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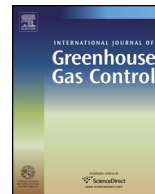| Location in article	Query / Remark: **click on the Q link to go** **Please insert your reply or correction at the corresponding line in the proof**
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Highlights

International Journal of Greenhouse Gas Control xxx (2013) xxx–xxx

NMR spectroscopy applied to amine–CO$_2$–H$_2$O systems relevant for post-combustion CO$_2$ capture: A review

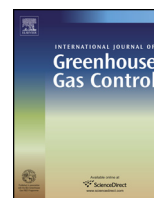Cristina Perinu, Bjørnar Arstad, Klaus-Joachim Jens[*]

- A survey of the NMR studies performed on amine–CO$_2$–H$_2$O systems is presented.
- Technical aspects of NMR experiments and methods are depicted.
- The main applications and corresponding results obtained by NMR are reported.
- NMR spectroscopy is a useful tool to identify and quantify liquid reaction products.

1 Review

NMR spectroscopy applied to amine–CO_2–H_2O systems relevant for post-combustion CO_2 capture: A review

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ABSTRACT

Nuclear Magnetic Resonance (NMR) spectroscopy is a powerful non-invasive analytical technique for chemical analyses since direct measurements at a molecular level can be performed. In this work, a survey of NMR spectroscopy applied for studies of CO_2 absorption in aqueous amine solvents (amine–CO_2–H_2O) relevant for post-combustion CO_2 capture is presented. Technical aspects of NMR experiments and the main applications with corresponding results are provided. The overview of the NMR literature in this field suggests that studies of amine–CO_2–H_2O systems can benefit from a further consideration of this spectroscopic technique.

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Contents

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Nomenclature

Symbols

1D	mono-dimensional
2D	two-dimensional
K	Kelvin (unit of temperature)
K_c	carbamate stability constant
k	rate constant
M (mol/l)	molar concentration (mole/litre)
ppm	part per million (unit)
T_1	spin-lattice (or longitudinal) relaxation time
S/N	signal to noise ratio
wt.%	weight percent
γ	activity coefficient

Acronyms and abbreviations

AEEA	2-(2-aminoethylamino)ethanol
AmineH$^+$	protonated amine
AMP	2-amino-2-methyl-1-propanol
AMPD	2-amino-2-methyl-1,3-propanediol
AP	2-amino-1-propanol
BEA	2-(butylamino)ethanol
COSY	correlation spectroscopy
DEA	diethanolamine or 2,2′-iminodiethanol
DEPT	distortionless enhancement by polarization transfer
DETA	diethylenetriamine
DMDEA$^+$	dimethyl-diethanolamine ion
DMMEA	2-(dimethylamino)ethanol
HMBC	Heteronuclear Multiple Bond Correlation
HSQC	Heteronuclear Single Quantum Correlation
HEA	N-(2-hydroxyethyl)acetamide
HEI	N-(2-hydroxyethyl)imidazole
HEF	N-(2-hydroxyethyl)formamide
MAPA	3-(methylamino)propylamine
MDEA	N-methyldiethanolamine or 2,2′-methyliminodiethanol
MEA	monoethanolamine or 2-aminoethanol
MEACOO$^-$	monoethanolamine carbamate
MEAH$^+$	protonated monoethanolamine
MMEA	N-methylethanolamine or 2-(methylamino)ethanol
NMR	Nuclear Magnetic Resonance
NOE	Nuclear Overhauser Effect
OZD	2-oxazolidone
PCC	post-combustion capture
PZ	piperazine or 1,4-diazacyclohexane
VLE	vapour-liquid equilibrium
SAR	sarcosine or N-methylglycine

Further acronyms and abbreviations in the Table A1 (Appendix A)

AA	amino acid
AHPD	2-amino-2-hydroxymethyl-1,3-propanediol
Abs	absorption experiments
ALA	L-alanine or (S)-2-aminopropionic acid
ATR-FTIR	attenuated total reflectance-Fourier transform infrared spectroscopy
BZ	benzylamine
Cf/Cd	carbamate formation/decomposition
CYS	cysteine
DAP	1,2-diaminopropane
DEAB	4-(diethylamino)-2-butanol
DEEA	2-(diethylamino)ethanol
Des	desorption experiments
DGA	diglycolamine or 2-(2-aminoethoxy)ethanol

DIPA	diisopropanolamine
EAE	2-(ethylamino)ethanol
EDA	ethylenediamine
f.e.p.	fast exchanging proton
GC/LC–MS	gas chromatography/liquid chromatography–mass spectrometry
GLY	glycine or aminoethanoic acid
homoPZ	homopiperazine
IBA	isobutylamine
IPAE	2-(isopropylamino)ethanol
MAE	2-(methylamino)ethanol
MORP	morpholine
MPZ	N-methylpiperazine
n.a.	not available
NRTL	non-random two liquid model
2-PE	2-piperidineethanol
PIPD	piperidine
4-PIPDM	4-piperidinemethanol
4-PIPDE	4-piperidineethanol
PRO	L-proline or (S)-pyrrolidine-2-carboxylic acid
PYR	pyrrolidine
RITE	base amines-additives
SER	L-serine or (S)-2-amino-3-hydroxypropanoic acid
TAU	taurine or 2-aminoethanesulphonic acid
TMORP	thiomorpholine

1. Introduction

1.1. Background

Processes utilizing aqueous amine solvents for chemical absorption of carbon dioxide (amine–CO_2–H_2O systems) are considered to be a robust separation technology to remove carbon dioxide (CO_2) from flue gas streams and will probably be deployed on a large scale in the years to come (Rochelle, 2009). However, the energy demands for CO_2 desorption and amine regeneration, corrosive nature of amines and their degradation represent the main drawbacks which limit their application (Ahn et al., 2011a). For rational improvement of the efficiency of post-combustion capture (PCC) by amine solvents and developments of new absorption systems, an accurate understanding of the underlying chemical processes (such as reaction kinetics, equilibria present and thermodynamics) involved in the capture and release of CO_2 is needed (Conway et al., 2012). In the context of PCC development, vapour-liquid equilibrium (VLE) models are critical tools for development and optimization of the gas–liquid absorption process (Faramarzi et al., 2009; Kontogeorgis and Folas, 2009). However, predictive thermodynamic VLE models are dependent on accurate determination of solvent composition and such data are often inferred through measurement of related variables that extend the data available for fitting. Nuclear Magnetic Resonance (NMR) spectroscopy allows direct access to the chemical composition of CO_2 capture solvents (speciation) and therefore more object functions usable for fitting parameters are provided. Furthermore, by monitoring speciation of the whole cyclic process of CO_2 capture, it is possible to obtain information on reaction mechanisms, kinetics of reaction, factors influencing reaction conditions (such as the chemical structures of the amines), amine capacities and CO_2 solubility (Jakobsen et al., 2008; Yang et al., 2009).

Before entering more detailed issues, a few words about NMR spectroscopy is useful as background. NMR is a non-invasive analytical technique which allows the study of atoms that have nuclei with a magnetic moment (i.e. a spin quantum number of

the nucleus different from zero). Some examples are the following isotopes: ^{1}H, ^{13}C, ^{15}N NMR data are usually presented as spectra showing peaks (reported along an axis with units ppm, parts per million) that correspond to the different nuclei in the molecules. Depending on NMR experiments, interpretation of the data leads to information on chemical structure and dynamics of compounds/materials. A strong quality of the NMR technique is that peak areas are also directly proportional to the number of nuclei contributing to the signals and, with some care, quantitative analyses of compounds are hence possible. Another advantageous feature of NMR is that unknown compounds (e.g. reaction and degradation products) can also be characterized and quantified without the use of any standard reference (Böttinger and Hasse, 2008).

In spite of the potential and practical importance of NMR spectroscopy, so far only a limited number of studies have been reported in the literature on investigation of liquid phase composition of amine–CO$_2$–H$_2$O systems. However, interest in NMR spectroscopy is growing, as evidenced by the increased number of publications in recent years (Fig. 1).

In this work we provide a survey of approximately 50 articles published up to spring 2013 where NMR has been applied for studies of aqueous amine solvents for CO$_2$ capture. Recently, Shi et al. published a review on the use of NMR for development of VLE models (Shi et al., 2012a) and we reported a short overview of ^{13}C NMR studies on aqueous amine systems relevant for CO$_2$ capture (Perinu et al., 2013). The present review gives an extensive survey of all types of NMR experiments and all possible applications, including methods and main results.
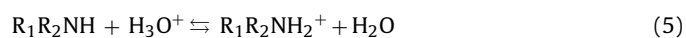
1.2. Outline

The present review is structured as follows: Section 2 gives an overview of the main chemical reactions involved in the amine–CO$_2$–H$_2$O systems, including the main issues of concern, and lists the main class of amine absorbents studied by NMR spectroscopy. In Section 3, technical aspects of NMR experiments and methods used to obtain quantitative data are discussed. The main applications and results obtained by NMR are reported in Section 4, while Section 5 provides some final considerations on the range of applicability of NMR spectroscopy in this field.

## 2. Overview of amine–CO$_2$–H$_2$O system chemistry

The absorption of CO$_2$ in aqueous amine solvents involves several parallel reactions that give rise to a large number of species in the liquid phase (Eqs. (1)–(7)).

Reaction rates and equilibrium constants for the water dissociation (1), the hydration of CO$_2$ (2), dissociation of carbonic acid (3) and bicarbonate (4) are known (Edsall, 1969; Pocker and Bjorkquist, 1977), as well as the protonation constants for many amines (5) (Hamborg and Versteeg, 2009; Perrin, 1965).

$$H_2O + H_2O \leftrightarrows H_3O^+ + OH^- \tag{1}$$

$$CO_2 + H_2O \leftrightarrows H_2CO_3 \tag{2}$$

$$H_2CO_3 + H_2O \leftrightarrows HCO_3^- + H_3O^+ \tag{3}$$

$$HCO_3^- + H_2O \leftrightarrows CO_3^{2-} + H_3O^+ \tag{4}$$

$$R_1R_2NH + H_3O^+ \leftrightarrows R_1R_2NH_2^+ + H_2O \tag{5}$$

On the other side, the reaction of CO$_2$ with amine compounds is critical and still merits further investigations. In particular, primary and secondary amines (with the exception of those that are so-called sterically hindered amines) in water react with CO$_2$ to form

carbamate with a stoichiometric loading of 0.5 mol CO$_2$/mol amine, as indicated in the following condensed reaction:

$$2R_1R_2NH + CO_2 \leftrightarrows R_1R_2NCOO^- + R_1R_2NH_2^+ \tag{6}$$
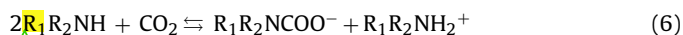
In contrast, the reaction between tertiary (and some sterically hindered) amines and CO$_2$ can be described with the base catalysis of CO$_2$ hydration as proposed by Donaldson and Nguyen (Donaldson and Nguyen, 1980; Fernandes et al., 2012) and loadings of 1.0 mol CO$_2$/mol amine are achieved in the following way:

$$R_1R_2R_3N + CO_2 + H_2O \leftrightarrows HCO_3^- + R_1R_2R_3NH^+ \tag{7}$$
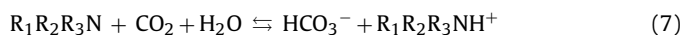
Reaction (7) is more efficient than 6 in terms of CO$_2$ absorption capacity, but reactions of primary and secondary amines with CO$_2$ show faster kinetics. However, during the CO$_2$ desorption/amine regeneration step, the energy demand for the reverse of 6 is higher than 7 due to the stability of carbamates (Sartori et al., 1987). A considerable number of publications on carbamate formation are found in literature, but only a few of these propose empirical reaction mechanisms that adequately model the measured gas absorption data (Caplow, 1968; Crooks and Donnellan, 1989; Versteeg et al., 1996). Experimental evidence of the chemistry associated with carbon dioxide and aqueous amine solvents (mechanism of reaction, equilibrium and rate kinetics constants) and of the factors that influence carbamate formation is still scarce (Aroua et al., 1997; McCann et al., 2009b). Quantum mechanical modelling has provided some insight into the chemistry and possible mechanistic pathways, but still needs experimental validations (Arstad et al., 2007; da Silva and Svendsen, 2004; Guido et al., 2012; Iida and Sato, 2012; Maiti et al., 2011).

At the present, most of the NMR studies on amine–CO$_2$–H$_2$O systems deal with alkanolamines, which are the most common chemical absorbents for the removal of acid gases. In addition, ammonia (Ahn et al., 2011a,b; Holmes et al., 1998; Mani et al., 2006; Pellegrini et al., 2010; Rowland et al., 2011), amino acid (Ciftja et al., 2013; Hartono et al., 2011; Hook, 1997; Xiang et al., 2012) and various other amine systems have also been examined by NMR (Conway et al., 2012; Fernandes et al., 2012; García-Abuín et al., 2012; Hartono et al., 2006; Kim et al., 2011a; McCann et al., 2011b; Mergler et al., 2011; Paul et al., 2008; Yang et al., 2012). Among the latter, piperazine (PZ), a cyclic diamine, is the most commonly studied (Bishnoi and Rochelle, 2000, 2002; Böttinger et al., 2008; Conway et al., 2013; Cullinane and Rochelle, 2005; Derks et al., 2010; Ermatchkov et al., 2003; Hartono et al., 2013; Kim et al., 2011b). Table A1 in Appendix A lists amine–CO$_2$–H$_2$O systems investigated by NMR collected in the present manuscript.

3. Experimental NMR methods

3.1. NMR Experiments

Out of various one- and two-dimensional (1D and 2D) NMR experiments, single pulse ^{1}H and ^{13}C NMR experiments are the most common ones for studies of amine–CO$_2$–H$_2$O systems. However, one paper has reported single pulse ^{15}N NMR experiments with the aim to evaluate the electron releasing and withdrawing effects of substituents on the background of ^{15}N chemical shift changes (Yoon, 2003) and Ciftja et al. have reported the use of DEPT (Distortionless Enhancement by Polarization Transfer) experiments to identify the primary, secondary and tertiary ^{13}C atoms of the species (Ciftja et al., 2011, 2013). Two-dimensional (2D) NMR experiments, like e.g. COSY (Correlation Spectroscopy), HSQC (Heteronuclear Single Quantum Correlation) and HMBC (Heteronuclear Multiple Bond Correlation), are quite often reported to define and/or check the chemical structure of the species in solution (Ballard et al., 2011; Bishnoi and Rochelle, 2000, 2002; Böttinger
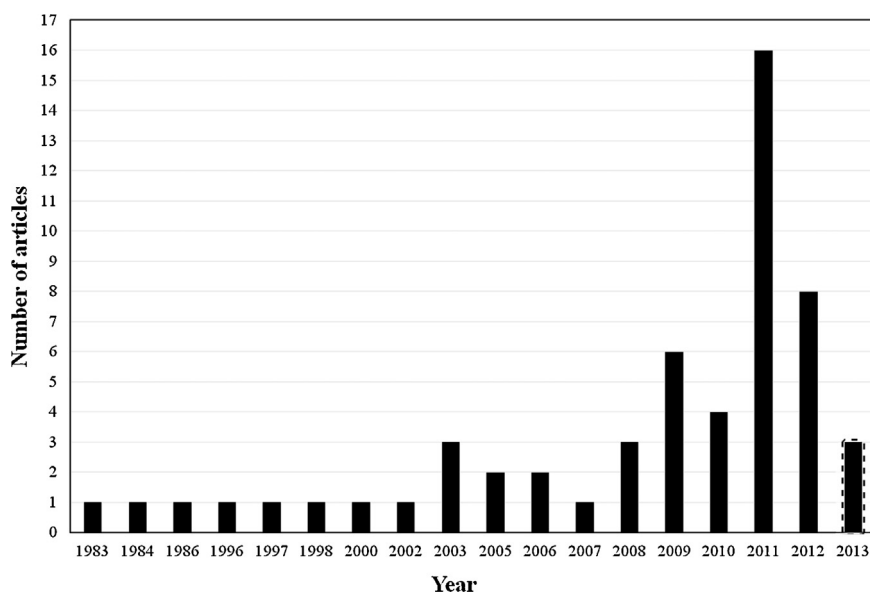
Fig. 1. Graph of the number of articles, dealing with NMR spectroscopy, per year. The traced column corresponding to the year 2013 reports the papers up to spring 2013.

et al., 2008; Bottinger and Hasse, 2008; Ciftja et al., 2012, 2013; Cullinane and Rochelle, 2005; Derks et al., 2010; Fan et al., 2009; Hartono et al., 2006, 2011; Jakobsen et al., 2008; Kim et al., 2011a,b; Ma'mun et al., 2006; McCann et al., 2009b).

Since the main goal of many works is often the estimation of the relative amounts of species, most of the papers deal with quantitative NMR studies and only few of them exclusively report qualitative evaluation for novel amine–CO_2–H_2O systems (García-Abuín et al., 2012; Hartono et al., 2006, 2011; Paul et al., 2008; Rowland et al., 2011).

For quantitative analyses, ^{1}H NMR is fast and reliable but not all the species in solution can be observed (like e.g. carbonate and bicarbonate). Thus, mostly ^{13}C NMR experiments are used to study the species distribution in amine–CO_2–H_2O systems because direct information of all interacting species, with the exception of H_2O, H_3O^+ and OH^-, can be gathered (Fig. 2).

In addition, ^{13}C NMR has a greater potential than ^{1}H NMR for the study of complex organic systems, due to the broad spectral range and, usually, an absence of interference between peaks. However, ^{13}C NMR suffers from poor sensitivity due to a relatively weak molar receptivity (0.0159 relative to ^{1}H) and a slow relaxation of the ^{13}C spins back to thermal equilibrium again (Bharti and Roy, 2012; Claridge, 1999). Specifically, in amine–CO_2–H_2O systems, there are different carbons of interest and some of them have relatively long spin-lattice (or longitudinal) relaxation time (T_1), leading to long measuring times (e.g. hours). In particular, ^{13}C atoms in the carboxylic groups of carbamates and in HCO_3^-/CO_3^{2-} have relaxation times much longer than those observed for carbons with bounded hydrogens (i.e. CH, CH_2 and CH_3).

Quantitative ^{13}C NMR data on amine–CO_2–H_2O systems are mainly used to develop and/or support VLE thermodynamic models (like e.g. by comparing experimental and predicted speciation) (Ahn et al., 2011a,b; Barth et al., 1984; Böttinger et al., 2008; Bottinger and Hasse, 2008; Chakraborty et al., 1986; Holmes et al., 1998; Jakobsen et al., 2005; Ma'mun et al., 2006; Shi et al., 2012b) and to obtain information on species distribution for investigating the reaction mechanisms and the factors influencing the CO_2 absorption/desorption processes in aqueous amine solvents (Ballard et al., 2011; Barzagli et al., 2009, 2010, 2011; Ciftja et al., 2012; Goto et al., 2011b; Yamada et al., 2012; Hook, 1997; Jakobsen et al., 2008; Kim et al., 2011b; Mani et al., 2006; Park et al., 2003; Rowland et al., 2011; Yang et al., 2009, 2012).

Concerning ^{1}H NMR analyses, quantitative experiments are combined with quantitative ^{13}C data in order to confirm speciation (Ballard et al., 2011; Böttinger et al., 2008; Bottinger and Hasse, 2008; Kim et al., 2011a; Ma'mun et al., 2006) and some kinetic and equilibrium studies on primary, secondary and sterically hindered amines deal with speciation calculated only by using ^{1}H NMR data (Conway et al., 2013, 2011, 2012; Ermatchkov et al., 2003; Fernandes et al., 2012; McCann et al., 2009a,b, 2011a,b; Xiang et al., 2012). As with the quantitative ^{13}C experiments, quantitative ^{1}H NMR data are also used in studies where the main goals are the development of thermodynamic models (Bishnoi and Rochelle, 2000, 2002; Cullinane and Rochelle, 2005; Derks et al., 2010; Fan et al., 2009; Hartono et al., 2013).

3.2. Quantitative measurements: parameters and error analysis

The sensitivity of NMR spectroscopy is considered to be well suitable for engineering applications, as reliable quantification of peak area fractions down to 0.05% is possible (Maiwald et al., 2003). To achieve accuracy with an error of less than 1.0% it is important to set proper NMR parameters so that the intensities of the peaks can be directly linked to the amount of species. Some features of specific importance are the setting of the recycle delay time between each pulse, which must be at least 5 times the longest T_1 of the nuclear spins in combination with a 90° pulse angle. Further, to improve the integration accuracy, a signal to noise (S/N) of circa 250:1 is recommended and it can be achieved by setting a proper number of scans (also known as transients). Concerning the selection of the pulse sequence, the single-pulse NMR sequence is widely used to acquire quantitative ^{1}H NMR spectra, while for quantitative ^{13}C NMR experiments, the inverse gated decoupling sequence is a good choice to annul the differential Nuclear Overhauser Effect (NOE) which creates an influence by neighbouring hydrogen atoms on the ^{13}C signal integral and therefore precludes quantitative analyses. With the necessary precautions to ensure that the acquired data reflects the relative ratios of the species within the sample, appropriate processing of the spectra can further enhance the results (Bharti and Roy, 2012; Claridge, 1999).

From our survey of NMR studies performed so far on amine–CO_2–H_2O systems, there is not much information on the parameters that decide if a NMR experiment is quantitative or not and actually most of the papers dealing with quantitative proton
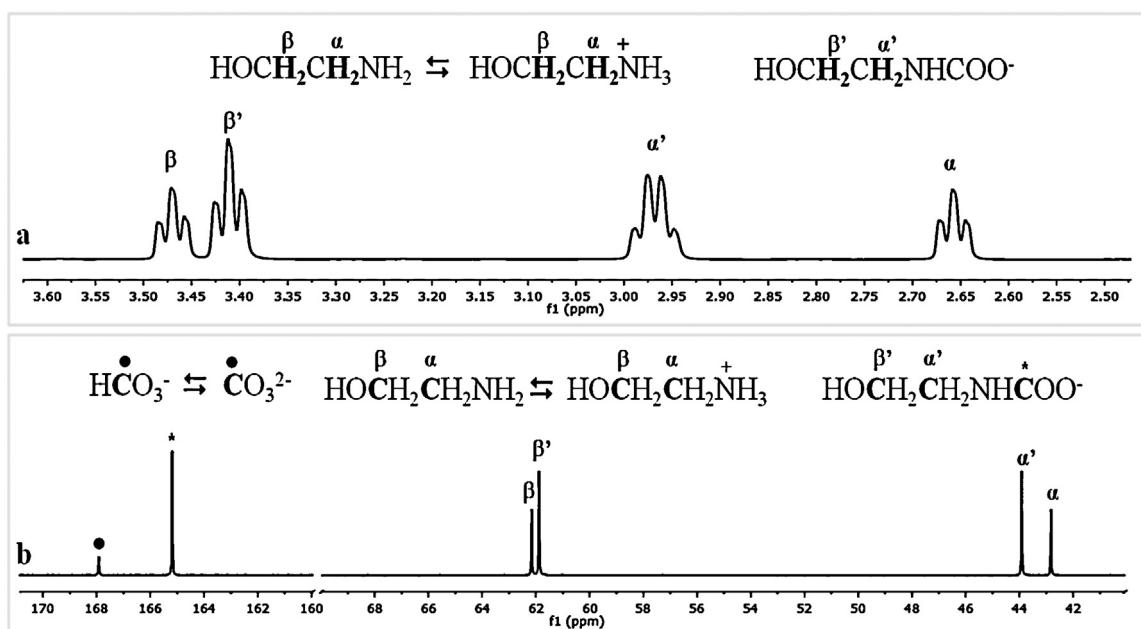
Fig. 2. ^{1}H NMR (a) and ^{13}C NMR (b) spectra of an aqueous monoethanolamine (MEA) solution loaded with CO_2.

experiments do not provide experimental parameters. An exception is represented by Kim et al. (2011a) where, to calculate the relative area ratios of the peak's species, a recycle delay of 1 second and 32 scans are reported (Kim et al., 2011a). Furthermore, in Fernandes et al., 2012 and in Hartono et al., 2013 a recycle delay of 3.98 seconds and 16 scans (Fernandes et al., 2012) and a recycle delay of 2 seconds and 128 scans (Hartono et al., 2013) are documented, respectively.

Concerning quantitative ^{13}C NMR studies, they are carried out by using the inverse gated decoupling sequence, but the basis for the setting of recycle delays is often not fully reported. T_1 values are indeed presented only by a few authors. In 1984, Barth et al. reported ^{13}C NMR studies of aqueous alkanolamines-CO_2-H_2O systems (about 0.5 M of starting amine concentration) using a recycle delay of 150 seconds based on estimation of the T_1 which was lower than 30 seconds for the ^{13}C of the carbonate/bicarbonate species and the carboxylic group of the carbamate (Barth et al., 1984). In the studies performed on various aqueous alkanolamine systems by Yang et al. (2009, 2012) and by Yamada et al. (2012), the longest T_1 was taken into account to set the recycle delay time and, by the inversion recovery method, it was estimated to be of circa 10 seconds for the ^{13}C of carbamate and carbonates. Recently, Ciftja et al. reported an extensive list of [13]C T_1 values for CO_2 loaded aqueous solutions of amines (30 wt. %) and blended amine-amino acids and it was observed that the relaxation times for the ^{13}C nuclei could vary significantly when moving from single amine to mixed amine systems. For instance, it has been reported that the T_1 values for ^{13}C of HCO_3^-/CO_3^{2-} in the different systems are in the range of 3.5–16.3 seconds. The authors have explained this to be related to the change in chemical environment such as pH and ionic strength (Ciftja et al., 2013).

Usually, in these studies reported above, the number of scans was in the range of 32–512, depending on several factors such as the sensitivity of NMR instruments, concentration of the species, and so on.

In some other papers, even if the T_1 values are not reported, long relaxation times of the nuclei under study are taken into consideration. Indeed, Bottinger et al. have reported a recycle delay up to 60 seconds and up to 512 scans (Bottinger and Hasse, 2008). For 2-amino-2-methyl-1-propanol (AMP)-CO_2-H_2O

and for monoethanolamine (MEA)-CO_2-H_2O-Fe^{2+}, Ciftja et al. have reported a recycle delay of 150 seconds and 300 scans (Ciftja et al., 2011, 2012), while Kim et al. (2011a,b) reported a recycle delay of 120 s and scans up to 1024 for quantitative analyses of PZ and homoPZ in blend with K_2CO_3.

In 1998 Holmes et al. studied ammonia-CO_2-H_2O (about 6 M of starting ammonia concentration) systems using only 5 s of recycle delay, even though measured T_1 values were of 28.9 and 29.2 s for the carbons of HCO_3^-/CO_3^{2-} and NH_2COO^-, respectively. Actually, in this last study NMR spectra were used to determine the ratios between carbamate and carbonate/bicarbonate signals and, by using a short recycle delay, a 6% of variation in the area ratios between the peaks was found (Holmes et al., 1998). Similarly, in 2011 Goto et al. reported quantitative ^{13}C NMR spectra obtained with a recycle delay of 30 s and 400 scans because, also in this case, only the ratios between amine carbamate and carbonates signals were considered (Goto et al., 2011a,b). Indeed, observations that the ^{13}C of carboxylic functional groups of amine carbamate and of bicarbonate/carbonate have similar relaxation times justify the use of a recycle delay shorter than 5 times the longest T_1 since only their ratios are evaluated.

In other studies, when a short recycle delay was set, a higher number of scans was used, like e.g. recycle delay of 30 s and 2000–3000 scans (Barzagli et al., 2009, 2010; Park et al., 2003). In particular, in the studies by Barzagli et al., only the relative peak areas of the ^{13}C atoms of the CH_2-CH_2 amine backbone were taken into consideration, leading to quantification of the carbamate and amine species, but hence not of the carbonates.

Concerning the errors and uncertainty in quantitative NMR analyses, there is little information in the papers of this review. The uncertainty in the determination of areas of different peaks within the same molecule was found to be 1–3% in ^{1}H NMR (Böttinger et al., 2008; Hartono et al., 2013; McCann et al., 2009b) and 2–5% in ^{13}C NMR spectra (Barzagli et al., 2009; Böttinger et al., 2008). Concerning the error propagation in the species calculation, this was found to be ±0.1%, whereas that in the determination of the area of peaks using the curve fitting was found to be ±1% (Ciftja et al., 2013). In some other papers, the error in percent of the calculated number of moles was evaluated with respect to the total moles given by the sample preparation. In Jakobsen et al. (2005),

the error of the calculated moles of alkanolamines was estimated to be in the range of 3.8–12.3% for the NMR experiments acquired at 293.15 K and of 8.8–24.2% for those acquired at 313.15 K. Similarly, in Bottinger and Hasse (2008) the relative deviations from the total number of moles were estimated to be lower than 3% for the amines and lower than 5% for CO_2 mole fractions (only in few case 10% deviation was achieved) (Böttinger et al., 2008). In general, it has been observed that the accuracy in defining the area integrals is also dependent on temperature and electrolyte concentration (Böttinger et al., 2008; Jakobsen et al., 2005).

3.3. Deuterated and reference solvents

In liquid NMR spectroscopy, deuterated solvents are needed for field-frequency stabilization (called locking) and for homogenization of the magnetic field (called shimming) before the experiment is started. In principle, deuterated species can alter the nature of the studied mixture but, generally, it is assumed (and in some case demonstrated) that any hydrogen-deuterium exchange on the amino nitrogen does not affect the electronic NMR environment of the nuclei of the neighbouring atoms, such as CH, CH_2, CH_3 (Cullinane and Rochelle, 2005; Ermatchkov et al., 2003).

Deuterated water (D_2O) is the most used "lock" compound for NMR studies of amine–CO_2–H_2O systems. In some works, amine solutions are prepared with 100% of D_2O, resulting in an amine–CO_2–D_2O system (Bishnoi and Rochelle, 2000, 2002; Choi et al., 2012; Ermatchkov et al., 2003; Fan et al., 2009), but in other works samples are prepared with only 10% D_2O (Ballard et al., 2011; Barzagli et al., 2009, 2010, 2011; Ciftja et al., 2013; Cullinane and Rochelle, 2005; Derks et al., 2010; Hartono et al., 2013; Jakobsen et al., 2005; Mani et al., 2006) or with 100% H_2O (Ahn et al., 2011a,b; Fernandes et al., 2012; McCann et al., 2009a,b, 2011b; Xiang et al., 2012; Yang et al., 2009). When 100% H_2O is used, the "lock" solvent is usually inside a capillary which is inserted in the NMR tube, or the experiments are performed without any deuterated solvent, as for on-line NMR spectroscopy (Böttinger et al., 2008; Bottinger and Hasse, 2008).

Selected compounds are used as chemical shift reference solvents and/or as standards for quantitative purpose and they are used as internal or external standards. As internal standard, a known amount of a reference is dissolved in a known volume of sample, whereas as external standard it is inserted in a sealed capillary which is placed into the NMR tube (Ahn et al., 2011a,b; Ballard et al., 2011; Conway et al., 2012; Fernandes et al., 2012; McCann et al., 2009a,b, 2011b). The choice of an external standard could be motivated by the intent of avoiding any sort of interference of the standard with the solution.

In amine–CO_2–H_2O systems, the NMR experiments are mainly performed by using the following reference solvents: 1,4-dioxane (Ballard et al., 2011; Choi et al., 2012; Ciftja et al., 2011, 2012, 2013; Fan et al., 2009; Hartono et al., 2006; Holmes et al., 1998; Jakobsen et al., 2005; Kim et al., 2011a; Yang et al., 2012), acetonitrile (Ahn et al., 2011a,b; Barzagli et al., 2009, 2010, 2011; Mani et al., 2006), 3-(trimethylsilyl)-propionic acid sodium salt (Conway et al., 2012; Fernandes et al., 2012; McCann et al., 2009a,b, 2011b; Xiang et al., 2012) or tetramethylsilane (Barth et al., 1984; Yamada et al., 2012; Jakobsen et al., 2008; Yang et al., 2009)

3.4. Quantification of fast-exchanging proton species

A well-known phenomena in NMR is that inter- and intramolecular exchanging nuclei may lead to modulations of the NMR signals. Depending on how fast the chemical exchange rate is, the different signals may coalesce and appear at an average chemical shift, which value also depends on the relative amount of the species componing the signal. In the context of the present work, intermolecular exchanging proton species appear with a common peak. In particular, it is not possible to distinguish between molecular and protonated forms of the amines, as well as between bicarbonate and carbonate, and only the sum of their concentrations can be quantified by NMR (Fig. 2). However, to assess the relative amount of each of them, various methods have been utilized.

In 1996, Suda and Mimura calculated the distribution of all the chemical species in amine–CO_2–H_2O solutions by combining the ^1H peak area of carbamate and amine/protonated amine to the charge and material balances, and dissociation constants and ion product of water (Suda and Mimura, 1996). Later, in 1998 Holmes et al. performed ^{13}C NMR analyses of ammonia–CO_2–H_2O mixtures and, by taking into account the peak positions, the area ratios and the carbon balance, they presented a method to calculate the concentrations of carbonate, bicarbonate and carbamate (Eqs. (8)–(10)) (Holmes et al., 1998).

$$[HCO_3^-] = \frac{168.09 - S}{(168.09 - 160.33)(1 + R)}[CO_2]_0 \qquad (8)$$

$$[CO_3^{2-}] = \frac{S - 160.33}{(168.09 - 160.33)(1 + R)}[CO_2]_0 \qquad (9)$$

$$[NH_2COO^-] = \frac{R}{1 + R}[CO_3]_0 \qquad (10)$$

In these formulas ((8)–(10)), 160.33 and 168.09 are the chemical shift values for 100% bicarbonate and 100% carbonate, respectively; S is the chemical shift of the carbonate/bicarbonate signal observed in the ^{13}C NMR spectra of CO_2 loaded amine solution; R is the ratio of the area of carbamate peak to the area of bicarbonate/carbonate signal and $[CO_2]_0$ is the carbon balance.

In the literature this method was applied, not only for ammonia chemical systems (Ahn et al., 2011a; Pellegrini et al., 2010), but also for the calculation of carbonate and bicarbonate concentrations in AMP–CO_2–H_2O systems (Ciftja et al., 2011). In this last case, the molecular and protonated amines were determined according to the dissociation constant of the amine and to the pH measured for each loaded sample, as also reported in some other NMR studies (Fan et al., 2009).

To calculate the relative amounts of two rapidly equilibrating components showing a common signal in the NMR spectra, calibration experiments have also been carried out. Standard aqueous solutions of free amine and protonated amine (amineH$^+$), as well as of HCO_3^- and CO_3^{2-}, are prepared and mixed in different appropriate ratios and the variations in chemical shifts are plotted against the variable parameter. In general, for amines it is observed that the protonation has a major effect on atoms distant two covalent bonds from the site of protonation. Specifically, the signals of the carbon in beta and of the proton in alpha position to the nitrogen of amines are more influenced by protonation than other nuclei, resulting in significant changes in the chemical shift (Jakobsen et al., 2008). Concerning the carbonate species, increasing the bicarbonate/carbonate ratio leads to a shift towards lower ppm values of the signal in the ^{13}C NMR spectra. The first time such calibration experiments were reported dates back to 1982, where Abbott et al. acquired ^{13}C NMR spectra of CO_2 (aq), HCO_3^- (aq) and CO_3^{2-} (aq) for a wide range of pHs (Abbott et al., 1982). Later, in 2003, Park et al. identified protonated organic species by comparing the ^{13}C NMR spectra of the loaded amine solutions with those of aqueous amine solutions prepared by adding different aliquot of hydrochloric acid (HCl) (Park et al., 2003). In 2005, Jakobsen et al. performed titration curves for a series of amine/amineH$^+$ and for HCO_3^-/CO_3^{2-}, reporting the change in chemical shift of the ^{13}C signals of the calibrating solutions as a function of the pH (Jakobsen et al., 2005). In similar studies, the change in chemical shift have been plotted as a function of the species ratios (Barzagli et al., 2009, 2010, 2011; Mani et al., 2006; Shi et al., 2012b), since the resonance frequency

of the ^{13}C nuclei depends on the electronic chemical environment of the atoms of the fast-exchanging proton species.

For quantitative purposes, the calibration experiments performed so far are exclusively based on ^{13}C NMR spectroscopy. However, to investigate the 2-(2-aminoethylamino)ethanol (AEEA) absorbent, titrated with HCl or loaded with CO_2 at 293.15 K, qualitative ^{1}H NMR experiments were also carried out (Jakobsen et al., 2008).

3.5. Variable temperature and high pressure NMR experiments

NMR experiments on amine–CO_2–H_2O systems are mostly performed on samples withdrawn from the equilibrated amine solutions after the absorption and/or desorption processes. However, there are reported NMR studies with variable temperature and/or pressure (Ahn et al., 2011a; Böttinger et al., 2008; Bottinger and Hasse, 2008; Cullinane and Rochelle, 2005; Jakobsen et al., 2005; Park et al., 2003). These sorts of NMR studies can provide information not only on the species distribution but also on the CO_2 solubility in aqueous amines (Park et al., 2003; Tomizaki et al., 2010).

With varying temperatures, the environment of the magnetic nuclei becomes different and these changes are observed in the NMR spectra because of the exchange between sites and other dynamic processes. In 2005, Jakobsen et al. investigated the liquid phase composition of MEA-, N-methyldiethanolamine (MDEA)- and 2-(butylamino)ethanol (BEA)-CO_2-H_2O systems, acquiring ^{13}C NMR spectra at temperatures ranging from 293.15 K to 363.15 K. Quantitative analysis was performed only for spectra acquired at 293.15 K and 313.15 K, because broadening of peaks were observed at higher temperatures (Jakobsen et al., 2005). Importantly, during the study of ammonia–CO_2–H_2O systems at temperatures higher than 343.15 K, CO_2 bubble formations occurred. It was also observed that, at increased temperatures (293.15–333.15 K), the ammonia carbamate peak was not affected by temperature change, while the carbonate/bicarbonate signal significantly moved towards lower chemical shift in the ^{13}C NMR spectra, which corresponds to an increase of bicarbonate to the detriment of carbonate (Ahn et al., 2011a).

High pressure NMR experiments can be performed using specific high-pressure NMR tubes, which are made of chemical resistant glass and hermetic stoppers and the samples can be kept under vacuum or pressure for long time (Park et al., 2003). Moreover, for studies under process conditions, flow NMR probes can be used in a wide range of temperatures and pressures. On-line NMR experiments were carried out for the study of individually and blended MEA, diethanolamine (DEA), MDEA and PZ, applying pressures up to 25 bar and temperatures between 293.15 K and 353.15 K (Böttinger et al., 2008; Bottinger and Hasse, 2008). The set up of on-line NMR experiments requires systematic studies to optimize flow rates (which affect magnetization and relaxation) and to perform solvent suppression. Since deuterated solvents are too expensive to be used in process engineering applications like this, no field-frequency stabilization (lock) can be used and NMR magnets with excellent field stability is a prerequisite as well as accurate homogeneity of the magnetic field (Maiwald et al., 2003).

4. Results and applications

4.1. Speciation of amine–CO_2–H_2O systems in absorption experiments

As described above, speciations of amine–CO_2–H_2O systems are of particular interest in order to derive information on species
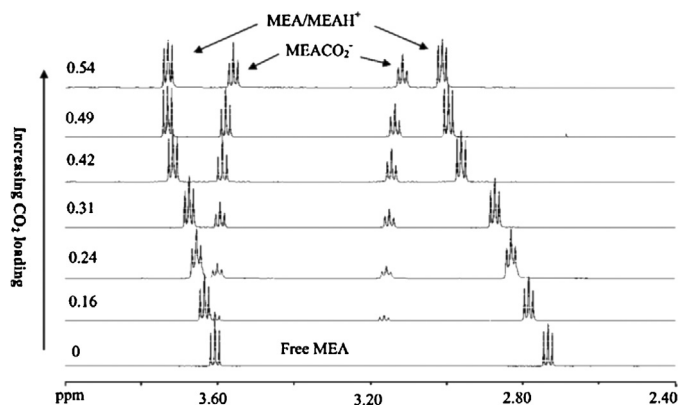

Fig. 3. Stacked ^{1}H NMR spectra for 5.0 M MEA solution with varying CO_2 loading at 295.65 K.
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distribution and hypothesis on reaction mechanism, as well as for kinetic and thermodynamic tasks.

Typically, in a MEA–CO_2–H_2O system, at increasing CO_2 loadings, an increment of amine carbamate is observed, as well as of bicarbonate and protonated amines. At CO_2 loadings higher than 0.5 mol CO_2/mol MEA, the protonated amine concentration continues to rise at the expense of carbamate, and the released carbon dioxide will react to bicarbonate (Bottinger and Hasse, 2008; Jakobsen et al., 2005). Characteristic ^{1}H and ^{13}C NMR spectra of MEA at varying CO_2 loadings are shown in Fig. 3 (Fan et al., 2009) and Fig. 4 (Jakobsen et al., 2005), respectively.

A common feature observed is that by varying the CO_2 loading most of the NMR signals change positions. The signals corresponding to the nuclei of MEA/MEAH$^+$ shift to the left (high ppm values) in the ^{1}H NMR spectra and to the right (low ppm values) in ^{13}C NMR spectra, due to an increase of protonated amines. On the other hand, the ^{13}C signal corresponding to HCO_3^-/CO_3^{2-} moves towards lower chemical shifts, due to an increase of bicarbonate concentration. Concerning the carbamate species, the change in ^{1}H and ^{13}C chemical shifts at increasing CO_2 loadings is much smaller than that observed for the amines. In this regard, by a ^{1}H NMR investigation, McCann et al. in 2011 suggested that the —COO^- group of carbamate amine is protonated (—$COOH$), rather than the nitrogen group as previously suggested with the zwitterionic mechanism (Caplow, 1968; McCann et al., 2011b).

Similarly, quantitative and qualitative information on amine–CO_2–H_2O reaction products with different chemical structures, such as secondary, tertiary and sterically hindered amines, can be gathered by the analyses of NMR spectra. For instance, Choi et al. in 2011 performed a ^{13}C NMR study on AMP, a primary steric hindered amine, and MDEA, a tertiary amine, and demonstrated that the absorption reactions involve completely different mechanisms. AMP and MDEA have high absorption capacities and follow the same pathway (Eq. (7)) in absorbing CO_2. MDEA shows a high bicarbonate concentration even at low loadings, whereas in AMP solutions the bicarbonate concentration increases at increasing loadings as primary and secondary amines (Choi et al., 2012).

Ammonia solutions have also been investigated and the analyses of the NMR spectra have led to hypothesis on the reaction mechanism. In particular, it has been observed that as the absorbed amount of CO_2 in the ammonia solution increases, the carbamate peak decreases, but that of bicarbonate/carbonate increases. Moreover, by the drop in pH, the amount of bicarbonate increases, as it is detected in the NMR spectra where the bicarbonate/carbonate
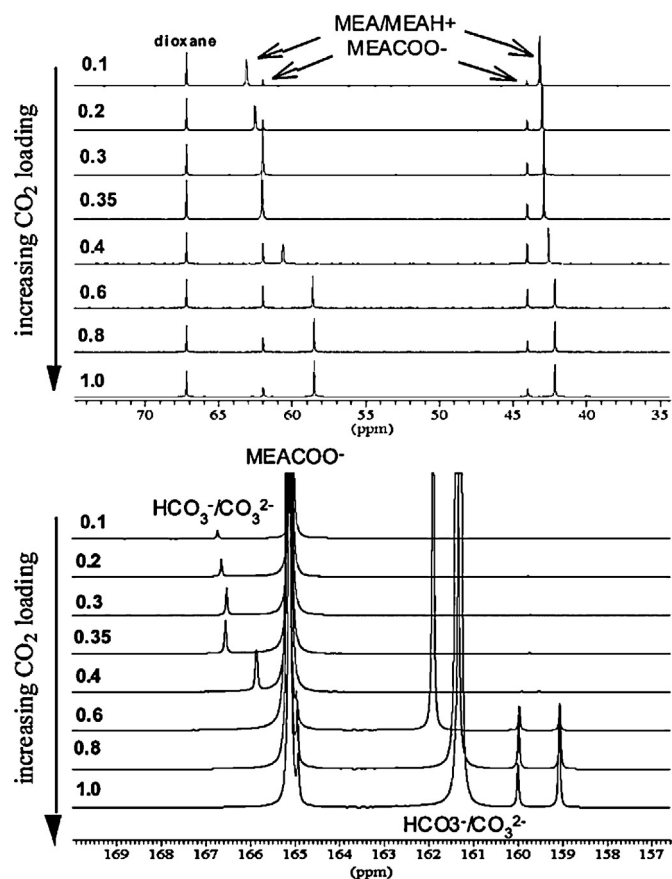
Fig. 4. Stacked ^{13}C NMR spectra for 30 wt.% MEA solution with varying CO_2 loading at 293.15 K.

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signal moves towards lower ppm values (Ahn et al., 2011a,b; Holmes et al., 1998; Mani et al., 2006).

Recently, Ciftja et al. reported 1D and 2D NMR experiments to identify the main oxidative degradation products of MEA (5 M) loaded with CO_2 in the presence of Fe^{2+} (aq). In particular, ^{13}C NMR experiments were used to quantify the identified degradation products, such as N-(2-hydroxyethyl)imidazole (HEI), 2-oxazolidone (OZD), N-(2-hydroxyethyl)formamide (HEF). The NMR results were in good agreement with those obtained by GC/LC–MS on the same solutions and, although N-(2-hydroxyethyl) acetamide (HEA) was not quantified, some additional signals in the NMR spectra were detected but the corresponding compounds were neither identified nor quantified in this study (Ciftja et al., 2012).

In 2007, Hartono et al. performed ^{13}C NMR investigations on aqueous diethylenetriamine (DETA) to identify the species really formed in solution after CO_2 absorption, among the 18 potential DETA species. Although DETA has three nitrogen atoms in the molecule, which can react with CO_2, no traces of tricarbamate were observed (Hartono et al., 2006).

In 2008 Jakobsen et al. performed NMR studies and quantum mechanical calculations for the study of 2-(2-aminoethylamino)ethanol (AEEA), a diamine novel absorbent. AEEA, primary carbamate AEEA and secondary carbamate AEEA were the major species identified by NMR. In this study, the NMR chemical shifts were also predicted by quantum mechanical calculations and compared to experimental NMR spectra. The overall results suggested that most species are populated by conformers

with some degree of intramolecular hydrogen bondings which could influence the absorption reactions (Jakobsen et al., 2008).

4.2. Speciation of blended amine–CO_2–H_2O systems in absorption experiments

Mixed amines have become attractive because the best characteristics of the single amines can be combined to improve the efficiency of CO_2 absorption (like e.g. increasing the rate of absorption). Problems of data analyses might appear due to the larger complexity of the solutions but, even if the spectra can be quite complex, information from ^{13}C NMR experiments on the species distribution in the liquid phase of amine mixtures can be gathered. Blends of PZ and MDEA have found widespread consideration due to the high absorption rate of PZ (which rate constant is found to be a factor of 10 higher than that of other alkanolamines, such as MEA) and the low reaction enthalpy of MDEA (Bishnoi and Rochelle, 2002; Fu et al., 2012). The NMR studies on this type of blends are mainly dealing with the species distribution for input to thermodynamic models (Bishnoi and Rochelle, 2002; Böttinger et al., 2008; Derks et al., 2010). In these works the species have been quantified by ^{1}H (Bishnoi and Rochelle, 2002; Derks et al., 2010) and/or ^{13}C NMR experiments (Böttinger et al., 2008) and, if needed, the chemical structures have been identified by HSQC experiments. For instance, in Bottinger et al. the following components were identified and quantified: PZ/protonated PZ, carbamate/protonated carbamate PZ, dicarbamate PZ, MDEA/protonated MDEA, dimethyl-diethanolamine ion (DMDEA$^+$), DEA/protonated DEA, carbonate/bicarbonate and carbon dioxide. Moreover, products formed from DEA and unidentified byproducts were observed but not quantified (Böttinger et al., 2008). This study points out that, although the high potential of this blend, degradation and secondary products can be issues of concern for its application in PCC technology. However, hypothesis on reaction mechanisms could lead to a rational design of amine/blended amine systems according to the demands in this field.

Recently, Ballard et al. have published a NMR study on the reaction of CO_2 with a series of mixed aqueous amine systems (MEA, N-methylethanolamine (MMEA), MEA-PZ, MEA-MDEA, MMEA-PZ). ^{13}C NMR experiments were performed to calculate carbamate and bicarbonate concentrations (it was assumed that no carbonate was formed) at increasing loadings and reaction time. Quantitative ^{1}H NMR experiments were used to confirm ^{13}C quantitative results, whereas HSQC NMR spectra were performed to define or confirm structures. Observation of trends of the species distribution in blended amines–CO_2–H_2O systems led to the following hypothesis on the mechanism of reaction: For primary and secondary amines the relative rates of reaction of each amine are not just a measure of the rate coefficients for carbamate formation, but more a reflection of the relative thermodynamic stabilities of each amine carbamate (Ballard et al., 2011).

A qualitative ^{13}C NMR study on amine aminoacids salts, which are an attractive alternative to alkanolamines, is also found in literature (Hartono et al., 2011). In order to observe the neutralization effect of the aminoacids in loaded samples, sarcosine (SAR) was blended with organic and inorganic bases, 3-(methylamino)propylamine (MAPA) and potassium (K^+), respectively. It was observed that, in the presence of CO_2, the MAPA-SAR system showed more species than the SAR-K system and was explained to be probably due to the presence of the carbamate species coming from the reaction of CO_2 with both SAR and MAPA, which limits the complete neutralization of the aminoacids by blending equinormal amounts.

Moreover, ^{13}C NMR spectroscopy has also been applied to identify reaction product species in a study on the mass transfer of CO_2

into aqueous ammonia with a series of promoters (Rowland et al., 2011).

The application of NMR spectroscopy on blended amines and the information that can be obtained demonstrate once again the wide range of applicability of this technique which allows the study of relatively complex chemical systems, such as blended amine–CO_2–H_2O systems.
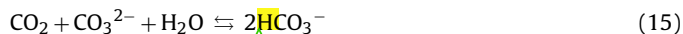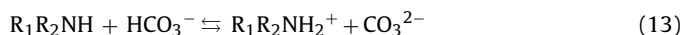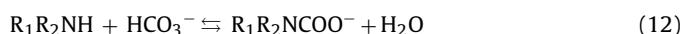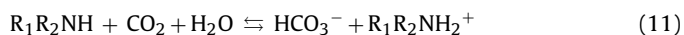
4.3. Speciation of single and blended amines–CO_2–H_2O systems in absorption-desorption experiments

Most of the studies on amine–CO_2–H_2O systems focus on the improvement of the absorption efficiency of the amine solvents, but the improvement of regeneration efficiency of the absorbent have also been considered in some works.

In 1997, Hook et al. dealt with a series of sterically hindered aminoacid salts to investigate the influence of the substituents on amine structure in the overall CO_2 capture process. In this study, ^{13}C NMR spectroscopy was applied to quantify the levels of carbamate and carbonate (reported as the sum of carbonate and bicarbonate). They found that substituents in alpha position to the nitrogen increased absorption capacities with an overall reduction in absorption rate. However, as the degree of substitution was increased, the proportion of carbamate remaining in the equilibrated desorbed solution decreased (Hook, 1997).

In 2009, Yang et al. performed experiments of absorption and desorption for a series of amines (MEA, MMEA, MDEA, 2-amino-2-methyl-1,3-propanediol (AMPD), PZ) at different concentrations (2–4 M). Using ^{13}C NMR, speciations were examined during both absorption and desorption of CO_2. Assuming that carbonate was not formed, they measured the amount of bicarbonate and carbamate as a function of reaction time in both absorption and desorption steps. For instance, they demonstrated that PZ rapidly reacts with CO_2 but, after heating for 60 min at 363.15 K, the enriched solution still maintained 61% of the CO_2, leading to a low desorption efficiency of PZ (Yang et al., 2009). Similarly, in 2012, they studied the influence of amine chemical structure on the amine's capacity of CO_2 capture, using quantitative ^{13}C NMR experiments. In particular, they focused on the effect of varying the carbon chain length from 2 to 6 methylene spacers between the two functional groups in primary and secondary alkanolamines and diamines. Here, the need of rationalizing the design of amine absorbents on the basis of factors (such as chemical structure) influencing the absorption and desorption of CO_2 was a focal point. In particular, NMR can be a useful tool to investigate the amine solvents based on the different chemical structures (Yang et al., 2012).

Recently, Barzagli et al. reported ^{13}C NMR investigations on several individual or blended alkanolamines (MEA, MMEA, 2-(dimethylamino)ethanol (DMMEA), DEA, MDEA, AMP) at different concentrations (0.167–2.00 M) in both absorption and desorption-regeneration processes (Barzagli et al., 2009, 2010, 2011). For instance, for the primary and secondary alkalonamines (MEA and MMEA respectively) it emerged that in the first 10 min of CO_2 desorption (carried out at 388.15 K and room pressure), the carbamate species increased, showing a trend similar to that observed in the absorption step. Since both the endothermic processes of desorption of CO_2 and regeneration of free amine are expected to occur via the reverse of the absorption reactions (Eqs. (11)–(15)), the trend of forming carbamate during the desorption step could easily be explained with the reverse of the reaction (14) (Barzagli et al., 2009).

$$R_1R_2NH + CO_2 + H_2O \leftrightarrows HCO_3^- + R_1R_2NH_2^+ \quad (11)$$

$$R_1R_2NH + HCO_3^- \leftrightarrows R_1R_2NCOO^- + H_2O \quad (12)$$

$$R_1R_2NH + HCO_3^- \leftrightarrows R_1R_2NH_2^+ + CO_3^{2-} \quad (13)$$

$$R_1R_2NCOO^- + CO_2 + 2H_2O \leftrightarrows 2HCO_3^- + R_1R_2NH_2^+ \quad (14)$$

$$CO_2 + CO_3^{2-} + H_2O \leftrightarrows 2HCO_3^- \quad (15)$$

In the study of AMP and MDEA, Barzagli et al. pointed out that, after each absorption/desorption cycle had reached the equilibrium, most of the captured CO_2 was stored in solution as HCO_3^- and CO_3^{2-} in both absorber and desorber solutions. In order to take advantage of the great absorption efficiency of AMP and great desorption efficiency of MDEA, these two amines were also studied in a mixture. An overall increased efficiency of the blend was observed and it was tentatively explained as due to the cooperative effects of the higher basicity of AMP, which increases both absorption efficiency and bicarbonate formation, and of the higher acidity of protonated MDEA, which facilitates amine regeneration according to reaction 16 (Barzagli et al., 2010).

$$HCO_3^- + R_1R_2NH_2^+ \leftrightarrows R_1R_2NH + CO_2 + H_2O \quad (16)$$
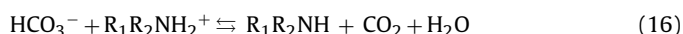
Concerning the thermal stability of amines at typical desorption temperatures, Barzagli et al. have performed ^{13}C NMR analyses to identify degradation products. They heated desorbed DEA, MDEA and AMP solutions for 14–16 days at 403.15 K or for 10 days at 388.15 K. In the ^{13}C NMR spectra no degradation products in either AMP and MDEA solutions were detected, while an amine degradation of about 0.4%/day in the DEA solutions was observed in both type of heating experiments. The degradation products were not identified due to a detection limit of ^{13}C NMR spectra analysis estimated to be about 0.5% (Barzagli et al., 2010, 2011).

4.4. Determination of carbamate stability constants

The calculation of carbamate stability equilibrium constants is a fundamental and important task because of the crucial role played by the carbamate formation reaction in the chemical systems under study. It is indispensable for determining and/or modelling the vapour-liquid equilibria in the CO_2 absorption process and for the calculation of the thermodynamics of the carbamate formation (Bishnoi and Rochelle, 2000; Conway et al., 2011; Ermatchkov et al., 2003; Fernandes et al., 2012; Jakobsen et al., 2005; McCann et al., 2011a). For equilibria in solution, activities of the chemical species are related to the ideal concentration by correction factors, called activity coefficients (γ), and the equilibrium constants measured in an ideal solution can be used to predict equilibria in non-ideal solutions. The carbamate stability constant (K_c) can be expressed as follows:

$$K_c = \frac{[RNHCOO^-]}{[RNH_2] \cdot [HCO_3^-]} \cdot \frac{\gamma RNHCOO^-}{\gamma RNH_2 \cdot \gamma HCO_3^-} \quad (17)$$

In Table 1, the values of carbamate stability constants ($\log K_c$) calculated from NMR data are reported. The distinction between $\log K_c$ (activity based) and apparent $\log K_c$ (non-activity based) is shown in different columns. All the constants are determined on a molar scale (mol/l), with the exception of the PZ $\log K_c = 1.80$ (mol/kg based) (Ermatchkov et al., 2003) and AMP $\log K_c = -0.33$ (molar fraction based) (Ciftja et al., 2011).

For most of the studies no efforts have been made to experimentally distinguish the protonated and free form of amines, as well as carbonate and bicarbonate, which in addition do not have resonating protons in ^{1}H NMR spectra. For PZ the possibility of forming the dicarbamate species is also explored and, based on ^{1}H NMR data, the equilibrium constant at 298.15 K is estimated to be $2.62 E^{-6}$ (molar fraction based).

The carbamate stability constants calculated by Jakobsen et al. in 2005 are provided in Table 2 because these values are reported differently. In this study the NMR data is treated as follows: the activity based carbamate stability constants are measured at

Table 1

Comparison of the main carbamate stability constants ($\log K_c$) obtained by NMR speciation.

Amine	NMR experiment	Activity based $\log K_c$	Non-activity based $\log K_c$
MEA	^{13}C		1.10 (313.15 K)[h]
	^{1}H	1.51 (303.15 K)[a]	
	^{1}H	1.54 (303.15 K)[b,c]	
	^{1}H	1.76 (298.15 K)[d]	
	^{1}H	1.86 (298.15 K)[e]	
DEA	^{1}H	0.92 (298.15 K)[d,f]	
	^{13}C		0.30 (313.15 K)[h]
AP	^{1}H	0.98 (298.15 K)[d]	
	^{1}H	0.72 (303.15 K)[b]	
AMP	^{13}C		<−1 (313.15 K)[h,i]
	^{13}C		−0.33 (298.15 K)[j]
	^{1}H	<−0.7 (303.15 K)[b]	
PZ	^{1}H	1.80 (283.15–333.15 K)[g]	
	^{1}H	1.49 (298.15 K)[d]	

[a] McCann et al. (2009a).
[b] McCann et al. (2011b).
[c] McCann et al. (2009b).
[d] Fernandes et al. (2012).
[e] Conway et al. (2011).
[f] Conway et al. (2012).
[g] Ermatchkov et al. (2003).
[h] Sartori and Savage (1983).
[i] Chakraborty et al. (1986).
[j] Ciftja et al. (2011).

Table 2

Activity based carbamate stability constants for MEA–CO_2–H_2O at 293.15 K and 313.15 K, obtained from NMR speciation in Jakobsen et al. (2005) and compared to literature (Jakobsen et al., 2005; Sartori and Savage, 1983).

Amine	NMR experiment	K_c in Sartori and Savage	K_c in Jakobsen et al.
MEA	^{13}C	4.5 E^{-4} (293.15 K)	4.76 E^{-4} (293.15 K)
	^{13}C	1.44 E^{-3} (313.15 K)	1.29 E^{-3} (313.15 K)

293.15 K and 313.15 K for the equation of carbamate reversion ($MEACOO^- + H_2O \leftrightarrows MEA + HCO_3^-$). NMR speciations are expressed in molar fractions and the correction factors are estimated by the use of the extended UNIFAC model by Poplsteinova (Jakobsen et al., 2005).

4.5. Kinetic studies

In amine–CO_2–H_2O systems, a number of simultaneous reactions occur at the same time and the rates of the reactions, in particular the reaction of CO_2 with amines, are fast. Spectrophotometric measurements do not allow the direct observation of the reactions and advanced analyses of the measured data are required.

Although ^{13}C NMR spectroscopy is an attractive tool for the study of solution composition, the measuring times are too long for formation kinetics in amine–CO_2–H_2O systems. Real-time NMR spectroscopy can be a valid tool to achieve kinetic information but it can be technically and analytically challenging. The best option for carrying out kinetic studies by NMR spectroscopy is the use of ^{1}H NMR which allows fast measurements and accurate quantitative integrations.

Since 2009, a research group of New Castle (Australia) has reported kinetic analyses on amine solvents from ^{1}H NMR spectroscopy, often combined with stopped-flow investigations (Conway et al., 2011, 2012, 2013; McCann et al., 2009b; Xiang et al., 2012). For instance, in McCann et al., 2009, kinetics studies were performed by rapidly mixing aqueous solutions of MEA/HCl and solutions of $KHCO_3$ at different pH conditions. The establishment of equilibria was monitored by automatically acquiring ^{1}H NMR spectra at intervals appropriate for the rate of reaction and the concentrations of MEA/MEAH$^+$ and MEA carbamate were determined as a function of time. Analysis of the data consisted of non-linear data fitting and all the kinetic measurements, which included NMR and stopped flow data, were analyzed in one global analysis and the rate constants were calculated (McCann et al., 2009b).

In Table 3, the rate constants for the reversible reactions of carbonic acid, bicarbonate and carbon dioxide with MEA are reported (Conway et al., 2011, 2012; McCann et al., 2009a,b).

5. Conclusions

In order to advance the development of CO_2 capture technologies utilizing absorption by aqueous amine solvents, detailed understanding of chemical reaction equilibria, kinetics and thermodynamics are important. Hence, detailed knowledge of the species (identification and quantification) formed in single and blended amine–CO_2–H_2O systems during the absorption and desorption/regeneration steps is required. In this regard, NMR spectroscopy has been applied with success for speciation in such systems in order to gather information on the compound distribution at equilibrium conditions.

NMR spectroscopy is hampered by relative low sensitivity and, especially for quantitative purposes, measurement times may therefore be long (such as hours for ^{13}C NMR experiments). However, with proper NMR experiment parameters and analyses, quite accurate results and detailed insight of the chemical equilibria and dynamics of the involved species can be provided.

Most NMR works are based on samples withdrawn from equilibrated amine solutions, but also studies in which the reactions are directly monitored with NMR are found in literature, such as pressure or temperature dependent experiments and some kinetic studies.

Table 3

Kinetic constants for MEA–CO_2–H_2O system derived from ^{1}H NMR data.

Reaction	Rate constants for forward-reactions	Rate constants for back-reactions
(I) $MEA + H_2CO_3 \leftrightarrows MEACOOH + H_2O$	$K_I = 1.02$ E^3 M^{-1} s^{-1} [a]	$k_{-I} = 7.8$ E^{-3} s^{-1} [a]
	$K_I = 9.16$ E^2 M^{-1} s^{-1} [b,d]	$k_{-I} = 5.14$ E^{-3} s^{-1} [b,d]
(II) $MEA + HCO_3^- \leftrightarrows MEACOO^- + H_2O$	$K_{II} = 3.8$ E^{-4} M^{-1} s^{-1} [a]	$k_{-II} = 2.0$ E^{-5} s^{-1} [a]
	$K_{II} = 1.05$ E^{-3} M^{-1} s^{-1} [b,d]	$k_{-II} = 7.43$ E^{-5} s^{-1} [b,d,e]
	$K_{II} = 6.0$ E^{-3} M^{-1} s^{-1} [c]	$k_{-II} = 8.3$ E^{-5} s^{-1} [c]
(III) $MEA + CO_2$ (aq) $\leftrightarrows MEACOOH$	$K_{III} = 6.11$ E^3 M^{-1} s^{-1} [b,d]	$k_{-III} = 29.8$ s^{-1} [b,d,f]

[a] McCann et al. (2009a).
[b] McCann et al. (2009b).
[c] Conway et al. (2011).
[d] Kinetic measurements are based on both ^{1}H NMR and stopped-flow measurements.
[e] k_{-II} is computed as $k_{-II} = (k_{II}k_{-I}K_{IV})/(k_I K_V)$ where $K_{IV} = [RNHCOOH]/[RNHCOO^-][H^+]$ and $K_V = [H_2CO_3]/[HCO_3^-][H^+]$.
[f] k_{-III} is computed, based on the principle of microreversibility, as $k_{-III} = (k_{III}k_{-I}k_{-VI})/(k_I k_{VI})$ where k_{VI} is referred to CO_2 in equilibrium with H_2CO_3.

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Table A1

Scheme of the amines and processes analyzed, type of NMR experiments and related contribution.

References	Amines	Type of process analyzed	Quantitative ^{1}H	Quantitative ^{13}C	Qualitative ^{1}H	Qualitative ^{13}C	2D	Other	NMR determination of f.e.p. species	NMR contribution
Ahn et al. (2011b)	NH$_3$	Abs		x					x	• Monitoring of process and validation of the thermodynamic simulation
Ahn et al. (2011a)	NH$_3$	Abs/Des		x					x	• Monitoring of process at variable T (293.15–333.15 K) and validation of the thermodynamic simulation
Ballard et al. (2011)	MEA-MMEA, MEA-PZ, MEA-MDEA, MMEA-PZ	Abs	x	x		x				• Measurements of carbamates and bicarbonate concentrations as a function of time and CO$_2$ loadings to investigate reaction mechanism
Barth et al. (1984)	MEA, DGA, DEA, DIPA	Abs		x						• Speciation for the determination of the thermodynamic parameters of the equilibrium for carbamate formation
Barzagli et al. (2009)	MEA, MMEA, DMMEA	Abs/Des		x					x	• Speciation to investigate chemical equilibria during the whole CO$_2$ capture process
Barzagli et al. (2010)	DEA, MDEA, AMP (individually and blend)	Abs/Des		x					x	• Speciation to investigate chemical equilibria during the whole CO$_2$ capture process. Analysis of the thermal stability of the amines
Barzagli et al. (2011)	DEA, MDEA	Abs/Des		x					x	• Speciation to investigate chemical equilibria during the whole CO$_2$ capture process. Analysis of the thermal stability of the amines
Bishnoi and Rochelle (2000)	PZ	Abs	x			x	x			• NMR data combined with pH, equilibria solubility and ionic conductivity data to obtain speciation. NMR estimation of dicarbamate equilibrium constant of PZ
Bishnoi and Rochelle (2002)	PZ-MDEA	Abs	x			x	x			• NMR data used to verify electrolyte NRTL model at high loading
Böttinger et al. (2008)	MDEA, PZ-MDEA	Abs	x	x		x				• Speciation, identification of byproducts and use of experimental data to develop a thermodynamic model
Bottinger and Hasse (2008)	MEA, DEA	Abs	x	x		x				• Speciation, identification of byproducts and use of experimental data to develop a thermodynamic model
Chakraborty et al. (1986)	AMP	Abs		x						• Estimation of the carbamate stability constant. A thermodynamic model is tested against experimental equilibrium data
Choi et al. (2012)	AMP, MDEA	Abs		x						• Investigation of the reaction mechanism
Ciftja et al. (2011)	AMP	Abs		x					x	• Speciation and determination of the non-activity based carbamate stability constant
Ciftja et al. (2012)	MEA/FeSO$_4$	Oxidative degradation	x	x	x	x		DEPT		• Identification and quantification of the main degradation products
Ciftja et al. (2013)	MEA, DEA, AMP, DEEA, PZ, EDA, GLY, ALA, TAU, SER, PRO, SAR	Abs	x	x	x	x		DEPT		• Determination of the T_1 values for the ^{13}C nuclei of species in CO$_2$ loaded solutions of amines and blended amine–aminoacids
Conway et al. (2011)	MEA	Cf/Cd	x							• NMR data used in a global analysis to generate rate and equilibrium constants for the reaction of HCO$_3^-$ and MEA
Conway et al. (2012)	MEA, DEA, MORP, TMORP, 4-PIPDM, 4-PIPDE, PIPD, PYR	Cf/Cd	x							• NMR data used in a global analysis to generate rate and equilibrium constants for the reaction of HCO$_3^-$ and MEA
Conway et al. (2013)	PZ	Cf/Cd	x							• NMR data to study the kinetic pathways with stopped-flow measurements
Cullinane and Rochelle (2005)	PZ/K$_2$CO$_3$	Abs	x			x	x			• Speciation to develop a thermodynamic model
Derks et al. (2010)	PZ-MDEA	Abs	x			x	x			• Speciation to develop a quaternary thermodynamic model
Ermatchkov et al. (2003)	PZ	Abs	x							• Speciation and determination of equilibrium constants
Fan et al. (2009)	MEA	Abs	x		x	x	x			• Speciation to modify a VLE model for MEA–CO$_2$–H$_2$O system
Fernandes et al. (2012)	MEA, AP, DEA, PIPD, 4-PIPDM, 4-PIPDE, MORP, PZ, MPZ, PYRR, NH$_3$	Cf	x							• NMR data fitted in a global analysis to determine carbamate stability constants for deriving enthalpy and entropy parameters
García-Abuín et al. (2012)	BZ, DAP, PYRR	Abs			x	x				• Species distribution as a function of time and loadings
Goto et al. (2011b)	MEA, AMP, DEA, EAE, IPAE, MDEA, PZ, RITE	Abs/Des		x						• Determination of carbamate and bicarbonate anions ratios to define the CO$_2$ absorption mechanism
Goto et al. (2011a)	MEA, AMP, DEA, EAE, IPAE, MDEA	Abs/Des		x						• Determination of carbamate and bicarbonate anions ratios to define the CO$_2$ absorption mechanism
Hartono et al. (2006)	DETA	Abs			x	x				• Identification of the main products

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Table A1 (*Continued*)

References	Amines	Type of process analyzed	NMR experiments Quantitative ^{1}H	^{13}C	Qualitative ^{1}H	^{13}C	2D	Other	NMR determination of f.e.p. species	NMR contribution
Hartono et al. (2011)	K-SAR, MAPA-SAR	Abs			x	x	x			• Identification and comparison of the main products
Hartono et al. (2013)	AMP, PZ (individually and in blend)	Abs	x							• NMR speciation and titrations data are modelled to define interaction parameters for thermodynamic models
Holmes et al. (1998)	NH₃	Abs			x				x	• Experimental concentrations compared to data obtained by theoretical model
Hook (1997)	AA, MEA, AMP	Abs/Des			x					• Speciation to investigate the effect of structural steric hindrance on CO₂ capture process
Jakobsen et al. (2005)	MEA, BEA, MDEA	Abs			x				x	• Speciation (determined at 293.15 K and 313.15 K) to refine VLE model and determine the carbamate stability constants
Jakobsen et al. (2008)	AEEA	Abs			x	x	x			• Investigastigation of protonation effect on amine chemical shift. Identification of main products and characterization of the system at molecular level supported by quantum mechanical calculation
Kim et al. (2011a)	homoPZ-K₂CO₃	Abs	x		x	x	x			• Identification of CO₂ absorption mechanism by defining the species formed in solution and their distribution. Calculation of the relative ratios of the species based on ^{1}H peak areas
Kim et al. (2011b)	PZ, PZ-K₂CO₃	Abs			x	x	x	x		• Identification of the species formed in solution and investigation of the species distribution. Calculation of the relative ratios of the species based ^{13}C peak areas
Ma'mun et al. (2006)	AEEA	Abs	x	x			x			• Speciation to validate the predicted speciation obtained from a thermodynamic model
Mani et al. (2006)	NH₃	Abs	x			x			x	• Speciation to perform chemical investigations
McCann et al. (2009b)	MEA	Cf	x							• Rate and equilibrium constants measurements based on NMR and stopped-flow data
McCann et al. (2009a)	MEA	Cf	x							• Rate and equilibrium constants measurements based on NMR data
McCann et al. (2011a)	MEA, DEA, NH₃	Cf	x							• A calorimetric study where the determination of carbamate equilibrium constants for MEA are NMR based
McCann et al. (2011b)	MEA, PA, IBA, AP, AMP, MDEA	Cf	x							• Determination of carbamate stability and protonation constants based on NMR data
Mergler et al. (2011)	MEA, EDA, ALA, TAU, CYS	Abs/des	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.		• Study based on VLE and ATR-FTIR. High T NMR used to validate desorption measurements
Park et al. (2003)	MEA, AHPD	Abs			x				x	• High pressure NMR experiments to investigate the effect of steric hindrance of amine on CO₂ solubility and absorption
Paul et al. (2008)	2-PE	Abs				x				• NMR data used to confirm the interpretation of kinetic data
Pellegrini et al. (2010)	MEA, DGA, NH₃	Abs			x					• NMR data obtained for ammonia are compared to simulation data
Rowland et al. (2011)	NH₃ promoted with PZ, H₃BO₃ and GLY	Abs				x				• Support to the study of the factors influencing mass transfer
Sartori and Savage (1983)	MEA, DEA, AMP	Abs			x					• Carbamate stability constants are reported (data are referred to a private communication)
Shi et al. (2012b)	DEAB	Abs			x				x	• Speciations to develop a VLE model
Suda and Mimura (1996)	MEA, MAE, EAE, BEA, MDEA	Abs	x						x	• Speciations to clarify the characteristic behaviour of dissolved state of CO₂ in aqueous alkanolamines
Xiang et al. (2012)	SAR	Cf/Cd	x							• By a global data fitting of ^{1}H NMR and stopped-flow measurements, rate and equilibrium constants for the reaction between HCO₃⁻ and amine are calculated
Yamada et al. (2012)	MEA, EAE, IPAE	Abs/Des			x					• Speciation to evaluate the CO₂ capacities. NMR and VLE analyses to provide insights into the absorption mechanisms and the influence of structures
Yang et al. (2009)	MEA, MMEA, MDEA, AMPD, PZ	Abs/Des			x					• Chemical investigation by the determination of carbamate and bicarbonate concentrations as a function of time and loadings
Yang et al. (2012)	I-II alkanolamines and diamine at increasing chain lenght	Abs/Des			x					• Chemical investigation by the determination of carbamate and bicarbonate concentrations as a function of time and loadings
Yoon (2003)	MEA, AMP, AMPD, AEPD	Abs			x			^{15}N		• Study of electron releasing and withdrawing effects of substituents for identification of CO₂ absorption capacity of amines

Based on this survey, it appears that NMR spectroscopy can give important contributions to the advance of new efficient amine–CO_2–H_2O systems.

Appendix A.

Amines, type of processes analyzed, NMR experiments and the corresponding contribution for each manuscript included in this review are reported in Table A1.

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