and hydrolysis constants as a function of pK_b, the above linear relationships are not observed anymore (Figure 3).

Figure 3 shows that at increasing steric hindrance on the alpha carbon to the N atom, there is a deviation from the trend line observable for non-hindered primary alkylamines. A similar result, as shown in Figure 3, has been observed for several other related alkyl and alkanol amines [5, 7, 17].

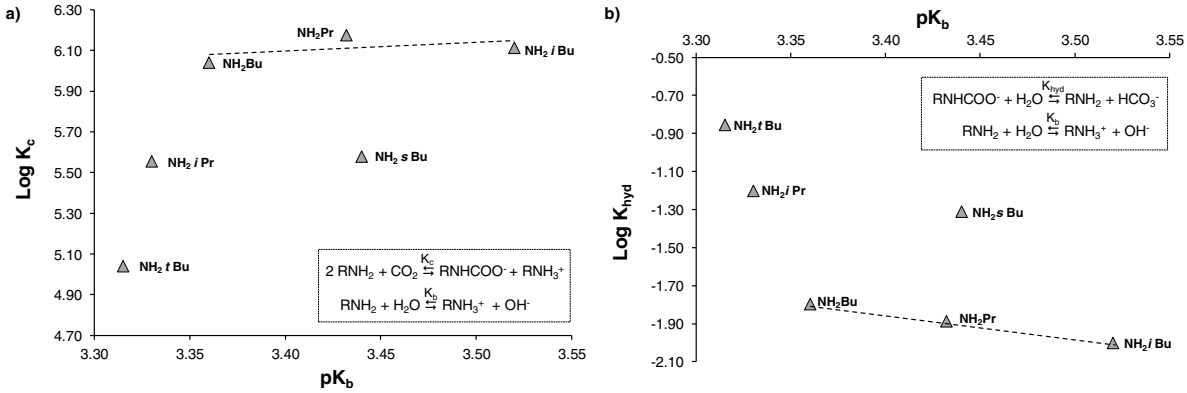


Figure 3. pK_b values as a function of a) carbamate forming equilibrium constants (Log K_c) and b) carbamate stability equilibrium constants (Log K_{hyd}) of aqueous primary non-hindered and hindered alkyl amines.

The discrepancy between the ^{15}N NMR chemical shift and the pK_b relationships may rely on the fact that the ^{15}N NMR chemical shift is a measure of the relative electron density on the N atom in respect to molecular structure and medium effects, whereas the pK_b is a measure of the proton accepting strength of a Brønsted base in water [7].

The Brønsted basicity scale is indeed built on the base-dissociation constant of Brønsted bases in water (reaction 5).

$$RNH_{2(aq)} + H_2O_{(l)} \leftrightarrows [RNH_3]^+_{(aq)} + [OH]^-_{(aq)} \quad (5)$$

For amines, the ammonium ion solvation term is considered to give an important contribution to the position of the reaction equilibrium and is thought to be the main reason for the "anomalous order" of substituent effects in amines [16]. Apparently this basicity scale contains some contributing components which do not directly reflect factors affecting the carbamate forming reaction. So far, only in a closely related series of non-hindered primary or secondary amines, a linear Brønsted relationship has been found [5, 7, 17, 18].

On the other hand, with respect to the ^{15}N NMR data, it is interesting to note that even sterically hindered amines, like e.g. tert-butylamine, are part of the linear relationships. The origin of the steric hindered amine effect on the carbamate formation reaction has been proposed to be due to electron charge transfer from the nitrogen nucleus to the substituting methyl group bonded to the carbon in alpha position to the N atom [19]. Recently, however, the effect of the methyl group has been suggested to be rather stereochemical than electronic [20]. Our ^{15}N NMR chemical shift data obtained so far on sterically hindered amines are consistent with the theory indicating steric hindrance in amines to be an electronic effect.

The ^{15}N NMR chemical shift is a useful parameter to investigate amine reactivity also in terms of reaction kinetics [13]. Figure 4 shows a linear relationship between the kinetic constants for carbamate formation (reaction 3) and the ^{15}N chemical shift values of aqueous primary alkyl amines, including steric hindered alkyl amines.

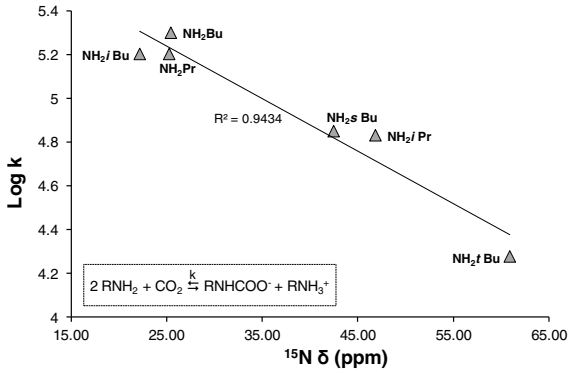


Figure 4. ^{15}N NMR chemical shifts (δ) values of aqueous primary non-hindered and hindered alkyl amines (2 M, before CO_2 loading) as a function of carbamate forming kinetic constants (Log k, $M^{-1}min^{-1}$).

So far, the results shown in Figure 2 and 4 suggest that a correlation between K_c, K_{hyd}, k and the ^{15}N NMR chemical shifts of amines can be found. Such correlation could be useful for predictive estimation of carbamate–related reaction constants, in both thermodynamic and kinetic terms.

4. Conclusions

^{15}N NMR spectroscopy is a useful tool for amine reactivity characterization since it can provide information about the lone electron pair availability on the nitrogen nucleus through the measured chemical shift values, which depend on molecular structure and medium effects. In this study, trough ^{15}N NMR measurements, it was confirmed that, as expected, the electron density on the nitrogen atom changes as a function of the type of solvent used, which may lead to a change of amine reactivity.

Moreover, a linear correlation between log K_c, log K_{hyd}, log k and the ^{15}N NMR chemical shifts of aqueous primary non-hindered and hindered alkyl amines was found. Such correlations could be useful for predictive estimation of carbamate forming and carbamate stability (hydrolysis) equilibrium constants as well as carbamate forming kinetic constants of amine absorbents for CO_2 capture.

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