NMR Analysis of Various Amine-CO$_2$-H$_2$O Systems
Interactions for Studies of Vapour-Liquid Equilibrium
and Catalyst Aided and Unaided Solvent Regeneration

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Huancong Shi, candidate for the degree of Doctor of Philosophy in Engineering, has presented a thesis titled, *NMR Analysis of Various Amine-CO₂-H₂O Systems Interactions for Studies of Vapour-Liquid Equilibrium and Catalyst Aided and Unaided Solvent Regeneration*, in an oral examination held on November 8, 2013. The following committee members have found the thesis acceptable in form and content, and that the candidate demonstrated satisfactory knowledge of the subject material.

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Abstract

The removal of CO₂ by chemical absorption and regeneration has been researched for decades. CO₂-amine interactions in solvent chemistry have been studied via the Vapour-Liquid Equilibrium (VLE) model. Databases for VLE models have been generated either through software simulators or conventional pH meter + Nuclear magnetic resonance (NMR) experiments. Studies have focused mostly on single amines solutions (MEA, MDEA, BEA, AMP, etc.) below 40ºC. Limitations have restricted research in VLE modeling. Solvent regeneration or CO₂ stripping studies have also been of research interest for years. However, the heat duty is very high, even with stripping performed at reboiler temperatures around 120-140ºC.

Two methods, the conventional (pH + NMR) method and a newly developed NMR calibration method presented, were used to obtain and compare the ion speciation data of VLE model in terms of both accuracy and a wider range of operating conditions. The novel NMR method involved both 1D and 2D NMR methods. The 1D NMR analyses included $^{13}$C chemical shifts test samples and area integration tests of the specific $^{13}$C NMR peaks for carbamate and bicarbonate/carbonate. The 2D NMR involved $^1$H vs $^1$H and $^1$H vs $^{13}$C tests to detect intermolecular interactions. NMR analyses of single and blended solvents showed typical but more accurate concentrations of major ions that changed with CO₂ loading. The application of NMR analysis widened the operating range to
quaternary amine systems and higher temperature regions, for which the ion speciation of the blended amine systems could be completely elucidated and quantified of various MEA-DEAB-CO$_2$-H$_2$O solutions at 24°C, from 40 to 70°C.

In solvent regeneration, the apparatus and procedures were used for amine regeneration studies with single and blended amine systems + two specific solid acid catalysts, Al$_2$O$_3$ and H-ZSM-5. The primary amine was not energy efficient because of few HCO$_3^-$ ions to reduce the energy requirement for MEAH$^+$ deprotonation. The effect of adding a tertiary amine (in blended amine) facilitated the heat duty reduction because of adding two components, R$_3$N and HCO$_3^-$ to cut the free energy gaps. DEAB generated more HCO$_3^-$ with tertiary amines resulting in a much lower heat duty, even though MDEA is less energy demanding than DEAB as it is less basic as per the energy diagram. The addition of solid acid catalysts during regeneration results in a further reduction of the energy cost because strong acidic catalysts facilitated the release of medium acidic oxides CO$_2$. Al$_2$O$_3$ (Lewis acid) was more effective in the lean region because it replaced the role of HCO$_3^-$ (negligible < 0.25); while H-ZSM-5 (Brønsted acid) was effective throughout the loading range within (0.15-0.50) because it donated protons. The combination of a blended amine (e.g., MEA-DEAB-CO$_2$-H$_2$O) with solid acid catalysts (especially H-ZSM-5) for regeneration was able to cut the energy cost by up to 60% compared to MEA even at 90°C, which implies that hot water (95-98°C) can be used as the heat source instead of steam, reducing plant disruption.
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Nomenclature

AMP  2-amino-2-methyl-1-propanol
DEA  diethanolamine
DEAB 4-(diethylamino)-2-butanol
K_{DEABH+} DEABH⁺ dissociation constant, mol/L
K_{eq} chemical reaction equilibrium constant
MDEA methyldiethanolamine
MEA monoethanolamine
NOE Nuclear Overhauser Effect
n  number of data points
n_{HCl} number of moles of HCl added during the titration, mol
n₀_{DEAB} initial DEAB amount, mol
S  standard variance for experimental system
T  absolute temperature, K
V_{total} total liquid volume after titration, L
2D NMR  two dimensional nuclear magnetic resonance spectroscopy,

COSY  2D NMR correlation spectroscopy

HMQC  2D NMR Heteronuclear Multiple Quantum Correlation

**Greek letter**

δ  chemical shift, ppm

σ  standard variance for real system

μ  real value
Chapter 1 General Introduction and Background

1.1 CO₂ Absorption and Regeneration in post combustion CO₂ capture

1.1.1 CO₂ capture and Storage (CCS) technology

CO₂ capture from industrial flue gases has been an important issue for years. Therefore, research and development (R&D) for cost-effective CO₂ capture technologies is important. If CO₂ emission rates can be reduced at facilities with the application of advanced cost-effective technologies, the consequences of global warming can be minimized. Carbon Capture and Storage (CCS) is expected to contribute about 20% of global greenhouse gas (GHG) emission reductions by the middle of the 21st century. [1]

CO₂ capture via post-combustion with chemicals is an amine scrubbing process removes a large amount of CO₂ from industrial gas streams. The exhaust gases or flue gases from coal-fired power plants are treated with a chemical process for reducing CO₂ emissions. [1] The flue gas is exposed to chemicals that absorb or dissolve CO₂, and CO₂ is separated effectively from chemisorption.

Amines are among the favoured chemicals for CO₂ absorption because of their low cost, efficiency, and effectiveness. They are relatively environmentally friendly, too. Therefore, the application of amines in this area is well understood in terms of solvent chemistry because they have been used in gas treating for years. [1]
1.1.2 Solvent chemistry: amine and CO₂-amine interaction

For most CO₂ capture processes, major research has been focused on process integration or development of improved solvents for CO₂-amine interactions in order to reduce the overall heat duty. Process integration involves the study of industrial systems related to CO₂ capture, usually in a heat exchanger network (HEN) and process optimization in a pilot plant design. This thesis is mainly focused on solvent improvement and partly on catalytic amine regeneration. The chemical properties of a variety of amine solutions are studied, tested, and compared as optimized solutions for CO₂ absorbents. The studies of CO₂ amine interactions focus on CO₂-amine bond generation in absorption and on CO₂-amine bond cleavage in regeneration.

A recently published collection of research articles covered the range of CO₂ capture technologies in a variety of aspects. Three parts are described in a review related to solvent chemistry. The first is a reaction equilibrium and vapour-liquid equilibrium (VLE) study through specific NMR analysis technologies. [2], the second focuses on reaction kinetics of CO₂ absorption [3], and the third is a pKa analysis of a variety of amines. The three reviews were written in the order of equilibrium to transfer analysis or from steady state to dynamic state. Part 5a [2] of the review series presents a review of VLE models in solvent chemistry. The purpose of this thesis is to understand chemical reactions and certain properties of water soluble amines and their interactions with CO₂.
1.1.3 Solvent regeneration or CO$_2$ stripping technology

The second part of the thesis is focused on solvent regeneration or (CO$_2$ stripping) with two effective approaches: improved solvents and the application of catalysts.

For the past few decades, amine regeneration studies have been a major challenge for cost effective CCS technologies, especially for scaled-up pilot plant studies. The conventional amine regeneration is performed under a rebuilder with steam as a heat source, and the operating temperature is about 120-140ºC. CO$_2$ can be regenerated out of the loaded amine solution properly, but the energy cost is huge, because the boiling point of an aqueous amine solution is about 100ºC. A large amount of heat is consumed in the vaporization of water, which is a huge waste. Figure 1.1 lists a relative energy distribution plot of amine regeneration from previous studies within ITC. [6] More than 85% of the energy is spent on water vaporization as waste heat. However, when the blended amine system is applied, the heat duty is greatly reduced compared to a single MEA solution and energy efficiency is increased.[6]

Therefore, studies have been performed to reduce the heat duty for amine regeneration. A 2009 perspective in Science described the problems with the conventional amine scrubbing process for CCS technology. [7] The conventional amine solution for CO$_2$ absorption and regeneration pilot plants is 30wt% MEA (5M), the theoretical minimum energy requirement is 0.11 MWh/ton CO$_2$ (437 kJ/kg CO$_2$) and the heat duty of the pilot plant in the US in 2006 was 0.37
MWh/ton CO₂ (1468 kJ/kg CO₂). The expected heat duty needs to be reduced to 0.20 MWh/ton CO₂ (793 kJ/kg CO₂). Generally, effective approaches to achieve this goal are either by solvent or process improvements. [7]

Fig. 1.1 Distribution of energy associated with reboiler heat duty for blended alkanolamines.

The reboiler heat duty of MEA-MDEA blended solutions (4.0 kmol/m³ amine concentration, 0.50 mol/mol rich loading). [6]

a. Most heat is wasted on vapourization of single amine MEA.
b. A lower ratio of energy was spent on vaporization of the MEA/MDEA mixture but more was expended on the reaction due to the MDEA and bicarbonate.

1.2. Research Targets and purpose of this study

The research objectives of the VLE model are focused on two types of amines and amine solutions: MEA (primary amine), DEAB (tertiary amine), single amine solutions and blended amine solutions. MEA is commercially available and well known. However, DEAB is a novel synthesized amine from ITC, (not commercially available). Some research has been completed at ITC on fundamental studies of the physical and chemical properties of pure DEAB and DEAB solutions. Meanwhile, research on CO₂-DEAB interactions such as reaction kinetics and mass transfer behaviour have been completed as well.

Therefore, by combining the VLE models of the DEAB-CO₂-H₂O system with results on solvent properties, reaction kinetics, and mass transfer, a very strong and comprehensive database can be generated for the DEAB solution and blended MEA-DEAB mixture. Since DEAB is used throughout this thesis, an introduction to its molecular identity is necessary.

Molecular Identification of DEAB: structure and NMR spectra

The novel amine DEAB has been synthesized within ITC. It is hard to interpret the NMR spectra of the amine solutions containing DEAB without a clear molecular identity. The molecular identification of DEAB is important, and it was demonstrated in the present research with simulative molecular structure + \(^1\)H and \(^{13}\)C NMR spectra.
The molecular structure of DEAB and DEABH$^+$ is plotted in Figure 1.2 with the $^{13}$C NMR spectra and labeling of carbon atoms. DEAB and DEABH$^+$ possess the same NMR spectra in the liquid phase because of fast-proton exchange. DEAB is a tertiary amine, which has 8 carbon atoms but only 6 groups of carbon in the $^{13}$C spectra because of symmetry. One NMR peak may represent more than one carbon atom in the molecule. This is a tricky characteristic of NMR spectra. There are 6 peaks in the $^{13}$C spectra, which represent 6 types of carbon for DEAB. They are clearly labelled on NMR spectra and molecules for convenience.

The $^1$H spectra of DEAB is also introduced in Fig 1.2. It is more complex than $^{13}$C spectra because there are more $^1$H peaks in DEAB and the split rules of $^1$H peaks are also complicated. $^1$H NMR and $^{13}$C NMR spectra consist of molecular IDs for organic compounds. Most analyses of NMR spectra in the present research are focused on $^{13}$C NMR spectra for either single or blended amine systems.
$^{13}$C NMR spectra of DEAB
Fig. 1.2 The molecular structure of DEAB and protonated DEAB (DEABH\(^+\)), the \(^{13}\)C and \(^1\)H NMR spectra of DEAB / DEABH\(^+\). \(^{a,b,c}\)

a. The 6 groups of carbon are numbered as C\(_1\) to C\(_6\) in spectra with the exact order of chemical shift from small to large. The specific carbons on the NMR spectra are labeled on the molecular structure.

b. The \(^1\)H NMR spectra of DEAB is complex. Standard peaks \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta = 3.89\) ppm (tq, 1H), 2.58-2.69 ppm (m 3H), 2.52 ppm (dt, 1H), 2.31 ppm (sex, 2H), 1.48-1.58 ppm (m, 1H), 1.39 ppm (dq, 1H), 1.10 ppm (d, 3H), 1.00 ppm (t, 6H).

c. The \(^1\)H NMR spectra was not emphasized as the present research is focused on \(^{13}\)C NMR spectra.
The comprehensive databases include equilibrium conditions (VLE) and dynamic conditions (reaction kinetics and mass transfer). They are very useful for the selection and design of optimized amine solvents for CO$_2$ capture processes under absorption and regeneration sections. Therefore, the “experimental” ion speciation data of VLE models are needed at higher operating temperatures.

The ion speciation plot of the VLE model illustrates the driving forces behind mass transfer of CO$_2$ into amine solutions, which is very important for CO$_2$ absorption and regeneration. Based on Film Theory, mass transfer of CO$_2$ is determined in eqn (1.1):

$$N_A = K_g P (y_{Ae} - y_A^*) = K_f (C_A^* - C_{AL}) \quad (1.1)$$

$A$ refers to CO$_2$

The concentration of $C_A^*$ is the research focus in VLE models, as it indicates the exact amount of CO$_2$ dissolved in the amine solution at equilibrium. Moreover, when CO$_2$ is dissolved in amine solutions, many reactions take place (Reaction scheme in Chapter 2.1.2). Three major anions are generated, which originate from CO$_2$: carbamate [RNH-COO$^-$], bicarbonate [HCO$_3^-$] and carbonate [CO$_3^{2-}$]; with trace amounts of [CO$_2$]$_0$ at very rich loading. The mole fraction of CO$_2$ in the gaseous phase $y_A^*$ is determined by $C_A^*$ or $y_A^*$ in the solution. The solubility curve (PCO$_2$ vs. loading $\alpha$) can clearly describe the relationship in the gas-liquid phase.

Moreover, the cations [AmineH$^+$] and neutral compounds [Amine] are also of research interest. The detected ion concentrations are grouped into organized ion speciation tables or plots in the database. With ion speciation plots handy, the
concentrations of major chemicals at any CO$_2$ loading in the solutions can be detected with ease (Chapter 1.2).

The ion speciation plots of the VLE models also indicate the maximum CO$_2$ loading for specific amine solutions, which are related to the “cyclic capacity” of amine solutions. For example, the maximum loading of the MEA-DEAB (5M/1.25 M) blended amine solvent is about 0.52-0.54 mol CO$_2$/ mol amine, which exhibits the limits of absorption. When CO$_2$ loading of this amine solution is close to 0.5, the driving force of CO$_2$ absorption is relatively small. (The loading of the MEA solution can reach 0.6 mol/mol with the long-term introduction of CO$_2$ over several hours [8] but 0.52-0.54 was a maximum under normal operating conditions).

The solubility curve of the VLE model is also applicable for regeneration operation design of the separation train in Chapter 7. A comparison of the operation line vs. solubility curve can be very useful for conventional regeneration operations at high temperature. Figure 1.3 clearly demonstrates the application of the solubility curve for amine regeneration, which is effective for gaseous phase. [6] Moreover, the ion speciation plots of the VLE models can compensate for the deficiency of the solubility curve in liquid phase in this research for a detailed and comprehensive amine regeneration analysis as an upgrade. Beyond the VLE models, two types of solid catalysts (Al$_2$O$_3$ and HZSM-5) are selected with combinations of three amine solutions (MEA, MEA-MDEA and MEA DEAB) to discover the most energy efficient catalytic amine regeneration process as a novel
solution.

Fig. 1.3 McCabe-Thiele diagrams for CO₂ stripping operation at different lean-CO₂ loadings:

(a) low lean-loading region; (b) high lean-loading region.[6]
1.3 Background and Analytical methodology, NMR spectroscopy

The previous sections (1.1-1.2) provided a broad introduction to the fundamental background, research focus, and direct approach of the research.

This research contains many contributions. A novel amine DEAB is introduced; a novel NMR calibration method is developed, and applied to new areas: the quaternary aqueous systems of blended amine and a higher temperature region 40-70°C. Therefore, some additional academic details are discussed, which is necessary and helpful for further analysis.

NMR (Nuclei Magnetic Resonance) Spectroscopy: A research technique that exploits the magnetic properties of certain atomic nuclei to determine physical and chemical properties of atoms or the molecules in which they are contained. It relies on the phenomenon of nuclear magnetic resonance and can provide detailed information about the structure, dynamics, reaction state, and chemical environment of molecules.

Chemical Shift: In NMR spectroscopy, the chemical shift \( \delta \) (ppm) is the resonant frequency of a nucleus relative to a standard. Often the position and number of chemical shifts are diagnostic of the structure of a molecule.

Amine-CO\(_2\)-H\(_2\)O systems: The important research objectives as part of solvent chemistry. As long as the CO\(_2\)-amine interactions reach chemical equilibrium, there are 8-9 cations, neutral molecules, and anions in the solutions, which will draw a lot of research interest. NMR analysis was applied to this complex system to detect the equilibrium models.
VLE *(Vapour–liquid equilibrium)* model: A condition wherein a liquid and its vapour (gas phase) are in equilibrium with each other, or a condition or state where the rate of evaporation (liquid changing to vapour) equals the rate of condensation (vapour changing to liquid) on a molecular level such that there is no net (overall) vapour-liquid inter-conversion.

Ion Speciation *(Speciation of ions)*: The changing concentration of varying forms of an ion (cation or anion) as the pH of the solution changes. In specific NMR analysis of this Part 5(a), ion speciation refers to the changing concentrations of varying ionic forms of amine/amineH⁺, carbamate, and bicarbonate/carbonate as the CO₂ loading of the solution increase from lean to rich, with pH value decreasing from strong base to weak base.

CO₂ loadings: The molar loading, which is the exact amount of CO₂ absorbed per each moles of amine, with the units “mol CO₂/mol amine” or “mol/mol”. The loading can be tested with analytical titration and a Chittick apparatus.

1.3.1. VLE models of CO₂ - amine Interaction for both absorption and regeneration

The reaction equilibrium for the CO₂-amine interaction study is the research focus of the solvent chemistry study [2] and objective of this research. As is well known, CO₂ is an acid gas and amines are basic compounds. Thus, the CO₂–amine reactions belong to a category of acid-base reactions. VLE models provide very important databases of chemical process designs in both absorption and
regeneration columns. Beyond absorption, VLE models are also very applicable in design of the separation train of G-L systems in industry, such as in amine regeneration. There are few studies where experimental VLE plots are successfully generated at higher temperatures, with the exception of this research, because of the difficulties with conventional pH + NMR techniques, which will be discussed in Chapter 6.

The CO₂-amine interactions are reversible to favour both absorption and regeneration processes. Under temperatures as low as 25°C, CO₂ chemically bonds to amines to facilitate absorption of CO₂ from flue gases. At regeneration conditions (120°C), CO₂ is regenerated from the amine solution with heat and stored.

At equilibrium, the reactions seem to be “stopped” on the macro level, since ion concentrations remain unchanged. However, at the molecular level, reversible reactions take place continuously and the reaction rates of forward reactions and backward reactions are the same. The reaction schemes of ion interactions are complicated (Chapter 2.1.2). Multiple cations, anions, and neutral chemicals interact with each other.

Beyond chemical reaction equilibrium, VLE (Vapour Liquid Equilibrium) analysis is emphasized in this research. Because of the gaseous CO₂ and liquid amine solutions, the reactions of CO₂-amine are not homogeneous but Gas-Liquid heterogeneous. The fact of mass transfer of CO₂ into amine solutions from the bulk of the gas into the bulk of the liquid is not negligible along with the reaction. When
the overall Amine-CO₂-H₂O system reaches vapour liquid equilibrium; not only does the reaction reach equilibrium, but also does the mass transfer in both phases reaches equilibrium. The velocity of CO₂ diffusion from gas to liquid is the same as that from liquid to gas.

Ion speciation plots of VLE models can either be generated by software simulation or by experimental detection. Simulation data are easy to generate with software. Figure 1.4 shows a typical example of a simulative ion speciation plot of MEA-CO₂-H₂O systems under 40 and 120°C with an electrolyte Non-Random Two-Liquid (e-NRTL) model. [2] With any vertical dashed line on the specific loading, mole fractions of different ions are detected and depicted as the horizontal dashed line automatically. With the tested CO₂ loading, it is also very convenient to obtain the exact ion concentrations of the major compounds in the solution, such as [MEA], [MEAH⁺], [MEA-COO⁻] and [HCO₃⁻]. This is feasible.

However, the simulation plots are not accurate compared to experimental plots. For example, the top plot at 120°C of the MEA solution system is not practical because the boiling point of water is 100°C. It violates the exact practical conditions. Moreover, for the bottom plot at 40°C, the maximum loading of CO₂ under normal operation conditions was around 0.52-0.55 mol CO₂/mol amine based on our experimental tests. The simulation data at higher loading (0.60-1.00) was not practical, either. Therefore, only the left part of the plot separated by the solid line was useful.
Fig. 1.4 Simulated Liquid-phase speciation and concentration in a 2.5 M MEA solution with CO₂ loadings from 0 to 1 at temperatures of (a) 40 and (b) 120 °C. 


b. With the vertical and horizontal dashed line, it is very easy to detect the ion concentrations of major compounds in the solution.

c. The solid line is the max CO₂ loading under experimental conditions in the research.
More practical and accurate ion speciation plots of VLE models should be generated from experiments with higher credibility. This is the exact aim of the first section of the research, to generate accurate ion speciation table/plots with experiments with specific NMR technology. The accurate plots of VLE models at room temperature are useful for absorption tests that at higher temperatures can provide much more sufficient and accurate information for amine regeneration studies.

In most cases, single amine solutions have been investigated experimentally by peer researchers at room temperature [2]. Different amines MEA, MDEA, BEA, and AMP have been tested and published, [2] which were very helpful and illustrative.

However, this research focused on VLE models of blended amine systems (MEA-DEAB) rather than single amines (DEAB), which are more complex and difficult to analyze because they are quaternary systems. The results would be very illustrative and practical as long as the technical difficulties were overcome. The author tested DEAB-CO₂-H₂O as another special tertiary amine [4] in Chapter 4, which represents a fundamental study of the amine. Meanwhile, a novel NMR calibration method was developed and is discussed briefly in Chapter 4. The novel experimental analyses of VLE plots of blended MEA-DEAB-CO₂-H₂O are discussed in Chapter 5. The NMR analyses method for higher temperatures of blended Amine-CO₂-H₂O with NMR calibration are
discussed in Chapter 6. Amine regeneration analysis of blended Amine-CO$_2$-H$_2$O with different packing is discussed in Chapter 7.

1.3.2 Targeted Major ions of single and blended Amine-CO$_2$-H$_2$O systems

Major ions of the CO$_2$-amine systems are grouped into three categories: bicarbonate/carbonate ($\text{HCO}_3^\text{-}/\text{CO}_3^{2\text{-}}$), carbamate ($\text{RNH-COO}$), and AmineH$^+$/Amine. Their exact concentrations under CO$_2$ loadings have to be tested with high accuracy.

However, these ion concentrations in the Amine-CO$_2$-H$_2$O solutions are hard to detect independently because many complicated reactions take place simultaneously, as a consequence of CO$_2$-amine interactions. Moreover, there is very fast proton exchange in $\text{HCO}_3^\text{-}/\text{CO}_3^{2\text{-}}$ and AmineH$^+$/Amine. It is difficult to test these ions accurately with conventional analytical chemistry methods (titration, GC, HPLC, IR etc). These accurate results can be achieved with the NMR analysis technique. [2] The chemical shift can reflect the ratio of $\text{HCO}_3^\text{-}/\text{CO}_3^{2\text{-}}$ and AmineH$^+$/Amine.

1.3.3 Analysis methods: pH + NMR combination, NMR calibration.

A basic introduction of the applications of NMR technology is available elsewhere [5]. Here, the NMR analysis of this research is focused on the ion concentration detection of the Amine-CO$_2$-H$_2$O system. Two methods are introduced: the conventional method and a novel calibration method developed by the author [2, 4].
The conventional method, which was used by Polling and Jakobsen, is a combination of pH meter with NMR instrument. [4] The $^{13}$C NMR spectra can detect the concentration of bicarbonate ($\text{HCO}_3^-$/$\text{CO}_3^{2-}$) and carbamate (MEA-COO$^-$). The pH meter can detect the concentration of [H$^+$], and AmineH$^+$/Amine can be calculated based on the available deprotonation constant K or (acidic Ka) from literature.

The novel NMR calibration method can detect all the ions simultaneously, and with NMR analysis solely. The method to detect the $\text{HCO}_3^-$/$\text{CO}_3^{2-}$ and carbamate is the same, but detection of AmineH$^+$/Amine is based on the calibration of $^{13}$C NMR spectra, which establishes the relationship of protonation ratio $x$ with the position of chemical shift $\delta$ (ppm) of the amines directly.

The detailed methodology of novel NMR analysis includes $^{13}$C peak interpretation, data acquisition, with extra treatments. They are discussed in detail in Chapters 2 to 6 respectively. A brief literature review is given in Chapter 2, and the general experimental procedures of both methods are introduced in Chapter 3. The description of both methods is in Chapter 4, and the accuracy of both methods is validated, with analyses of blended amine systems in Chapter 5. Calibration method of NMR analysis of samples at high temperature is in Chapter 6.
1.3.4 Ion Speciation tables and plots

After NMR analyses of the amine systems, the ion speciation tables and plots represent the desired results from detected ion concentrations. From chemical shift $\delta$ of $^{13}$C NMR tests, the ion concentrations can be detected, and two types of tables and figures can be generated: data ion concentration $C_A^*$ and with mole fraction $x_A^*$ [4]. These two types of plots are similar to each other, since both reflect the amount of chemicals in the solution. The mole fraction plot is more apparent, practical, and useful than the ion concentration, which is plotted in a consistent format such as Figure 1.4. However, different units are used for both calculations. The unit for ion concentration $C$ is mol/L, and for mole fraction, $x$, it is dimensionless.

The moles of all the compounds need to be calculated, including amineH$^+$, amine, carbamate, HCO$_3^-$, CO$_3^{2-}$, and water (only for mole fraction). The concentrations and mole fractions for each compound were calculated in Equations 1-1 and 1-2 below:

Concentration: $C[HCO_3^-] = \frac{nHCO_3^-}{V_{total}}$  

(1-2)

Mole fraction: $x_{HCO_3^-} = \frac{nHCO_3^-}{[n\text{amineH}^++n\text{amine}+n\text{carbamate}+nHCO_3^-+nCO_3^{2-}+nH_2O]}$  

(1-3)

In Chapter 4, both concentration and mole fraction calculations are performed on DEAB-CO$_2$-H$_2$O solution since the ternary systems are easy to study. However, from Chapter 5 to 7, only the ion concentrations are calculated for blended amine MEA-DEAB-CO$_2$-H$_2$O systems because the quaternary systems are more complex
than ternary systems. Ion concentration tables and plot are more convenient than mole fraction without loss of accuracy.

1.3.5 Common thermodynamic model and catalysis for amine regeneration.

Chapter 7 is a relatively independent part, which emphasizes the amine regeneration analysis. It is applied the ion speciation plot of VLE models in Chapter 6 for the purpose of regeneration study. Chapters 3-6 are mostly focused on NMR analysis of various amine solutions to generate VLE models, which are more related and consistent. However, beyond the background of VLE models, there is other background knowledge that needs to be introduced in regeneration studies. It includes thermo dynamic models such as Free Energy, PES diagram, and principle of catalysis.

Free energy $\Delta G$: is well known, amine regeneration requires a large amount of heat because the reactions taking place in the regeneration column are strong endothermic reactions. This qualitative statement is far from sufficient and more accurate estimations of energy requirement are needed. This can be solved with Free energy requirement $\Delta G$. The free energy of the reactions in amine regeneration can demonstrate the quantitative energy gaps from reactant to product (fresh CO$_2$ + amine). The free energies of amine regeneration reactions under specific temperatures reflect the “theoretical minimum energy” requirement of amine regeneration directly. This information is very useful and illustrative, and it is emphasizes that the Free energy $\Delta G$ calculations were different from standard
value $\Delta G^\circ$, since the operation was not under standard conditions (25°C) but catalytic regeneration conditions (90°C).

The Potential Energy Surface (PES) diagram was introduced as well. The PES diagram reflected the “relative free energies” for reactant, product, and intermediates during the reaction pathways. This is a very powerful method which can demonstrate the energy difference (energy peaks and valleys) clearly along the reaction. The energy gap (requirement) and activation energy can also be measured from the PES diagram directly, which indicates the extend of difficulty of regeneration.

Role of catalysis are introduced here. It is known that the role of catalyst can facilitate the reaction rate in both forward and backward reactions by decreasing the activation energy $E_a$, but it cannot change the free energy gaps $\Delta G$ of the reactions from the thermodynamic models. Therefore, it has been considered in the past that the application of catalysts would not be energy effective.

From our study, the application of catalyst is not aimed at changing the free energy requirement, but is used to accelerate the reaction rate and therefore increase the energy distribution or efficiency onto regeneration. As mentioned in section 1.1.3, for the current pilot plant (2006), the theoretical energy requirement is 0.11 MWh/ton CO$_2$ (437 kJ/kg CO$_2$) but the realistic energy requirement is 0.37 MWh/ton CO$_2$ (1468 kJ/kg CO$_2$). Such data indicate a very low energy efficiency (<30%) for the current CO$_2$ pilot plant. The goal of adding catalyst is to increase the energy efficiency in order to distribute the energy efficiently to the reaction,
but not to decrease the theoretical energy minimum, which is hardly changeable. This idea is novel and crucial for our regeneration analysis in Chapter 7. The idea of applying catalyst is a novel approach in the study of amine regeneration because it involves an alternative solution for regeneration energy reduction, outside of normal solvent improvement and process integration. [7]

1.4 Thesis objectives and Thesis outline.

1.4.1 Research Objective

The research objective is focused on two types of NMR analysis (pH + NMR & NMR calibration analysis) onto the single amine solution DEAB-CO$_2$-H$_2$O and quaternary amine solution MEA-DEAB-CO$_2$-H$_2$O at room temperature and higher temperature up to 70°C, for ion speciation tables and plots of VLE model. The ion speciation plots of different solutions at different temperatures are the desired research results.

The regeneration is focused on the catalytic study of 3 amine solutions: MEA-CO$_2$-H$_2$O, MEA-MDEA-CO$_2$-H$_2$O, MEA-DEAB-CO$_2$-H$_2$O systems, with three types of catalytic conditions: non-catalyst as reference state, Al$_2$O$_3$ as a typical Lewis acid, H-ZSM-5 as a typical Brønsted acid. Nine different typical cases were studied and the catalytic amine regeneration curves were developed.

1.4.2 Scope of the thesis

The NMR analysis is focused on 1D analysis, some 2D NMR analysis were performed as a start-up test of quaternary MEA-DEAB-CO$_2$-H$_2$O systems, but 2D is not emphasized. For the 1D NMR analyses, $^{13}$C NMR tests are researched in
detail for different amines, but \(^1\)H is applied briefly only for molecular ID of DEAB and MEA.

For the amine regeneration studies, the reflux condenser was used for as a batch reactor for regeneration study. The steady state analyses of amine scrubbing process with packing column are discussed elsewhere. This research just describe the catalytic regeneration curves, without detailed kinetics and mechanistic studies yet.

1.4.3 Thesis outline

The research is written in the integrated article format in which Chapters 2, 4, 5, 6 and 7 are the actual original manuscripts submitted for publication. Each of the five chapters is a standalone chapter with separate and relevant introduction, literature review, experiment, results and discussion, and conclusion sections.

The following detailed sets of objectives for the main work of the research:

1. Chapter 2, the literature review, which involved NMR analysis of amine-CO\(_2\)-H\(_2\)O solutions for ion speciation plots. Several papers related to amine regeneration and CO\(_2\) stripping processes were discussed, and the previous catalytic amine regeneration processes were briefly discussed.

2. Chapter 3, the introduction of general experimental procedures of NMR analysis (pH + NMR and NMR calibration) and regeneration study.

3. Chapter 4, \(^{13}\)C NMR of ternary DEAB-CO\(_2\)-H\(_2\)O systems with ion speciation plot of VLE models at 24.5°C, both methods (pH + NMR and
NMR calibration) are performed.

4. Chapter 5, $^{13}$C NMR of quaternary MEA-DEAB-CO$_2$-H$_2$O systems with ion speciation plot of VLE models at 24ºC, both methods (pH + NMR and NMR calibration) are performed.

5. Chapter 6, $^{13}$C NMR of quaternary MEA-DEAB-CO$_2$-H$_2$O systems with ion speciation plot of VLE models at 40-70ºC, with NMR calibration method.

6. Chapter 7, amine regeneration studies for various amine solutions and catalysts discussed in section 1.4.1.

1.5 References


The details of T1 relaxation times (or “relaxation delay”) can be referred to the contents at Chapter 5: Data acquisition, Page 68-71. The experimental procedures of complex 2D NMR techniques can be referred to the contents at Chapter 10: Multidimensional NMR, Page 171-200.


Chapter 2 General Literature Review

This chapter reviews the literature review that currently focuses on the ion speciation analysis with NMR instrument and solvent regeneration modeling speciation analysis to amine based CO\textsubscript{2}-capture.

2.1 NMR analysis of amine solutions of VLE models

This is Part 5(a) of special review series on recent progress and new development of the post combustion carbon-capture (PCC) technology using reactive solvents. NMR (nuclear magnetic resonance) spectroscopy is an important method in analytical chemistry to test the functional groups and molecular structures of organic compounds. This methodology has been recently applied into the field of CCS (carbon capture and storage) in terms of solvent chemistry aspects for solvent development of new CO\textsubscript{2} capture processes. NMR has been used for testing of new amines and amine-CO\textsubscript{2}-H\textsubscript{2}O systems with \textsuperscript{1}H and \textsuperscript{13}C spectra for a number of years [1]. This chapter is a comprehensive review of most of the recent research papers that have applied NMR spectroscopy to analysis of a variety of amines and amine-CO\textsubscript{2}-H\textsubscript{2}O systems for multiple purposes, mostly for vapour-liquid equilibrium (VLE) model analysis, and for some other researches as well as kinetic analyses.

NMR spectroscopy is an indispensable methodology in organic chemistry for work with synthesized chemicals. [2] The functional groups, the carbon backbones, and C-C double and triple bonds can be detected directly, mostly with liquid phase \textsuperscript{1}H and \textsuperscript{13}C spectra. Detailed NMR instrumentation operations can be
referred to the specific “Liquid NMR manual”[101] Moreover, in the field of carbon capture and storage (CCS) technology, NMR spectra have been applied into test the ion species in the complicated amine-CO$_2$-H$_2$O systems to develop the vapour-liquid equilibrium (VLE) models, which are discussed in detail in Part 5(a). This can be considered an important part in the field of solvent chemistry, beyond absorption solubility and kinetics, which are discussed in Parts 5(b) and 5(c), respectively.

This section focuses on the equilibrium of CO$_2$ absorption into water soluble amines, which exhibits vapour-liquid and chemical equilibrium. The former involves Henry's constant and the latter involves reaction thermodynamics. [3] In this research field, the ion speciations and the exact concentrations of cations, free molecules, and anions at different CO$_2$ loadings are of research interest, and ion speciations were detected with NMR spectroscopy and combined with other equilibrium methods.[1, 4, 5] The experiments generate very useful plots of ion speciation for different amines at different temperatures, which are the so-called VLE plots. VLE plots provided a very important database for the CO$_2$-amine reaction kinetics study in Part 5(b). The reactant’s (amine) rate of conversion $X_A$ was expressed as $(C_{A0}-C_A^*)/C_{A0}$, where the $C_A^*$ is the equilibrium concentration. However, the experimental equilibrium concentrations of major ions were difficult to detect because the major ions have strong interactions (see reaction scheme). With the experimental “VLE plot” of some CO$_2$-amine-H$_2$O systems generated with NMR analysis, all the major ion concentrations were tested and grouped in
one plot with respect to different CO₂ loading from lean to rich amine. The major ion concentrations can be obtained directly based on a given CO₂ loading at a given temperature, which can facilitate the tests of main ion concentrations in industrial CO₂ absorbent systems.

2.1.1 NMR analysis of amine-CO₂-H₂O systems

As is mentioned above, NMR techniques were mostly applied to identify / verify the structures and functional groups of chemicals, for qualitative analysis. However, the NMR spectra in Part 5(a) are applied for the quantitative analysis of certain ion concentrations. To establish a useful relationship between the chemical shift δ (ppm) and concentration C (mol/L) of certain ions was the foundation of this research, which has to be laid first.

After several trials in early research work, NMR spectroscopy became a very effective technique that can test ion concentrations directly due to its several advantages. The specific species in the solution possess their own chemical shifts both in ¹H and ¹³C NMR spectra.[1,4] The chemical shift of carbamate and bicarbonate/carbonate in ¹³C NMR spectra are quite different, and they can be easily distinguished. Moreover, from the ¹³C NMR spectra, the ratio of HCO₃⁻ / CO₃²⁻ can be detected directly based on the exact chemical shift of the peak. The proton transfer phenomenon was too fast to detect by NMR spectra, then the peak of HCO₃⁻ / CO₃²⁻ is one integral peak. However, the “position” (chemical shift) of the peaks can itself, illustrate the ratio of these two components directly.[7a] This is based on such equations as the following: the chemical shifts of pure bicarbonate
and carbonate at 25.0 °C were 160.33 ppm and 168.09 ppm respectively; then, the ratio of bicarbonate and carbonate were listed as: \( \frac{\text{CO}_3^{2-}}{\text{HCO}_3^-} = \frac{(\delta - 160.33)}{(168.09 - \delta)} \), where \( \delta \) is the chemical shift of the bicarbonate / carbonate mixture (160.33 < \( \delta \) < 168.09 ppm). [7a]

Some other research groups applied a pH meter with NMR technology to detect the ion speciaions. [1,4] The pH meter was applied to test the free amine and protonated amines with aid of acidic constant \( K_a \), while the NMR was applied to test the carbamate, bicarbonate, and carbonate. With this combination, a large number of amine-CO\(_2\)-H\(_2\)O systems have been tested and their VLE models plotted successfully.

Based on the detailed investigation, the research group at the International Test Centre for CO\(_2\) Capture (ITC) have recently developed a new method of NMR analysis of amine (DEAB)-CO\(_2\)-H\(_2\)O systems to develop the VLE model. [5] This method does not require the aid of pH meters. Both AmineH\(^+\) / amine species and HCO\(_3^-\) / CO\(_2^2-\) were tested simultaneously, more accurate results were achieved. This method seems to be the most up-to-date and advantages approach in this field, and it can be readily applied in amine regeneration analyses/CO\(_2\) stripping.

### 2.1.2 Reaction Schemes: fundamental chemistry of CO\(_2\)-amine interactions

Before the development of VLE models and chemical equilibrium, reaction schemes had to be studied in detail with acknowledgment of the complexity of the solvent systems. As long as the acidic gas CO\(_2\) was introduced into basic
water-soluble amine systems, several typical reactions would occur automatically. After the amine-CO$_2$-H$_2$O systems reached both vapour-liquid equilibrium (VLE) and chemical equilibrium, the systems were converted into complicated solutions containing multiple cations, free molecules, and anions, simultaneously. For instance, some part of the amine will convert to protonated amine (AmH$^+$), and the rest will convert to carbamate. Meanwhile CO$_2$ will convert to bicarbonate (HCO$_3^-$) and carbonate (CO$_3^{2-}$), and a small proportion of water will be protonated, as well. These assumed “three-role” amine-CO$_2$-H$_2$O systems will eventually contain 8-9 ionic or neutral species in the solution, the concentrations of which are also constrained by their reaction equilibrium and mass balance equations.

For the VLE model of single amine-CO$_2$-H$_2$O systems, there are two categories of amines having different chemical reactions while they interact with CO$_2$. The first steps were the same, which is the CO$_2$ in the gaseous phase absorption into liquid solution and reached the vapour-liquid-equilibrium. The CO$_2$ will either bind the amine to generate carbamate, mostly, or release the protons to generate bicarbonate / carbonate and reached chemical equilibrium. The primary and secondary amines such as MEA and DEA belong to the first group, where the carbamate is the major component except that bicarbonate/carbonate will dominant at rich CO$_2$ loadings. Sterically-hindered amine AMP also belongs to the first group by reaction scheme since it is primary amine, but the major component is not carbamate but bicarbonate and carbonate. AMP is special and will be discussed later. The tertiary amines such as MDEA, TEA, and DEAB, belong to the second group,
which contains bicarbonate / carbonate only. Chemical reactions of these two categories of amines are listed below, with amines labeled with MEA and MDEA as paradigms. All the ionic reactions are reversible while the system reaches equilibrium:

MEA [3] as RNH₂:

Overall reaction: \( 2 \text{MEA} + \text{CO}_2 \rightarrow \text{MEA-COO}^- + \text{MEA}^- + \text{H}_2\text{O} \) \hspace{1cm} (2.1)

Initial reaction: \( \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \leftrightarrow \text{H}_2\text{CO}_3(\text{l}) \) \hspace{1cm} (2.2)

Ionic reaction: MEA + CO₂ + H₂O ↔ MEA-H⁺-COO⁻ (zwitterion) + H₂O \hspace{1cm} (2.3)

MEA-H⁺-COO⁻ (zwitterion) + H₂O ↔ MEA-COO⁻ (carbamate) + H₃O⁺ \hspace{1cm} (2.4)

\[
\begin{align*}
\text{H}_3\text{O}^+ + \text{MEA} & \leftrightarrow \text{MEA}^- + \text{H}_2\text{O} \hspace{1cm} (2.5) \\
\text{H}_2\text{CO}_3 + \text{H}_2\text{O} & \leftrightarrow \text{HCO}_3^- + \text{H}_3\text{O}^+ \hspace{1cm} (2.6) \\
\text{HCO}_3^- + \text{H}_2\text{O} & \leftrightarrow \text{CO}_3^{2-} + \text{H}_3\text{O}^+ \hspace{1cm} (2.7)
\end{align*}
\]

Carbamate exchange reaction: MEA-COO⁻ +H₂O ↔ HCO₃⁻ + MEA \hspace{1cm} (2.8)

MDEA [1] as R₃N same as DEAB:

Overall reaction: \( \text{MDEA} + \text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{MDEA}^- + \text{HCO}_3^- \) \hspace{1cm} (2.9)

Initial reaction: \( \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \leftrightarrow \text{H}_2\text{CO}_3(\text{l}) \) \hspace{1cm} (2.2)

Ionic reaction: \( \text{H}_2\text{CO}_3 + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}_3\text{O}^+ \) \hspace{1cm} (2.6)

\[
\begin{align*}
\text{H}_3\text{O}^+ + \text{MDEA} & \leftrightarrow \text{MDEA}^- + \text{H}_2\text{O} \hspace{1cm} (2.10) \\
\text{HCO}_3^- + \text{H}_2\text{O} & \leftrightarrow \text{CO}_3^{2-} + \text{H}_3\text{O}^+ \hspace{1cm} (2.7)
\end{align*}
\]

2.1.3 VLE model development for ion speciation plots

As mentioned previously, the ion speciation plot of MEA-CO₂-H₂O has been studied since the 1980. The amounts of ions and neutral molecules were not independent in tested amine-CO₂-H₂O systems because the systems reached
vapour-liquid equilibrium (VLE) status and chemical equilibrium under experimental conditions. (Theoretically, it takes a very, very long time to reach chemical equilibrium, but we assume it reached equilibrium under experimental definitions when the variation of concentrations were negligible.) At constant temperature, the concentration of cations and anions did not change at certain CO$_2$ loading. Therefore, the exact concentration or mole fraction of the cations and anions and neutral molecules of specific amine are of great interest for researchers. Temperature is a very important factor in the VLE models. Even for the same system, for example, MEA-CO$_2$-H$_2$O, the ion speciation plots of the VLE model at 40°C and 120°C are quite different [3,6] because their reaction equilibrium constants K are different at different temperatures. Usually, VLE models are plotted under CO$_2$ absorption conditions from 20-45°C, since absorption is the primary research interest.

The VLE models of a variety of amine-CO$_2$-H$_2$O solutions have provided important and useful databases for the purposes of optimized amine selection for CO$_2$ absorption. Some researchers prefer to apply the software to simulate the equilibrium conditions computationally and plot the simulated VLE model. [3, 6] The early work was performed by Austen et al. In 1989, this group applied the electrolyte-Non Random-Two-Liquid (NRTL) equation, which focused on the thermodynamically consistent manner. [6] Later on, Liu et al. followed Austen's work and applied the same NRTL method to the same MEA-CO$_2$-H$_2$O system but added the influence of chemical equilibrium constants, Henry's constant,
experimental data, and data regressions.[3] Liu discussed VLE models both at absorption and desorption conditions in detail. The equilibrium constants of the carbamate reversion reaction as well as important interaction parameters of the electrolyte NRTL model, were carefully fitted to experimental data.[3] Then, a very useful VLE model was plotted based mostly on simulation. However, only the VLE plot of CO$_2$ absorption was considered to be accurate and useful, and the VLE plot of desorption was not. Because water vaporized at 120°C, the simulation of MEA-CO$_2$-H$_2$O showed a substantial deviation from the actual experiments. Figure 2.1 shows the simulated VLE model of the ion speciation of a MEA-CO$_2$-H$_2$O system under absorption and desorption conditions [3]. From the figures, it is clear that with the increase of CO$_2$ loading, the concentration of ions will change, either increasing or decreasing, or increasing first and then decreasing after reaching the apex.

However, simulation data are not as persuasive as experimental results. Most research groups prefer specific analytical methods to develop the VLE experimentally. However, a number of conventional analytical methods cannot detect the exact concentrations of AmH$^+$ / Am and HCO$_3^-$ / CO$_3^{2-}$ directly because very fast proton exchange exists in these aqueous systems. The sum of these two species was not difficult to test, but the exact ratios of these groups are difficult to determine. Consequently, most researchers eventually applied the equilibrium constant K to calculate the ion species with pH value as evaluation.
Fig. 2.1  Liquid-phase speciation and concentration in a 2.5 M MEA solution with CO₂ loadings from 0 to 1 at temperatures of (a) 40 and (b) 120 °C.

original reference paper: Figure 4.

2.2 Major NMR analysis of amine by other research groups

2.2.1 NMR analysis with amine for VLE model

The application of NMR spectroscopy to CO₂ reaction with water originated in 1960[8], Abott et al. performed NMR analysis with CO₂-H₂O system to detect bicarbonate and carbonate in 1981. [9] The interaction of CO₂ with H₂O, Henry's constant was the research focus.

In 1996, Suda et al. studied the chemical species in amine solution based on a series of electroneutrality, material balance, and equilibrium constants in combination with NMR; however, only limited data were provided. [10] Later, in 1998, Polling et al. performed NMR analysis of the ion speciation of NH₃-CO₂-H₂O systems with both ¹H and ¹³C spectra.[7a] This was an important paper that developed several useful equations for concentrations calculation of carbamate and bicarbonate/carbonate and the ratio of bicarbonate vs carbonate. These equations were widely applied in the field of NMR analysis of amine-CO₂-H₂O systems. Figure 2.2 has employed such equations from Polling, it was created by Usubharatana P. from ITC in his thesis. [12]
**Fig. 2.2** Calculation procedure flowcharts for ions concentration evaluation.

Original reference Figure 7.2 [12]
Equation (2.11) demonstrates that the ratio of carbamate and bicarbonate / carbonate is directly proportional to the area of $^{13}$C peaks. Since there are two different types of peaks in the $^{13}$C spectra, the areas of these two types of $^{13}$C peaks represents the amount of these two species, where the bicarbonate / carbonate possess one peak only. Equation (2.12) is the concentration of carbamate, which is related to the original CO$_2$ loading. Equations (2.13) and (2.14) are the concentrations of bicarbonate and bicarbonate, where 168.09 and 160.33 ppm [7a] is the chemical shift of pure CO$_3^{2-}$ and HCO$_3^-$ respectively at 25°C. If the system is not processed under that temperature, researchers should test the chemical shift of pure samples beforehand and replace it into the equations.

\[
\text{[NH}_2\text{CO}_2^-]/\text{[HCO}_3^-] + \text{[CO}_3^{2-}] = R \quad (2.11a)
\]

or carbamate / (bicarbonate + carbonate) = $R$ \hspace{1cm} (2.11b)

\[
\text{[NH}_2\text{CO}_2^-] = \frac{R}{(1+R) \times [\text{CO}_2]_0} \quad (2.12)
\]

\[
\text{[CO}_3^{2-}] = \frac{(\delta - 160.33)}{(168.09-160.33)(1 + R) \times [\text{CO}_2]_0} \quad (2.13)
\]

\[
\text{[HCO}_3^-] = \frac{(168.09 - \delta )}{(168.09-160.33)(1 + R) \times [\text{CO}_2]_0} \quad (2.14)
\]

The [CO$_2$]$_o$ represents the exact amount of CO$_2$ absorbed into the aqueous amine solution, where CO$_2$ have been converted to bicarbonate and carbonate already. The original CO$_2$ concentration is needed for mass balance calculation.\n
$[\text{CO}_2]_o = C_{\text{Amine0}} \times \text{loading } \alpha$. Beyond these useful equations, Polling reported another phenomenon which is that with the rise of temperature, the chemical shift will decrease for all the six cases. [7a] However, he did not mention the cations of NH$_4^+$ in the solution since this species is undetectable under either $^{13}$C or $^1$H NMR.
F. Mani et al. [7b] did the similar work for the VLE models with NH$_3$-CO$_2$-H$_2$O by NMR analysis in 2006. The system was tested at 293K with 2.5M NH$_3$, with the added of CO$_2$, the PH of the solution was recorded as well. They applied several equilibrium constant K of complicated CO$_2$-NH$_3$ interactions with pH value of the solution to calculate the exact ion concentrations of NH$_4^+$, NH$_3$, NH$_2$-CO$_2^-$, HCO$_3^-$, CO$_3^{2-}$ in the system. As mentioned before, $^{13}$C NMR spectra can only exhibit the peaks for NH$_2$-CO$_2^-$ and HCO$_3^-$/CO$_3^{2-}$. They applied the similar conventional method, NMR + pH meter. The results they resent is also a VLE model with ion speciation, but the x axis is not the CO$_2$ loading anymore, but the pH value of solution, which is not a standard VLE plot, however, it is useful in practical field, as long as the pH of the system was tested, all mole fraction is known.

In 2005, Jakobsen et al. performed NMR analysis of a variety of amine system and plotted multiple VLE models based on Polling's equations. [1]The systems of CO$_2$ introduced into water soluble MDEA, MEA and DEA solutions were studied at 20, 40, 70, and 90°C at loadings from 0.1 -1.0 (mole CO$_2$) / (mole amine). They developed the conventional method of combining a pH meter and NMR spectra; a pH meter was applied to study AmH$^+$ / Am ratio, and NMR were applied for carbamate, and bicarbonate / carbonate analysis. Several VLE plots were generated for both carbamate (MEA, BEA) and bicarbonate (MDEA) and they proved very important. Beyond the VLE models, the group reported the $^{13}$C chemical shifts of amine carbon types and their range when the amine was protonated. This
demonstrated the fact that the chemical shift of carbon peaks will shift either upfield or downfield with protonation at different scales.[1] This paper is a very typical example of NMR analysis of both primary, secondary, and tertiary amines. However, they failed to perform a detailed analysis of the types of shift and calibration as reported by Shi in the ITC group.[5]

In 2008, Böttinger et al. performed an online NMR spectroscopy of ion speciations of MEA-\textsubscript{CO}_2-H\textsubscript{2}O and DEA-\textsubscript{CO}_2-H\textsubscript{2}O at weight fraction of 0.2 and 0.3 g/g, under 293-353K (15-80°C).[11a] Both \textsuperscript{1}H and \textsuperscript{13}C NMR analyses were conducted for both solutions at 293, 313, and 333K, and MEA was also tested at 353K. Therefore, they plotted accurate VLE models of the two systems. However, they also applied the area integration method of \textsuperscript{1}H to the MEA and DEA systems, which can determine the ratio of MEAH\textsuperscript{+}/MEA vs carbamate. (Equation 2.15). Therefore, the concentrations of carbamate and MEAH\textsuperscript{+}/MEA can be detected as well from Equation 2.16 and 2.17 based on the mass balance. However, they did not apply the pH method to distinguish the exact concentrations of MEAH\textsuperscript{+} / MEA because these two species possess one type of peaks based the effect of fast proton exchange. Their free MEA species were developed with simulation models but not from experiments, which is a disadvantage.

\[
\frac{[\text{MEAH}^+] + [\text{MEA}]}{[\text{MEA-\textsubscript{COO}^-}]} = R \quad (2.15)
\]

\[
[\text{MEA-\textsubscript{COO}^-}] = \frac{1}{(R+1)} \times [\text{MEA}]_o \quad (2.16)
\]

\[
[\text{MEAH}^+] + [\text{MEA}] = \frac{R}{(R+1)} \times [\text{MEA}]_o \quad (2.17)
\]

Meanwhile Böttinger et al. performed another online NMR spectroscopy for
MDEA-CO$_2$-H$_2$O and MDEA-PZ-CO$_2$-H$_2$O in the same year.[11b] The methodology is the same as last work,[16a] from 293-313K, with mass fraction of MDEA at 0.2g, 0.3g, 0.4g/g solution. For the VLE model of MDEA-CO$_2$-H$_2$O, he plotted the MDEAH$^+$/MDEA and HCO$_3^-$/CO$_3^{2-}$ separately into two plots, and his NMR experimental data cannot distinguish the exact concentration of MDEAH$^+$/MDEA and HCO$_3^-$/CO$_3^{2-}$ again. For the quaternary solutions MDEA-PZ-CO$_2$-H$_2$O, the experiment was operated at 293-313K, with mass fraction of MDEA at 0.3 g/g and PZ (piperazine) 0.1g/g. They plot the ion speciation of MDEAH$^+$/MDEA, HCO$_3^{2-}$/CO$_3^{2-}$ and PZH$^+/PZ/PZ(H_2)^+$ and PZCOO$/PZ(COO^−)_2$ separately, this work can be a good example of the NMR analysis of VLE models of quaternary solutions, however, they are using 1D, not 2D. If the 2D NMR analysis were performed on the systems, some better results will be generated as well.

In conclusion, several groups performed NMR analysis of the VLE model in CO$_2$ absorption process studies with different amine-CO$_2$-H$_2$O systems,[1,4,5,7a,12,15] as well as H$_2$O-CO$_2$ systems. [8, 9] NMR was used successfully in combination with other equilibrium relationships, such as PH meter and K constant. The individual ionic concentrations had not been evaluated independently, and just relied on NMR spectra, except in the ITC groups studies. Finally, a novel methodology to detect the ionic concentrations with $^{13}$C NMR spectra alone was developed by the ITC group and it proved to more accurate and efficient than the conventional approach. [5]
2.3 NMR analysis of amines and Amine-CO$_2$-H$_2$O systems at ITC

2.3.1 NMR analysis of MEA-CO$_2$-H$_2$O VLE model

As is well known, MEA is the most commonly applied amine in CO$_2$ absorption. It has a number of advantages over other commercial alkanolamines: (a) it is a strong basic amine with a very quick reaction rate (second to piperazine PZ), yielding high purity, has low CO$_2$ leakage, and is suitable for CO$_2$ capture processes; (b) atomic economics: the lowest molecular weight and, thus the highest absorption capacity on a weight basis with a low cost; (c) thermally stable and less likely to undergo thermal degradation; (d) relatively low solubility for hydrocarbon which reduces the hydrocarbon loss in the process.[3]

In 2008, Usbharatana [12] developed the very useful and applicable NMR analysis “Standard Flowchart” for MEA-CO$_2$-H$_2$O systems based on the review of previous work [1, 4, 7a], which is shown in Figure 2.2. This flowchart of experimental procedures can be applied to all amine-CO$_2$-H$_2$O systems (primary, secondary and tertiary amines) with NMR analysis. Anyone who is interested in this field can perform the experiments successfully with aid of Figure 2. This is another major contribution to this field from ITC. Meanwhile, in 2009 Fan et al. performed NMR analysis of MEA-CO$_2$-H$_2$O experimentally for $^1$H and $^{13}$C at 22.5°C with loading from 0.0 to 0.54 and generated an ion speciations plot.[4] He applied the conventional NMR analysis method (NMR combined with a pH meter). Figure 2.3 represents the plot of ion species concentrations vs CO$_2$ loading from the NMR experiments [4], which matched the simulation results from both Austen and
Fig. 2.3 Plots of the amine species mole fraction against the CO$_2$ / MEA molar loading.

Original Figure 3[4].
Some conclusions were drawn from this work: Ion species in the MEA-CO$_2$-H$_2$O system were studied qualitatively and quantitatively by NMR spectroscopy. As the acidity increased upon CO$_2$ absorption, the MEA / MEAH$^+$ peaks were shifted downfield (chemical shift decrease), whereas the carbamate peaks were shifted upfield in the $^1$H NMR spectra. In contrast, in the $^{13}$C NMR spectra, the peaks of MEA / MEAH$^+$ were shifted upfield (chemical shift increase), but the carbamate peaks remained unchanged. The ratio of amine species was based only on the $^1$H NMR peak areas and, therefore, was not affected by the error in the calibration. The ratio of amine species was tested by calculating the $^1$H NMR peak integration ratio and the pH value of the solution. The VLE model was modified with the NMR results.

2.3.2 Novel amine synthesis and NMR identification

Synthesis and development of novel amine are the advantages of ITC group in CO$_2$ capture. During the past several years, the group has designed several novel amines and also succeeded in synthesizing some. For instance, DEAB (4-Diethylamino-2-butanol) was developed as a novel tertiary amine for CO$_2$ absorption. It reacts with CO$_2$ as MDEA chemically, but DEAB is more effective, with quick absorption, large cyclic capacity, and lower regeneration energy. Several papers have been published on the physical properties, reaction kinetics, mass transfer, and other aspects of this amine. [13-15]

Meanwhile, NMR techniques were applied to identify and verify the structure of DEAB. Figure 1.2 displays the molecular structure and $^1$H and $^{13}$C NMR spectra.
The $^{13}$C spectra of DEAB was very important for our NMR analysis from Chapter 4-6.[5]

2.3.3 NMR analysis of MEA-MeOH-CO$_2$-H$_2$O:

In 2009, some initial work was performed on the NMR analysis of ion speciation of MEA-MeOH-CO$_2$-H$_2$O.[12] When methanol was mixed with water soluble MEA systems, the liquid mass transfer flow rate increased. This system required NMR analysis of ion speciation. Moreover, Usubharatana has performed some basic experiments in Fig. 2.4 and 2.5. [12] The 1D NMR analysis of the MEA-MeOH-CO$_2$-H$_2$O system was very close to that of the MEA-CO$_2$-H$_2$O solution. The detailed interactions of MEA with MeOH remain unknown, since the 1D NMR spectra had technical limitations (unable to establish the relationship of $^1$H and $^{13}$C peaks within one molecule).
Fig. 2.4 Chemical shift of the peaks of the $^{13}$C spectra for MEA/MEAH$^+$ at 27°C. “S1 and S2” represents δ1 and δ2 of two $^{13}$C peaks of MEA, HO-CH$_2$ and –CH$_2$-NH$_2$

Original Figure 7.3 from reference[12]:

46
Fig. 2.5 Particular species concentrations for sample of 5M MEA at 27°C

Reference [12]
2.4 NMR analysis of amine-CO$_2$-H$_2$O systems for other purposes.

Beyond analysis of VLE models, NMR has been applied to testing amine systems for other purposes, including qualitative determination, carbamate stability analysis, and kinetics analysis as well.

In 2003, Ermatchkov et al. performed simple $^1$H NMR on the ion speciation of PZ-CO$_2$-D$_2$O systems for the purpose of calculation of equilibrium constant $K$ of formation of carbamates from PZ. [17] They tried the $^1$H NMR to achieve that. From the $^1$H NMR spectra, only limited data were obtained, At 333.15K, they can only get the PZDCOO$^-$/PZD$_2^+$COO$^-$, PZ(COO$^-$)$_2$ and PZD$_2$/PZD$_3^{3+}$/PZD$_4^{2+}$ only three type of concentrations, due to the fast proton exchange phenomena. They cannot test the exact ion concentration of each species. Finally, they just predicted the ion speciation plot based on thermodynamic equilibrium constant evaluation. [17] Moreover, the $^1$H NMR spectra only is not enough, the $^{13}$C NMR should be applied into the systems.

In 2007, Hartono et al performed qualitative determination of ion species in DETA (diethylenetriamine)-H$_2$O-CO$_2$ system with $^{13}$C NMR Spectra. [18] This work applied $^{13}$C NMR for functional group identification. Since DETA contains three N atoms in the molecule, which can react with CO$_2$ in three different ways, and the ratio of DETA interaction with CO$_2$ was not narrowed to a regular amine-CO$_2$ reaction stoichiometric ratio of 1:1, either, because the DETA contains more than one NH$_2$ functional groups, it can react with CO$_2$ at stoichiometric ratio of 1:1, 1:2 or even 1:3 theoretically. Thus, there are 18 potential DETA-CO$_2$ species in the
system. Figure 2.10 demonstrates these species. Therefore, the group performed $^{13}$C
NMR analysis of this complicated systems to identify the existence of these potential products. After a detailed analysis of the carbamate groups and bicarbonate/carbonate peaks, the results indicated that carbamate, dicarbamate, and $\text{HCO}_3^- / \text{CO}_3^{2-}$ species are the main species formed in the system. No clear indication was found of a tricarbamate species or of free $\text{CO}_2$. 

**Fig. 2.6** Potential DETA species in DETA-H$_2$O-CO$_2$ system: p, primary amine; s, secondary amine; pp, two primary amines; ps, primary and secondary amines.

Original Figure 1.

from reference:

In 2009, Yang et al performed a quantitative $^{13}$C NMR analysis of CO$_2$ reaction with amines. [19] Amines, bicarbonate, carbamate and the time-resolved total amount of CO$_2$ were drawn. Figure 2.11 indicated results for aqueous amine in both absorption and desorption conditions. Note that in terms of the chemical equilibrium of the VLE models and ion speciations, they focused on chemical kinetics with the time-resolved CO$_2$ absorption amount at 40°C. With the NMR method, they applied the integration of $^{13}$C peaks and correlated the area to the exact amount of their results. Moreover, they tested MEA, MMEA, MDEA, AMP, and PZ under both absorption and desorption conditions (40 and 120°C respectively) and also used the exact time-resolved amount of bicarbonate and carbamate. This paper mainly introduced a novel quantitative method of CO$_2$ absorption kinetics. Researchers can draw the rate laws of proper reactions easily with this group's time-resolved products.

In the same year, Conway et al. performed other kinetics study and mechanism of carbamate formation of CO$_2$-MEA species.[20a,b] Their result focused on the kinetics study of CO$_2$ react with MEA, and $^1$H NMR analysis was just an aid for two sets of analysis: 1) chemical equilibrium studies where different ion concentrations of MEA, carbonate and acid were mixed;[20b] 2) Kinetic studies were performed by rapidly mixing different amounts of MEA, carbonate and HCl and the establishment of the equilibrium was followed by taking NMR spectra at 1-2 minute intervals.[20a,b] Their $^1$H NMR did not provide enough data for the specific ion concentration. For instance the $^1$H NMR can only analyze the MEAH+/MEA
and carbamate species, it cannot estimate the concentration of bicarbonate/carbonate, which are analyzed by $^{13}$C NMR. $^1$H NMR spectra cannot provide the exact concentration of MEA and MEAH$^+$, either.

**Fig. 2.7** Absorption of CO$_2$ with MEA (4M and 2M) at room temperature and 40°C

a) 4M at room temp, b) 2M at room temp, c) 4M at 40°C, d) 2M at 40°C.

Original Figure 3. From Reference below:

In 2011, Yang et al applied the same method of 13C NMR analysis of CO\(_2\) reaction with mixed amine (MEA + MMEA, MEA + PZ, MEA + MDEA, MMEA + PZ, MDEA + PZ).[21] They determine the time-resolved ion speciation in mixtures in two different amines again. The time-dependent major ions such as carbamate, bicarbonate, and 1st and 2nd amine carbamate of PZ were published. These results can be a useful database of kinetics of CO\(_2\) -mixed amine interactions. They made the discovery that primary and secondary amines can compete with each other for a limited amount of CO\(_2\) but then rapidly equilibrate, most likely via a rapid exchange reaction between carbamate and free amine. Tertiary amines such as MDEA cannot reach equilibrium rapidly via this mechanism since the reaction velocity of CO\(_2\)-MDEA was slow.

In the same year, Corway et al. [20c] performed similar reaction kinetics study for CO\(_2\) and HCO\(_3^−\) with MEA interactions; similar to previous work [24a,b], what they emphasized is carbamate formation. The kinetics they study is the carbamate exchange reactions and overall CO\(_2\)-MEA reactions. Their work focused mostly on the kinetics analysis, the \(^1\)H NMR spectra was an aid to test the carbamate formation. The operation temperature was 25.0°C with 0.05 M MEA and 0.1 M HCO\(_3^−\) at high PH value. They perform \(^1\)H NMR analysis of the solution at predetermined time interval after the reaction to detect kinetics data and also for carbamate formation constant.

In 2011, Ciftja et al. performed \(^{13}\)C NMR spectroscopy on the carbamate stability of AMP-CO\(_2\)-H\(_2\)O systems. [22] This group applied the same VLE model
methodology for amine-CO$_2$-H$_2$O systems, but they did not generate the ion speciation plot. A table of ion species was generated for carbamate stability constant calculation, and this work can be considered as derivative research of the VLE model. AMP is a sterically-hindered primary amine, which can react with CO$_2$ and generate carbamate, but this carbamate is very unstable with the existence of bicarbonate. The strong competition of carbamate and bicarbonate/carbonate was the research focus. In their experiments, by increasing the loading from 0 to 0.62, the relative intensity of the carbamate peaks increased. The effects of protonated AMP and carbamate formation upon increasing the amount of CO$_2$ in the system were demonstrated. Based on the mole fractions of AMPCO$_2^-$, HCO$_3^-$ and AMP, the stability constant and were calculated and the data were plotted.
2.5 Summary and Related developments

2.5.1 Summary

This chapter reviewed most of the research of solvent chemistry of CO$_2$ capture: NMR analysis of CO$_2$-amine interaction. Most research groups focused on the NMR analysis of a variety of amine-CO$_2$-H$_2$O systems to detect the exact ion speciation of the complex systems and generate VLE models. Moreover, some basic NMR analyses were applied for novel amine structure identification and verification from ITC.[23]

Some other research works focused on carbamate product identification, carbamate stability analysis and time-resolved CO$_2$-amine kinetics studies, among others. These works are also important and interesting in field of solvent chemistry and will exploit more applications of NMR analysis of amine-CO$_2$ interactions. Especially for the NMR analysis for CO$_2$-Amine-H$_2$O kinetics study, it will be a very useful method to test the time-resolved ion concentrations for both amines and bicarbonate/carbonate.

2.5.2 Related researches within the thesis

The ternary amine DEAB-CO$_2$-H$_2$O will be tested for VLE model in Chapter 4. The solutions of MEA-DEAB-CO$_2$-H$_2$O will be tested as a start of “quaternary systems” (four-role systems) with both NMR analysis methods in Chapter 5 at room temperature, in Chapter 6 at higher temperature. For the complicated quaternary amine A-amine B-CO$_2$-H$_2$O systems, many detailed preparation has to be made to perform experiment carefully, [101] Some 2D NMR analysis has been
performed on the systems and will be emphasized in the VLE models of the more complicated amine A-amine B-CO$_2$-H$_2$O systems in Chapter 6. The relationship for the $^1$H and $^{13}$C for the complex solution will be both the challenge and research interest in the field.

**Executive Summary of VLE models of amines**

- The NMR analysis of Amine-CO$_2$-H$_2$O system of VLE model was very useful for the solvent chemistry as a database as an aid to kinetics analysis. This chapter mainly focused on the equilibrium of the system: VLE and reaction equilibrium, which can be applied for selection of amine as CO$_2$ absorbent and database for kinetics study. The ion concentrations of major components in reaction scheme is the main research interest.

- In the late 1980’s researcher had managed to plotted the ion speciation plot with simulative model as e-NRTL. Later on, during the past 15 years, researchers have managed to develop very useful experimental approach to test the ion concentrations of the systems from NMR spectra. To establish the relationship of chemical shift $\delta$ with ion concentration C is the key for the experiments.

- In ITC groups, a standard flowchart of experimental procedure of NMR analysis was generated. The conventional method is combination of pH meter with NMR analysis of MEA and DEAB. ITC has generated a standard flow chart for the researchers in the field.

- Some other works which applied NMR analysis for other tests of the carbamate stability and CO$_2$-Amine kinetics interaction were also very useful. They can
be the connection for part 5(a) and other section part 5(b) of the review series.

2.6 Available brief review of catalytic Solvent regeneration

Solvent regeneration studies have not been a major research topic until 2000. Most conventional regeneration studies involved pilot plant studies, which require an integrated chemical process. A recent review was published about the pilot plant operation of PCC capture technology. [24]

According to literature, the conventional methods to reduce heat duty of the amine scrubbing process are either from solvent improvement or from process improvement [25]. However, even with such improvements, the heat duty was still high. The heat duty reduction has been a major research challenge in the field [25]. The details of solvent improvements onto the regeneration pilot plant are discussed in chapter 7.1. We have also performed similar process studies, it turned out the blended amine solutions require less heat than single amines (Fig 1.1).

For catalytic solvent regeneration or CO₂ stripping processes, the idea of catalysts application into conventional CO₂ pilot plant was not developed until 2007, and it was developed within ITC only. A recent patent in our group was disclosed in 2011, which included adding solid catalysts into both the absorption and regeneration columns. [26] The idea of solid catalysts and catalysis to facilitate carbamate breakdown was clearly introduced therein. There is a common rule in catalytic CO₂ capture processes, which is emphasized here. Since CO₂ is an acidic gas, basic catalysts can facilitate absorption and acid catalysts can facilitate regeneration based on acid-base theory. A solid base catalyst should be selected
for the CO₂ absorption process, and a solid acid catalyst should be selected for the solvent regeneration or CO₂ stripping process. Therefore, the selection criterion of catalysts of solvent regeneration is solid acid, either Lewis acid or Brønsted acid. In this research, Al₂O₃ was selected as a typical Lewis acid and H-ZSM-5 was selected as a typical proton donor / Brønsted acid. (Chapter 7)

2.7 References


7b. Mani F, Perunizzi M, Stopioni P. CO₂ absorption by aqueous NH₃ solutions:


24. Gelowitz, D, Supap, T., Abdulaziz, N., Sema, T., Idem, R. Tontiwachwuthikul,


101. Online liquid NMR manual: www.chtf.stuba.sk/cl/seminar/VnmrJLiquids.pdf. The details of T1 relaxation times (or “relaxation delay”) can be referred to Chapter 5: Data acquisition, Page 68-71. The 2D NMR techniques can be referred to Chapter 10: Multidimensional NMR, Page 171-200.
Chapter 3: General Experimental Section

3.1 NMR experiments (Chapter 4 - 6)

3.1.1 Materials and Chemicals

A novel tertiary amine, 4-(diethylamino)-2-butanol (DEAB), was synthesized in the laboratory at the International Test Centre for CO₂ Capture (ITC) using the method described in Tontiwachwuthikul et al. (2008). Briefly, the organic synthesis was performed by blending methyl vinyl ketone and diethylamine by addition of NaBH₄. After hours of synthesis, the ether or concentrate was removed. The regular distillation was performed to remove water and vacuum distillation were applied to obtain DEAB products. Finally, DEAB with a purity of 95% was produced for the experiments. The molecular identity of DEAB is shown in Figure 1.2.

MEA, with a purity of 99%, was supplied from Sigma Aldrich. CO₂, with a purity of 99.9%, was supplied from Praxair Inc., Canada. D₂O was used for the signal lock for ¹³C NMR spectroscopy. The pH values were recorded using a pH meter (Accumet AB 15 m) standardized with pH 4, 7, and 10 buffer solutions for both Ka constant detection and NMR analysis. The standard hydrochloric acid (HCl) 1.0 M solution and NaHCO₃ and Na₂CO₃ (Sigma-Aldrich Co., Canada), with purities of 99.9%, were used for titration and NMR reference analysis.

Aqueous solutions of MEA, DEAB had to be prepared and the exact amount (mass) of MEA/DEAB and water needed to be calculated. Then, the volume of
amine and water could be calculated with the density available. Solutions can be prepared after the volumes of amine and water were prepared with a cylinder. The concentration of MEA is close to 5M and that of DEAB varies from 0.5-2.0 mol/L.

3.1.2 NMR instruments

Two types of NMR instruments were used for the analysis, a model Varian Mercury 500 MHz NMR spectrometer and a 300MHz NMR spectrometer. The NMR results in Chapter 4 were tested with a 500 MHz instrument at ITC, and the results from Chapters 5 and 6 were tested with a 300 MHz instrument from the Department of Chemistry, University of Regina.

A variety of Amine-CO$_2$-H$_2$O systems with various CO$_2$ loadings (0-0.8 mol CO$_2$/mol amine) and concentrations were carefully prepared in NMR tubes. The $^{13}$C NMR spectroscopy was recorded with a sample mixed with drops of D$_2$O 10% as the signal lock, using either the Varian Mercury 500 MHz or 300 MHz NMR spectrometer to test the samples within different temperature regions.

Most of the NMR analyses were performed with 1D $^{13}$C NMR techniques, with peak detection and sometimes with peak area integration. A small part of the 2D NMR analysis was performed onto the blended MEA-DEAB-CO$_2$-H$_2$O solution, with two 2D models, Correlation Spectroscopy (COSY) and Heteronuclear Multiple Quantum Correlation (HMQC), respectively.

3.1.3 CO$_2$ loading Tests of samples

The CO$_2$ loading tests were performed with a Chittick apparatus under
standard operating conditions. The CO$_2$ loading is the x axis of the ion speciation plot, which represents the conditions of the solution; small loading refer to “lean” solutions and large loading refer to “rich” solutions. The loading tests are performed in a standard Chittick apparatus. When 2ml amine solutions are pipetted into a 250 mL flask, 10 ml distilled water is added to dilute the sample, and 3-4 drops of methyl orange is added as indicator. The color of the sample is orange.

Then the flask, with solution, is properly sealed with a rubber cock which is connected to the chittick apparatus which is properly adjusted. The 1M HCl standard solution is applied to the titrate amine solution in the flask. The titration is run until the colour of the solution turns pink/red, which indicates the end point. After the volume of HCl is recorded as $V_{HCl}$, the same amount of HCl is added to the flask to thoroughly remove CO$_2$. The volume of gas was recorded as $V_{CO_2}$. Therefore, the concentration and CO$_2$ loading of amine can be calculated accurately:

$$C_{amine} = C_{HCl} \times \frac{V_{HCl}}{2} = 0.5 \ V_{HCl} \ (mol / L) \ (3.1)$$

$$\text{Loading } \alpha = \frac{V_{CO_2} - 2 \times V_{HCl}}{24.45 \times V_{HCl}} \ (mol \ CO_2 / mol \ amine) \ (3.2)$$

3.1.4 General NMR analysis procedures (1-6)

A large number of NMR experiments were performed on the single blended amine solutions within Chapters 4-6. The experiments are briefly discussed here; the detailed procedures can be referred to in each chapter.

1. Amine-CO$_2$-H$_2$O sample preparation:
After the amine solution is prepared at a specific concentration in a beaker, CO₂ is introduced into the solutions for 30-60 seconds. Then, the water soluble system is converted from a binary system (Amine-H₂O) into a ternary system (Amine-CO₂-H₂O) under specific loadings (Step 1).

2. The conventional pH + NMR method:

A pH meter is placed in the beaker to test the pH value of the solution (Step 2). Then, another 2 mL solution is pipetted and collected into another flask for the CO₂ loading test (Step 3). Approximately 500 μL of solution is pipetted and collected into an NMR tube, and 10% of the D₂O is added into the NMR tube to lock the signal (Step 4). Finally, the CO₂ loading test is performed for 2 ml of sample prepared in Step 2 with a standard Chittick apparatus (Step5).

Then, the procedures for Steps 1-5 are repeated 7-8 times. When additional CO₂ is introduced into the beaker, the new pH value needs to be tested; new samples need to be collected into NMR tubes and pipetted and tested for CO₂ loading. The amine samples possess different CO₂ loadings, from lean to rich, because extra CO₂ is introduced into the solution every round.

The ¹³C NMR tests are initiated after 7-8 NMR tubes are prepared with 10% D₂O added into each NMR tube. The D₂O is required to lock the signal of the amine solution, and even though the exact ion concentrations are diluted in the NMR tube, the relative ratio of ions is the same. The ratios can aide accurate detection of the ions of original amine solutions, via the data acquisition method.
described in the following section.

**3. Basic data acquisition:**

Useful data can be obtained from the experimental procedures. Detailed equations for data acquisition of different amines are described in Section 5.2.4 for experiments at room temperature and Section 6.2.2 for experiments at higher temperatures, respectively. Even though they are discussed in two chapters, the methods are similar and consistent with different parameters for different operational temperatures.

The ratio of AmineH\(^+\) to amine can be estimated with the pH value + equilibrium constant. The CO\(_2\) loading of each sample can be tested, and the ratio of carbamate to the sum of bicarbonate + carbonate and the ratio of bicarbonate to carbonate are obtained with NMR analysis. The ion concentrations of the major 7 components (MEAH\(^+\) / MEA, DEABH\(^+\) / DEAB, HCO\(_3\)\(^-\) / CO\(_3\)\(^2-\), and Carbamate) in the solution are accurately calculated with the ratios (AmineH\(^+\) / Amine, HCO\(_3\)\(^-\) / CO\(_3\)\(^2-\), and Carbamate / [HCO\(_3\)\(^-\) + CO\(_3\)\(^2-\)])). Thus, the tables and figures of ion speciation for a VLE model are generated as a useful database for this research.

**4. The novel NMR calibration method**

**4.1 Calibration sample preparation and collection:**

In this research, standard MEA and DEAB solutions are selected for calibration before the NMR test for the prepared amine-CO\(_2\)-H\(_2\)O system. First, the standard MEA / DEAB solution (5.0 M MEA and 1.0 M) is prepared separately, and 2 ml and 10 ml of solution are pipetted into a beaker and diluted to
20 ml. Then, a standard titration is performed with HCl to detect the end point. Approximately 10 ml of HCl is consumed by the system, and the exact amount of HCl is recorded as V1.

Secondly, another 2 ml of solution is pipetted and diluted into 50 ml. Then, 300-500μL of solution is collected into NMR tube #1, after which the HCl is titrated slowly into the dilute amine solution again. For every 20% of V1, HCl titration is completed and 300-500μL of solution is collected in the NMR tubes. This procedure is repeated several times.

Finally, 7 NMR tubes, with various protonation ratios at 0, 20%, 40%, 60%, 80%, 100%, and 120% are prepared at room temperature for the \(^{13}\text{C}\) NMR analysis to generate calibration curves for both amine systems.

4.2 Calibrations curves generation and selection of \(^{13}\text{C}\) peaks:

\(\text{D}_2\text{O} (10\%)\) is added to the NMR tubes of the 7 samples, and then, the \(^{13}\text{C}\) NMR test is performed on each sample. The NMR samples were tested with NMR instruments, where the instrument holds the operation temperatures at constant values, stabilized at 24, 40, 50, 60, and 70°C. The chemical shifts of the carbons were not the same but were shifted slightly in a regulated trend for the amines with different protonation ratios. Therefore, the relationship between the chemical shift (\(\delta\)) and protonation ratio (\(x\)) is directly established. Thus, several calibration curves (\(\delta\) vs \(x\)) are generated, but only the lines with \(R^2 > 0.99\) are selected as a qualified calibration curve because of a strict condition: higher accuracy.

One curve is selected (\(C_2\)) for MEA and 2 to 3 curves are selected (\(C_1, C_3,\)
and C₆) for DEAB. The equations are grouped in Table 6.1.2 as an important database from 24-70°C. The ion concentrations for the amineH⁺/amine can be calculated directly from calibration equations for samples for MEA or DEAB solution. Moreover, the protonation ratio of H⁺/Amine needs to be very accurate in the titration, but the concentration of the amine solution does not have to be the same as the calibration curve because the protonation “ratios” of the calibration curve are applicable for most amines with different concentrations. In this research, the calibration curve is valid for the MEA solution (0-5.0M), DEAB solution (0-2.0 M), and blended amine systems from 24 to 70°C.

5. NMR analysis with peak positions and area integration

Steps 1-5 in section 3.1.3 are mostly required to prepare amine-CO₂-H₂O samples, except the pH test (Step 2). After Steps 1, 3, 4, and 5 are repeated 7-8 times, 8 NMR samples are collected for the NMR analysis.

The ¹³C NMR is performed with specific temperatures with the NMR samples of the amine-CO₂-H₂O systems. The tests were performed at 24.5°C for the single amine solutions of DEAB, they are performed at 24.0°C for the MEA-DEAB mixture and the higher temperature tests are performed at 40, 50, 60, and 70°C. Special treatment is required on the NMR tube for the NMR tests under higher temperatures. Paraffin is applied to seal the cap of the NMR tube for higher temperature tests to avoid CO₂ leakage.

The ¹³C NMR tests for peak positions are performed for 64 scans, but for the area integration, some parameters need to be reset to avoid the NOE (nuclear
overhauser effect) where the decoupling is off, and 256 scans are needed to achieve high accuracy for the ratios of area integration. The processing of 64 scans takes 0.5-1 minute, and that of 256 scans take approximately 10 minutes.

6. 2D NMR analysis

Only a few 2D NMR analyses are performed on the blended amine system MEA-DEAB-CO₂-H₂O beyond the 1D NMR tests for most experiments in this research. ¹³C vs. ¹H was plotted with Heteronuclear Multiple Quantum Correlation (HMHCQ) and ¹H vs. ¹H with COSY methods.

3.2 Solvent regeneration tests/ CO₂ stripping (Chapter 7)

3.2.1 Amine Solution preparation and catalyst selection

Three different amine solutions were prepared for the regeneration process. Two liters of MEA (5M), MEA-MDEA (5M/1.25M), and MEA-DEAB (5M/1.25) solutions were prepared with the same method as in Section 3.1.1, except the quantity of amine was large, which required synthesis of large amounts of DEAB.

The catalyst of Al₂O₃ beads (3 mm diameter) are commercially available, which is usually applied as a catalyst support. The pelletized catalyst H-ZSM-5 (1-2 mm diameter) was purchased from Zeo-Chem. About 100 g of each catalyst were needed.

3.2.2 Experimental equipment and procedures for solvent regeneration

The amine regeneration was performed under a typical recirculation apparatus (reflux-condenser) for organic chemistry. Two liters of rich amine solutions were stored in 5 L flasks and heated to 90-95°C under continuous
stirring. The catalysts were weighed and placed in the solution. The weight of catalysts vs. the weight of solutions is approximately 1/40. The condenser is placed on the top of the flask to allow the exit of CO\textsubscript{2} but to retain the steam. The start time is the moment at which the temperature reached 90ºC. The CO\textsubscript{2} loading test was performed at 2, 6, and 9 hours of regeneration. Two millimeters of solution were pipetted, and the loading was tested with a Chittick apparatus each time. The detailed procedures are discussed in Chapter 6.2.1.
Chapter 4  1D NMR Analysis of DEAB-CO$_2$-H$_2$O Solution

4.1 Introduction

At present, carbon dioxide (CO$_2$) capture process has become a major consideration in order to mitigate the global warming and climate change problems caused by CO$_2$ emissions. The technology that applies a proper amine solution as an absorbent has been studied for decades. Recently, the novel amine, 4-(diethylamine)-2-butanol (DEAB), has been developed and synthesized at International Test Centre for CO$_2$ Capture (ITC) for use in CO$_2$ capture processes.[1-3] It was found that DEAB, which is considered as a tertiary amine since it has three carbon atoms attached to the nitrogen atom, has very high CO$_2$ absorption capacity. The absorption capacity of DEAB is competitive with piperazine (PZ) and higher than that of 2-amino-2-methyl-1-propanol (AMP), methyl diethanolamine (MDEA), monoethanolamine (MEA), and diethanolamine (DEA).[2,3] Also, it has been found that the regeneration energy of DEAB is lower than that of MDEA, DEA, and MEA, respectively.[2] Regarding to these outstanding performance characteristics, DEAB is now being considered as a promising alternative solvent for capturing CO$_2$. However, the exact ion speciation of DEAB-CO$_2$-H$_2$O system is required to comprehensively understand the CO$_2$ absorption and kinetics behaviour. The ion concentrations of major cations and anions in the DEAB-CO$_2$-H$_2$O system, such as free DEAB, protonated DEAB (DEABH$^+$), bicarbonate (HCO$_3^-$), and carbonate (CO$_3^{2-}$), need to be determined.
Numbers of NMR analysis have been performed on the vapour-liquid equilibrium (VLE) model in CO₂ absorption process studies within amine-CO₂-H₂O systems[4-7], as well as H₂O-CO₂ systems.[8] Reliable estimation of liquid phase composition plays a key role in the VLE model; however, useful information on particular species concentrations is difficult to detect by traditional phase equilibrium measurements for the activity coefficient models.[4] NMR experiments can provide detailed information about the liquid phase composition that serves this purpose. In the conventional method of combining pH measurement and ¹³C NMR analysis, the concentrations of amine and protonated amine were calculated using the measured pH value (from pH meter) and the dissociation constant of protonated amine, while the concentrations of HCO₃⁻ and CO₃²⁻ can be determined based on ¹³C NMR analysis. On the other hand, in the novel ¹³C NMR calibration technique developed in the present work, the concentrations of all major species (i.e., amine, protonated amine, HCO₃⁻, and CO₃²⁻) can be determined based on ¹³C NMR analysis alone.

In the present work, the dissociation constant of protonated DEAB (DEABH⁺) were determined by titration technique. In addition, the ion speciation results obtained from the newly developed methodology were then compared with those obtained from the method of combining pH measurement and NMR analysis, which is the conventional method as was done in the literature.[4-7]
4.2 Some Properties of Novel Amine DEAB

4.2.1 DEAB and chemical reaction schemes

Novel tertiary amine, DEAB, was synthesized in the solvent synthesis laboratory at ITC with method described in Tontiwachwuthikul et al.[1] The structure of DEAB is shown in Fig. 4.1. Aqueous solutions of DEAB were prepared by adding distilled water to the desired concentration.

Since DEAB is considered as a tertiary amine, thus, it does not react directly with CO$_2$ but it acts as a base that catalyzes the hydration of CO$_2$. The major chemical reactions within DEAB-CO$_2$-H$_2$O systems are listed in reactions 4.1–4.4. All the cations and anions as well as the neutral compound free DEAB and CO$_2$ loading can be determined with proper experiments. The concentration of free DEAB and DEABH$^+$ can be determined by (i) DEABH$^+$ dissociation constant K together with pH value analysis (conventional method) and (ii) $^{13}$C NMR peaks calibration (novel method developed in this work). Meanwhile, the CO$_2$ loading can be measured by titration with Chittick CO$_2$ analyzer with the reverse of reaction 4.3.[5,9] The construction of the apparatus and the measurement procedure of CO$_2$ loading can be found in the literature.[9] Also, the experimental equipment and procedure have been validated with conventional amines (i.e., MEA, DEA, MDEA, and AMP) in our previous work.[2] The concentration of bicarbonate and carbonate are measured by $^{13}$C NMR analysis from reactions 4.3 and 4.4.[6]
Fig. 4.1 Molecular structure of DEAB 4-(diethylamine)-2-butanol, C₈H₁₈ON.
Basic reaction scheme in DEAB-CO$_2$-H$_2$O systems can be expressed as:

\[
\text{CO}_2 + \text{H}_2\text{O} + \text{DEAB} \leftrightarrow \text{HCO}_3^- + \text{DEABH}^+ \quad (4.1)
\]
\[
\text{DEAB} + \text{H}^+ \leftrightarrow \text{DEABH}^+ \quad (4.2)
\]
\[
\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 \leftrightarrow \text{H}^+ + \text{HCO}_3^- \quad (4.3)
\]
\[
\text{HCO}_3^- \leftrightarrow \text{CO}_3^{2^-} + \text{H}^+ \quad (4.4)
\]

### 4.2.2 DEABH$^+$ dissociation constant determination

Since the dissociation constant of DEABH$^+$ in aqueous solution is not available in the literature, the K value should be measured carefully in preparation for the further calculation of DEAB and DEABH$^+$ concentrations using the conventional method. The experimental and calculation procedures for dissociation constant can be found in the work of Kamps and Maurer[10], who studied the dissociation constant of MDEAH$^+$. The titration technique was validated using MEA. In the present work, ln $K_{\text{MEAH}^+}$ at 22°C in are found to be -22.3, while in the literature, it was found to be -23.2 (3.8% deviation). In addition, the titration was repeated several times at similar conditions then the average value was taken. The results showed that the deviation percentage of DEABH$^+$ dissociation constant measurement is 0.4%.

Based on the assumption that the solution is ideal (activity coefficient is 1), DEABH$^+$ dissociation constant K can be calculated using Eq 4.5. The concentration of H$^+$ in the solution can be measured by pH meter. Bearing in mind that the disappearance of H$^+$ during titration is that reacts with DEAB to form DEABH$^+$ as shown in reaction 4.2, thus, the concentration of DEABH$^+$ can then
be calculated using the mass balance of protons as presented in eq 4.6. Lastly, the concentration of free DEAB can be calculated using the DEAB balance equation as shown in eq 4.7.

\[
K_{\text{DEAB}^+} = ([\text{DEAB}] [\text{H}^+]) / ([\text{DEABH}^+] \text{V}_{\text{total}})
\]  

(4.5)

\[
n\text{HCl} - [\text{H}^+] \text{V}_{\text{total}} = [\text{DEABH}^+] \text{V}_{\text{total}}
\]  

(4.6)

\[
([\text{DEAB}] + [\text{DEABH}^+]) \text{V}_{\text{total}} = n_0 \text{DEAB}
\]  

(4.7)

where \(n\text{HCl}\) is number of moles of HCl added during the titration, \(\text{V}_{\text{total}}\) is total liquid volume after titration, and \(n_0 \text{DEAB}\) is initial mole of DEAB, which can be determined by titration with 1.0 M HCl until methyl orange end point.[9]
Table 4.1 Dissociation constant $K_a$ for DEABH$^+$/DEAB solution at 24.5°C

<table>
<thead>
<tr>
<th>HCl amount (ml, 1.0 mol/L)</th>
<th>PH</th>
<th>$[H^+]$ (mol/L)</th>
<th>DEABH$^+$ (mol/L)</th>
<th>DEAB (mol/L)</th>
<th>Keq $^b$</th>
<th>$V_{tot}$ (ml)</th>
<th>ln K</th>
<th>T (°C)</th>
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<tr>
<td>0.0</td>
<td>11.72</td>
<td>1.91E-12</td>
<td>0.0000</td>
<td>0.0455</td>
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<td>24.5</td>
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<td>4.5 $^a$</td>
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<td>0.0007</td>
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<td></td>
<td>105.0</td>
<td></td>
<td>24.5</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ DEABH$^+$ dissociation constant $K_a$ calculation equations (eqs 4.6 and 4.7) are only valid within the ratio of DEAB/DEABH$^+$ of 0.1 to 10.0. The error will be extremely huge under edge conditions (0 and 4.5 ml), where the concentration of DEABH$^+$ or DEAB are near to zero. Therefore, the noise is comparable to scale of signal.

$^b$ The average value were obtained from four pH tests under the same DEAB concentration, which is repeated 4 times with very small errors. Therefore, the constant at room temperature will be $3.9 \times 10^{-11}$, ln K equals to -23.95$^b$. (pH meter used in this study provides 2 significant figures).
For example, from Table 4.1, 100 ml 0.91 M DEAB solution was prepared and titrated carefully until methyl orange end point for nDEAB. Then, 5 ml solution was pi-petted and diluted to 100 ml, and kept at room temperature. This diluted DEAB solution (0.0455 M) was then titrated with 5 ml of 1.0 M HCl standard solution slowly, to proceeding reaction 4.2. The pH meter was placed in the solution containing a magnetic stirrer for measuring the pH value. The pH of the solution was recorded after the addition of every 0.5 ml of 1.0 M HCl solutions. Similar process was repeated 4 times and the average pH value was taken. As mentioned earlier, [H+] was measured by pH meter, [DEABH+] and [DEAB] were calculated using mass balance equations (eqs 4.6 and 4.7). Finally, the dissociation constant K was then calculated using eq 4.5. The same procedure were also applied for determining the dissociation constant K of DEAB at 35 and 45°C.

4.2.3 $^{13}$C NMR analysis of DEAB and HCO$_3^-$ / CO$_3^{2-}$

The DEAB-CO$_2$-H$_2$O systems were prepared at various CO$_2$ loadings (0-0.8 mol CO$_2$/mol amine) and DEAB concentrations (0.52-1.97 M). The $^{13}$C NMR spectroscopy was recorded at 24.5°C, which is regarded as room temperature.

By comparison the $^{13}$C NMR peaks between MDEA and DEAB, it was found that the results are different. This is because the difference in chemical structures of MDEA and DEAB. MDEA exhibits three $^{13}$C NMR peaks at $\delta$=58.7-59.8 ppm (-CH$_2$-OH); $\delta$=57.3-59.6 ppm (-CH$_2$-N<), and $\delta$=41.7-42.7 ppm (CH$_3$-N<). However, DEAB exhibits six $^{13}$C NMR peaks for C$_1$-C$_6$ (as marked in Figure 2.2) at 10.2, 22.3, 33.9, 46.3, 48.56, 67.2 ppm, respectively.
Fig. 4.2: Protonated DEAB with its specific 6 carbon groups, these carbons are labelled in specific $^{13}$C chemical shift order from shielded region to deshielded region (low to high).
Due to the fast proton transfer reactions of eqs 4.2 and 4.4, it is impossible to distinguish between HCO$_3^-$/CO$_3^{2-}$, and between DEABH$^+$/DEAB in the NMR spectra. The $^{13}$C chemical shift of these proton exchanging species are represented by one common peak for HCO$_3^-$/CO$_3^{2-}$ and six common peaks for DEABH$^+$/DEAB. The chemical shift of Na$_2$CO$_3$ and NaHCO$_3$ solutions at 24.5°C (observed in this work) were detected at 160.716 and 168.467 ppm, respectively, which are very close to the results observed in Holmes et al.,[6] (which are 160.33 and 168.09 ppm, respectively at 25.0°C). From multiple sets of reference results of HCO$_3^-$/CO$_3^{2-}$ in Table 4.2, the trends are clear and matched well with the conclusion mentioned by Holmes et al.,[6] that the NMR peaks of pure HCO$_3^-$ and CO$_3^{2-}$ shift to the shielded region (chemical shift decreases) as temperature increases. Conversely, the NMR peaks shift to the larger chemical shift as temperature decreases.[6] The chemical shift of HCO$_3^-$/CO$_3^{2-}$ observed in this work (at 24.5°C) is 0.23% higher than that from the work of Holmes et al.,[6] (at 25.0°C). This matches well with the temperature deviation of 0.17%. Even though, there is no reference point for the size of the deviations and the magnitude of the temperature correction, the deviation of 0.23% different from the work of Holmes et al.,[6] is considered to be very small (the deviation causes by the different in temperature of 0.17%). Therefore, the sets of NMR data collected in this work are considered to be very accurate.
Table 4.2 $^{13}$C NMR chemical shift $\delta$ (ppm) of $\text{HCO}_3^-$/$\text{CO}_3^{2-}$ and pH of DEAB-$\text{CO}_2$-$\text{H}_2\text{O}$ solutions at various $\text{CO}_2$ loadings and concentrations at 24.5°C

<table>
<thead>
<tr>
<th>Sample #</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{\text{DEAB}} = 0.52$ (mol/L)</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>Loading</td>
<td>0.000</td>
<td>0.052</td>
<td>0.119</td>
<td>0.241</td>
<td>0.359</td>
<td>0.479</td>
<td>0.610</td>
<td>0.720</td>
<td>0.807</td>
</tr>
<tr>
<td>$\delta$ (ppm)</td>
<td>N/A $^a$</td>
<td>166.402</td>
<td>165.293</td>
<td>164.044</td>
<td>162.722</td>
<td>161.693</td>
<td>161.170</td>
<td>160.646</td>
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<tr>
<td>$C_{\text{DEAB}} = 0.98$ (mol/L)</td>
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<tr>
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<td>0.094</td>
<td>0.179</td>
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<td>0.409</td>
<td>0.545</td>
<td>0.702</td>
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<tr>
<td>$\delta$ (ppm)</td>
<td>167.035</td>
<td>166.581</td>
<td>166.054</td>
<td>165.468</td>
<td>164.751</td>
<td>163.938</td>
<td>162.737</td>
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<tr>
<td>$C_{\text{DEAB}} = 1.5$ (mol/L)</td>
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<td>0.113</td>
<td>0.169</td>
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<td>0.578</td>
<td>0.712</td>
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</tr>
<tr>
<td>$\delta$ (ppm)</td>
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<td>165.758</td>
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<td>163.996</td>
<td>163.337</td>
<td>162.466</td>
<td>161.660</td>
<td>160.957</td>
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<tr>
<td>$C_{\text{DEAB}} = 1.97$ (mol/L)</td>
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<td>$\delta$ (ppm)</td>
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<td>165.183</td>
<td>164.857</td>
<td>164.542</td>
<td>163.960</td>
<td>163.385</td>
<td>162.568</td>
<td>161.876</td>
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<td>$\text{NaHCO}_3$</td>
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<tr>
<td>$\delta$ (ppm)</td>
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<td>ref</td>
<td>160.27 $^b$</td>
<td>160.33 $^c$</td>
<td>161.4 $^d$</td>
<td>161.3 $^e$</td>
<td>161.3 $^e$</td>
<td>161.3 $^e$</td>
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</tr>
<tr>
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<tr>
<td>$\delta$ (ppm)</td>
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<td>ref</td>
<td>167.74</td>
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<td>168.9</td>
<td>169.5</td>
<td>169.5</td>
<td>169.5</td>
<td>169.5</td>
</tr>
</tbody>
</table>

$^a$ concentration of $\text{CO}_2$ was too low to detect from NMR analysis. The concentration of $\text{HCO}_3^-$/$\text{CO}_3^{2-}$ was calculated using charge balance equation (4.11)

$^b$ measured at 27°C.[14]

$^c$ measured at 25°C.[6]

$^d$ measured at 20°C.[4]

$^e$ measured at 32°C[15]. The sample of bicarbonate was mixing with acid and base.

The NMR instrument was not that accurate (10–100 MHz) either. This can be recognized as an exception.
4.2.4 Determination of ion concentration of HCO$_3^-$/CO$_3^{2-}$ and DEABH$^+$/DEAB

As suggested by Holmes et al.[6] the concentration of CO$_3^{2-}$ and HCO$_3^-$ can be calculated using eqs 4.8 and 4.9. The chemical shift of the HCO$_3^-$ and CO$_3^{2-}$ reflects the exact ratio of these two ions. The initial concentration of CO$_2$ ([CO$_2$]$_0$) can be determined using Chittick CO$_2$ analyzer.[9] However, the $^{13}$C NMR peak of HCO$_3^-$/CO$_3^{2-}$ is hardly detected at very low CO$_2$ loading. In this case, the concentration of HCO$_3^-$/CO$_3^{2-}$ can then be calculated using the simplified charge balance equation (eq 4.10), which is simplified from eq 4.11 based on the assumption that the trace amount of H$^+$ and OH$^-$ can be neglected.

$$[\text{CO}_3^{2-}] = \left(\frac{\delta - 160.716}{168.467 - 160.716}\right) \times [\text{CO}_2]_0 \quad (4.8)$$

$$[\text{HCO}_3^-] = \left(\frac{168.467 - \delta}{168.467 - 160.716}\right) \times [\text{CO}_2]_0 \quad (4.9)$$

$$[\text{DEABH}^+] = [\text{HCO}_3^-] + (2[\text{CO}_3^{2-}]) \quad (4.10)$$

$$[\text{DEABH}^+] + [\text{H}^+] = [\text{HCO}_3^-] + (2 \text{ CO}_3^{2-}) + [\text{OH}^-] \quad (4.11)$$

For the conventional method of determining the ion speciation, the pH method is applied in order to calculate the exact AmH$^+$/Am ratio.[4-7] Then, the ion concentration of free DEAB and DEABH$^+$ can be calculated using DEABH$^+$ dissociation constant K and pH value at a certain temperature.

Beyond the conventional method, a novel $^{13}$C NMR analysis methodology was developed based on the fact that the $^{13}$C NMR peaks will shift either upfield or downfield with protonation. Several researchers applied $^{13}$C NMR analysis on amine-CO$_2$-H$_2$O systems as well, but not for VLE models. They test the carbamate stability,[12] and the qualitative determination.[13] Similar to the case
of HCO\textsubscript{3}/CO\textsubscript{3}\textsuperscript{2-}, the chemical shift (position) of \textsuperscript{13}C NMR peaks of DEAB/DEABH\textsuperscript{+} also represent relative amount of initial DEAB and DEABH\textsuperscript{+}. The only difference between DEABH\textsuperscript{+}/DEAB and HCO\textsubscript{3}/CO\textsubscript{3}\textsuperscript{2-} is \textsuperscript{13}C NMR spectra of DEABH\textsuperscript{+}/DEAB exhibits by 6 peaks but that of HCO\textsubscript{3}/CO\textsubscript{3}\textsuperscript{2-} exhibits only 1 peak. The calibration curves of \textsuperscript{13}C NMR spectra of DEABH\textsuperscript{+}/DEAB can be established at various protonation ratios (ratio of initial DEAB concentration and DEABH\textsuperscript{+} concentration). The liquid samples are then examined using \textsuperscript{13}C NMR for the spectra. Thus, the concentrations of DEAB and DEABH\textsuperscript{+} can be calculated based on the developed NMR calibration curves. Therefore, in the case of novel \textsuperscript{13}C NMR calibration method, the pH test and acid dissociation constant Ka do not needed.

4.3 Results and Discussion

4.3.1 DEABH\textsuperscript{+} dissociation constant analysis using pH meter

The pH values (each value is averaged from four pH tests) of DEAB solution titrated with HCl solution at 24.5°C are listed in Table 4.1. The DEABH\textsuperscript{+} dissociation constant K values were calculated from Eqs 4.5 to 4.7. For example, at 24.5°C, the DEABH\textsuperscript{+} dissociation constant K for the 0.5 to 4.0 ml were taken into consideration, with the average value of 3.9\times10\textsuperscript{-11} mol/L (\text{ln} K_{\text{DEABH+}} = -23.96) (The subscript of 4 in -3.94\times10\textsuperscript{-11} mol/L was done in order to note the two significant digits obtained from pH measurement using the pH meter. This notation was made to ensure all the data were considered accurate and reliable). This value is higher than that of MEAH\textsuperscript{+} (\text{ln} K_{\text{MEAH+}} = -25.62 at 24.5 °C)[11] but lower than
that of MDEAH$^+$ (ln $K_{\text{MDEAH}^+}$ = -23.73 at 24.5°C).[4,10] This result indicated that the binding energy of DEAB with protons is smaller than that of MEA but higher than that of MDEA. The same method was applied for DEAB at 35 and 45°C. The DEABH$^+$ dissociation constant $K$ value was found to be $4.50 \times 10^{-11}$ mol/L (ln $K$ = -23.82) and $7.80 \times 10^{-11}$ mol/L (ln $K$ = -23.27), respectively;

Then, the predictive correlation of the DEABH$^+$ dissociation constant $K$ can be established as: ln $K_{\text{DEABH}^+}$ = -13.46 – 3147.5/T(K) with $R^2$ = 0.87, valid within temperature range of 24.5 to 45°C.

4.3.2. $^{13}$C NMR results and pH value of the DEAB-CO$_2$-H$_2$O systems

Table 4.2 demonstrates the exact chemical shift of HCO$_3^-$/CO$_3^{2-}$ of the DEAB-CO$_2$-H$_2$O system at various CO$_2$ loadings (0-0.8 mol CO$_2$/mol amine) and DEAB concentrations. In total, 36 samples with four different DEAB concentrations (i.e., 0.52, 0.98, 1.5, and 1.97 M) were tested. The pH test was also performed at DEAB concentrations of 1.50 and 1.97 M in order to generate ion speciation plot with conventional pH measurement as reference sets. It was clearly observed from Table 4.2 that for each concentration, along the samples from lean to rich amine solutions, the pH value and the chemical shift of the HCO$_3^-$/CO$_3^{2-}$ ratio decrease as CO$_2$ loading increases. This is plausible since acidic CO$_2$ gas is introduced into basic amine solution, the pH of solution is found to decrease. After CO$_2$ is dissolved in water, it will generate carbonic acid (H$_2$CO$_3$) and then releases protons. At very low loading conditions, the excessive DEAB accepts protons and generates CO$_3^{2-}$, which became one of the major components in the solution. By
increasing CO$_2$ loading, more protons are released, and CO$_3^{2-}$ starts to accept protons and converts to HCO$_3^-$, resulting in an increasing of HCO$_3^-$ component. Therefore, the chemical shift of HCO$_3^-/CO_3^{2-}$ decreased and finally reached to 100% DEABH$^+$ and HCO$_3^-$. 

The data in Table 4.2 show that the pure HCO$_3^-$ and CO$_3^{2-}$ have similar chemical shifts under certain conditions. However, the chemical shift of HCO$_3^-$ and CO$_3^{2-}$ were found to be slightly different from the literature.[4,6,14,15] After a careful analysis, it has been found that the main reason is the operating temperature. The chemical shift of HCO$_3^-$ and CO$_3^{2-}$ are slightly different under different operation temperatures. This is because the chemical shift of HCO$_3^-$ and CO$_3^{2-}$ is directly related to VLE equilibrium constants, which are very sensitive to temperature. For example, the chemical shift of HCO$_3^-$ and CO$_3^{2-}$ obtained in this work at 24.5 °C are 160.712 and 168.467 ppm, respectively. But those observed from Usubharatana[14] at 27.0 °C are 160.27 and 167.74 ppm, respectively. Note that the NMR instruments used in the work of Usubharatana[14] and this work were the same. Therefore, the chemical shift of pure HCO$_3^-$ and CO$_3^{2-}$ (NaHCO$_3$ and Na$_2$CO$_3$ solution) should be tested before the NMR analysis of amine-CO$_2$-H$_2$O system instead of quoting the reference data directly.

**4.3.3. A novel $^{13}$C NMR calibration curve of the DEAB/BEABH$^+$ system**

$^{13}$C NMR analysis of DEABH$^+$/DEAB exhibits 6 peaks. Even though DEAB molecule contains 8 carbon atoms, 6 types of carbons can be observed because of structural symmetry as shown in Figs 4.3.1 and 4.3.2. These 6 carbons were labeled
as \( C_1 \) to \( C_6 \) in numerical order of their \(^{13}\text{C} \) chemical shift from smallest to largest.

The entire chemical shifts at various protonation ratios (ratio of concentrations of added \( \text{H}^+ \) and initial DEAB) of 0:1, 0.2:1, 0.4:1, 0.6:1, 0.8:1, 1:1, and 1.2:1 are recorded and plotted as calibration curves in Table 4.3 and Figure 4.3. The ratio of 1.2:1 was prepared (\( n\text{H}^+: n\text{DEAB} = 1.2 :1 \)) to ensure that the sample was fully protonated.

### Table 4.3 \(^{13}\text{C} \) calibration table of DEAB protonation at 24.5°C

<table>
<thead>
<tr>
<th>( \delta_{\text{DEAB}} ) (ppm)</th>
<th>Mole ratio of ( \text{H}^+ ) and DEAB (( n\text{H}^+: n\text{DEAB} ))</th>
<th>( \Delta \delta ) (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_1 )</td>
<td>10.206</td>
<td>9.902</td>
</tr>
<tr>
<td></td>
<td>9.510</td>
<td>9.107</td>
</tr>
<tr>
<td></td>
<td>8.723</td>
<td>8.435</td>
</tr>
<tr>
<td></td>
<td>8.435</td>
<td>-1.771</td>
</tr>
<tr>
<td>( C_2 )</td>
<td>22.307</td>
<td>22.314</td>
</tr>
<tr>
<td></td>
<td>22.321</td>
<td>22.329</td>
</tr>
<tr>
<td></td>
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<td>47.666</td>
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<tr>
<td></td>
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</table>

The entire chemical shifts at various protonation ratios (ratio of concentrations of added \( \text{H}^+ \) and initial DEAB) of 0:1, 0.2:1, 0.4:1, 0.6:1, 0.8:1, 1:1, and 1.2:1 are recorded and plotted as calibration curves in Table 4.3 and Figure 4.3. The ratio of 1.2:1 was prepared (\( n\text{H}^+: n\text{DEAB} = 1.2 :1 \)) to ensure that the sample was fully protonated.

### Table 4.3 \(^{13}\text{C} \) calibration table of DEAB protonation at 24.5°C

<table>
<thead>
<tr>
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<th>Mole ratio of ( \text{H}^+ ) and DEAB (( n\text{H}^+: n\text{DEAB} ))</th>
<th>( \Delta \delta ) (ppm)</th>
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</thead>
<tbody>
<tr>
<td>( C_1 )</td>
<td>10.206</td>
<td>9.902</td>
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<tr>
<td>( C_2 )</td>
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<td>-1.487</td>
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The entire chemical shifts at various protonation ratios (ratio of concentrations of added \( \text{H}^+ \) and initial DEAB) of 0:1, 0.2:1, 0.4:1, 0.6:1, 0.8:1, 1:1, and 1.2:1 are recorded and plotted as calibration curves in Table 4.3 and Figure 4.3. The ratio of 1.2:1 was prepared (\( n\text{H}^+: n\text{DEAB} = 1.2 :1 \)) to ensure that the sample was fully protonated.

### Table 4.3 \(^{13}\text{C} \) calibration table of DEAB protonation at 24.5°C

<table>
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<tr>
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<td>0.044</td>
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<tr>
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<td>( C_5 )</td>
<td>48.563</td>
<td>48.680</td>
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<tr>
<td></td>
<td>48.823</td>
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<tr>
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<tr>
<td>( C_6 )</td>
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</tr>
<tr>
<td></td>
<td>65.731</td>
<td>-1.487</td>
</tr>
</tbody>
</table>
Fig. 4.3.1 Calibration curves and equations of $^{13}$C chemical shift of C$_1$, C$_3$, and C$_6$.

Fig. 4.3.2 $^{13}$C NMR spectra of loaded DEAB (0.4 mol CO$_2$/mol amine) at 24.5°C

Using Varian Mercury 500 MHz NMR spectrometer with VnmrJ Software (details on NMR analysis can be found in the liquid NMR manual;
From Table 4.3 and Fig. 4.3, 6 carbon $^{13}$C NMR peaks can be categorized into two groups, those in the shielded region and the deshielded region. The chemical shift of C₁, C₃, and C₆, which is considered to be shielded region, decreases as protonation ratio increases at -1.77, -2.00, and -1.49 ppm, respectively. On the other hand, the chemical shift of C₂, C₄, and C₅, which is considered to be deshielded region, increases as protonation ratio increases at 0.04, 1.35, and 0.66 ppm, respectively. After comparing the range of peak shifting, the shielded region (C₁, C₃, and C₆) was selected as a calibration set. Even though, the range of peak shifting of C₄ is comparable with those of C₁, C₃, and C₆, the chemical shift of C₄ (deshielded region) is in a different chemical environment from those of C₁, C₃, and C₆ (shielded region). Therefore, the chemical shift of C₄ was not included in the calibration curved in order to avoid the systematic error. The correlations of these 3 calibration curves (C₁, C₃, and C₆) were established in Figure 4.3. The average value of the three protonation ratios (which were calculated from the correlations for C₁, C₃, and C₆ calibration curves) was collected for the aid of being used to calculate the exact concentration of both DEAB and DEABH⁺.

This novel method for determining the protonation ratio has several advantages. First of all, this method no longer required a pH test. The NMR analysis can be independently determined the ratio of AmH⁺/Am and HCO$_3^-$/CO$_3^{2-}$ for most Amine-CO$_2$-H$_2$O independently. Secondly, the calibration method just takes some effort in the preparation, but it is a much easier sample analysis, the calibration method generates the results of speciation of DEABH⁺/DEAB and HCO$_3^-$/CO$_3^{2-}$.
simultaneously, which minimize the systematic error of performing pH test before NMR analysis.

This novel method has not been recognized because of two major reasons: (i) pH test is convenient since the acid dissociation constant $K$ value is available from literature. It can provide the $\text{AmH}^+/\text{Am}$ ratio right away, and (ii) only one chemical shift can be used as calibration curve for several amines. For instance, MEA has a simple structure, with two $^{13}$C peaks at 63.7 (CH$_2$OH) and 42.9 (CH$_2$NH$_2$) ppm, but only one of which can be used for calibration ($\Delta\delta = -4.2$ ppm).[5] The other $^{13}$C peak hardly changes with protonation ($\Delta\delta = -0.8$ ppm).[5] Under this condition, one reference curve would be less accurate for analysis. For other amines with more complicated structure (e.g., AMP, DEA, and MDEA), they contain multiple peaks in $^{13}$C spectra, which can be used as calibration curves. Jakobsen et al.[4] have also published the $^{13}$C chemical shift range of MDEA. For MDEA, the molecule possess three types of carbon peaks, -CH$_2$-OH, (δ=58.7-59.8 ppm), -CH$_2$-N< (δ=57.3-59.6 ppm), and CH$_3$-N< (δ=41.7-42.7 ppm). Jakobsen et.al.[4] have already acknowledged the change of δ $^{13}$C with protonation (increase CO$_2$ loading and decrease pH of the system). However, they did not perform the further analysis of the different types of shift (upfield and downfield) or find out the relationship of change of $^{13}$C chemical shift with protonation.

4.3.4. Ion speciation plot of DEAB-CO$_2$-H$_2$O system using combination of $^{13}$C NMR analysis and pH test (conventional method)

For the conventional method of combining the pH test with $^{13}$C NMR
analysis, the ratio of DEABH⁺/DEAB were obtained using the pH value and
DEABH⁺ dissociation constant K. Based on thes method, the ion speciation
(concentration of DEABH⁺, DEAB, HCO₃⁻, and CO₃²⁻) at 24.5°C and various CO₂
loadings (0-0.8 mol CO₂/mol amine) and initial DEAB concentrations (1.50 and
1.97 M) are reported in Table 4.4 (can be found in SI). The results were plotted as
solid lines in Figs 4.4 and 4.5.

Table 4.4 Ion Speciation (mole fraction) of 1.50 and 1.97 M DEAB-CO₂-H₂O
solutions at 24.5°C using conventional method of combining pH test and NMR
analysis

<table>
<thead>
<tr>
<th>CO₂ loading mol/mol Am</th>
<th>xDEAB</th>
<th>xDEABH⁺</th>
<th>xHCO₃⁻</th>
<th>xCO₃²⁻</th>
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<td>0.0044</td>
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<tr>
<th>CO₂ loading mol/mol Am</th>
<th>xDEAB</th>
<th>xDEABH⁺</th>
<th>xHCO₃⁻</th>
<th>xCO₃²⁻</th>
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<td>0.0062</td>
<td>0.0417</td>
<td>0.0251</td>
<td>0.0044</td>
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*a*solution without CO₂ loaded. The trance amount of absorbed from the air is
neglected.
Fig. 4.4 Ion speciation (mole fraction) plot of DEAB-CO$_2$-H$_2$O system at 24.5°C and initial DEAB concentration of 1.50 M (solid lines are obtained from conventional method of combining pH test and NMR analysis; and dashed lines are obtained from novel $^{13}$C NMR calibration method).

Fig. 4.5 Ion speciation (mole fraction) plot of DEAB-CO$_2$-H$_2$O system at 24.5°C and initial DEAB concentration of 1.97 M (solid lines are obtained from conventional method of combining pH test and NMR analysis; and dashed lines are obtained from novel $^{13}$C NMR calibration method).
4.3.5. Ion speciation plot of DEAB-CO$_2$-H$_2$O system using a novel $^{13}$C NMR calibration method

For the novel $^{13}$C NMR calibration method, the ion speciation (concentration of DEABH$^+$, DEAB, HCO$_3^-$, and CO$_3^{2-}$) was analyzed using $^{13}$C NMR. The results at 24.5°C and various CO$_2$ loadings (0-0.8 mol CO$_2$/mol amine) and initial DEAB concentrations (0.52, 0.98, 1.50, 1.97 M) are reported in Table 4.5. The results (at only 1.50 and 1.97 M) were plotted as dashed lines in Figures 4.4 and 4.5, together with the results obtained from the conventional method. The results of 0.52 and 0.98 mol/L were plotted in Figure 4.6 and 4.7, in format of mole fraction. The data was originated from Table 4.5.
Fig. 4.6 Ion speciation (mole fraction) plot of 0.52 mol / L DEAB-CO$_2$-H$_2$O system at 24.5 °C responded to Table 4.5, with NMR calibration.

Fig. 4.7 Ion speciation (mole fraction) plot of 0.98 mol / L DEAB-CO$_2$-H$_2$O system at 24.5 °C responded to Table 4.5, with NMR calibration.
Table 4.5 Ion Speciation (mole fraction) of 0.52, 0.98, 1.50, and 1.97 M DEAB-CO$_2$-H$_2$O solutions at 24.5°C using NMR calibration

<table>
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<th>CO$_2$ loading (mol CO$_2$ / mol amine)</th>
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<tr>
<td></td>
<td>0.52</td>
</tr>
<tr>
<td>C3</td>
<td>33.533</td>
</tr>
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<td>C6</td>
<td>66.720</td>
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<th>CO$_2$ loading (mol CO$_2$ / mol amine)</th>
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<td>0.98</td>
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<tr>
<td>C3</td>
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<td>HCO$_3$ / CO$_2^-$</td>
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<tr>
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<td>C6</td>
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<th>C$_{DEAB}$ (mol/L)</th>
<th>CO$_2$ loading (mol CO$_2$ / mol amine)</th>
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</tr>
<tr>
<td>C3</td>
<td>33.533</td>
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<tr>
<td>C6</td>
<td>66.720</td>
</tr>
<tr>
<td>HCO$_3$ / CO$_2^-$</td>
<td>165.699</td>
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</table>

*a The $^{13}$C NMR peaks is hard to detect because of the low concentration, the ratio of DEABH$^+$ was calculated based on the charge balance equation (eq 4.11).*
In the conventional method of combining pH test and $^{13}$C NMR analysis, the concentrations of $\text{HCO}_3^-$, and $\text{CO}_3^{2-}$ are determined using NMR analysis, while the concentrations of amine and protonated amine are calculated using predictive equation of dissociation constant $K_a$, concentrations of $\text{H}^+$ and $\text{OH}^-$ via pH test, and mass balance equations (eqs 4.10 and 4.11). In the novel method of $^{13}$C NMR calibration curve, all concentrations of $\text{HCO}_3^-$, $\text{CO}_3^{2-}$, amine, and protonated amine can be determined using the NMR analysis. Thus, the pH test and dissociation constant $K_a$ are not needed. As can be seen in Figure 4.3, the chemical shift of DEAB changes as protonation reaction proceed. However, this novel technique is not applicable in the case of amine that has simple chemical structure, such as MEA. This is because only two $^{13}$C NMR peaks can be detected at 63.7 ppm (CH$_2$OH) and 42.9 (CH$_2$NH$_2$) ppm. Moreover, one peak is found to rarely change as protonation proceed with $\Delta \delta = -0.8$ ppm.[5] The novel technique is suitable for the amine that has more complex structure (e.g., MDEA, DEAB, and AMP) since several calibration curves can be used for the aid of more accurate results.

In addition, it can be observed from Figs. 4.4 and 4.5 that the DEAB concentration decreases as CO$_2$ loading increases. This is due to the CO$_2$-DEAB-water reaction and the DEAB protonation, as shown in eqns 4.1 and 4.2, respectively. As a result, the protonated DEAB concentration, DEABH$^+$, increases as CO$_2$ loading increases. One of the major products, which is $\text{HCO}_3^-$, is found to increase as CO$_2$ loading increases. As CO$_2$ loading increases (which means more CO$_2$ is introduced to the system), $\text{HCO}_3^-$ is formed due to CO$_2$ reacting with
DEAB-water and CO$_2$ reacting with water, as shown in eqns 4.1 and 4.3, respectively. The last major component, which is CO$_3^{2-}$, is found to increase and reached to a maximum, then decrease as CO$_2$ loading increases. At the lean loading of CO$_2$, the solution contains excessive DEAB where the solution is a strong basic (pH > 10). At this point, CO$_3^{2-}$ is observed to be a major component rather than HCO$_3^-$.

However, after introducing more CO$_2$ (CO$_2$ loading is increased), the solution turned to be weaker basic (pH < 10). Thus, CO$_3^{2-}$ is converted to HCO$_3^-$ as a reverse reaction of eqn 4.4. After comparing the ion speciation of DEAB with that of conventional tertiary amine (i.e., MDEA), it was found that almost 100% of DEAB is converted to DEABH$^+$ at rich CO$_2$ loading of 0.8 mol CO$_2$/mole amine, but only 67% of MDEA is converted to MDEAH$^+$ at rich CO$_2$ loading of 0.8 mol CO$_2$/mole amine. It can be inferred from this observation that DEAB possesses stronger proton affinity than MDEA. Therefore, DEAB is found to be a stronger Brønsted base (has higher pKa value) than MDEA (pKa at 25 °C of DEAB and MDEA are 10.4 and 10.2, respectively). As mentioned by Versteeg et al.[17], and da Silva and Svendsen[18], the reaction rate constant for CO$_2$ absorption can be simply predicted using pKa as: the higher pKa, the faster reaction kinetics. Thus, it can be said that DEAB has faster reaction kinetics than MDEA. This observation is in good agreement with our kinetics analysis of DEAB using a laminar jet absorber$^{19}$. Moreover, the ion speciation of DEAB was compared with that of conventional primary amine (i.e., MEA). The results showed that 100% of MEA is converted to MEAH$^+$ at CO$_2$
loading of 0.7 mol CO\textsubscript{2}/mole amine.[5] Thus, it can be inferred that MEA possesses stronger proton affinity (pKa of MEA is 11.1) than DEAB and MDEA, respectively. This is because of MEA (which is primary amine) is more reactive than DEAB (which is tertiary amine).

4.4. Conclusions

1. The DEABH\textsuperscript{+} dissociation constant was calculated using pH test technique over a temperature range of 24.5-45°C and can be expressed as a function of temperature in Kelvin as: \[ \ln K_{\text{DEABH}^+} = -13.46 - 3147.5/T(\text{K}) \] with \( R^2 = 0.87 \).

2. A novel calibration method of \(^{13}\text{C}\) NMR spectra was successfully developed and applied for the first time to detect AmH\textsuperscript{+}/Am (which is DEABH\textsuperscript{+}/DEAB) ratio. In addition, the novel method is more convenient since the samples can be treated with NMR analysis right away and additional pH test beforehand is not required, which might minimize operational error.

3. Based on the protonation ratio observed from ion speciation, MEA (100% of MEA is protonated at 0.8 CO\textsubscript{2} loading) seems to be a better absorbent than DEAB (almost 100% of DEAB is protonated at 0.8 CO\textsubscript{2} loading) and MDEA (only 67% of MDEA is protonated at 0.79 CO\textsubscript{2} loading), respectively.
4.5 Reference


(8) Patterson, A.; Ettinger, R. Nuclear magnetic resonance studies of the carbon dioxide-water equilibrium. Z. Elektrochem. 1960, 98.


of Regina, SK, Canada, 2009.


Chapter 5  1D NMR Analysis of Blended MEA-DEAB Solutions

Part I: the VLE Model under room temperature 24°C

New procedures were developed for using the recently developed 1D NMR calibration method for quantitative liquid phase speciation analysis of a complex quaternary CO₂ loaded blended amine solution such as MEA-DEAB-CO₂-H₂O at room temperatures respectively representing CO₂ stripping and absorption conditions. The ion speciation analyses were performed in conjunction with the corresponding vapor-liquid equilibrium (VLE) of the system to estimate the CO₂ capture performance of the system. Accurate speciation was performed for a quaternary amine system using four concentrations consisting of 5.0M MEA blended with 0.5, 1.0, 1.5 and 1.25 M DEAB solutions with different CO₂ loadings at 24°C.

5.1 Introduction

The reliable estimation of the liquid phase composition or speciation of CO₂-amine-H₂O systems in conjunction with the corresponding vapor-liquid equilibrium (VLE) relationship constitutes a useful database for CO₂-amine interactions for CO₂ absorption and stripping operations. The VLE model at room temperature reflects CO₂ absorption, and that at temperatures > 90°C reflects amine regeneration. The 1D $^{13}$C NMR analysis of CO₂ loaded water soluble amine have been performed for years to test the ion speciation of ternary Amine-CO₂-H₂O system for the purpose of VLE model analysis.[1] Most of the research reported[1]
were accomplished mainly with conventional NMR analysis (pH + NMR) method for single amine solutions: Amine-CO$_2$-H$_2$O, such as MEA, BEA, MDEA, DEA, AMP, and NH$_3$, etc.[1-4] A pH meter was applied to determine the ratio of AmineH$^+$ / Amine based on the acidic constant $K_a$ ($K_{amineH^+}$) from the literature, while the NMR analysis was applied to determine the ratio of carbamate (HO-CH$_2$-CH$_2$-NH-COO$^-$) to the sum of bicarbonate and carbonate (HCO$_3^-$ and CO$_3^{2-}$), as well as the ion concentrations of bicarbonate and carbonate (HCO$_3^-$ and CO$_3^{2-}$) with the use of appropriate equations.[1-4] Usbharatana [5] generated a useful standard flow chart of this kind of experimental treatment which can be regarded as the standard approach for the “conventional (pH + NMR) method”.

A review of the literature [1, 6] shows three major characteristics of most of the previous works. These are: the limitation to ternary system (i.e. CO$_2$ loaded, single aqueous amine solutions), use of conventional pH + NMR method, and the use of low operating amine solution temperature (about 20-45ºC). These aspects can also constitute the limitation in the application of the NMR method for speciation analysis. In particular, the limitation to ternary systems does not allow taking advantage of blended amine systems, which are more energy efficient than single amine systems.[7] Our current study is intended to broaden the boundaries of operation in two corresponding aspects: extension to quaternary system (CO$_2$ loaded aqueous blended amine solutions), use of 1D NMR calibration method (i.e. elimination of pH tests).

According to Shi et al. [1] most of the successful NMR research for
speciation in the literature has been focused on the ternary system (essentially CO$_2$
loaded single amine solutions). There are scant reports of successful experimental
tests for the quaternary systems such as blended amine Böttinger et al. [8] have
performed NMR analysis of blended amine systems MDEA-PZ-CO$_2$-H$_2$O from
293 to 333 K (20 to 60 ºC), which seems to be the first trial for blended amines.
However, their ion speciation plot was accurate for only the ternary
MDEA-CO$_2$-H$_2$O but far from accurate for the quaternary MDEA-PZ-CO$_2$-H$_2$O
as reported by the authors.[8]

Li and Mather generated the ion speciation plot of MEA-MDEA-CO$_2$-H$_2$O
system by simulation but most of the parameters had to be corrected in order to
obtain realistic estimates.[9] Also, Edali [10] performed VLE plots of
MEA-MDEA-CO$_2$-H$_2$O systems (wt. ratio of 7/23) by numerical simulation using
COMSOL software. It is not shown how well the simulation results would fare
with experimental results since no experimental values were reported, thus
making it imperative to generate the speciation plots from accurate and
quantitative analytical chemistry methods.

In addition, based on analysis reported in the literature, the ternary system
(e.g. MEA-CO$_2$-H$_2$O) has five components such as MEAH$^+$, MEA, carbamate,
HCO$_3^-$, and CO$_3^{2-}$ with simple molecular structures. Also, DEAB-CO$_2$-H$_2$O
contains 4 major components that are detectable: DEABH$^+$, DEAB, HCO$_3^-$, and
CO$_3^{2-}$. On the other hand, a quaternary amine system (e.g. MEA-DEAB-CO$_2$-H$_2$O)
has 7 major ions and neutral compounds, namely, MEAH$^+$, MEA, carbamate,
DEABH⁺, DEAB, HCO₃⁻, and CO₃²⁻. For such systems, the NMR spectrum is complex with 11-12 peaks resulting from the complexity of CO₂-amine interactions within the solution and giving rise to increased difficulty of spectra interpretation for identifying the various species.

On the issue of NMR analysis technology, it has been pointed out by Jakobsen et al. [2] that with pH + NMR method, the individual ionic concentrations have not been evaluated independently solely from NMR data but always in combination with a thermodynamic model and/or equilibrium relationships. However, our recent results generated using our NMR calibration method shows that for the ternary system such as amine-CO₂-H₂O, the ion concentrations plot for the VLE model can be measured independently.[6] Using the ¹³C NMR calibration method, the DEAB-CO₂-H₂O solution was completely analyzed.[1, 6] Such analyses allowed the identification and confirmation of the molecular structure of a newly synthesized DEAB solvent.[6] It is possible to apply the NMR calibration method onto the complex quaternary MEA-DEAB-CO₂-H₂O systems to generate accurate speciation plots.
5.2 Experimental investigation of VLE plots of blended amine system:

5.2.1 Chemical Reaction Scheme

The chemicals for NMR analysis were discussed in Section 3.1.1. The chemical reaction schemes of the CO$_2$ interaction with primary amine MEA and tertiary amine DEAB were described in detail [1][2]. The major difference between MEA and DEAB is the existence of carbamate. The basic reaction schemes related to the direct CO$_2$-amine interaction are listed below, and 7 major ions are displayed in equations (5.1 to 5.7). Reaction 5.7 was the typical carbamate exchange reaction, which indicated the carbamate and bicarbonate can convert to each other with the existence of MEA. All the concentrations of cations, anions, the neutral compounds, as long as the CO$_2$ loading can be determined via proper experiments, either by pH method + NMR or by the novel NMR calibration method. Thus, all the reactions including the 7 major ions are presented here:

$$\text{CO}_2 + \text{MEA} \leftrightarrow \text{MEA-H}^+\text{-COO}^- \leftrightarrow \text{MEA-COO}^- + \text{H}^+ \quad (5.1)$$

$$\text{MEA} + \text{H}^+ \leftrightarrow \text{MEAH}_+ \quad (5.2)$$

$$\text{CO}_2 + \text{H}_2\text{O} + \text{DEAB} \leftrightarrow \text{HCO}_3^- + \text{DEABH}^+ \quad (5.3)$$

$$\text{DEAB} + \text{H}^+ \leftrightarrow \text{DEABH}^+ \quad (5.4)$$

$$\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 \leftrightarrow \text{H} + \text{HCO}_3^- \quad (5.5)$$

$$\text{HCO}_3^- \leftrightarrow \text{CO}_3^{2-} + \text{H}^+ \quad (5.6)$$

$$\text{MEA-COO}^- + \text{H}_2\text{O} \leftrightarrow \text{MEA} + \text{HCO}_3^- \quad (5.7)$$
5.2.2 Accuracy validation of pH method and NMR calibration analysis.

This is a unique set of experimental tests beyond Section 3.1.4. The NMR analysis of carbamate and bicarbonate/carbonate are the same for both methods. The difference is the analysis of AmineH⁺/Amine for the protonation ratio. Accuracy validation tests were performed to compare the deviations from the measured protonation ratio of MEA by the pH method or NMR calibration method to the highly accurate titrated protonation ratio. The titrated protonation ratio was recorded first. For the pH method, 100 mL of 0.10M MEA solution was prepared for 1.0M HCl titration. The solution was also tested with a pH meter. A magnetic stirrer was used in the beaker to establish equilibrium more quickly; the stirring was continuous throughout the titration. The pH value was recorded for every addition of 1 mL 1.0 M HCl standard solution during titration until 10 mL of HCl was added. The measured protonation ratio was calculated based on the pH value and equilibrium constant K from the literature. (Table 5.1.1)

Several sample tubes were prepared for the NMR calibration method,[6] with protonation ratios of nHCl vs. nMEA of 0.0, 0.2, 0.4, 0.6, 0.8, 1.0, and 1.2. The \(^1\)H and \(^{13}\)C NMR analysis of MEA was performed on the 7 samples at 24.0°C. Since MEA possesses two \(^1\)H and two \(^{13}\)C peaks, four calibration curves are generated in the calibration analysis. After comparison, the calibration line with a minimum deviation and \(R^2 > 0.99\) is selected as the standard calibration line, which is \(C_2\) (58-63 ppm) (Table 5.1.2 and Fig. 5.1). Therefore, any protonation ratio \(x\) of MEA can be calculated based on the chemical shift \(\delta\) of \(C_2\). The direct correlations of \(x\)
and δ have been established with a calibration curve.[1, 6] The protonation ratio obtained from HCl titration was regarded as the most accurate value, while the protonation ratio from the pH and K values, as well as the protonation ratio from NMR calibration, were regarded as the estimated values for which the accuracies required validation. (Table 5.2 Fig 5.2)

5.2.3 The overall experimental procedures for both methods.

The experimental procedures were introduced in Sections 3.3.1 and 3.3.2. However, the two methods can be combined to simplify the overall experimental procedures, which are described below.

Sample preparations were performed after the accuracy validation tests were performed and the NMR calibration curves were obtained. A standard typical blended amine solution (e.g. 50 mL of 5.0M MEA + 1.0M DEAB) was prepared in a beaker. Pure CO₂ was introduced into the solution for 45-60 seconds. The solution was tested with a pH meter while stirring with a magnetic stirrer. The pH value was not recorded until the pH value remained unchanged signifying the solution had reached equilibrium. Then 800 μL of the solution was collected into the NMR sample tube and recorded as #1 (the first loaded sample), and then 2 mL of the parent solution was pipetted and titrated for CO₂ loading (α₁) with a Chittick apparatus.[15]

The first sets of experimental procedures were completed for the first NMR sample with the introduction of CO₂ into the solution, pH testing, NMR sample collection, sample pipetting, and a loading test. This generated the pH value and
CO₂ loading. Eight NMR samples with 8 different CO₂ loadings (α₁ to α₈) covering the range from lean to rich CO₂ loading, were prepared for each blended amine concentration to generate a full range database. The analytical procedure was repeated 8 times, once for each CO₂ loading. CO₂ was introduced into the first 4 NMR samples for 60-90 s., CO₂ introduction for the next 4 sample (#5-#8) took longer (90-150s) because of the increased CO₂ loading, resulting in a slow CO₂ absorption rate. For sample #8, the CO₂ was introduced for 240s to reach the maximum loading (0.51-0.52 mol CO₂/mol amine). After the 8 CO₂-loaded NMR samples for each of blended MEA-DEAB quaternary system were collected, the samples were added to 400 μL D₂O for ¹³C NMR analysis., the full VLE plot was generated with CO₂ loading ranging from 0 to 0.52 mol/mol for the 5M/1.0M MEA-DEAB solution using the pH value, CO₂ loading, and NMR spectra.

An NMR analysis was performed immediately after preparation of each sample and two different sets of post NMR spectrum collection procedures were performed. The first set was used to test the chemical shift, δ. The second set was used to integrate the area of specific peaks for carbamate and bicarbonate/carbonate with specific parameter settings.[3] The area integration was performed from #4 to #8, where the peaks of bicarbonate/carbonate were detectable. Most of the CO₂ in the aqueous solution of the lean CO₂ loading samples (#1 to #3) was converted to carbamate with undetectable bicarbonate. This analysis at 24°C (room temperature) concluded the ion speciation data generation for one amine concentration based on the full use of two different methods (pH value + NMR results or NMR results).
This procedure was repeated for all the other concentrations 5M/0.5M, 5M/1.5M and 5M/1.25M.

5.2.4 Data Acquisition of Major Ions

The NMR spectra interpretation was not complicated for simple ternary amine solutions such as MEA-CO$_2$-H$_2$O and DEAB-CO$_2$-H$_2$O, from which the $^{13}$C NMR peaks can be directly selected and utilized in the equations of data acquisition.[4, 6] However, the NMR spectra for quaternary systems MEA-DEAB-CO$_2$-H$_2$O were much more complex than that of the ternary system, which increased the difficulty in the NMR spectra interpretation. Extra procedures were needed for the spectral interpretation of the NMR calibration techniques. These were: peak assignment, $Z_0$ correction and peak area integration; these were performed before the actual data acquisition from eqns (5.8-5.20) and ion concentration calculations. The extra procedures cannot be neglected if accurate results are to be obtained from the quantitative NMR analysis of quaternary amine solutions. The procedures for an NMR quantitative analysis assist in generating accurate speciation data.

**Part A: $^{13}$C NMR spectra interpretation**

The data acquisition procedure has been evaluated by Usubharatana [5] with a standard flowchart to describe the pH + NMR method. Since the blended amine system is more complicated than the single amine, it becomes essential to develop procedures for NMR spectra interpretation of an ion concentration analysis.

**Peak Assignment:** In order to facilitate NMR spectra interpretation, the
NMR peaks were assigned to 4 categories, which represent different ions and compounds in Fig 5.3.1. About 11-12 peaks were obtained from the $^{13}$C NMR spectra, which represent 7 major ions and neutral compounds in the solution. MEAH$^+$ / MEA possess 2 peaks, $C_1$ and $C_2$ and DEABH$^+/DEAB$ possess 6 $^{13}$C peaks, $C_1$ to $C_6$. Carbamate possesses 3 peaks and HCO$_3^- / CO_3^{2-}$ possesses 1 peak. When the CO$_2$ loading is small, the peak of HCO$_3^- / CO_3^{2-}$ is undetectable and negligible. Only one peak of carbamate and one peak of bicarbonate/carbonate need to be analyzed for the conventional pH + NMR analysis method since the ratio of AmineH$^+/Amine$ are tested with a pH meter.

**Z$_0$ correction:** Because of the protonation effect, samples with higher loading contain more cations and anions in the solution, which increases the ionic strength. The increased ionic strength affects the magnetic field of the NMR instruments, which shift the resonance of the overall $^{13}$C NMR peaks to the shielded region ($\delta$ decrease). As such shifts do not result from the protonation but from the chemical surroundings which affect the standard of “0 ppm”, the phenomena affect the accuracy of the calibration curves. For example, given samples #7 and #8 of 5M/0.55M MEA/DEAB, the chemical shift of $C_1$ of DEABH$^+/DEAB$ is 8.14 and 8.10 ppm, which is out of the range of the NMR calibration curve of $C_1$ 8.40-10.22 ppm. In the present work, a Z$_0$ line correction was performed to adjust the chemical shifts back to the range. The correction of this work was based on the assumption that the $C'_3$ of carbamate remains unchanged as an internal standard. This assumption was reasonable because the
the chemical shift of carbamate hardly changes with protonation.[2] The samples at one amine concentration set were considered to possess the same $\delta$ of $C'_{3}$ of carbamate as was demonstrated in the results. After the zero line correction, the chemical shift of DEABH+/DEAB was corrected to 8.40-8.42 ppm, which is close to 100% of protonation.

**Peak Area integration**: This step is necessary to calculate the exact ion concentration of carbamate (HO-CH$_2$-CH$_2$-NH-$\underline{\text{COO}^{'}}$) and bicarbonate/carbonate ($\text{HCO}_3^{-} / \text{CO}_3^{2-}$) from NMR spectra (see Fig. 5.3.2) With the specified treatment, the two peaks were integrated under operating conditions where the NOE was neglected and the decoupling was off.[3] The ratio of the integrated peak area reflects the ratio of C atoms for HO-CH$_2$-CH$_2$-NH-$\underline{\text{COO}^{'}}$ and $\text{HCO}_3^{-} / \text{CO}_3^{2-}$, which is the same as the ratio of the ionic concentration for each compound. The ion concentrations of carbamate, bicarbonate, and carbonate can be accurately calculated based on NMR spectra of the integrated peak area (see Fig. 5.3.2) and eqns (5.17) - (5.20). It is not necessary to integrate two other $^{13}$C peaks of carbamate because the peak $C'_{3}$ is adequate to reflect the carbamate in the systems.

**Part B. Data Acquisition for ion speciation of both methods**

NMR spectra cannot distinguish compounds of AmineH$^+$ and Amine due to the fast proton transfer effect.[1, 2, 6] The exact concentration of each compound was generated with the pH method and NMR calibration method. With respect to the pH method, the concentrations were calculated from eqns (8), (9), (12) and (13) with pH and Ka values from the literature. [3, 6] The calibration lines from the
NMR calibration methods were available for MEA (eqn 10) and DEAB (eqns 14, 15) from calibration curves obtained from experiment. The K values and calibration equations are sensitive to temperature. The exact concentration of AmineH⁺ and Amine were calculated from the K ratio and eqns (10), (11), (14), (15) and (16) at the experimental temperatures.

The sum of the ion concentrations for carbamate, bicarbonate and carbonate were calculated from the CO₂ loading in eqn (17), following the mass balance of CO₂. The ratio of the ion concentration for the exact concentration of carbamate and the sum of bicarbonate with carbonate is exactly the ratio of the integrated area for the ¹³C peaks at a specific condition: the absence of Nuclear Overhauser Effects (NOE).[3] The concentration of carbamate was calculated from eqns (17) and (18) while the concentrations of HCO₃⁻ and CO₃²⁻ were calculated from eqns (19) and (20).[3] The chemical shifts for the NaHCO₃ and Na₂CO₃ solutions were estimated under a standard temperature of 24.0°C as 160.769 ppm and 168.488 ppm and are parameters for the equations, respectively. The values are close to Poling’s reference data at 25.0 °C [3] and close to the previous data obtained at 24.5 °C. [6]

All seven major ions in the blended amine solutions were calculated accurately with both methods from eqns (8) to (20) since they are applicable to pH + NMR and NMR calibration methods.
Data acquisition equations:

**MEAH\(^+\)/MEA:** \[ Ka = [H^+] \times \frac{[MEA]}{[MEAH^+]} \] (5-8)

\[
\ln K_a = \frac{-5851.11}{T} - 3.3636 \quad (5-9) \quad [7,10] \quad \text{(pH method)}
\]

\[ C_b: \quad \delta = -0.0551 \times 100\% + 63.247 \] (5-10) \quad \text{(NMR calibration)}

\[ [MEA] + [MEAH^+] = nMEA_0 \] (5-11)

**DEABH\(^+\)/DEAB:** \[ Ka = [H^+] \times \frac{[DEAB]}{[DEABH^+]} \] (5-12)

\[
\ln K_a = \frac{-3147.5}{T} - 13.46 \quad (5-13) \quad [2] \quad \text{(pH method)}
\]

\[ C_1: \quad \delta = -0.01828 \times 100\% + 10.228 \] (5-14)

\[ C_3: \quad \delta = -0.02065 \times 100\% + 33.959 \] (5-15)

\[ [DEAB] + [DEABH^+] = nDEAB_0 \] (5-16)

**MEA-COO\(^-\):**

\[
\frac{[\text{MEA-COO}^-]}{[\text{HCO}_3^-] + [\text{CO}_3^{2-}]} = R \quad (5-17)
\]

\[
[\text{MEA-COO}^-] = \frac{R}{1 + R} [\text{CO}_2]_0
\]

\[
= \frac{R}{1 + R} \alpha \times ([\text{MEA}]_0 + [\text{DEAB}]_0) \quad (5-18) \quad [7]
\]

**HCO\(_3\^-\) / CO\(_3\)^{2-}\):**

\[
[\text{CO}_3^{2-}] = \frac{\delta - 160.769}{7.719(1 + R)} [\text{CO}_2]_0
\]

\[
= \frac{\delta - 160.769}{7.719(1 + R)} \alpha \times ([\text{MEA}]_0 + [\text{DEAB}]_0) \quad (5-19)[7]
\]

\[
[\text{HCO}_3^-] = \frac{168.498 - \delta}{7.719(1 + R)} [\text{CO}_2]_0
\]

\[
= \frac{168.498 - \delta}{7.719(1 + R)} \alpha \times ([\text{MEA}]_0 + [\text{DEAB}]_0) \quad (5-20) [7]
\]
5.3 Results and Discussion

5.3.1 NMR calibration of the MEA solution

MEA possess two $^1$H peaks and two $^{13}$C peaks, one set for the $\text{–CH}_2$OH group and the other for the $\text{–CH}_2$NH$_2$ group. The chemical shifts for the MEAH$^+$ / MEA mixture were tested with $^1$H and $^{13}$C probes and are listed in Table 5.1.2, with C$_2$ selected as the standard calibration curve (in Fig 5.1) for two reasons: 1) the $^{13}$C chemical shift was most significant (-5.354 ppm) and 2) the linear deviation was minimal: $R^2 = 0.9952$. Only lines with $R^2 > 0.99$ were chosen to achieve a higher accuracy from the calibration method. Figure 5.1 shows the NMR calibration curve for MEA under 24.0 °C. The NMR calibration curve for DEAB can be found in the literature [2] or in Chapter 4. C$_1$ and C$_3$ were chosen for the calibration curve and derived using equations 5.15 and 5.16 [2].
Table 5.1.1 PH test of MEA solution with protonation at 23°C.

<table>
<thead>
<tr>
<th>V HCl</th>
<th>protonation rate</th>
<th>PH</th>
<th>$[\text{H}^+]$</th>
<th>MEA/MEA+</th>
<th>MEA+ %</th>
<th>Deviation %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>10.94</td>
<td>1.14815E-11</td>
<td>32.41</td>
<td>2.99</td>
<td>2.99</td>
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<tr>
<td>1</td>
<td>10</td>
<td>10.36</td>
<td>4.36516E-11</td>
<td>8.53</td>
<td>10.50</td>
<td>0.50</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>10.08</td>
<td>8.31764E-11</td>
<td>4.47</td>
<td>18.27</td>
<td>1.73</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>9.87</td>
<td>1.34896E-10</td>
<td>2.76</td>
<td>26.60</td>
<td>3.40</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>9.69</td>
<td>2.04174E-10</td>
<td>1.82</td>
<td>35.43</td>
<td>4.57</td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>9.53</td>
<td>2.95121E-10</td>
<td>1.26</td>
<td>44.23</td>
<td>5.77</td>
</tr>
<tr>
<td>6</td>
<td>60</td>
<td>9.35</td>
<td>4.46684E-10</td>
<td>0.83</td>
<td>54.55</td>
<td>5.45</td>
</tr>
<tr>
<td>7</td>
<td>70</td>
<td>9.16</td>
<td>6.91831E-10</td>
<td>0.54</td>
<td>65.02</td>
<td>4.98</td>
</tr>
<tr>
<td>8</td>
<td>80</td>
<td>8.91</td>
<td>1.23027E-09</td>
<td>0.30</td>
<td>76.78</td>
<td>3.22</td>
</tr>
<tr>
<td>9</td>
<td>90</td>
<td>8.53</td>
<td>2.95121E-09</td>
<td>0.13</td>
<td>88.80</td>
<td>1.20</td>
</tr>
<tr>
<td>10</td>
<td>100</td>
<td>6.83</td>
<td>1.47911E-07</td>
<td>0.00</td>
<td>99.75</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Total \( \text{Keq} = 6.7042 \times 10^{-12} \) (296, 15 K) 3.10

Table 5.1.2 $^1\text{H}$, $^{13}\text{C}$ chemical shift of 5M MEA solution with protonation at 24 °C.

<table>
<thead>
<tr>
<th>$\delta_{\text{MEA}}$ ppm</th>
<th>Protonation rate (%)</th>
<th>$\Delta\delta$ ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>2.644</td>
<td>2.666</td>
<td>2.750</td>
</tr>
<tr>
<td>3.508</td>
<td>3.497</td>
<td>3.539</td>
</tr>
<tr>
<td>H2</td>
<td>42.866</td>
<td>42.412</td>
</tr>
<tr>
<td>C1</td>
<td>63.294</td>
<td>62.210</td>
</tr>
</tbody>
</table>

Fig. 5.1 NMR calibration curve of C$_2$ of MEA at 24°C.
5.3.2 Accuracy validation test for the pH method and NMR calibration method.

Table 5.1.2 presents the pH test for the MEA solution under 23.0°C. The measured protonation ratios, based on different pH values, were obtained based on Equations 5.21 and 5.22. The $K_{eq}$ value was obtained from the literature [6] and the concentration of $[H^+]$ was calculated based on its pH value. $K_{eq}$ was similar to $K_a$ for the deprotonation reaction (equation 5.2) but the concentration of water $[H_2O]$ is included in equation 5.21 and not included in equation 5.8. The difference between the $K_{eq}$ and $K_a$ values was based on different equations 5.9 and 5.22 [6,8,11]. The calculated AAD% for the pH method was 3.1% and 3.4% for AAD% was 3.4% where the start and end points (0 ml and 10 ml HCl) were excluded throughout the 11 measured points. The pH test, the data were considered to be more accurate for the pH test where the ratio of $[Am]/[AmH+]$ was within the range of 0.1 to 10.0, where pH value was in the range of $pK_a \pm 1$. Table 5.2 indicates the pH method was considered very accurate with an AAD% of 3%, which validates the accuracy of conventional pH + NMR methods as used by other researchers [1].

Deprotonation constant $K_{eq}$ for MEA:

\[
K_{eq} = \frac{[H_3O^+] [MEA]}{[MEA H^+] [H_2O]} \quad (5-21)
\]

\[
\ln K_{eq} = - \frac{6166.116}{T} - 4.90737 \quad (5-22) [6]
\]
### Table 5.2 Validation of Accuracy of NMR Calibration and pH Test.

<table>
<thead>
<tr>
<th>Real ratio %</th>
<th>by PH test %</th>
<th>D%</th>
<th>by NMR&lt;sup&gt;a&lt;/sup&gt; calibration&lt;sup&gt;a&lt;/sup&gt;</th>
<th>D%</th>
<th>by NMR&lt;sup&gt;b&lt;/sup&gt; calibration&lt;sup&gt;b&lt;/sup&gt;</th>
<th>D%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.99</td>
<td>2.99</td>
<td>-0.85</td>
<td>0.85</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>10</td>
<td>10.50</td>
<td>0.50</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>18.27</td>
<td>1.73</td>
<td>18.82</td>
<td>1.18</td>
<td>18.32</td>
<td>1.68</td>
</tr>
<tr>
<td>30</td>
<td>26.60</td>
<td>3.40</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
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<tr>
<td>50</td>
<td>44.23</td>
<td>5.77</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>54.55</td>
<td>5.45</td>
<td>63.21</td>
<td>3.21</td>
<td>63.94</td>
<td>3.94</td>
</tr>
<tr>
<td>70</td>
<td>65.02</td>
<td>4.98</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>80</td>
<td>76.78</td>
<td>3.22</td>
<td>82.63</td>
<td>2.63</td>
<td>83.82</td>
<td>3.82</td>
</tr>
<tr>
<td>90</td>
<td>88.80</td>
<td>1.20</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>99.75</td>
<td>0.25</td>
<td>96.19</td>
<td>3.81</td>
<td>----</td>
<td>----</td>
</tr>
</tbody>
</table>

| Average      | 3.100        | 1.953 |                                 |      | 2.375                           |      |
| Deviation %  | 3.424 (exclude 0% and 100%) |      |                                 |      |                                 |      |

<sup>a</sup>: This method applies to the equations used to obtain the 6-point calibration line in Figure 5.1.

<sup>b</sup>: This method applies to a similar method of NMR calibration, but excludes the point in the calibration line. For instance, to validate the dot (20%, 62.210 ppm), the calibration line is generated based on 5 points and the δ = 62.210 ppm is fitted into the line, after which the protonation rate is calculated as 18.32%. This method is more accurate than method 1 because the point and calibration line are independent.
In addition, Table 5.2 also exhibits the accuracy of the NMR calibration test. The protonation ratios for the calibration were calculated from the equation in Fig. 5.1 or eqn (5.10). The deviations for the measured protonation values from the NMR calibration method (similar to either of the pH meter methods) with respect to the titration values are labeled as “D%”, representing the absolute deviation of the analysis methods with respect to the highly accurate value. The measured protonation ratio \( x \) by the NMR calibration test1 was obtained from the detected chemical shift \( \delta \) of the MEA/MEAH\(^+\) based on the equations from Fig. 5.1.

Moreover, the NMR calibration test2 was performed to validate the accuracy under stricter conditions. This method generated a new calibration curve for \( C_2 \) but excluded the point itself. For instance, to validate the accuracy of point (20%, 62.210 ppm), the test1 (with the calibration equation in Fig.5.1 which includes the point) has a higher accuracy (18.82%) over test2 (with the calibration equation which excludes the point) (18.32%), because the point (20%, 62.210) itself was part of the calibration curve. A new calibration line was generated for test2 based on the other 5 points with protonation ratios of 0%, 40%, 60%, 80%, and 100%. Then, the chemical shift of 62.210 ppm was placed in the new calibration equation which generated a new protonation ratio \( x' \) (18.32%). The ratio was compared to “20%” and the absolute deviation “D%” of the measured protonation for the NMR calibration test2 was calculated. test2 was stricter because the point (20%, 62.210 ppm) and the new calibration curve were totally independent. From Table 5.2, the AAD% of the NMR test1 and test2 methods were 1.9% and 2.4%, respectively.
The accurate results indicate that both methods are accurate and the NMR calibration test1 (with an AAD% less than 2%) or test2 (with an AAD% less than 2.5%) was more accurate than the pH method. Fig. 5.2 represents the AAD% of the titration value compared to three methods corresponding to Table 5.2.

The higher accuracy of the NMR calibration compared to the pH test is reasonable because the pH test is an indirect measurement of testing \([H^+]\) despite the fact there are advantages to the procedure. The NMR calibration test is a direct measurement of the compounds since the chemical shift \(\delta\) of MEA/MEA\(^+\) is directly related to the protonation ratio \(x\).[1, 6]

![AAD% validation of PH and NMR method](image)

**Fig. 5.2** Accuracy Validation of pH test and NMR calibration test.
5.3.3 The $^{13}$C NMR spectra and results of pH and $^{13}$C NMR methods.

Figure 5.3.1 represents the $^{13}$C NMR spectra for the MEA-DEAB-CO$_2$-H$_2$O solution. All the chemical shifts need to be studied carefully. The 12 peaks from each sample, with 8 samples in one concentration, were assigned into 4 categories and organized in Table 5.3. Table 5.3 represents the concentrations of the 5.0 M + 0.58M, 5.0 M + 1.0 M, 5.0M + 1.5 M, and 5.0M + 1.25 M (MEA + DEAB) blended amine solutions.

Fig. 5.3.1 represents a typical $^{13}$C NMR spectrum for the MEA-DEAB-CO$_2$-H$_2$O solution. The peak of C$_3'$ for carbamate and HCO$_3^-$/CO$_3^{2-}$ needs to be studied with the pH + NMR method. However, all the chemical shifts need to be carefully studied for accurate NMR calibration. The 12 peaks of each sample were assigned into 4 categories and organized in Table 3 for 24ºC and Table S4.4 for 70ºC. Table 3 only represents the concentrations of 5.0 M + 0.58M (MEA + DEAB) blended amine solutions.

**Peak assignment** From Fig. 5.3.1 and Table 5.3, the components of MEAH$^+$/MEA at 24ºC possess two $^{13}$C peaks, C$_1$ (41.7-42.9 ppm) and C$_2$ (57.9-63.3 ppm). C$_2$ was chosen as the calibration curve. DEABH$^+$ / DEAB possess six peaks with 8 C atoms, as discussed previously.[6] C$_1$ (8.4 – 10.2 ppm) and C$_3$ (31.9-33.9 ppm) were chosen as standard calibration curves.[6] HCO$_3^-$ / CO$_3^{2-}$ exhibits one peak (160.7-168.5 ppm). The 9 peaks were strongly affected by protonation, which shifted to a shielded region (δ decrease with protonation). Carbamate (HO-CH$_2$-CH$_2$-NH-COO$^-$) has three peaks, C'$_1$ (43.4~43.5 ppm), C'$_2$ (61.4~61.5
ppm), and C’₃ (164.5~164.7 ppm) in the shielded region to de-shielded region (low δ to high δ), which changed little with protonation.[2] Based on the phenomena, the δ of C’₃ for carbamate was regarded as an internal standard for the NMR analysis to correct the Z₀.

**Z₀ correction** Table 5.3 reflects the Z₀ line correction from the original and corrected data. This correction was needed for the ¹³C NMR peak analysis because the deviation of the chemical shifts originated from the ionic strength of the solution interaction with the NMR instruments. For example, in Table 5.3, the chemical shift of C’₃ from the carbamate of sample #1(No.1) was 164.702 ppm, but the chemical shift in sample #8 (No.8) was 164.373 ppm. This minute difference (0.329 ppm) was negligible for regular NMR analysis of the molecular structure. This deviation has to be corrected for a calibration analysis. The minimum value of C₁ from DEAB was 8.40 ppm (100% protonation), but C₁ from some samples decreased to 8.060 ppm in Table 3, which is out of the range of the calibration curve (8.4 – 10.2 ppm) due to the Z₀ shift.

The peak shifts did not result from protonation (H⁺) but from the deviation of the Z₀ value. There are more ions in the system with a higher loading. The increased ionic strength affects the NMR instrument’s magnetic field, resulting in a change in the Z₀ value. The “Lock” signal for Z₀ (D₂O) ranged from 422 to 522, which resulted in a slightly deviated position from zero (0 ppm). This slight difference (0-0.5 ppm) results in a slight deviation in all the chemical shifts because an NMR reflects the difference in resonant frequency f between the chemicals and the
Therefore, a $Z_0$ correction was performed to fit the calibration equations to maintain accuracy. The $C'_3$ peaks of carbamate (164.373-164.658 ppm) from samples #2 to #8 were corrected to sample #1 (164.702 ppm) for every 8 samples with the same concentration in Table 3. Thus, the differences (0 – 0.5 ppm) were applied to every NMR peak for each spectrum of samples #2 to #8. The peaks from the carbamate were more consistent, and the chemical shift $\delta$ of the peaks fit the range of calibration curves after the technological/instrumentation corrections were implemented.
Fig. 5.3.1 The typical $^{13}$C NMR spectra of blended amine solution (MEA-DEAB-CO$_2$-H$_2$O) at 24.0°C.

a. This is an example of the $^{13}$C NMR spectra for the 5.0M-1.0 M MEA-DEAB mixed system at loading $\alpha_7$.

b. Two peaks, Ca, Cb, represent MEA/MEAH$^+$ and possess the same sets of $^{13}$C peaks. C$_1$-C$_6$ represent DEAB/DEABH$^+$ which is similar to MEA/MEAH$^+$. Cx represents HCO$_3^-$ / CO$_3^{2-}$. The relative ratio of free versus protonated compounds was determined by the position of the chemical shift with the calibration curve from equations 5.8 to 5.20.

c. The remaining 3 peaks represent carbamate, which changes very little with protonation. They may shift 0.2-0.4 ppm based on the slightly different $Z_0$ values based on the NMR data from supplementary materials.
Table 5.3 The $^{13}$C NMR results for 5.0 M MEA + 0.5 M ~ 1.50 M DEAB solutions at 24.0 °C a, b, c, d

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<th>Sample #</th>
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<th>Carbamate</th>
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a. A zero line correction was needed for the high accuracy NMR calibration method because the Z0 of resonance varied (0.0-0.5 ppm) for different samples. This minute difference is negligible for ordinary NMR tests for chemical identification, but this correction is necessary for the calibration curve. This correction is made on the standard Z0 value (0 ppm) for the spectra and the corrected data is chosen for data acquisition. All the chemical shifts should be altered by the same value. The criterion for the correction is to match the C3 of carbamate with the same value from sample #1 in each group.

b. The results for the other concentrations are provided in Tables 5.3

c. The red data was selected for the ion concentration calculation in Table 5.4.

d. The ion concentrations were measured with titration, which can only detect the sum of the amine concentrations. The solution was prepared for the 5M MEA + 0.5-1.5 M DEAB system, therefore, some deviation were also labelled to exhibit the deviation.
### (2). 5.0 M MEA + 1.0 M DEAB (± 0.025 M)

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### (3). 5.0 M MEA + 1.50 M (± 0.025 M) DEAB

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125
### Table 1.4

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(4). 5.0 M MEA + 1.25 M (±0.025 M) DEAB
**Area Integration** Fig. 5.3.2 reflects the peak area integration of carbamate and bicarbonate/carbonate. The concentration of the sum of carbamate and bicarbonate/carbonate was the same as $[\text{CO}_2]_0$ in the liquid phase based on the mass balance of CO$_2$. The ratio of the integrated peak area reflects the ratio of C atoms for HO-CH$_2$-CH$_2$-NH-\text{COO}^-$ and HCO$_3^-$ / CO$_3^{2-}$, which is the same as the ratio for the ionic concentration. The integrated peak area of carbamate to bicarbonate/carbonate was 85.48% to 14.52%, which is the exact composition of two compounds in the MEA-DEAB-CO$_2$-H$_2$O system. In addition, 85.48% of ‘$[\text{CO}_2]_0$’ in the liquid phase was converted to carbamate and the rest was converted to bicarbonate and carbonate.

![Carbamate and HCO$_3^-$ / CO$_3^{2-}$](image)

**Fig. 5.3.2** The integration spectra of $^{13}$C NMR test of bicarbonate and carbamate.

a. This integration was performed with the NMR technique without NOE, without decoupling, as in Colin’s research [6]. The integration of the area of the two $^{13}$C peaks represents the concentration of C atoms for MEA-COO$^-$ and HCO$_3^-$ / CO$_3^{2-}$, respectively. The area ratio reflects the direct ratio of ion concentrations between carbamate and the sum of bicarbonate/carbonate.
5.3.4 Ion speciation tables and VLE plots of blended amine systems.

Figure 5.4 represents the VLE plot of the MEA-MDEA-CO$_2$-H$_2$O system with software simulation by Edali [5]. Since MDEA is the major component, the ion concentration of HCO$_3^-$ was large.

The ion speciation tables of blended amine systems MEA-DEAB-CO$_2$-H$_2$O were generated with the NMR spectra, tables of NMR results, and the data acquisition equations 5.8 to 5.20. Table 5.4 represents four concentration sets: 5.0 M MEA + 0.55 M DEAB ($\pm$ 0.025M), 5.0M A + 1.0 M B ($\pm$ 0.025), 5.0 M A + 1.50 M B ($\pm$ 0.025M), and 5.0 M A + 1.25 M B ($\pm$ 0.025M) (where A is MEA, B is DEAB). The titration can only detect the concentrations of the overall amine solutions (A+B), but it cannot specify MEA from DEAB as there are small deviations in the ion concentration around 0.025M. The additional 0.025M of amine can either be MEA or DEAB or a mixture of both. Since the deviation in concentration was small, the concentration of blended amine solution was regarded as accurate.

From the tables, it is clear the VLE plots from the pH method and NMR calibration method can be generated. “Tot” represents the sum of HCO$_3^-$/CO$_3$$^{2-}$, which is much less than carbamate. The maximum percentage of bicarbonate/carbonate within [CO$_2$]$_0$ was no higher than 22%, which indicated the major formulation of CO$_2$ in aqueous solution was carbamate and not bicarbonate. This is reasonable because the ratio of MEA to DEAB was 5:0.5 to 5:2, 10 to 2.5 times and the stability of carbamate was larger than bicarbonate.
Fig. 5.4 Ion speciation in aqueous MDEA/MEA $^a$ (23/7 wt. ratio 1.9 M: 1.1M) solution with CO$_2$ loading ($\alpha$) from 0 to 1.0 at 298 K for a 2-D absorption rate/kinetics model. (Application of FEM COMSOL software to predict the composition of species) [5].

a. The major ions in this simulation are of MDEA not MEA [5]. This is the major difference between the simulation plot vs. the experimental plot.
Table 5.4 Ion concentrations of MEA-DEAB-H₂O-CO₂ mixture for different concentrations at 24 °C. a–d

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<th>DEABH⁺</th>
<th>C-mate</th>
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<th>CO₃²⁻</th>
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### 5.0 M MEA + 1.5 M DEAB ± 0.025 M

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<th>MEAH⁺</th>
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### Note
- Ion Concentrations mol/L
- Samples are identified by their number, and each sample is characterized by its loading in mol/L and the method used for measurement (NMR).
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<td>(24°C)</td>
<td>0.082</td>
<td>2.320</td>
<td>0.018</td>
<td>1.257</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<td></td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

a. The NMR calibration test applies the equations in Fig. 5.1 for MEA, and the calibration eqns (5.14, 5.15) for C₁ and C₃ with DEAB.[6] The chemical shift of C₆ (65-67 ppm) is close to C₆ from MEA (58-63 ppm) and C₂ from carbamate (61.47-61.5ppm). C₆ was not selected as the calibration line to simplify.

b. The deprotonation constant K.equ of MEA was obtained from the literature with eqn (5.9).[4] K.equ from DEAB was obtained from previous work.[6] The ion concentrations generated from the pH method are listed in blue.

c. The concentration of carbamate is calculated with eqn (5.17).[3] The ratios of carbamate and bicarbonate/carbonate were generated with peak area integration.

d. The number in the brackets is the total concentration of HCO₃⁻ + CO₃²⁻, which is based on eqn (5.18).[3] The ion concentration for specific components (HCO₃⁻ & CO₃²⁻) was based on eqns (5.19, 5.20).[3] The chemical shifts of the HCO₃⁻ and CO₃²⁻ samples were tested with the NaHCO₃ and Na₂CO₃ solutions.[6]
The VLE plot can be generated from Table 5.4 as in Figures 5.5 (1-5) with the NMR calibration method. The VLE plot obtained from the pH method can be combined with data obtained from the NMR as shown in Figure 5.5(5) and listed in Table 5.4. The VLE plots are similar in Figure 5.5 and the results are consistent with some trends. The results can facilitate further solvent chemistry studies for blended amine systems in the field. The first four figures are analyzed with the NMR calibration method, and the fifth is analyzed according to the 5.0 + 1.25 (+0.025) M MEA/DEAB systems and the pH + NMR method.
(1) Ion speciation plot of 5.0 + 0.55 M MEA/DEAB amine system

(2) Ion speciation plot of 5.0 + 1.0 M MEA/DEAB amine system
(3) VLE plot of ion speciation of 5.0 + 1.50 M MEA/DEAB amine system

(4) Ion speciation plot of 5.0 + 1.25 M MEA/DEAB amine system
(5) Ion speciation plot of 5.0 + 1.25 M MEA/DEAB amine with pH + NMR

**Fig. 5.5 (1-5)** Ion speciation of 5.0 ± 0.5~1.50 (± 0.025) M MEA/DEAB systems 24°C
The ion speciation tables for MEA-DEAB-CO$_2$-H$_2$O were generated with NMR spectra, tables of NMR data (in supplementary information), and the data acquisition eqns (5.8) to (5.20). The exact ion concentration tables for various ion concentrations plots of VLE models from Fig. 5.5 are clearly grouped (1-5). Fig. 5.5 represents four concentration sets: 5.0M/0.55M of MEA/DEAB ($\pm$0.025M), 5.0M/1.00M of MEA/DEAB ($\pm$0.025M), 5.0M/1.50M of MEA/DEAB ($\pm$0.025M), and 5.0 M/1.25M MEA/DEAB ($\pm$0.025M). The overall ion concentration for blended amine has a $\pm$ 0.025M deviation, with the exact ion concentration grouped in Table 5.4. “Tot” in Table 5.4 represents the sum of the ion concentration for HCO$_3^-$/CO$_3^{2-}$, which is calculated and recorded in parentheses. The maximum percentage of bicarbonate/carbonate within $[CO_2]_0$ was no higher than 22% (5M/1.5M) at 24°C, which indicates the predominant formulation for CO$_2$ in aqueous solution was carbamate but not bicarbonate. The concentration of carbonate (CO$_3^{2-}$) was negligible. Carbamate was the predominant format for CO$_2$ in the solution because MEA is the major fraction in the solution. A VLE plot was generated from Table 5.4 with the NMR calibration method as shown in Fig. 5.5. This type of result can facilitate CO$_2$ absorption studies for blended amine systems.

Successful application of the conventional pH + NMR method to the quaternary amine system was proven in the experimental procedure. Thus, the ion concentrations from the pH + NMR method were also collected in Table 5.4. The VLE plot for the pH method, combined with NMR, is shown in Fig. 5.5 (5) from the
5M/1.25M MEA-DEAB solution with corresponding data from the pH test. The VLE plots are similar and consistent with the calibration.

The ion concentrations of free MEA decreased with increased loading, since MEA was converted to MEAH$^+$ and carbamate while interacting with CO$_2$. Ion concentrations of MEAH$^+$ increased at a slower rate in the beginning and slightly faster at higher loadings after all the DEAB was protonated. There are two proton acceptors in the lean loading region, free MEA and free DEAB, but there is only one proton acceptor (MEA) in the rich loading region after the free DEAB has been exhausted. The same trend applies to free DEAB, which decreased to zero with protonation, and DEABH$^+$ simultaneously increases to its maximum [DEAB]$_0$. The carbamate increased from zero, reached a maximum and then decreased slightly after reaching an apex, which is consistent with previous NMR results.[2, 4] The CO$_3^{2-}$ concentration was limited and close to zero throughout, and the HCO$_3^-$ began to increase with a loading > 0.4 mol/mol. The concentration of bicarbonate was undetectable from the NMR spectra at lean concentrations. The trends for MEA and DEAB are consistent with the single amine solutions from previous research.[2, 4]

VLE plots of the quaternary amine systems can be successfully generated with pH + NMR methods. Few researchers have ever succeeded in generating the VLE plot of quaternary amine systems, because most have only studied two peaks of NMR spectra: C$_3'$ of carbamate and bicarbonate/carbonate with the conventional pH + NMR method. Jakobsen et al.[2] created a VLE plot for the MEA-CO$_2$-H$_2$O
and MDEA-CO$_2$-H$_2$O systems with the conventional pH with NMR method, but the VLE plot only contains four loadings plotted with every amine concentration. In the current tests, 8 samples of each blended amine solutions were tested from 0 to the maximum CO$_2$ loading, which contain complete information about an ion speciation plot. The NMR calibration method exhibited many advantages compared to the pH + NMR method, with higher accuracy and greater convenience. It solely and simultaneously generated all the results from experiments. It can also be applied to the other blended amine systems.

5.4 Conclusions

1. The accuracy validation test for the pH + NMR method and NMR calibration test were performed on a typical aqueous MEA solvent. The results indicated the pH method was accurate with an AAD% of about 3%, and the NMR calibration method was slightly more accurate with an AAD% of about 2%. The pH + NMR method and NMR calibration method can be applied to a quaternary MEA-DEAB-CO$_2$-H$_2$O for a VLE model analysis as a typical example of RNH$_2$-R’$_3$N-CO$_2$-H$_2$O systems. This NMR calibration method is applicable to a blended amine system and can generate a useful database, at room and higher temperatures. It is very important to perform an NMR peaks calibration first, and perform peak assignment, peak area integration, zero line correction onto spectra interpretation, and data acquisition in order to generate accurate ion speciation data.

2. The full data acquisition approach has been successfully developed for the
complex quaternary amine systems has with both methods for the VLE model. It can be applied to other binary blended amine R\textsubscript{N}H\textsubscript{2}-R\textprime{}\textsubscript{3}N-CO\textsubscript{2}-H\textsubscript{2}O systems as well if amine K values are available from the literature and corresponding NMR calibration curves are prepared beforehand. The equations are still applicable, with calibration equations and parameters replaced with other amines.

3. The ion speciation plots for a blended amine are similar to that of a single amine. Carbamate is more stable than bicarbonate. The major form of CO\textsubscript{2} in aqueous systems is the carbamate (HO-CH\textsubscript{2}-CH\textsubscript{2}-NH-COO\textsuperscript{−}) rather than bicarbonate (HCO\textsubscript{3}⁻) for a blended amine system composed mainly of MEA. The concentration of carbonate CO\textsubscript{3}^{2−} is from negligible to zero. A tertiary amine (such as DEAB) reacts in the solution as a proton acceptor / Brønsted base.
5.5 References


www.chtf.stuba.sk/cl/seminar/VnmrJLiquids.pdf (online address)
Chapter 6  1D NMR analysis of blended amine systems at higher temperature and introduction to 2D spectra studies

part II: the VLE Model under high temperature and 2D NMR

This chapter includes the first application of a 1D NMR calibration technique performed on the novel blended amine solution (MEA-DEAB-CO₂-H₂O) in a high temperature region from 40 to 70°C. An NMR analysis was performed on the 5M / 1.25M solutions to detect ion speciation data for a VLE model, in a temperature region where conventional pH meter testing is not applicable. The predicted ion speciation plot under 90°C can be generated through data extrapolation based on the VLE models, ion concentration tables and plots at 24, 40, 50, 60 and 70°C. This predicted plot facilitates an amine regeneration study. Moreover, 2D NMR analysis was performed on the blended amine solution to illustrate the interaction of the H-C bond.

6.1 Introduction

Chapter 5 already applied the pH+ NMR and NMR calibration method onto the quaternary amine systems at room temperature, chapter 6 applied NMR calibration methods for MEA-DEAB-CO₂-H₂O solutions of 5M/1.25M MEA/DEAB molar ratio at 40, 50, 60 and 70°C. The ion speciation plots at 90°C were then extrapolated based on the plots generated at 24, 40, 50, 60 and 70°C. Chapter 5, and 6 can be regarded as an integrated section of NMR analysis of
blended MEA-DEAB-CO₂-H₂O systems from 24-90°C.

Analysis at low temperatures does not allow for the study of the roles of different species as they affect the energy requirements for solvent regeneration, the step of which constitutes about 70% of the operating cost for amine-based CO₂ capture. Our current study is intended to broaden the boundaries at higher operating amine solution temperatures (40 – at least 70 °C).

According to Shi et al. [1] most of the successful NMR research for speciation in the literature has been focused on the ternary system (essentially CO₂ loaded single amine solutions). There are scant reports of successful experimental tests for the quaternary systems such as blended amine Bötinger et al. [8] have performed NMR analysis of blended amine systems MDEA-PZ-CO₂-H₂O from 293 to 333 K (20 to 60 °C), which seems to be the first trial for blended amines. However, their ion speciation plot was accurate for only the ternary MDEA-CO₂-H₂O but far from accurate for the quaternary MDEA-PZ-CO₂-H₂O as reported by the authors.[8]

Given the huge benefit of amine blends in reducing the heat duty for solvent regeneration [7] the need to quantify the ion species as they affect regeneration heat duty, and the complexity of the chemical interactions in such systems, it is highly desireable to develop an accurate method for speciation and VLE analysis of quaternary systems at higher temperatures.

In the case of operating temperature, it is known that VLE models and speciation analysis performed at room temperature can only effectively reflect the
CO₂ absorption process. This implies that it is necessary to generate the ion speciation plot at higher temperatures in order to enable the study of the solvent regeneration process for CO₂ stripping, which would typically occur at temperatures ≥ 90°C.[7] It is known that any method that uses the pH method is restricted to lower temperatures. In conformance, some NMR analytical works have been reported without the use of a pH meter. But such NMR results have not been shown to provide accurate ion speciation results.[2, 8] Jakobsen et al.[2] attempted the sole use of ¹³C NMR analysis only without the pH test at 70 and 90°C for rich MEA solution for carbamate stability test. This conflicted in terms of temperature with their NMR analysis for the VLE models of MEA solutions which were performed at 20 and 40°C. Also, Böttinger et al.[11] performed ¹H and ¹³C NMR analysis of MEA-CO₂-H₂O and DEA-CO₂-H₂O for ion concentration plots at temperatures ranging from 15 to 80°C without a pH meter. However, their methods could not distinguish between protonated amines and free amines (MEAH⁺/MEA, DEAH⁺/DEA), as expected. As such, the researchers plotted the sum of the concentrations, resulting in inaccurate representation of the speciation plots.[11]

While the NMR instrument can test amine-CO₂-H₂O samples up to 90°C,[2] a pH meter is unable to go up to such temperatures. Also, while the pH meter along with the Ka of amineH⁺ can distinguish AmineH⁺/amine⁻ it can only test the solution at temperatures < 45°C at such environments for the amine-CO₂-H₂O system. Without pH tests, the ion speciation plots are incomplete and therefore
inaccurate since $^1$H and $^{13}$C NMR peaks alone cannot distinguish AmineH$^+$/Amine because of fast proton exchange. The NMR calibration method like any other NMR method can perform tests at high temperatures. For example, (1) NMR can test samples up to 70-90°C under specific operating conditions; (2) NMR calibration curves can distinguish AmineH$^+$/amine independently.[6] Thus, it appears possible the ion speciation can be obtained solely from an NMR analysis for quaternary amine solutions at higher temperatures with calibration procedures.

6.2 Experimental investigation of 1D and 2D NMR

6.2.1 Experimental analysis of major ions from blended amine solution

$\text{HCO}_3^- \text{/ CO}_3^{2-}$ analysis

As mentioned previously, the chemical shift of bicarbonate/carbonate ($\text{HCO}_3^-/\text{CO}_3^{2-}$) is very sensitive to temperature. The exact chemical shifts of $\text{Na}_2\text{CO}_3$ and $\text{NaHCO}_3$ solutions needed to be tested and recorded under different temperatures; 40, 50, 60 and 70°C. The variations of the chemical shift are small: for $\text{NaHCO}_3$, $\Delta \delta = +0.06$ ppm and for $\text{Na}_2\text{CO}_3$, $\Delta \delta = +0.20$ ppm. It was not accurate to directly quote data from the literature.

NMR calibration analysis of amines

NMR analyses of MEA and DEAB solutions were performed in order to generate the calibration curves in preparation for the experiments, as mentioned in Section 3.3.2. Several calibration sample tubes were prepared with protonation ratios of nHCl vs. nMEA$_0$ at 0.0, 0.25, 0.50, 0.8, 1.0, and 1.2. The ratios of nHCl vs. nDEAB$_0$ for DEAB were 0.0, 0.20, 0.40, 0.6, 0.8, 1.0, and 1.2. The $^{13}$C NMR
analysis was performed on the 13 samples at several temperatures; 40, 50, 60 and 70°C.

However, MEA-DEAB-CO$_2$-H$_2$O, C$_1$ and C$_3$ were selected as calibration curves (Section 5.2) for the blended amine systems. [8] C$_6$ was not selected to simplify the calibration process since the chemical shift of C$_6$ is close to that of MEA and carbamate. There are 3 calibration lines at one specific temperature, one line for MEA and two lines for DEAB. All of the curves were linear with a high accuracy ($R^2 > 0.99$). They were grouped as a set of standard calibration curves under that temperature. Therefore, the direct correlations between the chemical shift $\delta$ and protonation ratio $x$ for MEA and DEAB were established with calibration equations.

Another property of the calibration method is that the chemical shifts of the samples are sensitive to the operating temperature. For example, the chemical shifts of $^{13}$C from the same MEA sample at 24, 40, 50, 60, and 70°C were different. Therefore, four sets of calibration curves were applied at 40, 50, 60, and 70°C, to detect the ion concentrations of amines. (Fig 6.1, Table 6.1)

**NMR analysis of MEA-DEAB-CO$_2$-H$_2$O samples**

The formal experimental procedure was performed after the calibration tests were completed. The blended amine solution was prepared (50 ml 5.0 M MEA + 1.25 M DEAB $\pm$ 0.025 M). Pure CO$_2$ was introduced into the solution for 45-60 seconds. Then, 800 µL of solution was collected into the NMR sample tube and recorded as sample #1 (the first loaded sample), and then 2 ml of solution was
pipetted and titrated for CO₂ loading as α₁ with a Chittick apparatus [9]. The procedures were repeated 8 times for each CO₂ loading in preparation for 8 samples as a full database (α₁ to α₈). After 8 NMR samples were prepared, the NMR tubes were tightly sealed with paraffin to ensure no leakage of CO₂ gas.

The NMR calibration process was similar at high temperatures as it was at room temperature except (i) the top of the NMR tube was sealed with paraffin to avoid gas leakage, and (ii) the steps related to the pH test were not completed. The latter tests were performed with 5M/1.25M MEA-DEAB solutions at 40, 50, 60 and 70°C. A separate experiment using the 5M/1.25M MEA-DEAB solution with a loading of 0.50 mol CO₂/mol total amine was completed at 70°C whereby the sample was put in a vial, tightly sealed with paraffin and kept in a water bath at 70°C for 10 min. The loading only changed to 0.49 mol CO₂/mol of total amine. Thus, the experimental error in relation to trace amounts of CO₂ leakage was negligible.

2D NMR analysis

The 2D NMR was performed on sample #1 of blended amine with low CO₂ loading. The correlation spectroscopy COSY mode pulse sequence was applied to plot the ¹H vs ¹H 2D spectra of this sample. The pulse sequence of the Heteronuclear Multiple Quantum Correlation (HMQC) method was applied to plot the ¹H vs ¹³C 2D spectra of this sample. The relaxed delay and acquisition times were 1.0 and 0.213 seconds, respectively. For the COSY model, the width of both axes were 4803.1 Hz with the same elements. The width of ¹H was 4803.1
Hz and that of $^{13}$C was 12837.0 Hz for the HMQC model. Details regarding the 2D NMR instruments can be obtained from the online manual [11].

### 6.2.2 Data acquisition method with calibration curves

The difference between the current project and the project described in Chapter 5 is the omission of the pH method. The reaction schemes are listed in equations 5.1-5.7. All the equations and thermodynamic models related to pH testing were excluded because the NMR calibration method tested the sample independently. Current data acquisition was focused on the $^{13}$C NMR spectra in terms of peak assignment, zero line correction, and area integration, as in Chapter 5. After a zero line correction, the $^{13}$C chemical shifts for MEA-COO$^-$ were the same as sample #1, an internal standard, for all 8 samples. The chemical shifts for the same sample only varied with temperature. The data acquisition method is similar to that described in Section 5.2.5, with equations (6.1) to (6.9) but the parameters in the equations differed at different temperatures.

Moreover, the exact equations (6.1), (6.3) to (6.4) and (6.8) to (6.9) are only suitable for the NMR results at 40°C. The calibration equations are different at 50, 60, 70°C, and the exact chemical shift of bicarbonate and carbonate differ. However, equations (6.5) to (6.7) are applicable in all the temperature regions (24 -70 °C) because no parameters are involved.

The three calibration equations (6.1), (6.3), and (6.4), for amine samples tested at other temperatures (50, 60, and 70 °C), should be replaced with the correct equations for a specific temperature (Table 6.1.2). Moreover, the chemical
shift $\delta$ of $\text{HCO}_3^-$ and $\text{CO}_3^{2-}$ in equations (6.8) and (6.9) [10] should be replaced with the correct variable in Table 6.1.1 and specific temperature, since they are very sensitive to the operating temperature.[7] Most formats for the equations are similar and consistent with the exception of several parameters. It must be emphasized that 160.798 and 160.313 ppm are the chemical shifts for $[\text{CO}_3^{2-}]$ and $[\text{HCO}_3^-]$ at 40°C, the exact chemical shift needs to be replaced under operating temperatures to reach the high accuracy of the experimental data [7] for equations 6.8 to 6. 9. It is inappropriate to quote the data directly from the literature because the two values are very temperature sensitive [7].

**MEAH’/MEA:**

<table>
<thead>
<tr>
<th>Equation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_0$: $\delta = -0.0550 \times 100% + 63.475$ (40 °C)</td>
<td>(6.1)</td>
</tr>
<tr>
<td>$[\text{MEA}] + [\text{MEAH}^+] = n\text{MEA}_0$</td>
<td>(6.2)</td>
</tr>
</tbody>
</table>

**DEABH’/DEAB:**

<table>
<thead>
<tr>
<th>Equation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_1$: $\delta = -0.0188 \times 100% + 10.443$ (40 °C)</td>
<td>(6.3)</td>
</tr>
<tr>
<td>$C_3$: $\delta = -0.0216 \times 100% + 34.218$ (40 °C)</td>
<td>(6.4)</td>
</tr>
<tr>
<td>$[\text{DEAB}] + [\text{DEABH}^+] = n\text{DEAB}_0$</td>
<td>(6.5)</td>
</tr>
</tbody>
</table>

**MEA-COO’:**

$$\frac{[\text{MEA- COO}^-]}{[\text{HCO}_3^-]+[\text{CO}_3^{2-}]} = R \quad \text{(NMR peak area integration)} \quad (6.6)[10]$$

$$[\text{MEA} - \text{COO}^-] = \frac{R}{1+R} [\text{CO}_2]_0$$

$$= \frac{R}{1+R} \alpha \times ([\text{MEA}]_0 + [\text{DEAB}]_0) \quad (6.7) \ [7]$$

**HCO$_3$’ / CO$_3^{2-}$:**

$$[\text{CO}_3^{2-}] = \frac{5-160.798}{7.515(1+R)} [\text{CO}_2]_0 = \frac{5-160.798}{7.515(1+R)} \alpha \times ([\text{MEA}]_0 + [\text{DEAB}]_0)(40°C) \quad (6.8) \ [7, 10]$$

$$[\text{HCO}_3^-] = \frac{168.313-\delta}{7.515(1+R)} [\text{CO}_2]_0 = \frac{168.313-\delta}{7.515(1+R)} \alpha \times ([\text{MEA}]_0 + [\text{DEAB}]_0)(40°C) \quad (6.9)[7, 10]$$
6.3 Results and Discussion

6.3.1 Calibration of MEA and DEAB solutions from 40-70°C

The exact $^{13}$C NMR spectra of the standard MEA and DEAB solutions are grouped in Table 6.1.1 with their typical chemical shifts. The spectra of bicarbonate and carbonate were also recorded at 40, 50, 60, and 70°C.

It is apparent that the chemical shifts for MEA and DEAB increase with an increase in temperature from 24 to 70°C. This phenomenon was also observed by Jakobsen et al. (2005), and the observed trend is consistent with the present research results [7]. The chemical shift moves to the de-shielded region ($\delta$ increase) with an increase in temperature. However, the scales were not the same: MEA, $\Delta\delta = +0.70$ ppm, DEAB, $\Delta\delta_1 = +0.52$ ppm and $\Delta\delta_2 = +0.80$ ppm. The trend is evident from Figures 6.1.1 to 6.1.2. the trend is not clear in the chemical shifts of bicarbonate and carbonate, where they did not change to the same degree as the amines. They seemed to randomly deviate from an average value: NaHCO$_3$, $\Delta\delta = +0.06$ ppm and Na$_2$CO$_3$, $\Delta\delta = +0.20$ ppm. The average values for the samples, in the temperature range from 24-70 ºC, are 160.781 ppm for NaHCO$_3$ and 168.444 ppm for Na$_2$CO$_3$, respectively. This is due to the equilibrium constant K. The chemical shift of bicarbonate hardly changes with temperature, but carbonate shifts 0.20 ppm. It is inappropriate to assume the chemicals increase the chemical shift at the same scale. The average value can be selected as an approximation for a similar NMR analysis.
Table 6.1.1 $^{13}$C NMR data for MEA, DEAB solutions with protonation and bicarbonate/carbonate under high temperature

<table>
<thead>
<tr>
<th>Compound</th>
<th>T °C</th>
<th>Protonation ratio %</th>
<th>Δδ ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0</td>
<td>25</td>
</tr>
<tr>
<td>MEA C$_2$</td>
<td>40.0</td>
<td>63.550</td>
<td>62.093</td>
</tr>
<tr>
<td></td>
<td>50.0</td>
<td>63.697</td>
<td>62.225</td>
</tr>
<tr>
<td></td>
<td>60.0</td>
<td>63.843</td>
<td>62.364</td>
</tr>
<tr>
<td></td>
<td>70.0</td>
<td>63.990</td>
<td>62.452</td>
</tr>
<tr>
<td>DEAB C$_3$</td>
<td>40.0</td>
<td>34.208</td>
<td>33.820</td>
</tr>
<tr>
<td></td>
<td>50.0</td>
<td>34.406</td>
<td>33.996</td>
</tr>
<tr>
<td></td>
<td>60.0</td>
<td>34.574</td>
<td>34.172</td>
</tr>
<tr>
<td></td>
<td>70.0</td>
<td>34.743</td>
<td>34.362</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>T °C</th>
<th>(δ) ppm</th>
<th>average</th>
<th>Carbonate</th>
<th>T °C</th>
<th>(δ) ppm</th>
<th>average</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCO$_3^-$</td>
<td>24.0</td>
<td>160.769</td>
<td>CO$_3^{2-}$</td>
<td>24.0</td>
<td>168.488</td>
<td></td>
</tr>
<tr>
<td></td>
<td>24.5</td>
<td>160.716</td>
<td></td>
<td>24.5</td>
<td>168.467</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40.0</td>
<td>160.798</td>
<td></td>
<td>40.0</td>
<td>168.313</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50.0</td>
<td>160.754</td>
<td></td>
<td>50.0</td>
<td>168.401</td>
<td></td>
</tr>
<tr>
<td></td>
<td>60.0</td>
<td>160.820</td>
<td></td>
<td>60.0</td>
<td>168.475</td>
<td></td>
</tr>
<tr>
<td></td>
<td>70.0</td>
<td>160.828</td>
<td>160.781</td>
<td>70.0</td>
<td>168.518</td>
<td>168.444</td>
</tr>
</tbody>
</table>
Fig. 6.1.1 NMR calibration of MEA from 40 – 70°C.
Fig. 6.1.2 NMR calibration of DEAB (C₁ and C₃) at from 40-70°C.

Table 6.1.2 NMR calibration equations for MEA and DEAB at different temperatures

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>Chemicals</th>
<th>Equations of labeled C δ = f(x) 0 &lt; x &lt; 100</th>
<th>of calibration lines x = f⁻¹(δ)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>24.0</td>
<td>MEA C₂</td>
<td>δ = -0.0551 x + 63.247</td>
<td>0.995</td>
<td>x = (63.247 - δ)/0.0551</td>
</tr>
<tr>
<td></td>
<td>DEAB C₁</td>
<td>δ = -0.0182₈ x + 10.228</td>
<td>0.998</td>
<td>x = (10.228 - δ)/0.0183</td>
</tr>
<tr>
<td></td>
<td>DEAB C₃</td>
<td>δ = -0.0206₅ x + 33.959</td>
<td>0.998</td>
<td>x = (33.959 - δ)/0.0206₅</td>
</tr>
<tr>
<td>40.0</td>
<td>MEA C₂</td>
<td>δ = -0.0550 x + 63.47₅₉</td>
<td>0.998</td>
<td>x = (63.47₅₉ - δ)/0.0550</td>
</tr>
<tr>
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<td>DEAB C₁</td>
<td>δ = -0.0188 x + 10.44₃₉</td>
<td>0.998</td>
<td>x = (10.44₃₉ - δ)/0.0188</td>
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<tr>
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<td>DEAB C₃</td>
<td>δ = -0.0216 x + 34.21₈₃₉</td>
<td>0.998</td>
<td>x = (34.21₈₃₉ - δ)/0.0216</td>
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<tr>
<td>50.0</td>
<td>MEA C₂</td>
<td>δ = -0.0550 x + 63.61₃₃₉</td>
<td>0.998</td>
<td>x = (63.61₃₃₉ - δ)/0.0550</td>
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<td>DEAB C₁</td>
<td>δ = -0.0186 x + 10.5₈₄₃₉</td>
<td>0.994</td>
<td>x = (10.5₈₄₃₉ - δ)/0.0186</td>
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<td>DEAB C₃</td>
<td>δ = -0.0216 x + 34.3₉₈₃₉</td>
<td>0.995</td>
<td>x = (34.3₉₈₃₉ - δ)/0.0216</td>
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<tr>
<td>60.0</td>
<td>MEA C₂</td>
<td>δ = -0.0551 x + 63.7₆₂₅₉</td>
<td>0.999</td>
<td>x = (63.7₆₂₅₉ - δ)/0.0551</td>
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<td>DEAB C₁</td>
<td>δ = -0.018₈ x + 10.7₂₂₃₉</td>
<td>0.996</td>
<td>x = (10.7₂₂₃₉ - δ)/0.018₈</td>
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<td>DEAB C₃</td>
<td>δ = -0.022₀ x + 34.₅₇₂₉</td>
<td>0.9₉ₗ</td>
<td>x = (34.₅₇₂₉ - δ)/0.022₀</td>
</tr>
<tr>
<td>70.0</td>
<td>MEA C₂</td>
<td>δ = -0.055₈ x + 63.₈₉₆₆₉</td>
<td>0.₉₉₉</td>
<td>x = (63.₈₉₆₆₉ - δ)/0.05₉₈</td>
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<td>DEAB C₁</td>
<td>δ = -0.01₈₉ x + 10.₈₆₃₉</td>
<td>0.₉₉₇</td>
<td>x = (10.₈₆₃₉ - δ)/0.0₁₈₉</td>
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<td>DEAB C₃</td>
<td>δ = -0.02₂₄ x + 3₄.⁷₆₉₉</td>
<td>0.₉₉₇</td>
<td>x = (3₄.⁷₆₉₉ - δ)/0.0₂₂₄</td>
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</table>
Based on the chemical shifts in Table 6.1.1, the calibration curves for MEA and DEAB can be generated from Figs 6.1.1 to 6.1.2, one for C₂ of MEA and two for C₁ and C₃ of DEAB. All the calibration curve lines were generated with linear regression. The equations are clearly listed. The chemical shifts in the calibration curves increase simultaneously with increasing temperature.

Finally, the calibration equations were grouped in Table 6.1.2 under various temperatures. They are regarded as highly accurate because \( R^2 > 0.990 \) is the selection criteria for the calibration curve [7][8]. It is not necessary to duplicate the calibration tests with the recorded calibration curves. The ratio \( x \) and exact concentrations of AmineH⁺/Amine can be calculated based on the chemical shift \( \delta \) with certain \(^{13}\text{C}\) NMR spectra of prepared MEA and DEAB samples shown in Fig 5.3.1. Each set of equations is suitable for the NMR spectra of blended amine samples at concentrations of 0-5M MEA and 0-2M DEAB in the 24-70 °C temperature range and 0 – 0.52 mol/mol loading.

6.3.2 \(^{13}\text{C}\) NMR spectra analysis of blended amine samples

The NMR analyses were performed on the 8 samples at intervals from 40 to 70°C. The data from the NMR spectra are grouped in Table 6.2, from 6.2.1 to 6.2.4. All five tables (5.3, 6.2.1 – 6.2.4) were similar because the same set of samples were tested from 24-70°C. The approach with each table was consistent, including peak assignment, \( Z_0 \) line correction, and peak area integration, as in Section 5.2.3. Table 6.2.4 (70°C) is presented as an example as this is the highest
operating temperature ever reached; the remaining three tables are also available.

The chemical shifts of carbamate also increase with an increase in temperature for the typical $^{13}$C peaks of MEA-COO$^-$ at 164.5-165.0 ppm. The chemical shift of sample #1 is the foremost research interest, second to the $Z_0$ line correction. The change in chemical shift for sample #1 from 24 to 70°C was $\Delta \delta = + 0.45$ ppm, which is inconsistent with the shift for MEA, (+ 0.70 ppm).

The details of the original NMR spectra have been described. The peak assignment and peak area integration are demonstrated in Figure 5.3.1. The methods are similar and consistent and can be widely applied to other blended amine systems.
Table 6.2.1 – 6.2.4 $^{13}$C NMR spectra of MEA-DEAB-CO$_2$-H$_2$O solution at
40-70°C

Table 6.2.1 $^{13}$C chemical shift of MEA-DEAB-CO$_2$-H$_2$O solution 40°C $^a$

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<th>MEA/MAH$^a$</th>
<th>DEAB / DEAB$^a$</th>
<th>Carbamate</th>
<th>HCO$_3$-</th>
<th>HCO$_2$-</th>
<th>Cx</th>
<th>area ratio</th>
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<td>0 reference</td>
<td>0</td>
<td>42.837 61.590</td>
<td>10.440 22.489 34.208 46.433 49.769 67.432</td>
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<td>160.798 168.313</td>
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<tr>
<td>5.0 M MEA+ 1.275 M DEAB</td>
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<td>42.639 62.305</td>
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<td>160.798 168.313</td>
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<td>0.2282</td>
<td>42.404 61.565</td>
<td>9.297 22.599 32.875 47.004 49.960 66.121</td>
<td>43.386 61.683 164.724</td>
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<td>8.902 22.511 32.443 47.143 48.931 65.814</td>
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Table 6.2.2 $^{13}$C chemical shift of MEA-DEAB-CO$_2$-H$_2$O solution 50°C

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<th>loading (mol CO$_2$ / mol Am)</th>
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<th>DEAB / DEAB$^a$</th>
<th>Carbamate</th>
<th>HCO$_3$-</th>
<th>HCO$_2$-</th>
<th>Cx</th>
<th>area ratio</th>
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<td>10.594 22.635 34.406 46.616 49.960 67.572</td>
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<td>41.957 58.990</td>
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158
### Table 6.2.3 $^{13}$C chemical shift of MEA-DEAB-CO$_2$-H$_2$O solution 60°C

<table>
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<th>δ (ppm)</th>
<th>loading</th>
<th>MEA/MEAH$^+$</th>
<th>DEAB / DEABH$^+$</th>
<th>Carbamate</th>
<th>HCO$_3$/CO$_2$ $^+$</th>
<th>Cx</th>
<th>area ratio</th>
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<td>Sample #</td>
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<td>C$_5$</td>
<td>C$_1$</td>
<td>C$_2$</td>
<td>C$_3$</td>
<td>C$_4$</td>
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### Table 6.2.4 $^{13}$C chemical shift of MEA-DEAB-CO$_2$-H$_2$O solution 70°C

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<th>Carbamate</th>
<th>HCO$_3$/CO$_2$ $^+$</th>
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<td>Sample #</td>
<td>mol CO$_2$/mol Am</td>
<td>C$_4$</td>
<td>C$_5$</td>
<td>C$_1$</td>
<td>C$_2$</td>
<td>C$_3$</td>
<td>C$_4$</td>
</tr>
<tr>
<td>0 reference</td>
<td>0</td>
<td>43.381</td>
<td>63.900</td>
<td>10.843</td>
<td>22.855</td>
<td>34.743</td>
<td>46.894</td>
</tr>
<tr>
<td>5.0 M MEA+ 1.275 M DEAB</td>
<td></td>
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<tr>
<td># 1 origin</td>
<td>0.1903</td>
<td>42.902</td>
<td>62.584</td>
<td>9.993</td>
<td>22.884</td>
<td>33.637</td>
<td>47.231</td>
</tr>
<tr>
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<td># 2 origin</td>
<td>0.2582</td>
<td>42.675</td>
<td>61.858</td>
<td>9.532</td>
<td>22.797</td>
<td>33.183</td>
<td>47.334</td>
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<td># 3 origin</td>
<td>0.3311</td>
<td>42.419</td>
<td>60.950</td>
<td>9.151</td>
<td>22.716</td>
<td>32.751</td>
<td>47.502</td>
</tr>
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</tr>
<tr>
<td># 4 origin</td>
<td>0.4173</td>
<td>42.192</td>
<td>59.983</td>
<td>8.924</td>
<td>22.701</td>
<td>32.516</td>
<td>47.693</td>
</tr>
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<tr>
<td># 5 origin</td>
<td>0.4538</td>
<td>41.936</td>
<td>59.148</td>
<td>8.711</td>
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<tr>
<td># 6 origin</td>
<td>0.4703</td>
<td>41.855</td>
<td>58.885</td>
<td>8.660</td>
<td>22.570</td>
<td>32.194</td>
<td>47.590</td>
</tr>
<tr>
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</tr>
<tr>
<td># 7 origin</td>
<td>0.4869</td>
<td>41.789</td>
<td>58.665</td>
<td>8.624</td>
<td>22.562</td>
<td>32.172</td>
<td>47.568</td>
</tr>
<tr>
<td># 7 correction</td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td># 8 origin</td>
<td>0.5262</td>
<td>41.738</td>
<td>58.511</td>
<td>8.580</td>
<td>22.540</td>
<td>32.121</td>
<td>47.554</td>
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<tr>
<td># 8 correction</td>
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<td></td>
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</tr>
</tbody>
</table>

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### 6.3.3 Ion speciation table and plots of VLE model from 40-70°C

After obtaining successful results from analysis at room temperature, the NMR calibration method was applied to the VLE model analysis of quaternary amine systems at higher temperatures, up to 70°C. The adjusted experimental NMR data shown in Tables 6.2.1 to 6.2.4 were after same treatment of peak assignment, $Z_0$ correction and peak area integration. The ion concentration tables for the major ions were calculated with specific calibration equations; They are grouped in Table 6.3 with data acquisition eqns (6.1-6.9). The ion concentrations for the major components $[\text{MEA}] / [\text{MEAH}^+]$, $[\text{DEAB}] / [\text{DEABH}^+]$, $[\text{HCO}_3^-] / [\text{CO}_3^{2-}]$ and $[\text{MEACOO}^-]$ were calculated from 40 - 70°C as shown in Table 6.3 and plotted in Fig. 6.2.

Therefore, four ion speciation plots were generated from 40 to 70°C as shown in Fig. 6.2 with the trends shown. This is the first time a 1D NMR analysis was performed on any blended amine system to successfully generate a VLE speciation plot at high temperature. Jakobsen et al.[2] tried NMR analysis on carbamate at 70 and 90°C to detect the dynamic NMR phenomena but not an ion speciation plot. Böttinger et al.[8, 11] tried a similar analysis on ternary and quaternary systems but were unsuccessful. The ratios of bicarbonate/carbonate over carbamate increase with increasing temperature at similar ratios, monotonically. The minimum CO$_2$ loadings, where bicarbonate was detectable, decreased from 0.418 mol CO$_2$/mol amine (at 24°C) down to 0.333 mol CO$_2$/mol amine (at 70°C) when the temperature was increased from 24 to 70°C. This is
evident in Fig. 6.2. This indicates the carbamate exchange reaction, eqn. (22), is endothermic and carbamate breakdown is facilitated under heat to generate the bicarbonate.

**MEA-COO\(^-\) + H\(_2\)O ⇌ MEA + HCO\(_3\)^- \text{ carbamate exchange (6.10)}**

**Table 6.3** Ion concentration (mol/L) tables of MEA-DEAB-CO\(_2\)-H\(_2\)O solution (5M – 1.25 M ± 0.025 M) under different temperature, from 24 to 70°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>loading</th>
<th>24(^\circ)C</th>
<th>40(^\circ)C</th>
<th>50(^\circ)C</th>
<th>sum of</th>
<th>160.769</th>
<th>168.488</th>
<th>160.798</th>
<th>168.313</th>
<th>160.754</th>
<th>168.401</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>MEA</td>
<td>MEAH(^+)</td>
<td>DEAB</td>
<td>DEABH(^+)</td>
<td>C-mate</td>
<td>HCO(_3^+)/CO(_3^{2-})</td>
<td>HCO(_3^-)</td>
<td>CO(_3^{2-})</td>
<td>HCO(_3^+)/CO(_3^{2-})</td>
<td>HCO(_3^-)</td>
</tr>
<tr>
<td>#0</td>
<td>0.000</td>
<td>5.000</td>
<td>0.000</td>
<td>1.275</td>
<td>0.000</td>
<td>0.000</td>
<td>N / A</td>
<td>0.000</td>
<td>0.000</td>
<td>N / A</td>
<td>0.000</td>
</tr>
<tr>
<td>#1</td>
<td>0.190</td>
<td>3.014</td>
<td>0.792</td>
<td>0.758</td>
<td>0.517</td>
<td>1.194</td>
<td>N / A</td>
<td>0.000</td>
<td>0.000</td>
<td>N / A</td>
<td>0.000</td>
</tr>
<tr>
<td>#2</td>
<td>0.258</td>
<td>2.240</td>
<td>1.140</td>
<td>0.530</td>
<td>0.745</td>
<td>1.620</td>
<td>N / A</td>
<td>0.000</td>
<td>0.000</td>
<td>N / A</td>
<td>0.000</td>
</tr>
<tr>
<td>#3</td>
<td>0.331</td>
<td>1.428</td>
<td>1.494</td>
<td>0.278</td>
<td>0.997</td>
<td>2.078</td>
<td>N / A</td>
<td>0.000</td>
<td>0.000</td>
<td>N / A</td>
<td>0.000</td>
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<tr>
<td>#4</td>
<td>0.417</td>
<td>0.673</td>
<td>1.708</td>
<td>0.100</td>
<td>1.175</td>
<td>2.619</td>
<td>N / A</td>
<td>0.000</td>
<td>0.000</td>
<td>N / A</td>
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</tr>
<tr>
<td>#5</td>
<td>0.454</td>
<td>0.365</td>
<td>2.009</td>
<td>0.040</td>
<td>1.235</td>
<td>2.625</td>
<td>0.222</td>
<td>0.187</td>
<td>0.035</td>
<td>0.355</td>
<td>0.316</td>
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<tr>
<td>#6</td>
<td>0.470</td>
<td>0.267</td>
<td>2.136</td>
<td>0.007</td>
<td>1.268</td>
<td>2.597</td>
<td>0.355</td>
<td>0.316</td>
<td>0.039</td>
<td>0.465</td>
<td>0.442</td>
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<tr>
<td>#7</td>
<td>0.487</td>
<td>0.190</td>
<td>2.219</td>
<td>0.001</td>
<td>1.274</td>
<td>2.591</td>
<td>0.465</td>
<td>0.442</td>
<td>0.022</td>
<td>0.674</td>
<td>0.653</td>
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<tr>
<td>#8</td>
<td>0.521</td>
<td>0.143</td>
<td>2.266</td>
<td>0.000</td>
<td>1.275</td>
<td>2.598</td>
<td>0.674</td>
<td>0.653</td>
<td>0.021</td>
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</tr>
</tbody>
</table>

161
<table>
<thead>
<tr>
<th>Sample</th>
<th>loading</th>
<th>5.0 M A+ 1.25 M B</th>
<th>60°C</th>
<th>Ion Concentrations mol/L</th>
<th>70°C</th>
<th>Ion Concentrations mol/L</th>
<th>sum of</th>
<th>160.828</th>
<th>168.475</th>
<th>160.828</th>
<th>168.518</th>
</tr>
</thead>
<tbody>
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<td>#7</td>
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<td>0.301 2.228 0.000 1.275 2.471</td>
<td>0.584 0.568 0.016</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>#8</td>
<td>0.521</td>
<td>0.236 2.361 0.000 1.275 2.403</td>
<td>0.869 0.857 0.012</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

5.0 M A+ 1.25 M B

50 M A+ 1.25 M B solution under 24°C (Same as Figure 5.5(4))
Fig. 6.2 Ion speciation plot of MEA-DEAB-CO$_2$-H$_2$O solution (5.0 M + 1.25 M ± 0.025 M) under 40-70°C
6.3.4 Predicted ion speciation table and plots at 90°C

The NMR instrument becomes unstable beyond 70°C according to experimental observations. The experimental NMR analysis was discontinued. However, other researchers have performed NMR analysis of amine samples up to 90°C.[2] The ion speciation plot of the VLE models around 90°C was the present research interest because the VLE models under amine regeneration conditions were important for amine regeneration tests.[7, 12] The exact ion concentrations at this temperature were not measured using NMR analysis. However, the ion speciation table and plot were predicted using the current experimental results in Table 6.4 and Figs. 6.3. Three ratios: MEA/MEAH⁺, DEAB/DEABH⁺, and carbamate/bicarbonate illustrate the extrapolation with respect to temperature. All three ratios decreased with an increase in temperature. The first two were obtained from the literature, [2, 6] and the third was obtained from the NMR spectra via experimental measurements. This revealed an increased concentration of MEAH⁺, DEABH⁺, and bicarbonate (HCO₃⁻) and a decreased concentration of free MEA, DEAB, and carbamate. The predicted ion concentrations at 90°C were calculated and grouped in Fig. 6.4 (Table 6.5). The accuracy of the table and figures are better than the simulation results and comparable with the experimental data. The CO₂ loading in Fig. 6.4, where bicarbonate ions began to be detectable, was 0.253 mol CO₂ / mol amine at 90°C.
Table 6.4 Predicted Ion concentration plot of MEA-DEAB-CO₂-H₂O solution at 90°C

<table>
<thead>
<tr>
<th>Sample #</th>
<th>loading</th>
<th>90 °C</th>
<th>Ion Concentrations mol/L</th>
<th>sum of</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>MEA</td>
<td>MEAH⁺</td>
<td>DEAB</td>
</tr>
<tr>
<td>#0</td>
<td>0.000</td>
<td>5.000</td>
<td>0.000</td>
<td>1.275</td>
</tr>
<tr>
<td>#1</td>
<td>0.190</td>
<td>2.909</td>
<td>0.897</td>
<td>0.550</td>
</tr>
<tr>
<td>#2</td>
<td>0.258</td>
<td>2.180</td>
<td>1.200</td>
<td>0.307</td>
</tr>
<tr>
<td>#3</td>
<td>0.331</td>
<td>1.402</td>
<td>1.520</td>
<td>0.030</td>
</tr>
<tr>
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<td>0.417</td>
<td>0.760</td>
<td>1.913</td>
<td>0.000</td>
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<td>0.454</td>
<td>0.480</td>
<td>2.157</td>
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<td>0.345</td>
<td>2.267</td>
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<td>2.367</td>
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<td>0.521</td>
<td>0.283</td>
<td>2.485</td>
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</table>

Fig. 6.3 Predicted Ion speciation plot of MEA-DEAB-CO₂-H₂O (5.0 M + 1.25 M ±0.025 M) under 90°C
6.3.5 Studies of bicarbonate and carbonate

Bicarbonate and carbonate are important ions within the solutions. According to the ion concentration tables, the carbonate $\text{CO}_3^{2-}$ is negligible for blended amine systems. The bicarbonate $\text{HCO}_3^-$ is important in the blended amine system. The concentrations of $\text{HCO}_3^-$ began to increase with an increase in $\text{CO}_2$ loading and temperature; more bicarbonate was detected because additional bicarbonate was generated from the endothermic carbamate breakdown in eqn (22). The ion concentration of bicarbonate is utilized in the amine regeneration analysis [7]. Therefore, the existence and maximum concentration of bicarbonate have to be examined separately. However, the major challenge is the concentration of $\text{HCO}_3^-$ which is very sensitive to three factors: the $\text{CO}_2$ loading $\alpha$, operating temperature, and ratio of tertiary amine vs. primary amine $\beta$. It is difficult to generate an applicable equation $[\text{HCO}_3^-] = f(\alpha, T, \beta)$ directly because of the complex relations.

Therefore, a simplified way involves selection of the exact data or data extrapolation from the ion speciation from Figs. 6.2 and 6.3 (Table 6.3 and 6.4). The resulting data are given in Fig. 6.4 (Table 6.5) which clearly lists the maximum concentrations of bicarbonate at maximum $\text{CO}_2$ loading as a function of temperature. This is plotted for the 5M/1.25M MEA-DEAB-$\text{CO}_2$-$\text{H}_2\text{O}$ solution at maximum loading $= 0.52 \text{ mol CO}_2 / \text{ mol amine}$ and shown in Fig. 6.4 (Table 6.5). The maximum
concentration of bicarbonate increased from 0.653 mol/L at 24°C to 1.021 mol/L at 90°C. The maximum concentration of bicarbonate is almost 80% of the concentration of the original tertiary amine (n₀DEAB, 1.275 mol/L) under amine regeneration conditions. The lean amine solution contains a negligible amount of bicarbonate because almost all of the CO₂ is converted to carbamate. Trace amounts of bicarbonate are initially detectable at certain – loadings (the turning point) with an increase in CO₂ loading. There was negligible bicarbonate at 24°C until the CO₂ loading reached 0.41 mol/mol, until it reached 0.25 mol/mol at 90°C. The ion concentration of bicarbonate increases with temperature, but the minimum CO₂ loadings at which trace bicarbonate become detectable decrease. The solid dots represent the data from experimental tests, and the hollow dots represent the prediction data at 90°C.
Table 6.5 Turning point of detectable amount of HCO$_3^-$ and maximum concentration of HCO$_3^-$ in MEA-DEAB-CO$_2$-H$_2$O solutions (5M: 1.25M) under 24 - 90°C

<table>
<thead>
<tr>
<th>Temperatures of VLE model (°C)</th>
<th>24.0</th>
<th>40.0</th>
<th>50.0</th>
<th>60.0</th>
<th>70.0</th>
<th>90.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>minimum CO$_2$ loading with detectable amount of HCO$_3^-$ (mol CO$_2$ / mol amine)</td>
<td>0.418</td>
<td>0.420</td>
<td>0.395</td>
<td>0.353</td>
<td>0.333</td>
<td>0.250</td>
</tr>
<tr>
<td>max concentration of HCO$_3^-$ (mol / L)</td>
<td>0.653</td>
<td>0.816</td>
<td>0.869</td>
<td>0.924</td>
<td>0.967</td>
<td>1.021</td>
</tr>
</tbody>
</table>

Fig. 6.4 The minimum CO$_2$ loading with a detectable amount of HCO$_3^-$ and maximum concentration of HCO$_3^-$ in MEA-DEAB-CO$_2$-H$_2$O solutions (5M/1.25M ± 0.025M) within 24-90°C.

a. This plot originated from the VLE plots (Fig 6.2, Fig 6.3) within 24-90°C throughout the temperature interval of CO$_2$ absorption and regeneration.

b. The solid dots were generated from the NMR experiments, and the circle was predicted.
6.3.6 2D NMR spectra

Finally, the 2D NMR analysis was performed to provide a useful database for the study of blended amine solutions. From the 1D NMR analyses, the blended system has 12 $^{13}$C peaks and 15-20 $^1$H peaks, which is very complicated and difficult to detect. Moreover, the connections in the H-C bond for the specific molecule are also complex. Therefore, 1D NMR spectra has limitations that require the application of a 2D NMR study.

Figure 6.5.1 provides a 2D NMR analysis with $^1$H vs $^{13}$C and $^1$H vs $^1$H plots under 24°C. However, the peaks of carbamate are not strong since the loading is low. There are 8 dots in Figure 6.5.1, two of which represent MEA and the rest (6) represent DEAB. The connection of the H-C bond is easily detected, which cannot be shown with 1D NMR spectra. In Figure 6.5.2, symmetric $^1$H vs $^1$H plots are demonstrated with correlation spectroscopy (COSY).[11] There are multiple types of connections for the H in MEA and H inside the DEAB. Further analysis may be applied to the 2D NMR analysis of blended amine systems, if possible.
Fig. 6.5.1 2D NMR spectra (\textsuperscript{1}H vs \textsuperscript{13}C) of MEA-DEAB-CO\textsubscript{2}-H\textsubscript{2}O solution at CO\textsubscript{2} loading 0.18 with HMQC mode.

Fig. 6.5.2 2D NMR spectra (\textsuperscript{1}H vs \textsuperscript{1}H) of MEA-DEAB-CO\textsubscript{2}-H\textsubscript{2}O solution at CO\textsubscript{2} loading 0.18 with COSY mode.
6.4 Conclusion

1. The calibration curve will shift to the de-shielded region (δ increase) with increasing temperature. Moreover, the points shift with increasing temperature at similar ratios in a consistent monotonic manner. The ratio of bicarbonate/carbonate vs. overall CO₂ loading increased from 20.60% to 29.82% for the sample at maximum CO₂ loading (0.528 mol/mol). This phenomenon indicates the carmabate exchange reaction is endothermic. More carbamate will break down and convert to bicarbonate at 90°C than at 24°C.

2. The ion concentration plot and speciation plot can be predicted at 90°C with the current experimental results. The accuracy of the predicted plot is comparable to the experimental tests and better than the simulation data. This plot is helpful for amine regeneration studies.
6.5 References


(5) Böttinger W.; Maiwald M.; Hasse H.; Online NMR spectroscopic study of species distribution in MEA-CO$_2$-H$_2$O and DEA-CO$_2$-H$_2$O. *Fluid Phase Equilib.* **2008**, *263*, 131.


### Appendix Table 1.1. $^{13}$C chemical shift calibration of MEA solutions protonation at different temperature

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>δ MEA ppm</th>
<th>Protonation rate (%)</th>
<th>Δδ ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>24.0</td>
<td>C1  42.837</td>
<td>9.504</td>
<td>41.848</td>
</tr>
<tr>
<td></td>
<td>C2  63.294</td>
<td>9.019</td>
<td>41.621</td>
</tr>
<tr>
<td>40.0</td>
<td>C1  42.837</td>
<td>9.504</td>
<td>41.848</td>
</tr>
<tr>
<td></td>
<td>C2  63.550</td>
<td>9.019</td>
<td>41.621</td>
</tr>
<tr>
<td>50.0</td>
<td>C1  42.837</td>
<td>9.504</td>
<td>41.848</td>
</tr>
<tr>
<td></td>
<td>C2  63.550</td>
<td>9.019</td>
<td>41.621</td>
</tr>
<tr>
<td>60.0</td>
<td>C1  42.837</td>
<td>9.504</td>
<td>41.848</td>
</tr>
<tr>
<td></td>
<td>C2  63.550</td>
<td>9.019</td>
<td>41.621</td>
</tr>
<tr>
<td>70.0</td>
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<td>41.848</td>
</tr>
<tr>
<td></td>
<td>C2  63.550</td>
<td>9.019</td>
<td>41.621</td>
</tr>
</tbody>
</table>

### Appendix Table 1.2. $^{13}$C chemical shift calibration of DEAB solutions protonation at different temperature

<table>
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<tr>
<th>Temp °C</th>
<th>δ DEAB ppm</th>
<th>Protonation rate (%)</th>
<th>Δδ ppm</th>
</tr>
</thead>
<tbody>
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### Appendix Table 6.1.1 The original data of NMR spectra for MEA with protonation

#### Appendix Table 6.1.2 The original data of NMR spectra for DEAB with protonation

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Chapter 7 Catalytic and non catalytic solvent regeneration during absorption-based CO\textsubscript{2} capture with single and blended reactive amine solvents

This chapter is composed of a paper submitted, for molecular potential energy surface (PES) diagrams of the deprotonation of a protonated amine (AmH\textsuperscript{+}) have been developed to elucidate the solvent regeneration process for CO\textsubscript{2} stripping from reactive solvents. The PES diagrams in combination with ion speciation plots of the vapour liquid equilibrium (VLE) model were then used to provide a better understanding of the reasons for the drastic reduction of energy required for CO\textsubscript{2} stripping from some amine solutions under certain operating conditions. Experiments for CO\textsubscript{2} stripping were performed using single and blended amines (namely, MEA, MEA-MDEA, MEA-DEAB (4-(diethylamine)-2-butanol)) with and without solid acid catalysts (Al\textsubscript{2}O\textsubscript{3} or HZSM-5) at 90-95 °C. The results showed that the CO\textsubscript{2} stripping performance decreased in the order: MEA-DEAB with HZSM-5 (38%) > MEA-DEAB with γ-Al\textsubscript{2}O\textsubscript{3} (40%) > MEA-MDEA with HZSM-5 (47%) MEA-DEAB with no catalyst (51%) > MEA with HZSM-5 (65%) > MEA-MDEA with γ-Al\textsubscript{2}O\textsubscript{3}/no catalyst (72%) > MEA with γ-Al\textsubscript{2}O\textsubscript{3} (90%), all relative to MEA with no catalyst (100%). The results further show that the addition of MDEA or DEAB (as tertiary amines) in a blended solvent provided R\textsubscript{3}N and HCO\textsubscript{3}\textsuperscript{-}, which split and thus decreased the free energy gaps. On the other hand, even though MDEA is intrinsically less basic as per the energy diagram, DEAB generated a lot more HCO\textsubscript{3}\textsuperscript{-} resulting in a tremendously lower heat duty. γ-Al\textsubscript{2}O\textsubscript{3} (Lewis acid) was more effective in the CO\textsubscript{2} lean region by contributing HCO\textsubscript{3}\textsuperscript{-},
which is negligible in the CO\textsubscript{2} lean region, whereas H-ZSM-5 (Brønsted acid) is effective throughout the loading range by donating protons.

7.1 Introduction

Carbon capture, utilization and storage (CCUS) is a major option that can be used to mitigate carbon dioxide emissions which is blamed for global warming and climate change. The amine-based post-combustion capture of CO\textsubscript{2} is regarded as one of the mature technologies that can be employed in CCUS. The major drawback of this technology is that the energy required for the process, especially during solvent regeneration for CO\textsubscript{2} stripping, is still too high [1]. Recently, Rochelle [2] has highlighted the approaches that could be used to minimize the heat required for regeneration. Using the bench mark solvent of 30 wt % (5 kmol/m\textsuperscript{3}) MEA aqueous solutions, the optimized energy required has been reported to be in the range from 2057-3165 kJ/kg of CO\textsubscript{2} according to data from the literature in the 1980’s [3]. More recent heat duty of the main amine scrubbing pilot plants in the US, utilizing the same solution, was reported to be 0.37 MWh/tonne CO\textsubscript{2} (1468 kJ/kg CO\textsubscript{2}) in 2001 and 0.51 MWh/ton CO\textsubscript{2} (2023 kJ/kg CO\textsubscript{2}) in 2006, respectively [2], which shows that heat duty had been greatly decreased. According to Rochelle [2], the theoretical minimum is estimated to be (0.11 MWh/ton CO\textsubscript{2} or 437 kJ/kg CO\textsubscript{2}), which is hardly achievable because this is essentially the heat of the chemical reactions. This researcher suggested that the two significant methods to cut heat duty to achieve the expected value were solvent optimization and process integration.
The heat duty is considered to be more specific to operating conditions such as
temperature (T) and pressure (P) with less dependence on process configurations,
with the exception of process integration and heat optimization [4]. A number of
researchers have reported measures that have been used to effectively reduce heat
duty [1,2,4-6]. These include the development a series of different novel solvents,
which can reduce the heat duty from 1.738 to 0.409 MWh/tonne CO₂,(6895 to 1623
kJ/kg CO₂) and reflux ratio of H₂O/CO₂ from 0.7 to 0.1 [7]. Recently, efforts have
been made to improve Heat Exchanger Network (HEN) optimization, which
exhibits a good potential to improve energy efficiency of an overall power plant
with a reduction in the energy penalty for CO₂ capture from 19.4% to 15.9% [8].

Other methods such as the blending of amines to reduce the regeneration
energy compared to MEA have been reported [1]. According to the literature, when
various tertiary amines such as MDEA are blended with MEA, it results in the
reduction of the energy requirements and an increase in the capture efficiency [4,5].
Based on our earlier studies [1], a huge heat-duty reduction could be achieved with
blended amine solutions (MEA/MDEA at a ratio of 4:1) (67000 BTU/1b-mol or
3534.6 kJ/kg CO₂) instead of a single MEA solution (78000 BTU/1b-mole or
4115.0 kJ/kg CO₂) at lean loading of 0.25 – 0.35 mol/mol (Appendix Fig. 7.1a,
7.1b). Similar conclusions have been drawn [4] with energy efficiency plots of
MEA and blended MEA/MDEA (Fig 1.1. A large amount of heat (>80% of heat) is
used for water vaporization for MEA solutions, and only approximately 50% of
heat is used for vaporization for blended MEA:MDEA (1:1) solution [4]. Also,
amine regeneration was improved significantly by Agar’s group with specific blended amines such as dipropylamine (DPA) and improved PCC processes such as a combined improvement for the capture process and power generation process [6,7]. (Appendix Fig. 7.2) The measures still have not achieved regeneration energy of acceptable or theoretical levels. Also even though the experimental measures have been employed to reduce energy penalty, no explanation has been provided as the basis for the reductions[1, 4-7].

Recently, Idem et al. [9] have reported the application of solid acid catalysts to solvent regeneration for CO₂ stripping [9]. HZSM-5 and Al₂O₃ catalysts were used proved to be effective catalysts for CO₂ stripping from single MEA solutions. With HZSM-5 catalyst, the solvent regeneration process was greatly facilitated with a decreased operating temperature from 120-140 °C to 90-95 °C [9]. This ensured that the heat duty was significantly reduced at a lower temperature range with significantly less water vaporization. The heat duty obtained at the lab scale was 1.56 GJ/ton CO₂ (1560 kJ/kg CO₂), compared with 3.53 GJ/tonne CO₂ (3530 kJ/kg CO₂) from the pilot plant [1]. Following these, other researchers have applied Al₂O₃ sphere to amine regeneration [6], and Al₂O₃ was found to be useful for solvent regeneration with specific lipophilic amines such as dipropylamine (DPA) Di-sec-butylamine (DsBA), and N,N-dimethylcyclohexylamine (DMCA). This paper not only presents experimental results for catalyst-aided amine regeneration, but also, provides a better understanding of the circumstances behind the use of novel tertiary amines or amino alcohols, and solid acid catalysts to drastically
reduce the heat of regeneration. Also in the paper, we develop catalytic carbamate breakdown and/or AmineH\(^+\) deprotonation mechanisms [9] applicable to catalytic and non-catalytic regeneration processes as well as single and blended amines similar to the computational potential energy surface (PES) diagram developed for the Zwitterion mechanism by Xie et al.[10]. This paper also used the NMR technique to experimentally obtain the ion speciation plot to accompany the VLE model. Both the measures were then used to provide a better understanding of the reasons for the drastic reduction of energy required for CO\(_2\) stripping from some amine solutions under the operating conditions reported in this paper. Experiments for CO\(_2\) stripping were performed using single and blended amines (namely, MEA, MEA-MDEA, MEA-DEAB (4-(diethylamine)-2-butanol)) with and without solid acid catalysts (Al\(_2\)O\(_3\) or HZSM-5) at regeneration temperatures in the range of 90 – 95 °C. The results are presented and discussed in this paper.
7.2 Experimental Section

7.2.1 Chemicals and catalysts

DEAB (4-(diethylamine)-2-butanol) was synthesized according to the method reported recently [11,12]. The CO₂ had a purity of 99.9% and was obtained from Praxair Inc., Mississauga, Ontario, Canada. Standard 1.0 M hydrochloric acid (HCl) solution and MEA, MDEA, (Sigma-Aldrich Co., Oakville, Ontario, Canada), with purities of 99.9%, were used for titration and the Chittick apparatus was applied for the CO₂ loading test [13]. Gamma-Alumina (γ-Al₂O₃) and HZSM-5 catalysts were purchased from Zeochem, US

7.2.2 Solvent Regeneration process

A typical recirculation device (Fig. 7.1) was designed for solvent regeneration for CO₂ stripping. About 2L of the prepared amine solutions of the required formula, amine concentration and CO₂ loading were placed in a 3000 ml reaction flask used as a batch reactor. Pure CO₂ was introduced into the amine solutions over a period of 1 hour to load the amine solution with CO₂. The CO₂ loading was set at 0.5 mol/mol amine at the start for all the amine solutions. A condenser was placed on the top with a thermometer in an adaptor to monitor the temperature. A heater was used to provide heat at a predetermined fixed rate which kept the temperature at between 85-95 ºC. A magnetic stirrer was used in the flask for stirring the mixture. Time was not recorded until the operating temperature of > 85 °C was reached. Heating was required throughout the reaction to ensure the temperature was maintained at between 85-95 ºC for 9 h (540 minutes). Samples were taken by
pipetting 2 mL of sample from the 2 L flask at periods of 120, 240, 360, 480 and 540 mins after the temperature had reached 85°C, and used to perform CO₂ loading tests. The regenerated amine CO₂ loading (α) vs. heating time (min) curve was then generated to study the regeneration process. About 25-30 g of catalysts were added for catalytic regeneration, with mass ratio of catalyst : solution around 1 / 80.

Fig. 7.1 The simplified apparatus of regeneration process, the reflux condenser.
7.2.3 Formulation of Potential Energy Surface (PES) Diagrams

The potential energy surface diagrams for various scenarios was formulated based on reactions typically involved in solvent regeneration, which according to Caplow [1968], can be categorized into (A) Carbamate breakdown (eqn 1), and (B) AmineH⁺ deprotonation (eqns 2 and 3). For primary and secondary amines (e.g. MEA and DEA, respectively), both categories are included because the amines are regenerated from both carbamate (MEA-COO⁻) and protonated amines (MEAH⁺). For tertiary amines, the focus is only on type B reaction because of negligible carbamate content.

- Zwitterion mechanism of Carbamate formation and breakdown with protons:
  \[
  \text{MEA-COO}^- + \text{H}_3\text{O}^+ \leftrightarrow \text{Zwitterion} \leftrightarrow \text{MEA} + \text{CO}_2 \uparrow \quad (7.1)
  \]

- AmH⁺ deprotonation process of single amine MEA-CO₂-H₂O (One-step):
  \[
  \text{MEA}^\text{H}^+ + \text{H}_2\text{O} \leftrightarrow \text{MEA} + \text{H}_3\text{O}^+ \quad (7.2) \Delta G_0
  \]

- AmH⁺ deprotonation process for blended amine MEA-MDEA/DEAB-CO₂-H₂O:
  Multi-step process for MEA-MDEA solution without bicarbonate (lean region):
  \[
  \text{MEA}^\text{H}^+ + \text{MDEA} \leftrightarrow \text{MEA} + \text{MDEA}^\text{H}^+ \quad (7.3.1) \Delta G_1
  \]
  \[
  \text{MDEA}^\text{H}^+ + \text{H}_2\text{O} \leftrightarrow \text{MDEA} + \text{H}_3\text{O}^+ \quad (7.3.2) \Delta G_2
  \]
  Where \( \Delta G_0 = \Delta G_1 + \Delta G_2 \), and DEAB can replace MDEA for MEA-DEAB system.

- AmH⁺ deprotonation process with bicarbonate can be written as follows:
  - Overall step for MEA reaction with bicarbonate: (To be consistent with 7.2)
  \[
  \text{MEA}^\text{H}^+ + \text{H}_2\text{O} + \text{HCO}_3^- \leftrightarrow \text{MEA} + \text{H}_3\text{O}^+ + \text{HCO}_3^- \quad (7.2) \Delta G_0
  \]
  - Multi-step process for MEA-MDEA/DEAB solution with bicarbonate: (7.3)
\[
\text{MEAH}^+ + \text{HCO}_3^- \leftrightarrow \text{MEA} + \text{H}_2\text{CO}_3 \quad (7.3.3) \quad \Delta G'_0
\]

\[
\text{MEAH}^+ + \overbrace{\text{MDEA}} \leftrightarrow \text{MEA} + \overbrace{\text{MDEA}H^+} \quad (7.3.3a) \quad \Delta G_1
\]

\[
\overbrace{\text{MDEA}H^+ + \text{HCO}_3^-} \leftrightarrow \overbrace{\text{MDEA} + \text{H}_2\text{CO}_3} \quad (7.3.3b) \quad \Delta G_3
\]

\[
\text{H}_2\text{CO}_3 + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{HCO}_3^- \quad (7.3.3c) \quad \Delta G_4
\]

For energy balance: \(\Delta G_0 = \Delta G_1 + \Delta G_2 = \Delta G_1 + (\Delta G_3 + \Delta G_4)\), where \(\Delta G_2 = \Delta G_3 + \Delta G_4\). With bicarbonate, the overall energy was reduced to \(\Delta G'_0 = \Delta G_1 + \Delta G_3 = \Delta G_0 - \Delta G_4\).

Related Reactions (2) = (3-3a) + (3-3b) + (3-3c); (3-3a) + (3-3b) = (2) − (3-3c)

\[
\text{H}_2\text{CO}_3 \leftrightarrow \text{H}_2\text{O} + \text{CO}_2 \uparrow \quad (7.3.4)
\]

Solvent regeneration requires a large heat duty because reactions (7.1 and 7.2) are strongly endothermic. From a reaction point of view, the protonated amines release protons to water, carbamate or bicarbonate, which facilitates carbamate and carbonic acid breakdown. However, based on acid-base theory, this is a very difficult step in the absence of the bicarbonate since the amine is a relatively strong base while water is neutral. Hence the large heat duty requirement for regeneration.

Since the reaction scheme is well known, quantitative energy diagrams for the reactions (7.1 and 7.2) can be generated even though this requires a detailed analysis as shown in order to accurately calculate the theoretical minimum energy requirement at a molecular level as the basis for the heat duty.
7.3 Results and discussion

7.3.1 Potential energy surface (PES) Diagrams for Carbamate breakdown and AmineH⁺ De-protonation

A. Carbamate breakdown

The PES of the Zwitterion mechanism for carbamate breakdown in this study was based on the estimation by Zhang et al. [6] obtained from computational techniques. The free energy was calculated with their software with different levels of theory. The CO₂ stripping pathway was initiated from the right to the left as the reverse of absorption. The calculated heat requirement of reaction 1 was 3.7 kcal/mol (15.47 kJ/mol). “Carbamate breakdown” via the Zwitterion mechanism is well known for primary and secondary amines [14]. This process requires a large amount of free protons and/or heat [9]. While heat sources such as steam are available to provide the heat, the availability of large amounts of free protons is limited because free protons are bonded to the amine, hence the difficulty for carbamate breakdown. According to the literature [6,9], the reaction energy diagram was not estimated quantitatively until recently. That is why we have relied on the recent and accurate estimates by Zhang et al.[6].

According to our earlier analysis of carbamate breakdown, any available free proton (H⁺) attacks the N atom of the carbamate (HO-CH₂-CH₂-NH-COO⁻). From an optimal molecular structure perspective, the proton is attached to the N atom, which converts the sp² hybridization of the N and C atoms into sp³, and breaks the de-localized N-COO⁻ conjugation simultaneously, and finally stretches the N-C
bond in preparation for N-C bond cleavage [9]. Therefore, this supports the assertion that the availability of large amounts of free protons (H\(^+\)) is extremely important. However, the pH value of the CO\(_2\)-rich MEA solutions is around 8-10, which indicates a great shortage of free protons as most protons have been bonded tightly to MEA in terms of MEAH\(^+\) [9], thereby constituting the major difficulty in CO\(_2\) stripping.

**B. De-protonation of AmH\(^+\)**

Fig. 7.2 represents the energy diagram for MEAH\(^+\) (or AmineH\(^+\) in general) deprotonation to H\(_2\)O which is the initial step for CO\(_2\) stripping. It is considered to first occur with the generation of “free protons, H\(^{++}\)”, which is key toward a subsequent carbamate breakdown. Both types of reactions are endothermic with strong heat requirements as shown in Fig. 7.2. The free energy requirement of the one-step deprotonation from the right side is large (about 73.4 kJ/mol at 25\(^\circ\)C). The energies shown are generated based on an experimental deprotonation constant K\(_a\) provided by Jacobsen et al. [15]. With a combination of carbamate breakdown and deprotonation of AmH\(^+\), the estimated free energy requirement of CO\(_2\) bond breaking with MEA from the current study is 88.9kJ/mol, which is close to the reference value of 85.6 kJ/mol reported by Kohl and Nielsen [16], with AAD of 3.85\%.
Fig. 7.2 Free Energy diagram of MEAH$^+$ to MDEA to water at 25 °C from reactions (7.2), (7.3.1) and (7.3.2). $^{a,b}$

a. For MEA, $\ln K_{eq} = \ln K_a - \ln [H_2O](4.00733) = \frac{6166.116}{T} - 4.90737 - 4.00733 \quad [15]$

b. For MDEA, $\ln K_{eq} = \ln K_a - \ln [H_2O](4.00733) = -819.7/T - 79.474 + 10.9756* \ln (T) - 4.00733 \quad [15]$
From thermodynamic analysis, cabamate breakdown appears to be complex but with less energy requirements. On the other hand, deprotonation of MEAH\(^+\) is simple but requires a larger amount of energy as shown in Figs. 7.3 and 7.4. The figures explain how the energy duty of deprotonation is huge for solvent regeneration for MEA solutions (73.4 kJ/mol at 25 °C (Fig. 7.3) and 78.2 kJ/mol at 90 °C (Fig. 7.4)). From the macroscopic view point, the energy penalty is much bigger than the free energy requirement. Sakwattanapong et al. [4] showed that a large fraction of the energy (> 85%) is wasted on water vaporization while heating the solution. This work reported that the reboiler heat duty was 3,767 kJ/kg CO\(_2\) (1.05 MWh/tonne CO\(_2\)) from a rich CO\(_2\) loading of 0.5 to a lean CO\(_2\) loading of 0.3. If most of the energy was spent on the reaction, the theoretical energy requirement would be reduced to 450 kJ/kg CO\(_2\) which is close to the theoretical minimum of 0.11MWh/ton CO\(_2\) (437 kJ/kg CO\(_2\)) with the same solution [2].
Fig. 7.3 Free energy requirement of proton transfer at 25 °C (i.e. from relatively strong base to water)

Fig. 7.4 Free energy requirement of proton transfer from relatively strong base to water at 90 °C (regeneration condition).\textsuperscript{a-d}

a. For MEA, \(\ln K_{eq} = \ln K_a - \ln [H_2O](4.00733) = 6166.116/T - 4.90737 - 4.00733\)

b. For MDEA, \(\ln K_{eq} = \ln K_a - \ln [H_2O](4.00733) = -819.7/T - 79.474 + 10.9756*\ln (T) - 4.00733\)

c. For bicarbonate, \(\ln K = 231.465 - 12092.1/T - 36.7816 \ln (T) [CO_2 + 2H_2O \leftrightarrow HCO_3^- + H_3O^+]\) The equations from a-c are from Jakobsen et al.[15].
d. For DEAB, K were obtained with pH test at 25°C and estimated at 90°C.

### 7.3.2 Role of Tertiary Amines in Blended Amine Solutions

Figure 7.2 also represents the energy diagram of reaction (7.3.1) and (7.3.2) as step-wise reactions at standard conditions. The energy gap of reaction (7.2) is $\Delta G_0 = \Delta G_1 + \Delta G_2 = 73.4$ kJ/mol. The role of the tertiary amine (e.g. MDEA or DEAB) is to split the energy of (7.2) from one difficult step $\Delta G_0$ into two less difficult steps (7.3.1 and 7.3.2) with $\Delta G_1 + \Delta G_2$, respectively. It is much easier for MEAH\(^+\) to release H\(^+\) to MDEA or DEAB initially than to H\(_2\)O directly because the tertiary amine is a stronger base than water. Although the overall free energy requirement appears to be the same, the overall reaction rate is greatly accelerated resulting in a reduced macroscopic energy penalty because the energy efficiency increases with significantly less energy wasted on water vaporization and other energy losses as demonstrated [4]. Therefore, a step-wise proton transfer, made possible by the presence of a tertiary amine, is what facilitates proton release into the solutions. Hence, it can be proposed that one of the roles of tertiary amines is very close to that of being a “catalyst”, which alters the reaction pathway, but does not change the thermodynamics nor the reactants / products [17]. It should be noticed that Fig. 7.2 represents the MEA-MDEA mixture as a simplified model without the bicarbonate (HCO\(_3\)\(^-\)) ion. However, bicarbonate ions could exist in the solution, as was detected with \(^{13}\)C NMR analysis [15]. Also, from the ion speciation plot of the MEA-DEAB (5M/1.25M) system, carbonate (CO\(_3\)\(^2-\)) ions were negligible but trace amounts of bicarbonate ions were detected at a loading $\geq 0.40$ at 24 °C and a loading $\geq 0.25$ at
90 °C as shown in Figs. 7.5, 7.6 and 7.7. Below those loadings, NMR analysis shows that the amounts of bicarbonate ions are negligible or undetectable. The PES diagram of Fig. 7.2 represents such conditions, which shows the role of tertiary amines in blended amines only as a catalyst because there is no involvement of the bicarbonate ions.

![Graph](image)

**Fig. 7.5** VLE and Ion speciation plot of MEA-DEAB-CO$_2$-H$_2$O system (5.0M/1.25M) at 24 °C).

This figure is similar to Fig. 5.5 (4), from the previous NMR analysis in Chapter 5.
**Fig. 7.6** VLE and Ion speciation plot of MEA-DEAB-CO$_2$-H$_2$O system (5.0M/1.25M) at 90 °C.

a. This plot was predicted from the experimental plots at 24, 40, 50, 60 and 70 °C, same as Fig 6.3 details were described in Chapter 6.

b. The existence of HCO$_3^-$ in the solution was at loading of 0.25 molCO$_2$ / mol amine at 90 °C, which is much smaller than 0.40 at 24 °C. For VLE models, higher temperature facilitates the bicarbonate generation of carbamate exchange. MEA-COO$^- +$ H$_2$O $\leftrightarrow$ MEA + HCO$_3^-$. 

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Fig. 7.7 The minimum CO₂ loading for existence of HCO₃⁻ and maximum concentration of HCO₃⁻ in MEA-DEAB- CO₂-H₂O solutions (5M/1.25M) from 24 to 90 ºC.

a. This figure is similar to Fig 6.4, the detailed analysis were refer to Chapter 6.

b. The bottom data series is the minimum CO₂ loading where HCO₃⁻ start to be detectable in the solution, below that loading, most of the CO₂ in liquid phase is converted to carbamate.

c. The top data series is the maximum concentration of HCO₃⁻ at rich loading of the blended amine.

d. The solid dots are experiment data from NMR analyses, the circle is predicted value from extrapolation based on the previous 5 sets of experiments.
7.3.3 Addition of Tertiary Amines and Bicarbonates in Blended Amine Solutions

The deprotonation reactions of tertiary amine with bicarbonate, which occurs at high CO₂ loading regions, can be explained with equations (7.3.3a, 7.3.3b) and the energy diagram in Fig. 7.8. The overall reaction energy was ΔG₂. The existence of bicarbonate splits the reaction into two steps, similar to Fig. 7.2. Based on the mechanism and as long as the protons attach to bicarbonate ions, it can be seen that there are two possible results, namely, either by releasing protons to water (7.3.3c) or splitting to CO₂ and H₂O directly equations (7.3.4). Bicarbonate has two roles, to act as a “catalyst” for deprotonation from DEABH⁺ or MDEAH⁺ to water, or to act as a “proton acceptor” to release CO₂ directly. As mentioned previously, it is much easier for MDEAH⁺ or DEABH⁺ to release H⁺ to HCO₃⁻ first than to H₂O directly since bicarbonate is more basic than water. The role of the catalyst does not change the free energy, but the role of the proton acceptor reduces the free energy of regeneration from ΔG₀ to ΔG'₀ which is equal to ΔG₁ + ΔG₃ = ΔG₀ - ΔG₄. MEAH⁺ releases protons to HCO₃⁻ to generate CO₂ directly as a short cut to solvent regeneration for CO₂ stripping.

It is seen from Figure 7.4 that the free energy of ΔG₀ (78.2 kJ/mol) at 90 °C is reduced to ΔG'₀ (21.9 kJ/mol). If the energy requirement of carbamate breakdown is very close to 15.47 kJ/mol under 90 °C, the estimated energy requirement of amine regeneration is cut from 93.7 (78.2+15.47) kJ to 37.4 (21.9+15.47) kJ. Theoretically, the updated energy requirement with the aid of bicarbonate is only 40%
of the original process. Therefore, if the blended solvents can bring more bicarbonate ions into the amine solution, then energy duty reduction will be facilitated.

Fig. 7.8 The Free energy diagram of reaction (3-3b) for amine blend with tertiary with bicarbonate (e.g. MDEAH$^+$ to HCO$_3^-$ to water) at 25 °C

a. For bicarbonate, ln K = 231.465 - 12092.1/T -36.7816 ln (T) at 25.0 °C
[CO$_2$+2H$_2$O$\rightarrow$ HCO$_3^-$ + H$_3$O$^+$] [15]
Without bicarbonate, there is only one pathway (1×1) to regenerate CO₂ (only one proton donor MEAH⁺ and one acceptor H₂O). However, with the tertiary amine and bicarbonate ions, there are two proton donors MEAH⁺ and MDEAH⁺ (DEABH⁺) and two proton acceptors HCO₃⁻ and H₂O. Four pathways (2×2) are available to generate CO₂, three of which require less energy than MEAH⁺ to H₂O.

\[
\begin{align*}
\text{MEA} & \quad \text{H}_2\text{O} & \text{MEA only, 1 pathway} \\
\text{MEAH}^+ & \quad \text{H}_2\text{O} & \text{MEA-MDEA/DEAB blended} \\
\text{MDEAH}^+ / \text{DEABH}^+ & \quad \text{HCO}_3^- & 2 \times 2 = 4 \text{ pathways}
\end{align*}
\]

A combination of information in Figs. 7.2 and 7.7 for the energy requirement was earlier plotted on Figs. 7.3 and 7.4 at 25 °C for absorption and 90 °C for regeneration conditions, respectively. Figs. 7.3 and 7.4 indicate the quantitative free energy requirements of proton transfer from MEA, MDEA or DEAB and HCO₃⁻ to H₂O accurately at the molecular level for both conditions. This plot can be regarded as quantitative proton affinity analysis within various Brønsted bases. Along the X axis, the proton is transferred from a relatively strong base (MEA) to a medium base (MDEA or DEAB) and subsequently, to a weak base (HCO₃⁻) and then neutral compound (H₂O) with heat. This is consistent with a typical example from any RNH₂ to R₃N and to HCO₃⁻ and neutral H₂O using acid-base theory. Thus, with the introduction of tertiary amine and HCO₃⁻ introduced into the solution, one direct step is split into three, and one extra, important proton acceptor (HCO₃⁻) is introduced. HCO₃⁻ directly generates CO₂ and protonation with different proton
transfer pathways with significantly less energy requirements. The overall regeneration process is also accelerated by small steps with significantly less energy duty at the macroscopic level because of significantly increased energy efficiency.

The overall regeneration processes proposed in Fig 7.4 can be used to explain the specific role of DEAB. DEABH$^+$ is more likely to release protons than MEAH$^+$. (1) Protons are released from tertiary amino alcohol, DEAB, initially and then react with either bicarbonate to directly release CO$_2$ or breakdown Carbamate to release CO$_2$ [14]. (2) The free DEAB then reacts with MEAH$^+$ to accept the protons with heat (7.3.3a), which regenerate fresh MEA. It is much more convenient for MEAH$^+$ to release protons to basic DEAB than neutral H$_2$O. (3) Again, DEAB is protonated to DEABH$^+$ and then deprotonated to water or bicarbonate. As long as the proton is removed out of AmH$^+$ in the system with CO$_2$ being emitted simultaneously, the overall endothermic process continues with both amines regenerated and most of the CO$_2$ exits the solution. The energy requirements are small in the beginning ($\Delta G'_{0} = \Delta G_1 + \Delta G_3$) and may be large after removal of all the bicarbonate ions ($\Delta G_{0} = \Delta G_1 + \Delta G_2$). Since the tertiary amine remains in the system, the rate of CO$_2$ release from the blended amine system is quicker than for the single primary amine.
7.3.4 Theoretical minimum regeneration energy requirement for the blended amine systems

The theoretical minimum energy requirement is an important criterion for amine regeneration based on assumptions that energy is solely spent on the reactions. It needed to be re-calculated in order to verify the accuracy of the PES diagram. The recorded energy for CO₂ to break chemical bonds with MEA is given as 85.6 kJ/mol at 25 ºC by Kohl and Nielsen [16] and the value obtained in our study is 88.9 (73.4+15.47) kJ/mol in Fig 3a which gives a 3.8% deviation.

The theoretical minimum energy for the 5M MEA solution (30% wt) is given in Fig 7.3 and was calculated at a maximum CO₂ loading of 0.50 mol/mol, where reactions (7.1) and (7.3.3) at a ratio of 1:1 were investigated. The free energy requirement of reaction (1) was assumed to remain ΔGₐ = 15.47 kJ/mol at 90 ºC, and that of MEAH⁺ to HCO₃⁻ was ΔG₀' = 21.9 kJ/mol. The energy requirement was calculated in equation (7.5) with a value of 425 kJ/kg CO₂, which is very close to the reference at 0.11 MWh/ton CO₂ (437 kJ/kg CO₂), with 2.5% AAD% [2].

Free energy requirements from 0.50 mol/mol of 5M MEA solution:

\[
\frac{n\text{MEAH}^+ \times \Delta G'_a + n\text{Carbamate} \times \Delta G'_c}{n\text{HCO}_3^- + n\text{Carbamate}} = \frac{1 \times 21.9 + 1 \times 15.47}{1+1} \frac{kJ}{mol \text{ CO}_2} = 18.69 \text{ kJ/mol CO}_2 (425 \text{ kJ/kg CO}_2)
\]

The same calculation was performed for the blended amine system at a maximum loading of 0.52 mol/mol, which included three reactions: (7.1), (7.3.3) and (7.3.3b). The free energy requirement of reaction (7.3.3b), deprotonation of
DEABH⁺ to bicarbonate, was ΔG₃ = 16.7 kJ/mol. The three reactions were also estimated with a stoichiometric ratio. The theoretical minimum energy was calculated in equation (7.6) with a value of 410 kJ/kg CO₂, close to that of the 5M MEA solution.

Energy requirement from 0.521 mol/mol of 5M/1.25M MEA/DEAB solution:

\[
\frac{n\text{MEAH}^+ \times \Delta G'_f + n\text{Carbamate} \times \Delta G_e + n\text{DEABH}^+ \times \Delta G_g}{n\text{HCO}_3^- + n\text{Carbamate}} = \frac{kJ}{mol \text{ CO}_2} = 18.02 \text{ kJ / mol CO}_2 (410 \text{ kJ/kg CO}_2)
\]

The calculations at a maximum CO₂ loading validated the accuracy of the PES diagrams in Figs. 7.3 and 7.4. Such calculations were made, assuming the three reactions stayed at the ratio of 1:1:1. However, for the real systems, bicarbonate was the limiting reagent and the regeneration process would take place within a range of CO₂ loading. Therefore, more practical calculations were computed for the PES diagram in Fig. 7.4 and the exact ion concentrations of Fig. 7.6 at 90 °C.

It is seen in Fig. 7.6 that when the CO₂ loading decreases from 0.50 to 0.30 mol CO₂/mol of amine, the ion concentration of MEAH⁺ decreases from 2.485 to 1.500 mol/L (0.985 mol/L MEA regenerated), DEABH⁺ decreases from 1.275 to 1.245 mol/L (0.03 mol/L DEAB regenerated), carbamate decreases from 2.232 to 2.078 mol/L and bicarbonate decreases from 1.040 to 0.04 mol/L. The concentration of DEABH⁺ did not change greatly, which verifies the previous mentioned regeneration process. It releases protons to water and bicarbonate while accepting protons from MEAH⁺ as a “catalyst”. DEABH⁺ regeneration is easier than MEAH⁺, and the amount of regenerated DEAB is considered to be bigger than MEA.
However, the VLE plots indicate the opposite whereby 0.98 mol MEA is regenerated compared to 0.03 mol DEAB. This result is reasonable because regenerated DEAB will accept protons from MEAH\(^+\) right away, which greatly facilitates the difficult MEA regeneration.

The protons released from MEAH\(^+\) and DEABH\(^+\) were 0.985+0.03 = 1.015 mol/L, which produces approximately 1.00 mol/L of bicarbonate. 0.985 mol/L of MEAH\(^+\) releases protons to bicarbonate as described in equation (7.3.3), and part of DEABH\(^+\) (0.015 mol/L) releases protons to bicarbonate and the rest (0.015 M) release to water, equation (7.3.3b).

Calculated from equation (7.7), the overall free energy requirement at 90 °C from loading of 0.52 to 0.30 mol/mol should be 21.9 kJ/mol CO\(_2\) (498 kJ/kg CO\(_2\)). This is a little bigger than 437 kJ/kg CO\(_2\) with a 5M MEA solution because it was calculated within the CO\(_2\) loading range.

The energy requirement for regeneration from 0.521 to 0.30 mol/mol is given as:

\[
\frac{\text{nMEAH}^+\times\Delta G_0 + \text{nCarbamate}\times\Delta G_c + \text{nDEABH}^+\times\Delta G_2}{\text{nHCO}_3^- + \text{n Carbamate}} = \frac{(2.485-1.500)\times21.9+(2.232-2.078)\times15.47+(1.275-1.245-0.015)\times16.7+0.015\times73.01}{1.000+(2.232-2.078)}
\]

\[
\frac{k J}{mol \text{ CO}_2} = 21.92 \text{ kJ / mol CO}_2 (498 \text{ kJ/kg CO}_2)
\]

Finally, this free energy calculation can be applied to other blended amines with different ratios. The theoretical energy requirement can be calculated at any specified loading range with high accuracy with combinations of PES diagrams and ion speciation plots of VLE models.
7.3.5 Amine solvent Regeneration for CO$_2$ Stripping with catalysts

Figures 7.9 and 7.10 show the PES diagrams with the resultant free energy gaps after the introduction of Al$_2$O$_3$ as a catalyst. It can be seen that the addition of further splits the energy gaps between MEAH$^+$ and H$_2$O and between HCO$_3^-$ and H$_2$O resulting in less heat requirements for regeneration for MEA solvent system and a solvent system of MEA blended with a tertiary amine, respectively. So, it became essential to study in detail the contributions of different types of solid acid catalysts. Nine sets of experiments were tested to evaluate the roles of solid Brønsted and Lewis catalysts as well as different tertiary amines in solvent regeneration. Fig. 7.11 shows the regenerated amine CO$_2$ loading vs. heating time (i.e. fixed heat input) plotted for three different amine solution systems: MEA only, MEA/MDEA and MEA/DEAB at a ratio of approximately 4:1. For all three systems, non-catalyst tests were initiated as a blank test, two additional types of catalysts were applied later; one was a solid Lewis acid, $\gamma$-Al$_2$O$_3$ and the other was a solid proton donor catalyst, HZSM-5. The regeneration tests were performed under 85-95 ºC for amine regeneration. From Fig. 11, it is apparent that the slope of CO$_2$ loading vs. time is steep in the beginning (i.e. CO$_2$ is quickly released) but the slope becomes less and less steep as time progresses. This verifies the existence of the “with bicarbonate” stage and “without bicarbonate” stage for amine regeneration. A typical example is that for MEA-DEAB-CO$_2$-H$_2$O, the transition point is at a CO$_2$ loading = 0.25 mol/mol for different stages in Fig 7.11. According to Figs. 7.6 and 7.8, this transition point for the two stages is a loading below which the bicarbonate
disappears. HCO$_3^-$ is exhausted at a loading of 0.25 mol CO$_2$/mol amine, and thus, the energy barrier increases from 21.9 to 78.2 kJ/mol (Fig. 7.4). Without bicarbonate, CO$_2$ production is difficult and the rate decreases greatly as seen from Fig. 7.11. This therefore presents a new methodology for the evaluation of the energy required for amine regeneration for CO$_2$ stripping by combining the PES plot (Fig. 7.4) with the speciation/VLE (Fig. 7.5 and 7.6) and the solvent regeneration plots (Fig. 7.11). Fig. 7.11 clearly shows the different stages of Amine regeneration for the nine cases. The regeneration rate was much faster with bicarbonate than without bicarbonate. Such phenomena can also be explained with Figs. 7.4, 7.6 and 7.7 at 90 ºC. The transition point is the CO$_2$ loading where at least trace amounts of bicarbonate HCO$_3^-$ can be detected. This method is also applicable for all amine solutions, MEA, MEA-DEAB and MEA-MDEA, with ion concentration plots from VLE models generated at 90 ºC or other temperatures of interest.
Fig. 7.9 Free Energy diagram of MEA with / without addition of Al₂O₃.

Fig. 7.10 Energy diagram of MEA-MDEA/DEAB with/without addition of Al₂O₃ at 90 °C.
Fig. 7.11 Experimental regeneration curves of MEA, MEA/MDEA, and MEA-DEAB at without catalyst and with catalysts.

a. The amine mixture was 2000 mL, with Al₂O₃ 25-30g, HZSM-5 25-30 g at ratio of 1/80 with solution
Regeneration with Catalysts $\gamma$-Al$_2$O$_3$ and H-ZSM-5

According to the literature, the use of catalysts cannot change the theoretical minimum thermodynamic energy requirement. However, they can accelerate the reaction and facilitate CO$_2$ release by increasing the energy efficiency, $\eta$, and reducing the overall energy penalty during the amine regeneration process. $\gamma$-Al$_2$O$_3$, a Lewis solid acid catalyst, was used as an electron acceptor to play the role of bicarbonate generator while H-ZSM-5, a Brønsted solid acid catalyst, was used as a proton donor to break down carbamate. Fig. 7.11 shows that both catalysts facilitate amine regeneration in the CO$_2$ lean loading region more than in the CO$_2$ rich loading region compared with the non-catalytic process. Consequently, with catalysts, the rate of CO$_2$ release increases especially in lean loading regions where the driving force for CO$_2$ stripping is low. Fig. 7.12 shows the heat duty for amine regeneration for CO$_2$ capture obtained for the catalytic and non catalytic processes at 120 min for all the amines relative to 5M MEA, which covers the CO$_2$ loading range of 0.50 – 0.20 mol CO$_2$/mol amine. It is to be mentioned that the calculated absolute energy duties are relatively high compared to literature values because the experiments were performed with a simplified recirculation process without any heat insulators that would prevent heat losses. Thus, a large amount of energy was lost to the surroundings. Despite the non-illustrative absolute energy duties, the energy requirements of the nine sets relative to MEA are very accurate because the same heating rate at the same temperature was applied to all the amine samples which had the same volume of samples stirred at the same stirring rate in the
reaction flask.

**Fig. 7.12** The Relative heat duty for solvent regeneration for CO₂ stripping for the first 120 minutes.
The three sets on the left side of Fig 7.12 are MEA solutions (single amine). It is seen that the addition of catalysts reduces the heat duty by 40-50% less than without catalyst. The three sets in the middle are MEA-MDEA solutions. The heat duty of mixture with/without alumina seemed to be the same. This is reasonable because Al$_2$O$_3$ duplicates the role of HCO$_3^-$, the effect of Al$_2$O$_3$ is negligible in the first 120 min, but it takes effect at longer periods (5-9 h as in Fig. 7.11). HZSM-5 worked better than γ-Al$_2$O$_3$ requiring less energy because it provides protons directly. The three sets on the right side are MEA-DEAB solutions where the heat duty of the mixtures was already low, and they behaved much better with γ-Al$_2$O$_3$ and more so with HZSM-5. Even without any catalyst, the heat duty of the blended MEA-DEAB (5M : 1.25M) was 961.4 kJ/mol, much smaller (51.4%) than the single amine (5M) MEA (1871.2 kJ/mol). With catalysts, heat duties were respectively 750.8 and 710.3 kJ/mol, which required 40.1 % and 38.0 % less energy for regeneration than the non-catalytic process with 5M MEA solution. The energy efficiency was greatly increased with blended MEA-DEAB mixtures with either catalyst. The ratio of heat duty with catalysts to those without a catalyst was 0.78 (750.8/961.4) to 0.74 (710.3/961.4), which was considered a catalysis enhancement factor of the blended MEA-DEAB systems.
7.3.6 Role of HCO₃⁻ concentrations: MDEA vs. DEAB

The existence of bicarbonate is essential for amine regeneration for CO₂ stripping, and is even more crucial than the presence of tertiary amines. This can explain the contradictions exhibited in Figs. 7.4 and 7.12 whereby the ΔG₃ of MDEA (7.2 kJ/mol) is much smaller than that of DEAB (16.7 kJ/mol) in Fig. 7.4, suggesting that the overall heat duty of MEA-MDEA should be less than that of MEA-DEAB under similar circumstances. However, the experimental results show the opposite as the MEA-DEAB system exhibited better energy efficiency. The theoretical energy estimation from PES requires the exact concentrations of converted MEAH⁺, MDEAH⁺, HCO₃⁻ and carbamate which were calculated from the ion speciation plot for the models. Fig. 7.4 was effective when reaction of protonated amine to bicarbonate was at ratio 1:1, same as reaction indicated, but HCO₃⁻ is the limiting reagent for MEAH⁺ and MDEAH⁺ or DEABH⁺. It has been shown that the DEAB solution contains more HCO₃⁻ than MDEA solution under the same loading and temperature (Table 7.1), based on early work comparing DEAB-CO₂-H₂O with MDEA-CO₂-H₂O [18]. Similarly, blended MEA-DEAB solutions contain more bicarbonate than MEA-MDEA at the same loading and concentrations as well. With more HCO₃⁻ in the solution, the regeneration was greatly facilitated because the energy requirement of MEAH⁺ deprotonation was small with bicarbonate (21.9 kJ/mol). This would become large (78.2 kJ/mol) if the bicarbonate disappears.
Table 7.1 Effect of HCO$_3^-$ of heat duty in blended amine solutions $^{a-e}$

<table>
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<th>DEAB</th>
<th>MDEA</th>
<th>MEA</th>
</tr>
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<tr>
<td>Energy to release H$^+$ to HCO$_3^-$</td>
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<td>23.11</td>
<td>12.64</td>
</tr>
<tr>
<td></td>
<td>90 °C</td>
<td>16.68</td>
<td>7.20</td>
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<td>HCO$_3^-$/amine ratio</td>
<td>20-25 °C</td>
<td>(24 °C)</td>
<td>(20 °C)</td>
</tr>
<tr>
<td>(max loading) $^b$</td>
<td>80-90 °C</td>
<td>(90 °C)</td>
<td>(80 °C)</td>
</tr>
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<td></td>
<td></td>
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<td>0.660</td>
</tr>
<tr>
<td>max[HCO$_3^-$] of 1.25M</td>
<td>90 °C</td>
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<td>0.810</td>
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<tr>
<td>Relative heat duty (%) $^c$</td>
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<td>71.90</td>
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<table>
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<td>1.0 M</td>
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<tr>
<td>Energy of MEAH$^+$ + H$_2$O $^d$</td>
<td></td>
<td>23.47</td>
<td>0.3 M</td>
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<td>total energy (kJ) $^e$</td>
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<td>1.3 M</td>
</tr>
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<td>90 °C</td>
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<td>0.81 M</td>
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<td>100</td>
</tr>
<tr>
<td>Heat duty</td>
<td></td>
<td>71</td>
<td>100</td>
</tr>
</tbody>
</table>

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a. The energy was obtained from Figure 7.3, 7.4.


c. This data is from Fig 7.12.

d. Reaction of MEAH$^+$ + H$_2$O occurs simultaneously with MEAH$^+$ + HCO$_3^-$, with the existence HCO$_3^-$, energy efficiency is higher because of more steps break the energy barrier from PES diagrams.

e. This calculation is also from Figure 7.3, 7.4.

f. The ratio of free energy requirement of DEAB / MDEA was 0.8:1, consistent with the inverse of HCO$_3^-$ concentration (1:0.8). For the realistic experiments, the ratio was even smaller, close to 0.70:1. This is reasonable since much extra energy is spent on MEA-H$_2$O processes in MEA-MDEA solution after exhaust ion of HCO$_3^-$. DEAB contains more HCO$_3^-$, which keeps the regeneration process under higher efficiency at a longer period.
7.4. Conclusions

1. The huge heat duty of a 5M MEA solution regeneration is due to the difficulty of deprotonation of MEAH⁺ to water and the great shortage of protons. The former reason results in the latter. The amine regeneration process originated from the endothermic proton transfer from a proton donor (MEAH⁺, MDEAH⁺) to proton accepter (HCO₃⁻, H₂O). Based on Brønsted acid-base theory, amines are a stronger base than bicarbonate HCO₃⁻, Al₂O₃ and water (neutral). The difficulty of proton transfer, which is controlled by proton affinity (basicity), decreases as follows: MEA > DEAB/MDEA > HCO₃⁻ (Al₂O₃) > H₂O.

2. It is very difficult to “manipulate” a direct proton transfer from a strong base MEA to neutral water. It is much easier to transfer from a strong base to a medium base and then to bicarbonate and to water via a stepwise pathway with heating. This is explained with the proposed reaction. A de-protonation process shifts from one-step to multi-steps from a stronger base (RNH₂) to a medium base (R₃N) and to weak base HCO₃⁻ and H₂O. The overall energy penalty of a blended amine is much lower than that of an MEA solution due less heat waste on water vaporization.

3. For the regeneration of blended MEA/MDEA or MEA/DEAB, a massive volume CO₂ was emitted from bicarbonate (HCO₃⁻), more so than carbamate. The amine regeneration process behaves poorly without bicarbonate. The addition of a tertiary amine can facilitate the regeneration process by splitting the energy barrier from one-step (ΔG₀) into two {ΔG₁; ΔG₂} without
bicarbonate. The energy barrier was decreased from $\Delta G_0$ to $\Delta G'_0$ with a bicarbonate effect. Regenerations should be performed at CO$_2$ loading with the existence of HCO$_3^-$.

Moreover, the combination of PES and VLE and amine regeneration plots is an accurate method for solvent regeneration energy study for CO$_2$ stripping on a molecular level.

4. The blended primary amine (MEA) with tertiary amine (DEAB or MDEA) is a useful technique for the amine regeneration for CO$_2$ stripping as a solvent improvement. $\gamma$-Al$_2$O$_3$ and HZSM-5 catalysts facilitate amine regeneration for CO$_2$ stripping of a solution in different ways.

5. MEA-DEAB with HZSM-5 appears to be the best approach thus far for amine regeneration at 90 - 95 °C.

6. We have shown, based on the reactions proposed for the amine regeneration process that heat duty can be reduced effectively by introducing either bicarbonate from a tertiary amine and/or solid acid catalysts while decreasing the temperature. These provide a novel and integrated approach for amine regeneration for CO$_2$ stripping using hot water instead of steam.
7.5 References


WO patent 2011/12013821.


Appendix of Chapter 7. Related Figures

Appendix Fig 7.1.a The experimental regeneration plot of pure MEA and MEA-DEAB mixture (4:1) in lab scale [Idem et al. 2006].

Appendix Figure 7.1.b The energy cost of amine regeneration from Pure MEA and MEA-MDEA mixture (4:1) in pilot plant [Idem et al. 2006].

a. The MEA-MDEA ratio of both figures was 4:1, which is the same as our current research, 5:1.25. The experimental results validated the fact that blended amine has less energy cost than single MEA solutions.
Appendix Fig. 7.2.a Solvent regeneration by nucleation with Al$_2$O$_3$ spheres [Zhang, J et al. 2012].

a. A1 is the absorption activator (amine in type II), and B1 is the regeneration promotor (Bi-sec-butylamine Type II).

b. From this figure, the CO$_2$ production speed was much faster when Al$_2$O$_3$ was placed in the system. The amine regeneration speed is increased with increased amount of Al$_2$O$_3$ added.

Appendix Fig. 7.2.b Intensification of CO$_2$ release with various methods.

a. The Al$_2$O$_3$ greatly increased the amine regeneration speed, which is also used as catalyst within this research as well. [Zhang, J et al. 2012]
Chapter 8  Overall Conclusions and Recommendations

8.1 Conclusions

1D NMR analysis (\(^1\)H and \(^{13}\)C) of water soluble amine systems DEAB-CO\(_2\)-H\(_2\)O (single) and MEA-DEAB-CO\(_2\)-H\(_2\)O (blended) have been performed to develop the VLE models for solvent chemistry studies of CO\(_2\) capture and storage. The ion speciation plots of the VLE models were generated based on ion concentration (mol/L) and mole fraction (\(x\)) for amine systems. Additional 2D analyses were also performed on blended amine systems.

The NMR calibration was developed by the author and validated with conventional pH + NMR methods as it was effective and accurate. Both methods were successfully applied to the single amine, DEAB-CO\(_2\)-H\(_2\)O and blended amine, and MEA-DEAB-CO\(_2\)-H\(_2\)O systems. Therefore, the reaction objective has been widened from ternary (single amine) to quaternary systems (blended amine) and from room temperature to high temperatures up to 70\(^\circ\)C. The operational conditions have been widened from CO\(_2\) absorption conditions to regeneration conditions.

Ion speciation tables and plots provided very useful databases, which are convenient to obtain exact ion concentrations of major compounds from the exact CO\(_2\) loading from off-line analysis. The ion speciation plot under room temperature is useful for CO\(_2\) absorption studies, and the predicted plot at 90\(^\circ\)C is useful for amine regeneration studies.

Several useful theoretical discoveries were made for the amine regeneration
studies. The combination of the PES diagram (of CO₂-amine reaction) + VLE plot (of blended amine solution) + regeneration curve (with catalysts) was generated as a new development method for regeneration analysis. The PES diagram estimates the free energy requirement of amine regeneration on a molecular level, the ion speciation plot demonstrates the exact concentrations of major ions (especially bicarbonate HCO₃⁻) of the solutions under regeneration conditions, and the regeneration curves detected the two stages of amine regeneration of fast and slow stages with the introduction of catalysts and improved amine solutions.

**Summary:**

1. The statement: “single ionic concentrations have **NOT** been evaluated independently or solely from NMR spectra, but it can always be calculated in combination with a thermodynamic model and/or equilibrium relationships” (Jakobsen et al. 2005) was disproved with NMR calibration methods developed in the research. The NMR spectra alone can detect all the ion speciation plots of amine-CO₂-H₂O systems.

2. This method was even more accurate (AAD% of 1.9 %) than the conventional pH + NMR method (AAD% of 3.1 %). Moreover, the application of the NMR calibration method can be widened to blended amine solutions (quaternary systems) and high temperatures up to 70°C, which make it possible to predict ion speciation plots at 90 °C for CO₂ stripping studies, where the pH + NMR method can only reach 40 - 45°C.

3. The calibration curves of MEA, DEAB were generated and applicable for
all the single or blended amines containing MEA/DEAB, at a wide range of concentrations (0-5M MEA, 0-2M DEAB), CO₂ loading (0-0.52 mol/mol) and operating temperatures (24-70°C). With certain NMR amine samples tested, the concentration of amineH⁺/amine can be calculated from their chemical shifts δ (ppm), and it is unnecessary to duplicate the calibration process.

4. The amine regeneration studies can be developed with new sets of academic methodologies: the Potential Energy Surface (PES) diagrams of major amine regeneration reactions, the experimental ion speciation plots of VLE models for solutions at 90°C to perform analyses of solutions, and the introduction of solid catalysts into packing to cut heat duty.

5. The expected heat duty of a CO₂ pilot plant should be as low as 0.2 MWh/ton CO₂ (793 kJ/kg CO₂). From the studies in this research, the amine regeneration energy can be greatly reduced with three procedures: bicarbonate introduction from blended amine systems, solid catalysts, and lower operating temperatures of 90-95°C.

6. The introduction of tertiary amines provides bicarbonate (HCO₃⁻) in the solution, which is a key factor for amine regeneration. The bicarbonate also splits the regeneration process into two stages, fast and slow. The blended amine is preferred to a single amine as a better solvent. The introduction of solid catalysts makes it possible for the amine regeneration process to be performed below 100°C, which saves a huge amount of heat for water
vaporization. The solid acid catalyst Al$_2$O$_3$ duplicates part of the role of bicarbonate in the lean CO$_2$ region where bicarbonate is exhausted. The other catalyst H-ZSM-5 provides protons into the solutions to facilitate CO$_2$ production.

7. The catalytic packing should be applied to MEA/DEAB blended amine with solid acid catalyst (H-ZSM-5 or Al$_2$O$_3$) under lower regeneration temperatures of around 90-95°C, with hot water (95-98°C) as the heat source instead of steam.

8.2 Recommendations

The research was finished successfully the following further work is recommended:

1. The catalytic reactions of carbamate formation and breakdown should be investigated. Such as the mechanisms for the heterogeneous catalytic process and models, compared to the classic, non-catalytic Zwitterion mechanism proposed in 1968.

2. The reaction kinetics of catalytic carbamate formation and breakdown, the rate models, elementary steps, rate determines steps, catalytic activation energies will be of research interest for further analysis.

3. It is time to develop a novel amine scrubbing process which integrates the catalytic packing with the two other methods: solvent improvement and process improvement at an optimized ratio to cut the overall heat duty of the process.