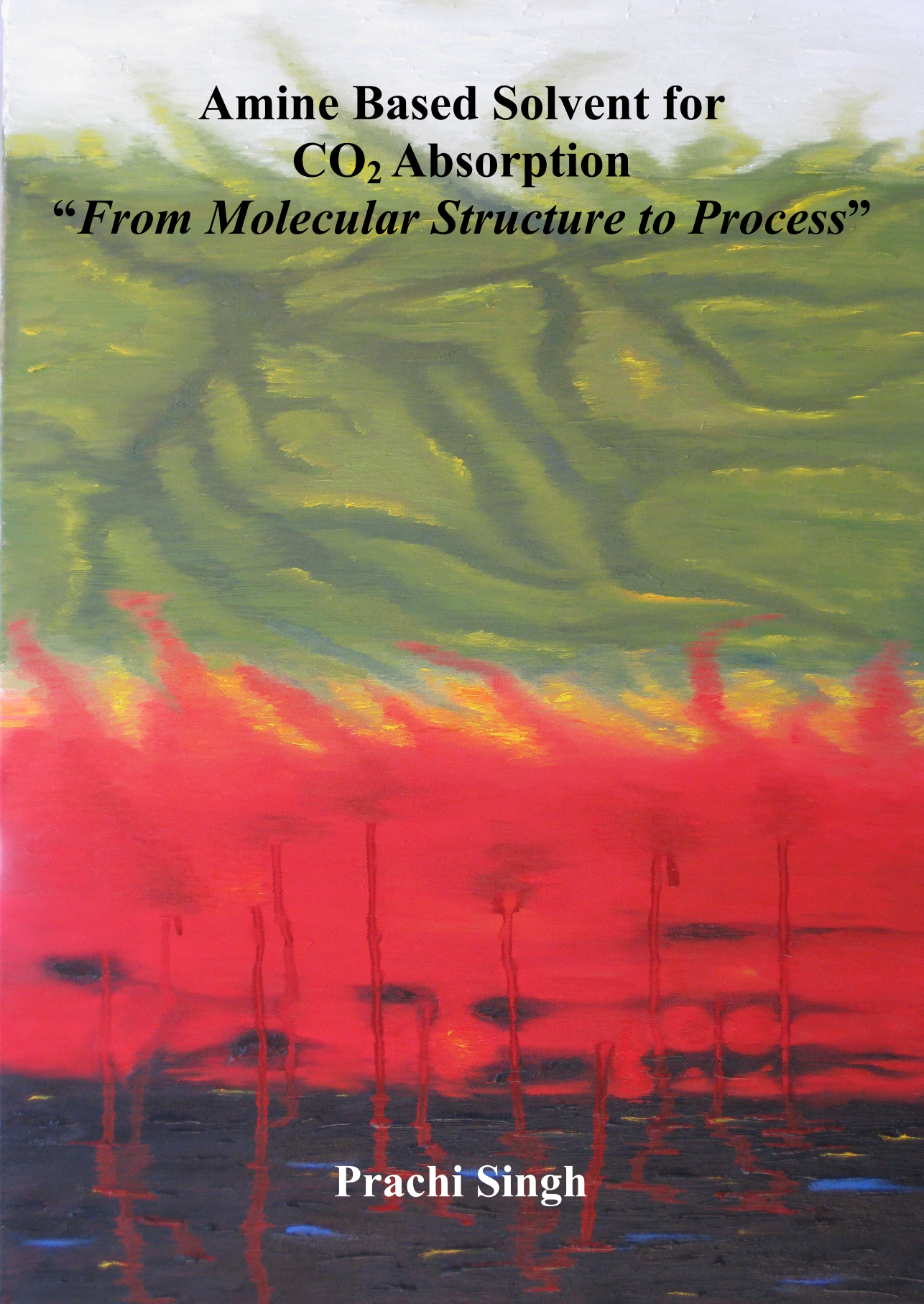
Amine Based Solvent for CO_2 Absorption

"*From Molecular Structure to Process*"



Prachi Singh

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Dit proefschrift is goedgekeurd door de promotor:
Prof.dr.ir. W. P. M. van Swaaij

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AMINE BASED SOLVENT FOR CO_2 ABSORPTION
"*FROM MOLECULAR STRUCTURE TO PROCESS*"

PROEFSCHRIFT

ter verkrijging van
de graad van doctor aan de Universiteit Twente,
op gezag van de rector magnificus,
prof.dr. H. Brinksma,
volgens besluit van het College voor Promoties
in het openbaar te verdedigen
op woensdag 1 juni 2011 om 12.45 uur

door

Prachi Singh
geboren op 29 April 1979
te Meerut, Uttar Pradesh, India

Dit proefschrift is goedgekeurd door de promotoren:
Prof.dr.ir. W. P. M. van Swaaij
Dr.ir. D. W. F. Brilman

Dedicated to my
Guru Ji

Summary

Global warming is a well known, worldwide concern, most probably caused by increasing concentrations of CO_2 and other greenhouse gases in the earth's atmosphere, due to human activities. Especially the production of electricity is a major contributor, responsible for 41% of the world CO_2 emissions in 2008. Worldwide, the power sector relies heavily on coal, the most carbon-intensive of fossil fuels, and hence amplifying its share in global emissions. Carbon Capture and Storage (CCS) offers the opportunity to reduce the CO_2 emissions associated with the use of fossil fuels. Carbon dioxide capture with a regenerable solvent is considered to be a mature technology, since it is successfully applied as CO_2 removal technology in industrial applications. In order to make this technology more economical for post-combustion capture, especially in the power-sector, more research is required to identify solvents which require less energy and lead to lower solvent loss- and corrosion rates in this application. In this thesis, the development of improved, energy efficient amine based solvents is targeted, through experimental (screening) work and by a further understanding of the role of molecular structure on the solvent absorption properties for amine based solvents in a CO_2 absorption process.

Primary and secondary amines react with CO_2 forming carbamate-species. The degree of hydrolysis of these carbamate to form bicarbonate depends on several factors, such as its chemical stability, which is influenced by the temperature. Tertiary amines groups cannot react with CO_2 directly to form a carbamate, because these amines lack a free proton. Hence, tertiary amines act as a base and catalyze the hydration of CO_2, leading to the formation of bicarbonate. Carbamate stability and basicity are the major parameters determining the absorption capacity and regeneration energy requirement. From literature it was identified that steric hindrance is an important parameter in reducing the carbamate stability and is also affecting the basicity of amine based solvents. Steric hindrance is present at different levels (low to high) depending on the number of functional groups substituted at α-carbon next to the amine group. Therefore, the effect of molecular structure like the carbon chain length, functional groups and steric hindrance on the basicity of various amines was studied. It was noticed that for alkanolamine and diamine basicity increases with an increase in carbon chain length, whereas alkyl amine basicity was not affected by an increase in carbon chain length. Difference between two pKa constants for diamines was reduced with an increase in carbon chain length. Steric hindrance showed an increase in the basicity for primary alkanol amines, primary alkylamines and secondary alkylamines, illustrating the clear relationship between the molecular structure and the basicity of the solvents.

The relative carbamate stability for various amine based solvents for CO_2 absorption has been studied by quantum mechanical calculations. Various molecular structure effects like carbon chain length, steric hindrance, functional groups and different configurations of cyclic amines have been investigated using the SM8 solvation model in combination with gas phase reaction energies calculated with the B3LYP density functional method. The trends observed for carbamate stability are (qualitatively) compared with experimental data reported in literature. This work gives theoretical support to the trends observed in earlier experimental studies Singh et al. (2007, 2009) on the effect of the molecular structure.

To identify, and to confirm above mentioned-, effects of molecular structure for amine based solvents on their CO_2 absorption capacity and reactivity, solvent screening experiments were performed for CO_2 absorption and regeneration conditions. The absorption of pure CO_2 was performed at 30°C and atmospheric pressure to assess a preliminary indication on the initial absorption rate and absorption capacity (or rich loading). The regeneration of CO_2 from saturated solvents was performed at 80°C and atmospheric pressure to determine the lean loading at pseudo equilibrium. Evaluation of desorption capacity (lean loading) at this relatively low temperature may point out more directly towards a more energy efficient solvent. Results showed that an increase in chain length between the amine and different functional groups in the absorbent structure, results in a decrease of the absorption rate, whereas the absorption capacity was increased in most of the absorbents. A steric hindrance effect was noticed when an alkyl group side chain was present at the alpha–carbon next to the amine group in the absorbent structure. An increase in the number of amine groups, up to 4 amine groups in the absorbent structure, results in an increase of absorption capacity, but also a higher lean loading. Aromatic amines substituted with alkyl groups showed slight increase in an initial absorption rate and absorption capacity. Cyclic saturated diamine substituted with a hydroxyl group by a side chain at the cyclic ring showed the lowest lean loading at pseudo equilibrium when compare to that of other functional group (alkyl or amine) substitution at cyclic ring.

Further study was done to evaluate these amine based solvents for CO_2 absorption capacity and reactivity at low CO_2 partial pressure, more close to flue gas emissions conditions. The CO_2 cyclic capacity (difference in rich and lean CO_2 loading) of various potential aqueous amine-based solvents was determined by performing CO_2 absorption experiments at 30°C and 10 kPa CO_2 partial pressure and regeneration at 90°C and atmospheric pressure. 1,7-Diaminoheptane and 1,6 Hexanediamine, N,N' dimethyl showed under the conditions studied comparatively high cyclic loadings of 0.81 and 0.85 mole CO_2/mole amine respectively. Aqueous solutions of 1,6 Hexanediamine, N,N' dimethyl of 0.5 and 2.55 mole/L concentration were selected to study solubility of CO_2 at different CO_2 partial pressure ranging from 1 up to 40 kPa, 30°C and at 1 atmosphere. The CO_2

solubility in 2.55 mole/L 1,6 Hexanediamine, N,N' dimethyl was found to be approximately twice as that of 2.5 mole/L MEA at lower CO_2 partial pressure.

Solubility experiments for CO_2 absorption have been performed for 0.5, 1 and 2.5 mole/L aqueous solution of 1,6 Hexamethylenediamine (HMDA) at 20, 30 and 40°C. The isothermal absorption capacity for CO_2 as function of HMDA concentration has been presented and the absorption enthalpy of CO_2 in 1 mole/L HMDA was calculated.

A study towards the kinetics of CO_2 in aqueous solutions of 1,6 Hexamethyl diamine (HMDA) and 1,6 Hexamethyl diamine, N,N' di-methyl (HMDA, N,N') was performed at concentrations ranging from 0.5 to 2.5 mole/L and temperatures from 10 up to 30°C. The kinetics data were determined by CO_2 absorption experiments using a stirred cell reactor with a flat interface between gas and liquid. These new CO_2 solvents were identified in earlier work for their high CO_2 capacity and limited corrosiveness. The reaction order with respect to HMDA was found to vary from 1.4 to 1.8 with increasing temperature. The secondary diamine HMDA, N,N' was found to be very reactive towards CO_2 and showed a lower temperature dependency. Additionally, the effect of CO_2 loading on the kinetics was studied for 0.5 mole/L aqueous solutions of HMDA and HMDA, N,N' at 20°C. Both solvents are from absorption kinetics point of view good candidates for further evaluation as solvent (-component) for CO_2 capture.

Based on above experiences, new amine based solvent formulations for CO_2 recovery from flue gasses were tested in a continuous flow pilot plant located at Shell Technology Centre, Amsterdam. The new formulations successfully passed an additional test on corrosivity and operability. Main focus of the pilot plant tests is the study of the energy requirement (MJ/kg CO_2) for these solvents. The two most promising solvents tested in this study were an aqueous solution of 26.74 wt% AMP (2-amino-2-methyl-1-propanol) + 11.91 wt% HMDA and a 51 wt% solution of "New solvent". At 90% (± 3%) CO_2 recovery the 51 wt% New solvent was found to be the most energy efficient one, requiring 2.48 and 2.26 MJ/kg CO_2 for 5 and 10 vol% CO_2 inlet concentration respectively. The mixture of AMP with HMDA required 3.62 and 3.41 MJ/kg CO_2 for 5 and 10 vol% CO_2 inlet concentration respectively, still considerable better than that for the MEA as a reference solvent. These new solvents therefore have attractive properties for CO_2 removal from flue gas, where energy consumption is an important factor.

In this thesis an improved understanding of the interaction between amine structure and CO_2 capture properties was developed, as well as a few potential solvents for post-combustion CO_2 capture. This is expected to benefit the development of even better solvents for CO_2 capture in the future.

Samenvatting

De opwarming van de aarde is een bekende, wereldwijde aangelegenheid, die zeer waarschijnlijk te relateren is aan de stijgende concentratie van CO_2 en andere broeikasgassen in the atmosfeer, mede veroorzaakt door menselijke activiteiten. Vooral de productie van elektriciteit uit fossiele brandstoffen levert daarbij een grote bijdrage. Deze is, ter illustratie, verantwoordelijk voor 41% van de wereldwijde CO_2 emissies in 2008. Wereldwijd is de energiesector sterk afhankelijk van het gebruik van kolen, de meest CO_2 intensieve fossiele brandstof, waardoor het aandeel in de wereldwijde emissies van anthropogeen CO_2 nog eens wordt versterkt. CO_2-afvangst en -opslag (CCS) biedt een mogelijkheid om de CO_2 emissies naar de atmosfeer, die geassocieerd zijn met het gebruik van fossiele brandstoffen, te reduceren.

Het afvangen van koolstofdioxide uit een gasstroom door middel van een regeneratief oplosmiddel wordt vaak gezien als een volwassen technologie, welke reeds succesvol als CO_2 verwijderingstechnologie industriëel wordt toegepast. Om deze technologie economisch aantrekkelijker te maken voor toepassing op rookgassen in de energie sector is additioneel onderzoek nodig om oplosmiddelen te identificeren die minder energie verbruiken en die leiden tot minder verlies aan oplosmiddel en minder corrosie van de gebruikte apparatuur. De doelstelling van dit proefschrift is derhalve de ontwikkeling van verbeterde, energie-efficiënte- en op amine gebaseerde oplosmiddelen. Dit wordt gedaan door het uitvoeren van verkennende karakteriserings-experimenten (‘screenen’) alsmede door middel van het verkrijgen van inzichten van het effect van de molecuulstructuur op de absorptie eigenschappen voor deze op amine gebaseerde oplosmiddelen in een CO_2 absorptie proces. Dit laatste wordt bereikt door zowel experimenteel als in de theoretische studies systematisch de effecten van de molekuulstructuur te onderzoeken.

Primaire en secundaire amines reageren met CO_2 waarbij carbamaten gevormd worden. De mate van hydrolyse van deze carbamaten en het vormen van bicarbonaat hangt af van verschillende factoren, zoals de chemische stabiliteit van het carbamaat, welke afhankelijk is van de temperatuur. Tertiaire amine groepen kunnen niet direct reageren met CO_2 tot carbamaten, omdat deze componenten een vrije proton in de aminegroep missen. Dientengevolge treden tertiaire amines alleen op als base en katalyseren zo de hydratatie van CO_2, waarbij bicarbonaat wordt gevormd.

Voor primaire en secundaire amines zijn de carbamaat stabiliteit en amine basiciteit de belangrijkste parameters welke de absorptie capaciteit en benodigde

regeneratie energie bepalen. In de literatuur wordt een belangrijke invloed toegeschreven aan sterische hinder op de carbamaat stabiliteit en op de basiciteit van de amine gebaseerde oplosmiddelen. Sterische hinder kan plaatsvinden op verschillende niveaus (van laag tot hoog), afhankelijk van het aantal gesubstitueerde functionele groepen op het α-koolstof atoom, direkt naast de amine groep. Daarom is het effect van de molecuulstructuur, zoals (met name) de lengte van de koolstofketen, de aanwezigheid van functionele groepen en sterische hinder op de basiciteit van de verschillende amines bestudeerd. Het is gebleken dat de basiciteit voor alkanolamines en di-amines steeg met toenemende lengte van de koolstofketen, terwijl voor alkyl amines de lengte van de koolstofketen nagenoeg geen invloed heeft op de basiciteit. Het verschil tussen de twee pKa constanten voor di-amines neemt af bij toenemende lengte van de koolstofketen tussen beide aminegroepen. Sterische hinder gaat gepaard met een toename in de basiciteit voor primaire alkanolamines, primaire alkyl amines and secundaire alkyl amines, hetgeen een duidelijke relatie laat zien tussen de molecuulstructuur en basiciteit van de oplosmiddelen.

De relatieve carbamaat stabiliteit van de diverse-, op amine gebaseerde oplosmiddelen voor CO_2 absorptie zijn bestudeerd door middel van kwantummechanische berekeningen. Enkele effecten van de molecuulstructuur, zoals de lengte van de koolstofketen, sterische hinder, de aanwezigheid van functionele groepen en verschillende configuraties van cyclische amines zijn onderzocht met behulp van het SM8 model voor de solvatie energie in combinatie met gasfase reactie energieën, berekend met de kwantummechanische B3LYP methode. De waargenomen trends voor de carbamaat stabiliteit zijn (kwalitatief) vergeleken met experimentele data uit de literatuur en geobserveerde trends uit de eigen experimentele studies naar het effect van de molecuulstructuur.

Om bovengenoemde effecten van de molecuulstructuur van amine gebaseerde oplosmiddelen op de CO_2 absorptiecapaciteit en reactiviteit te bestuderen en de theoretisch bepaalde trends te bevestigen, zijn er screening experimenten uitgevoerd onder CO_2-absorptie en -regeneratie condities. De absorptie van CO_2 is uitgevoerd bij 30°C en atmosferische druk om een indicatie te krijgen van de initiële absorptiesnelheid en absorptie capaciteit (‘rich loading’). De regeneratie van CO_2 verzadigde oplosmiddelen is uitgevoerd bij 80°C en atmosferische druk om de verarmde belading (‘lean loading’) bij pseudo evenwicht te bepalen. Evaluatie van deze verarmde belading kan, bij de toegepaste, relatief lage temperatuur wijzen op een energie-efficiënt oplosmiddel. Resultaten laten zien dat een toename van de lengte van de koolstofketen tussen de aminegroep en de verschillende functionele groepen in de oplosmiddelstructuur een afname van de absorptie snelheid tot gevolg had. De absorptie capaciteit steeg daarentegen voor de meeste oplosmiddelen. Het effect van sterische hinder was zichtbaar als er een alkyl zijketen verbonden was met het α-koolstof naast de amine groep in de molekuulstructuur. Een toename in het aantal amine groepen, tot vier amine

groepen in de oplosmiddelstructuur, resulteert in een toename van de capaciteit onder zowel absorptie als onder regeneratie condities. Aromatische amines, met alkyl substituenten laten een lichte toename zien in initiële absorptie snelheid en absorptie capaciteit. Cyclische verzadigde diamines, welke een hydroxyl groep hebben opgenomen in een zijketen van de cyclische ring laten een lagere verarmde belading zien bij pseudo evenwicht in vergelijking met een alkyl zijgroep.

In een vervolg onderzoek zijn deze op amine gebaseerde oplosmiddelen verder onderzocht op de CO_2 absorptie capaciteit and reactiviteit bij lage CO_2 partiaalspanning, vergelijkbaar met die onder rookgas condities. De cyclische capaciteit voor CO_2 voor de verschillende potentiële-, in water opgeloste, amine-gebaseerde absorptiemiddelen is bepaald door middel van CO_2 absorptie experimenten bij 30°C en 10 kPa CO_2 partiaalspanning en voor regeneratie bij 90°C en atmosferische druk. 1.7-Diaminoheptaan en 1,6-Hexaandiamine, N,N'-dimethyl lieten onder de onderzochte condities gelijkwaardige, hoge cyclische beladingen zien van respectievelijk 0.81 and 0.85 mol CO_2 per mol amine. Water gebaseerde oplossingen van 1,6 Hexaandiamine en 1.6-Hexaandiamine, N,N-dimethyl zijn derhalve geselecteerd om, bij een concentratie van 0.5 en 2.55 mol/l, de oplosbaarheid van CO_2 bij verschillende partiaalspanningen in het bereik van 1 tot 40 kPa bij 30°C nader te bepalen. De CO_2 oplosbaarheid in 2.55 mol/L 1,6-Hexaandiamine, N,N'-dimethyl bleek ongeveer tweemaal de oplosbaarheid van CO_2 in 2.5 mol/L Mono-Ethanol amine (MEA, commercieel beschikbaar (referentie-) oplosmiddel) bij lage CO_2 partiaalspanning.

Verdere oplosbaarheidsexperimenten voor CO_2 absorptie zijn uitgevoerd voor 0.50, 1.0 and 2.5 mol/L oplossingen van 1,6-Hexamethyleendiamine (HMDA) in water bij 20, 30 en 40°C. De isotherme absorptiecapaciteit voor CO_2 als functie van de HMDA concentratie is gepresenteerd en de daarmee gepaard gaande absorptie enthalpie voor CO_2 in 1 mol/L HMDA is berekend.

Een studie naar de absorptie kinetiek van CO_2 in water gebaseerde oplossingen van HMDA en 1,6-Hexamethyleendiamine, N,N'-dimethyl is uitgevoerd bij concentraties variërend van 0.5 tot 2.5 mol/L and temperaturen tussen 10 en 30°C. Deze nieuwe CO_2 oplosmiddelen zijn geselecteerd op basis van de voorafgaande studies vanwege hun hoge CO_2 capaciteit en gelimiteerde corrosieve eigenschappen. De CO_2 absorptie experimenten zijn uitgevoerd in een geroerde celreactor met een vlak grensvlak tussen het gas en de vloeistof. De reactieorde voor HMDA bleek te variëren tussen 1.4 en 1.8. Het secundair diamine HMDA, N,N' bleek zeer reactief te zijn ten opzichte van CO_2. Verder is het effect van CO_2 belading op de kinetiek bestudeerd voor 0.5 mol/L HMDA en HMDA, N,N' oplossingen bij een absorptietemperatuur van 20°C. Beide oplosmiddelen zijn vanuit het gezichtspunt van absorptie kinetiek zeer geschikte kandidaten voor verdere evaluatie als oplosmiddel (-component) voor CO_2-afvangst.

Gebaseerd op bovenstaande ervaringen zijn nieuwe, op amine gebaseerd oplosmiddel formuleringen voor CO_2 terugwinning uit rookgas getest in een continu bedreven proefinstallatie in de laboratoria van het "Shell Technology Centre" in Amsterdam. De nieuwe formuleringen hebben succesvol additionele testen op corrosiviteit en gebruiksgemak doorstaan. De belangrijkste doelstelling van deze proefinstallatie testen was de bepaling van de vereiste energiebehoefte (in MJ/kg CO_2) voor de regeneratie van deze oplosmiddelen. De twee meest veelbelovende oplosmiddelen getest in deze studie waren een watergebaseerde oplossing van 26.7 gewichtsprocent AMP (2-amino-2-methyl-1-propanol) met 11.9 gewichtsprocent HMDA alsmede een 51 gewichtsprocent oplossing "New Solvent", eveneens gebaseerd op voorafgaand werk. Bij 90% (±3%) CO_2 terugwinning bleek de 51%-oplossing "New Solvent" het meest energie efficiënt. Slechts 2.48 en 2.26 MJ/kg CO_2 is nodig voor de regeneratie van het oplosmiddel bij een gasstroom met een inlaat concentratie van respectievelijk 5 en 10 volumeprocent CO_2. Het mengsel van AMP met HMDA heeft respectievelijk 3.62 en 3.41 MJ/kg CO_2 nodig voor regeneratie bij dezelfde ingaande gasstromen met een inlaat concentratie van 5 en 10 volumeprocent CO_2. Deze resultaten zijn significant beter (20-50%) dan die voor het referentie oplosmiddel MEA, zoals bepaald in dezelfde proefinstallatie. Deze nieuwe oplosmiddelen hebben derhalve aantrekkelijke eigenschappen voor CO_2 verwijdering uit het rookgas van electriceitscentrales, waarbij energie consumptie een belangrijke factor is.

In dit proefschrift is de interactie tussen de amine structuur en CO_2 afvang eigenschappen nader onderzocht en in kaart gebracht. Daarnaast is een aantal potentiële oplosmiddelen voor CO_2 afvang uit rookgas geïdentificeerd en gekarakteriseerd. De verwachting is dat de opgedane kennis ten goede komt aan de verdere ontwikkeling van nog betere oplosmiddelen voor CO_2 afvangst in de toekomst.

CONTENTS

1
Introduction

1.1. Global warming

There is considerable scientific evidence that the risk of irreversible and potentially catastrophic environmental changes, like unstoppable melting of polar land ice or Arctic tundra, will increase significantly if global warming reaches 2°C or more above the pre-industrial temperature, which is around 1.2°C above today's level. This global warming effect is ascribed to the increasing concentrations of CO_2 and other greenhouse gases in the earth's atmosphere. Figure 1 shows the increase in the observed average surface temperature over the years. According to the United Nation-Intergovernmental Panel on Climate Change (IPCC) and the IPCC projects a further global warming of minimally 1.8 to 4°C in this century, and in the worst case 6.4°C, is expected. This can be avoided if international community acts to cut down greenhouse gas (GHG) emissions. Among the greenhouse gasses, CO_2 is seen as the main contributor.

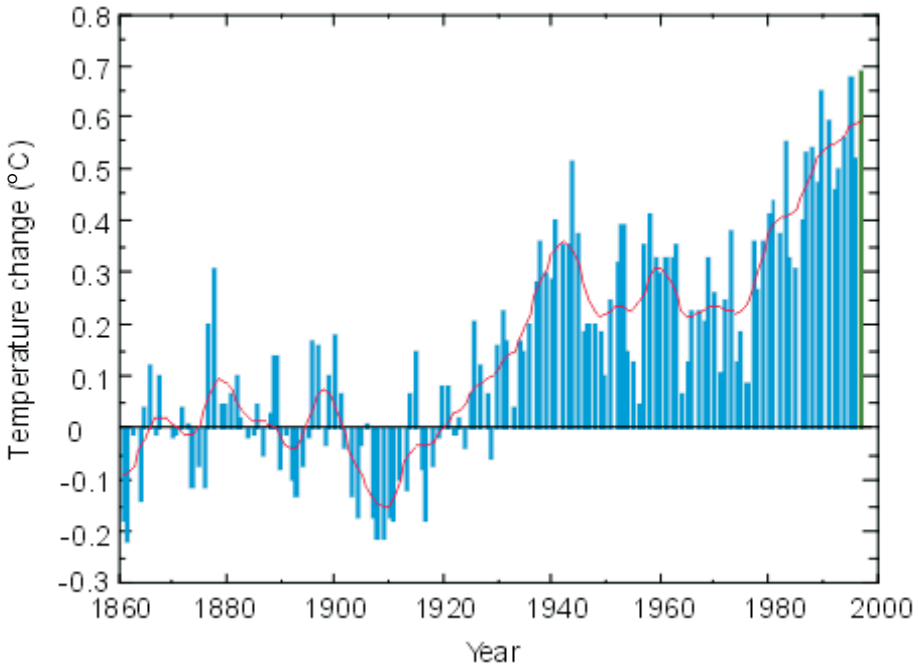

Figure 1, The observed change in global mean temperature at ground level (Source UK Met. Office).

Through the Kyoto Protocol (1997), developed countries agreed to reduce their CO_2 emissions by 5.2% below their 1990 levels. European Union (EU) has even agreed in 2008 to reduce GHG emissions to 20% below 1990 levels by 2020. However, given the increasing fossil energy consumption, the CO_2 emission level is likely to continue increasing, so even greater reductions in the CO_2 emissions will be required in the future. It was calculated that, for example, emissions of CO_2

may need to be reduced by more than 60% by 2100, in order to stabilise the atmospheric concentration of CO_2 at no more than 50% above its current level.

1.2. CO_2 emission

Figures 2 and 3, shows the upward trend of CO_2 emission in the early years of the 21st century. Fossil fuels are the dominant form of energy utilized in the world (86%) and account for around 75% of the anthropogenic CO_2 emissions (IPCC, 2001c).

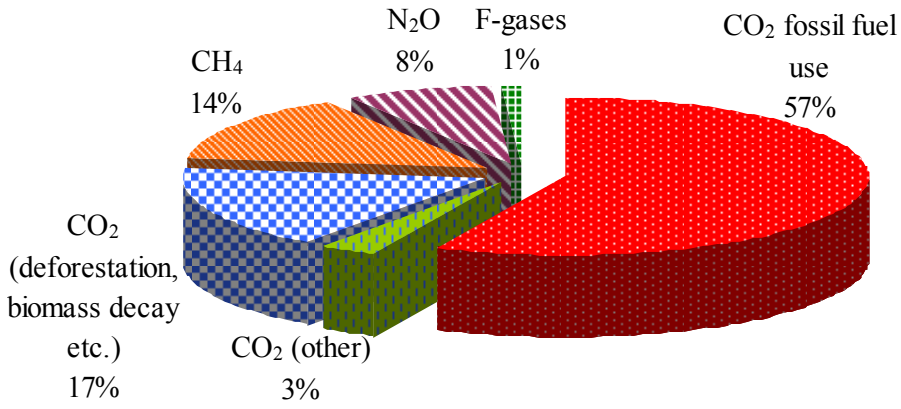

Figure 2, Share of different Greenhouse gases in total global emissions in 2004 (IPCC, 2007).

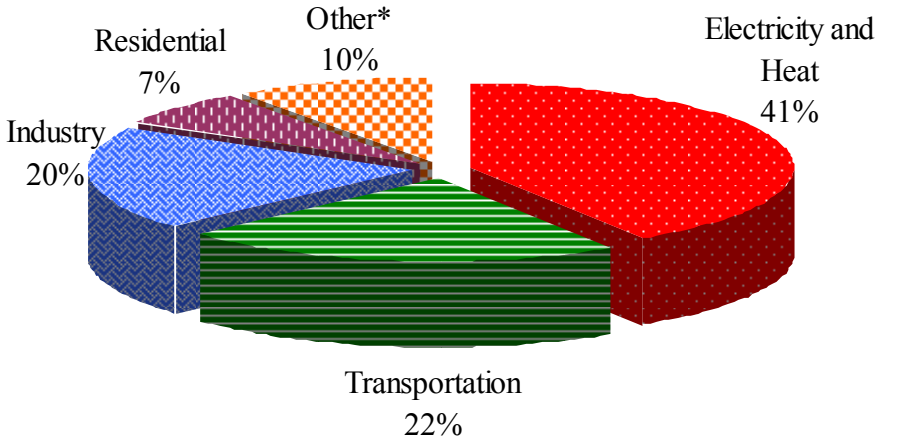

Figure 3, World CO_2 emission by sector 2008 (IEA, 2010).
*Other includes commercial/public services, agriculture/forestry, fishing, energy industries other than electricity and heat generation, and other emissions not specified elsewhere.

Electricity and heat generation and transportation are the sectors which produced two-thirds of global CO_2 emissions in 2008 (Figure 3). Generation of electricity and heat (also known as public utilities) was by itself the main contributor to the CO_2 emissions and responsible for 41% of the world CO_2 emissions in 2008. Worldwide, the electricity and heat sector relies heavily on coal, which is the most carbon-intensive fossil fuels. Countries such as Australia, China, India, Poland and South Africa produce between 69% and 94% of their electricity and heat through the combustion of coal. The future emissions intensity of the electricity and heat sector depends strongly on the fuel that will be used to generate the electricity and on the share of non-emitting sources from renewable sources and nuclear energy. By 2030, the World energy outlook (WEO) 2009 projects that demand for electricity will be almost twice as high as the current demand, driven by rapid growth in population and in income in the developing countries, by the continuing increase in the number of electrical devices used in homes and commercial buildings and by the growth in electrically driven industrial processes.

These trends underline the demand to develop technologies to reduce CO_2 emission associated with the use of fossil fuels. Carbon dioxide Capture and Storage (CCS) offers this opportunity to reduce CO_2 emission.

1.3. Carbon Capture and Storage (CCS)

CCS is defined as a system of technologies that integrates CO_2 capture, transportation and geological storage (see Figure 4). Each stage of CCS is in principle technically available and has been used commercially for many years (IEA 2008b). However, various competing technologies, with different degrees of maturity, are competing to be the low-cost solution for each stage within the CCS value chain. For CO_2 capture, different technologies are being used by industry to remove CO_2 from gas streams, where it was an undesirable contaminant or needed to be separated as a product gas. There are currently three primary methods for CO_2 capture; post-combustion capture, pre-combustion capture and oxy-fuel processes. Post-combustion capture involves scrubbing CO_2 from the flue gas from a combustion process. Oxyfuel combustion refers to combustion of fuel using pure oxygen, thereby produce a CO_2-rich gas. In a pre-combustion process gasification is followed by CO_2 separation prior to the use of the produced hydrogen as a fuel gas.

CO_2 transport is done for over 30 years in North America; over 30 metric tonnes of CO_2 from natural and anthropogenic sources are transported per year through 6200 km of CO_2 pipelines in the USA and Canada, mainly for enhanced oil recovery (EOR) IEA GHG (2009). CO_2 is transported at high pressure through a network of pipeline. Ships, trucks and trains have also been used for CO_2 transportation in early CCS demonstration projects and in regions with inadequate storage.

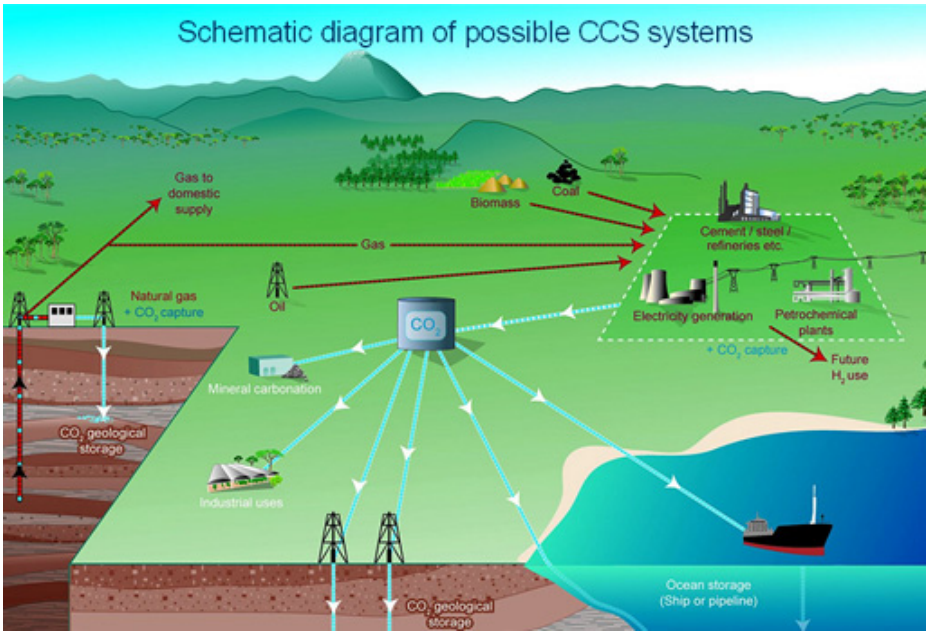

Figure 4, The Carbon Capture and Storage (CCS) process (Source IPCC).

CO_2 storage involves the injection of supercritical CO_2 into a geologic formation. On geological timescales this CO_2 will partly be fixed in minerals by carbonation reactions. There are three common options for geological CO_2 storage; saline aquifers, oil and gas reservoirs, and deep unminable coal seams (IEA, 2008b). It is expected that saline aquifer formations provide the largest storage capacities quantities for CO_2, followed by oil and gas reservoirs. A number of projects involving the injection of CO_2 into oil reservoirs have been conducted, primarily in the USA and Canada. Most of these projects use the CO_2 for enhanced oil recovery (EOR).

1.4. CO_2 capture technology development

The three different types of CO_2 capture process are as follows:

1.4.1. Pre-combustion capture power plants

In pre-combustion carbon dioxide capture, CO_2 is separated from the fossil fuel (coal or natural gas) before combustion. Figure 5 shows the schematic picture of CO_2 pre-combustion capture process. The principle of this process is to first convert the fossil fuel into synthesis gas ($CO+H_2$). In Figure 5 steam reforming is indicated, but in many cases gasification by partial oxidation with oxygen and steam will be used. This synthesis gas is send to a shift reactor (not indicated in Figure 5) where it reacts with steam to produce a mixture of CO_2 and H_2. Then CO_2

is separated from the (high pressure) gas mixture and H_2 is send to the turbine to be combusted.

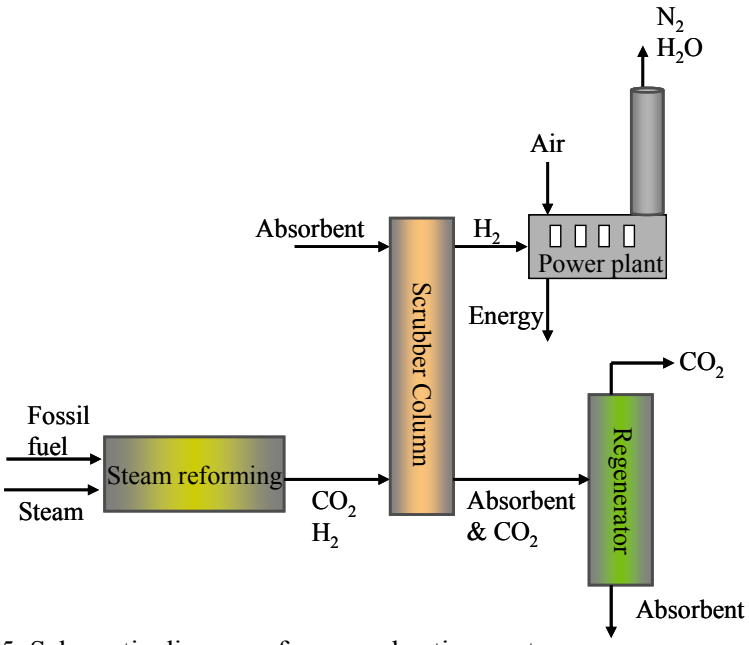

Figure 5, Schematic diagram of pre-combustion capture.

In this technology development is ongoing to reduce the amount of steam required to perform the water gas shift reaction from CO and steam to CO_2 and H_2. Combining CO_2 sorption with water-gas shift activity is an alternative promising technology under development. Other development activities focus on increasing the efficiency of the gas turbine used to combust H_2 and the development of other separation methods like pressure swing adsorption, electrical swing adsorption, gas separation membranes and cryogenics.

1.4.2. Oxy-combustion capture power plants

In traditional fossil fuelled power plants, combustion of fuel is carried out using air, and the nitrogen (N_2) in the air ends up in the flue gas. However, also pure oxygen (O_2) can be used, together with recycled flue gas, as an alternative to air for fuel combustion, see Figure 6. Such a process is called an oxyfuel combustion process. This has the advantage that the flue gas only contains steam and CO_2, which can easily be separated by cooling. The water is condensed and after phase separation a CO_2 rich gas-stream is obtained. Up to 100 percent CO_2 can be captured in this process. In oxy-combustion processes, the air separation unit is the most expensive part.

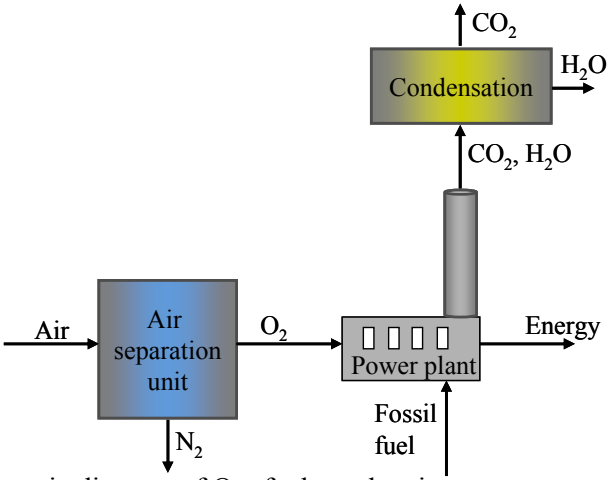

Figure 6, Schematic diagram of Oxyfuel-combustion capture.

Air separation is commercially done using cryogenic distillation, an optimized and mature technology leaving little room for further improvement. Oxy-fuel processes have a further disadvantage that they are difficult to implement as a retro-fit option for existing installations.

1.4.3. Post-combustion capture power plants

Carbon dioxide post-combustion capture is considered to be one of the most mature capture technologies, since there is a good experience and reputation of this type of technology within many other industrial applications (Rao et al., 2002).

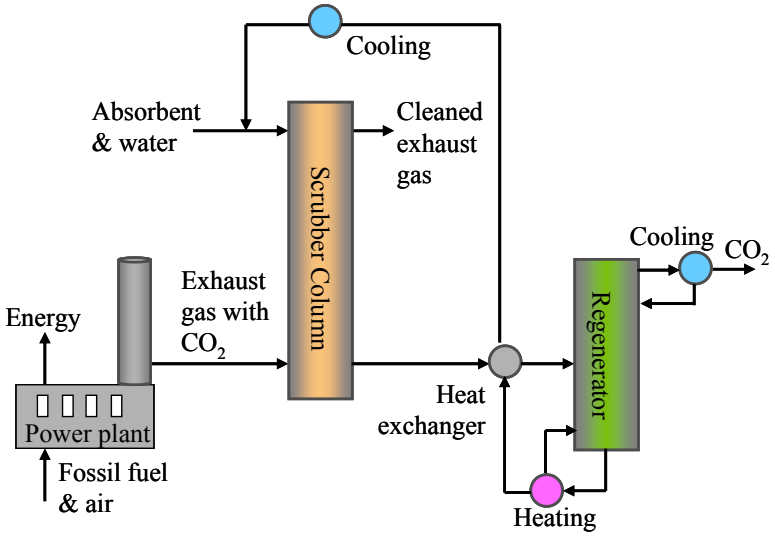

Figure 7, Schematic diagram of post-combustion capture.

Separation of CO_2 from gas mixtures is a commercially applied technology which is in use at hundreds of locations around the world. There are many small facilities in operation today using amine based solvents to capture significant flows of CO_2 from flue gas. However, this technology has yet to be fully demonstrated at the scale of a commercial-scale power plant (up to 500 ton CO_2/hr). The general chemical absorption process of CO_2 from flue gas is shown schematically in Figures 7 & 8. This process is based on the reversible characteristic of the temperature dependent reaction of CO_2, and other acid gases, with aqueous solutions of amine based absorbents. The flue gas of a power plant is first cooled (and desulphurized) before it is brought into contact with the solvent. The flue gas is pumped through an absorption column where CO_2 reacts with the amine based absorbent at temperatures between, typically, 40 to 60°C. The flue gas is then washed to remove water and solvent droplets/vapour at the top of absorber column. The CO_2-rich solvent is send to the top of the stripper column. In this column, heat is used to free the CO_2.

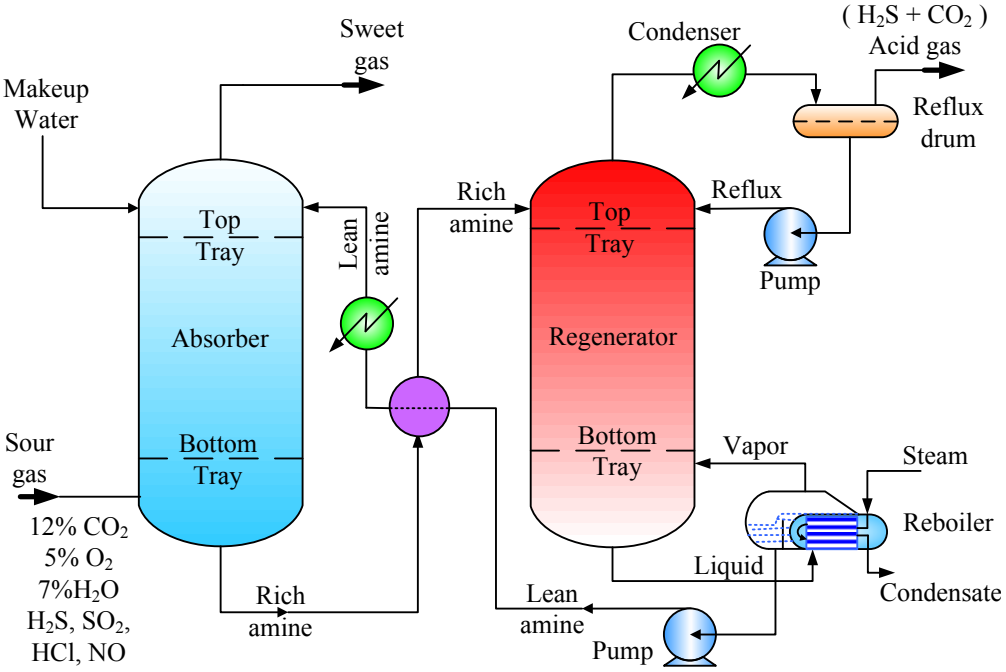

Figure 8, Schematic representation of a flue-gas CO_2 absorption process.

The regeneration of the solvent takes place at a temperature between 100 and 140°C. This heat is generated in a reboiler from steam extracted from the power cycle. The pressure of the regeneration process is nearly atmospheric. The gas stream from the stripper is a CO_2/H_2O mixture. The H_2O is recovered by a condenser, after which the CO_2 is pressurized to be send for transportation. Heat from the CO_2-lean solvent is then transferred to the CO_2-rich solvent in a heat

exchanger referred as a lean-rich heat exchanger. Although the post-combustion capture is a mature technology, considerable R&D efforts are undertaken, as there is a need for new solvents requiring less energy for regeneration, solvents showing lower solvent loss rates via degradation and evaporation and less equipment corrosion. Furthermore alternative process (stripper-) configurations and alternative means of capturing CO_2, such as membrane separations, chemical looping and solid adsorption processes are being studied. Most of these alternative separations technologies are still in the R&D stage, but may be able to improve the overall efficiency of the process in the future.

1.5. Commercial solvents for CO_2 post combustion capture process

The development of aqueous solutions of alkanolamines as absorption liquid for acidic gases started with the work by R.R. Bottoms for which a patent was granted in 1930 (Kohl et al. 1997). Triethanolamine (TEA) was the first alkanolamine commercially available and was used in these early gas-treating plants. Other alkanolamines were subsequently introduced into the market as possible acid-gas absorbents. Monoethanolamine (MEA), Diethanolamine (DEA), and Methyldiethanolamine (MDEA) are alkanolamines that proved to be of principal commercial interest for gas purification (Kohl et al. 1997). Triethanolamine was found to be less attractive mainly due to its low absorption capacity (resulting from higher equivalent weight), its lower reactivity and its relatively poor stability. Diisopropanolamine (DIPA) (Bally, 1961) was used to some extent in the Adip process and in the Sulfinol process, as well as in the SCOT process for Claus plant tail gas purification but gradually displaced by Methyldiethanolamine (MDEA) in these applications In addition to aqueous solutions of single solvents, more and more mixtures of amines with various additives (e.g. for corrosion inhibition or absorption rate promotion) are introduced in the market and being used. A different class of acid gas absorbents, the sterically hindered amines, was disclosed by EXXON Research and Engineering Company (Anon., 1981; Goldstein, 1983; Sartori and Savage, 1983).

Hence, from above it is clear that commercially available solvents are continuously being improved with respect to their performance for CO_2 absorption. In following section an overview is given on the effect of solvent characteristics on the economics of a CO_2 post combustion capture process, as they determine among other things the energy use (e.g. for regeneration and for heating/cooling the circulating absorption liquid), the solvent losses (via degradation and evaporation) and the capital costs (size of absorber and desorber equipment and heat exchanger). The most important characteristics, summarized in Figure 9, are the solvent CO_2 loading (cyclic capacity), the chemical binding energy, the absorption rate and the absorption- and desorption temperatures (Peeters et al., 2007). When CO_2 compression is included, the chemical binding energy is responsible for over 40% of the regeneration energy requirements and about 25% of the energy penalty in a state-of-the-art Monoethanol amine (MEA)-based processes (Peeters et al., 2007).

A low binding energy often comes together with a low reactivity towards CO_2 and, similarly, a high absorption rate is normally accompanied by a high binding energy. The absorption rate determines the required absorber dimensions and is important as the capital costs of absorber make up about 40% of the total costs of the amine-based CO_2 post combustion capture plant (IEA GHG, 2004).

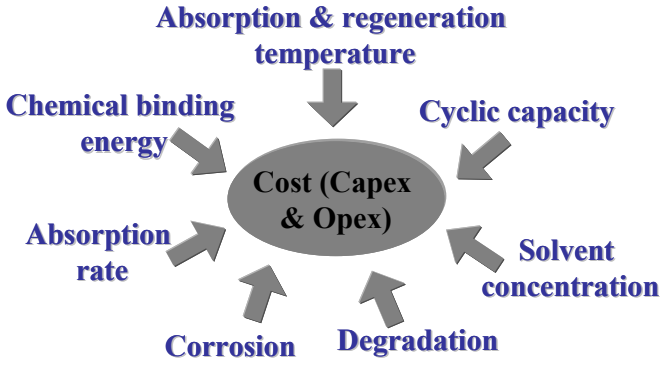

Figure 9, Various solvent parameters affecting CO_2 post combustion capture economics.

The cyclic loading of the solvent is the difference between lean and rich CO_2 loading (see Figure 8) in terms of mole of CO_2 per kilogram solvent. A high cyclic loading will result in lower solvent circulation flow rate in the amine plant, which will influence the dimensions of the solvent heat exchanger, the amine pumps, the reboiler, the absorber, and piping. High cyclic loading will also lower the electricity consumption of the amine pumps and the energy required for solvent heating. In addition, a smaller absorber will lower the flue gas blower energy requirements and dimensions.

The absorption temperature determines the costs and the energy requirements of the flue gas coolers. Bringing the absorption temperature closer to the desorption temperature will decrease the costs of the solvent heat exchanger. For CO_2 capture in a power-plant setting, the desorption temperature determines the temperature of the steam that has to be extracted from the steam turbine. Bolland and Undrum (2003), showed that there is a strong dependency between the energy output of the steam cycle and the steam temperature. For specific solvents, lowering desorption temperature will mean a higher lean CO_2 loading and thus a smaller cyclic loading.

Counteracting this with higher solvent concentrations is not always possible, due to the corrosive nature of amine based solvents. The stability of the amine based solvent and the specific solvent costs are also important characteristics with respect to Opex (operational cost), influencing the solvent make-up and replacement costs. Furthermore, evaporative losses and associated health risks and the impact on the environment are becoming increasingly important. The solvent replacement cost is

strongly dependent on the solvent costs. For MEA, the share of the solvent replacement costs is about 8% of the incremental cost of electricity (COE). Formation of degradation products are thought to play an important role in the corrosion (Chakravarti et al., 2001). The corrosion mainly affects the stripper, reboiler and lean-rich heat exchangers. Reducing the degradation rate will thus result in lowering the Opex and the Capex of the critical parts in the CO_2 capture plant.

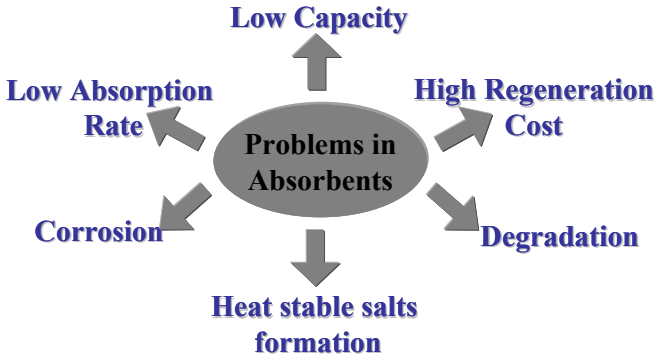

Figure 10, Existing problems in commercial amine based solvents.

Despite several studies on (individual) aqueous amine based solvents in past, the above mentioned aspects are still not entirely met by the current commercial solvents for CO_2 absorption (see Figure 10). An improved understanding on the relationship between the molecular structure of the amine based solvent and its performance as CO_2 absorbent is desired to be able to develop improved solvents for CO_2 absorption in the future.

1.6. Thesis objectives and outline

This thesis focuses on the development of an energy efficient solvent for a CO_2 post-combustion absorption process, by evaluating the absorption properties of amine-based solvents with different molecular structure, as illustrated in Figure 11.

To achieve this goal, first knowledge on structure-activity relationships for amine based absorbents for CO_2 absorption is developed, both by experimental work and (molecular) calculations. As a result, the knowledge should cumulate into the development of an improved, more energy efficient solvent for CO_2 absorption.

Chapter 2 focuses on understanding the reaction mechanism between an amine and CO_2 and on the identification of the solvent properties influencing their performance for CO_2 absorption. The amine group basicity and carbamate stability were found to be most important characteristics. The effect of different molecular structure on basicity was evaluated in this chapter.

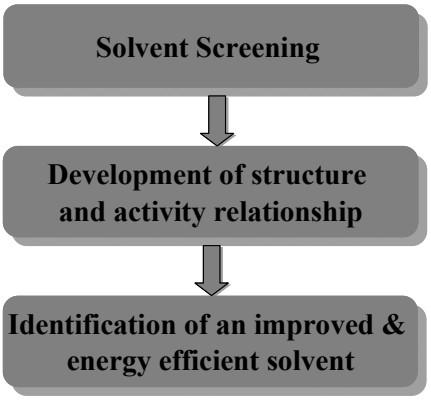

Figure 11, Thesis objective and overall outline.

In ***Chapter 3*** the effect of molecular structure on the stability of the carbamate, reaction product of the amine solvent with CO_2, was studied using quantum mechanical calculations.

Taking the knowledge gained in this work into account, a first round of solvent selection was made, based on basicity, solubility in water, cost, volatility and environmental hazard. This set of solvents will be used for experimental validation of trends identified in Chapter 2 and Chapter 3.

Solvent screening experiments were performed using CO_2 absorption and regeneration with selected solvents and the results thereof are reported in ***Chapter 4***. In these solvent screening experiments various solvent molecular structural aspects were tested on their influences on CO_2 absorption capacity, initial CO_2 absorption rate and regeneration capacity.

In ***Chapter 5***, for the more promising solvents identified in Chapter 4, subsequent solvent screening experiments were performed at low CO_2 partial pressure to determine their CO_2 absorption and regeneration capacity under more realistic conditions. From this work the potential solvents 1,6 Hexamethyl diamine (HMDA) and 1,6 Hexamethyl diamine, N,N' di-methyl (HMDA, N,N') were selected for further investigation.

In ***Chapter 6*** the CO_2 solubility for the selected solvent candidate 1,6 Hexamethyl diamine (HMDA) was determined experimentally at different solvent concentrations and temperatures. ***Chapter 7*** focuses on determining kinetics of CO_2 absorption in aqueous solution of 1,6 Hexamethyl diamine (HMDA) and 1,6 Hexamethyl diamine, N,N' di-methyl (HMDA, N,N'), using a stirred cell contactor.

Before testing the solvents in a pilot plant corrosion tests were performed, showing satisfactory performance. In ***Chapter 8*** the results of these corrosion tests are reported together with the CO_2 capture performance in the pilot plant. The performance of the solvents selected, including a combination of AMP with HMDA (2-Amino-2-methyl-1-propanol with 1,6 Hexamethylenediamine) and New Solvent, was very promising as their energy requirement at 90% CO_2 recovery was significantly lower (25% for AMP/HMDA and 50% for the New Solvent) than for the MEA reference runs.

Hence, within this study, in addition to the effects studied for the relation between solvent molecule structure and CO_2 capture properties, promising- and energy efficient solvent candidates for (post-combustion) CO_2 capture have been identified.

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2

CO_2 absorption with amine based solvents: Insight in the effect of molecular structure on solvent properties

Primary and secondary amines based solvents can react with CO_2 to form carbamates. The degree of hydrolysis of these carbamates to form bicarbonate depends on the chemical stability of the carbamate, which is influenced by the temperature and solvent molecular structure. The carbamate stability is an important parameter determining the CO_2 absorption capacity and the CO_2 regeneration energy requirement. From literature it also identified that steric hindrance is an important parameter in reducing the carbamate stability and is also affecting the basicity of amine based solvents. It is also noticed that the level of steric hindrance (low to high) depends on the number and type of functional group substituted at α-carbon to the amine group, affecting the solvents characteristics for CO_2 absorption capacity and CO_2 absorption kinetics accordingly. From literature, it is further clear that the presence of different functional groups (like hydroxyl-, alkyl-, acid groups) and that the presence of more than one amine group or a cyclic structure of the molecule are affecting amine based solvents CO_2 absorption properties, most directly reflected in their basicity.

The effect of carbon chain length, different functional group and steric hindrance on the basicity of various amines was therefore studied more systematically. It was noticed that for alkanolamine and diamine basicity increases with an increase in carbon chain length. Still alkyl amine basicity was not affected by increase in carbon chain length. The difference between the two pKa constants for diamines was reduced with an increase in the carbon chain length. The steric hindrance effect showed an increase in the basicity for primary alkanolamine, primary alkylamine and secondary alkylamine. Whereas, diamines basicity was not influenced by steric hindrance. The effects of molecular structure aspects like carbon chain length, different functional groups and steric hindrance on the carbamate stability is identified as important topic for further study. An improved understanding thereof is expected to assist in the development of improved solvents for CO_2 absorption.

2.1. Introduction

For a CO_2 capture process using (aqueous) amine-based solvents, the absorption/desorption characteristics of the amine based solvents determine the operational and material (O&M) costs, most directly via the energy use and solvent losses, and indirectly it also influences the capital costs via the size and specifications of the process equipment required. The most important characteristics for a regenerative CO_2-solvent are therefore the chemical binding energy, the absorption rate, the cyclic solvent CO_2-loading and the absorption- and desorption temperatures. Further important characteristics with respect to O&M costs and the impact on the environment include the stability of the solvent towards thermal and oxidative degradation in combination with the specific solvent costs, secondary effects with respect to e.g. equipment corrosion or eco-toxicity due to possible degradation products and solvent losses due to its volatility.

When CO_2 compression is included in the CO_2 capture process evaluation, the chemical binding energy is responsible for over 40% of the regeneration energy requirements and about 25% of the energy penalty for state-of-the-art Monoethanolamine (MEA)-based CO_2 capture processes (Peeters et al., 2007). In general, a lower value for the chemical binding energy corresponds with a lower absorption rate, leading to an increased size for the absorption equipment and consequently a higher capital expenditure. The desorption rate, on the other hand is positively effected as CO_2 is easily released. This is, however, a much less important variable because the desorption rate is normally much higher than the absorption rate (due to much higher operation temperature in regenerator). The absorption rate determines the required absorber dimensions. Because the capital costs of absorber make up about 40% of the total costs of an amine plant (IEA GHG report, 2004), there is a strong coupling between absorption rate and the total capital costs. Additionally, a change in absorber size will directly effect the energy requirements and capital costs of the flue gas blower, which is by itself responsible for increase in both the energy penalty and the overall absorption plant costs. Although the dependency of both capital costs and energy requirements on the absorption rate is high, a further improvement of the absorption rate is in itself not considered to be a major development target in the available literature. It is, however, important that the absorption rate for the newly developed solvents should not be significantly below than that of MEA-based reference solvents, when the other parameters are changed, especially the chemical binding energy of the solvent.

The effective loading (or cyclic loading) of the solvent is the difference between lean- and rich loading in terms of mole of CO_2 per kilogram solvent, cycling between the absorber and desorber unit. A high effective solvent loading leads to a smaller solvent circulation in the amine plant, which will influence the dimensions of the lean-rich solvent heat exchanger, the amine pumps, the reboiler, the absorber etc. It will also lower the electricity consumption of the amine pumps and the

energy required for solvent heating. In addition, a smaller absorber will lower the flue gas blower energy requirements and dimensions, as already described by Bolland and Undrum (2003). The amine pumps have a minor share in the energy penalty (3%), but a much larger share (12%) in the capital costs of the capture plant. The costs of the lean-rich heat exchanger are relatively small about 2% of the absorption plant costs. For a specific solvent, the optimal value of the effective loading is determined by the combined effect of the following process parameters: absorption temperature, desorption temperature and absorbent concentration. The absorption temperature determines the costs and the energy requirements of the flue gas coolers. Bringing the absorption temperature closer to desorption temperature will decrease the costs of the solvent heat exchanger. The desorption temperature determines the (minimum) temperature and amount of the steam required in the desorber which in a power-plant should probably be extracted from the steam turbine. As shown by Bolland and Undrum et al. 2003, there is a strong dependency between the energy output of the steam cycle and the steam temperature. For specific solvents lowering desorption temperature will result in a higher lean loading and thus a smaller effective loading, as discussed earlier.

Other solvent-related parameters can also play a decisive role in the development of a suitable solvent for CO_2 absorption. In addition to aspects related to safety issues (toxicity of the amine or its degradation products) and solvent losses (via degradation or evaporation) also the corrosiveness of the solvent is an issue. As many amine-based absorbents are corrosive, there are limitations with regard to the concentration at which they can be economically applied. These maximum solvent concentrations can, however, be increased when corrosion inhibitors are used.

Considering above mentioned solvent parameters influencing the cost of CO_2 absorption process, it is important to develop a clear understanding on the solvent molecular property influencing its CO_2 absorption characteristics. An improved understanding may prove to be very valuable in the search for a suitable solvent or to develop tailor-made molecules that could carry out the chemical absorption of CO_2 in light of above mentioned process requirements. So far, these aspects have received little attention in literature, particularly in engineering science. Often the attention has been focused on e.g. facilitated-transport phenomena, whereas relatively little emphasis has been placed on a fundamental understanding of the molecular chemistry of these systems. Based on various literature sources it is tried to present a comprehensive overview of the reaction mechanisms and the effect of molecular structure aspects, like steric hindrance, amine basicity and the effect of different functional groups, on the characteristics relevant to CO_2 absorption.

In the next sections, first an overview of literature is presented on the reactions and reaction mechanisms as well as on the effects of steric hindrance and the presence of functional groups and the (resulting) basicity of the amine-based solvents.

Subsequently the results for a more systematic investigation of the effect of molecular structure on the basicity of amine based solvents will be presented.

2.2. Reaction mechanism

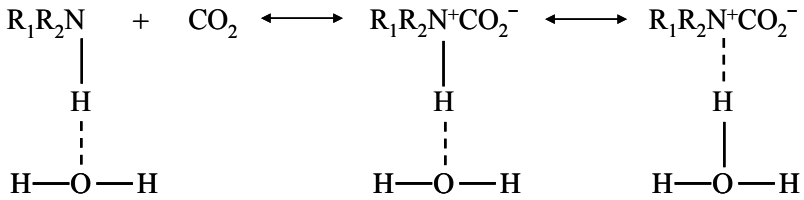
2.2.1. Primary and Secondary amines

Caplow (1968) introduced a reaction mechanism for the reaction between CO_2 and amine based solvents on the formation of a zwitterion followed by the removal of a proton by a base B:

$$CO_2 + R_1R_2NH \longleftrightarrow R_1R_2NH^+COO^- \quad (1)$$

$$R_1R_2NH^+COO^- + B \longleftrightarrow R_1R_2NCOO^- + BH^+ \quad (2)$$

R_1 and R_2 represents substituted group attached to the amine group; B represents a base molecule which may be a hydroxyl ion, water or an amine-functionality.

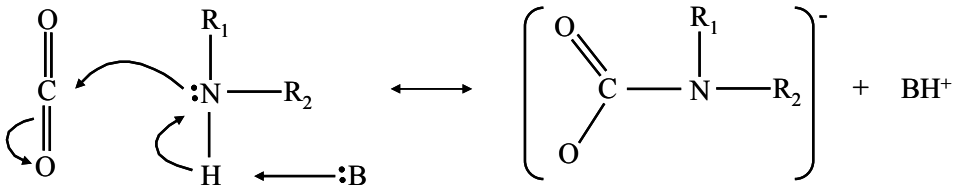


In the mechanism shown below CO_2 forms a bond to the hydrated amine group (with a hydrogen on the amine weakly bonded to the oxygen of water) forming a zwitterion in a first step. In a second step the deprotonation of the amine takes place in presence of base molecule. The intermediate species in the reaction is a zwitterion. One important feature of the mechanism proposed by Caplow (1968) is the assumption that a hydrogen bond is formed between the amine and a water (base) molecule before the amine reacts with the CO_2 molecule. Danckwerts et al. 1979 introduced this mechanism into the chemical engineering literature, and Blauwhoff et al. 1984 and Mahajani and Joshi 1988 showed that this mechanism reconciled much of the data in the literature, especially for Diethanolamine (DEA) and other secondary amines. Although Danckwerts and other investigators after considering that the zwitterion species to be attacked by a base which extracts a proton in their work, they ignore the suggestion that the amine group may be hydrated before forming the zwitterion. More recent da Silva and Svendsen (2004) and Ohno et al. 1999 suggested on the basis of quantum mechanical calculations that any zwitterion species is likely to be very unstable. The zwitterion may be an entirely transient state (giving a single-step mechanism), it may be a short-lived species or it may be a transition state.

Crooks and Donnellan (1989), proposed a single step, termolecular mechanism:

$$B + R_1R_2NH + CO_2 \longleftrightarrow R_1R_2NCOO^- + BH^+ \quad (3)$$

Here, B is a base molecule. In this termolecular mechanism, the bonding between amine and CO_2 and the proton transfer takes place simultaneously.



2.2.2. Carbamate stability and bicarbonate formation

The carbamate formed, either via the termolecular or zwitterion mechanism, tends to undergo hydrolysis, thereby forming a bicarbonate species:

$$R_1R_2NCOO^- + H_2O \longleftrightarrow R_1R_2NH + HCO_3^- \quad (4)$$

The degree of hydrolysis of the carbamate species depends on several factors, such as its chemical stability, which is strongly influenced by the temperature. In studies by Caplow (1968) the kinetics of carbamate formation and -breakdown for different types of amines were investigated. It was found in that study that the carbamate formation equilibrium constant showed a nonlinear relationship with the with pKa (basicity) of the solvent, which suggests that factors other than basicity play a role in the formation and breakdown of carbamate. McCann et al. 2010 shows that the amines with a lower pKa values typically show lower carbamate equilibrium constants.

CO_2 can also react directly in aqueous amine systems to form bicarbonate. The formation of bicarbonate from CO_2 and water is a well known reaction, which can be described by following three (related) reactions.

$$CO_{2\,(aq)} + H_2O \longleftrightarrow H_2CO_3 \quad (5)$$

$$CO_{2\,(aq)} + OH^- \longleftrightarrow HCO_3^- \quad (6)$$

$$H_2CO_3 + OH^- \longleftrightarrow HCO_3^- + H_2O \quad (7)$$

Bicarbonate can again be deprotonated by a base molecule (B).

$$HCO_3^- + B \longleftrightarrow CO_3^{2-} + B \quad (8)$$

The base molecule is usually an amine molecule or a hydroxyl ion (OH^-). By itself carbonate formation is, however, a rather slow reaction. It has been observed that

this reaction proceeds more quickly in the presence of amine molecules, an effect to be considered besides the direct effect of the amines as bases (Donaldsen and Nguyen, 1980). This is in line with the statement by Sharma and Danckwerts (1963) that Brønsted bases can catalyze the formation of bicarbonate.

2.2.3. Tertiary amines

Tertiary amines groups cannot react with CO_2 directly to form a carbamate, because these amines lack a free proton (Blauwhoff et al., 1984). According to Donaldsen and Nguyen 1980 and Rinker et al. 1995, the tertiary alkanolamines act as a base and catalyze the hydration of CO_2, leading to the formation of bicarbonate. The complete mechanism of the reaction of CO_2 with a tertiary alkanolamine might be summarized by the formation of a hydrogen bond between free amine and water and involves the lone-pair electrons of nitrogen enhancing the reaction between water and CO_2 (Blauwhoff et al. 1984, Rinker et al. 1995, Barth et al. 1984). The reaction mechanism includes the following reactions:

$$CO_{2\,(aq)} + H_2O \longleftrightarrow H_2CO_3 \qquad (9)$$

$$CO_{2\,(aq)} + OH^- \longleftrightarrow HCO_3^- \qquad (10)$$

$$CO_2 + R_1R_2R_3N + H_2O \longleftrightarrow R_1R_2R_3N^+H + HCO_3^- \qquad (11)$$

This reaction, Eq. (11), is less exothermic than that between CO_2 and primary and secondary alkanolamines, in which a carbamate is formed, see Mathonat et al. 1998, Littel et al.1990 and Hikita et al.1977. The tertiary alkanolamines react in equimolar ratio with CO_2 and this confers to them a CO_2 loading capacity of 1 mole of CO_2/mole of amine (Linek et al. 1994, Mimura et al. 1995). Moreover, the pH of the solution is also a factor that will influence the CO_2 absorption rate for aqueous solutions of tertiary alkanolamines. Notably, the weak basicity of Triethanolamine (TEA), pKa = 7.76 at 25°C seems to decrease the absorption rate. Of particular interest, a prior study has also revealed that tertiary alkanolamines are more easy to regenerate and loose less of their absorption capacity after (several) regeneration cycles compare to the primary alkanolamines, Lin et al. 2000.

2.2.4. Other reactions

In addition to above mentioned reactions of the amine with CO_2 and the formation of carbonate and bicarbonate, the ionization of water and the protonation of the amine species play a role.

Ionization of water:

$$OH^- + H_3O \longleftrightarrow 2H_2O \qquad (12)$$

Protonation of amine molecule:

$$R_1R_2NH + H_2O \longleftrightarrow R_1R_2NH_2^+ + OH^- \quad (13)$$

Amine molecules can act as a base and they are usually the strongest and dominating base present in the aqueous system: water is a weak base, the hydroxyl-ion (OH^-) is a strong base, but only present in small quantities. Bicarbonate is a very weak base (da Silva 2005) and will not extract a proton from water nor from the amine molecules.

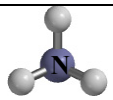
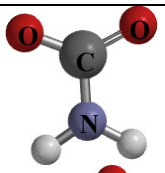
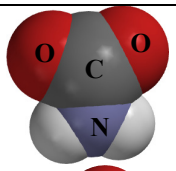
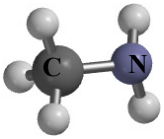
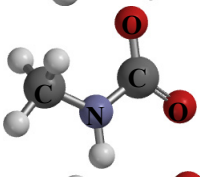
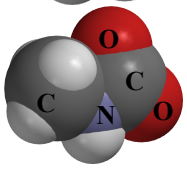
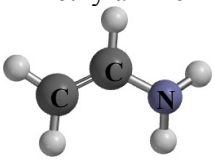
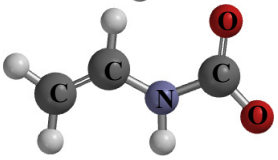
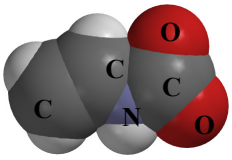
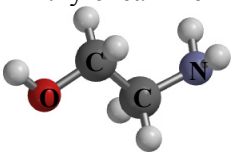
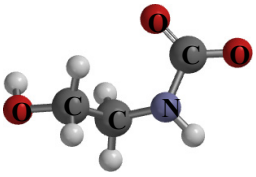
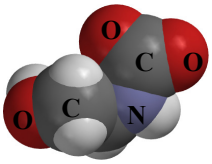
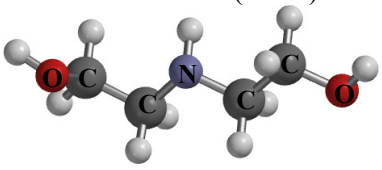
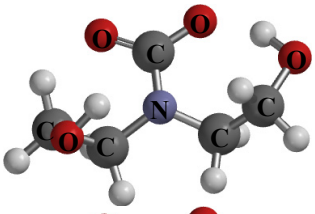
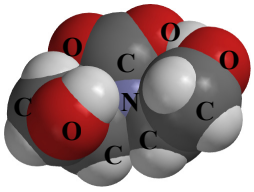
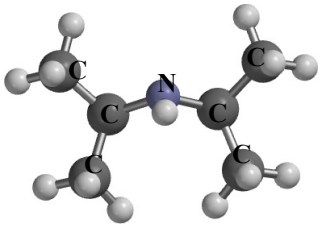
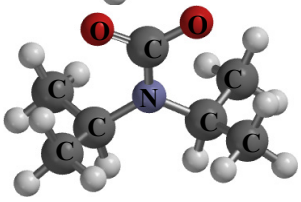
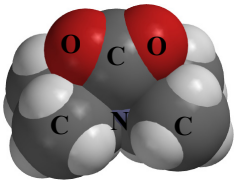
The effect of the molecule structure of the amine is reflected in several characteristics, relevant for its performance as solvent in CO_2 capture. Often the effect of molecular structure on its performance is discussed in terms of 'steric hindrance', in view of functional groups present and their effect on e.g. the 'amine basicity', as these aspects are conceptually easy to envisage ('steric hindrance') or relatively easy to measure ('basicity').

2.3. Steric hindrance

Sterically hindered amines have been defined as amines for which either a primary amino group is attached to a tertiary carbon atom or a secondary amino group is attached to a secondary or tertiary carbon atom. Bosch et al. 1989 studied experimentally the kinetics of CO_2 absorption in aqueous solution of MEA, DEA, DIPA (Diisopropylamine) and sterically hindered amines like AMP (2-Amino-2-methyl-1-propanol) and PE (2-Piperidine ethanol). The results showed that CO_2 absorption rates of conventional amines such as MEA, DEA and DIPA reduce drastically on approaching a liquid loading of a 0.5 mole CO_2/mole amine. Whereas, sterically hindered amines AMP, PE do not show a deteriorated CO_2 absorption rates at even higher CO_2 loadings.

Another sterically hindered amine for CO_2 absorption, 2-amino-2-hydroxymethyl-1,3-propanediol (AHPD) was studied by Park et al. 2003. It was found that the equilibrium CO_2 loading of aqueous AHPD solution in high CO_2 partial pressure range (above 4 kPa) was much higher when compared to that of aqueous MEA solution, but lower at lower CO_2 partial pressures.

Table 1, Molecular structure of non-sterically hindered and sterically hindered amine based compounds, their carbamate forms and tertiary amine.

Compounds	**Amine-Carbamate**	**Amine-Carbamate (Space filling molecular model)**
Non-sterically hindered amine		
 Ammonia		
 Methylamine		
 Ethyleneamine		
 Monoethanolamine or Ethanolamine (MEA)		
 Diethanolamine (DEA)		
 Diisopropylamine (DIPA)		

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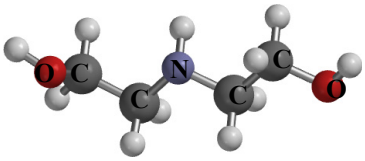
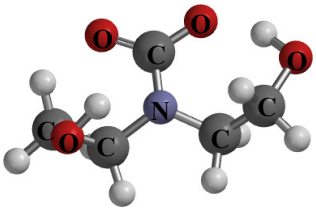
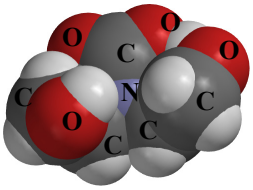
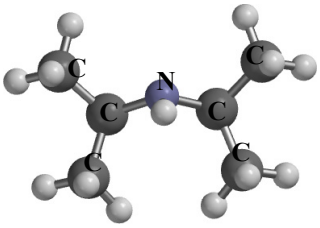


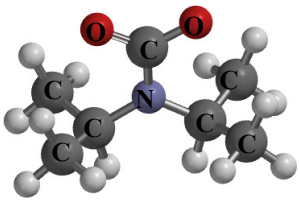
Diethanolamine (DEA)

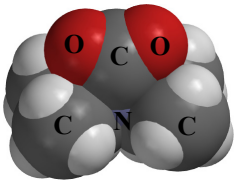


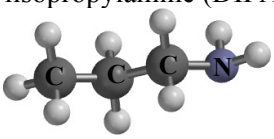




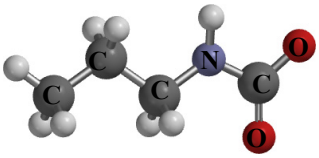
Diisopropylamine (DIPA)

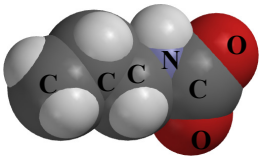


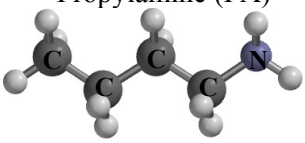




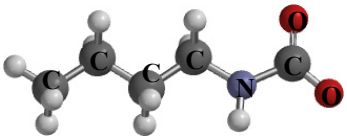
Propylamine (PA)

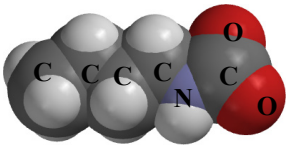


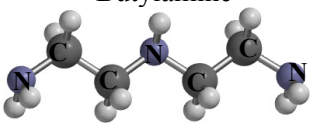




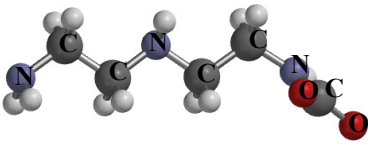
Butylamine

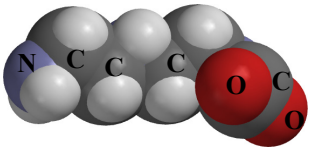


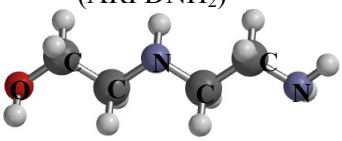




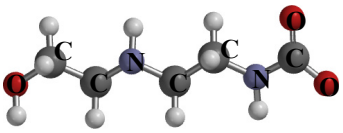
N-(2-aminioethyl)-1,3-propanediamine ($ARPDNH_2$)

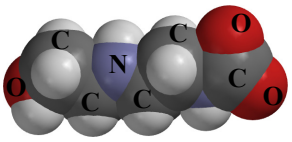


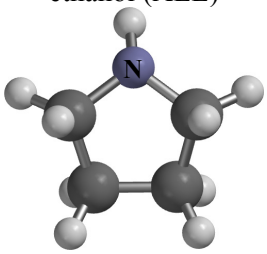




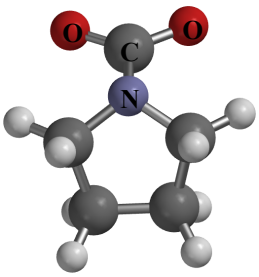
2-(2-aminoethylamino) ethanol (AEE)

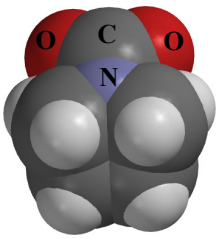






Pyrrolidine





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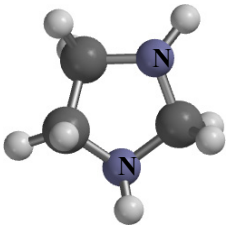
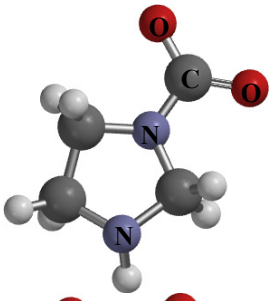
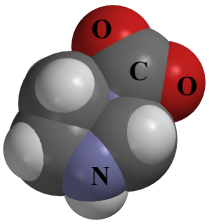
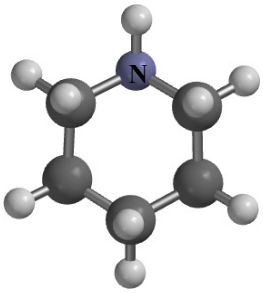


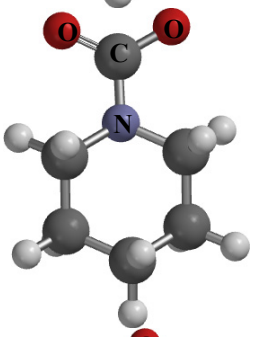
Imidazole

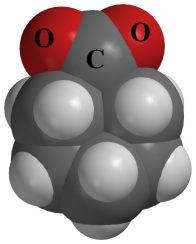


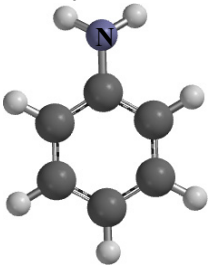




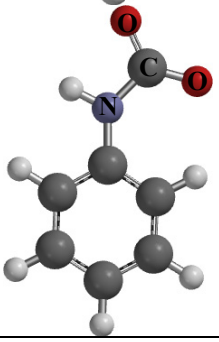
Pyridine

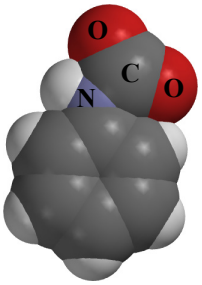




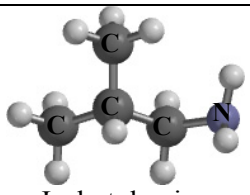


Aniline

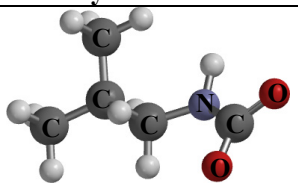


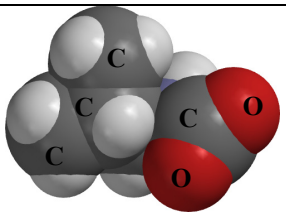


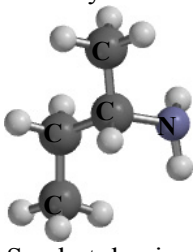
Sterically hindered amine



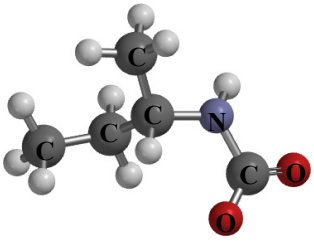
Isobutylamine

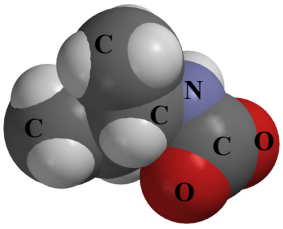






Sec-butylamine





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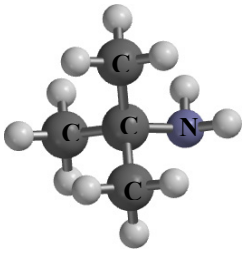
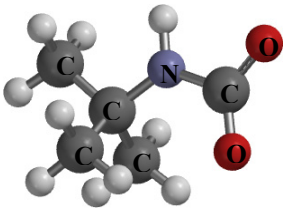
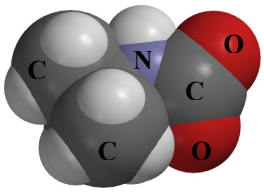
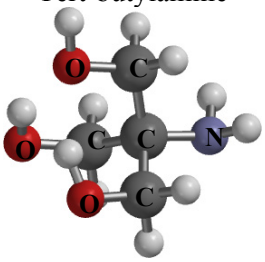
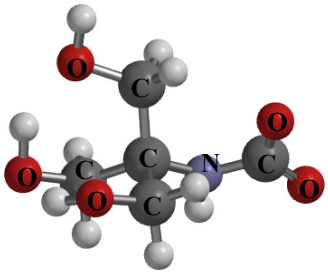


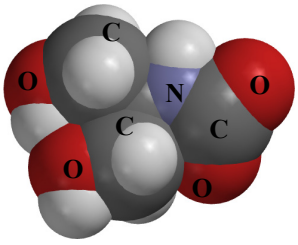




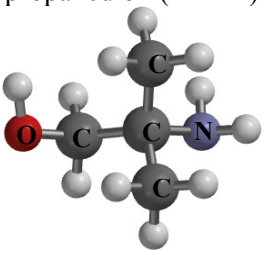
Tert-butylamine

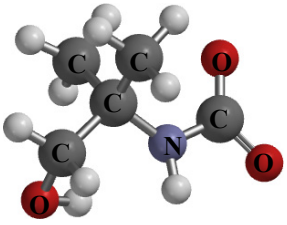


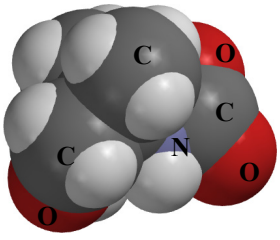




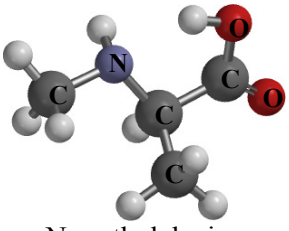
2-amino-2-hydroxymethyl-1,3-propanediol (AHPD)

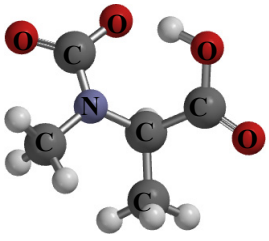


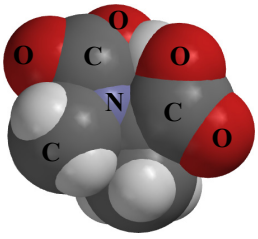




2-Amino-2-methyl-1-propanol (AMP)







N-methylalanine

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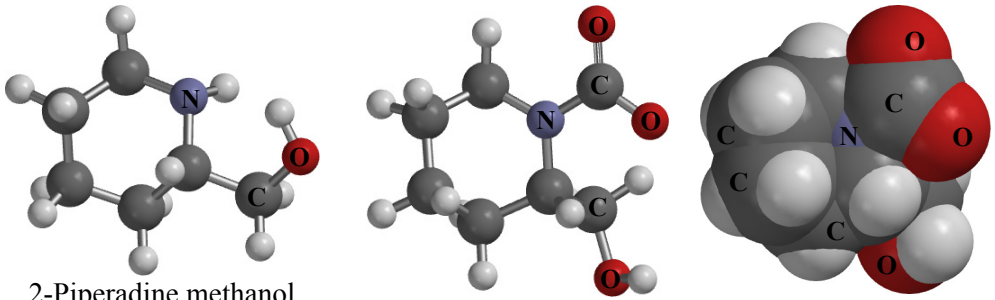
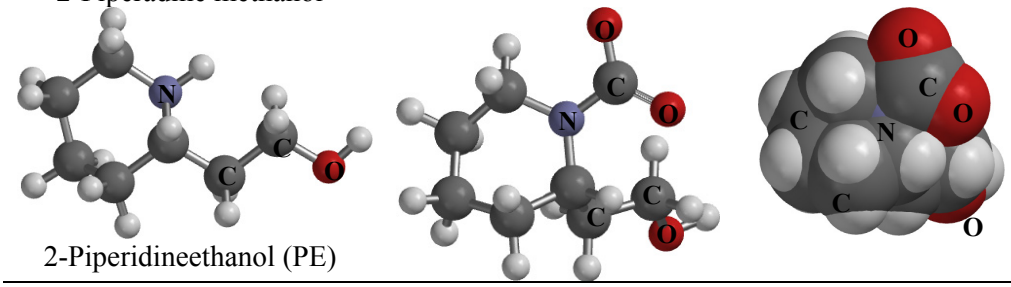
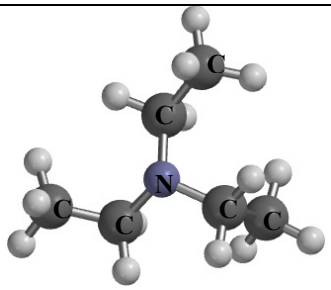


2-Piperadine methanol

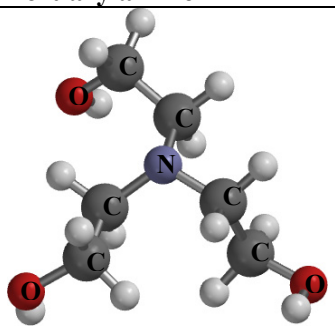


2-Piperidineethanol (PE)

Tertiary amine



Triethylamine



Triethanolamine (TEA)

The bulky structure of AHPD is hindering both the formation of carbamate anions as well as bicarbonate ions at low partial pressure and hence the CO_2 solubility of aqueous MEA, provided by the relatively large amount of carbamate formed, dominates in this region. With increasing partial pressure, there is a 'cross-over' of the CO_2 solubility, based on the reaction stoichiometry of the bicarbonate versus the carbamate formation for AHPD.

Sartori et al. 1994 studied primary amines which were used for acid gas separation applications and having methyl substituents attached at the alpha carbon atom next to the nitrogen atom in the molecular structure. Sartori attributed the favourable behaviour of these amines (higher CO_2 solubility) to the relative instability of the carbamate species. This was described due to the instability of the carbamate species to constraints imposed by the alkyl groups attached to the amine group. In non-sterically hindered amines, like N-butylamine, the rotation around the N-COO^- bond is unrestricted in the carbamate species, whereas in sterically hindered amines

like Tert-butylamine, the rotation around the N-COO^- bond in the carbamate species is only possible if the bulky substituent is compressed. Consequently, the carbamate of Tert-butylamine is much less stable than that of n-butylamine. Table 1 shows molecular structure of various non-sterically hindered and sterically hindered amine compounds and their carbamate forms. Two type of molecular structure model are shown for carbamate species, one normal and another space filling molecular model from which the limitation in the rotation around N-COO^- bond can be noticed clearly for the sterically hindered amines.

Singh et al. (2008, 2009, 2010) studied the effect of molecular structure on CO_2 absorption rate and capacity for various amines, including sterically hindered ones. Sec-butylamine (having a methyl group at the alpha carbon next to the amine group) and Iso-butylamine (having a methyl group at the beta carbon to the amine group) were studied experimentally for CO_2 absorption and regeneration. It was noticed that CO_2 absorption loading was higher in the case of Sec-butylamine when compared to that of Iso-butylamine. For the CO_2 regeneration experiments a higher degree of regeneration was achieved for Sec-butylamine when compared to that of Iso-butylamine. Hook (1997) studied different type of amines including sterically hindered amines like AMP (two methyl groups at the alpha-carbon to the amine group) and N-methylalanine (one methyl group at the alpha-carbon to the amine group) for CO_2 absorption and regeneration by performing experiments and by doing NMR studies to determine the carbamate, bicarbonate and carbonate concentration in solution. It was found that the presence of two methyl groups at the alpha carbon next to the nitrogen molecule reduces the stability of the carbamate but the effect of one methyl group at alpha carbon next to the amine group is however insufficient to induce full conversion of the carbamate species into bicarbonate.

McCann et al. (2010) studied the carbamate stability for different sterically hindered amines by NMR analysis. In this study the amines were selected on the basis of their level of steric hindrance present at the amine group in the molecular structure. The amines with the lowest sterical hindrance studied were Propylamine (PA) and MEA. The highest steric hindrance among the amines studied was in Isobutylamine and AMP. It was found that an increase in the level of steric hindrance resulted in a decreased carbamate stability. Simultaneously, the high sterically hindered amines investigated in this study had a low pKa value. Chakarborty et al. (1988) investigated the changes in the electronic characteristics due to various substituents on the alpha carbon atom adjacent to the amine group in sterically hindered amines. It was identified that a methyl group substitution at the alpha-carbon atom in primary amines and amino alcohols leads to a subtle but significant changes in the electronic environment of the nitrogen atom donor site. At the donor site the lone electron pair orbital of nitrogen interacts with the Π Me and Π Me* methyl group orbital. These interactions result in the donor species having a lower charge at the donor site and a higher and more delocalized HOMO

(highest occupied molecular orbital) i.e. making it a weaker base. The bond between the nitrogen and the hydrogen atom (N-H) weakens on the substitution of a methyl group at the alpha-carbon atom next to the nitrogen group.

Carbamate stability was studied by da Silva et al. 2006 for various amine based solvent including AMP and MEA by using ab initio calculation methods and a free energy of perturbation method. From quantum mechanical calculations it was suggested that the AMP-carbamate species shows some steric interaction between the methyl group substituent and the carbon atom of CO_2, as the (OH)C-N-C(COO^-) angle tightens from 114.53^o in MEA-carbamate to 111.38^o in AMP-carbamate, suggesting that the N-atom, together with carbamate functionality, is forced away from one of the methyl groups. Moderate sterically hindered amines are characterised by high rates of CO_2 absorption and high capacities of CO_2, making them very suitable for the removal of CO_2 and the bulk, non-selective removal of CO_2 and H_2S. A severely sterically hindered amine has a much lower CO_2 absorption rate, making it more suitable for the kinetically selective removal of H_2S in the presence of CO_2.

2.4. Functional group

Amine based solvents characteristics for CO_2 absorption and their basicity are found to be affected by structural effects in their molecular structure. In the study by Caplow (1968) the Brønsted relationship (between amine basicity and CO_2 reaction kinetics) for various amines was developed. A nonlinear correlation was observed in the Brønsted relationship and for compounds that showed a large deviation from the observed trend lines in the Brønsted plot it was suggested that molecular structure will play a role. In that study amines showing a low reactivity were Aniline and Imidazole. The low reactivity of Aniline was explained by electron withdrawal effects by the carboxyl functional group and preventing resonance involving the nitrogen atoms unshared electron pair in the benzene ring. The low reactivity for Imidazole was explained on the basis of the transition state for the Imidazole carbamate, whose formation is possibly destabilized by the loss of the aromatic resonance involving nitrogen atoms' unshared electron pair.

Molecular structural effects were also identified in the study of different amines for CO_2 absorption by Graeme et al. 2009. In this study 2-Piperidine ethanol and 2-Piperidine methanol achieved a CO_2 absorption capacity of approximately 1 mole CO_2/mole amine. Graeme et al. 2009 explained that these compounds show a high CO_2 absorption capacity due to the distance between hydroxyl group from the cyclic ring, which is suitable to form a stable intramolecular hydrogen bond with the nitrogen atom in a five or six member ring shape molecular structure. Intramolecular hydrogen bond formation between amine and hydroxyl groups have been estimated by Cacelia et al. 2001, Goldblum et al. 1990 and from experimental data by Danckwerts et al. 1979 and Sharma et al. 1963. This intramolecular hydrogen bonding between hydroxyl and amine group may decrease the basicity

(pKa) for primary and secondary amines and may also destabilize carbamate formation.

da Silva et al. 2007 studied stability of carbamate by using a quantum mechanical ab initio method. They suggested that alcohol groups in the amine molecular structure tend to reduce the basicity, while alkyl groups tend to increase the basicity. For instance: by adding an alcohol group to Ethyleneamine, Ethanolamine is formed and the addition of this group leads to a reduced base strength of over 1 pKa unit. Ethylamine, having a one methyl group more than Methylamine, has a somewhat higher pKa. These effects are mainly due to stabilization through bonds. In literature on CO_2 absorption there has been a tendency to only consider sterical hindrance when discussing differences in reactivity towards CO_2 between different solvents. While steric hindrance may play a role in affecting amine reactivity towards CO_2, other effects like electron donation through bonds and solvation effects are in many amines likely to be at least as important in accounting for effect on the overall reactivity towards CO_2.

Bonenfant et al. 2003 studied molecular structural features for amine based solvents by performing CO_2 absorption experiments. In this study the CO_2 absorption capacity of various amines were found to increase in the order Pyridine < Ammonia < MEA < Pyrrolidine < Triethylamine < TEA (Triethanolamine) < AEE (2-(2-aminoethylamino) ethanol) < $ARPDNH_2$ (N-(2-aminioethyl)-1,3-propanediamine). In particular a low CO_2 absorption capacity for Pyridine was observed when compared to other tested amines. This might be due to the aromatic ring in Pyridine causes the lone electron pair of nitrogen atom to be located in a sp^2 hybrid orbital and that might decrease their accessibility for its binding to CO_2.

In contrast, a high CO_2 absorption capacity of Pyrrolidine was observed when compared to that of pyridine. This might be attributed to Pyrrolidine non-aromatic ring that can favour the accessibility of lone electron pair of the nitrogen atom to bind with CO_2. The relatively low CO_2 absorption capacity noticed for the primary amine Ammonia which might be associated with the formation of ammonium bicarbonate ($NH_4(C(=O)OHO)$ that limits the absorption capacity at approximate 0.5 mole CO_2/mole amine (Bai et al., 1997). In case of primary amines like MEA the CO_2 absorption capacity is limited to, again, around 0.5 mole CO_2/mole amine due to the formation of a stable carbamate, which by stoichiometry requires two amine molecules for one CO_2 molecule. The effect of two amine groups in the same molecular structure was identified by Bonenfant et al. (2003), who studied AEE (2-(2-aminoethylamino)ethanol). AEE was found to be having CO_2 absorption capacity of more than 1 mole CO_2/mole amine. This high CO_2 absorption capacity might be due to the presence of two amine groups that permits reaction with two moles of CO_2.

Singh et al. (2007, 2008, 2009 and 2010) did a systematic experimental study on the effect of molecular structure for various amine based solvents on CO_2 absorption and regeneration. In that study especially the effect of carbon chain length between amine groups and different functional groups was identified. It was noticed e.g. for diamines that a six carbon chain length between both amine groups increases the amine reactivity and absorption capacity for CO_2. It can be due to the fact that increasing the carbon chain to more than 4 carbon atoms between the groups at either end of the carbon chain minimizes the interaction of the functional groups (which apparently influences the reactivity and capacity negatively) and hence, in diamines with longer carbon chains between the amine groups, each amine group reacts individually. This results in an increase in the absorption capacity (mole CO_2 per mole amine) and reaction rate. Furthermore, it was found for saturated cyclic amines that substitution of amine group by a side chain enhances the CO_2 absorption capacity. Saturated cyclic amines were found to have a relatively low CO_2 absorption capacity.

Summarizing, steric hindrance is identified as an important factor in reducing the carbamate stability and is also affecting the basicity of amine based solvents. From above mentioned literature it was noticed that the presence of a second functional group (like hydroxyl group, alkyl group and more than one amine group) near the amine group and/or a cyclic structure are also affecting amine based solvents CO_2 absorption properties and their basicity. The carbon chain length ("distance") between the amine group and the other functional group was identified as important factor in this study. In above discussion emphasis has been given on the basicity as it is not only one of the most important parameters for the reactivity of amine based solvents, but since it is a good first indicator for the solvent properties, the changes in basicity can be used as an indicator for the effect of changes in the molecular structure in the amine based solvent properties. Therefore, in following section a systematic study is performed to identify the effects of changes in the molecular structure like carbon chain length, different functional groups and steric hindrance on the basicity of various amine based solvents.

2.5. Basicity

The dissociation constant (pKa) is one of the important factors in the selection of an amine based absorbent for acid gas removal, in the interpretation of the kinetic mechanism of the acid gas absorption in the amine based absorbent and serves as a first indicator of the reactivity of various amine-based absorbents towards CO_2. Dissociation constants provide the basic strength of the amine-based absorbent at a specific temperature. Their temperature dependency and reaction enthalpy will be reflected in the overall reaction enthalpy of CO_2 with the amine based solvent (McCann et al., 2008). When the basic strength is reduced, the tendency to remove a proton from the intermediate zwitterions formed during the reaction with CO_2 (see reaction mechanisms above) will be lower.

da Silva and Svendsen (2003) studied basicity of various amine based solvents by quantum mechanism ab initio calculations. In their study a general, qualitative explanation of the trends observed in the experimental pKa data was suggested. For alkanolamine based solvents the alcohol group in the molecule is electron-withdrawing and destabilizes the protonated form of the amine. This effect is mitigated by the alcohol groups forming hydrogen bonds to the amine protons. Most of the alkanolamines therefore have pKa values only slightly lower than those of methylamines of the same order. Morpholine has electron-withdrawing oxygen but cannot form hydrogen bonds and has therefore a relatively low pKa value. In Triethanolamine (TEA) the three ethanol groups present create a strong electron-withdrawing effect. In the protonated form, there is, however, only one amine proton that these groups can bond with, limiting the stabilizing effect of the hydrogen bonding. It was identified from the calculations that intramolecular hydrogen bonds play a crucial part in determining the pKa values and their temperature-dependency of alkanolamines.

Table 2, Inductive and resonance effects of substituent.

+I;	$-COO^-$, $-O^-$, $-NH^-$, -Alkyl, -OH
(acid-weakening)	
-I *	$-NH_3^+$, $-NR_3^+$, $-NO_2$, -CN, -F, -Cl, -Br, -I, $-CF_3$, -COOH,
(acid- strengthening)	$-CONH_2$, -COOR, -CHO, -COR, -OR, -SR, $-NH_2$, $-C_6H_5$
+M	-F, -Cl, -Br, -I, -OH, -OR, $-NH_2$, $-NR_2$, -NHCOR, $-O^-$,
(acid-weakening)	$-NH^-$, -alkyl
-M	$-NO_2$, -CN, -COOH, -COOR, $-CONH_2$, $-C_6NH_5$, -COR,
(acid-strengthening)	$-SO_2R$

*Approximately in decreasing order

From above mentioned literature it is confirmed that basicity to be influenced by different molecular structure. In the following section the factors that influence the basicity will be discussed. Qualitatively the factors that modify the pKa values are inductive, electrostatic and electron delocalization (mesomeric) effects, together with contributions from hydrogen bonding, conformational differences and steric effects.

2.5.1. Inductive and electrostatic effect

Work is required to remove a proton from a solvent molecule and to transfer it to an organic base. The amount of work done is influenced by the localizations and distributions of the dipoles and electrical charges. The inductive effects are transmitted through bonds in the molecule, in contradiction to the electrostatic effects which are thought to operate across the low dielectric cavity provided by the solute or through the solvent. Inductive effects would be expected to remain approximately constant in cis and trans isomers, the major difference in pKa values arise from differences in the electrostatic field effects. Since inductive and electrostatic effects usually operate in the same direction it is usually not possible

to separate them. A substituent is considered to have +I effect (acid-weakening) if its insertion into a molecule in place of a hydrogen atom increases the electron density at other points of the molecules. If, instead it decreases the electron density it has a –I effect and is acid-strengthening or base weakening.

2.5.2. Mesomeric effect

Mesomeric effects (+M) arise from π-electron delocalization ('resonance'). They contribute appreciably to the ease with which the strength of an acid or a base is modified by remote substituents, especially in aromatic or heteroaromatic systems that have ortho or para substituents (the mesomeric effect of meta substituent are negligible). Mesomeric effects may enhance or oppose inductive effects, as shown in Table 2.

2.5.3. Steric effect

The proton itself is so small that direct steric hindrance is seldom encountered in proton transfers. Steric hindrance can indirectly affect acidity or basicity by affecting the resonance (or mesomeric effect). As due to steric hindrance the resonance is reduced because the atoms are sterically forced out of the planarity.

2.5.4. Hybridization effect

Electrons of 2s orbitals tend, on average, to be much closer to the nucleus than electrons in 2p orbitals, since considering the shapes of the orbitals 2s orbitals are spherical and centred on the nucleus whereas 2p orbitals have lobes on either side of the nucleus and are extended into space. A change in coordination e.g. from a triple bonded basic atom (as in hydrogen cyanide, HCN) to a single bonded basic atom (as in methylamine, CH_3NH_2) implies a change in its formal hybridization from sp to sp^3, and a decrease in the electronegativity of the basic centre. This is a consequence of the decrease in the s-character of the hybrids, since s-electrons are more tightly bound than are p-electrons. On this basis, one may predict that the basicity trends should follow the sequence of $sp>sp^2>sp^3$. The same trend is followed by the charge densities at the basic centre lone electron pairs. The charge density at the lone electron pair and the intrinsic basicity increases as the contribution from the s-orbitals decreases Ijjaali et al. 1995.

2.5.5. Hydrogen bonding effect

Internal hydrogen bonding can greatly influence base strength. If internal hydrogen bonding can stabilize the isomer, the basicity will be decreased.

2.6. Evaluation of structural effect on basicity (pKa)

Considering the efforts made in literature on explaining the influence of amine basicity on the observed amine reactivity for CO_2, it is important to identify the effect of above mentioned molecular structure on the pKa value. Hence, a

systematic study of molecular structure on the pKa-value was performed for alkyl, alkanol and diamine based solvents, using experimental data as well as an established pKa-estimation method. The focus of this study was on the effect of molecular structure like carbon chain length, different amine groups like primary, secondary, tertiary and sterically hindered configurations. It should be noticed that sterically hindered amines were having one alkyl group substitution at α-carbon to the amine group in molecular structure. Hence, a lower level of steric hinderance will be present at amine group. It is important to clarify that some molecular structure might not exist in reality still a hypothetical structure was used as that will help in identifying the complete trend.

Table 3 shows the example of the molecular structure of the amine studied. The structure is categorized in three groups, Type A for primary amine group, Type B is for secondary amine group and Type C is for tertiary amine group alkanol, alkyl and diamine based solvents. It should be noticed that in diamine two amine groups are tagged with I^{st} and II^{nd} and only I^{st} amine group was secondary (Type C) and tertiary (Type D). Whereas II^{nd} amine group in diamine was kept primary for all type (A, B and C). Sterically hindered amines studied were having the same structure as non-sterically hindered amines in each type (A, B and C) except that the sterically hindered amines were substituted with one alkyl group at α-carbon to the amine group.

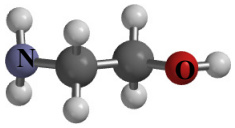
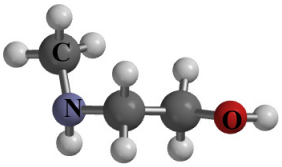
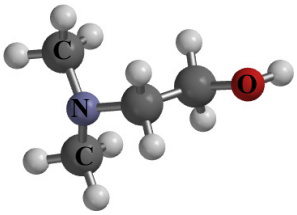
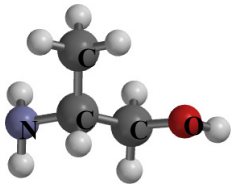
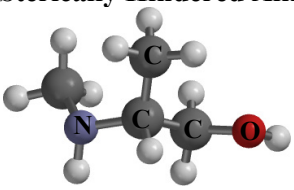
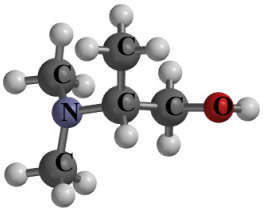
In diamine only I^{st} amine group was sterically hindered for all type (A, B and C). Whereas, II^{nd} amine group was primary and non-sterically hindered for all type (A, B and C). The carbon chain length for alkanol and diamines studied is increased from two to seven and for alkylamines carbon chain length studied is increased from one to six.

The pKa values presented in this section have been estimated by using ACD/pKa Phys. Chem. software by ACD/Labs. This ACD/pKa software uses the Hammett equation to estimate pKa of different amine based solvents. The Hammett Equation relates the relative magnitude of the equilibrium constants to a reaction constant ρ and a substituent constant σ.

$$\text{Log}\,(K_X / K_H) = \rho\,\sigma \quad \text{or} \quad pK_H - pK_X = \rho\,\sigma \tag{14}$$

The pKa value estimated from this ACD/pKa software refers to data valid for a temperature of 20°C. Error estimation from this software for this diverse set of compounds was estimated to be significantly less than 1 pKa unit. Table 4, shows the comparison of the experimental pKa values for some amines taken from literature Perrin 1965 with estimated pKa values from ACD/pKa software, showing a maximum deviation of around 0.5 pKa unit and average deviation of less than 0.1 pKa unit.

Table 3, Various amine based solvent molecular structure with primary (Type A), secondary (Type B) and tertiary amine (Type C) group and their sterically hindered forms.

Type A	Type B	Type C
Alkanolamine		
		
Sterically Hindered Alkanolamine		
		
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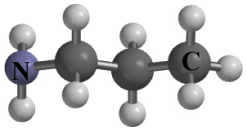	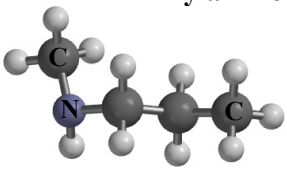	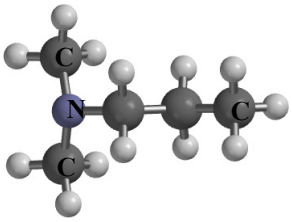
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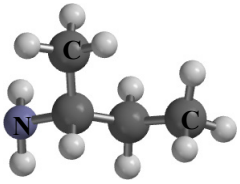
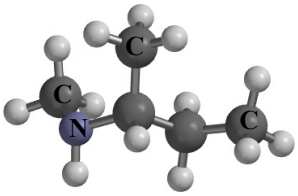
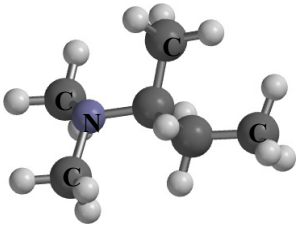
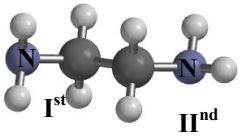
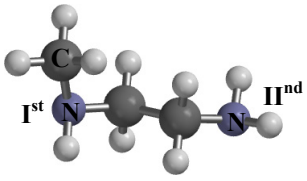
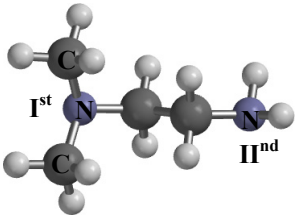
		
Diamine		
		

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Sterically Hindered Diamine

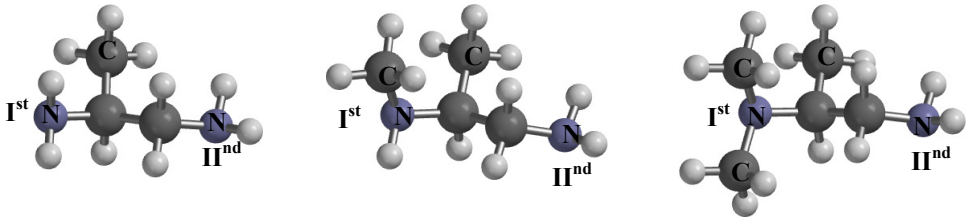

Table 4, Comparison of experimental pKa values (Perrin 1965) of some amines with estimated pKa* values.

Amine	Experiment Temp. °C	Experiment pKa	Estimated* Temp. °C	Estimated* pKa
Monoethanolamine (MEA)	20	9.65	20	9.16
3-amino-1-proponaol	20	9.96	20	9.91
4-amino-1-butanol	20	10.35	20	10.32
Ethylenediamine	20	10.08	20	9.89
1-3 Diamino propane	20	10.62	20	10.43
1,4-Diaminobutane	20	10.80	20	10.68
1,5-Diaminopentane	20	10.96	20	10.86
Hexadimethylenediamine	20	11.11	20	10.92
Ethylamine	20	10.81	20	10.64
Propylamine	20	10.71	20	10.66
Butylamine	20	10.78	20	10.69
n-Pentylamine	20	10.79	20	10.69
Sec Butylamine	20	10.56	20	10.74
Isobutylamine	20	10.48	20	10.72
Piperazine	20	9.86	20	9.90

* using ACD/pKa PhysChem software

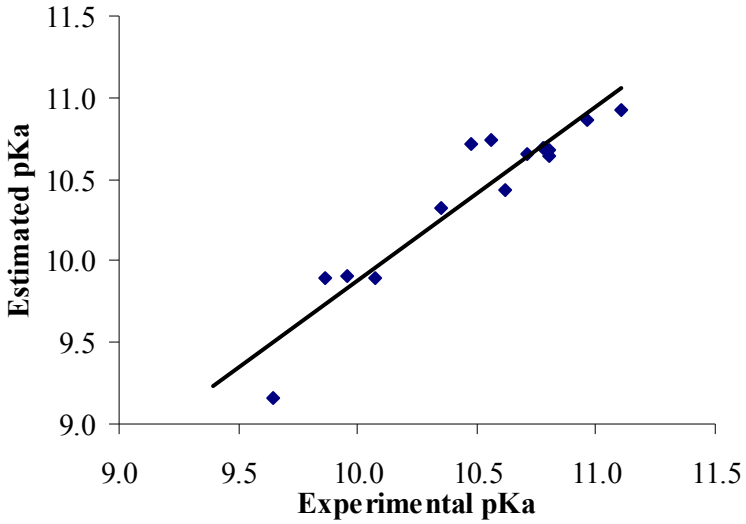

Figure 1, Parity plot of experimental pKa data vs. predicted pKa data by using ACD/pKa software at 20°C; $R^2 = 0.94$.

It can be noticed from Figure 1, that a plot of experimental pKa values vs predicted pKa values by using ACD/pKa software gives a linear trend with R^2 of 0.94. Hence, ACD/pKa software can be used with reasonable confidence and accuracy to estimate pKa values for the amines of different structure considered in this study.

2.6.1. Alkanolamine

Figure 2 shows the influence of the carbon chain length increase on the basicity for primary, secondary and tertiary alkanolamine based solvents. Table 3 shows molecule structure of two carbon chain length alkanol amine as an example. In this alkanolamine series molecule structure was kept same for all solvent molecules (as shown in Table 3) except carbon chain length was increased up to six carbon between amine and alkanol group. A hydroxyl group is electron withdrawing group, which will result in a lower electron density at nitrogen molecule. Hence, by increasing the distance between hydroxyl group and amine group the electron withdrawing effect is reduced and amine is protonated more easily and the basicity of alkanolamine is thus increased, as shown in Figure 2. It is interesting to notice that a secondary amine group in an alkanolamine molecule shows a higher basicity when compared to a primary amine group.

Alkanolamine with a tertiary amine group showed the lowest basicity. The increase in basic strength following the first two alkyl group at amine group is derived from the inductive effect (+I) of the alkyl group. The decrease following the third alkyl group has been attributed by 'back strain' overcrowding (Brown et al., 1944), but the more widely held opinion is that progressive number of alkyl groups on the N-

atom of the amine group eventually reduces its strength by decreasing the number of hydrogen atoms (in the cation) capable of forming stabilizing hydrogen bonds with water (Bell, 1960). Introducing steric hindrance effect by substituting one alkyl group at the alpha-carbon to the amine group in alkanolamine based solvents shows different effects on their basicity for primary, secondary and tertiary alkanolamine. It can be noticed that steric hindrance increases the basicity for primary alkanolamine while for secondary and tertiary alkanolamine basicity is only marginally influenced by steric hindrance.

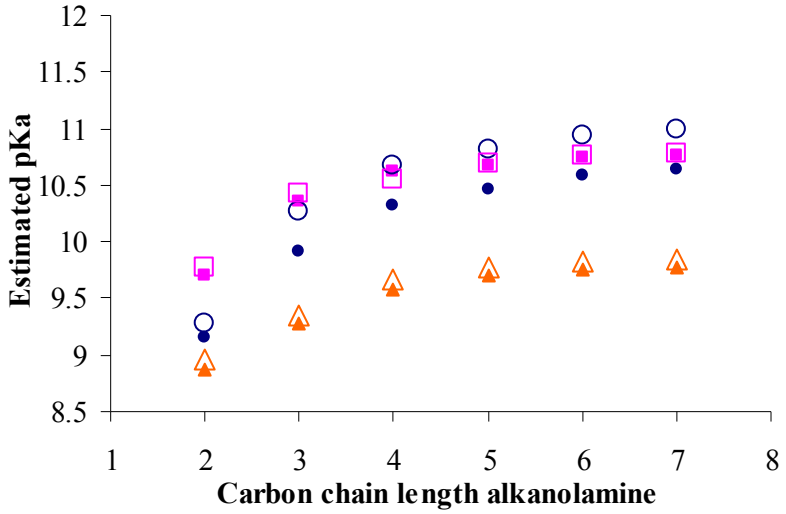

Figure 2, Effect of carbon chain length and sterical hindrance on pKa for various alkanolamine based solvents. ● Primary amine (Type A), ○ primary amine sterically hindered, ■ secondary amine (Type B), □ secondary amine sterically hindered and ▲ tertiary amine (Type C), △ tertiary amine sterically hindered.

It is interesting to notice that when sterically hindered primary alkanolamine with 2 carbon chain length the basicity is only slightly increased when compared to that of 3 carbon chain length. It can be suggested that the steric effect from the alkyl group is not strong enough to diminish the electron withdrawing effect coming from OH-group in two carbon chain length and the basicity is only slightly increased. Whereas in a three carbon chain length the sterically hindered primary alkanolamine the electron withdrawaing effect from hydroxyl amine is diminished and protonation of the amine group is done easily. In secondary and tertiary alkanolamine steric hindrance has little effect on the basicity.

2.6.2. Alkylamine

Figure 3, shows the influence of carbon chain length on the basicity (of I^{st} amine group) of primary (Type A), secondary (Type B), tertiary alkylamine (Type C) based solvents. Table 3 shows molecule structure of two carbon chain length alkyl

amine as an example. In this alkylamine series molecule structure was kept same for all solvent molecules (as shown in Table 3) except carbon chain length was increased up to six carbon between amine and alkyl group. It can be noticed that the basicity is not significantly influenced by an increase in the carbon chain length. When ammonia (pKa 9.3) is substituted by one-alkyl group, the pKa rises to 10.6; this effect does not depend on the size of the alkyl-group substituent (Albert and Serjeant, 1984).

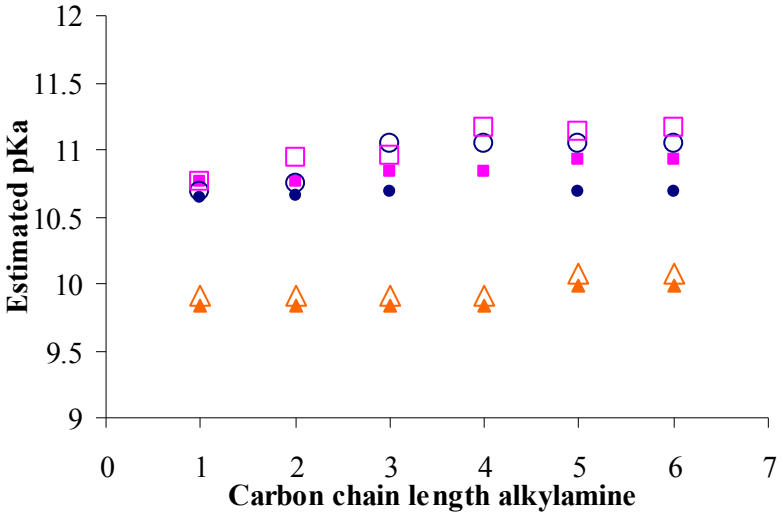

Figure 3, Effect of carbon chain length and sterical hindrance on pKa for various alkylamine based solvents. ● Primary amine (Type A), ○ primary amine sterically hindered, ■ secondary amine (Type B), □ secondary & sterically hindered and ▲ tertiary amine, △ tertiary amine & sterically hindered.

The effect on basicity for secondary and tertiary amine groups in alkyl amines follows the same trends as found above for alkanolamines. Again, the effect of an increase in the carbon chain length in secondary and tertiary amines on the basicity is limited. Steric hindrance was introduced to amine group in alkyl amine based solvents by an alkyl group substitution by side chains at the α-carbon to the amine group. Sterical hindrance effect on the basicity can be noticed for primary alkyl amines (Type A) when carbon chain length is 3 and higher (see Figure 3). Secondary alkyl amine showed an increase in basicity due to steric hindrance from 2 and higher carbon chain length. Whereas, no further significant increase in basicity was noticed in tertiary alkylamine (Type C) due to steric hindrance. The explanation on the steric hindrance on different amine groups (primary, secondary and tertiary) is same as that for alkanolamines.

2.6.3. Diamine

Figure 4 shows the effect of carbon chain length on the basicity for primary, secondary and tertiary diamine based solvents. Table 3 shows the molecular structure of two carbon chain length diamine based compounds as an example studied in this section.

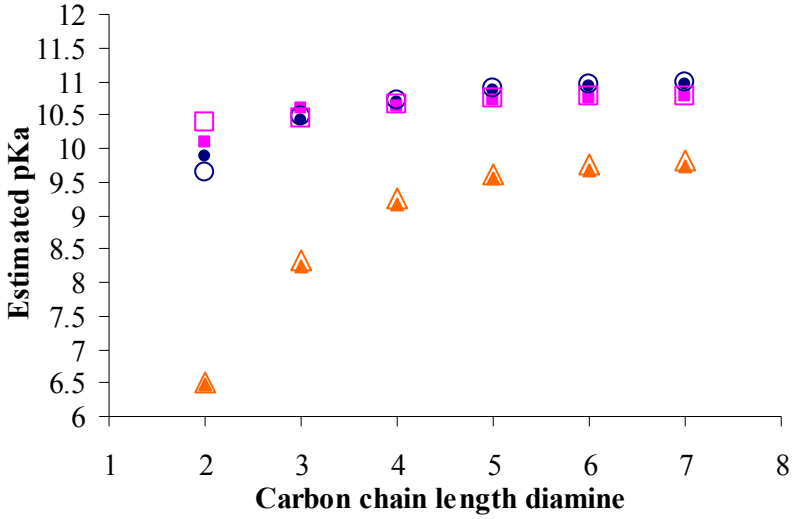

Figure 4, Effect of carbon chain length and sterical hindrance on pKa for various diamine based solvents. ● Both primary amine (Type A), ○ one primary amine (I^{st}) & one primary amine sterically hindered (II^{nd}), ■ one secondary amine (I^{st}) & one primary amine (II^{nd}) (Type B), □ one secondary amine sterically hindered (I^{st}) & one primary amine (II^{nd}), ▲ one tertiary amine (I^{st}) & one primary amine (II^{nd})(Type C), △ one tertiary amine sterically hindered (I^{st}) & one primary amine (II^{nd}).

It can be noticed that in primary, secondary and tertiary diamine based solvents the basicity is increased with an increase in chain length up to five carbon chain. A further increase in the carbon chain length doesn't influence the basicity. Sterical hindrance effect was introduced on one of the amine groups (I^{st} amine group, see Table 3) by an alkyl group substitution with side chain at the alpha carbon next to the amine group. It can be noticed that for tertiary amine the steric hindrance does not influence its basicity. Whereas, steric hindrance in primary and secondary diamine increases the basicity for the two carbon chain. Further increase in carbon chain in primary and secondary diamine sterical hindrance results in no influence on the basicity. Krueger (1967) explained that due to the intramolecular NH^{+}-----N hydrogen bond in monoprotonated diamines e.g. in Ethyelendiamine (2 carbon chain length primary diamine), the basicity is reduced.

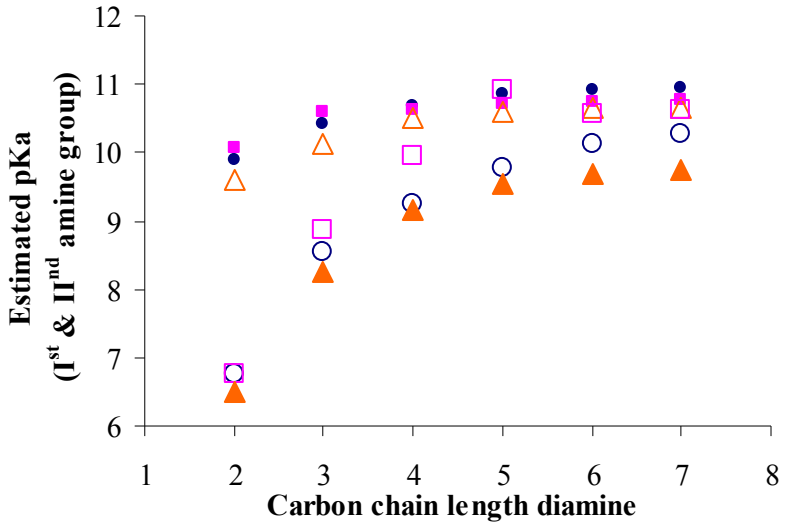

Figure 5, Effect of carbon chain length on two pKa for various diamine based solvents.
● I^{st} primary amine, ○ II^{nd} primary amine (Type A), ■ I^{st} secondary amine, □ II^{nd} primary amine (Type B) and ▲ I^{st} tertiary amine, △ II^{nd} primary amine (Type C).

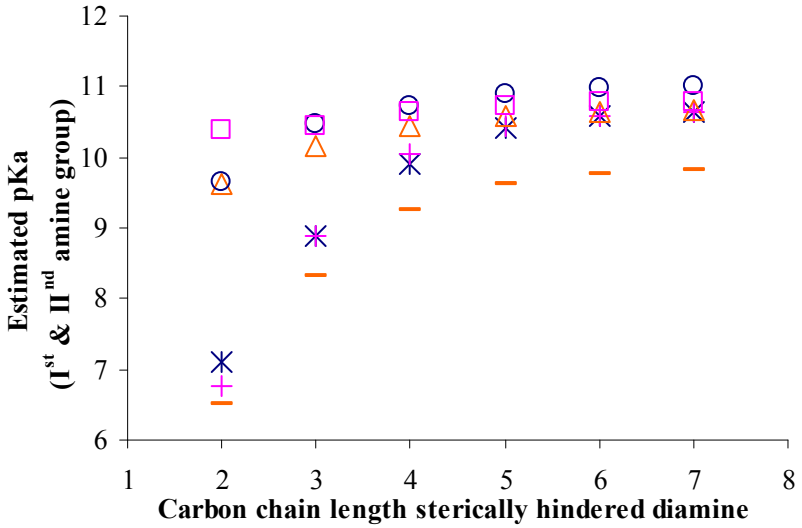

Figure 6, Effect of carbon chain length and steric hindrance on two pKa of various diamine based solvents. ○ I^{st} primary amine sterically hindered, * II^{nd} primary amine, □ I^{st} secondary amine sterically hindered, + II^{nd} primary amine, △ I^{st} tertiary amine sterically hindered, − II^{nd} primary amine.

This is caused by the decrease in electronegativity of opposite NH_3^+ due to the proton attracted by second amine group from solution since it is acting as a proton acceptor in an intramolecular hydrogen bond. Similar intramolecular hydrogen bond can be present in secondary diamines. Carbon chain lengths of 4 or higher in secondary diamine (N, N'-dimethyl-1-4-butanediamine) no intramolecular hydrogen bonds exists (Krueger 1967). Hence, introducing steric hindrance to one amine group in a 2-carbon chain length primary or secondary diamine reduces the possibility of intramolecular hydrogen bonding and enhances the basicity.

It is also interesting to notice that the influence on the basicity of both amine groups in diamine based solvent is influenced by carbon chain length. Figure 5, shows the both pKa values (first and second amine group) of primary, secondary and tertiary diamine based solvents. It can be noticed that the differences between pKa^1 (I^{st} amine group) and pKa^2 (II^{nd} amine group) varies greatly. Albert and Serjeant (1984) explained that this difference depends mainly on whether the two similar charges are near (and, hence, influencing each other) or distant, mutually hydrogen bonded or free as explained above. It can again be noticed from Figure 6, as the carbon chain length is increased the difference between two pKa constant of both primary secondary and tertiary sterically hindered amine group is reduced.

2.7. Conclusion

During CO_2 absorption in aqueous amine based solvents, primary and secondary amines react mainly with CO_2 forming carbamate, whereas tertiary amines act as a base (as they lack a free proton) and catalyze the hydration of CO_2 to form bicarbonate. The degree of hydrolysis of the carbamate formed to bicarbonate depends on the chemical stability of the carbamate, which is not only influenced by temperature but also depends on the molecular structure. The molecular structure determines the degree of sterical hindrance, the hybridization, the possibility to form intra-molecular or intermolecular hydrogen bonding and the presence of functional groups may further affect the electronic structure via their electron donating or –withdrawing character. Most of these effects are also reflected in the basicity of the amine species. Moreover, the basicity plays an important role in reaction mechanism and the overall reaction enthalpy. Hence in this study the molecular structure was systematically varied to study its effect on the basicity.

The effect of carbon chain length, different functional group and steric hindrance on the basicity of various amines was studied using validated pKa-software. It was noticed that alkanolamines and diamines the basicity increases with an increase in the carbon chain length. For alkyl amine the basicity was, however, only marginally affected by an increase in the carbon chain length. The difference between the two pKa constants for diamines was reduced with increasing carbon chain length, and hence decreasing mutual influence. The steric hindrance effect showed an increase in the basicity for primary alkanolamine, primary alkylamine and secondary alkylamine. Whereas hardly any influence of steric hindrance was

noticeable for the diamine basicity. Hence, a clear influence of the molecular structure on the basicity of the solvents was observed.

Although the trends identified in this work for the effect of molecular structure on the basicity can serve as first guidelines, it is recommendable to study further (both experimental as well as by modelling) the relationship between the carbamate stability and molecular structure as well as the effect on the reactivity towards CO_2 during absorption in aqueous solution, in order to create more insight in the process towards the development of an optimal solvent for CO_2 capture.

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3

Determination of the molecular structural effects on the carbamate stability for various amine based solvents by using ab Initio Method

The relative carbamate stability for various amine based solvents which are already used or are potential candidate for CO_2 absorption has been studied. Various molecular structural effects like carbon chain length, steric hindrance, functional groups and different cyclic amines have been investigated using SM8 solvation model and gas phase energies calculated with the B3LYP density functional method. The trends observed for carbamate stability are compared with experimental data reported in literature. Moreover this work gives theoretical support for trends observed in earlier experimental studies Singh et al. 2007, 2009 on the effect of the molecular structural effects for amine based solvents for CO_2 absorption.

3.1. Introduction

In order to make the CO_2 capture process based on aqueous amine-based solvents more energy efficient, there is a great demand to develop new improved solvents. To be able to develop new solvents it is desired to have a better understanding of the effect of the solvent structure on the CO_2 absorption characteristics. Hence, for that purpose experimental-based studies were performed to screen structure-activity relationships for various aqueous amine based solvents (Singh et al. 2007, 2008, 2009). In those studies various structural effects have been investigated and were identified for both CO_2 absorption (and regeneration) capacity as well as for the initial absorption rate. To give more background to these experimentally observed trends, it was considered useful to analyse these trends by quantum mechanical calculations for solvents of different molecular structure.

In the chemical absorption of CO_2 in aqueous amine based systems, the CO_2 is bound as either, carbamate, bicarbonate or carbonate form. If the equilibrium constants governing the formation of these species is known or can be predicted, the overall CO_2 absorption capacity of a solvent could be identified to a large extent. The relative carbamate stability of several amines used in CO_2 absorption processes has been studied by da Silva et al. 2004, 2006, using different solvation models together with gas-phase energies calculated with the B3LYP density functional method. Those studies showed that the carbamate stability could be predicted with a reasonable accuracy using these methods.

In this work these quantum mechanical calculations will be applied to determine the effect of the molecular structure on the carbamate stability. Solvents studied in this work were selected on the basis of earlier experimental work by Singh et al. 2007, 2008, 2009 & 2010 which included various alkanolamines, alkylamines, diamines and cyclic diamines. The effects that were investigated includes the carbon chain length, side chain at α-carbon position, alkyl group position in cyclic amine and the effect of a side chain with different functional groups on cyclic amines.

3.2. Methods

For the carbamate formation the following reaction is considered:

$$CO_2 + 2R_1NHR_2 \leftrightarrow R_1NR_2CO_2^- + R_1NR_2H_2^+ \quad (1)$$

where R_1NHR_2 is any primary or secondary amine molecule. R_1 and R_2 are functional group. For bicarbonate formation, the following reaction is considered:

$$CO_2 + 2H_2O \leftrightarrow HCO_3^- + H_3O^+ \quad (2)$$

Although no amine molecule appears in Eq.2, the extent to which this reaction will proceed is, in fact, governed by the strength of the amine as a base:

$$R_1NHR_2 + H_3O^+ \leftrightarrow R_1NR_2H_2^+ + H_2O \quad (3)$$

The present work involves the modelling of carbamate stability; so that the performance of different amine solvents can be compared. For the formation of a carbamate, an alternative equilibrium can be set up that does not involve the base molecule. This is the carbamate formation starting from bicarbonate:

$$HCO_3^- + R_1NHR_2 \leftrightarrow R_1NR_2CO_2^- + H_2O \quad (4)$$

If the mole-fraction-based activity of water is assumed to be 1 and if H_3O^+ is written as H^+, Eq.5 and Eq.6 are obtained for equilibrium constant for Eq.3 and Eq.4 respectively:

$$K_a = \frac{a^+_{R_1NH_2R_2}}{a_{R_1NHR_2} a^+_H} \quad (5)$$

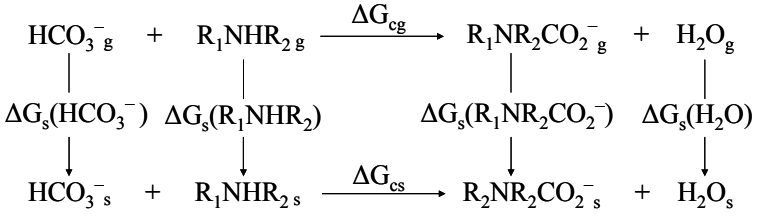
Similarly, the following equilibrium constant is obtained for the formation of carbamate (Eq.4):

$$K_c = \frac{a_{R_1NR_2CO_2^-}}{a_{R_1NHR_2} a_{HCO_3^-}} \quad (6)$$

The carbamate equilibrium constant from Eq.1 (K_{c2}) can be expressed as a product of the equilibrium constants of Eq.2, 3, and 4:

$$K_{c2} = K_2 K_a K_c \quad (7)$$

where, K_2 is the equilibrium constant of Eq.2. Therefore, the interactions between an amine species and CO_2 in solution can be described by two equilibrium constants: K_a and K_c. Although there are also other reactions that occur, these are independent of the amine present in the system. From knowledge of these equilibrium constants K_a and K_c, the amount of CO_2 captured and the energy consumption of the process can be estimated. When these constants can be estimated for arbitrary molecular structures, the effect of variations in the molecular structure can be investigated. On the basis of the thermodynamic cycle, the reaction energy in solution ΔG_{cs} can be divided into two contributions:



$$\Delta G_{cs} = \Delta G_{cg} + \Delta\Delta G_s \quad (8)$$

Where ΔG_{cg} is

$$\Delta G_{cg} = \Delta G_g(R_1NR_2CO_2^-) + \Delta G_g(H_2O) - \Delta G_g(R_1NHR_2) - \Delta G_g(HCO_3^-) \quad (9)$$

and

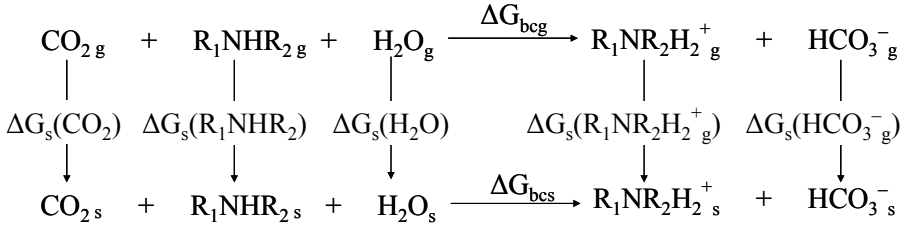
$$\Delta\Delta G_s = \Delta G_s(R_1NR_2CO_2^-) + \Delta G_s(H_2O) - \Delta G_s(R_1NHR_2) - \Delta G_s(HCO_3^-) \quad (10)$$

Formation of bicarbonate can be written as follows:

$$CO_2 + R_1NH\,R_2 + H_2O \leftrightarrow R_1N\,R_2H_2^+ + HCO_3^- \quad (11)$$

If the mole-fraction-based activity of water is assumed to be 1, then equilibrium constant can be written as follows:

$$K_{bc} = \frac{a_{R_1NR_2H^+}\, a_{HCO_3^-}}{a_{R_1NHR_2}\, a_{CO_2}} \quad (12)$$



$$\Delta G_{bcs} = \Delta G_{bcg} + \Delta\Delta G_s \quad (13)$$

Where ΔG_{bcg} is

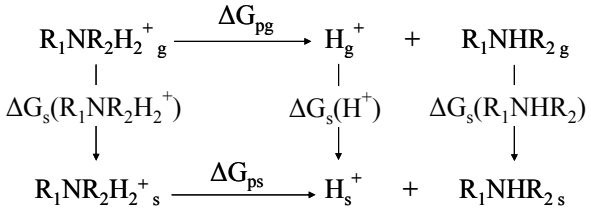
$$\Delta G_{bcg} = \Delta G_g(R_1NR_2H_2^+) + \Delta G_g(HCO_3^-) - \Delta G_g(H_2O) - \Delta G_g(R_1NHR_2) - \Delta G_g(CO_2) \quad (14)$$

$$\Delta\Delta G_s = \Delta G_s(R_1NR_2H_2^+) + \Delta G_s(HCO_3^-) - \Delta G_s(H_2O) - \Delta G_s(R_1NHR_2) - \Delta G_s(CO_2) \quad (15)$$

The basicity is one of the more important properties for amine based solvents. Equilibrium constant K_a for base reaction is given in Eq.5. There is accurate experimental data available in literature, which can be used to calculate the free energy of protonation (ΔG_{ps}) for various amine-based solvents. The free energy of protonation in aqueous solution (ΔG_{ps}) is related to K_a by equation (16) the following equation:

$$\Delta G_{ps} = -2.303\ RT \log K_a \quad (16)$$

Where R is the Universal gas constant and T is the temperature (K). The calculations are based on the following thermodynamic cycle.



3.3. Computational Aspects

The Spartan 8 programme (Wavefunction Inc.) was used to perform the molecular calculations presented in this study. For the modelling of gas-phase bicarbonate formation energies, standard ab initio calculations have been used. Density functional models were used to calculate the gas-phase energy. Gas phase calculations were performed at the equilibrium geometry level. Optimization of geometry has been studied extensively by da Silva et al. 2003 and Cramer 2002. From their studies the B3LYP/6-311+G(d,p) model was found to be suitable basis model for gas phase energy calculations.

For the calculation of solvation energies, several models are available. The density functional model SM8 was found to be suitable to calculate solvation energies and hence used in this work to calculate the energy of solvation. The SM8 model is a Semiemperical model that provides fairly accurate solvation energies for neutral species. All solvation energy calculations were done as single-point energy calculation using the B3LYP/6-31+G(d) basis set as suggested by Marenich et al. 2007. Separate conformer searches were conducted for the amines and carbamate forms. The conformers that were observed to be the most stable in the gas phase were also assumed to be the most stable in solution.

The thermal corrections to the free energy, the zero point energies and the entropies were all calculated at the equilibrium geometry and density function model with B3LYP/6-311+G(d,p) basis set. These contributions are relatively small and are not expected to change significantly with the level of modelling. It should be noticed there are uncertainties in the present calculated solvation energies for ionic species. The applied methods are also much more reliable in calculating relative energy differences between solvents, than in calculating absolute reaction energies. Expected errors in relative energies between solvents are found to be in order of ± 1 kcal/mol.

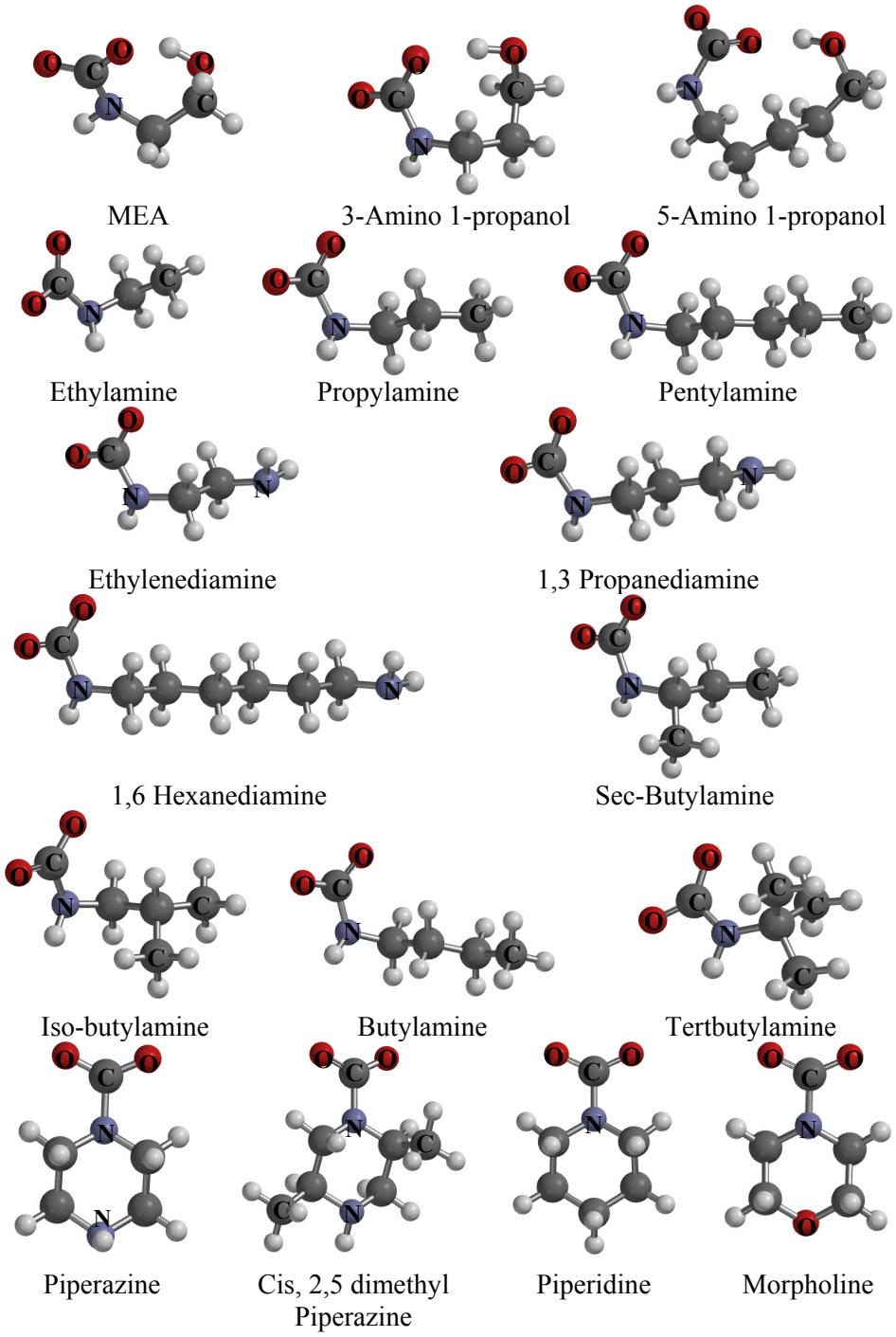


Figure 1, Carbamate forms of most stable amine conformer in solution.

3.4. Results and discussion

Figure 1, lists the molecular structures studied in this article. As it is mentioned in the introduction, the compounds chosen in this work were experimentally studied for CO_2 absorption and regeneration by Singh et al. 2007, 2009.

Table 1, Calculated gas phase carbamate and bicarbonate formation reaction energies for various amine based compounds.

Type of amine	Compound	$\Delta G_{cg}^{b,1}$ kcal/mol	$\Delta G_{bcg}^{b,2}$ kcal/mol
Alkanolamine	Monoethanolamine	-5.80	132.73
	3-Amino 1-propanol	-5.35	125.53
	5-Amino 1-propanol	-6.38	131.62
Alkylamine	Ethylamine	3.23	134.58
	Propylamine	3.26	133.40
	Pentylamine	2.87	131.86
Diamine	Ethylenediamine	2.94	126.09
	1,3 propanediamine	2.94	132.50
	1,6 hexanediamine	1.46	131.77
Side Chain	Sec-Butylamine	3.27	129.91
-Alkylamine	Iso butylamine	2.20	132.19
	Butylamine	2.48	132.46
	Tertbutylamine	6.93	129.19
Cyclic amine	Piperazine (Pz)	0.00	125.76
	Cis, 2,5 dimethyl piperazine	0.57	138.34
	Piperidine	1.77	124.49
	Morpholine	-1.41	135.52

[b]Gas phase energies are given at the B3LYP/6-311+G(d,p) level with thermal energy correction given at the B3LYP/6-311+G(d,p) level at 298.15K and 1atm. [1]Reaction energy for Eq.4. [2]Reaction energy for Eq.11.

The calculated carbamate and bicarbonate reaction energies for the selected amine based compounds are shown in Tables 1-3. Experimental pKa values are also given in Table 2, which are taken from literature (Perrin, 1965). These pKa values will be used to calculate the carbamate equilibrium constant from Eq.7 (K_{c2}). The geometries of the most stable conformers for the selected amines carbamate forms studied in this work are shown in Figure 1. As explained in the work of da Silva et

al. 2006 the carbamate molecules tend to form intramolecular hydrogen bonds between the alcohol-group H atoms and CO_2-group oxygen atoms. For the amines themselves, intramolecular hydrogen bonding between the amine groups and the alcohol groups were also identified. da Silva et al. 2006 concluded that the carbamate conformers which are found to be the most stable ones in the gas phase (vacuum) remain the most stable in solution as well. In this work it will be assumed that these conformers with intramolecular hydrogen bonds for alkanolamines in gas phase will also dominate in solution.

Table 2, Experimental pKa data from literature (Perrin 1965) and calculated solvation energies for various amine based compounds.

Type of amine	**Compound**	**Exp. Basicity**	**Solvation Energy (kcal/mol)**		
		pKa* (-)	Am	AmH^+	$AmCO_2^-$
Alkanolamine	Monoethanolamine	9.6	-8.40	-74.08	-77.29
	3-Amino 1-propanol	10.0	-8.15	-67.59	-71.79
	5-Amino 1-propanol	10.5	-8.70	-78.90	-69.96
Alkylamine	Ethylamine	10.8	-3.77	-75.90	-77.13
	Propylamine	10.7	-3.55	-74.54	-76.50
	Pentylamine	10.8	-3.56	-73.57	-75.56
Diamine	Ethylenediamine	10.1	-7.40	-69.13	-79.62
	1,3 propanediamine	10.6	-8.17	-78.11	-80.70
	1,6 hexanediamine	11.1	-7.78	-77.82	-79.46
Side Chain	Sec-Butylamine	10.6	-2.37	-69.55	-74.26
-Alkylamine	Iso butylamine	10.5	-2.88	-71.91	-75.04
	Butylamine	10.8	-3.38	-73.92	-75.98
	Tertbutylamine	10.7	-2.03	-68.46	-72.80
Cyclic amine	Piperazine (Pz)	9.9	-8.82	-67.71	-75.97
	Cis, 2,5 dimethyl piperazine	9.7	-6.45	-63.37	-73.90
	Piperidine	11.3	-4.11	-63.74	-72.37
	Morpholine	8.5	-7.60	-68.70	-72.52

*Experimental pKa values presented in this table are at 20°C. Solvation energies are given at the SM8 / B3LYP/ 6-31G(d) level.

However, it is clear that in solution, this intramolecular hydrogen bonding will compete with hydrogen bonding to the water molecule in solution. It can be noticed from Figure 1 that in diamine based compounds possibility of intramolecular hydrogen bonding reduces as the carbon chain length increases in molecular structure between two amine groups. Table 1, show the results for gas-phase carbamate formation reaction energies (ΔG_{cg}) and gas-phase bicarbonate formation reaction energies (ΔG_{bcg}) which were calculated at the B3LYP level.

Table 3, Calculated free energies of carbamate and bicarbonate formation reaction in solution for various amine based compounds.

Type of amine	**Compound**	**ΔG_{cs} [b,1]**	**ΔG_{bcs} [b,2]**
		kcal/mol	kcal/mol
Alkanolamine	Monoethanolamine	-6.15	-2.02
	3-Amino 1-propanol	-0.45	-2.99
	5-Amino 1-propanol	0.90	-7.66
Alkylamine	Ethylamine	-1.59	-6.62
	Propylamine	-1.14	-6.67
	Pentylamine	-0.59	-7.23
Diamine	Ethylenediamine	-0.75	-4.72
	1,3 propanediamine	-1.05	-6.52
	1,6 hexanediamine	-1.68	-7.35
Side Chain	Sec-Butylamine	-0.08	-6.34
-Alkylamine	Iso butylamine	-1.42	-5.92
	Butylamine	-1.58	-7.15
	Tertbutylamine	4.69	-6.32
Cyclic amine	Piperazine (Pz)	1.39	-2.20
	Cis, 2,5 dimethyl piperazine	1.65	12.34
	Piperidine	2.04	-4.21
	Morpholine	2.21	5.34

[b]Solvation energies are given at the SM8 / B3LYP/ 6-31G(d) level with thermal energy correction are given at the B3LYP/6-311G+(d,p) level at 298.15 K and 1 atm. [1]Reaction energy for Eq.4. [2]Reaction energy for Eq.11.

Table 2, shows the solvation energies calculated with the continuum model. Table 3, presents the solvation energies for equations 4 and 11. The energies are based on the B3LYP gas-phase energies and SM8 solvation model.

Table 4, Calculated carbamate formation equilibrium constant at 298.15 K for various amine based compounds.

Type of amine	**Compound**	**$\Delta G\ K_{C2}$[b,3]** kcal/mol
Alkanolamine	Monoethanolamine (MEA)	-7.45
	3-Amino 1-propanol	-2.17
	5-Amino 1-propanol	-1.64
Alkylamine	Ethylamine	-4.45
	Propylamine	-3.87
	Pentylamine	-3.43
Diamine	Ethylenediamine	-2.62
	1,3 propanediamine	-3.66
	1,6 hexanediamine	-4.94
Side Chain -Alkylamine	Sec-Butylamine	-2.85
	Iso butylamine	-4.08
	Butylamine	-4.40
	Tertbutylamine	1.76
Cyclic amine	Piperazine (Pz)	-0.43
	Cis, 2,5 dimethyl piperazine	0.11
	Piperidine	-1.45
	Morpholine	2.46

[b]Thermal energy correction are given at the B3LYP/6-311G+(d,p) level at 298.15 K and 1 atm. [3]Reaction energy for Eq.7.

The assessment of the accuracy of these results will be discussed in comparison with experimental data later in this article. To calculate the energy for K_{c2} (Eq.7) experimental pKa data were used together with model data for Eq.2 and are shown in Table 4. The accuracy of carbamate stability estimation in this work is similar as from the work of da Silva (2006) on carbamate stability. It should be noticed that the present level of modelling used to calculate carbamate stability is sufficient to

give reasonably indication of various effects of the molecular structure for different amines.

3.5. Comparison with experimental data

In this section calculated carbamate and bicarbonate formation reaction energy will be discussed in relation to their molecular structure and the experimental data by Singh et al. 2007, 2009.

3.5.1. Alkanolamines

Figure 2 and Table 3, shows the calculations performed for alkanolamine based solvents to determine the effect of the carbon chain length between the alkanol- and amine group on their carbamate formation reaction energy ΔG_{cs} (kcal/mol) and their bicarbonate formation reaction energy ΔG_{bcs} (kcal/mol).

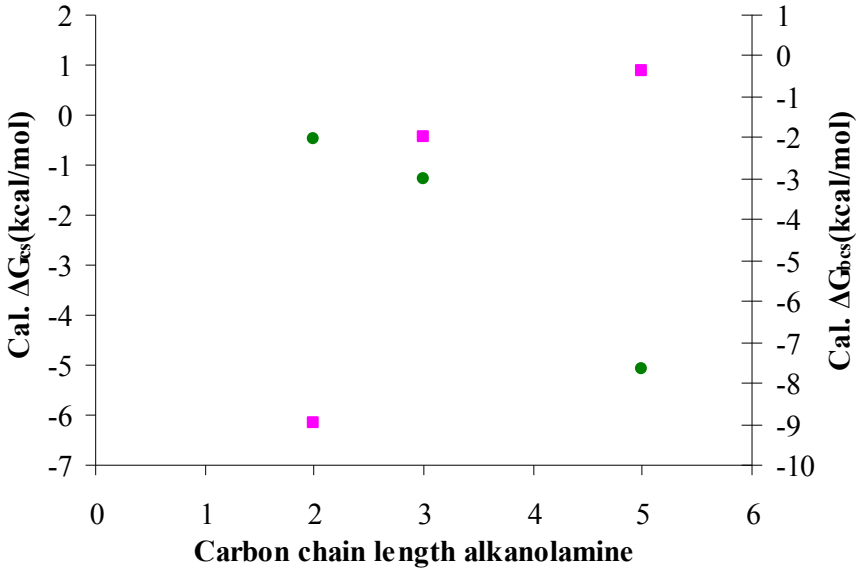


Figure 2, Effect of carbon chain length for alkanolamine based solvents on their ■ calculated carbamate formation reaction energy, ΔG_{cs} (kcal/mol) (left side) and ● calculated bicarbonate formation reaction energy, ΔG_{bcs} (kcal/mol) (right side).

It can be noticed that alkanolamine carbamate stability is strongly decreased when the carbon chain length is increased from 2 up to 5 C-atoms between the amine and hydroxyl group. This is due to the fact that the effect of electron withdrawing hydroxyl group on the nitrogen atom of amine group is reduced as carbon chain length increases and results in lower carbamate stability. The experimental pKa value is found to be increasing with an increase in the carbon chain length, see Table 2. When comparing these results with previous experimental work

performed for CO_2 absorption by Singh et al. 2007, it was noticed that the initial absorption rate was found to be decreased when the carbon chain length in alkanolamine was increased from 2 up to 5 for alkanolamine based solvents. It can now be stated that this is in line with the strongly reduced carbamate stability (as this reaction is faster) especially when going from 2 to 3 C-atoms. Figure 2 also shows that the bicarbonate reaction energy is increased (as this is exothermic reaction) with an increase in carbon chain length in alkanolamine based solvents. This is inline with the reduced stability of carbamate.

3.5.2. Alkyl amines

Figure 3 shows that increase in carbon chain length from 2 to 3 in alkylamine based solvents shows a slight decrease in the calculated carbamate stability while the experimental pKa values remain the same, see Table 2, 3.

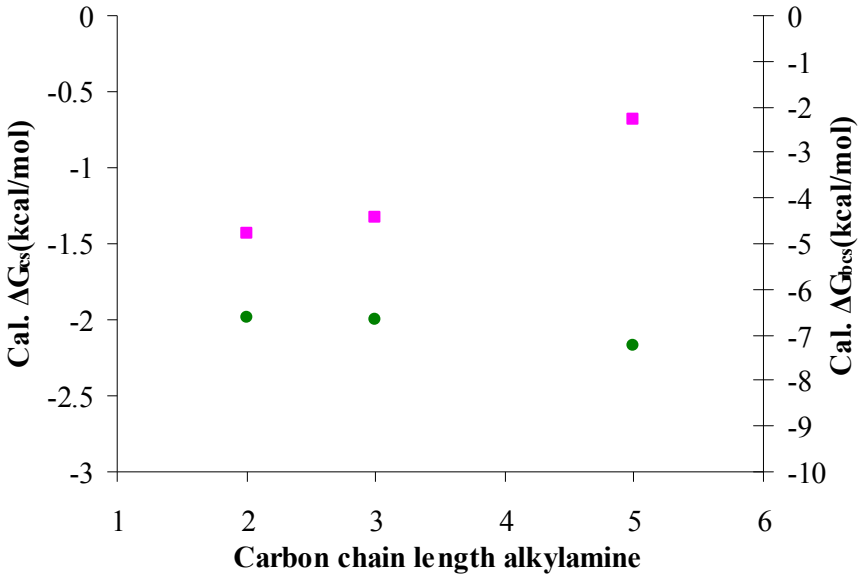


Figure 3, Effect of carbon chain length for alkylamine based solvents on their ■ calculated carbamate formation reaction energy, ΔG_{cs} (kcal/mol) (left side) and ● calculated bicarbonate formation reaction energy, ΔG_{bcs} (kcal/mol) (right side).

For the initial absorption rate in earlier experimental work, Singh et al. (2007), it was found that the initial absorption rate in alkyl amine increased with an increase in carbon chain length. This trend is not in line with the slightly decreasing carbamate stability, and the explanation for the increased initial absorption rate should be found in other effects, e.g. the surface activity of these compounds (Cents et al., 2005). Furthermore, the experimental absorption capacity was found to be decreased with an increase in carbon chain length from 2 to 5 carbon atoms Singh et al. 2007, which is in line with the decreased carbamate stability shown in

Figure 3. As the basicity of these alkyl amine based solvents remains the same and a similar trend was noticed for the bicarbonate reaction energy (see Figure 3).

3.5.3. Diamines

Figure 4 shows the carbamate and bicarbonate formation reaction energy for diamine based solvents. The most remarkable difference between the results presented in Figure 4 and those from Figures 2 and 3 is the increasing trend of the carbamate stability with increasing carbon chain length for the diamine series, whereas a decreasing stability was observed for the alkanolamines (Figure 2) and alkyl amines (Figure 3).

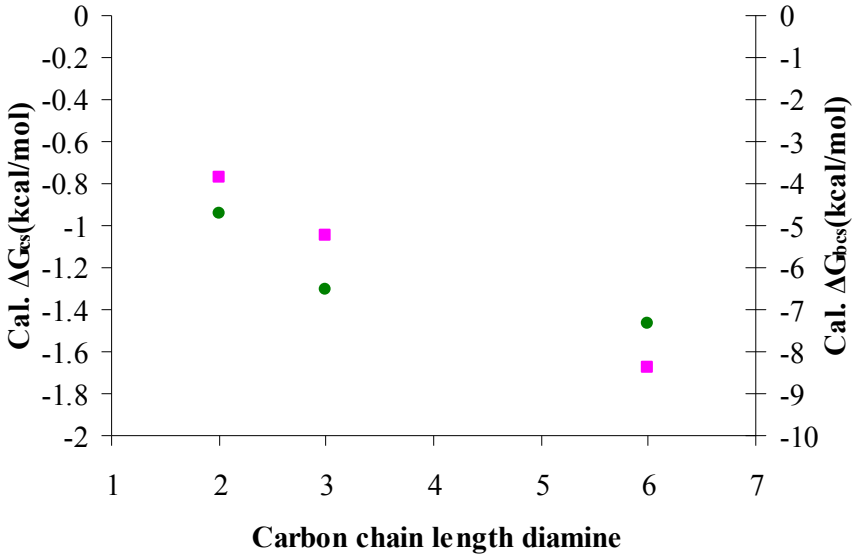


Figure 4, Effect of carbon chain length for diamine based solvents on their ■ calculated carbamate reaction energy, ΔG_{cs} (kcal/mol) (left side) and ● calculated bicarbonate formation reaction energy, ΔG_{bcs} (kcal/mol) (right side).

These results might be interpreted as indication for a stabilizing effect by internal hydrogen bonding. However, for the alkanolamines (near cyclic) conformations are observed for the most stable molecular configurations (conformers), as presented in Figure 1. The diamines do show, on the other hand, a more linear structure; maximizing the distance between the end-groups. For the diamine series, it should be noticed that in the calculations the second amine group was kept non-protonated. Especially when comparing Ethylenediamine with Monoethanolamine the basicity is higher while carbamate stability was lower for Ethylenediamine.

This is due to the presence of electron donating group nitrogen atom in Ethylenediamine.

In diamine based solvents increased stability with increasing carbon chain length between the charged end-groups seems logical from the point of view of optimizing charge distribution within the molecule. This is also reflected in the increasing pKa value with increasing carbon chain length. For the diamine based solvents the carbamate stability increases only slightly with an increase in carbon chain length, while the bicarbonate reaction energy increases strongly. This was also seen for the alkanol amine based solvents, but not for the alkyl amine based solvents, where the stability is already high for the compounds with low carbon chain lengths. The actual speciation of diamines studied in this work is however unknown. In equations 17-19 formation of di-carbamate (Eq.17), a protonated carbamate (Eq.18) and a double protonated species (Eq.19) are shown for these diamine based solvents.

$$2HCO_3^- + R_1HN_1N_2HR_2 \leftrightarrow {}^-OOCNR_1R_2NCOO^- + 2H_2O \quad (17)$$

$$HCO_3^- + R_1HN_1N_2R_2H_2^+ \leftrightarrow {}^-OOCN_1R_1N_2R_2H_2^+ + H_2O \quad (18)$$

$$2H_2O + 2CO_2 + R_1HN_1N_2HR_2 \leftrightarrow {}^+H_2R_1N_1N_2R_2H_2^+ + 2HCO_3^- \quad (19)$$

Table 5, Calculated gas phase carbamate and bicarbonate formation reaction energies for diamine based solvents.

Type of amine	Compound	ΔG_{cg} [b,4] kcal/mol	ΔG_{cg} [b,5] kcal/mol	ΔG_{bcg} [b,6] kcal/mol
Diamine	Ethylenediamine	53.91	-112.84	367.01
	1,3 Propanediamine	46.67	-119.18	343.95
	1,6 Hexanediamine	41.51	-117.16	310.63
	Piperazine (Pz)	54.42	-115.95	357.98
	Cis, 2,5 Dimethyl piperazine	58.36	-88.07	349.44

[b]Gas phase energies are given at the B3LYP/ 6-311+G(d,p) level with thermal energy correction given at the B3LYP/6-311+G (d,p) level at 298.15 K and 1 atm. [4]Reaction energy for Eq.17. [5]Reaction energy for Eq.18. [6]Reaction energy for Eq.19.

Table 5 and 7 shows the results from Eq.17-19. Table 6 shows the solvation energy for different species in diamine based solvents. It should be noticed that results from Table 5 and 7 cannot be directly compared with the results presented in Table 1 and 3. This is due to the fact that the species used in Eq.17, 18 and 19 are

different from Eq.4 and 11. Since in diamine amine based solvents the carbamate and bicarbonate formation equation can be written in more ways than shown in Eq.17-19. Hence, the carbamate and bicarbonate formation reaction energy, as calculated from equation 17, 18 and 19 is a first effort to develop more understanding for diamine based solvents. Further detailed computational calculations are required to give more accurate results for different forms of carbamate and bicarbonate formation for diamine based compounds.

Table 6, Calculated solvation energies for diamine based solvents.

Type of amine	**Compound**	**Solvation Energy (kcal/mol)**		
		$^{+}HAmH^{+}$	$CO_2^{-}AmCO_2^{-}$	$^{+}HAmCO_2^{-}$
Diamine	Ethylenediamine	-245.54	-201.99	-17.85
	1,3 Propanediamine	-226.24	-195.84	-16.34
	1,6 Hexanediamine	-193.05	-184.66	-11.66
	Piperazine (Pz)	-231.56	-199.07	-12.11
	Cis, 2,5 Dimethyl piperazine	-216.77	-193.52	-51.20

Solvation energies are given at the SM8 / B3LYP/ 6-31G(d) level.

Table 7, Calculated free energies of carbamate and bicarbonate formation reaction in solution for diamine based solvents.

Type of amine	**Compound**	$\Delta G_{cs}^{b,4}$	$\Delta G_{cs}^{b,5}$	$\Delta G_{bcs}^{b,6}$
		kcal/mol	kcal/mol	kcal/mol
Diamine	Ethylenediamine	-3.59	6.98	-9.28
	1,3 Propanediamine	-3.92	11.13	-12.27
	1,6 Hexanediamine	1.71	17.54	-12.79
	Piperazine (Pz)	1.25	8.19	-2.91
	Cis, 2,5 Dimethyl piperazine	8.37	-7.36	0.97

[b]Solvation energies are given at the SM8 / B3LYP/ 6-31G(d) level with thermal energy correction are given at the B3LYP/6-311G+(d,p) level at 298.15 K and 1 atm. [4]Reaction energy for Eq.17. [5]Reaction energy for Eq.18. [6]Reaction energy for Eq.19.

Table 7 shows that the 1,6 Hexanediamine is forming less stable di-carbamate when compared to 1, 3 Propanediamine and Ethylenediamine. Also the protonated

carbamate is less stable for 1,6 Hexanediamine when compared to 1,3 Propanediamine and Ethylenediamine. Ethylenediamine forms the most stable protonated carbamate. It can be noticed from Table 7 that Ethylenediamine has low value (-9.28 kcal/mol) for bicarbonate formation (based on equation 19) when compared to that of 1, 3 Propanediamine and 1, 6 Hexanediamine.

3.5.4. Side chain effect in alkylamines

Figure 5 shows the effect of side chain position on carbamate stability in alkylamine based solvents. It can be noticed that the Sec-butylamine showed less stable carbamate when compared to Isobutylamine and Butylamine.

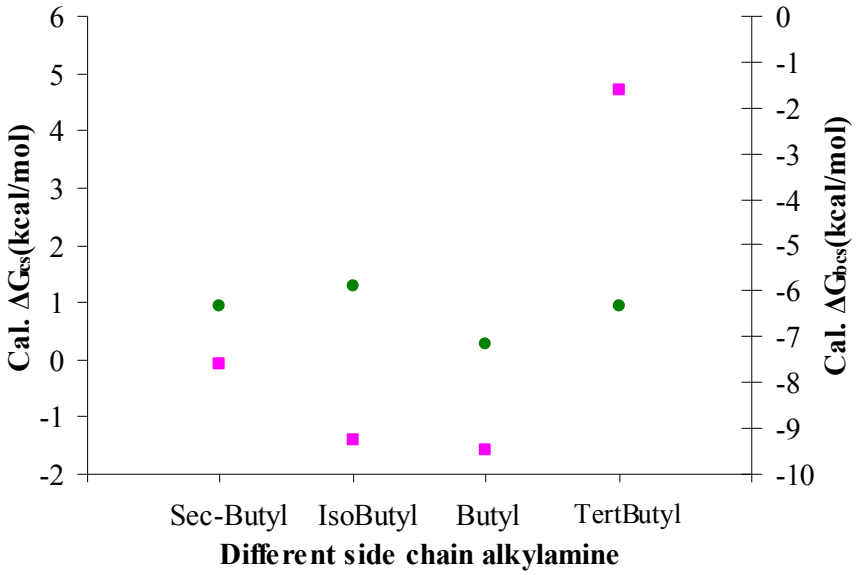


Figure 5, Effect of different side chain for alkylamine based solvents on their ■ calculated carbamate reaction energy, ΔG_{cs} (kcal/mol) (left side) and ● calculated bicarbonate formation reaction energy, ΔG_{bcs} (kcal/mol) (right side).

Hence, substitution of an alkyl group at the alpha carbon to the amine group in molecular structure as is the case in Sec-butylamine, reduces the carbamate stability by causing steric hindrance effect. This steric hindrance effect was also identified via CO_2 absorption capacity in experiments for these amines (Singh et al. 2009). It should be noticed that Tert-butylamine has the lowest energy for carbamate formation, corresponding with literature data (Chakraborty et al. 1988). This is due to the fact that substitution of two alkyl group at the alpha carbon to the amine group in molecular structure creates a strong steric hindrance effect. The lowest carbamate stability was observed for Tert-butylamine, ΔG_{cs} is even having a positive value; indicating that carbamate formation is unfavourable. The basicity of

these alkylamine based solvents is found to be quite similar ranging from 10.5 to 10.8 (see Table 2). The difference for bicarbonate formation reaction energy was also found to be small, as the values are in the range from -5.92 to -7.15 (see Figure 5 and Table 3).

3.5.5. Cyclic amines

Different cyclic amines were investigated in this study for their calculated reaction energy for carbamate formation and bicarbonate formation and the results are shown in Figure 6.

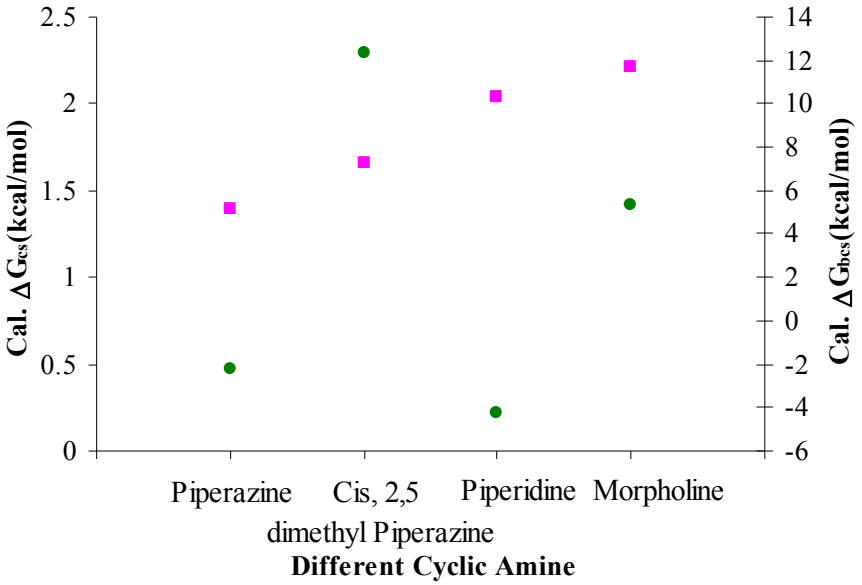


Figure 6, Effect of different cyclic amine based solvents on their ■ calculated carbamate reaction energy, ΔG_{cs} (kcal/mol) (left side) and ● calculated bicarbonate formation reaction energy, ΔG_{bcs} (kcal/mol) (right side).

The carbamate stability values for these cyclic amine ranges from 1.39 to 2.21, which is a relative small range. From Figure 6, it can be noticed that Morpholine, which has an electron withdrawing oxygen atom and a low base strength (pKa = 8.5), shows a low carbamate stability. Piperidine has an electron donating carbon atom in the back of the cyclic ring which results in a higher base strength (pKa = 11.3) and shows lower carbamate stability when compared to Morpholine. Figure 6 also shows that Piperazine has the highest carbamate stability. Cis 2, 5 dimethyl piperazine has two electron donating alkyl groups present at each nitrogen atom and has slightly lower basicity (pKa = 9.7) when compared to basicity of Piperazine. The carbamate stability of Cis 2, 5 dimethyl piperazine was found to be slightly lower than that of Piperazine.

Table 5 and 7 shows the carbamate reaction energy for Piperazine and Cis 2, 5 dimethyl piperazine based on equation 17 and 18. It can be noticed that dicarbamate of Cis 2, 5 dimethyl piperazine is less stable than that of Piperazine (see Table 7). Whereas, protonated carbamate is found to be more stable for Cis 2, 5 dimethyl piperazine than that of Piperazine. In Piperazine the presence of two electron donating nitrogen atoms makes it less basic (pKa = 9.9) when compared to piperidine and more basic when compared to morpholine. From Figure 6 it can be noticed that the trend observed for bicarbonate formation reaction energy (ΔG_{bcs}) is Morpholine > Piperadine > Piperazine which is reverse trend as for their experimental basicity, Table 2 (Piperadine < Piperazine < Morpholine). Table 7 shows that the bicarbonate formation reaction energy (based on equation 19) is lower for Cis 2, 5 dimethyl piperazine than that of Piperazine.

3.6. Conclusion

In this study the effect of molecular structural effect of different amines on their carbamate stability was investigated by calculating the quantum mechanical gas phase energies and the use of a solvation model. The effect of the carbon chain length on carbamate stability was studied for several classes of amine species, including alkanol amines, alkyl amines, diamine based compounds. Cyclic diamines were also evaluated on their carbamate stability. Additionally, for alkyl amines, the contribution of the steric hindrance effect on the calculated carbamate stability is studied. The bicarbonate formation energy was also studied for these amine solvents. In alkanolamine and alkyl amine based solvents it was found that an increase in carbon chain length between amine and hydroxyl group lowers the stability of carbamate. Steric hindrance was clearly identified in reducing the stability of carbamate for alkylamine based solvents. For the cyclic amine studied, Morpholine was found to be forming least stable carbamate due to the presence of electron donating oxygen group present in the structure. Piperazine was found to be forming most stable carbamate. The effect of carbon chain length in diamine based solvents was also investigated. Due to the presence of two amine functional groups in the molecular structure of diamine based solvents, further calculations are required to give more concrete results. Hence, from this work relative knowledge on carbamate stability for various amine based solvents has been developed. Therefore, from study it was noticed that the carbamate stability is influenced by presence of different functional group (electron withdrawing/electron donating), carbon chain length, steric hindrance and solvation effects. The results are in agreement with trends earlier observed in experimental data reported by Singh et al. 2007, 2009 and common knowledge on effects of steric hindrance. This (re-)confirms the usefulness of using computational chemistry for solvent development work in order to reduce extensive experimental screening and will help in developing better (understanding of-) amine based solvents for CO_2 absorption.

Acknowledgement
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Finally, I would like to express my deepest thanks to my Late Professor Michiel Groeneveld, who gave tremendous support to initiate this research in collaboration with SINTEF.

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4

Structure and activity relationships for CO_2 absorption and regeneration for various aqueous amine based absorbents

A study to determine the effect of molecular structure on CO_2 absorption capacity and reactivity was performed for various amine based absorbents for CO_2 absorption and regeneration. The absorption of pure CO_2 was performed at 30°C and atmospheric pressure to assess a preliminary indication on the initial CO_2 absorption rate and absorption capacities (or rich loading). The regeneration of CO_2 from saturated solvents was performed at 80°C and atmospheric pressure to determine the lean loading at pseudo equilibrium. Evaluation of desorption capacity (lean loading) at this relatively low temperature may point out more directly towards a more energy efficient solvent. Results showed that an increase in carbon chain length between the amine and different functional groups in the absorbent structure, result in a decrease of the absorption rate whereas the absorption capacity was increased in most of the absorbents. Results showed that an increase in carbon chain length (up to four carbon atoms) between the amine and hydroxyl group groups in the solvent structure, results in a lower lean loading at pseudo equilibrium. The steric hindrance effect was noticed when side chain with alkyl group was present at the alpha–carbon to the amine group in the absorbent structure. An increase in the number of amine groups up to 4 amine group in the absorbent structure, results in an increase of absorption capacity up to 2.5 mole CO_2/mole amine. Whereas a higher lean loading was observed with an increase in number of amine groups. Aromatic diamines substituted with alkyl groups at 2^{nd} and 5^{th} position showed a slight increase in the initial absorption rate and absorption capacity. Aromatic diamines substituted with a hydroxyl group on a side chain at the cyclic ring showed the lowest lean loading of 0.38 mole CO_2/mole amine at pseudo equilibrium compared to other functional group substitution at the cyclic ring of saturated diamine based absorbents. Additionally, the effect of basicity on the absorbents CO_2 absorption and regeneration characteristics was investigated. These results were also compared with those obtained from quantum mechanical calculations on different molecular structural effects on carbamate stability performed in Chapter 3.

4.1. Introduction

Although the absorption of acid gases such as CO_2 in aqueous amine based solvents like e.g. MEA (Monoethanolamine) from natural gas can be considered proven technology, the removal of CO_2 from flue gases is not as straightforward as expected. In these oxygen containing systems problems such as degradation, precipitation, corrosion, foaming etc., affect more the process substantially. Furthermore, in the currently used systems a major part (up to 40%) of the operational cost is caused by the solvent regeneration, Peeters et al. 2007. In industrial processes, high temperatures (>100°C) are used to regenerate MEA solutions. Usually steam is applied to provide the heat of reaction and enabling the transport of CO_2 out of the reactor. The regeneration process is usually done at elevated temperatures, as the chemical kinetics of regeneration increases with temperature and the reaction equilibrium shifts favourably to release CO_2. The energy consumption in the stripper reboiler is estimated to be 15-30% of the net power production of a coal-fired power plant for about 90% CO_2 removed. The development of solvents with lower regeneration energy requirement has therefore been identified as priority research and development objective for amine based CO_2 capture systems.

In the development of a better solvent it is necessary to have a clear understanding how various solvent properties influence the reactivity characteristic towards CO_2. The dissociation constant (pKa value) is one of the important factors in the selection of an amine based absorbent for acid gas removal or in the interpretation of the kinetic mechanism of the absorption of the acid gas in the amine based absorbent. Earlier in this thesis, (Chapter 2) the basicity of various amine based solvents was evaluated to determine the effect of carbon chain length and steric hindrance in alkanol, alkyl and diamine based solvents. It was found that an increase in the carbon chain length in alkanol and diamine results in an increase in their basicity. While in alkylamine based solvents the basicity was not affected with an increase in carbon chain length. This clearly shows the effect of molecular structure (carbon chain length and in combination with functional groups) to be relevant, but non-trivial.

The effect of molecular structure was also investigated in Chapter 3 by evaluating the carbamate stability using quantum mechanical calculations for various amine based solvents, building on earlier work performed by da Silva et al. (2007) who drew attention on the influence of molecular structure on the CO_2 absorption characteristics. In literature according to Chakraborty et al. (1986) the introduction of substituents at the α-carbon to the amine group creates a carbamate instability, which causes the carbamate hydrolysis to go faster, thereby increasing the amount of bicarbonate formed, and hence allowing for higher CO_2 loadings. Sartori and Savage (1983) suggested this instability was due to the steric hindrance created by these α-substituents. Chakraborty et al. (1988) examined the electronic effects of

such substituents and proposed that substitution at the α-carbon atom results in an interaction of the π and π* methyl group orbital with the lone electron pair of the nitrogen atom. This interaction could reduce the charge at the nitrogen, resulting it in a softer base, which again results in a weakening of the N-H bond. These effects allow an increase of the hydrolysis by the hydroxide (hard base) in the solution. The steric hindrance would be expected to slow down the rate of the initial reaction with CO_2 to some extent, but as one mole of amine is released upon hydrolysis of the carbamate, the level of amine available for reaction with CO_2 increases.

For solvent selection and development, the approach of evaluating a large number of solvents through a complete and rigorous (rate based) simulation model of the chemical absorption- desorption process, would require a huge data-set of physico-chemical data (solvent viscosity, density, diffusivities, kinetics data, equilibrium model) and a tedious task which could not be performed for even a few solvents in a short time. Moreover, studies devoted to a systematic investigation of molecular structural effects for amine based absorbents for CO_2 absorption and regeneration are scarce in literature. Therefore, an attempt is made to provide an experimental basis for comparison with the results found for molecular structure - activity characteristics of various amines based CO_2 absorbents, as studied in Chapter 2 and 3 in this thesis. For this, a screening method has been developed for the absorption of CO_2 and desorption of CO_2 from various loaded amine based aqueous absorbents. The main aim of this investigation is to perform the screening of aqueous, amine-based solvents with various molecular structures on their absorption characteristics with respect to CO_2 absorption capacity and reactivity. Another focus is to investigate the CO_2 regeneration behaviour of various amine based solvents at low temperature and atmospheric pressure, with respect to rapid regeneration rate and low evaporation solvents losses especially. Regeneration of CO_2 from various amine based absorbents was measured to assess the amount of CO_2 desorbed at 80°C.

From these solvent screening experiments the earlier identified effects of molecular structure on basicity (Chapter 2) and carbamate stability (Chapter 3) can be evaluated experimentally. The variables that were investigated experimentally in this study are the effect of carbon chain length, an increase in the number of functional groups, the effect of side chains substituents at the α & β-carbon position, the alkyl group position in cyclic (di)amines and the effect of side chains on cyclic (di)amines with different functional groups. A semi quantitative representation of these effects on the preliminary indication of initial rate of absorption for CO_2 is described, as well as on the CO_2 absorption capacity. Based on these results a better understanding of the effect of molecular structure on CO_2 absorption and desorption is targeted and may result in more advantageous amine based CO_2 absorbents.

4.2. Experiment

4.2.1. Absorption experiment set-up

The various amine based absorbents were tested in a screening apparatus (see Figure 1), where the relative rates of absorption and absorption capacity can be measured and compared to the MEA as a default case. This experiment set-up is similar to the experiment set-up used by Hook 1997. The apparatus is designed to operate at atmospheric pressure and temperature up to 40°C. Before starting the experiment the absorbent sample in absorbent vessel is degassed for approximate 1 hour. The temperature of the water bath was maintained at 30 ± 0.5°C. The carbon dioxide absorption was measured by following the volume changes of pure CO_2 in gas burette over 10 ml sample of an aqueous amine solution of 2.5 to 0.1 mole/L concentration, stirred at a constant rate for 200 minute at 1 atm. pressure.

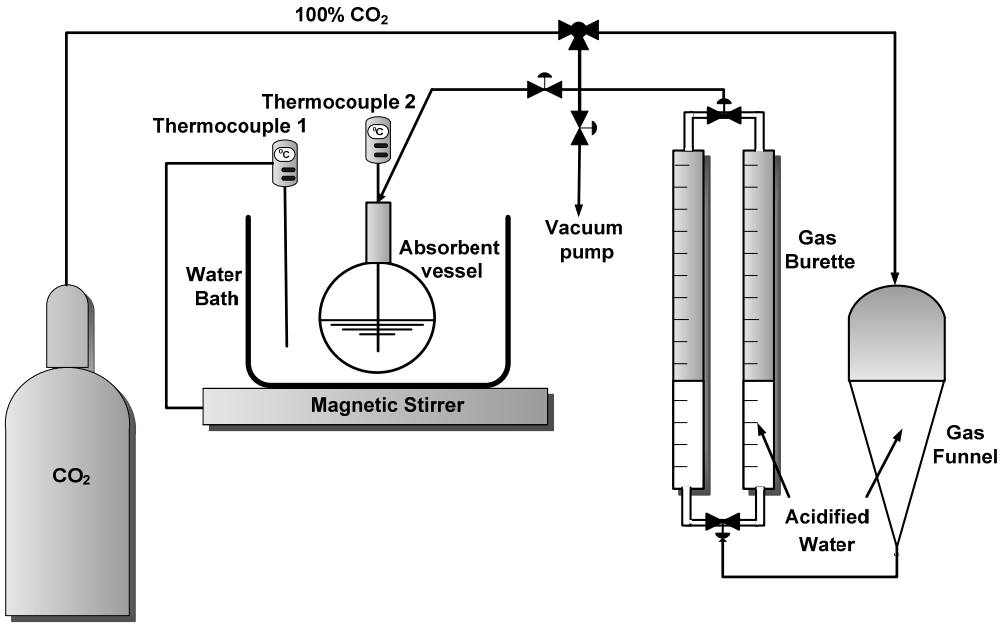


Figure 1, Schematic diagram of the experimental set-up for determining the CO_2 absorption capacity of various amine based absorbents.

4.2.2. Desorption experiment set-up

The various amine based absorbents were tested in a simple screening apparatus (see Figure 2), in which the desorption capacity at pseudo equilibrium can be measured and compared to the MEA (base case). Due to the selection of the lower temperature of 80°C for these experiments, compared to the commercial process CO_2 regeneration temperature of 120°C, complete equilibrium for these desorption experiments was difficult to achieve due to the relatively low experimental temperature and the minor amount of nitrogen fed to the system. In these

desorption experiments pseudo-equilibrium was defined, which for most of the absorbents will be close to their equilibrium composition. As desorption of CO_2 is faster compared to the absorption process, a desorption time of 20 minute was found to be sufficient for this preliminary evaluation. The apparatus was designed to operate at atmospheric pressure and temperatures up to 80°C. In a typical experiment first the solvent was degassed for sufficient time (approximately 2 hour) and then loaded by bubbling pure CO_2 with sufficient speed for approximately one hour at 30°C and atmospheric pressure in separate bubble column equipment. The contact area between gas and liquid was high and one hour was found to be sufficient time for the solvent to be saturated. Once the solvent was completely saturated, a sample was taken to determine the total CO_2 loading in the solvent by a desorption/titration procedure as described by Blauwhoff et al (1984). Once the total CO_2 loading was determined the known volume (40 ml) of a saturated amine sample was transferred into the desorption vessel (see Figure 2). The temperature inside desorption vessel was maintained at 80 ± 0.5°C. To ensure that the temperature in the absorbent solution during desorption remained constant, the solution is stirred continuously with a constant speed in every experiment. Saturated absorbent solution reached 80°C within approximate 2.5 minute.

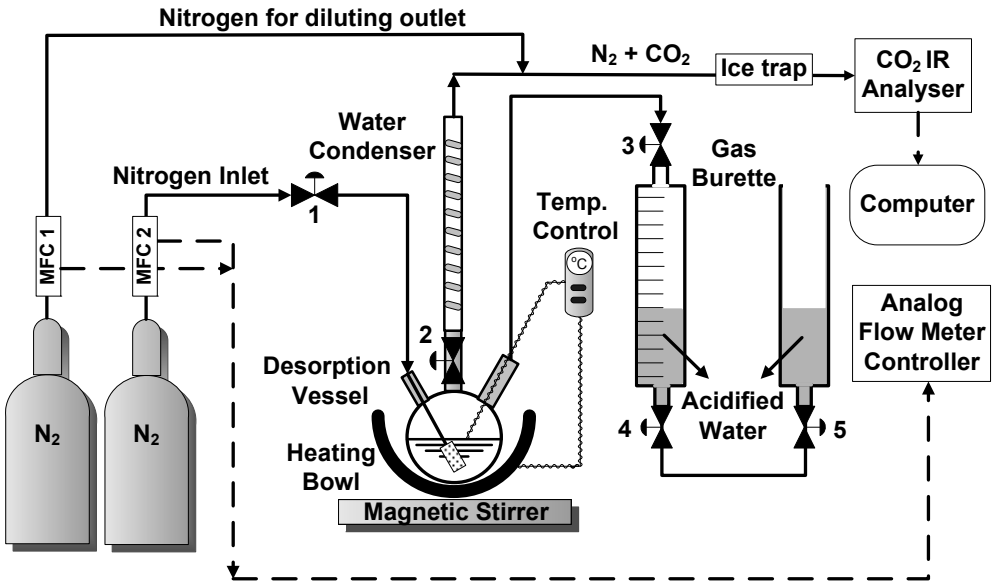


Figure 2, Schematic diagram of the experimental set-up for determining the CO_2 desorption capacity of various amine based absorbents.

The carbon dioxide released during this heating time is measured by a gas burette connected to the desorption vessel. When the solvent temperature is 80°C the valve of the gas burette is closed and the CO_2 is monitored by inline CO_2 IR detector. At the same time pure N_2 gas is bubbled through the saturated absorbent to increase the interfacial area for CO_2 desorption. The vapour leaving the desorption vessel

containing the CO_2 and N_2 is fed into a vertical condenser. The condenser was kept at a temperature of 20°C. The gas leaving the top of the condenser was at 25 ± 1°C and thus contained only about 3 vol% of water vapour. Furthermore, N_2 gas is added to the outlet stream as diluent before analysis. This diluted stream is passed through an ice trap with a temp of approximate 2°C to remove the remaining amount of water vapour from the stream.

Next this stream is send to CO_2 IR detector where the amount of CO_2 in the stream is measured. To ensure that there was no significant reduction of the partial pressure of CO_2 in the desorption vessel during the desorption experiment, the flow of N_2 gas is kept very low in the saturated absorbent. Hence the effect on CO_2 partial pressure was negligible in the desorption experiment. The complete desorption experiment was carried out at the prevailing atmospheric pressure, as the pressure-drop during the experiment was very small. The N_2 gas flows added to the desorption vessel and for dilution was kept constant in every experiment. After a certain time in this desorption experiment, when pseudo equilibrium is reached, the total CO_2 loading in the desorbed solvent is determined by desorption/titration procedure as described by Blauwhoff et al 1984. The time for each regeneration experiment was kept constant for 200 minutes.

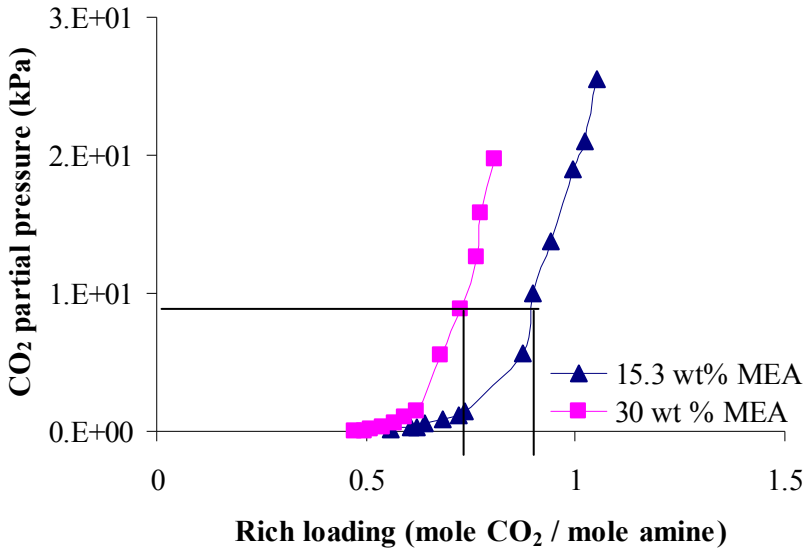


Figure 3, Solubility of CO_2 in 15.3 and 30 wt% MEA aqueous solution at 40°C (Keh-Perng Shen et al. 1992).

The amine concentration in the solution could vary with the type of compound only to e.g. molecular weight and solubility. As default MEA was chosen with a concentration of 2.5 mole/L. All absorbents tested showed good solubility in water, except for a few compounds. Due to the differences in solubility and molecular

weight, it is not possible to carry out all experiments at the same molar concentration and weight fraction. It was chosen to be, where possible, to carry out the experiments at a concentration of 2.5 mole/L. In some cases this was not possible, and this must be regarded as a drawback of this present screening technique as differences in the concentration may affect both the initial absorption rate as well as the total absorption capacity. The effect of solvent concentration is illustrated in Figure 3, in which the influence of the MEA wt% on the equilibrium pressure of CO_2 at constant loading is presented. The concentration of the absorbents were kept same for both absorption and regeneration experiment. Since in this research the main focus was still at a level of difference in chemical species as to their reactive properties for CO_2 absorption and regeneration, the present technique (with its limitations) was applied as a first screening of various amine based absorbents. The optimal operational concentrations for these absorbents are not yet known. All chemicals investigated (see Table 1 to 13) were purchased from Sigma Aldrich Chemical Co.

4.3. Results and discussion

Examination of the absorption data, using a pure CO_2 atmosphere, allows for a comparison of the absorption rates and capacity for the CO_2 solubility. From the initial absorption rate a preliminary indication can be obtained about the reactivity of various amine based aqueous solvents. Due to the mass transfer effects e.g. interfacial area and enhancement factor, that are contactor specific, no quantitative conclusions can be drawn from the (initial) absorption rates observed. However, since the absorption experiments for the different solvents are conducted under comparable conditions, differences in absorption rate arise mainly due to the differences in solvent specific physical and chemical properties, like e.g. interfacial tension, density and viscosity. Since these characteristics are also relevant for absorption under actual process conditions, the experiments provide a direct comparison of the overall performance.

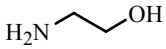
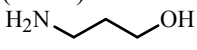
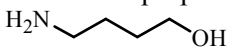
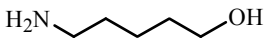
Examination of the desorption behaviour from a saturated amine based solvent, allows for a comparison of the desorption capacity (lean loading) defined as the amount of CO_2 that remains in the solvent at the experimental conditions at the end of the experiment. The solvents with the higher absorption capacity (higher rich loading) and lower desorption capacities (lower lean loading) are more suitable as they will decrease the solvent circulation rate in the CO_2 capture process. Hence, that will be economically beneficial for the whole CO_2 absorption process. All experiments were repeated three times for each absorbent and the experimental deviation (based on propagation of error) was estimated to be approximate 5%.

4.3.1. Effect of carbon chain length

In Figures 4(a & b), 5(a & b) and Table 1, the effect of an increase in the carbon chain length between the amine and hydroxyl group on the CO_2 initial absorption

rate and CO_2 absorption capacity of an alkanolamine based absorbents is shown. In these experiments the carbon chain length varied from two carbon chain (MEA) up to five (5-amino-1-pentanol) respectively.

Table 1, Effect of carbon chain length in aqueous alkanolamine based absorbents.

Solvent	**Conc.** mole/L	**Rich loading** mole CO_2 /mole amine	mole CO_2 /kg amine	**Lean loading** mole CO_2 /mole amine
 Monoethanolamine (MEA)	2.5	0.72	11.76	0.49
 3-Amino-1-propanol	2.5	0.88	11.63	0.45
 4-Amino-1-butanol	2.5	0.83	9.44	0.44
 5-Amino-1-pentanol	2.5	0.84	8.05	0.54

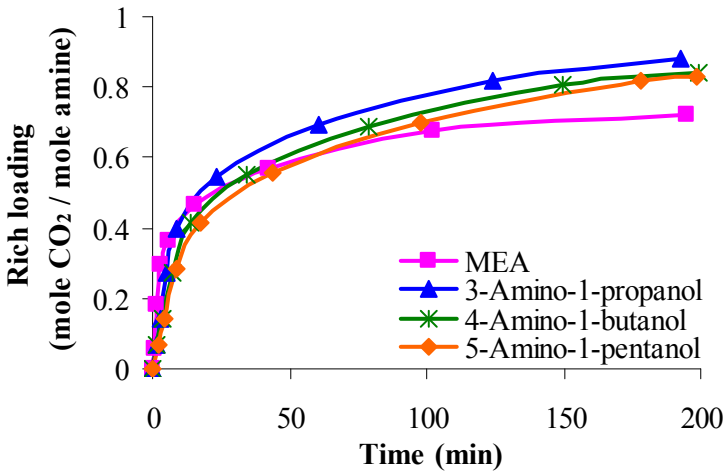


Figure 4(a), Influence of the carbon chain length in alkanolamine for the absorption of CO_2 in aq. absorbents.

In Figure 4(a), the overall results from CO_2 absorption are presented. It must be noticed that the concentration of all alkanolamine was kept to 2.5 mole/L. Increase in the carbon chain length resulted in a slight increase in CO_2 absorption capacity up to three carbon chain length from 0.72 to 0.88 mole CO_2/mole amine (see Table 1 and Figure 4(a) and 5(a)). The high rich loading in MEA of 0.72 mole CO_2/mole amine occurred due to the conversion of the carbamate to bicarbonate and hence

results in an increase in mole fraction of CO_2 that is a result of physical absorption (Poplsteinova et al. 2005).

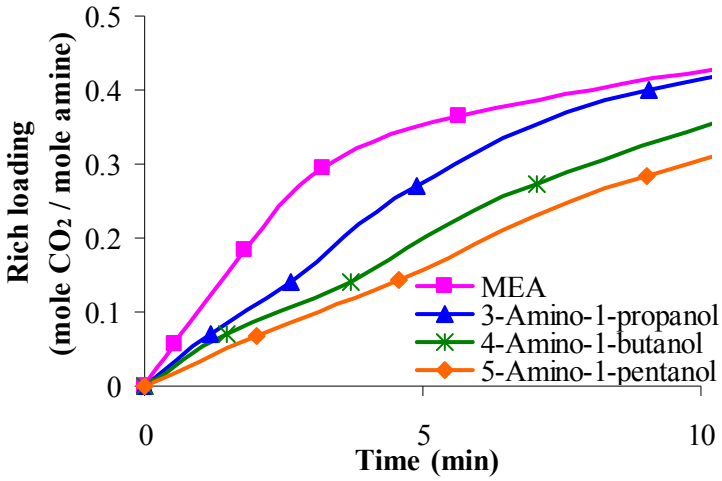


Figure 4(b), Influence of the carbon chain length in alkanolamine initial absorption rate for the absorption of CO_2 in aq. absorbents.

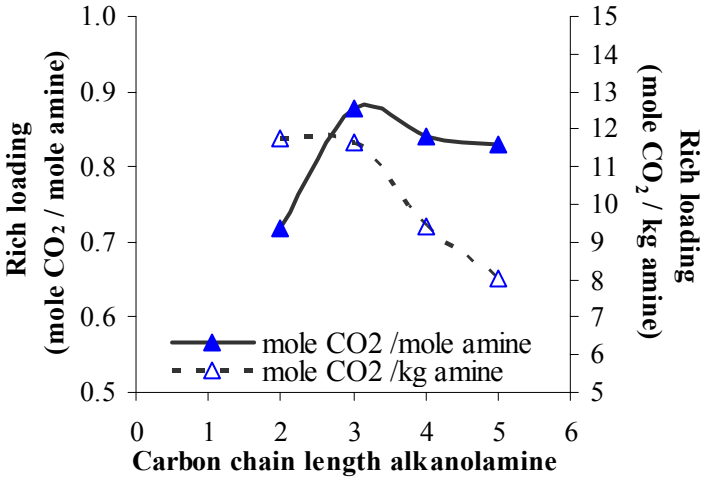


Figure 5(a), Influence of carbon chain length on the rich loading of CO_2 in aq. solution of alkanolamine absorbents.

Further increase in carbon chain length did not increase the absorption capacity, as it remains approximately the same. Figure 5(a) and Table 1 shows the total capacity of CO_2 absorption for various alkanolamine in mole CO_2/kg amine. Results show that the absorption capacity is decreasing from 11.76 to 8.05 mole

CO_2/kg amine with an increase in carbon chain length. This is mainly caused by increase in molecular weight which means less mole absorbent is present in the solution.

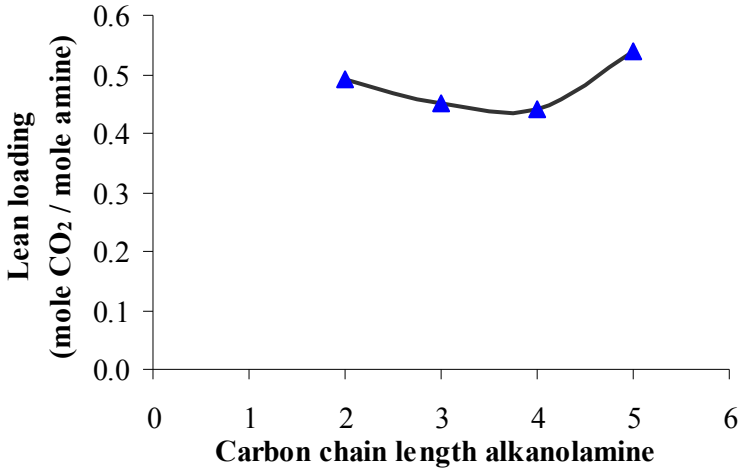


Figure 5(b), Influence of carbon chain length on the lean loading of CO_2 in aq. solution of alkanolamine absorbents.

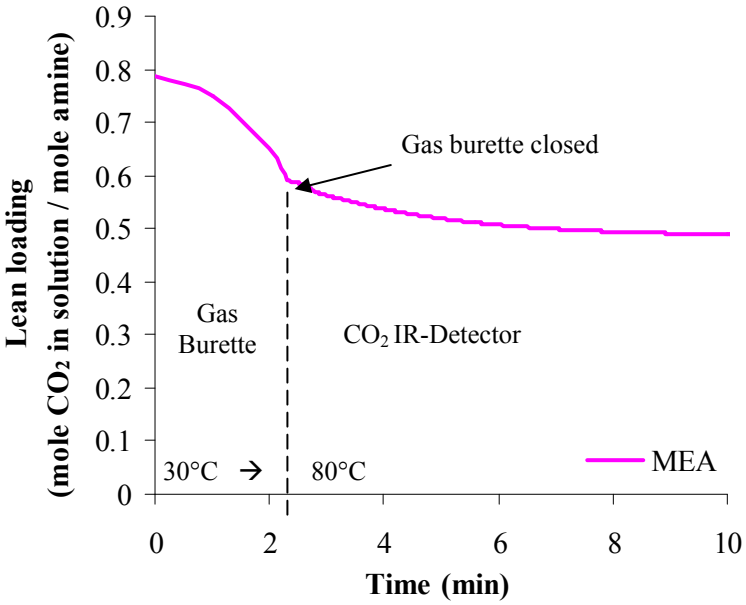


Figure 6(a), Detailed overview on desorption of CO_2 from 2.5 mole/L aqueous MEA solution at 80°C.

The effect of carbon chain length on the initial absorption rate for alkanolamine is clearly shown in Figure 4(b). Interestingly the pKa values for alkanolamine are only slightly increased from 9.65 to 10.46 (estimated pKa value at 20°C, Chapter 2) with an increase in carbon chain from 2 to 5 as showed in Chapter 2. The experimental result shows that increase in carbon chain length decreases the initial absorption rate in alkanolamine. The decrease in absorption rate might be due to an increased contribution of the bicarbonate formation reaction and less carbamate formation. This is in line with the results from quantum mechanical calculations, as presented in Chapter 3, for the study of the stability of the carbamate. In Chapter 3 it was found that the carbamate stability decreased with an increase in carbon chain length in alkanolamine based solvents. The absorption rate is the result of a complex interaction between hydrodynamics, mass transfer, kinetics and equilibrium no further conclusion can be made at this stage. The interpretation therefore it is not as straight forward as was expected on before hand. Overall for alkanolamine based solvents the absorption capacity and initial absorption rate is decreasing with increasing in carbon chain length.

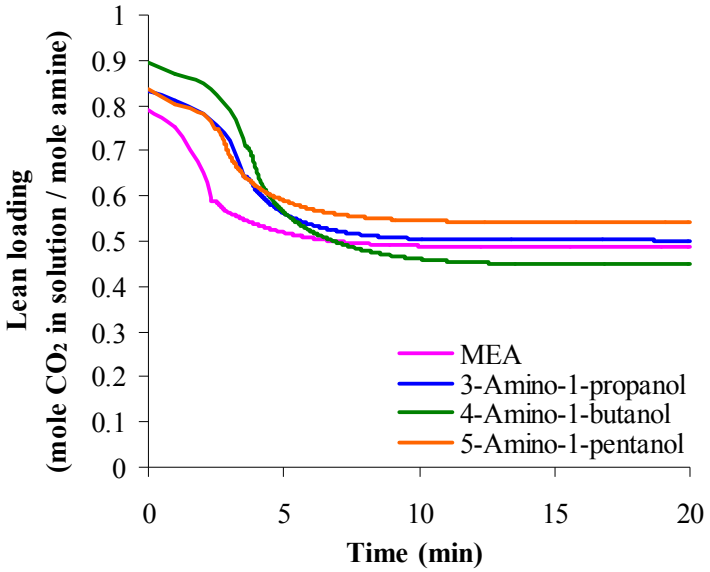


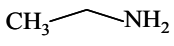
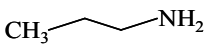
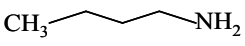
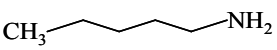
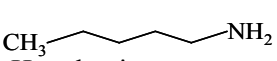
Figure 6(b), Influence of the carbon chain length in aqueous alkanolamine based absorbent for desorption of CO_2.

In Figure 6(a), 6(b) and Table 1, the effect of an increase in the carbon chain length between the amine and hydroxyl group on their CO_2 desorption behaviour for alkanolamine based absorbents is shown. In these experiments the carbon chain length varied from a two carbon (MEA) up to five (5-amino-1-pentanol) respectively. Figure 6(a) shows the result overview of the complete desorption experiments of CO_2 from 2.5 mole/L aqueous MEA solution, which is regarded as the base case. As it can be seen from Figure 6(a) in the beginning of the experiment

from t = 0 to 2.5 minutes desorption rate is influenced by the increase in temperature which is starting from 30°C up to 80°C. Desorption rate is increasing with increasing temperature. Hence, in this region desorption is affected by combination of phenomena; lower physical solubility, changing thermodynamic equilibrium and increasing kinetics with temperature. It is clear that neither qualitative nor quantitative conclusions can be presented during this period of experiments. Once the temperature of the absorbent solution reached 80°C, desorption rate would be more affected by chemical kinetics. In Figure 5(b), the overall results for alkanolamines are presented. Increase in the carbon chain length up to four carbon atoms results in a slight decrease in CO_2 lean loading down to 0.44 mole CO_2/mole amine (see Figure 5(b) and Table 1) and a higher value for the five carbon atom chain length.

In the alkylamine experiments the carbon chain length varied from two carbon chain (Ethyl amine) up to six carbon atoms (Hexyl amine) respectively. In Figure 7(a), the overall results for CO_2 absorption in alkylamines are presented. It must be noticed that the concentration of alkylamine up to five carbon chain (N-pentylamine) was kept to 2.5 mole/L but for the six carbon chain alkylamine (Hexylamine) the concentration was 0.1 mole/L and for this reason the results for Hexylamine are not included in Figure 7 (a & b) and 8 (a & b).

Table 2, Effect of carbon chain length in aqueous alkylamine based absorbents.

Solvent	**Conc.**	**Rich loading**		**Lean loading**
	mole/L	mole CO_2 /mole amine	mole CO_2 /kg amine	mole CO_2 /mole amine
 Ethylamine	2.5	0.91	20.10	0.48
 Propylamine	2.5	0.77	12.96	0.68
 Butylamine	2.5	0.86	11.74	0.59
 N-pentylamine	2.5	0.72	8.20	0.51
 Hexylamine	0.1	1.52	15.05	1.07

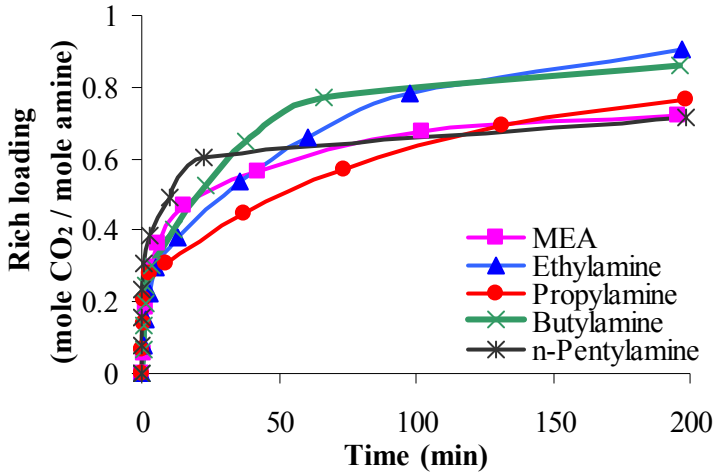


Figure 7(a), Influence of the carbon chain length for the absorption of CO_2 in aqueous solution of alkylamine based absorbents.

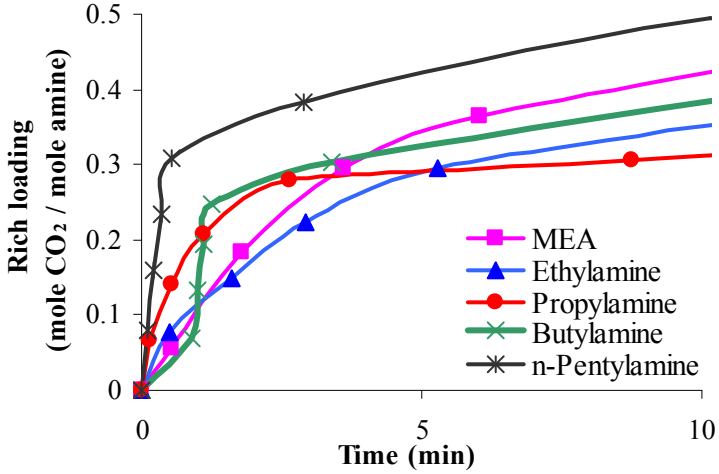


Figure 7(b), Influence of the carbon chain length on initial absorption rate for the absorption of CO_2 in aqueous solution of alkylamine based absorbents.

The influence of the carbon chain length in alkylamines is shown in Figure 7(a & b) and 8(a & b) and Table 2. No clear trends were obtained for the CO_2 absorption capacities of the alkyl amine compounds tested. Figure 7(b), shows that the initial absorption rate in alkylamines increases gradually with an increase in carbon chain length up to five carbon i.e. N-pentylamine. Hence, N-pentylamine might be an interesting absorbent on the basis of its high CO_2 initial absorption rate. The six

carbon chain alkylamine (Hexylamine) showed a very fast CO_2 absorption rate and high capacity (up to 1.52 mole CO_2/mole amine). Due to the much lower concentration of 0.1 mole/L applied for Hexylamine, it is difficult to draw clear conclusions for this solvent at this stage. The Hexylamine CO_2 absorption curve is shown in the Appendix in Figure 27.

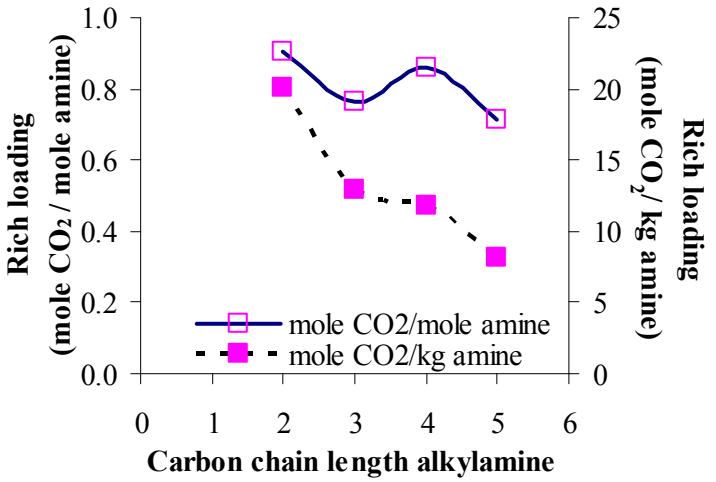


Figure 8(a), Influence of the carbon chain length on rich loading of CO_2 absorption in aqueous solution of alkylamine absorbents.

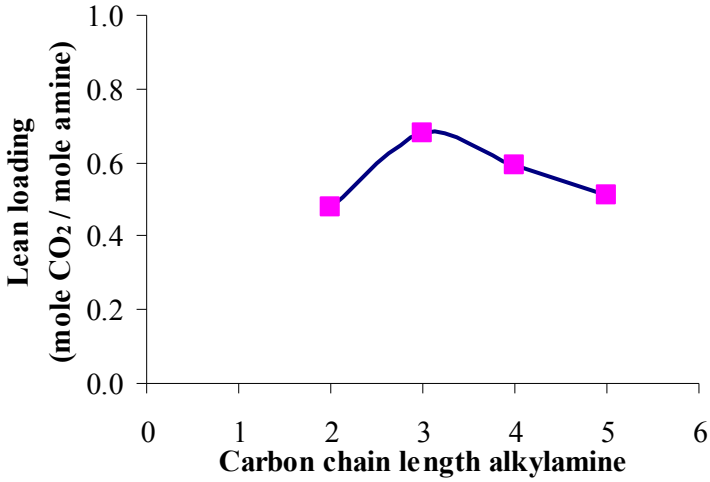


Figure 8(b), Influence of carbon chain length on the lean loading of CO_2 in aqueous solution of alkylamine absorbents.

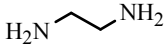
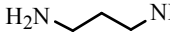
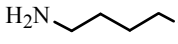
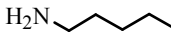
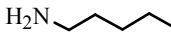
Comparing the mole of CO_2 absorbed per kg of amine in Figure 8(a) shows that the ethylamine has the highest CO_2 concentration of 20.1 mole CO_2/kg amine (see Table 2) due to its lowest molecular weight. The absorption capacity decreases

with an increase in carbon chain length up to five carbon chain (N-pentylamine) 8.2 mole CO_2/kg amine. From Figure 8(b) and Table 2, the results shows that an increase in the carbon chain length from a two carbon (Ethylamine) to a three carbon (Propylamine) the CO_2 lean loading is increased. Further increase in the carbon chain length from 3 to 5 carbon results in a decreased CO_2 lean loading.

The basicity of alkylamine was found not to be influenced with an increase in the carbon chain length. From quantum mechanical calculation it was found that the increase in carbon chain length decreases the carbamate stability when carbon chain is increased from 3 to 5 carbon in alkylamine. An increase in carbon chain length results in a weaker N-C bond in the carbamate species, but apparently the N-C bond is still not weak enough to have a strong contribution of the hydrolysis reaction of the carbamate to form bicarbonate. Therefore, the major concentration of CO_2 in liquid remains in the form of carbamate species and hence, the absorption capacity is not significantly affected with an increase in carbon chain length for alkylamine.

In diamine based absorbent experiments the carbon chain length was varied from two carbon (Ethylenediamine) up to seven (1, 7-Diaminoheptane) respectively. It must be noticed that the used concentrations for diamines up to six carbon chain (Hexamethylenediamine) was kept at 2.5 mole/L.

Table 3, Effect of carbon chain length in aqueous diamine based absorbents.

Solvent	**Conc.**	**Rich loading**		**Lean loading**
	mole /L	mole CO_2 /mole amine	mole CO_2 /kg amine	mole CO_2 /mole amine
 Ethylenediamine	2.5	1.08	17.93	0.84
 1,3-Diamino propane	2.5	1.30	17.66	0.94
 1,4-Diaminobutane	2.5	1.26	14.29	0.94
 Hexamethylenediamine	2.5	1.48	12.71	0.95
 1,7-Diaminoheptane	1.5	1.34	10.28	0.95

However, due to the low solubility in water, the concentration of seven carbon chain (1, 7-Diaminoheptane) was kept at 1.5 mole/L. The CO_2 absorption curve of 1, 7-Diaminoheptane is shown in Appendix, Figure 28.

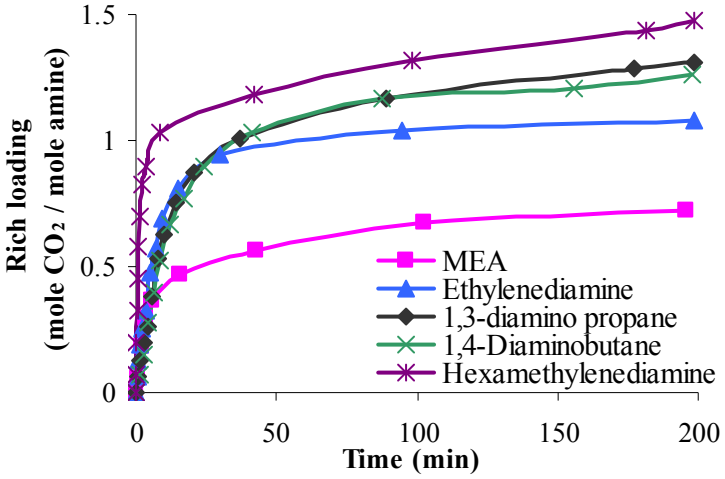


Figure 9(a), Influence of the carbon chain length for CO_2 absorption in aqueous diamine based absorbents.

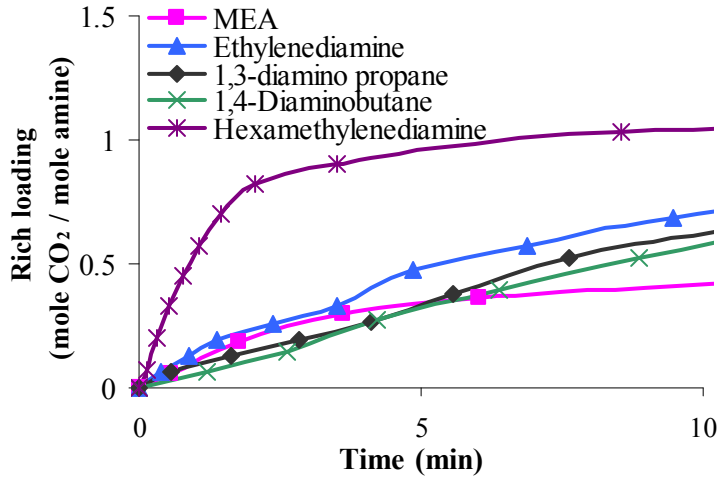


Figure 9(b), Influence of the carbon chain length on initial absorption rate for CO_2 absorption in aqueous diamine based absorbents.

In Figure 9(a), the overall results on CO_2 absorption in diamine based absorbents are presented. An increase in the carbon chain length in diamine results in an increase in their CO_2 initial absorption rate and capacity from 1.08 to 1.48 mole CO_2/mole diamine (see Figure 9(a), 10(a) and Table 3). This might be caused by

the decrease in the stability of the carbamate with an increase in the carbon chain length between the amine groups or an increase of the stability of double protonated molecules, which may increase the CO_2 absorption capacity of these absorbents. The basicity of diamines was found to increase with an increase in carbon chain length up to 6 carbon atoms (see Chapter 2). The carbamate stability studied in Chapter 3 for diamine based solvents showed that diamines with one carbamate and with one protonated amine group also results in a decreased carbamate stability. Hence, from these results it can be suggested that an increase in carbon chain length in diamine indeed is beneficial to enhance the absorption capacity. Figure 9(a) shows that increase in carbon chain length decreases initial CO_2 absorption rate in diamines up to four carbon (1,4-Diaminobutane). However, further increase in carbon chain length up to six-carbon (Hexamethylenediamine), an exceptional increase in initial absorption rate was noticed.

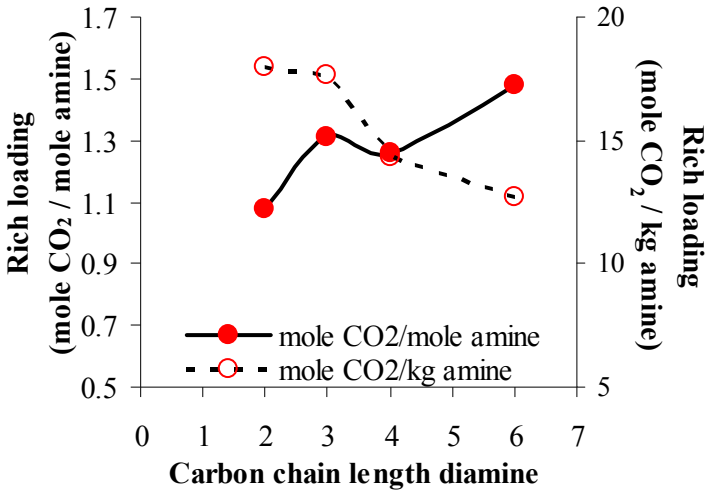


Figure 10(a), Influence of carbon chain length on rich loading of CO_2 absorption in aqueous diamine based absorbents.

From Figure 10(a) and Table 3, it can be noticed that in the diamine based solvents the absorption capacity increases from two (Ethylenediamine) to three carbon chain length absorbent (1,3-Diaminopropane) from 1.08 till 1.30 mole CO_2/mole amine respectively. This effect was also noticed in the carbamate stability as it was reduced with an increase in carbon chain length from 2 to 3 in Chapter 3. The slightly lower absorption capacity for 4 carbon chain length diamine (1,4-Diaminobutane) of 1.26 mole CO_2/mole amine could be an experimental error. The absorption capacity of six carbon chain length (Hexamethylenediamine) reaches up to 1.48 mole CO_2/mole amine (see Table 3 and Figure 10(a)). This might very well be caused by a formation of a hydrogen bond between the amine groups in this absorbent, thus creating a ring shaped structure. The Hexamethylenediamine absorption properties are comparable with cyclic amines such as Piperazine but the

carbamate was found to be much less stable for Hexamethylenediamine (see Chapter 3). Hence, Hexamethylenediamine was found to be an interesting absorbent based on its high CO_2 initial absorption rate and capacity. Figure 10 (a), also shows the comparison of diamines absorption capacities in mole CO_2/kg amine. Ethylenediamine has the highest absorption capacity for CO_2 up to 17.93 mole CO_2/kg amine.

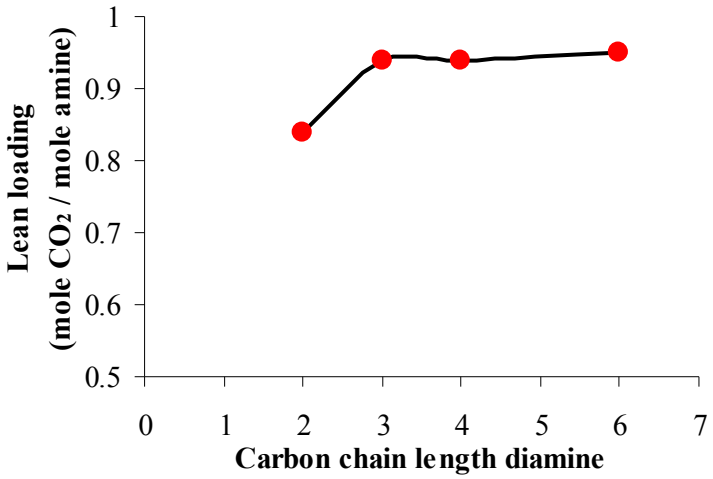


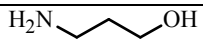
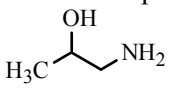
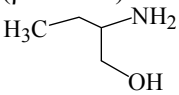
Figure 10(b), Influence of carbon chain length on lean loading of CO_2 absorption in aqueous diamine based absorbents.

From these results Ethylenediamine and Hexamethylenediamine could thus have a greater potential for CO_2 absorption. Figure 10(b) shows that an increase in the carbon chain length in diamine based absorbent results in an increase in the difference between rich and lean loading (i.e. cyclic capacity) as can be noticed in Hexadimethylenediamine (see Table 3). This might be caused by the effect from a decrease in stability of the carbamate with an increase in the carbon chain length. Therefore, the bicarbonate concentration may be higher and hence, higher amount of CO_2 is released.

4.3.2. Effect of functional group substitution by side chain

The position of different functional groups in the molecular structure of various amine based absorbents is an important factor for CO_2 absorption, as e.g. shown in the work by Chakraborty et al. (1986, 1988). In Figure 11(a & b), 12(a & b) and Table 4 the effect of the position of substituted hydroxyl groups is compared. Note that the concentration for 3-Amino-1-propanol, and 2-Amino 1-butanol was kept at 2.5 mole/L, whereas the concentration used for 1-Amino 2-propanol was 0.5 mole/L. In these experiments the hydroxyl group is positioned at the α-carbon (1-Amino 2-propanol) and β-carbon (2-Amino 1-butanol) to the amine group in the absorbent structure.

Table 4, Effect of side chain in aqueous alkanolamine based absorbents.

Solvent	Conc. mole/L	Rich loading mole CO_2 /mole amine	Rich loading mole CO_2 /kg amine	Lean loading mole CO_2 /mole amine
 3-Amino-1-propanol	2.5	0.88	11.63	0.50
 2-Amino-1-butanol (β-carbon)	2.5	0.88	9.86	0.37
 1-Amino-2- propanol (α-carbon)	0.5	1.14	15.24	0.86

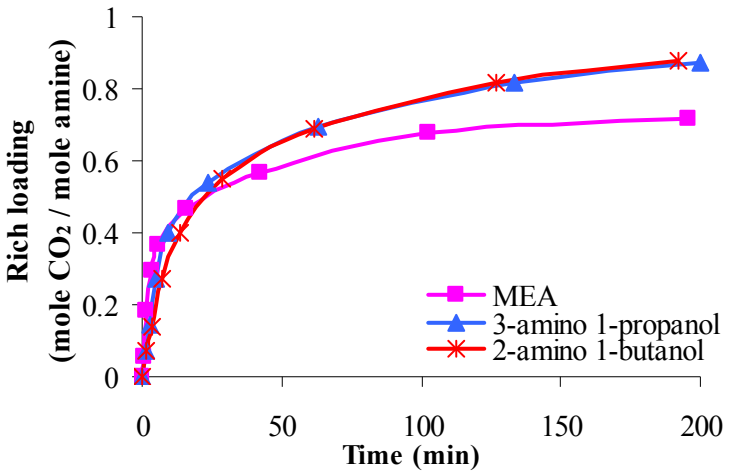


Figure 11(a), Influence of the hydroxyl group position on rich loading of CO_2 absorption in aqueous alkanolamine based absorbents.

The concentration of all alkanolamine absorbents was kept at 2.5 mole/L. It must be noticed that a substitution of an OH group on the β-carbon (2-Amino-1-butanol) to the amine group does not enlarge the CO_2 absorption capacity as it remains the same as that of non-substituted alkanolamine (3-Amino-1-propanol), see Table 4.

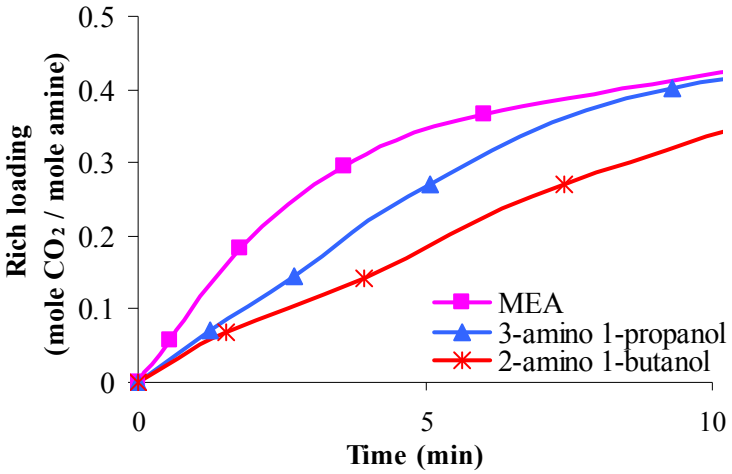


Figure 11(b), Influence of the hydroxyl group position on initial absorption rate of CO_2 absorption in aqueous alkanolamine based absorbents.

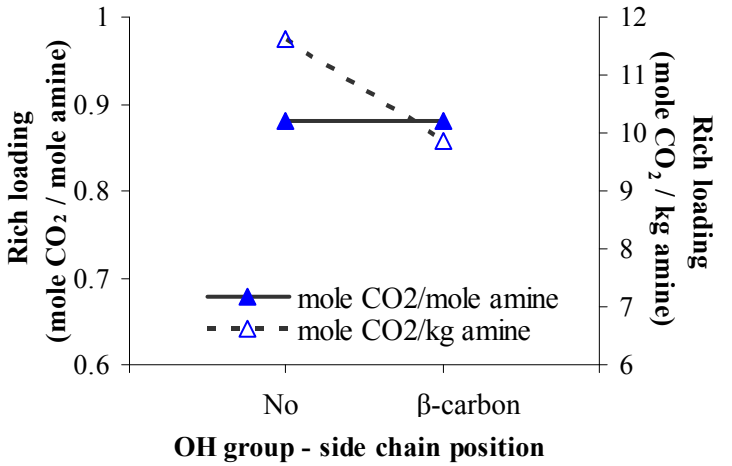


Figure 12(a), Influence of the hydroxyl group position on rich loading of CO_2 absorption in aqueous alkanolamine based absorbents.

It can be noticed that hydroxyl group at the α-carbon (1-Amino 2-propanol) to the amine group results in a higher CO_2 absorption capacity of 1.14 mole CO_2/mole amine but due to the much lower concentration of 1-Amino 2-propanol used in this experiment, no firm conclusions can be drawn on the hydroxyl group substitution at the α-carbon to the amine group from these results. Figure 30 in Appendix shows the CO_2 absorption curve for 1-Amino 2-propanol. Figure 11(b), shows that the

effect of a hydroxyl group substitution on α- and β-carbon next to the amine group on the initial absorption rate. In the experimental setup used the absorption rate is the result of a complex interaction between hydrodynamics, mass transfer, kinetics and reaction equilibria. So, no further conclusion can be made at this stage.

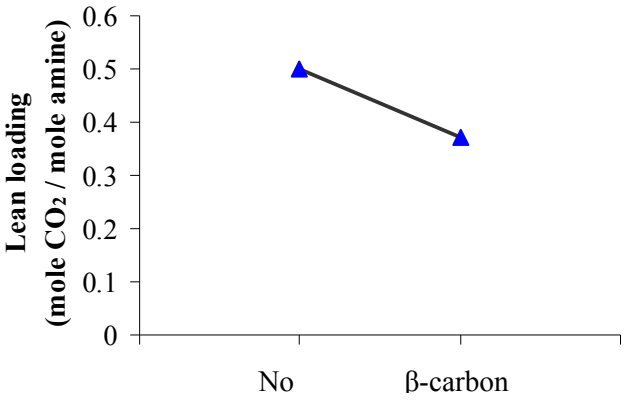


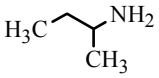
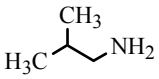
Figure 12(b), Influence of the hydroxyl group position on lean loading of CO_2 absorption in aqueous alkanolamine based absorbents.

In Figure 12(b) and Table 4 the effect of the position of substituted hydroxyl group can be compared on the lean loading of the respective solvents. It must be noticed that a substitution of a hydroxyl group on the β-carbon (1-Amino-2-propanol) to the amine group results in a lower lean loading of 0.37 mole CO_2/mole amine, when compared to that of non-substituted alkanolamine (3-Amino-1-propanol). Looking at that the rich loading was identical; the decrease lean loading implies an increased cyclic capacity. Considering the basicity of these absorbents, the basicity is reduced with a hydroxyl group substitution on β-carbon (1-Amino-2-propanol) to 9.19 when compared to that of non-substituted alkanolamine (3-Amino-1-propanol) which is 9.91. It is interesting to notice that when the hydroxyl group, which is an electron withdrawing functional group, is substituted at β-carbon to amine group the basicity reduces and the absorption capacity remains the same, but the lean loading is improved.

Furthermore, the effect of a methyl group substitution at α and β carbon to the amine group in alkylamines was investigated (see Figures 13 (a & b), 14 (a & b) and Table 5). The concentration of Butylamine, Sec-butylamine and Iso-butylamine used in the experiments was 2.5 mole/L. Substitution of the CH_3 group at the α-carbon (Sec-butylamine) to the amine group resulted in a slightly higher absorption capacity up to 0.84 mole CO_2/mole amine when compared with a CH_3 group substitution on the β carbon to the amine group (Iso-butylamine 0.78 mole

CO_2/mole amine) (see Table 5). This might be due to the fact that the substitution at the α-carbon position creates steric hindrance effect and thus lowers the stability of carbamate.

Table 5, Effect of side chain length in aqueous alkylamine based absorbents.

Solvent	Conc. mole/L	Rich loading mole CO_2 /mole amine	Rich loading mole CO_2 /kg amine	Lean loading mole CO_2 /mole amine
 Butylamine	2.5	0.86	11.74	0.59
 Sec-butylamine (α-carbon)	2.5	0.84	11.54	0.39
 Iso-butylamine (β-carbon)	2.5	0.78	10.54	0.47

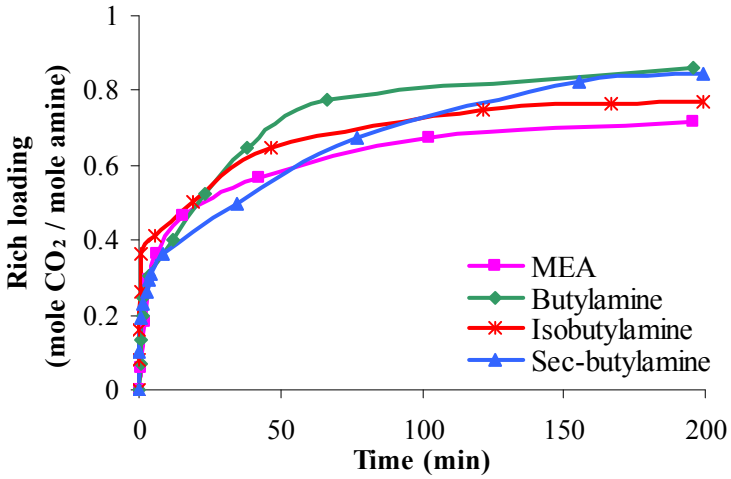


Figure 13(a), Influence of a methyl group substitution on rich loading of CO_2 absorption in aqueous alkylamine based absorbents.

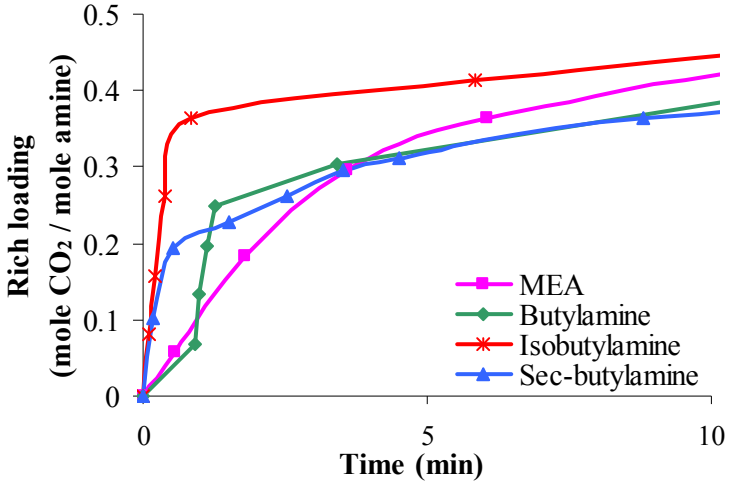


Figure 13(b), Influence of a methyl group substitution on initial absorption rate of CO_2 absorption in aqueous alkylamine based absorbents.

This means that the hydrolysis of the carbamate is enhanced which will drive the equilibrium towards bicarbonate. This effect is more pronounced when comparing the lean loading (see Table 5). Figure 13(b) shows that the effect of an alkyl group substitution on the CO_2 initial absorption rate. Results shows that the alkyl group substitution at the α-carbon (Sec-butylamine) to the amine group decreases the CO_2 initial absorption rate when compared to the substitution at the β-carbon (Iso-butylamine), possibly related to steric hindrance created at the amine group which results in decrease in the CO_2 initial absorption rate.

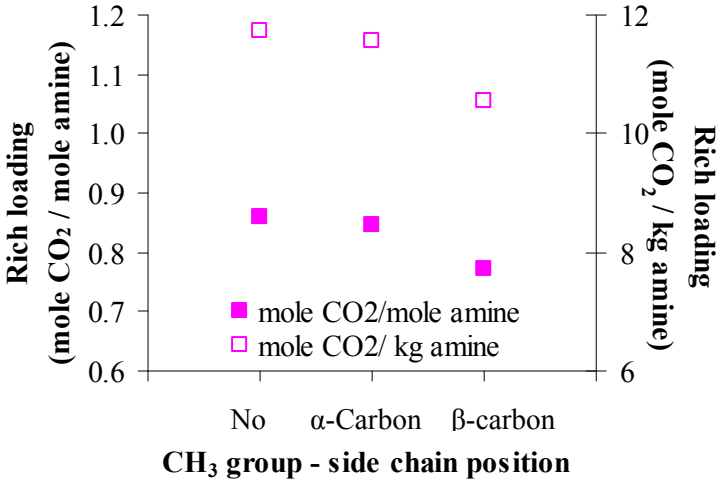


Figure 14(a), Influence of a methyl group substitution on rich loading for CO_2 absorption in aqueous alkylamine based absorbent.

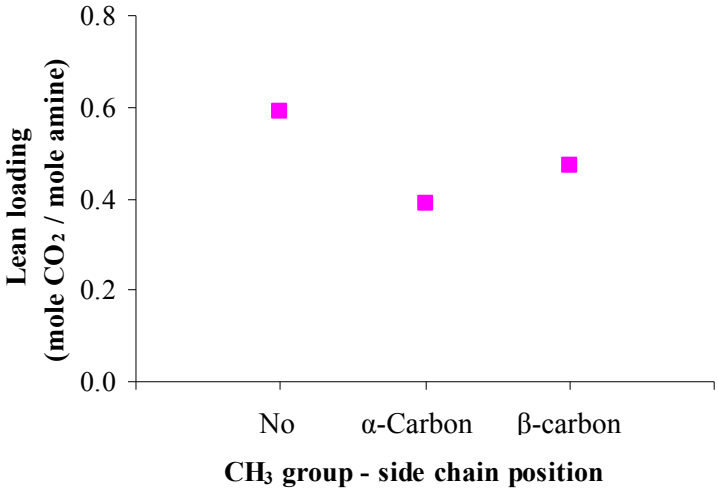
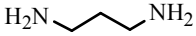
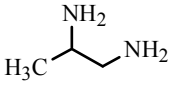


Figure 14(b), Influence of a methyl group substitution on lean loading for CO_2 absorption in aqueous alkylamine based absorbent.

A further relevant observation is that the substitution of alkyl group at α-carbon (Sec-butylamine) to amine group results in a lower lean loading of up to 0.39 mole CO_2/mole amine, when compared with alkyl group substitution at β-carbon to amine group (Isobutylamine) which has a lean loading of 0.47 mole CO_2/mole amine (see Table 5 and Figure 14(b)). Similar observations of α-carbon substitution, which creates the adverse effect of steric hindrance on amine-CO_2 absorption rates, have been made previously by Sartori and Savage (1983). In the quantum mechanical calculations in Chapter 3, it was clearly observed that the carbamate stability was reduced when alkyl group was substituted at α–carbon to the amine group (Sec-butylamine). Hence, from these experiments, the effect of substituents at the α-carbon atom is clearly confirmed to be an important molecular property which will results in an enhanced CO_2 absorption and regeneration capacity.

The influence of an amine group substitution by a side chain in diamine was also investigated, see Figure 15 (a & b), 16 (a & b) and Table 6. It should be noticed that the concentration of 1,2-Diamino propane and 1,3-Diamino propane was kept at 2.5 mole/L. The amine group substitution at the β-carbon to the amine group (1,2-Diamino propane) results in a slightly lower absorption capacity, 1.27 mole CO_2/mole amine, when compared with the non-substituted (1,3-Diamino propane), 1.30 mole CO_2/mole amine (see Table 6), and a significant lower lean loading thus resulting in s strongly improved cyclic capacity.

Table 6, Effect of side chain length in aqueous alkylamine based absorbents.

Solvent	Conc.	Rich loading		Lean loading
	mole/L	mole CO_2 /mole amine	mole CO_2 /kg amine	mole CO_2 /mole amine
 1,3-Diamino propane	2.5	1.30	17.66	0.91
 1,2-Diamino propane (β-carbon)	2.5	1.27	15.48	0.74

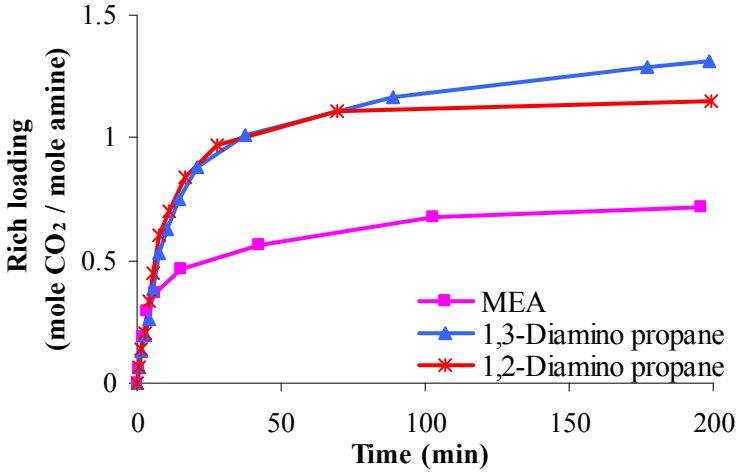


Figure 15(a), Influence of amine group substitution on rich loading of CO_2 absorption in aqueous diamine based absorbents.

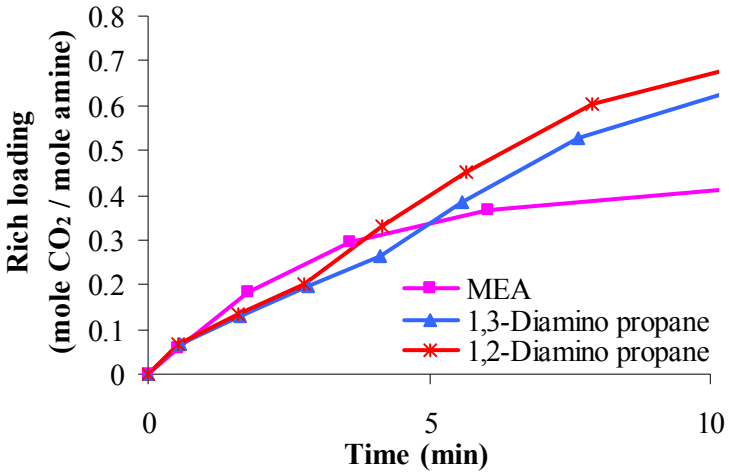


Figure 15(b), Influence of amine group substitution on initial absorption rate of CO_2 absorption in aqueous diamine based absorbents.

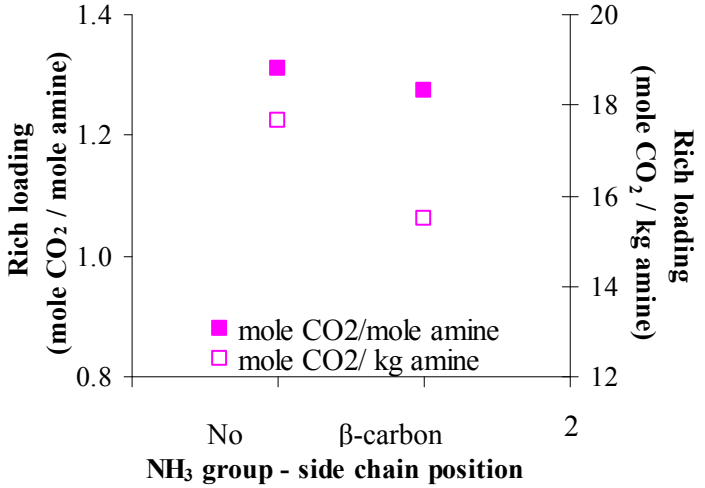


Figure 16(a), Influence of amine group substitution on rich loading of CO_2 absorption in aqueous diamine based absorbents.

The results from Figure 15(b) shows no significant effect on the initial absorption rate for the amine group substitution at β-carbon to the amine group (1, 2-Diamino propane) in comparison with the 1,3-Diamino propane. Figure 16(b) shows amine group substitution at β-carbon to amine group (1,2-Diamino propane) results in slightly lower lean loading up to 0.74 mole CO_2/mole amine when compared to that of non-substituted (1,3-Diamino propane) with a lean loading of 0.91 mole CO_2/mole amine (see Table 6).

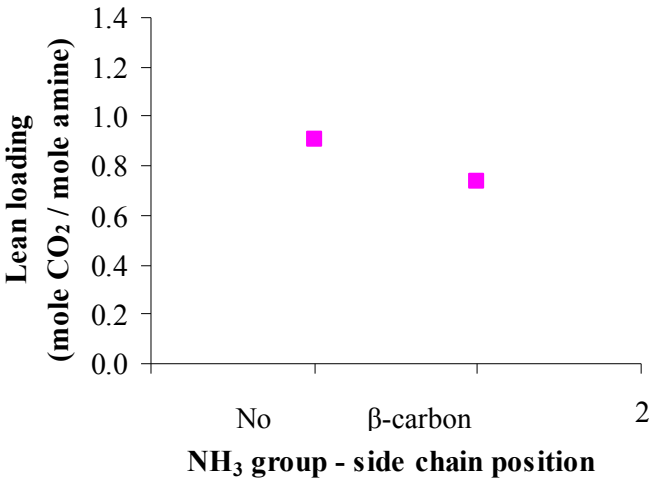


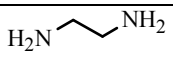
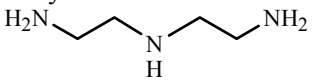
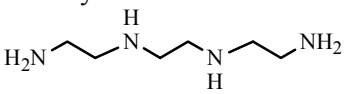
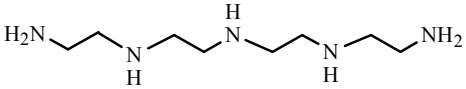
Figure 16(b), Influence of amine group substitution on lean loading of CO_2 absorption in aqueous diamine based absorbents.

When considering the basicity of these absorbents it is interesting to notice that the basicity (pKa) is reduced from 10.43 (1,3-Diamino propane) to 9.64 (1,2-Diamino propane) with an amine group substitution at β-carbon to amine group. In conclusion, the amine group substitution at β-carbon to the amine group has more effect on the regeneration than on the absorption capacity for CO_2.

4.3.3. Effect of number of functional groups

The next parameter studied is the effect of an increase in the number of functional groups was investigated In Figures 17 (a & b), 18(a & b) and Table 7, the result from the effect of an increase in number of amine groups in the absorbent structure are presented. It should be noticed that the concentration of Ethylenediamine, Diethylenetriamine and Triethylenetetramine was kept at 2.5 mole/L. Due to the high viscosity of Tetraethylenepentamine, the concentration used for this absorbent was kept at 0.5 mole/L.

Table 7, Effect of number of amine group in aqueous amine based absorbents.

Solvent	Conc. mole/ L	Rich loading mole CO_2 /mole amine	Rich loading mole CO_2 /kg amine	Lean loading mole CO_2 / mole amine
 Ethylenediamine	2.5	1.08	17.93	0.84
 Diethylenetriamine	2.5	1.83	16.51	0.76
 Triethylenetetramine	2.5	2.51	17.15	1.02
 Tetraethylenepentamine	0.5	3.03	15.98	0.74

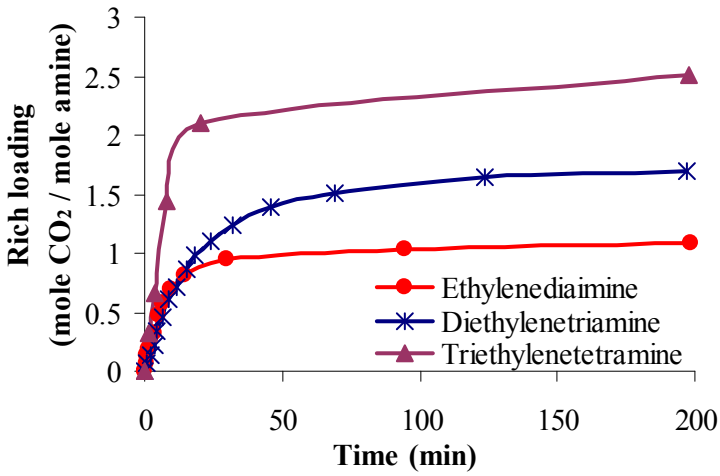


Figure 17(a), Influence of the number of amine groups on the absorption of CO_2 in aqueous amine based absorbent.

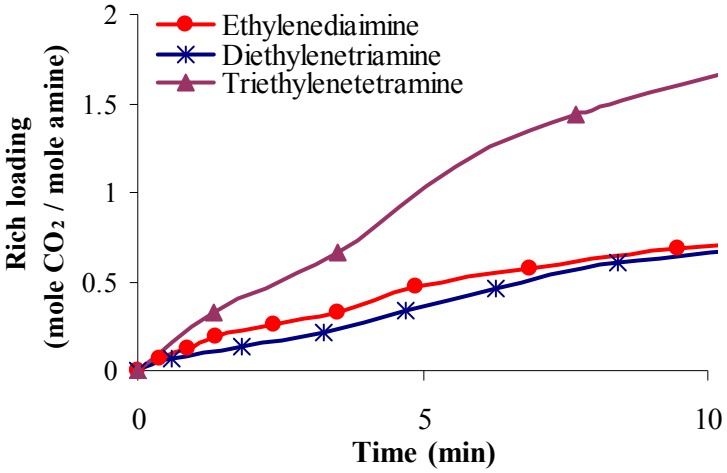


Figure 17(b), Influence of the number of amine groups on the initial CO_2 absorption rate in aqueous amine based absorbent.

Results from Figure 17(b) shows that an increase in the number of amine groups from 2 (Ethylenediamine) to 3 (Diethylenetriamine) the initial absorption rate remain the same, whereas there is a drastic increase in the initial absorption rate when the number of amine group increases up to 4 (Triethylenetetramine).

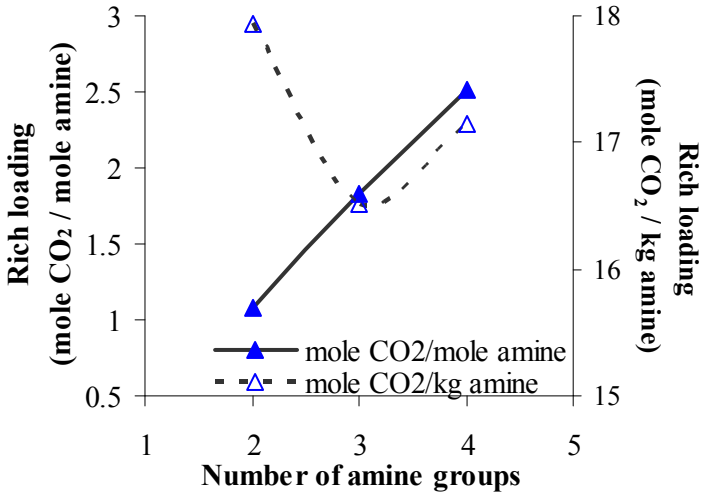


Figure 18(a), Influence of number of amine groups on rich loading of CO_2 absorption in aqueous amine based absorbents.

The effect of an increase in the number of amine groups on the CO_2 absorption capacity can be seen in Figure 17(a), 18(a) and Table 7. An increase in the number of amine group from 2 to 4 increases the absorption capacity from 1.08 to 2.51

mole CO_2/mole amine. Considering CO_2 absorption capacity in per amine functionality the CO_2 absorption capacity increases from 0.54 to 0.63 mole CO_2/amine group.

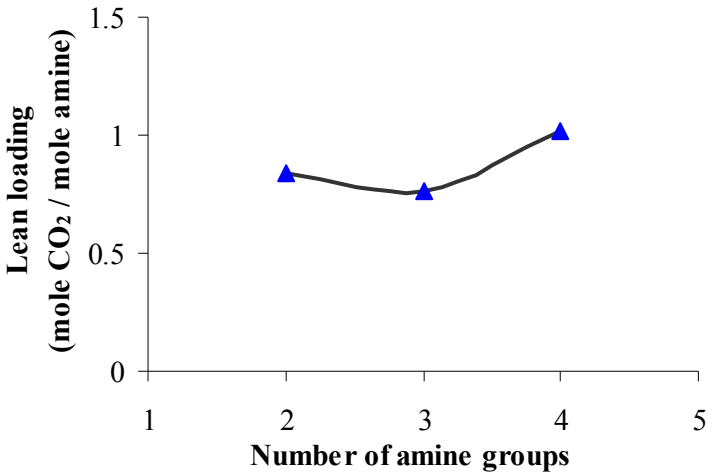


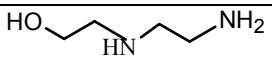
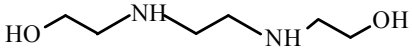
Figure 18(b), Influence of number of amine groups on lean loading of CO_2 absorption in aqueous amine based absorbents.

When the total absorption capacity of these absorbents were compared in unit of kg of CO_2 absorbed per mole of amine, results shows that the absorption capacity does not decrease with an increase in number of amine group in the structure. Ethylenediamine (where two amine groups are present) which could absorb CO_2 up to 17.93 kg CO_2/mole amine, whereas Triethylenetetramine (in which 4 amine groups are present) could absorb CO_2 only up to 17.15 kg CO_2/mole amine (see Table 7).

Results from Figure 18(b) show that an increase in the number of amine results in higher lean loading, but per amine functional group it decreases continuously from 0.42 mole CO_2/amine group (Ethylenediamine) to 0.25 mole CO_2/amine group (Triethylenetetramine). Cyclic loading (difference between absorption and lean loading) is thus increased with an increase in the number of amine groups but also per amine functional group (from 0.12 to 0.38 mole CO_2/amine group). The basicity was found to be not influenced with an increase in number of amine groups 2 till 4, as basicity only increase slightly from 9.89 (Ethylenediamine) to 10.07 (Triethylenetetramine). In Tetraethylenepentamine (5 amine group) the absorbent showed a very high absorption capacity and cyclic capacity. Note, however, that a fair comparison cannot be made on this solvent as the concentration of this solvent was significantly lower in these experiments. Figure 30 in Appendix shows the CO_2 absorption curve for Tetraethylenepentamine.

The effect of an increase in the number of hydroxyl groups was also investigated. The concentration of N-(2-Hydroxyethyl)ethylenediamine and N,N'-Bis(2-hydroxyethyl)ethylenediamine) was 2.5 mole/L. Results from diamine based absorbent with one (N-(2-hydroxyethyl) Ethylenediamine) and two hydroxyl groups (N,N'-Bis(2-hydroxyethyl)ethylenediamine) are presented in Figures 19 (a & b), 20 (a & b) and Table 8.

Table 8, Effect of number of hydroxyl group in aqueous amine based absorbents.

Solvent	**Conc.**	**Rich loading**		**Lean loading**
	mole /L	mole CO_2 /mole amine	mole CO_2 /kg amine	mole CO_2 /mole amine
 N-(2-hydroxyethyl) Ethylenediamine	2.5	1.15	11.09	0.70
 N,N'-Bis(2-hydroxyethyl) Ethylenediamine	2.5	1.20	8.07	0.41

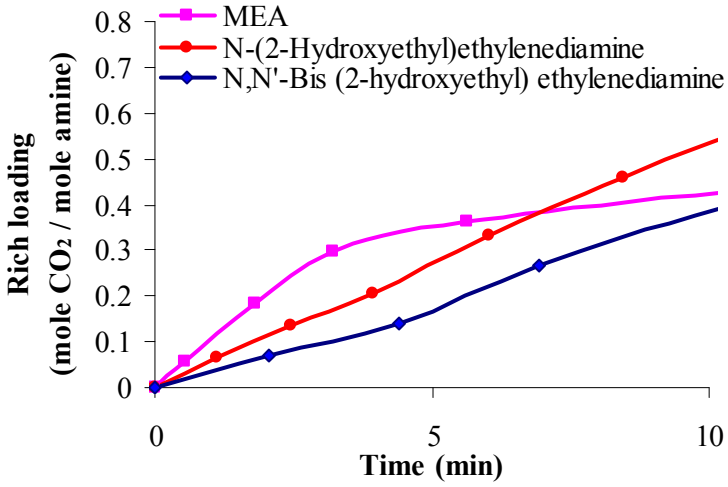


Figure 19(a), Influence of the number of OH groups on CO_2 absorption in aqueous alkanolamine based absorbents.

Figure 19(b) shows that the increasing the number of hydroxyl groups in diamine based absorbent structures results in a negative effect on the CO_2 initial absorption rate, resulting in a decrease in the CO_2 initial absorption rate.

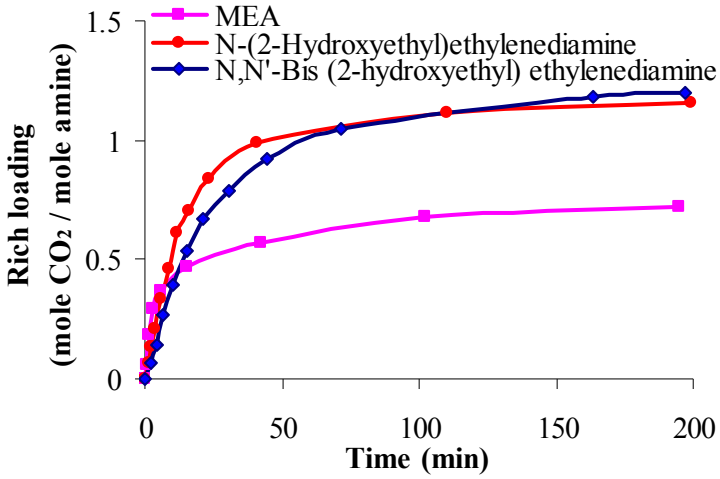


Figure 19(b), Influence of the number of OH groups on initial CO_2 absorption rate in aqueous alkanolamine based absorbents.

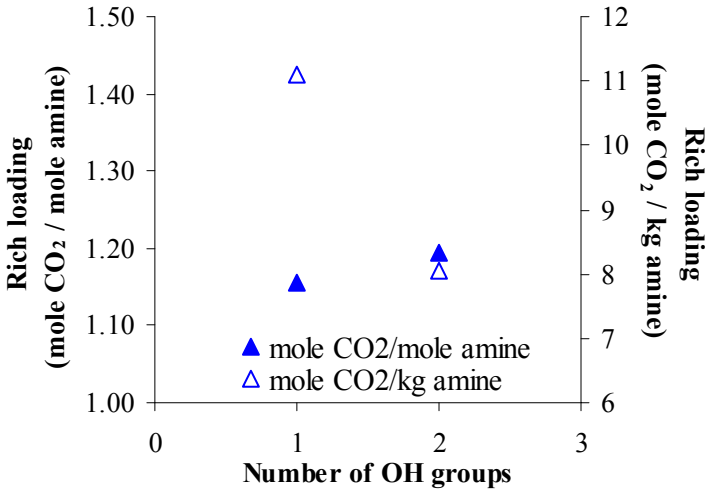


Figure 20(a), Influence of the number of OH groups on rich loading of CO_2 absorption in aqueous alkanolamine based absorbents.

This might be caused by the presence of a steric hindrance effect around both amine groups when two hydroxyl groups are present (N,N'-Bis(2-hydroxyethyl) ethylenediamine) or the exchange of the primary amine functionality for a secondary amine functionality. The basicity was only slightly reduced from 9.61 (N-(2-Hydroxyethyl) ethyelendiamine) to 9.4 (N,N'-Bis(2-hydroxyethyl) ethyelendiamine). From Figure 19(a) and Table 8 it is clear that an increase in the number of hydroxyl groups in the absorbent structure has no significant effect on the absorption capacity (mole CO_2/mole amine), but decreases in terms of (mole CO_2/kg amine) (see Table 8 and Figure 20(a)).

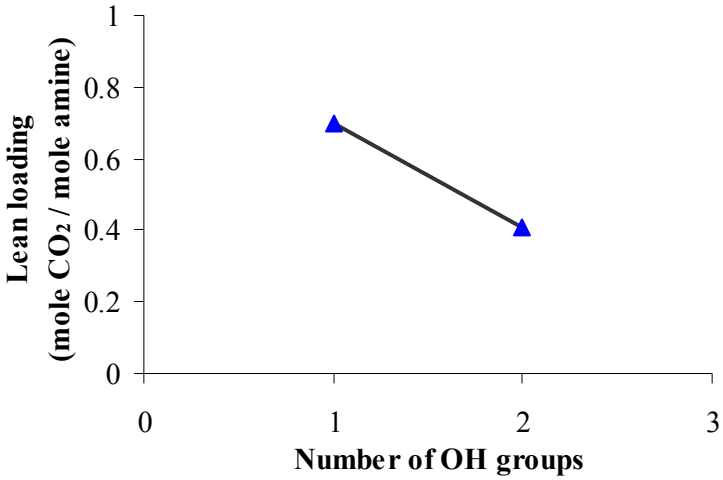


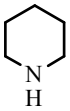
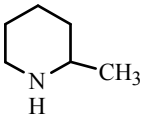
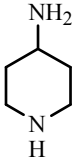
Figure 20(b), Influence of the number of OH groups on lean loading of CO_2 absorption in aqueous alkanolamine based absorbents.

Figure 20(b) shows that an increase in the number of hydroxyl groups in the diamine based absorbent significantly lowers the lean loading as for (N,N'-Bis(2-hydroxyethyl)ethylenediamine) the lean loading is 0.41 mole CO_2/mole amine. The basicity slightly reduced from 9.61 (N-(2-Hydroxyethyl) ethyelendiamine) to 9.4 (N,N'-Bis(2-hydroxyethyl)ethyelendiamine). The reduced basicity may cause a reduced carbamate stability and therefore result in a higher absorption capacity and lower lean loading for N,N'-Bis(2-hydroxyethyl)ethylenediamine.

4.3.4. Effect of functional groups in cyclic amines

Cyclic amines are generally considered to be potentially good absorbents for CO_2 absorption due to their fast CO_2 absorption rate and higher absorption capacities. Therefore, the effect of different substituted saturated and unsaturated cyclic amines was investigated.

Table 9, Effect of functional group substation in aqueous saturated cyclic amine based absorbents.

Solvent	**Conc.**	**Rich loading**		**Lean loading**
	mole/L	mole CO_2 /mole amine	mole CO_2 /kg amine	mole CO_2 /mole amine
 Piperidine	0.5	1.26	14.79	0.67
 2-Methylpiperidine	0.5	1.22	12.28	0.50
 4-Amino piperidine	0.25 (for rich loading) & 0.5 (for lean loading)	1.90	21.20	1.20

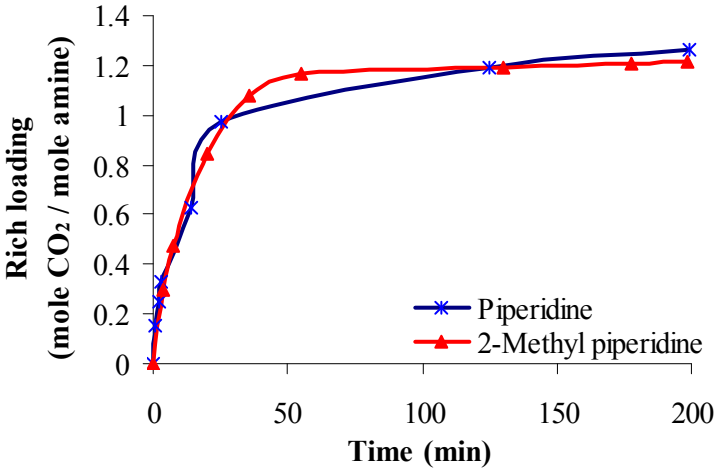


Figure 21(a), Influence of a function group substitution on CO_2 absorption in aqueous saturated cyclic amines based absorbents.

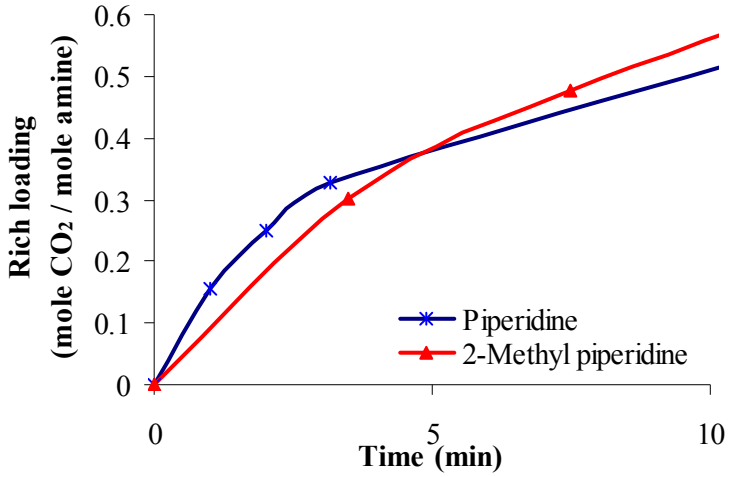


Figure 21(b), Influence of a function group substitution on initial CO_2 absorption rate in aqueous saturated cyclic amines based absorbents.

In Figure 21 (a & b), 22 (a & b) and Table 9 the comparison between saturated cyclic monoamine and similar compounds, substituted with an alkyl and amine groups, are presented. It must be noticed that the concentration of Piperidine and 2-Methylpiperidine was kept to be 0.5 mole/L, whereas for 4-Amino piperidine the concentration was kept 0.25 mole/L for absorption experiment and (initially) 0.5 mole/L during the regeneration experiment.

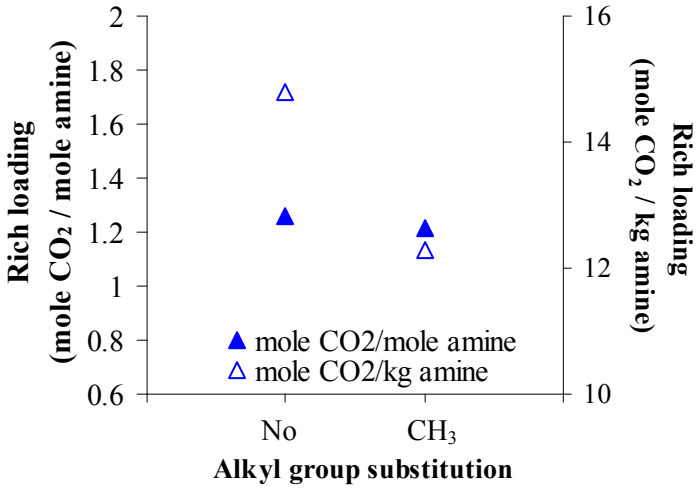


Figure 22(a), Influence of alkyl group substitution on CO_2 rich loading in aqueous saturated cyclic amines based absorbents.

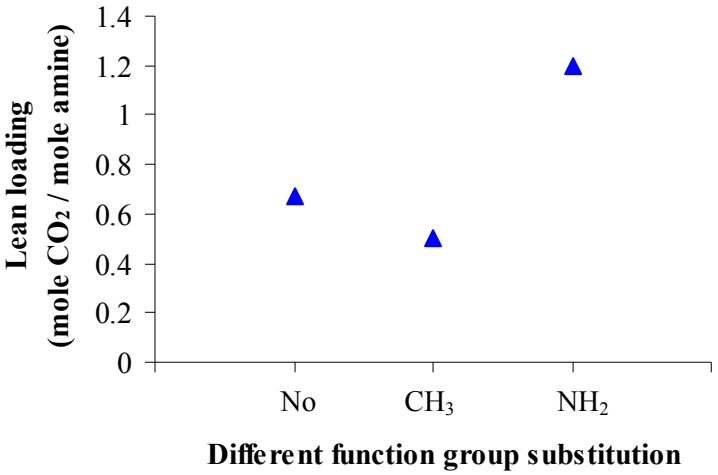
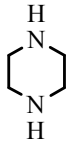
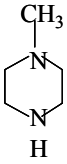
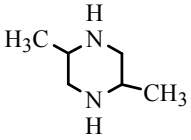


Figure 22(b), Influence of different functional group substitution on CO_2 lean loading in aqueous saturated cyclic amines based absorbents.

Therefore, only CO_2 rich and lean loading of 4-Amino piperidine is presented in the results. CO_2 absorption curve for 4-Amino piperidine is shown in Appendix, Figure 31. Still considering the difference between rich and lean loading (cyclic loading) for alkyl (2-methyl piperidine) and amine group (4-amino piperidine) substituted cyclic amine, it remains the same for both absorbents. The basicity of these absorbents was found to be in order of Piperadine (pKa=11.24) < 2-Methyl piperidine (pKa=11.3) < 4-Amino piperidine (pKa=11.7). Apparently, the increase in basicity does not negatively influence the regeneration of CO_2.

Figures 23(a & b), 24(a & b) and Table 10 show the effect of a methyl group substitution on saturated cyclic diamine based absorbents. The concentration of Piperazine, 1-Methylpiperazine and Trans piperazine, 2,5-Dimethyl was kept at 0.5 (± 0.1) mole/L. Figure 23(b) shows that a substitution of alkyl group doesn't affect the CO_2 initial absorption rate in saturated cyclic diamine. From Figure 24(a) and Table 10, it is clear that the absorption capacity with one methyl group substituted cyclic diamine, 2-Methyl piperazine is slightly lower when compared with a 2 methyl group substituted cyclic diamine, Trans piperazine 2,5-dimethyl (absorption capacity of 1.12 and 1.28 mole CO_2/mole amine, respectively).

Table 10, Effect of number of alkyl group substitution in aqueous saturated cyclic diamine based absorbents.

Solvent	Conc.	Rich loading		Lean loading
	mole /L	mole CO_2 /mole amine	mole CO_2 /kg amine	mole CO_2 /mole amine
 Piperazine	0.6	1.22	14.20	0.40
 1-Methyl piperazine	0.6	1.12	11.23	0.67
 Trans piperazine, 2,5-dimethyl	0.54	1.28	11.19	0.59

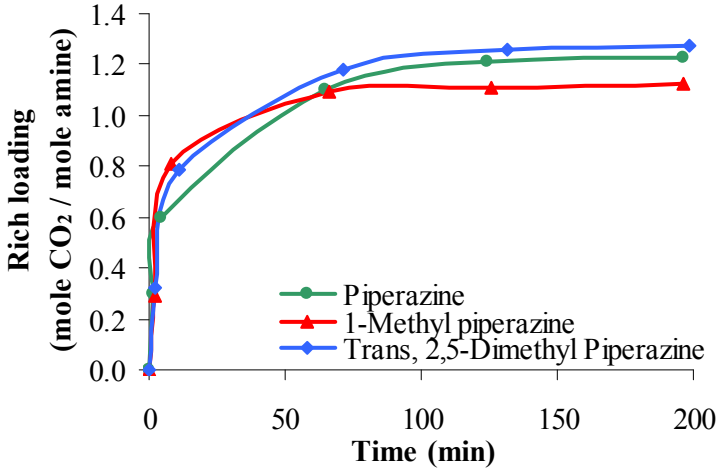


Figure 23(a), Influence of number of alkyl groups for CO_2 absorption in aqueous saturated cyclic diamine based absorbents.

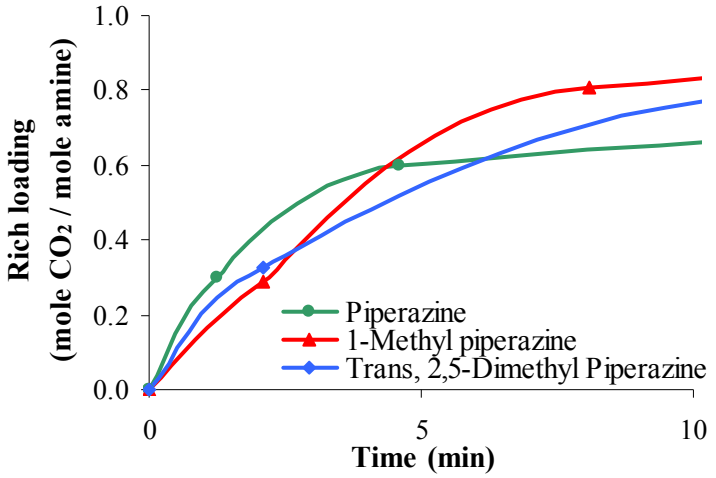


Figure 23(b), Influence of number of alkyl groups on initial CO_2 absorption rate in aqueous saturated cyclic diamine based absorbents.

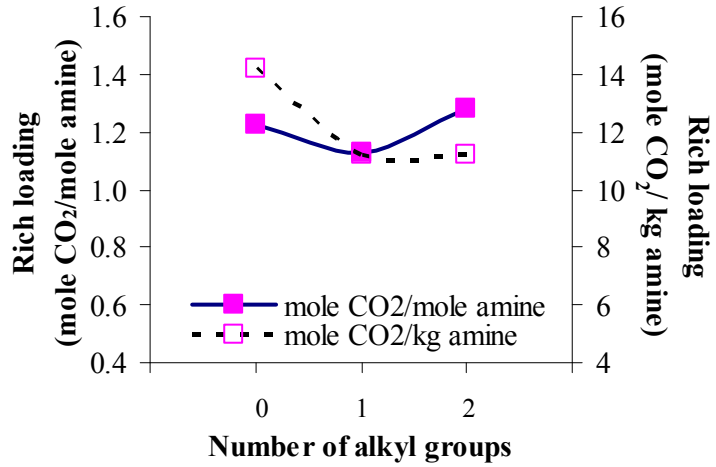


Figure 24(a), Influence of number of alkyl groups on CO_2 rich loading in aqueous saturated cyclic diamine based absorbents.

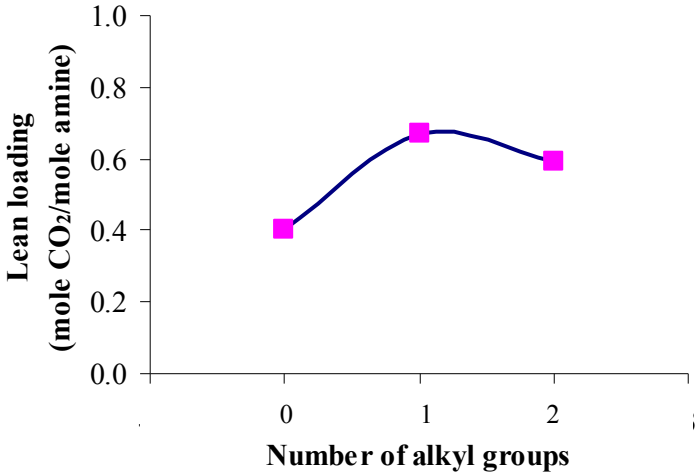
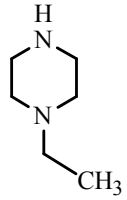
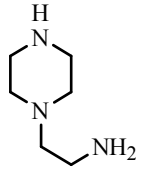
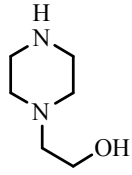


Figure 24(b), Influence of number of alkyl groups on CO_2 lean loading in aqueous saturated cyclic diamine based absorbents.

Results from Figure 24(b) and Table 10 shows that a substitution of one methyl group in the saturated ring at the 1st carbon position (1-Methyl piperazine) shows a significantly higher lean loading of 0.67 mole CO_2/mole amine and the two methyl group substitution (Trans-Piperazine, 2,5-dimethyl) a lean loading of 0.59 mole CO_2/mole amine. Piperazine, however, showed the lowest lean loading of 0.4 mole CO_2/mole amine and, hence results in the highest CO_2 cyclic capacity.

The effect of different functional groups in saturated cyclic diamines was also investigated. The concentration of N-ethylpiperazine, 2-(1-Piperazinyl)ethylamine and 2-(1-Piperazinyl) ethanolamine was kept to be at 1 mole/L. Figures 25(a & b), 26(a & b) and Table 11 shows the effect of a different functional (amine, alkyl and hydroxyl) group substitution at para position on the cyclic ring of saturated diamine.

Table 11, Effect of functional group substitution in aqueous saturated cyclic diamine based absorbents.

Solvent	Conc. mole/L	Rich loading mole CO_2 /mole amine	Rich loading mole CO_2 /kg amine	Lean loading mole CO_2 /mole amine
 N-ethyl piperazine	1.0	1.15	10.03	0.69
 2-(1-Piperazinyl) ethylamine	1.0	1.81	13.97	0.65
 2-(1-Piperazinyl)ethanol	1.0	0.84	8.41	0.38

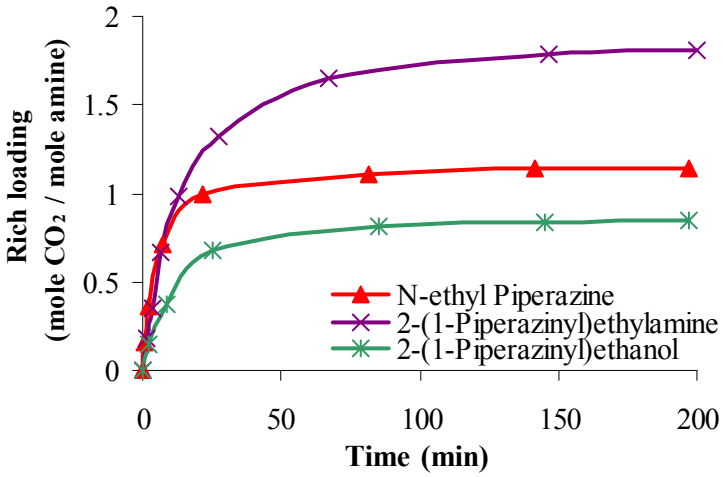


Figure 25(a), Influence of different functional groups for CO_2 absorption in aqueous saturated cyclic diamine based absorbents.

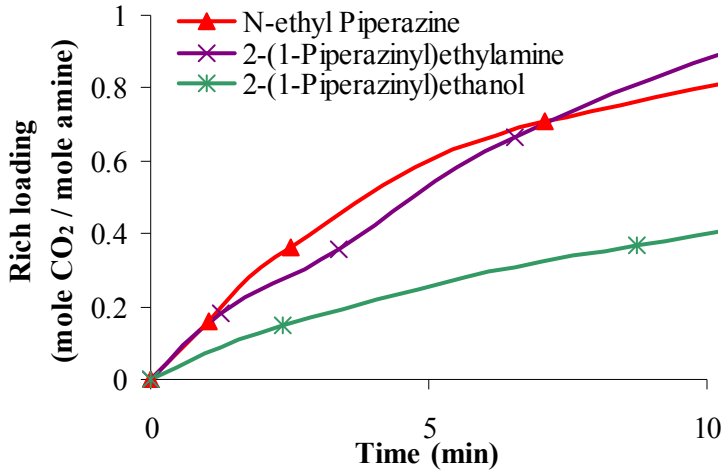


Figure 25(b), Influence of different functional groups on initial CO_2 absorption rate in aqueous saturated cyclic diamine based absorbents.

Comparing the results for N-ethylpiperazine and 2-(1-Piperazinyl)ethanol shows that the ethanol group substitution leads to both a lower rich loading and lower lean loading, but the net cyclic loading is essentially identical, Figure 25(b) shows that substitution with an amine and alkyl group in saturated diamines leads to comparable initial CO_2 absorption rates, whereas the hydroxyl group substitution resulted in a significant lower initial CO_2 absorption rate.

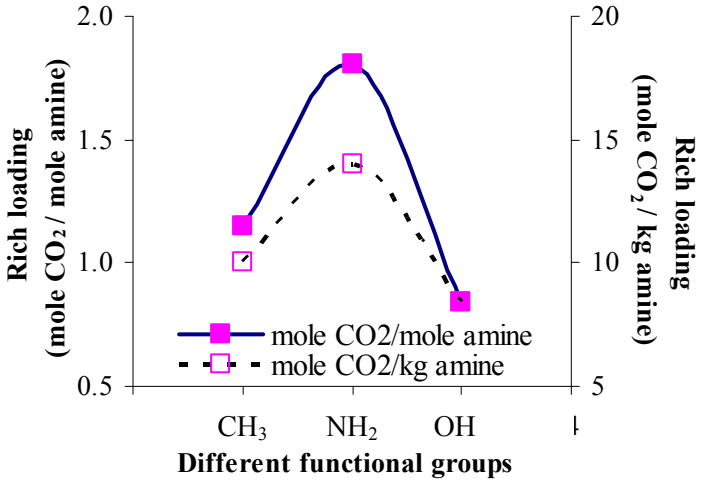


Figure 26(a), Influence of different functional groups for CO_2 rich loading in aqueous saturated cyclic diamine based absorbents.

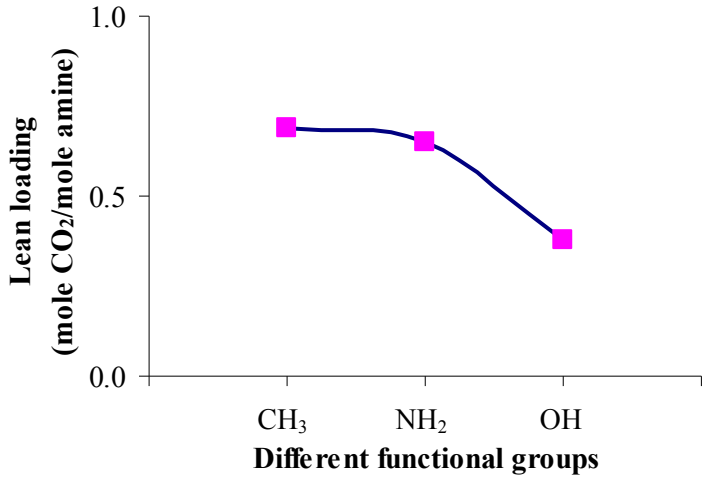
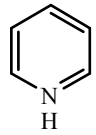
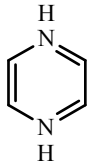
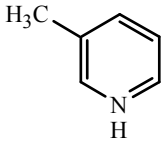
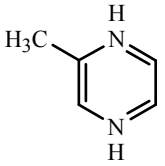
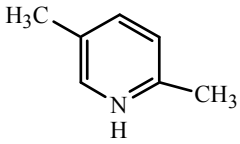
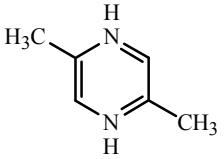
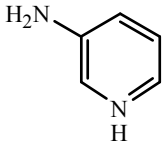
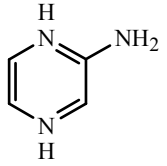


Figure 26(b), Influence of different functional groups for CO_2 lean loading in aqueous saturated cyclic diamine based absorbents.

The basicity of N-ethylpiperazine, 2-(1-Piperazinyl)ethylamine and 2-(1-Piperazinyl)ethanolamine was found to be 9.6, 10.11 and 9.27 respectively. The higher basicity of N-ethylpiperazine, 2-(1-Piperazinyl) ethylamine is due to electron donating effect of alkyl and amine group, which results in an increase in electron density at nitrogen atom and hence the amine group is faster protonated. This will result in a faster CO_2 absorption rate and increase in the CO_2 absorption capacity. The difference between rich and lean loading (cyclic loading) was the highest for the amine group substituted cyclic diamine, but this is obviously largely related to the increased number of amine-functionalities in the molecule. Nevertheless, the capacity per amine functional group is also the highest for this compound. Therefore, from these results it seems that using an amine group as substituted functional group can be used to enhance the performance of saturated cyclic diamine based solvents.

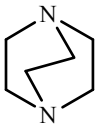
Unsaturated cyclic amines were also investigated (see Table 12). All unsaturated cyclic compounds showed a poor absorption rate and capacity. However, upon substitution with a methyl group at the 2^{nd} or two alkyl groups at the 2^{nd} and 5^{th} position in the unsaturated amines, an increase in the absorption capacity was found. Unsaturated amines substituted with an amine group with the side chain (i.e. Aminopyrazine) showed an increase in the CO_2 absorption capacity. The basicity of all absorbents mentioned in Table 12 was found to be lower than 6.3, which is insufficient to react with CO_2.

Table 12, Effect of different aqueous unsaturated cyclic amine based absorbent on CO_2 absorption.

Solvent	Rich loading mole CO_2 /mole amine	Solvent	Rich loading mole CO_2 /mole amine
 Pyridine	0.05	 Pyrazine	0.04
 2-Pyridylamine	0.28	 2-Methyl pyrazine	0.10
 2-,5-Lutidine	0.29	 2,5-Dimethyl pyrazine	0.11
 2-Methyl pyridine	0.06	 Aminopyrazine	0.12

Finally, the effect of different ring shapes was investigated. The concentration of Azetidine and DABCO was kept at 0.1 mole/L and 2.5 mole/L respectively. Table 13 shows that the small ring structure in Azetidine results in a very high CO_2 absorption capacity of 2.45 mole CO_2/mole amine but note that this value was obtained for a low amine concentration. The basicity of Azetidine was also found to be very high, 11.26. DABCO showed lower absorption capacities, 0.89 mole CO_2/mole amine. The low absorption capacity in DABCO might be caused by the presence of a bond between the two amine groups present in the saturated diamine ring.

Table 13, Effect of functional group substitution in aqueous saturated cyclic diamine based absorbents.

Solvent	Conc.	Rich loading		Lean loading
	mole /L	mole CO_2 /mole amine	mole CO_2 /kg amine	mole CO_2 /mole amine
 Azetidine	0.24	2.45	42.9	1.56
 DABCO (1,4-Diazabicyclo [2.2.2]octane)	2.5	0.89	7.95	0.35

The effect of other functional groups like ketone, aldehyde, ester, amide in amine based absorbents was also investigated for CO_2 absorption experiment. All of these compounds showed a very poor CO_2 absorption rates and capacities.

4.4. Conclusions

The present study revealed some effects of molecular structure for various amine based aqueous solvents on their CO_2 absorption and regeneration characteristics. Effect of carbon chain length was found to be an interesting molecular structural effect in alkyl, alkanol and diamine based absorbents. An exceptional increase in the CO_2 initial absorption rate and capacity was noticed for the six carbon chain length diamine Hexamethylenediamine. Also the CO_2 cyclic capacity was found to be higher for Hexamethylenediamine, when compared to that of other diamine solvents. In cyclic saturated diamine based absorbents substitution of a hydroxyl group by a side chain increases the absorption capacity and results in higher cyclic loading. Unsaturated amines showed poor absorption rates and capacities for CO_2 absorption. The effect of basicity (pKa) on the behaviour of absorbents CO_2 absorption and regeneration characteristic was also investigated, but no unique correlation with between pKa and absorption nor regeneration characteristic were identified. Hence, basicity cannot be taken as the only parameter in order to make the selection of a suitable absorbent for CO_2 absorption process. The results obtained from quantum mechanical calculations to investigate different structural effect on carbamate stability for various amine based absorbents in Chapter 3 were found to be consistent with most of the experimental results in this study. Hence, these screening experiments illustrate and validate clearly the occurrence of the effect of solvent molecular structure for CO_2 absorption and regeneration. The

results and trends presented here are believed to be advantageous in the development of an improved amine based CO_2 absorbent for CO_2 capture technologies. Moreover, a new potential solvent, Hexamethylenediamine, was identified as a potential new solvent and selected for further investigation in this work.

Acknowledgement
This research is part of the CATO programme, the Dutch national research programme on CO_2 Capture and Storage. CATO is financially supported by the Dutch Ministry of Economic Affairs (EZ) and the consortium partners (www.co2-cato.nl).
I would like to thank John P.M. Niederer and Prof. Geert F. Versteeg for supervising this work. I would like to acknowledge Benno Knaken for constructing the experimental set-up.

4.5. References

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Chakraborty A. K., Astarita G., Bischoff K. B. Damewood J. R. Jr., 1988, Molecular orbital approach to substituent effects in amine-CO_2 interactions. Journal of American Chemical Society, Vol. 110, pp 6947

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Kehn-Perng S., Meng-Hul L., 1992, Solubility of carbon dioxide in aqueous mixtures of monoethanolamine with methylenediethanolamine. Journal of Chemical Engineering, Vol. 37, pp 96-100

Peeters A. N. M., Faaij A. P. C., Turkenburg W. C., 2007, Techno-economic analysis of natural gas combined cycles with post-combustion CO_2 absorption, including a detailed evaluation of the development potential. International Journal of Greenhouse Gas Control, Vol. 11, pp 396 – 417

Poplsteinova J. J., Krane J. Svendsen H. F., 2005, Liquid-Phase composition determination in CO_2-H_2O-alkanolamine systems: An NMR study. Industrial Engineering Chemical Research, Vol. 44, pp 9894-9903

Sartori G., Savage D. W., 1983, Sterically hindered amines for CO_2 removal from gases. Industrial Engineering Chemistry Fundamentals, Vol. 22, pp 239-249

4.6. Appendix

In this study the solvent tested were at kept at concentration of 2.5mole/L still some solvents were tested at lower concentrations. This appendix contains additional data of such solvents which may be illustrative or useful for the reader, but are not included in the series where the molecular structure was varied, since these data were obtained at significantly different molar concentrations of the amine, which influences the results in such a way that differences observed can not be attributed to differences in the molecular structure, see Figure 27-31.

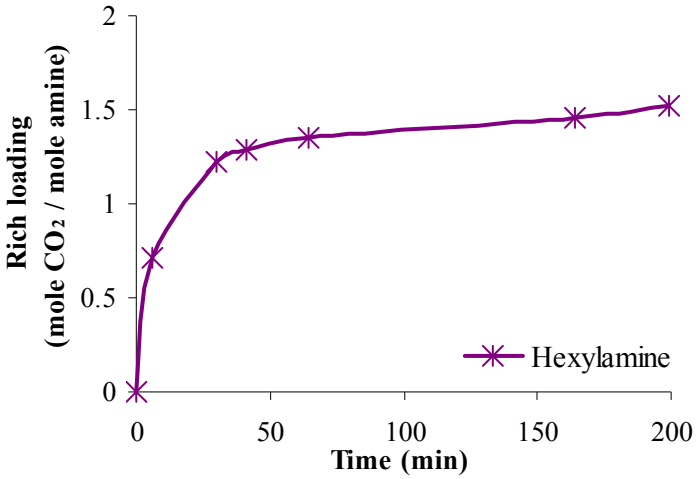

Figure 27, CO_2 absorption in 0.1 mole/L aqueous Hexylamine.

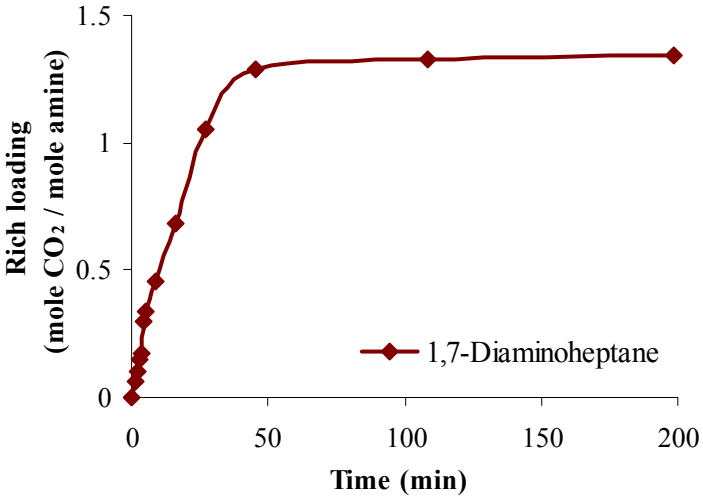

Figure 28, CO_2 absorption in 1.5 mole/L aqueous 1,7-Diaminoheptane.

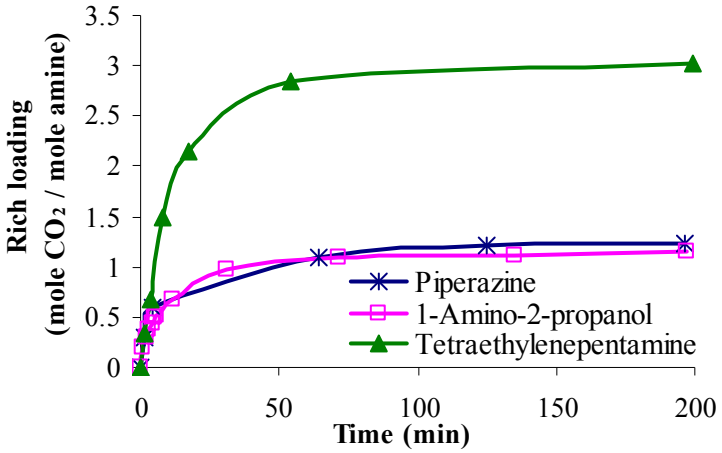

Figure 29, CO_2 absorption in 0.5 mole/L aqueous solution of different amine based absorbents.

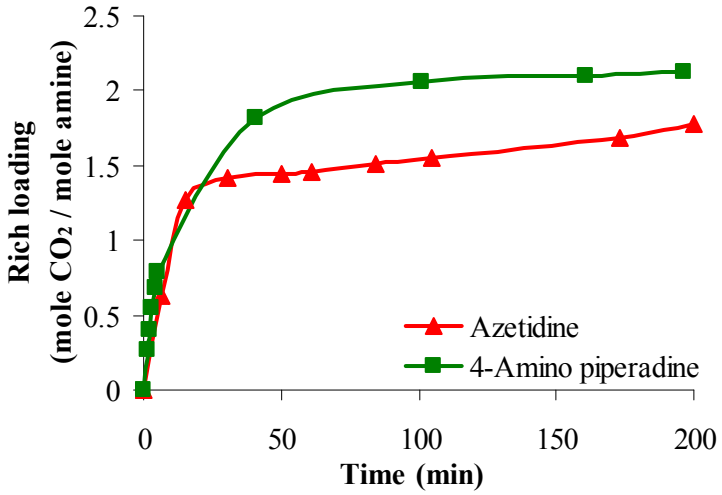

Figure 30, CO_2 absorption in 0.25 mole/L aqueous solution of different amine based absorbent.

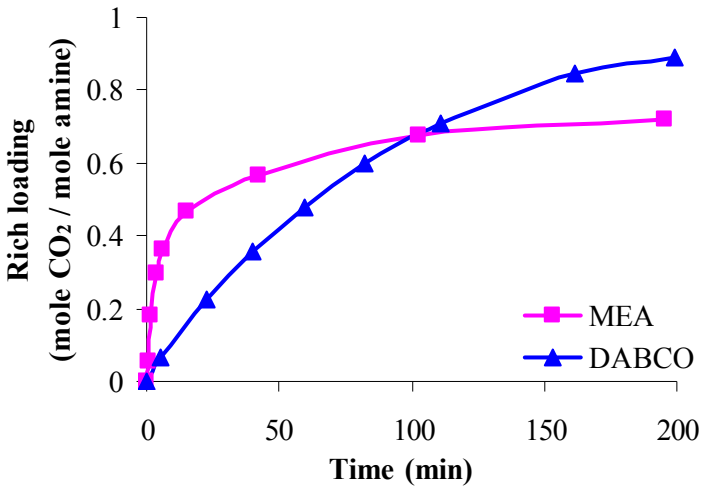

Figure 31, CO_2 absorption in 2.5 mole/L aqueous solution of DABCO (1,4-Diazabicyclo[2.2.2]octane).

5

Evaluation of CO_2 solubility in potential aqueous amine based solvents at low CO_2 partial pressure

The cyclic capacity of various potential aqueous amine-based solvents were determined by performing CO_2 absorption experiments at 30°C and 10 kPa CO_2 partial pressure and regeneration experiments at 90°C and atmospheric pressure. Comparison based on the molecular structural effect was made for the selected solvents on their CO_2 cyclic capacity and reactivity at low CO_2 partial pressure. 1,7-Diaminoheptane and 1,6-Hexanediamine, N,N'-dimethyl showed a high cyclic loading of 0.81 and 0.85 mole CO_2/mole amine respectively. Aqueous solutions of 1,6-Hexanediamine, N,N'-dimethyl of 0.5 and 2.55 mole/L concentration were selected to study solubility of CO_2 at different CO_2 partial pressure ranging from 1 up to 40 kPa, 30°C and at 1 atmosphere. The solubilities of CO_2 in aqueous 1,6-Hexanediamine, N,N'-dimethyl at 30°C were compared with CO_2 solubility in aqueous solution of MEA of similar solvent molar concentrations. The solubility of CO_2 in 2.55 mole/L 1,6-Hexanediamine, N,N'-dimethyl was found to be almost twice than that of 2.5 mole/L MEA at lower CO_2 partial pressure.

5.1. Introduction

Separation of carbon dioxide from a large amount of flue gas by chemical separation is known for many years and considered to be one of the most reliable and economical processes to capture the CO_2. Various studies for improving the capture process have been performed, however, the current applied technology for this separation is still expensive, both in terms of capital cost (capex) and operating cost (opex). The main cost items of the process are the size of the absorption tower and regenerator, and the lean/rich cross flow heat exchanger. High opex is related to the energy requirement for heating/cooling and regeneration of the solvent circulating in the process, corresponding to 76% of the total (Abu Zahra 2009). Other cost factors related to the use of the conventional solvents include solvent losses due to degradation, precipitation, corrosion, foaming and evaporation losses etc. Therefore, there is a scope for novel solvent systems to make the removal of carbon dioxide from flue gases a more energy- and cost effective process.

From the results obtained in previous work on structure and activity relationships for CO_2 absorption and regeneration with various aqueous amine based solvents, some novel solvents were identified (Singh et al. 2007, 2008). For example Hexylamine, 1,4 Diaminobutane and Hexamethylenediamine at 30°C and atmospheric CO_2 pressure reached CO_2 loadings up to 1.52, 1.26 and 1.48 mole CO_2/mole amine respectively. In that study, CO_2 absorption experiments were performed under pure CO_2 environment whereas, under real process conditions the CO_2 partial pressure is significantly lower e.g. 3.5-12 kPa. This can significantly affect the relative CO_2 solubility in solvents, and hence it is necessary to evaluate and compare potential solvents under low CO_2 partial pressure environment. In this work the more promising solvents have been selected from the previous screening experimental study (Singh et al. 2007, 2008), in which solvents were evaluated on the basis of their CO_2 absorption capacity and initial absorption rate. In addition to the cyclic capacity also solvent molecular structural effects at low CO_2 partial pressure were included in this work. Hence, some new solvent candidates, considered to be interesting from their molecular structural point of view, are also included in this work.

The cyclic capacity, which is defined as the difference between the CO_2 loadings of the CO_2 rich solvent and the CO_2 lean solvent, is a major factor in evaluating new solvents. A high cyclic capacity will result in a smaller solvent circulation flow rate in the amine plant, which will decrease the dimensions of the amine plant. This increase in cyclic capacity is expected to reduce the overall capital cost, reduce utility consumption and hence will result in decreased cost for CO_2 capture. The temperature effect on absorption and regeneration loading is an important factor, as a decrease in the difference between absorption and regeneration temperature will decrease the cost of energy consumption for solvent heating and cooling (Abu Zahra 2009, Peteers et al. 2007). In this work the cyclic capacity was determined

by first performing absorption experiments at 10 kPa CO_2 partial pressure and at 30 ±0.5°C by using single aqueous amine-based solvents. Once the solvent reached the equilibrium under absorption conditions, then regeneration of the solvent was done at 90 ±0.5°C by stripping the solvent with N_2 gas for approximately 5 hours. The total pressure in the bubble column reactor was kept at 1 atmosphere during both absorption and regeneration. Hence, in this work the cyclic capacity of various aqueous amine based solvents will be obtained for a relatively low regeneration temperature of 90°C. It is expected that this information will provide a preliminary indication on the solvent energy efficiency level, at least for mutual comparison within the set of solvents studied.

The optimal design and operation of absorption and regeneration columns requires more detailed knowledge of several parameters, with the most important one is the vapour-liquid equilibrium (VLE) of CO_2 in the solvents. Therefore, in this study solubility of CO_2 as function of CO_2 partial pressure was investigated for one of the most promising solvents (1,6-Hexanediamine, N,N'-dimethyl). VLE experiments were performed with the CO_2 partial pressure ranging from 1 up to 40 kPa and at a temperature of 30°C.

5.2. Experiment

The potential aqueous amine based solvents were tested in a screening apparatus where relative rates of absorption, equilibrium absorption capacity and regeneration capacity can be measured. More commonly used solvents such as Monoethanolamine (MEA), Diethanolamine (DEA), Diisopropanolamine (DIPA), and Piperazine (Pz) were taken as reference solvents for comparison. Most of the solvents tested in these experiments had a good solubility in water. However, for some amine based solvents the maximum concentration is limited. For this reason, the experiments were conducted at essentially two concentration levels (0.5 and 2.5 mole/L).

For a better comparison, reference experiments were performed for most commonly used solvents (MEA, DEA and DIPA) at the two different concentrations of 0.5 and 2.5 mole/L. Piperazine was tested only at a concentration of 0.5 mole/L in view of its limited solubility in water at room temperature. In the absorption experiments the solvents were treated with saturated CO_2 at 10 kPa partial pressure mixed with saturated N_2 as a make-up gas at temperature of 30 ± 0.5°C. Regeneration experiments, in which a small N_2 gas flow-rate was used as a stripping gas, were done at a temperature of 90 ± 0.5°C. The solvent screening experiments were performed at atmospheric pressure. The experiment conditions (temperature, pressure, amine concentration) were selected to enable direct comparison with previous results from Singh et al. (2007, 2008). The absorption experiments were continued until equilibrium was attained and for regeneration experiments the run-time was up to five hours.

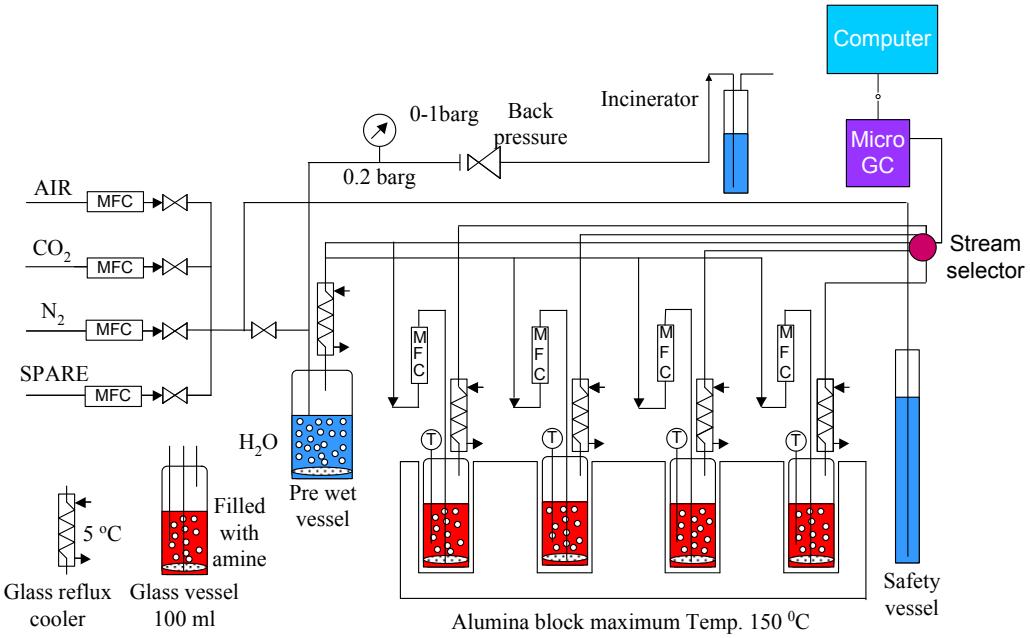

Figure 1, Schematic diagram of the experimental set-up used for solvent screening and vapour liquid equilibrium (VLE) experiment.

The experimental set-up consists of four identical bubble column reactors, which were placed inside an oven. In a typical experiment first fresh solution of known volume (80 ml) and of specific concentration was transferred into each reactor. To remove traces of CO_2 present into the solvent, it was stripped with saturated N_2 gas approximately for an hour. Once the temperature was stabilized in the reactor and CO_2 traces were removed from the solvent, the saturated inlet of 10 kPa CO_2 partial pressure, balanced with saturated N_2 gas was bubbled through the solvents. When the concentration of CO_2 in each outlet reached the inlet CO_2 concentration, the solvent was considered to have reached equilibrium. Subsequently, a regeneration experiment was performed at 90°C by stripping the solvent with saturated N_2 gas.

Each reactor outlet was connected to a condenser to avoid solvent losses by evaporation. The temperature of the condensers was kept at 5°C. An inline gas chromatograph (GC) was connected to all four outlets and also to the central inlet of the experiment set-up. Hence, CO_2 loading for absorption and regeneration experiment was determined by the inline GC. Each reactor was connected to a separate thermocouple and inlet mass flow controller (MFC). The regeneration experiments in this study were performed at 90°C, a lower temperature than in commercial stripper temperatures (around 120°C). In view of the lower temperature, and hence lower kinetics, the lean loading from the regeneration

experiments was determined after one hour of regeneration. It was found in preliminary experiments that a further reduction of the lean loading of the solvent for extended regeneration times (up to 5 hrs.) is limited. The lean loading thus determined after one hour seems to provide a fairly good indication of the obtainable lean loading, and was (for MEA) reasonable in line with literature data (see Table 2). It was therefore considered to be a sufficiently reliable benchmarking test for solvent regeneration. The gas flow rate in each reactor was kept constant for all experiments (10 nL/hr). A computer with Labview software was used to record the data from the experimental setup. CO_2 rich and lean loading from solvent samples was also determined by liquid sampling followed by GC analysis.

To determine vapour-liquid equilibrium data the same experiment set-up has been used. In these experiments absorption tests were done at 30°C and at 1 atm. The CO_2 partial pressure used for these experiments were 1, 5, 10, 20 and 40 kPa. In these experiments first the four parallel reactors were filled with a known volume (80 ml) of fresh solution of a specific concentration. Traces of CO_2 in the solvent were removed by stripping solvents with saturated N_2 gas. Once the temperature is stabilized in each reactor and CO_2 traces were removed, the saturated inlet gas having 1 kPa CO_2 partial pressure balanced with N_2 gas was bubbled through each solvent. The gas flow rate in each reactor was kept constant for every experiment (10 nL/hr). The CO_2 concentration in the outlet was recorded by the in-line GC. When the concentration of CO_2 in each outlet reached the inlet CO_2 concentration, the inlet stream was switched to 5 kPa CO_2 (again balanced with N_2 gas). Once again the CO_2 concentration in the outlet was noticed by inline GC. Similarly when the outlet CO_2 concentration reached the same concentration as the inlet gas flow, the CO_2 partial pressure in the inlet stream was increased again to a higher CO_2 partial pressure of 10 kPa. This procedure was repeated for 20 and 40 kPa CO_2 partial pressure experiments. To prevent solvent loss during these experiments, the condenser temperature for the outlet stream was kept around 5°C. All chemicals investigated were purchased (at high purity of around 99%) from Sigma Aldrich Chemical Co.

5.3. Results and discussion

Various aqueous amine based solvents have been compared for their absorption behaviour on the basis of the absorption and regeneration experimental results at CO_2 partial pressure of 10 kPa. The results, where saturation was reached for all solvents in absorption experiments at 30°C and regeneration was tested in experiments at 90°C, with the CO_2 lean loading determined after the first hour of regeneration, allow for a comparison of the solvents absorption capacity and also the cyclic capacity. In addition the CO_2 outlet concentration breakthrough curves from the absorption experiments were evaluated as they are believed to give an preliminary indication on the absorption rate, related to the reactivity of the various amine based solvents. For comparison, comparative data on the reaction kinetics of

the reference solvents used are presented in Table 1. In Table 2 literature data on the CO_2 solubility for these solvents is presented.

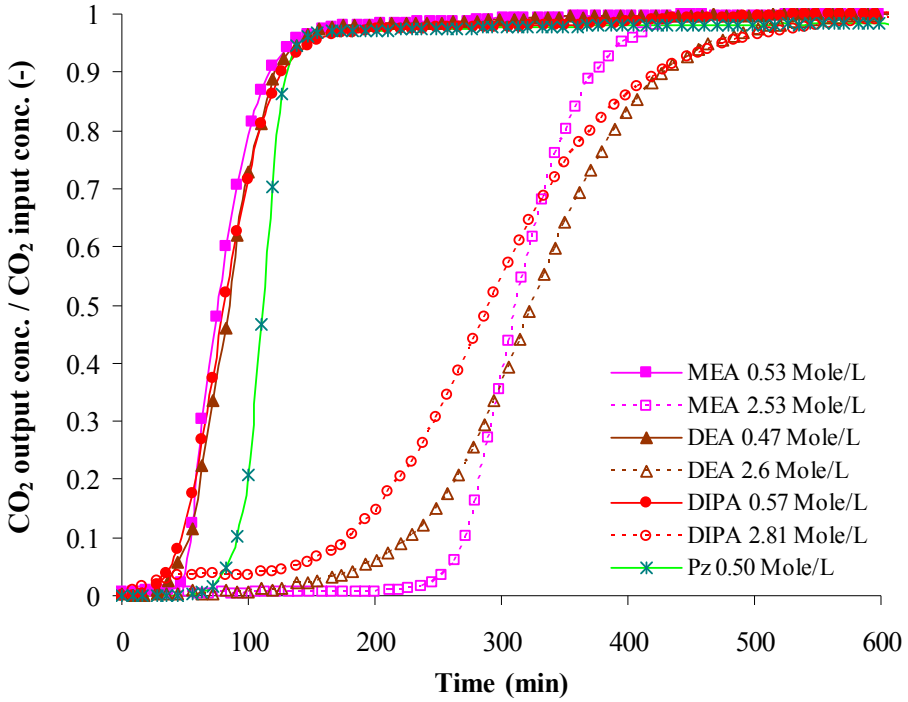

Figure 2, Breakthrough curve for CO_2 absorption in various reference solvents at 30°C.

Table 3, shows the rich and lean loading in mole CO_2/mole amine and also the cyclic loading of various aqueous amine based solvents. The repeatability of these experiments was within 5% deviation. In addition to the cyclic capacity, the absorption rate is important in the design of an absorption column. The (maximum) slope value (min^{-1}) shown in Table 3 is taken from the CO_2 absorption breakthrough curve over time (e.g. Figure 2). It is suggested here that the slope value gives an indication on the absorption rate for various solvents. It must be noticed that due to mass transfer effects, which are contactor specific, no quantitative conclusions can be presented based on these slope values. However, since all four parallel reactors are identical in design and are having a similar gas flow rate, the differences that may arise are mainly due to the variations in physical and chemical properties of the solvents like e.g. interfacial tension, density, viscosity and heat of absorption. Hence, a test like this allows one for direct comparison of the solvents under identical feed conditions. For preliminary comparison of the various solvents, the slope value (min^{-1}) from CO_2 outlet concentration breakthrough curve over time is preferred over the slope value from

the CO_2 loading curve loading (mole CO_2/mole amine) over time. It should also be noticed that the CO_2 loading in solvent near the breakthrough of the curve is close to the equilibrium loading in most of the solvents evaluated in this study.

Table 1, Literature data for reference solvents on the reaction between aqueous solvents and CO_2.

Solvent	**Conc.**	**Temp.**	**k_2**	**Reference**
	mole/L	°C	m^3 / mol sec	
Monoethanolamine (MEA)	1	25	6.97	Sharma (1965)
Diethanolamine (DEA)	1	25	1.24	Sharma (1964)
Diisopropylamine (DIPA)	1	25	0.4	Sharma (1964), Danwerts and Sharma (1966)

Table 2, Literature data for reference solvents on their CO_2 loading at low CO_2 partial pressure.

Solvent	**Conc.**	**CO_2 Partial Pressure**	**Temp.**	**CO_2 loading**	**Reference**
	mole /L	kPa	°C	mole CO_2 /mole amine	
Monoethanolamine (MEA)	2.5	15.70	40	0.56	Khen et al. 1992
	2.5	30.40	100	0.28	Murrieta et al. 1993
	4.9	8.60	30	0.44	Murrieta et al. 1993
	4.9	10.10	100	0.23	Murrieta et al. 1993
Diethanolamine (DEA)	0.5	6.89	25	0.69	Lee et al. 1972
	2.0	6.89	25	0.57	Lee et al. 1972
	2.0	10.70	30	0.59	Benamor et al. 2005
Diisopropylamine (DIPA)	2.5	10.00	40	0.41	Isaacs et al 1977
Piperazine (Pz)	0.6	10.92	25	0.98	Derks et al. 2005
	0.6	10.08	40	0.91	Derks et al. 2005
	0.6	10.41	70	0.76	Derks et al. 2005

Table 3, Solvent-screening results for 10 kPa CO_2 partial pressure absorption at 30°C and regeneration at 90°C, 1 atmosphere.

Solvent	**Solvent conc.**	**Rich loading**	**Lean loading**	**Cyclic loading**	**Abs. slope**
	mole/L	mole CO_2/ mole amine	mole CO_2/ mole amine	mole CO_2/ mole amine	min^{-1}
Reference solvents					
Monoethanolamine (MEA)	0.54	0.61	0.18	0.44	1.70E-02
Monoethanolamine (MEA)	2.53	0.52	0.27	0.25	1.01E-02
Diethanolamine (DEA)	0.48	0.66	0.18	0.48	1.45E-02
Diethanolamine (DEA)	2.60	0.50	0.25	0.25	5.29E-03
Diisopropanolamine (DIPA)	0.58	0.61	0.18	0.43	7.63E-03
Diisopropanolamine (DIPA)	2.81	0.42	0.19	0.22	4.45E-03
Piperazine (Pz)	0.51	0.87	0.07	0.80	2.56E-02
Effect of chain with OH group					
5-Amino-1-pentanol	2.51	0.52	0.34	0.18	7.30E-03
6-Amino-1-hexanol	0.51	0.58	0.18	0.40	1.46E-02
Effect of chain length with CH_3 group					
n-Pentylamine	2.57	0.35	0.25	0.10	1.05E-02
Hexylamine	0.13	0.99	0.67	0.32	3.10E-02
Effect of chain length in diamine based solvents					
1-3 Diamino propane	2.53	0.97	0.78	0.19	9.74E-03
1,4-Diaminobutane	2.58	1.09	0.87	0.22	5.64E-03
1,3-Propanediamine, N,N,N',N'-tetramethyl	2.56	0.95	0.54	0.41	1.46E-03
Hexamethylenediamine	2.54	1.11	0.89	0.21	5.16E-03
1,6-Hexanediamine, N,N'-dimethyl	0.49	1.51	0.66	0.85	1.06E-02
1,7-Diaminoheptane	0.51	1.34	0.53	0.81	9.92E-03
Effect of side chain effect					
Sec-Butylamine	2.53	0.59	-	-	5.42E-03
Iso Butylamine	2.58	0.39	-	-	8.40E-03

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1-2-Diamino propane	2.52	0.89	0.68	0.21	9.09E-03
N-(2-Hydroxyethyl) ethylenediamine	2.56	0.89	0.60	0.29	9.14E-03
Effect of number of NH_2 group					
Diethylenetriamine	2.47	1.43	1.08	0.34	6.67E-03
3,3'-Iminobis(N,N-dimethylpropylamine)	2.50	1.29	0.80	0.49	7.87E-03
N-(2-aminoethyl)1-3-propane diamine	2.54	0.92	0.57	0.35	3.33E-03
Triethylenetetramine	2.61	1.48	1.21	0.27	5.05E-03
Tris(2-aminoethyl) amine	2.55	1.50	1.42	0.08	3.63E-03
Different cyclic amine					
1-Methyl Piperazine	0.53	0.76	0.24	0.51	1.55E-02
Trans Piperazine, 2-5 dimethyl	0.57	0.93	0.44	0.49	1.18E-02
2-(1-Piperazinyl) ethylamine	2.50	1.08	0.79	0.29	5.96E-03
2-Methyl Piperazine	0.54	0.87	0.35	0.52	2.07E-02

Literature data on the kinetic rate constant k_2 (m^3/mol sec) for reference solvents (MEA, DEA, DIPA) is shown in Table 1. The rate constant, k_2 (m^3/mol sec) from Table 1, shows the following order for the reference solvents: MEA>DEA>DIPA. Similar order for these reference solvents (at 0.5 mole/L concentration) was also noticed from the steepness of the CO_2 breakthrough absorption curve (Figure 2) and hence also from the slope values determined from these curves (see Table 3). The CO_2 inlet concentration, amount of solvent, temperature, pressure, CO_2 flow rate etc. were the same for all absorption experiments. Hence, from the slope values shown in Table 3, it seems possible to have a preliminary indication on the relative absorption rate or reactivity of the various solvents.

The "slope value" presented in Table 3 is taken from the CO_2 absorption breakthrough curve for each solvents over the range from 0.2 to 0.6 (CO_2 outlet concentration / CO_2 inlet concentration). It is clear from Figure 2, that the CO_2 absorption break through curve for piperazine (0.5 mole/L) with a slope value of 2.56E-02 min^{-1} is much steeper when compared with the breakthrough absorption curve for 0.5 mole/L MEA (slope value = 1.01E-02 min^{-1}) see Table 3, in line with the common role of piperazine as absorption rate accelerator (activator). Table 2 shows the literature data of CO_2 loading (mole CO_2/mole amine) for reference solvents MEA, DEA, DIPA and Pz at low CO_2 partial pressure. Data represented in Table 2 is not exactly at the same combination of temperature, amine concentration and CO_2 partial pressure. However, it can nevertheless be concluded that the

experimental data as determined for the reference solvents in Table 3 is in acceptable agreement with literature data.

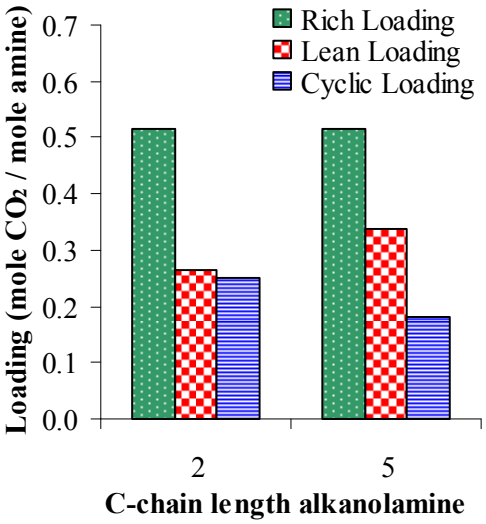

Figure 3, Effect of carbon chain length in alkanolamine based solvents for 2.5 mole/L concentration.

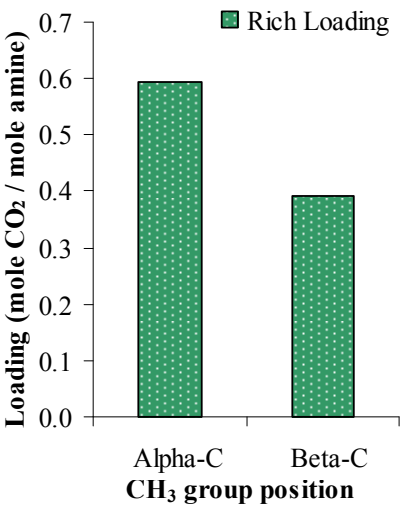

Figure 4, Effect of CH_3 group position to amine group in alkylamine based solvents for 2.5 mole/L concentration.

Results from Table 3 and Figure 3, shows that an increase in the carbon chain length for alkanolamine based solvents from 2 (in MEA) to 5 (5-amino-1-pentanol) between the amine and the hydroxyl group, results in an higher lean loading, whereas the rich loading remains essentially the same. Due to this effect the five carbon chain alkanolamine (5-amino-1-pentanol) shows a lower net cyclic capacity. Table 3 shows that for diamine based solvents an increase in carbon chain length results in an increased lean and rich loading, and shows only a marginal effect on the cyclic loading, see also Figure 5. This increase in lean loading with increase in chain length indicates that the carbamate stability is enhanced with increase in chain length in diamine-based solvents. For 1,7-Diaminoheptane (with seven carbon chain length) a high cyclic loading up to 0.81 mole CO_2/mole amine was found. It should be noted that the concentration for 1,7-Diaminoheptane was evaluated at a lower concentration of 0.5 mole/L.

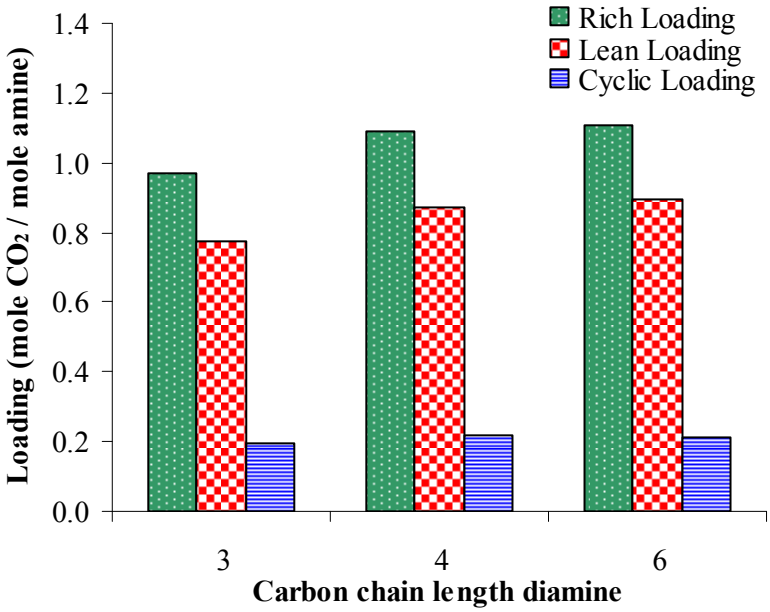

Figure 5, Effect of chain length in diamine based solvents for 2.5 mole/L concentration.

Steric hindrance effect was also noticed when comparing sec-butylamine and Isobutylamine (see Table 3 and Figure 4). For the structures with alkyl group substitution at the α-carbon next to the amine group (Sec-butylamine) the absorption capacity i.e. rich loading, is significant larger and reaches up to 0.59 mole CO_2/mole amine. An alkyl group substitution at β-carbon to the amine group (Isobutylamine) showed a lower rich loading of only 0.39 mole CO_2/mole amine. Interestingly, the absorption slope value was found to be lower for Sec-butylamine when compared with Isobutylamine. Hence, from these results clear effect of steric hindrance can be noticed at low CO_2 partial pressure. Due to the high vapour pressure of Sec-butylamine and Isobutylamine, the results from the regeneration experiments were not reliable.

Generally, tertiary amines show a lower reactivity towards CO_2 and a higher (cyclic) absorption capacity due to the formation of a significant amount of carbonate and bicarbonate species. These trends are confirmed in Table 3 for the species with the 1,3 diamino propane backbone structure. 1,3 propanediamine N,N,N',N' tetramethyl (tertiary form: 3 carbon chain length between two tertiary amine groups) shows a significant lower 'slope value', indicating slower absorption kinetics, and a much higher cyclic capacity when compared to the primary amine equivalent 1,3 diamino propane (3 carbon chain length between two primary amine group).

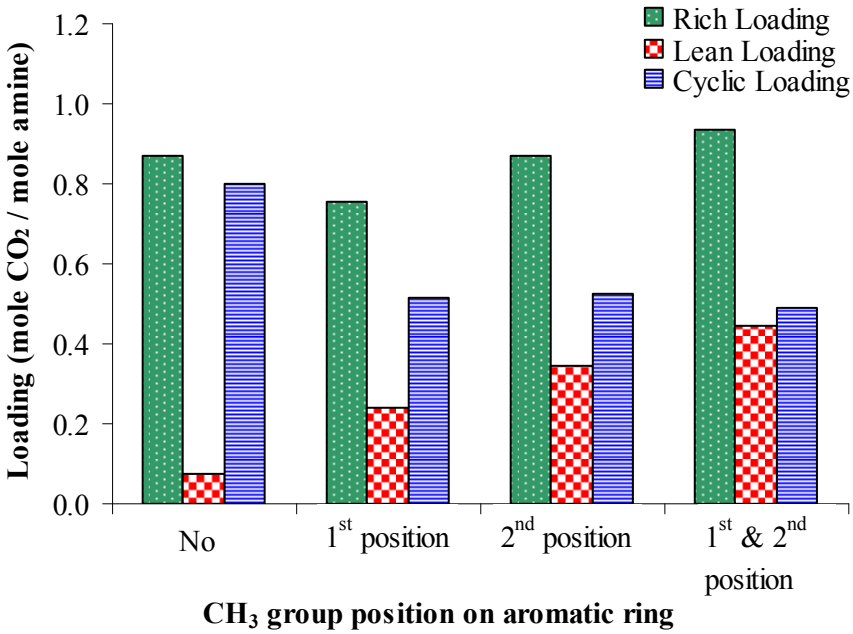

Figure 6, Effect of CH_3 group position in diamine based cyclic amine for 0.5 mole/L concentration.

The results of Table 3 and Figure 6 show, however, that for the cyclic diamine-based solvents, a substitution with alkyl or amine groups does not result in an enhanced cyclic loading. Figure 6 indicates that both the rich and lean loading increase when going from methyl substitution at the ortho (alpha) position to meta-position and both positions respectively, leaving the net cyclic capacity almost unaltered.

It should be noticed that the temperature used for regeneration experiments (90°C) in this work is much lower than normally applied in the commercial process temperature (around 120°C). As the CO_2 equilibrium loading normally decreases with temperature, the cyclic loading reported here could potentially be increased when, (still) absorbing at 30 °C and regenerating at e.g. 120 °C.

Table 4, Solvent-screening results in mole CO_2/L solution for 10 kPa CO_2 partial pressure absorption at 30°C and regeneration at 90°C, 1 atmosphere.

Solvent	**Solvent conc.** mole/L	**Rich end** mole CO_2 /L solution	**Lean end** mole CO_2 /L solution	**Net cyclic capacity** mole CO_2 absorbed /L solution
Reference solvents				
Monoethanolamine (MEA)	0.54	0.33	0.10	0.23
Monoethanolamine (MEA)	2.53	1.31	0.67	0.64
Diethanolamine (DEA)	0.48	0.31	0.09	0.23
Diethanolamine (DEA)	2.60	1.31	0.64	0.66
Diisopropanolamine (DIPA)	0.58	0.35	0.11	0.25
Diisopropanolamine (DIPA)	2.81	1.17	0.54	0.63
Piperazine (Pz)	0.51	0.44	0.04	0.40
Effect of chain with OH group				
5-Amino-1-pentanol	2.51	1.30	0.84	0.45
6-Amino-1-hexanol	0.51	0.30	0.09	0.21
Effect of chain length with CH_3 group				
n-Pentylamine	2.57	0.90	0.63	0.26
Hexylamine	0.13	0.13	0.09	0.04
Effect of chain length in diamine based solvents				
1-3 Diamino propane	2.53	2.45	1.96	0.49
1,4-Diaminobutane	2.58	2.81	2.25	0.56
1,3-Propanediamine, N,N,N',N'-tetramethyl	2.56	2.43	1.39	1.04
Hexamethylenediamine	2.54	2.81	2.27	0.54
1,6-Hexanediamine, N,N'-dimethyl	0.49	0.74	0.32	0.42
1,7-Diaminoheptane	0.51	0.68	0.27	0.42
Effect of side chain effect				
Sec-Butylamine	2.53	1.50	-	-
Iso Butylamine	2.58	1.01	-	-
1-2-Diamino propane	2.52	2.24	1.71	0.53

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N-(2-Hydroxyethyl) ethylenediamine	2.56	2.28	1.52	0.75
Effect of number of NH_2 group				
Diethylenetriamine	2.47	3.52	2.67	0.85
3,3'-Iminobis(N,N-dimethylpropylamine)	2.50	3.23	2.00	1.23
N-(2-aminoethyl)1-3-propane diamine	2.54	2.32	1.44	0.88
Triethylenetetramine	2.61	3.86	3.16	0.70
Tris(2-aminoethyl)amine	2.55	3.83	3.62	0.21
Different cyclic amine				
1-Methyl Piperazine	0.53	0.40	0.13	0.27
Trans Piperazine, 2-5 dimethyl	0.57	0.53	0.25	0.28
2-(1-Piperazinyl) ethylamine	2.50	2.71	1.99	0.72
2-Methyl Piperazine	0.54	0.47	0.19	0.28

The net effect on the cyclic capacity when the absorption temperature is simultaneously increased to 40-50°C would require significant additional experimental work. It is expected that the relative performance of the various solvents will not be very different when evaluating at 30°C (absorption) and 90°C (desorption) in comparison to e.g. 50°C for absorption and 120°C for desorption.

The volumetric CO_2 capacity (mole CO_2/L) is sometimes a more practical and relevant parameter than the CO_2 loading of in mole CO_2/mole amine, e.g. when determining the solvent circulation flow-rate between the absorber/regenerator column is an important parameter when evaluating new solvents. Hence, to give some insight on that Table 4 represents results for the various amine based solvents of Table 3 in mole CO_2/L solution. From these results a preliminary indication can be obtained on the solvent circulation rate requirement for particular solvent. It is known that solvent concentration plays an important role in reducing solvent circulation rate for e.g. in case of MEA (Abu Zahra 2009). In contrast to Table 3, Table 4 clearly shows the effect of concentration on solvent cyclic capacity (in mole CO_2/L solution), see reference solvents MEA, DEA and DIPA. Tertiary amine based solvents were found to show the highest cyclic capacities (mole CO_2/L solution) e.g. 1,3-Propanediamine, N,N,N'N'-tetramethyl and 3,3'-Iminobis(N,N-dimethylpropylamine).

Table 5, Comparison of Rich loading obtained at 10 kPa CO_2 Partial pressure and Pure CO_2 from Literature data (Singh et al. 2007 & 2008).

Solvent	Solvent conc.	10 kPa CO_2 Rich loading	Pure CO_2 Rich loading
	mole/L	mole CO_2 /mole amine	mole CO_2 /mole amine
Reference solvents			
Monoethanolamine (MEA)	2.53	0.52	0.72
Piperazine (Pz)	0.51	0.87	1.22
Effect of chain with OH group			
5-Amino-1-pentanol	2.51	0.52	0.83
Effect of chain length with CH_3 group			
n-Pentylamine	2.57	0.35	0.72
Hexylamine	0.13	0.99	1.52
Effect of chain length in diamine based solvents			
1-3 Diamino propane	2.53	0.97	1.30
1,4-Diaminobutane	2.58	1.09	1.26
Hexamethylenediamine	2.54	1.11	1.48
Effect of side chain effect			
Sec-Butylamine	2.53	0.59	0.84
Iso Butylamine	2.58	0.39	0.77
1-2-Diamino propane	2.52	0.89	1.27
N-(2-Hydroxyethyl)ethylenediamine	2.56	0.89	1.15
Different cyclic amine			
1-Methyl Piperazine	0.53	0.76	1.12
Trans Piperazine, 2-5 dimethyl	0.57	0.93	1.28

The effect of CO_2 partial pressure on CO_2 solubility for various solvents is important as the CO_2 loading capacity depends non-linearly on the CO_2 partial pressure. In earlier solvent screening work (Singh et al., 2007, 2008) the rich loading (mole CO_2/mole amine) at 30°C using pure CO_2 at atmospheric pressure was determined for some of the solvents at same concentration as in this study. Hence, the rich loading (mole CO_2/mole amine) of these solvents (now at 10 kPa CO_2) can be compared with the data reported earlier obtained at atmospheric CO_2 pressure, see Table 5. It is interesting to notice that for e.g. pentyl amine and isobutyl amine, the rich loading at 10 kPa CO_2 is almost reduced by half when compared with the rich loading at atmospheric CO_2 pressure, whereas for some

other solvents, e.g. 1,4-diamino butane and Hexamethylenediamine the effect of CO_2 partial pressure on their rich loading is much less pronounced.

Table 6, Solubility of CO_2 in aqueous solution of Monoethanolamine and 1,6-Hexanediamine, N,N'-dimethyl at 30°C.

Solvent	**Conc.**	**CO_2 Partial pressure**	**CO_2 loading**
	mole/L	kPa	mole CO_2 /mole amine
Monoethanolamine	0.5	0.88	0.51
(MEA)		4.80	0.59
		9.72	0.64
		19.87	0.70
		39.48	0.76
Monoethanolamine	2.5	0.88	0.49
(MEA)		4.80	0.54
		9.72	0.56
		19.87	0.60
		39.48	0.64
1,6-Hexanediamine, N,N'-dimethyl	0.51	0.89	1.19
(HMDA, N, N')		4.70	1.42
		9.40	1.54
		19.28	1.57
		39.71	1.60
1,6-Hexanediamine, N,N'-dimethyl	2.55	0.89	0.98
(HMDA, N, N')		4.70	1.11
		9.40	1.17
		19.28	1.23
		39.71	1.27

A further investigation has been performed on the CO_2 solubility at various CO_2 partial pressures for one of the more promising solvent candidates identified in this study; 1,6-Hexanediamine, N,N'-dimethyl, which is a secondary diamine based solvent with a six carbon chain between the amine groups and where each amine group is substituted once with an methyl group. Results presented earlier for this solvent showed a high cyclic capacity of 0.85 mole CO_2/mole amine, comparable or slightly higher than the value determined for piperazine (0.80 mole CO_2/mole

amine). While the cyclic loadings are quite comparable, interestingly, 1,6-Hexanediamine, N,N'-dimethyl showed a high rich loading of 1.51 mole CO_2/mole amine when compared with the rich loading of 0.51 mole/L Piperazine (0.87 mole CO_2/mole amine) and of 0.5 mole/L MEA (0.61 mole CO_2/mole amine). Not only the cyclic loading compares favourably, also the reactivity ('as indicated via the slope value') seems to be fairly high. The slope value of 1.06E-02 min^{-1} for 1,6-Hexanediamine, N,N'-dimethyl was found comparative with slope value of 0.5 mole/L MEA with slope value of 1.70E-02 min^{-1}. Additionally, 1,6-Hexanediamine, N,N'-dimethyl is reported to be non-corrosive from its MSDS. Hence, based on the above mentioned properties, 1,6-Hexanediamine, N,N'-dimethyl was selected, as potential CO_2 solvent for further evaluation of the CO_2 solubility.

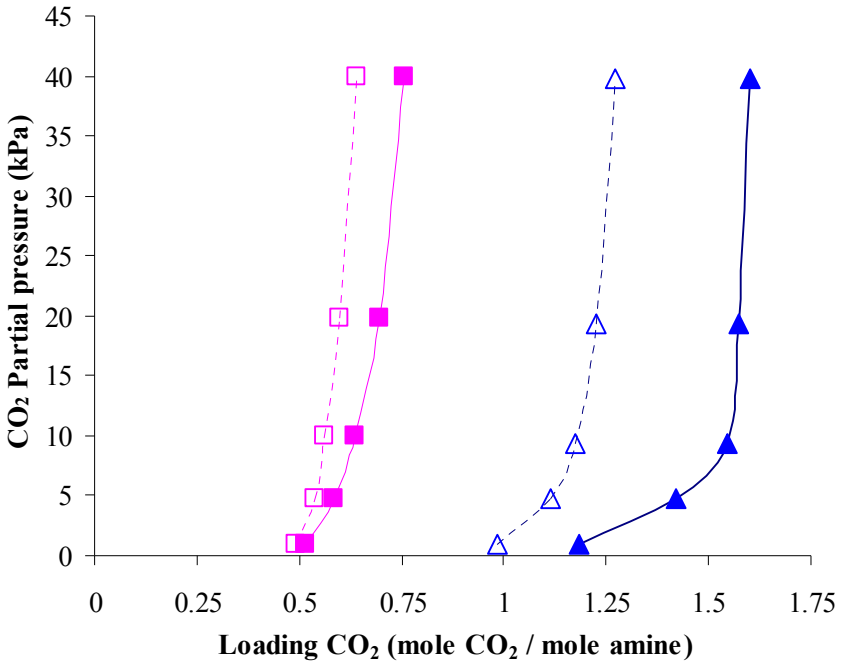

Figure 7, Loading capacity of CO_2 in different solvents at 30°C; ■ 0.5 mole/L MEA, □ 2.5 mole/L MEA, ▲ 0.51 mole/L 1,6-Hexanediamine, N,N'-dimethyl, △ 2.55 mole/L 1,6-Hexanediamine, N,N'-dimethyl.

The experimental solubility data for MEA and the potential solvent 1,6-Hexanediamine, N,N'-dimethyl, measured in the same equipment, is presented in Table 6 and is plotted in Figure 7. From Figure 7 it is clear that the obtainable rich loadings at all CO_2 partial pressure are much higher for the aqueous solution of 1,6-Hexanediamine, N,N'-dimethyl in comparison to aqueous solutions of MEA at 30°C. The solubility of CO_2 per mole of amine is decreased when the concentration of aqueous solution of 1,6-Hexanediamine, N,N'-dimethyl is increased from 0.51

mole/L to 2.55 mole/L. The solubility of CO_2 in 2.55 mole/L 1,6-Hexanediamine, N,N'-dimethyl is approximately twice the value for the solubility of CO_2 in a 2.5 mole/L MEA solution. The reason for high CO_2 solubility obtained for this solvent could be due to the effect from its molecular structure. The 1,6-Hexanediamine, N,N'-dimethyl molecular structure has two secondary amine groups with a six carbon chain in between. It is suggested that due this (apparently sufficiently long) six carbon chain length these two secondary amine groups are not influencing each other on reactivity and acts as individual amine groups. This is not trivial as carbamate formation on one of the amine-groups within the molecule may influence the reactivity of the other amine group. Which can results in forming less stable carbamate at both secondary amine groups. This molecular structural effect requires, however, further investigation before more general conclusions can be drawn. The high CO_2 absorption capacity of this solvent offers the possibility of strongly reducing the solvent circulation in a cyclic CO_2 absorption process.

5.4. Conclusion

The cyclic capacity of various aqueous amine based solvents was determined using low CO_2 partial pressure (10 kPa) during absorption at 30ºC and regeneration at 90ºC. By measuring the CO_2 breakthrough curves in the four parallel absorption vessels used in this study, also a first indication of the relative reactivity of the solvents studied was obtained. 1,7-Diaminoheptane and 1,6-Hexanediamine, N,N'-dimethyl showed a high cyclic loading of 0.81 and 0.85 mole CO_2/mole amine respectively. The effect of solvent molecular structure on the absorption characteristics (capacity, reactivity) of various solvents could be observed in this study. Steric-hindrance effect on absorption capacity was noticed for alkyl group substituted at α-carbon to the amine group. Also the effect of the carbon chain length in alkanolamine and diamine based solvents was identified. For the cyclic diamines studied, it was found that the one without substitution showed a higher cyclic loading when compared to that of substituted cyclic diamine.

1,6-Hexanediamine, N,N'-dimethyl was selected for further solubility study at various CO_2 partial pressure ranging from 1 up to 40 kPa, at 30°C and 1 atmosphere. The CO_2 solubility in 2.55 mole/L aqueous 1,6-Hexanediamine, N,N'-dimethyl is nearly twice the value of a 2.5 mole/L MEA solution at lower CO_2 partial pressure. The new solvent has therefore the potential to reduce the solvent circulation rate in CO_2 absorption processes. Additionally, considering the slope values observed from the breakthrough curves, the reactivity for 1,6-Hexanediamine, N,N'-dimethyl is reasonably high and the corrosiveness is also limited. Further investigation related to the CO_2 absorption kinetics for 1,6-Hexanediamine, N,N'-dimethyl at different temperatures will be performed.

Acknowledgement
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I would like to give my deepest thanks to my Late Professor Michiel Groeneveld, who gave tremendous support and guidance to my research.

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6

Solubility of CO_2 in aqueous solution of 1,6 Hexamethylenediamine (HMDA)

Solubility experiments for CO_2 absorption have been performed for 0.5, 1 and 2.5 mole/L aqueous solution of 1,6 Hexamethylenediamine (HMDA) at 20, 30 and 40°C. The isothermal absorption capacities of CO_2 as a function of HMDA concentration have been presented for partial pressures from 1 to 100 kPa. From the regressed VLE data the equilibrium partial pressure of CO_2 and the absorption enthalpy for CO_2 were evaluated for the same amine-group concentration, same CO_2-loading per amine group and the same temperature. HMDA solvent is compared very favourably to MEA with respect to equilibrium partial pressure and showed similar heat of absorption. The observed low corrosiveness makes HMDA an even more promising candidate-solvent for CO_2 capture.

6.1. Introduction

Alkanolamine aqueous solutions are widely used in gas treating processes to remove acid gases, such as CO_2 and H_2S, from natural, refinery, and synthesis gas streams. Industrially important alkanolamines are Monoethanolamine (MEA), Diethanolamine (DEA), di-2-propanolamine (DIPA), and N-methyldiethanolamine (MDEA). Aqueous MEA solutions have been widely used due to their high reactivity, low solvent cost, ease of reclamation, and low absorption of hydrocarbons. When the primary (or secondary) amine reacts with CO_2, stable carbamates are usually formed. The maximum CO_2 loading is limited by stoichiometry to 0.5 mole of CO_2/ mole of amine when carbamate formation is the only reaction. At high CO_2 partial pressures, however, carbamate may hydrolyze and generate free amines which can react with additional CO_2; thus, the CO_2 loading of MEA may exceed than 0.5 mole CO_2/mole MEA.

For a gas stream that contains both CO_2 and H_2S, an aqueous solution of the tertiary amine MDEA is found to be an appropriate solution for the selective removal of H_2S as MDEA does not form carbamates on reaction with CO_2 but acts as proton acceptor. In that case the dissociative absorption of H_2S is kinetically favoured over the absorption of CO_2 which is then determined by the relative slow reaction with water forming bicarbonate. Advantages of the use of MDEA solutions include their high loading capacity (about 1.0 mol of CO_2/mol of amine) and low enthalpy of reaction with the acid gases. The lower enthalpy of reaction leads to lower energy requirements for regeneration. However, the somewhat slower reaction rate of CO_2 absorption in aqueous solutions of tertiary amines (like MDEA) limits the use of MDEA and similar compounds.

The use of blended amines, a solution of two or more amines in varying compositions, considerably improves the absorption performance and leads to savings in energy requirements. Blended amines combine the absorption characteristics of the constituent amines such as a higher loading capacity and faster reaction rates. Blends of primary and tertiary amines, such as mixtures of MEA and MDEA, have been suggested for CO_2 removal. Nowadays, the addition of an accelerator or more specifically piperazine (PZ), to aqueous N-methyldiethanolamine (MDEA) solutions has found widespread application in the removal and absorption of carbon dioxide from process gases. The success of such a blend of a primary or secondary amine with a tertiary amine is based on the relatively high absorption CO_2 rate reaction with the former combined with the low heat of reaction of CO_2 with the latter, which, ideally, leads to higher rates of absorption in the absorber column and lower heats of regeneration in the stripper section. Sterically hindered alkanolamines have been proposed as commercially attractive solvents for removal of acid gases from gaseous streams. For example 2-amino-2-methyl-1-propanol (AMP), which is the sterical hindered form of MEA. Due to the bulkiness of the group attached to the tertiary carbon atom of AMP, the

formation of carbamate is inhibited when AMP reacts with CO_2. Therefore, the CO_2 loading of AMP can approach 1.0 mole of CO_2/mole of amine.

Singh et al. (2007, 2008, 2009 and 2010) studied various amine based solvents for CO_2 absorption and regeneration. During solvent screening Hexamethylenediamine, and it's secondary amine equivalent 1,6-Hexanediamine, N,N'-dimethyl showed a high CO_2 absorption capacity and high absorption rate when compared to MEA and other solvents. As corrosion is one of the important characteristic to be determined for the new solvent, an intrinsic corrosion test was performed using an iron solubility test performed at 130°C for 2 hour. The iron solubility for Hexamethylenediamine was found to be 3.5 ppm while for MEA the iron solubility under identical conditions was found to be 15 ppm. Therefore, 1,6 Hexamethylenediamine has confirmed and strengthened it's candidacy as a potential solvent for a CO_2 absorption process.

Thermodynamic equilibrium data for the carbon dioxide solubility determine the most important process parameters in an absorption-desorption cyclic process like solvent flow rate and energy requirement. Obviously, these two numbers play an important role in process economics and data for this thermodynamic equilibrium is therefore crucial. Hence, in this work vapour liquid equilibrium (VLE) data has been determined experimentally for 1,6 Hexamethylenediamine (HMDA).

6.2. Experimental section

Experimental data for the CO_2 solubility at various CO_2 partial pressures was obtained using a stirred cell reactor setup, which mainly consisted of a thermostatted vigorously stirred reactor (ca. 2L) connected to a calibrated gas vessel (see Figure 1). Both reactor- and gas supply vessel were equipped with a temperature and pressure indicator. In a typical experiment, a known amount of amine solution was transferred to the reactor vessel, after which the liquid was degassed by applying vacuum for a short while to remove all inert gases from the setup and dissolved gases from the amine solutions prior to the experiment. Next, the solution was allowed to equilibrate at the desired temperature and the (vapour) pressure was recorded. Then, the gas supply vessel was filled with pure carbon dioxide and the initial pressure in this vessel was measured. Next, the stirrer was switched on and a sufficient amount of CO_2 was fed from the gas supply vessel to the reactor. The gas supply to the reactor was closed and the content of the reactor was allowed to reach equilibrium - which was reached when the reactor pressure remained constant. The actual CO_2 partial pressure could be calculated from this final (equilibrium) reactor pressure corrected for the vapour pressure of the lean solution, thereby assuming that the solution vapour pressure is not influenced by the CO_2 loading.

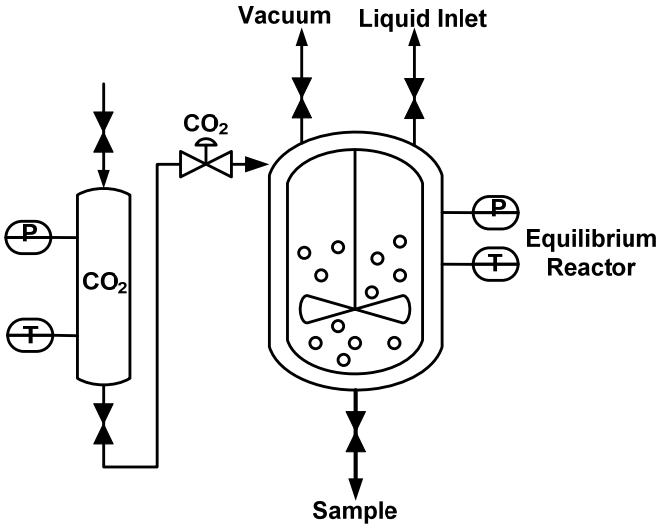

Figure 1, Schematic diagram of solubility experiment set-up.

The difference between initial and final pressure in the gas supply vessel, taking non-ideal behaviour for CO_2 in the gas phase into account, was used to calculate the corresponding CO_2 loading of the solution. These solubility experiments have been carried out for 1,6 Hexamethylenediamine concentrations of 0.5, 1 and 2.5 mole/L at 20, 30 and 40°C.

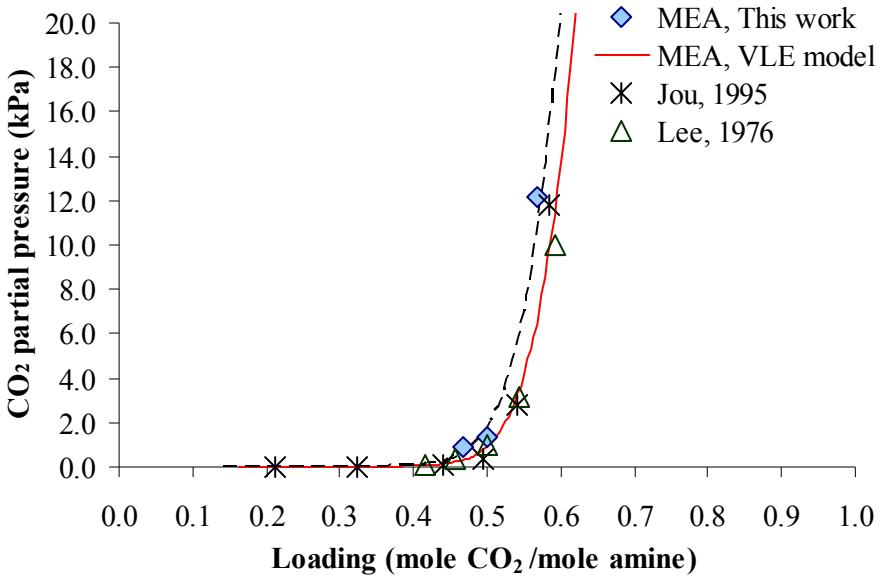

Figure 2, Comparison of the CO_2 solubility validation experiment for 2.5 mole/L aqueous solution of MEA at 25 °C with literature and model data.

To determine the accuracy of the experiment set-up, an experiment was performed for the CO_2 solubility in 2.5 molar aqueous solution of Monoethanolamine (MEA) at 25°C. Figure 2, shows experimental data together with literature data reported by Lee et al. (1976) and Jou et al. (1995). The data is quite in line with literature data. The model line from the concentration based equilibrium model for MEA model was calculated using the reaction equilibria reported in the VLE model by Aboudheir et al. (2003), for which an absolute standard deviation of about 12.5% is reported, still less than the typical uncertainty of VLE data (around 20%), according to Aboudheir et al. (2003). The reproducibility between various experiments was within ±5%. The experimental error in the data points presented in this work is estimated at maximally 0.01 unit (in loading) and 5 mbar (in CO_2 partial pressure) respectively. Equilibrium partial pressures below 1 kPa of CO_2 were considered to be unreliable for this measurement technique and are not reported here.

6.3. Results and Discussion

All experimentally obtained data on CO_2 solubility in aqueous solution of 0.5, 1 and 2.5 mole/L 1,6 Hexamethylenediamine (HMDA) at 20, 30 and 40°C with their corresponding partial pressure are listed in Tables 1 to 3.

Table 1, Experimental VLE data of CO_2 in a 0.5 mole/L aqueous solution of HMDA.

T = 20°C		**T = 30°C**		**T = 40°C**	
Loading mole CO_2 /mole amine	**PCO_2** kPa	**Loading** mole CO_2 /mole amine	**PCO_2** kPa	**Loading** mole CO_2 /mole amine	**PCO_2** kPa
1.29	2.64	1.22	2.50	1.21	2.16
1.37	3.82	1.31	3.61	1.29	3.79
1.46	5.77	1.38	5.67	1.36	5.95
1.54	8.85	1.46	8.36	1.43	9.10
1.62	13.72	1.53	12.64	1.50	13.88
1.69	20.98	1.59	18.18	1.56	20.16
1.75	32.16	1.65	26.06	1.62	28.10
1.80	46.77	1.70	35.95	1.66	37.13
		1.74	46.66	1.70	47.49
		1.77	59.45	1.74	58.44
		1.79	70.99	1.76	71.65
		1.81	80.50		

To determine the effect of temperature at fixed concentrations of HMDA on the solubility of CO_2, the partial pressures of CO_2 (PCO_2) (kPa) were plotted by the equilibrium loading (mole CO_2/mole amine). These results are summarized in Figure 3 to 5.

Table 2, Experimental VLE data of CO_2 in a 1 mole/L aqueous solution of HMDA.

T = 20°C		**T = 30°C**		**T = 40°C**	
Loading mole CO_2 /mole amine	**PCO_2** kPa	**Loading** mole CO_2 /mole amine	**PCO_2** kPa	**Loading** mole CO_2 /mole amine	**PCO_2** kPa
1.07	1.19	1.15	1.88	1.02	1.47
1.20	2.91	1.19	2.82	1.05	1.98
1.24	3.86	1.23	3.98	1.09	2.77
1.28	5.11	1.27	5.45	1.13	3.85
1.33	6.65	1.30	7.07	1.17	4.98
1.37	8.53	1.34	9.27	1.21	6.85
1.41	10.92	1.38	11.85	1.24	9.13
1.45	13.69	1.42	14.95	1.28	11.60
1.48	17.04	1.45	18.52	1.31	14.64
1.52	20.67	1.48	22.78	1.35	18.00
1.55	25.00	1.52	27.40	1.38	21.79
1.58	30.12	1.54	32.57	1.40	25.94
1.60	35.38	1.57	38.45	1.43	30.66
1.63	41.81	1.59	42.04	1.46	35.41
1.65	48.48	1.62	50.29	1.48	40.89
1.67	55.27				
1.69	62.57				

The effect of HMDA concentration on its CO_2 absorption capacity is shown in Figure 6, where absorption equilibrium of CO_2 in three different concentrations of HMDA is presented. The observed concentration dependency, the CO_2 equilibrium loading per amine group decreases with an increase in HMDA concentration at fixed temperature and -CO_2 partial pressure, is similar to what is normally found for aqueous MEA-solutions. Realizing that HMDA contains two primary amine groups, a comparison on a per-amine-group basis seemed relevant. The concentration effect for MEA and HMDA at a temperature of 40ºC and similar amine group concentrations is compared in Figure 7 (a & b).

Table 3, Experimental VLE data of CO_2 in a 2.5 mole/L aqueous solution of HMDA.

T = 20°C		**T = 30°C**		**T = 40°C**	
Loading mole CO_2 /mole amine	**PCO_2** kPa	**Loading** mole CO_2 /mole amine	**PCO_2** kPa	**Loading** mole CO_2 /mole amine	**PCO_2** kPa
1.05	1.81	1.04	1.86	1.01	1.87
1.07	2.23	1.06	2.40	1.02	2.43
1.09	2.69	1.07	3.03	1.04	3.33
1.10	3.30	1.09	3.77	1.05	4.36
1.12	3.98	1.11	4.65	1.07	5.53
1.14	4.74	1.12	5.63	1.08	6.95
1.15	5.58	1.14	6.72	1.10	8.46
1.17	6.53	1.15	7.95	1.11	10.02
1.19	7.55	1.17	9.35	1.13	11.87
1.20	8.66	1.18	10.92	1.14	13.66
1.22	9.97	1.20	12.52	1.16	15.84
1.24	11.31	1.21	14.24	1.17	17.98
1.25	12.61	1.23	16.09	1.18	20.43
1.27	14.19	1.24	18.09	1.19	22.92
1.28	15.84	1.25	20.30	1.21	25.75
1.29	17.52	1.27	22.47	1.22	28.32
1.31	19.38	1.28	24.89	1.23	30.97
1.32	21.28	1.29	26.93	1.24	33.73
1.33	23.37	1.30	29.39	1.25	36.46
1.35	25.59	1.31	31.93	1.26	39.28
1.36	27.88	1.32	34.45	1.27	42.23
1.37	30.18	1.33	36.98	1.28	45.04
1.38	32.72	1.34	39.46	1.28	48.08
1.40	35.43	1.35	42.01	1.29	50.99
1.41	38.12	1.36	44.72	1.30	53.91
1.42	40.79	1.37	47.46	1.31	56.21
1.43	43.47				
1.44	45.87				

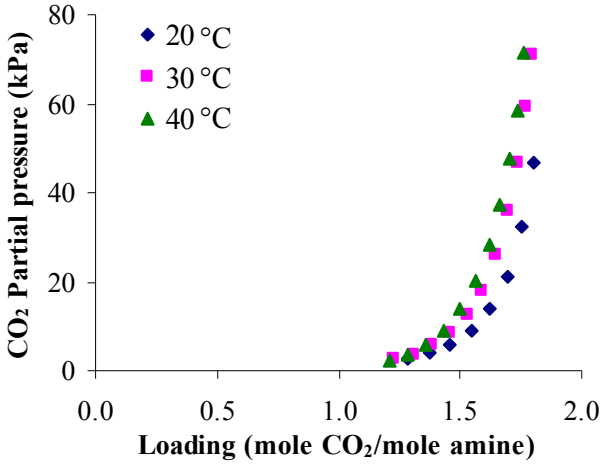

Figure 3, Equilibrium solubility of CO_2 in a 0.5 mole/L aqueous solution of HMDA.

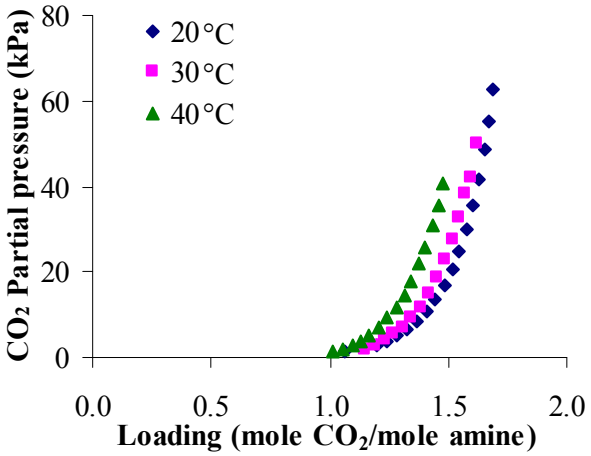

Figure 4, Equilibrium solubility of CO_2 in a 1 mole/L aqueous solution of HMDA.

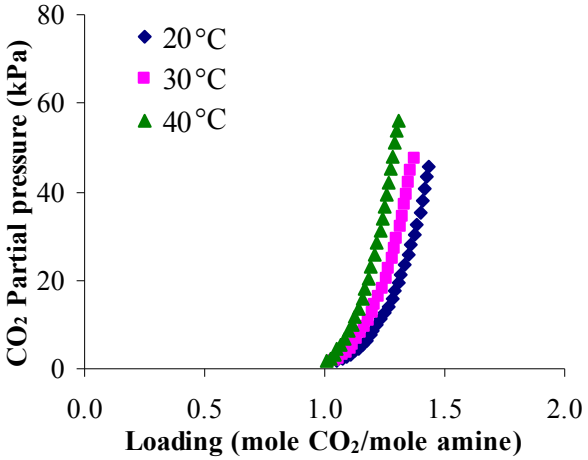

Figure 5, Equilibrium solubility of CO_2 in a 2.5 mole/L aqueous solution of HMDA.

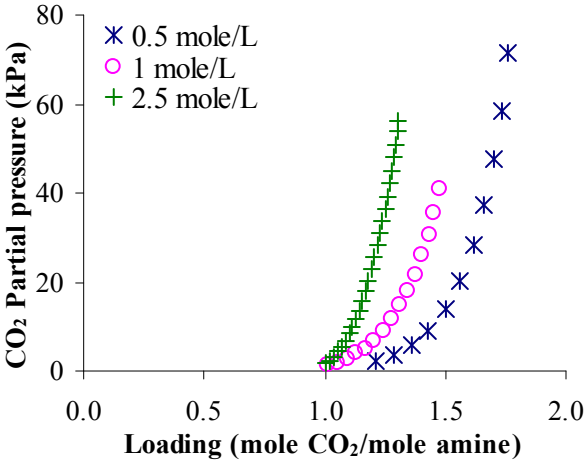

Figure 6, Equilibrium solubility of CO_2 at 40°C in an aqueous solution of HMDA.

It can be observed in Figure 7(a) that at similar amine group molar concentrations and at the same partial pressure, that the CO_2 solubility in HMDA solutions is significantly higher. This effect is stronger at higher loadings (higher CO_2 partial pressures). Alternatively, for a given amine loading, the equilibrium partial pressure of CO_2 for HMDA is a factor 3-8 lower than for MEA. Again, this effect

changes somewhat with loading and (not shown here) with temperature. The similarity of the curves is illustrated by Figure 7(b).

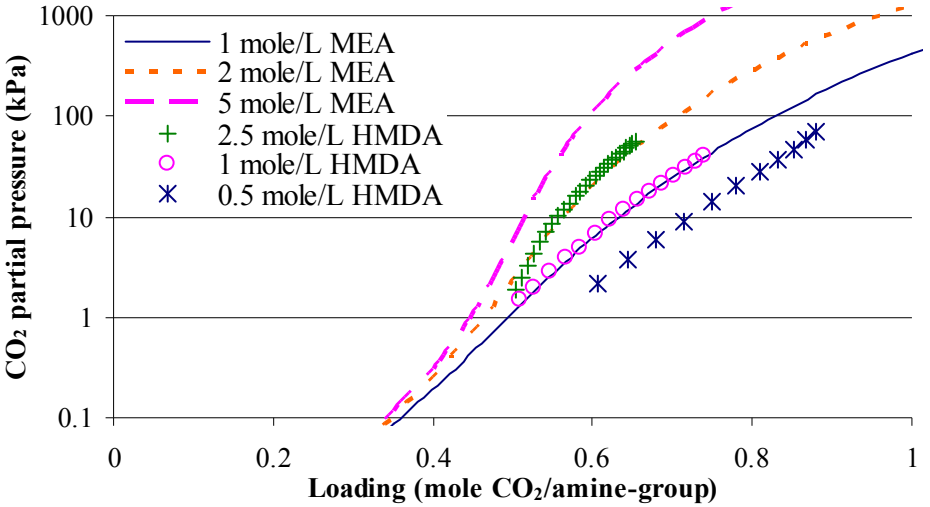

Figure 7 (a), Comparison of the effect of concentration on the CO_2 equilibrium solubility in aqueous solution of HMDA with MEA at 40°C.

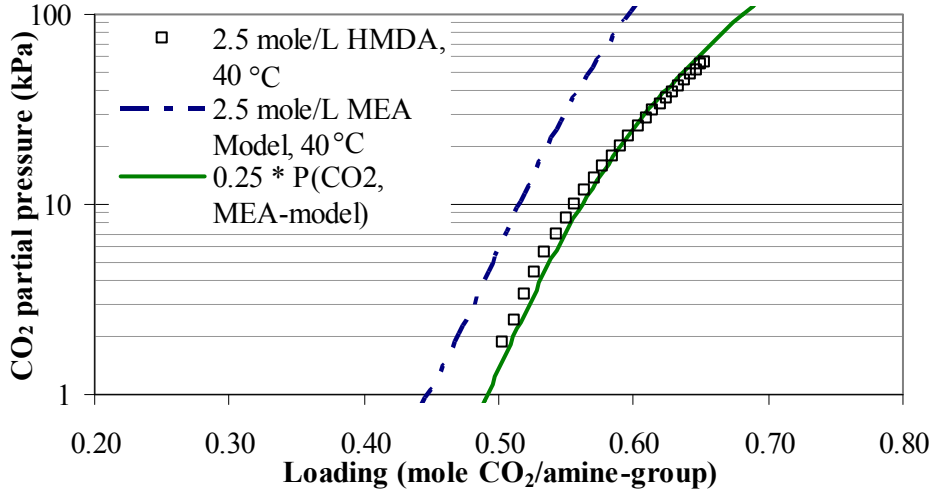

Figure 7 (b), Similarity of CO_2 partial pressure-loading curve for 5 mole/L MEA with 2.5 mole/L HMDA at 40ºC. Solid model line represents 25% of the CO_2-equilibrium pressure for 5mole/L MEA.

From the regressed CO_2 partial pressure – loading equilibrium data, the absorption enthalpies for CO_2 in aqueous HMDA solutions (ΔH_{abs}) were calculated on the basis of the following Gibbs-Helmholtz equation:

$$\frac{\Delta H_{abs}}{R} = \left(\frac{\partial \ln P_{CO_2}}{\partial (1/T)} \right)_{xCO_2} \quad (1)$$

Where x_{CO2} is the mole fraction CO_2 in the solution. The absorption enthalpies thus obtained are compared with the absorption enthalpies for CO_2 in aqueous MEA solutions at the same average temperature of 30ºC (using the VLE model mentioned earlier) and at the same loading per amine group.

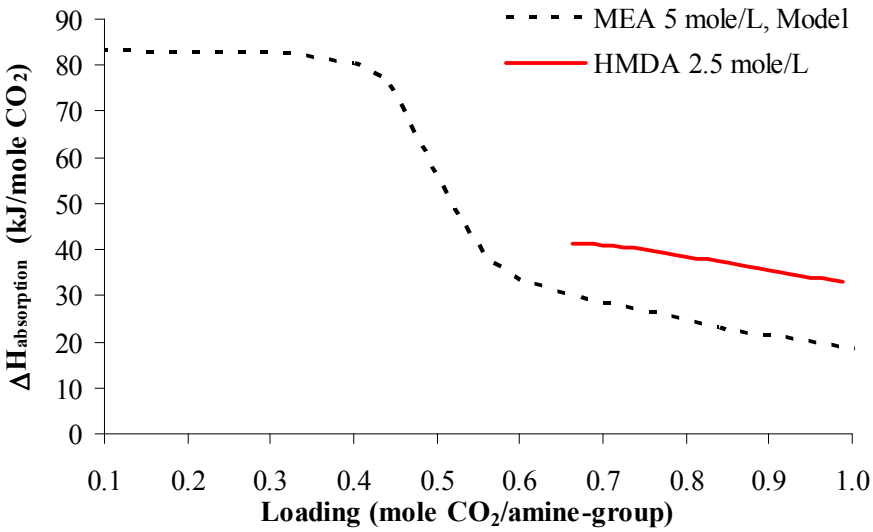

Figure 8, Enthalpy of CO_2 absorption for 2.5 mole/L HMDA compared with 5 mole/L MEA data (30ºC), calculated using the VLE model.

Table 6, Absorption enthalpies (ΔH_{abs})for HMDA and MEA, evaluated at 30ºC and at the same amine group concentration and loading).

HMDA				**MEA***	
Conc.	**Average Loading**		**ΔH_{abs}**	**Conc.**	**ΔH_{abs}**
mole/L	mole CO_2 /mole amine	mole CO_2 /amine-group	kJ /mole CO_2	mole/L	kJ /mole CO_2
2.5	1.25	0.63	40.54	5	33.62
1	1.45	0.73	33.54	2	31.4
0.5	1.7	0.87	29.1	1	28.2

*MEA VLE model.

It should be noticed that the results presented originate from a loading range where the (calculated) absorption enthalpy is quite sensitive to the loading, as indicated in Figure 8 where the calculated enthalpy for MEA as function of amine-group loading is presented.

As the enthalpy of absorption is strongly dependent on the CO_2 loading in the range studied, the calculated values may deviate 10-20% from actual values. If more accurate values are required, direct measurement of the absorption enthalpies is recommended.

6.4. Conclusion

The absorption equilibrium data of CO_2 in aqueous solution of 0.5, 1 and 2.5 mole/L 1,6 Hexamethylenediamine (HMDA) were measured at 20, 30 and 40°C for pressures in the range of 1 to 100 kPa. The equilibrium partial pressure of CO_2 is considerably lower than for aqueous MEA, compared at the same temperature and same amine-group concentration and amine-group loading. From the VLE data, the absorption enthalpies for CO_2 in HMDA solutions were found to be comparable to those for MEA, when evaluated at the same temperature and CO_2 loading per amine group, for the range of conditions studied.

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7

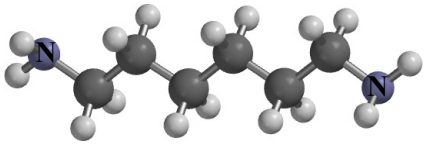
Kinetics study of carbon dioxide absorption in aqueous solutions of 1,6 Hexamethyldiamine (HMDA) and 1,6 Hexamethyldiamine, N,N' di-methyl (HMDA, N,N')

A study towards the kinetics of CO_2 in aqueous solutions of 1,6 Hexamethyl diamine (HMDA) and 1,6 Hexamethyl diamine, N,N' di-methyl (HMDA, N,N') was performed at concentrations ranging from 0.5 to 2.5 mole/L and temperatures from 283 up to 303 K. The kinetics data were determined by CO_2 absorption experiments using a stirred cell reactor with a flat interface between gas and liquid. These new CO_2 solvents were identified in earlier work for their high CO_2 capacity and limited corrosiveness. The experimental technique was validated using kinetic experiments for a 2.5 mole/L Monoethanolamine solution. In view of double amine functionality and the six carbon chain between the amine groups, attention was paid to whether the amine groups acted independently and whether or not internal cyclisation would affect the carbamate forming mechanism. The reaction order with respect to HMDA was found to vary from 1.4 to 1.8 with increasing temperature. Absorption experiments in an equimolar solution of HMDA with HCl, showed that the two amine groups react independently from each other towards CO_2. The reactivity of both diamines was more than five times larger than for Monoethanolamine. The secondary diamine HMDA, N,N' was found to be even more reactive towards CO_2. Additionally, the effect of CO_2 loading on the kinetics was studied for 0.5 mole/L aqueous solutions of HMDA and HMDA, N,N' at 293K. Both solvents are from absorption kinetics point of view good candidates for further evaluation as solvent (-component) for CO_2 capture.

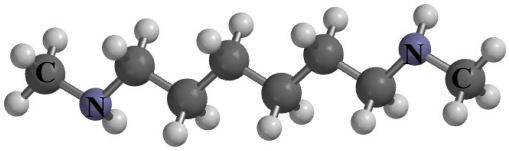
7.1. Introduction

Separation of carbon dioxide from a large amount of flue gas by chemical separation is known as one of the most reliable and economical processes. The separation is, however, expensive with standard industrial technology, both in terms of capital cost (capex) and operating cost (opex). The main cost items of the process are the size of the absorber and regenerator, and the lean/rich cross flow heat exchanger. High opex is related to the energy requirement for regeneration of the solvent circulating in the process, corresponding to 80% of the total. Other issues are associated with degradation, precipitation, corrosion, foaming, evaporation etc. Therefore, novel solvent systems are desired to be developed to make the removal of carbon dioxide from flue gases a more cost effective process.

Results obtained from previous work on development of new solvents for CO_2 absorption process with aqueous amine based solvents have revealed some new novel solvents (Singh et al., 2007, 2009, 2010). The potential solvents 1,6 Hexamethyldiamine (HMDA) and 1,6 Hexamethyl diamine, N,N' di-methyl (HMDA, N,N') (see Figure 1) showed an almost two times higher CO_2 absorption capacity when compared to conventional solvent e.g. Monoethanolamine (MEA) at similar amine concentration. For example, 0.5 mole/L 1,6 Hexamethyldiamine, N,N' di-methyl reaches up to 1.5 mole CO_2/mole amine at 10 kPa CO_2 partial pressure (similar CO_2 partial pressure in flue gas) at 30 ^oC temperature, 1 atm pressure. Interestingly, this solvents were found to be non-corrosive. Hence, 1,6 Hexamethyldiamine, N,N' di-methyl, shows great potential and deserving further investigation



1,6 Hexamethylenediamine (HMDA)



1,6 Hexamethylenediamine ,N,N'di-methyl (HMDA, N,N')

Figure 1, Molecular structure of selected diamine based solvents.

In order to be able to determine the dimension of the absorber in a CO_2 capture plant, information on the reaction kinetics of CO_2 with this new solvent is required. The absorption kinetics of CO_2 in aqueous solutions of 1,6 Hexamethyldiamine and 1,6 Hexamethyldiamine, N,N' di-methyl were determined at temperatures ranging from 283 up to 303 K and solvent concentration ranging from 0.5 up to 2.5 mole/L. In addition, the effect of CO_2 solvent loading is evaluated. In order to validate the experimental procedure reference experiments for the kinetics for a 2.5 mole/L aqueous monoethanolamine (MEA) solution were conducted.

7.2. Theory

7.2.1. Reaction Mechanism

In aqueous environment, 1,6 Hexamethyldiamine and 1,6 Hexamethyldiamine, N,N' di-methyl can react with CO_2 to form many different reaction products., 1,6 Hexamethyldiamine is a six carbon chain length diamine with two primary amine functionalities, whereas 1,6 Hexamethyldiamine, N,N' di-methyl, is a six carbon chain length diamine with two secondary amine functionalities.

In aqueous 1,6 Hexamethyldiamine and 1,6 Hexamethyldiamine, N,N' di-methyl solution, CO_2 can react with two primary amine or secondary amine group according to the following reactions:

Reaction (1): $R_1HNR_2NHR_1 + CO_2 + B \leftrightarrow R_1HNR_2NR_1COO^- + BH^+$

Reaction (2): $R_1HNR_2NR_1COO^- + CO_2 + B \leftrightarrow COO^-R_1NR_2NR_1COO^- + BH^+$

Reaction (3): $CO_2 + OH^- \leftrightarrow HCO_3^-$

Reaction (4): $CO_2 + H_2O \leftrightarrow H_2CO_3$

Where
R_1=CH_3 for HMDA, N,N' and R_1 = H for HMDA; R_2 = $(CH_2)_6$; B is any base present in solution ($R_1HNR_2NHR_1$, $R_1HNR_2NR_1COO^-$, + $R_1^+H_2NR_2NHR_1$, H_2O, OH^-).

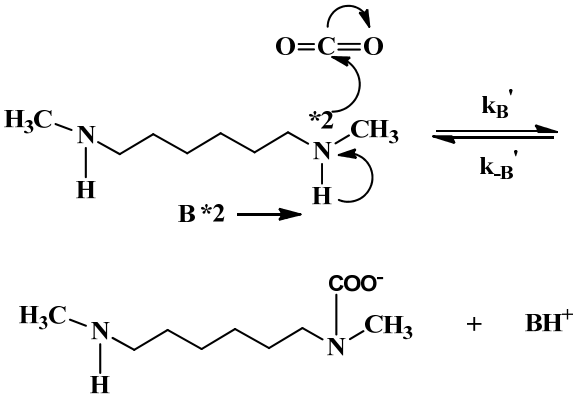
In principle, a diamine molecule (both for HMDA as well as for HMDA, N,N') can serve both as carbamate-former and proton-acceptor (base), leading to:

Reaction (5): $^+H_2R_1NR_2NHR_1 + CO_2 \leftrightarrow {}^+H_2R_1NR_2NR_1COO^-$

The aim of this work is to determine the overall CO_2 absorption kinetics and to identify if possible the most important reaction(s) and the corresponding mechanism(s) and kinetic constant(s) between CO_2 and the two amine groups present in 1,6 Hexamethyldiamine and 1,6 Hexamethyldiamine, N,N' di-methyl. Two well-known reaction mechanisms, discussed below, are generally used to describe the reaction between CO_2 and aqueous amines and are used to derive rate equations to correlate the kinetic rate constant(s).

7.2.2. Termolecular mechanism

Initially proposed by Crooks and Donnellan et al. 1989, the mechanism assumes that the amine bonding to CO_2 and the proton-transfer take place simultaneously. The mechanism was recently reviewed by da Silva and Svendsen et al. 2004. The reaction of the two secondary group of 1,6 Hexamethyldiamine, N,N' di-methyl with CO_2 is illustrated below:



(6)

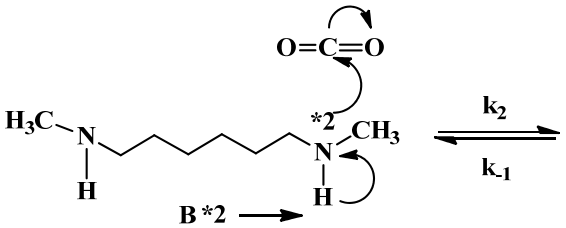
In above mechanism '*2' represents two loan electrons present at nitrogen and at base atom. For the carbamate formation reactions, with HMDA (or HMDA, N,N') and water as the dominating bases the forward reaction rate can be expressed as follows:

$$R_{CO2} = -\left(k_3^{am}\left[R_1HNR_2NHR_1\right] + k_3^{H2O}\left[H_2O\right]\right)\left[CO_2\right]\left[R_1HNR_2NHR_1\right] \qquad (7)$$

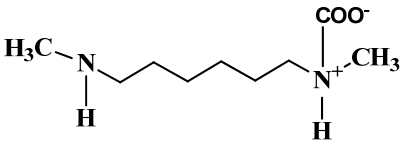
In this equation the reaction rate expressions for the termolecular reaction in which water acts as a base and the one in which $R_1HNR_2NHR_1$ acts as a base are added.

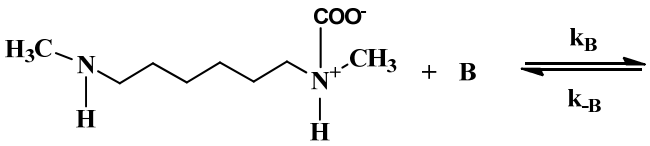
7.2.3. Zwitterion mechanism

Initially proposed by Caplow et al. in 1968 and reintroduced by Danckwerts et al. in 1984 this mechanism predicts the carbamate formation to proceed in two-steps, i.e. the reaction between CO_2 and the amine proceeds through the formation of a zwitterion (reaction for the secondary diamine HMDA, N,N' illustrated in (8a)) and the subsequent deprotonation of the zwitterions by a base B (secondary group see (8b))



(8a)





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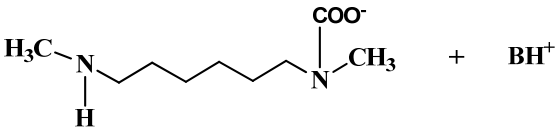

In above mechanism '*2' represents two loan electrons present at nitrogen and at base atom. Assuming the quasi steady-state condition for the zwitterions concentration and an irreversible deprotonation step, the kinetics rate equation is given by:

$$R_{CO2} = \frac{k_2 [CO_2][R_1HNR_2HNR_1]}{1+\frac{k_{-1}}{\sum k_B [B]}} = \frac{[CO_2][R_1HNR_2HNR_1]}{\frac{1}{k_2}+\frac{k_{-1}}{k_2}\frac{1}{\sum k_B [B]}} \qquad (9)$$

Where $\sum k_B[B]$ is the contribution of all bases present in the solution ($R_1NHR_2NHR_1$, $R_1NHR_2NR_1COO^-$, + $R_1^+HNR_2NH^+R_1$, H_2O, OH^-) for the removal of the protons. As e.g. Kumar et al. 2003 pointed out, there are two asymptotic situations for amines in aqueous solution:

In case the deprotonation of the zwitterions is very fast, or $k_{-1}/\sum k_B[B] << 1$, the kinetic equation reduces to simple second order kinetics, as found for primary alkanolamine such as MEA:

$$R_{CO2} = k_2[CO_2][R_1HNR_2NHR_1] \tag{10}$$

The reversed situation of case I occurs when $k_{-1}/\sum k_B[B] >> 1$. Now the kinetic rate expression reduces to Eq.11.

$$R_{CO2} = k_2[CO_2]\ \ [R_1HNR_2NHR_1]\left(\frac{\sum k_B[B]}{k_{-1}}\right) \tag{11}$$

As the reaction order is dependent on the contribution of the individual bases to the deprotonation of the zwitterions, this expression can account for a shift in reaction order in the amine concentration with changing amine concentration. This has been found in the kinetic rate expression for the reaction of CO_2 with many secondary alkanolamines (Versteeg et al., 1996).

Both asymptotic options I and II can not excluded on beforehand. The pKa value of these compounds is higher than the one for MEA, which would -based on the Brønsted plot technique –result in high deprotonation rates and thus could point towards behaviour type I. On the other hand, both amine groups in HMDA, N,N' are in fact secondary amines (like Diethanolamine (DEA)) for which a reaction order for HMDA, N,N' in excess of one is expected. In the case of HMDA and HMDA, N,N' a more specific situation may exist; in case a single diamine molecule simultaneously serves both functions of carbamate formation and proton acceptor.

7.3. Kinetics measurement

The reaction kinetics can be determined from the absorption rate in the reactive solution when measuring in the "pseudo-first-order reaction regime", with $R_{CO2} = k_{ov}[CO_2]$. For this, the following conditions for the Hatta-number (Ha) need to be satisfied (Westerterp et al., 1984):

$$2 < Ha << E_A^{\infty} \tag{12}$$

with

$$Ha = \frac{\sqrt{k_{ov} D_{CO2}}}{k_L} \tag{13}$$

and

$$E_A^{\infty} = \sqrt{\frac{D_{CO2,L}}{D_{Am,L}}}\sqrt{\frac{D_{Am,L}}{D_{CO2,L}}}\frac{[Amine]RT}{\nu_{Am}\, m_{CO2} P_{CO2,G}} \tag{14}$$

assuming the penetration model to be applicable and the reactions to be essentially irreversible. In the above equation the stoichiometric coefficient (ν_{Am}) for HMDA and HMDA, N,N' is one. This value is taken because both amine groups present in

these solvents are located far apart and, hence, it is expected that they will not influence each others reactivity.

As the reaction of CO_2 with amine is basically reversible, the infinite enhancement factor may become lower than suggested by Eq.14. A method to calculate the infinite enhancement factor for reversible reactions is given by Secor and Beutler (1967), and is more recently reviewed by Hogendoorn et al. (1997). The calculation of the infinite enhancement factor taking into account reversibility requires knowledge on the equilibrium constant, which is not available for the system under consideration. In this kinetic study, at the conditions applied, it is assumed that the reaction is essentially irreversible; i.e. the equilibrium is far on the products-side of the equation. This is supported by the low CO_2 equilibrium partial pressures (lower that for equivalent loadings for MEA, see Chapter 6).

For irreversible reactions, normally the Hatta number should be at least be five times smaller than the infinite enhancement factor to meet the condition of a pseudo-n-th order regime as indicated by Eq.12. For reversible reactions this margin should be even higher. In the pseudo-first-order regime the CO_2 absorption rate can then be described by:

$$J_{CO2} = \sqrt{k_{ov} D_{CO2,L}} \frac{m_{CO2} P_{CO2,G}}{RT} \tag{15}$$

In the absorption experiments the overall reaction rate constant was determined per experiment, in line with the following rate expression:

$$R_{CO2} = k_{ov} [CO_2] \tag{16}$$

In situation when CO_2 partial pressure is increased (i.e. results in decrease in infinite enhancement factor), depletion of amine concentration will start to occur at the gas liquid interface. This is an "intermediate regime" in which direct calculation of the kinetic rate constant k_{ov} from the CO_2 absorption flux and corresponding enhancement factor using Eq.15, is not possible. An approximate solution for this intermediate regime was given DeCoursey (1974):

$$E_{DC} = -\frac{Ha^2}{2\left(E_A^\infty - 1\right)} + \sqrt{\frac{Ha^4}{4\left(E_A^\infty - 1\right)^2} + \frac{E_A^\infty Ha^2}{\left(E_A^\infty - 1\right)} + 1} \tag{17}$$

From which Ha, and hence k_{ov}, can be determined from the experimental determined enhancement factor E. Equation 17 is suitable for an irreversible second order chemical reaction and is based on surface renewal theory proposed by Danckwerts. This "intermediate regime" can also be used for reversible chemical

reaction with the knowledge of equilibrium constant of the reaction, due to its influence on infinite enhancement factor. This regime is considered to be less attractive to derive kinetics reliably due to these mutual interactions.

For absorption rate experiments carried out in the pseudo-first-order regime, the flux should be independent of the liquid-side mass transfer coefficient k_L and thus the stirrer speed. This is generally a good check on the fulfilment of pseudo-first-order regime condition in Eq.12. Besides this, in the pseudo-first-order regime a linear relation between the flux and the CO_2 partial pressure is expected. So, even if the exact value of the infinite enhancement factor for the reversible reactions cannot be calculated, the independency of the flux on the stirrer speed and a linear relationship between the flux and the CO_2 partial pressure indicates that Eq.13 is fulfilled. As can be seen in Eq.16, the calculation of k_{ov} from the absorption flux requires, amongst other things, knowledge of the physical solubility parameter (m_{CO2}) for CO_2 in the reactive solutions is under consideration. Physical solubility parameter (m_{CO2}) for CO_2 will be determined via solubility measurements of the chemically inert N_2O in the reactive solutions and using the well-established N_2O-CO_2 analogy.

7.4. Experimental procedure

Experiments were performed in a (closed) stirred cell reactor (see Fig. 2). Carbon dioxide could be fed to the reactor from two gas supply vessel that had volumes of ~325 and ~85 ml, respectively, or directly from the gas cylinder. The pressure in the reactor, which has a volume of ~720 ml, could be kept constant by a pressure controller. The stirred cell, is a double walled glass reactor with thermostat, was closed by stainless steel flanges. Two separate operating stirrers were used to stir the gas and liquid phase separately.

A pressure transducer was connected on the reactor for monitoring the pressure in the reactor, and second one was connected to the gas supply vessels for determining the pressure in these vessels.

The experimental set-up allowed two operation modes:

Semi-batch operation: In this operation mode the pressure in the reactor was kept constant, and the pressure drop against time was measured in the gas supply vessel. In the pseudo-first order regime, the relation between the pressure and time in the gas supply vessel can be obtained from an instationary mass balance Hogendoorn et al., 1995.

$$P_{CO2,G,SupplyVessel}\Big|_t = P_{CO2,G,SupplyVessel}\Big|_{t=0} - \sqrt{K_{ov}\, D_{CO2,L}}\, \frac{m_{CO2} P_{CO2,G,Reactor}}{V_{G,SupplyVessel}}.t \quad (18)$$

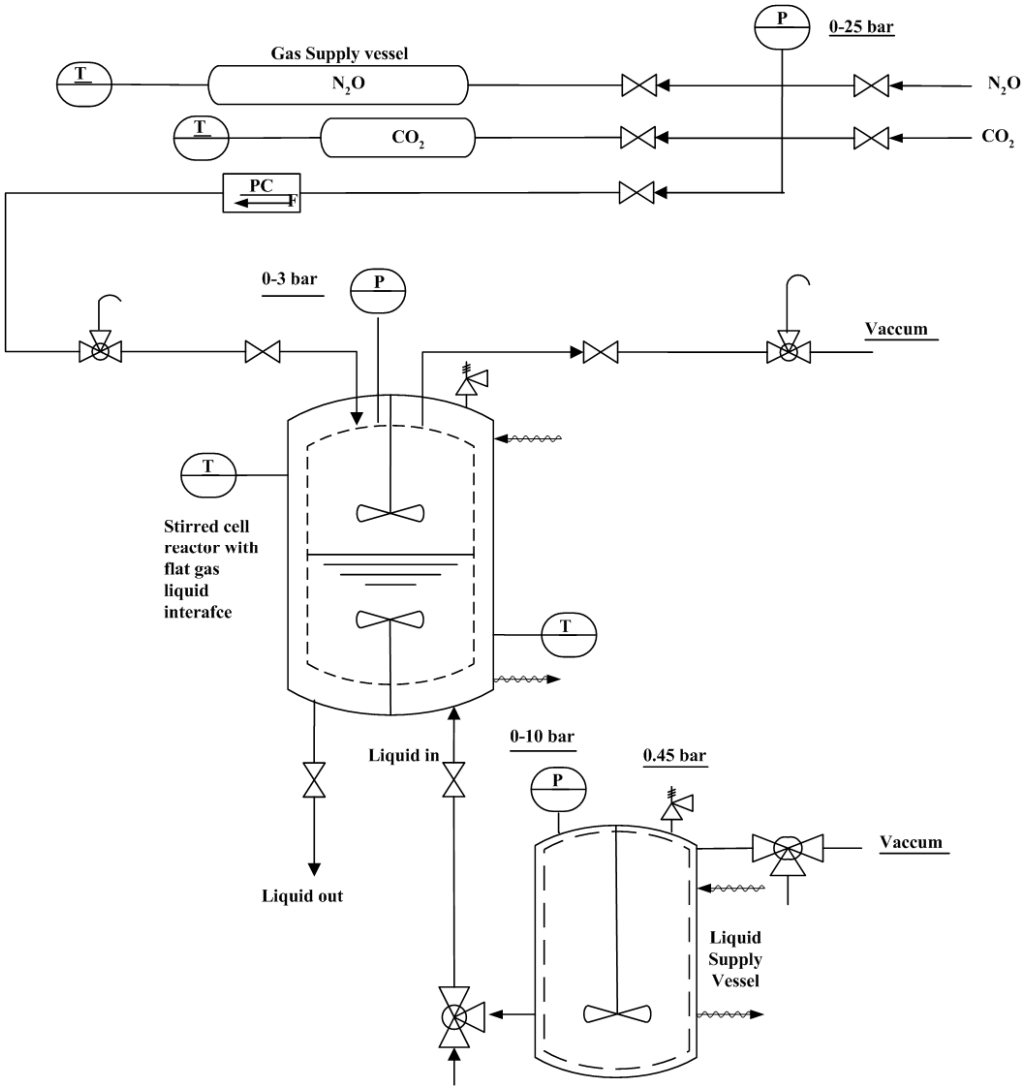

Figure 2, Schematic representation of the stirred cell reactor set-up.

Total batch operation: After admittance of the batch of gas, the reactor was closed, and the pressure drop in the reactor against time was measured. The relation between the pressure and time in the reactor, when closed, is given by Blauwhoff et al., 1984.

$$\ln P_{CO2,G,Reactor}\big|_t = \ln P_{CO2,G,Reactor}\big|_{t=0} - \sqrt{K_{ov}\, D_{CO2,L}}\,\frac{m_{CO2} A}{V_{G,Reactor}}.t \qquad (19)$$

When the reaction rate of CO_2 with the amine based absorbents is high (as expected with secondary amine), large Hatta numbers will be obtained. A large Hatta number has the consequence that the CO_2 partial pressure in the reactor must be very low (and hence the total pressure close to the water vapour pressure), to satisfy the second condition as stated by Eq.12 (Ha << E_A^{∞}).

7.5. Physical constants

7.5.1. Density, Viscosity and Diffusion coefficient

The density of 1,6 Hexamethyldiamine and 1,6 Hexamethyldiamine, N,N' di-methyl solution with concentration ranging from 1 up to 5 mole/L was measured with a commercial density meter (DMA-4500M, Anton Paar GMbH) at temperature ranging from 293 up to 353K.

Table 1, Density (kg.m-3), viscosity and estimated CO_2 diffusion coefficient of aqueous solution of 1,6 Hexamethylenediamine (HMDA) and 1,6 Hexamethylenediamine, N,N' di-methyl (HMDA,N,N').

Solvent	**Conc.**	**Temp.**	**Viscosity**	**Density**	**CO_2 Diffusion Coefficient**
	Mole. L^{-1}	K	Pa. sec	kg. m^{-3}	m^2. sec^{-1}
1,6 Hexamethylenediamine					
(HMDA)	1.01	293	1.8E-03	990.0	1.1E-09
		313	1.1E-03	981.5	1.8E-09
		333	7.0E-04	970.6	2.6E-09
	2.50	293	3.6E-03	976.6	6.6E-10
		313	1.9E-03	964.4	1.2E-09
		333	1.2E-03	950.9	2.0E-09
	5.04	313	5.2E-03	920.4	5.8E-10
		333	2.7E-03	904.1	1.1E-09
		353	1.7E-03	887.2	1.9E-09
1,6 Hexamethylenediamine, N, N' di-methyl					
(HMDA, N, N')	2.50	293	1.0E-02	977.3	3.0E-10
		313	4.6E-03	963.9	6.4E-10
		333	2.5E-03	949.4	1.2E-09

Table 1, shows the measured density for aqueous solution of 1,6 Hexamethyldiamine and 1,6 Hexamethyldiamine, N,N' di-methyl at different concentration and temperature. The viscosities of 1,6 Hexamethyldiamine and 1,6 Hexamethyldiamine, N,N' di-methyl solution with concentration ranging from 1 up to 5 mole/L was measured with an Ubbelohde-type viscometer at temperature ranging from 293 up to 353K. The viscometer was immersed in a large oil bath. The temperature was controlled with a constant temperature circulator to within ±0.05K. From the efflux time, the kinematic viscosity was calculated from the equation:

$$v = Ct \tag{20}$$

Where v is the kinematic viscosity; 'C' is a constant specific to the viscometer; t is the efflux time. End effect corrections were neglected in the calculation of the kinematic viscosity. The constant, 'C' in Eq.20 is given for each viscometer. Table 1, shows the measured viscosity for aqueous solution of 1,6 Hexamethyldiamine and 1,6 Hexamethyldiamine, N,N' di-methyl solution at different concentration and temperature. Each reported measurement was repeated with a maximum deviation in the kinematic viscosity of approximately ±0.05%.

A modified Stokes-Einstein relation given in Eq.21 (van Holst et al., 2009), was used to estimate the diffusion coefficient of CO_2. This CO_2 diffusion coefficient will be used in the determination of the kinetics using Eq.18 or Eq.19.

$$\left(D_{CO2,L}.\eta^{0.74}\right)_{H2O} = \left(D_{CO2,L}.\eta^{0.74}\right)_{Amine} \tag{21}$$

The diffusivity of CO_2 in water, as required in Eq.21, was determined with the following correlation by Versteeg and van Swaaij, 1988:

$$D_{CO2,Water} = 2.35\times10^{-6}.\exp\left(\frac{-2119}{T}\right) \tag{22}$$

The dynamic viscosity shown in Table 2, for 1,6 Hexamethyldiamine and 1,6 Hexamethyldiamine, N,N' di-methyl was determined by Eq.20. Table 1, shows the estimated diffusion coefficient for CO_2 in aqueous solution of 1,6 Hexamethyldiamine and 1,6 Hexamethyldiamine, N,N' di-methyl at different concentrations and temperatures.

7.5.2. Liquid side mass transfer coefficient (kL) and Physical Solubility (m)

The liquid-side mass transfer coefficient and physical solubility of N_2O in the actual aqueous amine solution used were measured simultaneously in a series experiments at various amine concentration and temperatures. These experiments were performed in the same experimental set-up as mentioned above, using the

batch mode procedure for gas absorption. In a typical experiment first a known volume of degassed aqueous amine solution was transferred into the reactor. Once the solvent reached equilibrium with temperature and its vapour pressure is recorded, N_2O gas was fed to the reactor from a N_2O gas cylinder, till a certain pressure is reached in the reactor. The volume of N_2O gas supply cylinder is 320ml.

Table 2, Liquid-side mass transfer coefficient, k_L, the physical solubility parameter, m_{N2O}, for N_2O and the estimated CO_2 solubility parameter, $m_{CO2,}$ in aqueous solutions of 1,6 Hexamethylenediamine (HMDA) and 1,6 Hexamethylenediamine, N,N' di-methyl (HMDA, N,N').

Solvent	**Conc.**	**Temp.**	**k_L**	**m, N_2O**	**Estimated CO_2 distribution coefficient, mCO_2**
	Mole $.L^{-1}$	K	m $.sec^{-1}$	(-)	(-)
1,6 Hexamethylenediamine					
(HMDA)	0.51	298	-	0.56	0.76
		303	-	0.50	0.69
		313	-	0.43	0.61
	1.01	298	1.2E-05	0.49	0.67
		303	1.3E-05	0.43	0.60
		313	1.9E-05	0.35	0.50
	2.56	298	1.0E-05	0.50	0.68
		303	1.2E-05	0.47	0.65
		313	1.9E-05	0.42	0.59
	5.04	313	1.1E-05	0.56	0.76
		333	1.8E-05	0.58	0.80
1,6 Hexamethylenediamine, N, N' di-methyl					
(HMDA, N, N')	2.50	299	9.0E-06	0.53	0.72
		304	9.5E-06	0.48	0.66
		315	1.4E-05	0.47	0.66
		334	2.6E-05	0.43	0.64

It should be noticed that during the gas feeding time the gas and liquid phase stirrer were stopped in order to minimize absorption of the N_2O during this time period. Once the N_2O gas is fed, the reactor is closed and the gas and liquid phase stirrer were switched on. The pressure drop over time in the reactor was recorded. The physical solubility of N_2O in the aqueous amine based absorbents was measured in the reactor vessel, having a volume of 700 ml, which was kept at the desired temperature and filled with the known volume of around 400 ml of solution by measuring the pressure drop due to absorption of the N_2O, The physical solubility of CO_2 was estimated using CO_2-N_2O analogy Laddha et al. 1981. Table 2, shows the results from 1,6 Hexamethylenediamine (HMDA) and 1,6 Hexamethylenediamine, N,N' di-methyl (HMDA, N,N'). It should be noticed that the liquid phase stirrer speed was kept constant during all experiments at approximately 130 rpm.

7.6. Results and Discussion

7.6.1. Validation of the experiment set-up

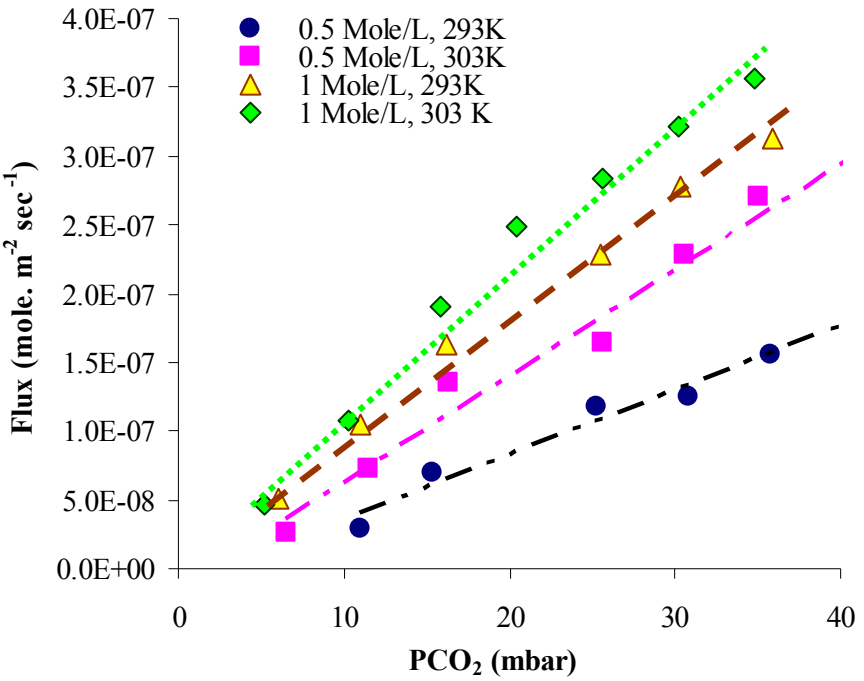

Figure 3, Comparison of CO_2 absorption flux (mole. m^{-2} sec^{-1}) in aqueous solution of 1,6 Hexamethylenediamine (HMDA) at 0.5 and 1.0 mole/L and temperatures of 293 and 303 K from batch mode experiments.

First experimental validation of the experiment set-up was carried out using operation mode 2 (see section experimental procedure) and using aqueous a solution of 2.5 mole/L Monoethanolamine (MEA) at 298K. The CO_2 absorption into an aqueous MEA solution was chosen in the present study because of its large collection of kinetic data available in literature. The second order rate constant for 2.5 mole/L MEA solution at 298K was found to be 5.52×10^3 L/ mole sec, which implies that for MEA the k_2 values determined in this study are in good agreement with published data, especially those reported by Aboudheir et al. 2003. This confirms that the experimental equipment and procedure can be used to determine CO_2 reaction kinetics fairly accurate. From Eq.15 it should be noticed that a plot of the flux versus CO_2 partial pressure at the interface will yield straight line. Figure 3, shows results of absorption experiments at 293 K and 303 K with varying CO_2 partial pressure for two amine concentrations of aqueous solutions of Hexamethylenediamine (HMDA; at 0.5 and 1 mole/L). Only experiments carried out in the regime where a linear relationship existed between pressure and flux were used in the interpretation of the experiments into reaction kinetics, as those experiments were carried out in the pseudo first order regime. It was checked experimentally that the absorption flux did not change on variation of the stirrer speed (while maintaining a flat interface). The CO_2 loading for each experiment was very low; maximally approximately 0.05 mole of CO_2 per mole of amine. The same procedure was followed for the aqueous solutions of 1,6 Hexamethylenediamine, N, N' di-methyl (HMDA, N, N').

7.6.2. Kinetics of Aqueous solution of 1,6 Hexamethylenediamine (HMDA) and 1,6 Hexamethylenediamine, N,N' di-methyl (HMDA, N,N')

The overall absorption kinetics of the CO_2 absorption reaction with aqueous 1,6 Hexamethylenediamine (HMDA) was determined at concentrations of 0.5, 1 and 2.5 mole/L and temperature ranging from 283 till 303 K. For the reaction of CO_2 with aqueous solution of 1,6 Hexamethylenediamine, N,N' di-methyl (HMDA, N,N') kinetics was determined at 0.5 mole/L concentration and temperature ranging from 283 till 303 K. Table 3, shows the overall kinetics determined by experiments for 1,6 Hexamethylenediamine (HMDA) and 1,6 Hexamethylenediamine, N,N' di-methyl (HMDA, N,N'). A list of governing Hatta numbers and corresponding (irreversible) infinite enhancement factors (according to Eq.12) is presented in Table 3.

Table 3, shows that in all cases the Hatta number is larger than two, but also that the ratio between the calculated instantaneous enhancement factor and the Hatta number is such that influence of diffusion on transport can not be fully excluded. Hence, although the experimental checks on mass transfer limitations were negative (i.e. no effect of stirrer speed and linear dependence on CO_2 partial pressure), it was decided to use the DeCoursey approach to determine the Hatta number from the experimentally determined enhancement factor. The ratio of the

diffusion coefficient of HMDA and HMDA, N,N' to that of CO_2, as required for the calculation of infinite enhancement factor, was estimated using the Wilke-Chang method.

Table 3, Experimental data on absorption rate for aqueous solution of 1,6 Hexamethylenediamine (HMDA), 1,6 Hexamethylenediamine, N,N'di-methyl (HMDA, N,N') and equimolar concentration of 1,6 Hexamethylenediamine (HMDA) and Hydrochloric acid (HCl).

Solvent	**Conc.**	**Temp.**	**P_{CO2}**	**$m_{CO2} . (k_{ov} . D_{CO2})^{0.5}$**	**k_{ov}**	**Ha**	**E_{inf}**
	Mole $.L^{-1}$	K	mbar	m $.sec^{-1}$	sec^{-1}	(-)	(-)
1,6 Hexamethylenediamine							
(HMDA)	0.51	283	11.2	1.9E-03	4.4E+03	135	1.1E+03
	0.51	295	11.2	2.7E-03	8.5E+03	274	1.3E+03
	0.51	304	6.7	3.2E-03	1.3E+04	341	2.6E+03
	1.01	284	8.4	3.1E-03	1.5E+04	243	3.2E+03
	1.01	293	10.3	3.8E-03	2.5E+04	458	3.1E+03
	1.01	304	10.6	4.3E-03	3.5E+04	544	3.8E+03
	2.56	283	9.4	4.2E-03	8.2E+04	444	8.1E+03
	2.56	293	8.9	5.7E-03	1.0E+05	837	9.5E+03
	2.56	303	9.4	7.0E-03	1.2E+05	909	9.9E+03
1,6 Hexamethylenediamine, N, N' di-methyl							
(HMDA, N, N')	0.51	284	8.3	3.1E-03	1.1E+04	213	1.5E+03
	0.51	294	8.2	3.7E-03	1.6E+04	370	1.8E+03
	0.51	303	9.1	4.1E-03	2.0E+04	431	2.0E+03
1,6 Hexamethylenediamine + Hydrochloric acid							
(HMDA : HCl)	1:1	293	8.4	3.7E-03	2.4E+04	451	3.9E+03

Figure 4 and Table 3, show the effect of temperature on the overall rate constant for 1,6 Hexamethylenediamine (HMDA) and 1,6 Hexamethylenediamine, N,N' di-methyl (HMDA, N,N'). It is clear from these results that the temperature and concentration are affecting kinetics for CO_2 absorption. It can be noticed that the absorption kinetics for 0.5 mole/L HMDA, N,N' are significantly faster than that for 0.5 mole/L HMDA. Figure 5, shows the effect of concentration for the overall rate constant at different temperature for 1,6 Hexamethylenediamine (HMDA).

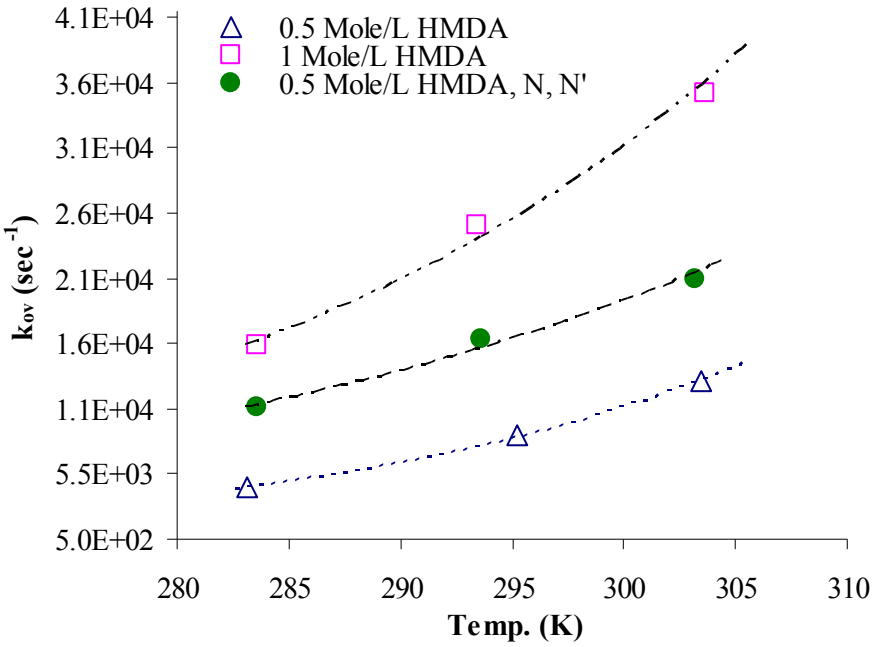

Figure 4, Effect of temperature on overall reaction rate k_{ov} (sec^{-1}) for 1,6 Hexamethylenediamine (HMDA) and 1,6 Hexamethylenediamine, N,N' di-methyl (HMDA, N,N').

Starting from Eq.9, derived for the zwitterion model, it was found by model analysis, when trying to fit the shapes of the curves for the different temperature series, that $k_{-1} / \sum k_B [B]$ decreases with increasing temperature and amine concentration, having a value in the range of around 1 to 10, hence intermediate to the extremes indicated by Eq.10 and 11. Furthermore, it appears that both amine and water play a role and that the temperature dependency (activation energy) for the deprotonation reaction with the dominating base (k_B) is significant higher (around factor 10) than the one for the reverse reaction (k_{-1}).

Table 4, shows that the determination of the kinetics using Eq.17, gives and overview of the overall kinetics constant with an uncertainty of 10-33%. To evaluate further a graphical representation between all experimentally observed enhancement factors and the calculated Hatta numbers based on DeCoursey approximation-using the kinetics presented in Table 4, and physical constants presented in Table 3 and 2, is shown in Figure 6. It can be noticed from Figure 6, that the experimental absorption rates presented in Table 3, and predictions from the DeCoursey equation are in good agreement with each other.

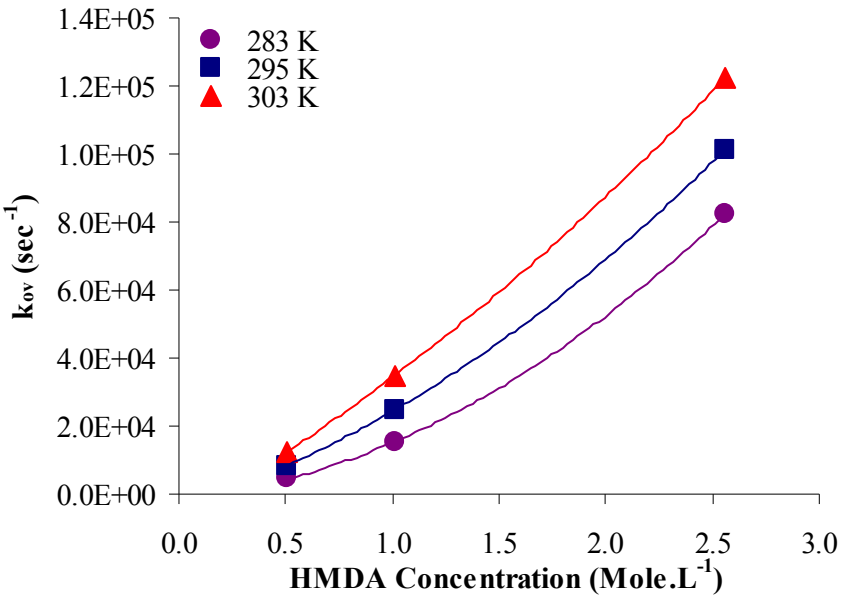

Figure 5, Effect of temperature on overall reaction rate k_{ov} (sec^{-1}) for 1,6 Hexamethylenediamine (HMDA) and 1,6 Hexamethylenediamine, N,N' di-methyl (HMDA, N,N').

When using the reaction equation derived for the termolecular mechanism, Eq.7, a nearly similar fit of the data can be obtained. On basis of the limited data set, no discrimination can be made with respect to the reaction mechanism for the carbamate formation. The suggested bimolecular mechanism, where one amine group of the molecule acts as proton acceptor and the other one as carbamate former, is not likely, (especially at the lower temperature) as this would suggest linear relationships between k_{ov} and the amine concentration, which was not observed for the experiments at 283K and 295K.

To be able to compare the corresponding second order rate constant from the apparent kinetics k_{ov} resulting from the experimental data and from DeCoursey approximation with literature data, the reaction order was taken one for HMDA and HMDAN,N', in line with the majority of literature on the kinetics of CO_2 with a wide variety of aqueous (alkanol)amines. Table 4, shows the kinetic rate constant (k_2) based on experiment data and DeCoursey approximation method. It can be noticed from Table 4, that the DeCoursey relation (based on an irreversible enhancement factor) for HMDA shows similar reaction rate value as calculated from experimental data. The results obtained with the DeCoursey relation are considered to be the most accurate, since the pseudo first order criteria are may not

be fully satisfied (see Table 3). The second order rate constant obtained from DeCoursey approximation is used in further discussion.

Table 4, Results from the reinterpretation of the experimental kinetics date based on DeCoursey approximation method.

Solvent	Conc.	Temp.	Ha - PFO[a]	k_{ov}-PFO	Ha-DC[b]	k_{ov}-DC	k_2 -PFO	k_2-DC
	Mole $.L^{-1}$	K	(-)	sec^{-1}	(-)	sec^{-1}	L $.mole^{-1}$ $.sec^{-1}$	L^1 $.mole^{-1}$ $.sec^{-1}$
1,6 Hexamethylenediamine								
(HMDA)	0.51	283	135	4.4E+03	138	4.4E+03	8.4E+03	8.7E+03
	0.51	295	274	8.5E+03	307	1.1E+04	1.5E+04	2.1E+04
	0.51	304	341	1.3E+04	373	1.5E+04	3.2E+04	3.0E+04
	1.01	284	243	1.5E+04	241	1.5E+04	1.7E+04	1.5E+04
	1.01	293	458	2.5E+04	490	2.8E+04	2.4E+04	2.8E+04
	1.01	304	544	3.5E+04	601	4.2E+04	4.0E+04	4.2E+04
	2.56	283	444	8.2E+04	434	7.9E+04	2.5E+04	3.1E+04
	2.56	293	837	1.0E+05	857	1.1E+05	3.4E+04	4.1E+04
	2.56	303	909	1.2E+05	966	1.4E+05	4.8E+04	5.4E+04
1,6 Hexamethylenediamine, N, N' di-methyl								
(HMDA, N, N')	0.51	284	213	1.1E+04	220	1.1E+04	2.1E+04	2.2E+04
	0.51	294	370	1.6E+04	413	2.0E+04	3.1E+04	3.9E+04
	0.51	303	431	2.0E+04	506	2.8E+04	4.0E+04	5.6E+04
1,6 Hexamethylenediamine + Hydrochloric acid								
(HMDA : HCl)	1:1	293	451	2.4E+04	473	2.6E+04	2.4E+04	2.6E+04

PFO= Pseudo First Order; DC = DeCoursey.
[a]Hatta number is calculated by assuming pseudo first order behaviour (Table 3).
[b]Hatta number is calculated by data regression.

When assuming that the reaction rate for 1,6 Hexamethylenediamine is first order in the amine concentration and first order in CO_2, Figure 7, shows the comparative data for the second order rate constant of 2.5 mole/L 1,6 Hexamethylenediamine (HMDA) with the literature value of 2.5 mole/L MEA from Aboudheir et al. 2003 and 2.5 mole/L Ethylenediamine (EDA) from Li et al. 2007.

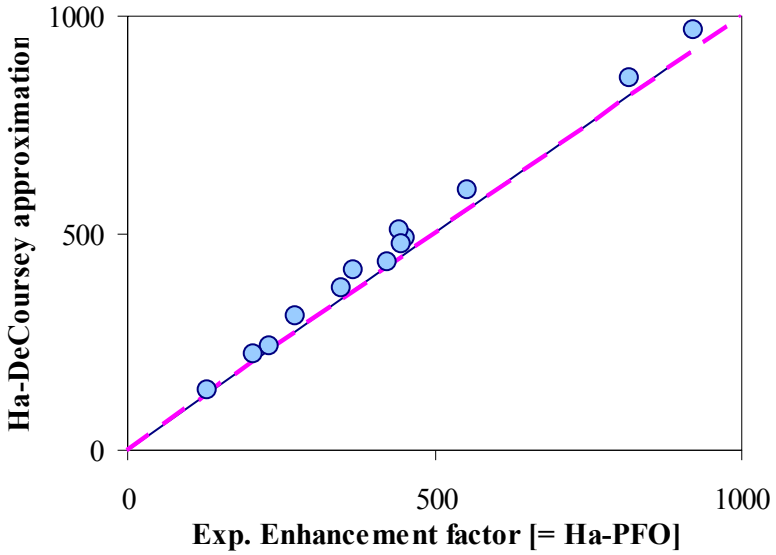

Figure 6, Parity plot of experimental enhancement factor and Hatta number from DeCoursey approximation using the irreversible infinite enhancement factor.

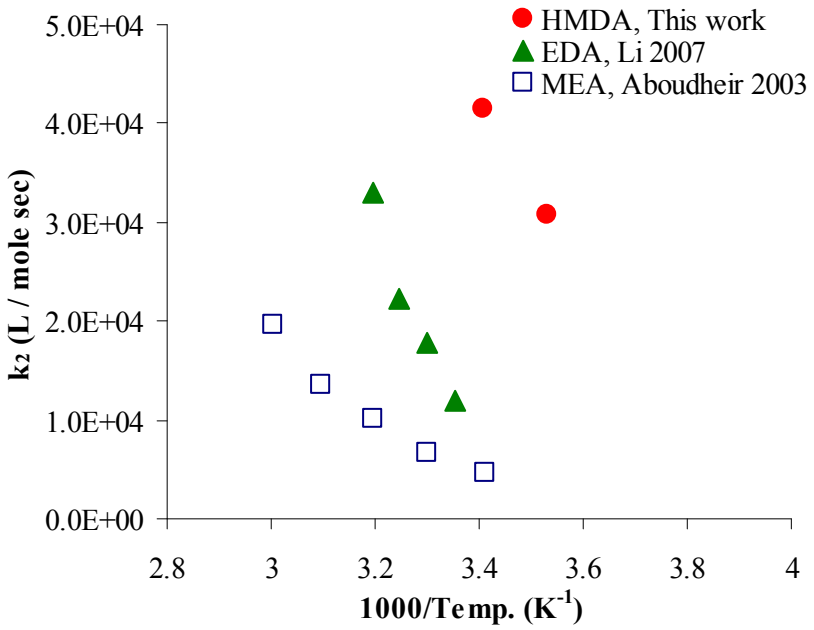

Figure 7, Comparison of second order reaction rate constants for HMDA, EDA (Li, 2007) and MEA (Aboudheir et al. 2003), 2.5 mole/L.

Figure 7, shows that 1,6 Hexamethylenediamine shows an almost 10 times higher intrinsic kinetic rate constant than for MEA. It is interesting to notice that the intrinsic kinetic rate constant for the HMDA (6 carbon chain length diamine) is much higher than for the EDA (2 carbon chain length diamine).

The data presented in presented in Table 3, for all HMDA concentration and temperature is used to study the mechanism of HMDA and CO_2 reaction. A log-log plot was made between apparent kinetics rate k_{ov} versus amine concentration to identify the reaction order with respect to HMDA. From the experimental data, the apparent reaction order for 1,6 Hexamethylenediamine (HMDA) was found to be in the range of 1.4 (for 303 K series) till 1.8 (for the 283 K series) with an average of about 1.5.

Correlation of the apparent, indicative rate constants as a function of temperature, obtained for HMDA and using the two different mechanistic models (one based on the zwitterion mechanism and one on basis of the termolecular mechanism) and one correlation based on simple, overall power-law kinetics results in as follows:

The Zwitterion mechanism:

$$k_2 = 2.0\times10^{6}\ \exp\left[-\frac{2500}{T}\right] \quad (\text{for } k_{-1} = 1.10^{-5}\ s^{-1}) \tag{22}$$

$$k_3^{am} = 5.10^{-10}\ \exp\left[-\frac{120}{T}\right] \tag{23}$$

$$k_3^{H2O} = 4.5\times10^{-6}\ \exp\left[-\frac{4000}{T}\right] \tag{24}$$

The Termolecular mechanism:

$$k_3^{am} = 2.00\times10^{4}\exp\left[-\frac{4400}{T}\right] \tag{25}$$

$$k_3^{H2O} = 1.0\exp\left[-\frac{2300}{T}\right] \tag{26}$$

Or using powerlaw kinetics: $$k_2 = 2.5\cdot10^{6}\ \exp\left[-\frac{4400}{T}\right][Am]^{1.5} \tag{27}$$

The average error using these correlations show average deviations of around 15% with a maximum of around 30-40% Above correlations are therefore only useful as first estimation for temperatures ranging from 283-303K and HMDA concentration from 0.5 to 2.5 mole/L.

Table 5, The second order rate kinetics of various amines.

Solvent	k_2 L .mole^{-1} .sec^{-1}	pKa	Temp. K	Conc. Mole/L	Source
HMDA	4.2E+04	10.8	304	1	This work
HMDA, N,N'	5.6E+04	11.1*	303	0.5	This work
EDA	1.7E+04	9.8	303	0.26 - 0.67	J. Li et. al. 2007
DETA	3.5E+04	9.5^{+}	305	1	A. Hartono et. al. 2009
Pz	9.0E+04	9.7	303	1	P. Derks et. al. 2006
MEA	6.7E+03	9.3	303	1	A. Aboudheir et. al. 2003
DEA	5.1E+03	8.9	303	1	E. B. Rinker et. al. 1996

Experimental pKa values at 303K taken from literature Perrin (1665). +pKa value at 303K estimated from correlation proposed by Hartono 2009, *pKa value at 293K estimated by ACD/pK_a software.

For the absorption of CO_2 in aqueous solution of 1,6 Hexamethylenediamine (HMDA) and 1,6 Hexamethylenediamine, N,N' di-methyl (HMDA, N,N') no literature data is available for comparison. Therefore in Table 5, the rate constant (DeCoursey approximation) for 1,6 Hexamethylenediamine (HMDA) and 1,6 Hexamethylenediamine, N,N' di-methyl (HMDA, N,N') is shown together with results for Diethylenetriamine, DETA (Hartono et al., 2009), Ethylenediamine, EDA (Li et al., 2007), Piperazine, Pz (Derks, 2006) and Monoethanolamine, MEA (Aboudheir et al., 2003). The results suggested that 1,6 Hexamethylenediamine (HMDA) and 1,6 Hexamethylenediamine, N,N' di-methyl (HMDA, N,N') show significantly faster kinetics than MEA, DEA and DETA, but lower than Piperazine, which has a cyclic structure.

Possibly, an intramolecular cyclic configuration adds to the reactivity of the HMDA species. The positive effect of cyclic structures was earlier recognized by Cullinanne and Rochelle 2006. Figure 8, shows the Brønsted relationship HMDA, HMDA, N,N' and other primary and secondary amine based solvents. It should be noticed that the experimental pKa (basicity) values presented in Table 5 and Figure 8, are taken from literature (Perrin 1665). In Figure 8 and Table 5, pKa value for DETA at 303K was estimated by correlation give in literature (Hartono 2009). Due to unavailability of experimental pKa data for solvent HMDA, N,N', this pKa value for HMDA, N,N' was estimated by use of ACD/pK_a software (avg. error of 0.5%) at 293K. In Figure 7, the linear correlation between the logarithm of k_2 (m^3 / mole .sec) and pKa for temperatures up to 303K for primary and secondary

aqueous alkanolamine, as proposed by Versteeg and van Swaaij 1996 (Eq.28) is presented as a straight line.

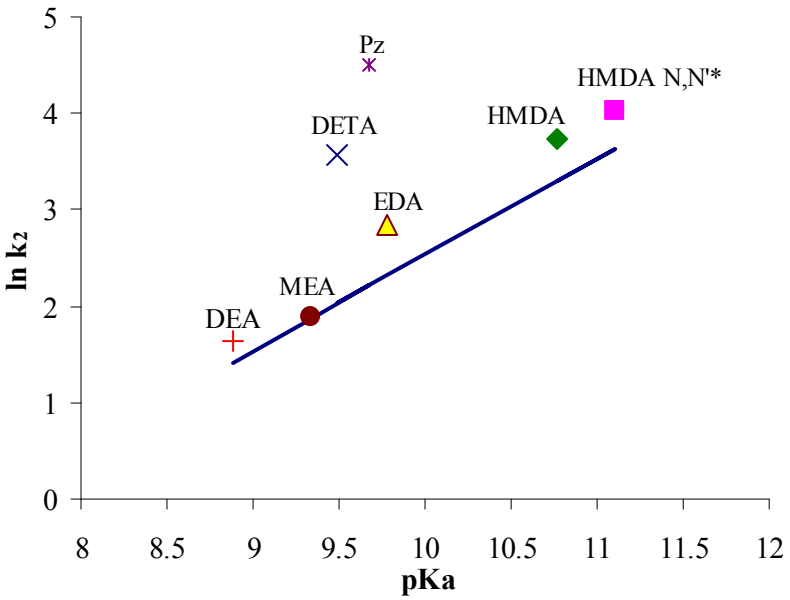

Figure 8, Brønsted plot for primary and secondary amine based solvents at 303K *pKa value is at 293K estimated by ACD/pK_a software.

$$\ln k_2 = pKa + 17.60 - \left(\frac{7188}{T}\right) \tag{28}$$

In Figure 8, Piperazine is much higher compared to other primary and secondary amine, as it is a cyclic amine, for which probably a different Brønsted relationship exists (Derks, 2006). Similarly, the deviation of DETA could be due to the presence of two primary and one secondary amine group present in its molecular structure. It can be noticed from Figure 8, that for HMDA, HMDAN,N' and EDA are in similar range and reasonably in line with the correlation by Versteeg and van Swaaij 1996.

7.7. Kinetics of CO_2 with protonated 1,6 Hexamethylenediamine (HMDA)

Considering the effect of molecular structure, it has been mentioned by Albert et al. 1984 that a carbon chain length of more than 4 carbon atoms in between two diamines groups diminishes the influence of these groups on each other. This effect was identified in aliphatic diamine on basis that for more than four carbon atoms the basicity of both amine groups was found to be similar to each other Albert et al.

1984. The effect of carbon chain length on basicity of both amine groups was confirmed in Chapter 2. The HMDA basicity of both amine groups was estimated to be pKa^1 =10.92; pKa^2 =10.13 respectively at 20°C. On this basis for 1,6 Hexamethylenediamine (HMDA) the two primary amine groups at either end of a 6 carbon chain length in between, both amine group should be equally reactive. To test this, a CO_2 absorption experiment was performed in an equimolar (1:1) solution of hydrochloric acid (1 mole/L) and 1,6 Hexamethylenediamine (HMDA) (1 mole/L). Hydrochloric acid (HCl) was chosen, since it, being a strong acid, will protonate the most basic groups in solutions irreversibly and thus converts all HMDA molecules to $HMDAH^+$ (protonated HMDA). For simplicity reasons, it is assumed that the presence of the chloride ions does not influence the reaction (rate) or the mass transfer process, even though it must be noted that its concentration is identical to the $HMDAH^+$ concentration in solution. First, batch mode experiments were performed to determine the CO_2 partial pressure at which the conditions for operating in the pseudo first order regime were satisfied. Apparent pseudo first order behaviour was found at CO_2 partial pressures below about 15 mbar. Again, experimental conditions were adjusted to keep the maximum carbon dioxide loading low to minimize the influence of reversibility of the reaction. In all experiments, the loading never exceeded 0.002 mole CO_2 per mole $HMDAH^+$.

Results from semi batch mode kinetic experiment for (partially) protonated 1,6 Hexamethylenediamine (HMDA) are shown in Table 3 and 4. It is obvious from these results that the molar diamine concentration is more important than the number of amine groups. Since the flux for the partially protonated amine solution is similar to the one for the non-protonated solvent, it seems that both amine groups react individually/independently to CO_2 as the second amine group shows a similar second order rate constant, when the first one is protonated.

7.8. Effect of CO_2 loading on kinetics

In a typical CO_2 absorption process, where the amine solution cycles between absorber and stripper, the amine based solvent is always partially loaded with CO_2. Hence, it is required to identify the effect of such a CO_2 loading on the absorption rate for these new solvent. Kinetic experiments were performed at 293 K for aqueous solutions of 1,6 Hexamethylenediamine (HMDA) and 1,6 Hexamethylenediamine, N,N'di-methyl (HMDA, N,N') at 0.51 mole/L concentration for both solvents. These experiments were performed in semi batch mode and using 20 mbar CO_2 partial pressure in most of the experiments. When the CO_2 loading increased, the CO_2 equilibrium partial pressure increased significantly and the kinetic experiments were performed at higher than 20 mbar CO_2 partial pressure.

Table 6, Experimental data on the effect of CO_2 loading on absorption rate for aqueous solution of 1,6 Hexamethylenediamine (HMDA) and 1,6 Hexamethylenediamine, N,N'di-methyl (HMDA,N,N') at 0.51 Mole/L concentration and 293.14 K temperature.

Solvent	**Conc.**	**Temp.**	**P_{CO2}**	**$m_{CO2} . (k_{ov} . D_{CO2})^{0.5}$**	**CO_2 Loading**	**k_{ov}**
	Mole. L^{-1}	K	mbar	m. sec^{-1}	mole CO_2 / mole amine	sec^{-1}
1,6 Hexamethylenediamine (HMDA)	0.51	294	10.7	2.8E-03	0.06	1.1E+04
	0.51	294	11.1	2.5E-03	0.18	9.0E+03
	0.51	294	10.4	2.3E-03	0.30	6.8E+03
	0.51	294	10.7	2.0E-03	0.41	5.4E+03
	0.51	294	9.6	1.9E-03	0.51	4.6E+03
	0.51	293	11.9	1.2E-03	0.64	1.9E+03
	0.51	293	11.1	8.0E-04	0.87	7.7E+02
	0.51	293	11.1	4.8E-04	0.99	2.7E+02
	0.51	293	12.2	2.9E-04	1.10	9.5E+01
	0.51	293	12.2	2.0E-04	1.21	4.7E+01
	0.51	293	14.2	1.2E-04	1.23	1.6E+01
1,6 Hexamethylenediamine, N, N' di-methyl (HMDA, N, N')	0.51	294	10.4	3.2E-03	0.25	1.3E+04
	0.51	284	9.9	3.2E-03	0.30	1.2E+04
	0.51	294	10.7	3.0E-03	0.46	1.3E+04
	0.51	294	9.6	2.8E-03	0.57	1.1E+04
	0.51	294	10.5	2.3E-03	0.66	7.2E+03
	0.51	294	10.3	1.9E-03	0.81	4.8E+03
	0.51	294	10.2	1.5E-03	0.91	3.1E+03
	0.51	294	10.1	1.2E-03	1.04	1.8E+03
	0.51	294	9.5	1.1E-03	1.17	1.6E+03
	0.51	294	10.3	6.2E-04	1.30	4.6E+02
	0.51	294	7.9	6.5E-04	1.39	5.1E+02
	0.51	294	8.7	4.1E-04	1.48	2.0E+02
	0.51	294	7.1	3.6E-04	1.55	1.5E+02
	0.51	294	11.7	1.4E-04	1.59	2.2E+01
	0.51	293	17.5	1.3E-04	1.62	1.8E+01
	0.51	294	23.8	1.2E-04	1.66	1.7E+01
	0.51	294	17.1	8.8E-05	1.69	9.0E+00
	0.51	294	27.0	4.8E-05	1.72	2.7E+00
	0.51	294	26.0	3.2E-05	1.75	1.2E+00

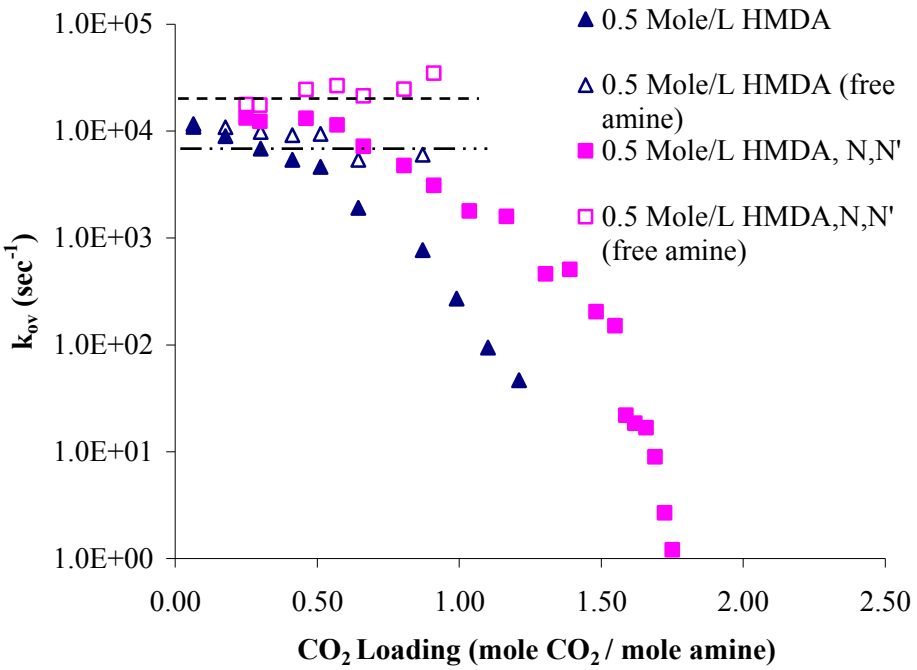

Figure 9, Effect of CO_2 loading on absorption rate in aqueous solution of 0.5 Mol/L 1,6 Hexamethylenediamine (HMDA) and 0.5 Mol/L 1,6 Hexamethylenediamine, N,N'di-methyl (HMDA, N,N') at 293K.

Results from the Table 6 and Figure 9, show that for both HMDA and HMDA, N,N' solvents the apparent overall rate constant decrease drastically as CO_2 loading (α_{CO2})is increasing in the solvent. This decrease in the second order rate constant can largely be explained on the basis of decrease in the free amine and hydroxyl ions concentrations with increasing CO_2-loading in the solution. This is shown in Figure 9, where the k_{ov} value is plotted both as determined on a total amine concentration and as calculated using on a free amine"-basis using k_{ov} (free amine) = k_{ov} / (1-α_{CO2}). Comparable trends for the effect of loading on kinetics were recently published by Simons et al. (2010). For comparable CO_2 loading the kinetics for 1,6 Hexamethylenediamine, N,N'di-methyl (HMDA, N,N') were found in all case to be higher when compared to 1,6 Hexamethylenediamine (HMDA) at the same CO_2 loadings. However, the difference in kinetic rate constant increases strongly with increasing loading, which may suggest that either the reaction orders in the (free) amine concentration are significantly different, or that the HMDA, N,N' species forms more bicarbonate product, resulting in higher remaining free amine concentration at a certain loading.

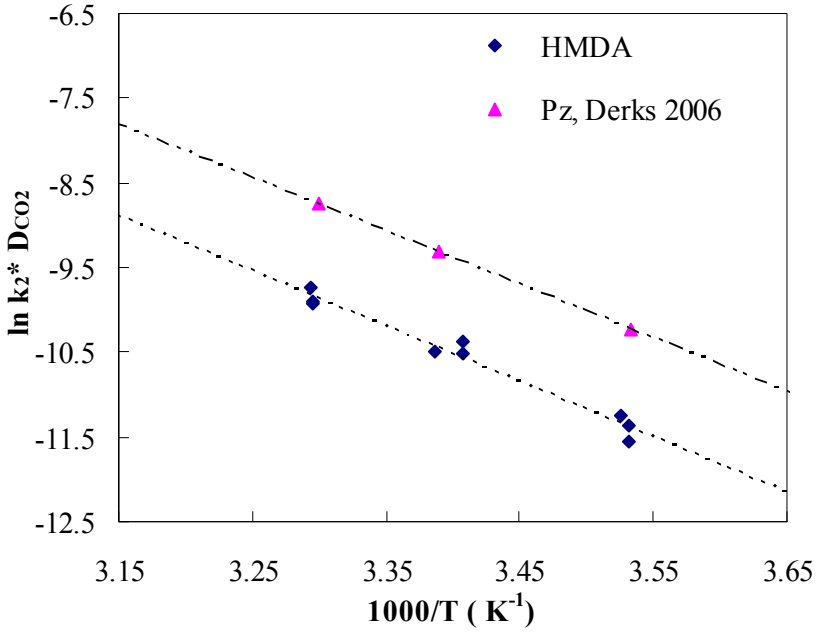

Figure 10, The Arrhenius plot of the second order rate constant for the reaction of CO_2 with aqueous solution of 1,6 Hexamethylenediamine (HMDA) and compared with Piperazine data from Derks 2006.

The temperature dependence of the apparent forward second order kinetic rate constant for 1,6 Hexamethylenediamine (HMDA) can be described by an Arrhenius type relationship for kinetic rate constants (DeCoursey approximation) for 1,6 Hexamethylenediamine (HMDA). Due to lack of experimental diffusion coefficient data, and to avoid the influence from estimated diffusion coefficients, the rate multiplied with diffusion coefficient of CO_2, $k_2.D_{CO2}$ is plotted in Figure 10. Piperazine correlation for second order rate constant and diffusion coefficient with temperature proposed by Derks et al. 2006, is also plotted in Figure 10 for comparison.

The temperature dependence of the apparent forward second order kinetic rate constant and diffusion coefficient for 1,6 Hexamethylenediamine (HMDA) is described by Eq.29 respectively:

HMDA:
$$k_2 \cdot D_{CO2} = 1.2 \cdot 10^5 \cdot \exp\left(-\frac{6.5 \cdot 10^3}{T}\right) \qquad (29)$$

The apparent temperature of the diffusion coefficient of CO_2 in aqueous (amine) solutions is in the order of 2.1 K (see Versteeg et al. 1996). Therefore, activation temperature of the reaction amounts to on an average 4.4 ± 0.3K. Hence, the activation energy for HMDA was found to be close to that for MEA (36.6 kJ/mole, Aboudheir et al., 2003) and Piperazine (35.0 kJ/mole, Cullinanne and Rochelle et al., 2006).

7.9. Conclusion

Kinetics experiments were performed for aqueous solution of concentration ranging from 0.5 till 2.5 mole/L for 1,6 Hexamethylenediamine (HMDA) and 0.5 mole/L for 1,6 Hexamethylenediamine, N,N' di-methyl (HMDA, N,N') at temperature ranging from 283 till 303 K, using a stirred cell reactor set-up. The reaction orders were found to be one for CO_2 and for the amine (1,6 Hexamethylenediamine, HMDA) it varied with temperature between 1.4 to 1.8 with an average of about 1.5 for the range of temperatures investigated. Kinetic experiments using an equimolar concentration of 1,6 Hexamethylenediamine (HMDA) and hydrochloric acid (HCl) showed that the reactivity of the second amine-group (with the first one being protonated) is similar to the reactivity of the first amine group in aqueous HMDA solutions without hydrochloric acid addition. This suggests that there is no mechanistic interaction between the both amine groups of one molecule by an intra molecular cyclisation configuration in the transition state during carbamate formation. Nevertheless, the CO_2 absorption kinetics found are significantly higher than for MEA, which was taken as reference solvent.

Further, the effect of CO_2 loading on the reactivity of the HMDA and HMDA, N,N' solutions was studied and the observed decrease in reactivity could be attributed to a large extent to the decrease in the free amine concentration. From comparison with conventional solvents as MEA, it can be concluded on basis of absorption kinetics that both 1,6 Hexamethylenediamine (HMDA) and 1,6 Hexamethylenediamine, N,N' di-methyl (HMDA, N,N') have potential as new solvent for CO_2 capture.

Nomenclature

A	Gas liquid interface area (m^2)
$D_{i,j}$	Diffusivity of component i in j phase (m^2/s)
E	Enhancement factor (-)
E_A^{∞}/E_{inf}	Infinite enhancement factor defined by Eq.15 (-)

E_{DC}	DeCoursey enhancement factor by Eq.17 (-)
k_2	Second order rate constant (m^3/ mole s)
k_{-1}	Zwitterion mechanism rate constant (/s)
k_B	Zwitterion mechanism deprotonation rate constant, (m^3/ mole s)
$k_{3B'}$	Termolecular mechanism rate constant (m^6 / $mole^2$ s)
k_3^{am}	Deprotonation kinetic rate constant (m^3/ mole s)
$k_3^{H_2O}$	Deprotonation kinetic rate constant (m^3/ mole s)
k_L	Liquid phase mass transfer coefficient (m / s)
k_{ov}	Overall rate constant (/s)
R_{CO2}	Rate of reaction of CO_2 (mole/m^3 s)
m_{CO2}	Physical solubility parameter for CO_2 ($([CO_2]_L/[CO_2]_G)_{eq}$) (-)
$P_{i,j}$	Partial pressure of component I in phase j (kPa)
R	Universal gas constant (8.3143) (J / mole K)
T	Temperature (K)
η	Dynamic viscosity (mPa s)
ν	Stoichiometric coefficient in Eq.15 (-)
α_{CO2}	CO_2 loading (mole CO_2/mole amine)
ρ	Density ($kg.m^{-3}$)

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8
Pilot Plant Evaluation

New amine based solvent formulation for CO_2 recovery from flue gasses have been tested in a continuous flow pilot plant located at Shell Technology Centre, Amsterdam. These new formulations are based on previous screening testes and additional pre-selection test on corrosivity and operability.

Two most promising solvents tested were aqueous solution of 51 wt% New solvent and 26.74 wt% AMP + 11.91 wt% HMDA. Main focus of this study is to identify the energy requirement (MJ/Kg CO_2) for these solvents. In this study CO_2 absorption was done at 40°C, 1.3bar and regeneration at 120ºC, 2.0-2.2 bar. These experiments were performed for 5 and 10 vol% CO_2 inlet concentration. Results from these new solvents were compared to more conventional solvents; aqueous solutions of MEA 31 wt%, AMP 30 wt% + PZ 5 wt% and AMP 35.6 wt%. At 90% (± 3 %) CO_2 recovery 51 wt% New solvent was found to be the most energy efficient 2.48 and 2.46 (MJ/Kg CO_2) for 5 and 10 vol% CO_2 inlet concentration respectively. 26.74 wt% AMP + 11.91 wt% HMDA was found to be having energy requirement of 3.62 and 3.41 (MJ/Kg CO_2) for 5 and 10 vol% CO_2 inlet concentration respectively. The results show that these new solvents have attractive properties for CO_2 removal from flue gas, where energy consumption is an important factor.

8.1. Introduction

Carbon dioxide is a greenhouse gas that contributes to global warming and climate change. Post combustion capture of carbon dioxide (CO_2) is undoubtedly the most versatile technology for mitigating greenhouse gas (GHG) emissions from existing fossil fuel-fired electric power plants. It is also one of the technologies that can supply huge amounts of CO_2 to be used as flooding agent in enhanced oil recovery. One of the most attractive methods to remove CO_2 from diluted, low-pressure gas streams is by absorption with chemical reaction using aqueous alkanolamine solutions. The reference solvent for this type of process is a 30 wt.% aqueous solution of Monoethanolamine (MEA) which, however, has the drawback of a high energy requirement for solvent regeneration, leading to an efficiency penalty up to 15 percentage points in the efficiency of fossil fuelled power plants.

A wide variety of alkanolamines exists along with Monoethanolamine (MEA) including Diethanolamine (DEA), Di-2-propanolamine (DIPA), Methyldiethanolamine (MDEA), 2-amino-2-methyl-1-propanol (AMP) and Piperazine (Pz). Some of these amine based solvents are already applied in industry for many years. These alkanolamines show clear differences in their performance during CO_2 absorption when using e.g. packed columns for contacting the flue gas with the absorption liquid. The first difference pertains to their reactivities or rates of CO_2 absorption. Primary and secondary amines such as MEA and DEA are very reactive compared to tertiary amines like MDEA and thus are able to realize high removal fractions for CO_2 in the absorbers. The second difference between primary and secondary on one hand and with tertiary amines on the other hand is that primary and secondary amines have the limitation that their maximum CO_2 loading capacity based on reaction stoichiometry is at best 0.5 mole of CO_2 per mole of amine. Whereas, tertiary amines such as MDEA have an equilibrium CO_2 loading capacity that approaches 1.0 mole of CO_2 per mole of amine which can result in lower solvent circulation rates.

The third difference is the energy requirement for solvent regeneration. The stripping of CO_2 from MEA or DEA solutions requires significant more energy as compared to MDEA solution. The heat duty for solvent regeneration can constitute up to 40% of the total operating costs in a CO_2 capture plant Abu Zahra, 2009, including solvent heating up, water evaporation and CO_2 release, which on their turn are determined by cyclic loading capacity and carbamate (or bicarbonate) stability. Other operating costs concerns are solvent corrosiveness and solvent chemical instability, which are suggested by literature studies. For better process economics it is essential to find more efficient solvents, tailored for CO_2 post combustion capture.

A further major challenge for the carbon dioxide removal for flue gas from power plants using post combustion capture technology is the enormous capacity required

to treat the flue gas. In typical applications flue gas flow rates are of the order of a few thousands of tons per hour corresponding to millions of cubic meters flue gas per hour, and hundreds of tons of carbon dioxide per hour. At present there are several commercial processes available for CO_2 capture in post combustion systems. So far, there is no application of full scale CO_2 capture in power plants, even though test facilities using flue gas slipstreams exist. In most commercial CO_2 capture processes an aqueous solution of MEA (amine based solvent) is used. Mitsubishi Heavy Industries together with Kansai Electric, employ other patented chemical solvents – sterically hindered amines called KS-1, KS-2 or KS-3. The regeneration heat of KS solvents is said to be ~ 3 GJ/t CO_2, i.e. 20 % lower than that of MEA with ~ 3.7 GJ/t CO_2 (Mangalapally et al., 2009).

Mixed amines have been reported to maximize the desirable qualities of the individual amines. Thus, the specific goal with respect to the use of mixed amines is to have a solution consisting of tertiary and primary amines or tertiary plus secondary amines that, in comparison with single amine based systems, retains much of the reactivity of primary or secondary amines at similar or reduced solvent circulation rates and offers low regeneration costs similar to those of tertiary amines, due to enhanced bicarbonate formation and a higher CO_2 cyclic capacity. Consequently, by blending a primary or secondary alkanolamine with a tertiary alkanolamine, bulk CO_2 removal is easily accomplished while regeneration energy costs are minimized. In addition, another degree of freedom (the amine concentration) is gained. The amine concentration can be altered to achieve precisely the desired separation for a given process configuration. Substantial reductions in energy requirements and modest reduction in solvent circulation rates have been reported for amine blends relative to the corresponding single amine system of similar total amine concentration (Idem et al., 2006). Simulation studies have shown that, for CO_2 loadings below 0.5 mol CO_2 / mol amine, MDEA + MEA and MDEA + DEA blends containing 2 kmol/m^3 of each amine produced an equilibrium CO_2 partial pressure of the amine blend that is intermediate between those of the corresponding single amine based systems of equivalent total amine concentration. For higher CO_2 loadings, the equilibrium partial pressures in blended amine systems were less or comparable with those of single amine based systems. Furthermore, experiments on CO_2 solubility in aqueous blends of MEA + MDEA and DEA + MDEA have confirmed that equilibrium solution CO_2 loading is influenced mostly by the blended solvent compositions under conditions that are typical for industrial regenerators (Idem et al, 2006).The addition of small amounts of MEA to AMP results in a significant enhancement of CO_2 absorption rates (Sakwattanapong et al., 2009).

In previous work (Singh et al., 2010) single amine solvents were screened for their CO_2 loading capacity and cyclic capacity using regeneration at 90ºC. In addition, preliminary information on their reactivity during absorption conditions was obtained. For further evaluation of the applicability of selected amines in low-cost

post combustion CO_2 capture solvent systems, pilot plant testing was considered valuable and a necessary next step. This pilot plant study, from which the results are presented in this study, was enabled by the permission and support to use the absorption/desorption pilot plant unit (ASAP) for removal of carbon dioxide located at the Shell Technology Centre Amsterdam. Amines selected for the solvent (mixtures) were based on the results obtained during the experimental solvent screening activities (Singh et al., 2010) and subsequently formulated into a blend of amines.

Main objective of this study is the proof-of-principle runs for the new solvents including a first round optimization on solvent circulation rate, the evaluation of the energy requirements for solvent regeneration and, simultaneously, a check on possible operational hurdles.

8.2. Solvent selection and solvent formulation

In order to determine the optimal solvent formulation for pilot plant test, a pre-test to screen various solvent combinations was performed in a solvent screening unit (experimental set-up explained in detail in Chapter 4). Main focus of these pre-test solvent screening experiments was to identify the suitable solvent formulation on the basis of solvent maximum concentration, rich CO_2 loading, lean CO_2 loading and cyclic CO_2 loading. Other solvent issue like e.g. foaming tendency, crystallization, viscosity changes etc. could also be identified from these experiments. In these solvent pre-test solvent screening experiments, CO_2 absorption was done at 20°C and atmospheric pressure with 20 vol% CO_2 inlet feed concentration. Regeneration of the solvent tested was carried out at 90°C and atmospheric pressure. AMP solution has been introduced as a commercially attractive co-solvent for HMDA, since it has a loading capacity of up to 1 mol of CO_2 per mole of AMP. It showed an excellent absorption characteristics and is easy to regenerate, higher degradation resistance and a lower corrosion rate in comparison with more conventional amines as MEA and MDEA, Aboudheir et al. 2006. Hence AMP was chosen in the present investigation as a base solvent in combination with HMDA for solvent formulation in the pre-tests. Additionally, and based on the results obtained during earlier solvent screening activities (Singh et al., 2010), selected amines were formulated into a propriety blend of amines (called 'New Solvent') which exact composition cannot be disclosed here.

Table 1 shows the results from different AMP+HMDA combinations and the New Solvent combination used during pre-test experiments. The importance of pretesting is illustrated by the reported results for AMP 2.5 mole/L + HMDA 1.50 mole/L, where a reliable regeneration experiment could not be obtained due to the high foam formation during experiment. Furthermore, it can be noticed that solvent formulation Nr.1 has a higher cyclic capacity when compared to that of solvent Nr.3, see Table 1.

Table1, Solvent pre-test screening results from solvent screening experiments at 20 vol% CO_2 inlet Conc.

No.	Amine concentration				Rich loading	Lean loading	Cyclic loading	Abs. slope
	mole /L	wt%	mole /L	wt%	mole CO_2 /mole amine	mole CO_2 /mole amine	mole CO_2 /mole amine	min^{-1}
	AMP		**HMDA**					
1	3.0	26.7	1.0	11.6	0.94	0.16	0.78	3.39E-03
2	2.5	22.3	1.5	17.9	0.98	-	-	4.31E-03
3	2.5	22.3	2.5	29.8	0.94	0.31	0.63	2.69E-03
	New Solvent							
1	3.0	51.1	-	-	1.58	0.17	1.41	3.21E-03

8.2.1. Corrosion Test

In addition to CO_2 capture/regeneration characteristics, the corrosiveness of the solvent also needed to be evaluated before starting pilot plant testing. For all solvents tested an intrinsic corrosion test was performed. This is an iron solubility test performed at 130°C for 2 hour. The iron solubility results for Hexamethylenediamine, the New Solvent and MEA (for reference) are presented below.

Table 2, Iron solubility test for MEA, Hexamethylenediamine (HMDA) and New Solvent.

Solvent	Iron solubility ppm
MEA	15
HMDA	3.5
New Solvent	2.5

Based on the pre-test solvent screening experiments and the corrosion test results, an aqueous solution of 26.74 wt% AMP + 11.91 wt% HMDA and an aqueous solution of the 51 wt% New Solvent were found to be suitable for pilot plant testing.

8.3. Experiment Section

8.3.1. Chemicals

Monoethanolamine (MEA), 2-Amino-2-Methyl 1-propanol (AMP), Piperazine (Pz), Hexamethylenediamine (HMDA) and New Solvent components have been purchased from Sigma Aldrich with a purity of 99%. These solvents were diluted with dematerialised water to the desired concentrations.

8.3.2. Shell Pilot Plant (ASAP; ID4001)

The ASAP unit (shortened for Amine Screening Apparatus) is a bench scale unit that is capable to test different amine solutions to sweeten several kinds of sour gases under various conditions. The ASAP unit consists of two columns; the Absorber (C-200) and the Regenerator (C-300) (see Figure 2). The length of absorber and regenerator is 150 cm and the internal diameter is 28mm. These columns are packed with structured packing type Ex laboratory packing (Sulzer Chemtech Ltd) shown in Figure 1 below. This packing has a surface area of $1735 m^2/m^3$. This high surface area ensures good contacting between gas and liquid. The diameter of this packing element is 28 mm, which is same as columns internal diameter. The absorber column is filled up to 145 cm with this packing. The regenerator is filled up to 130 cm with this packing. The columns are insulated so that exothermic and endothermic heat effects can be monitored.

Figure 1, Structured packing for ASAP Unit provided by Sulzer Chemtech Ltd.

Sour feed gas of a certain composition is fed into the bottom of the absorber. In the absorber, feed gas will be brought into contact in counter current direction with the amine solvent, which is circulating continually through the absorber-regenerator system. The sour components in the feed gas dissolve in the amine solution by an exothermic reaction. The sweetened off gas is cooled in condenser (E200) to remove vaporised water from the off gas stream. The amine solvent which is loaded in the absorber with sour components from the feed gas stream must be regenerated by stripping before it can be used again in the absorber. In the regenerator (C300) the loaded amine solvent was stripped from its sour components by means of steam generated from the boiling amine solution in the reboiler (E310) of the regenerator. Loaded or fat solvent is warmed up to 100°C and fed in the top of the Regenerator. In the bottom of the regenerator the amine solvent is boiling at approximately at 124°C and at 2 bar. During the trip down of the loaded solvent, the sour components will come out of the solvent and the solvent become unloaded or lean again. The sour off gas will be cooled in condenser (E300) to remove vaporised water. There is a possibility to improve the stripping by adding nitrogen strip gas in the boiling solvent at the bottom of the regenerator. Liquid samples were taken at every experiment from absorber and

regenerator to determine CO_2 rich and lean loading by doing separate gas chromatography analysis. The concentrations of components in the feed- and off-gasses are continuously monitored using a Varian CP-4900 micro gas chromatographic (GC). Honeywell process control software is used to run the ASAP unit unmanned and continuously. The process data were stored in the computer.

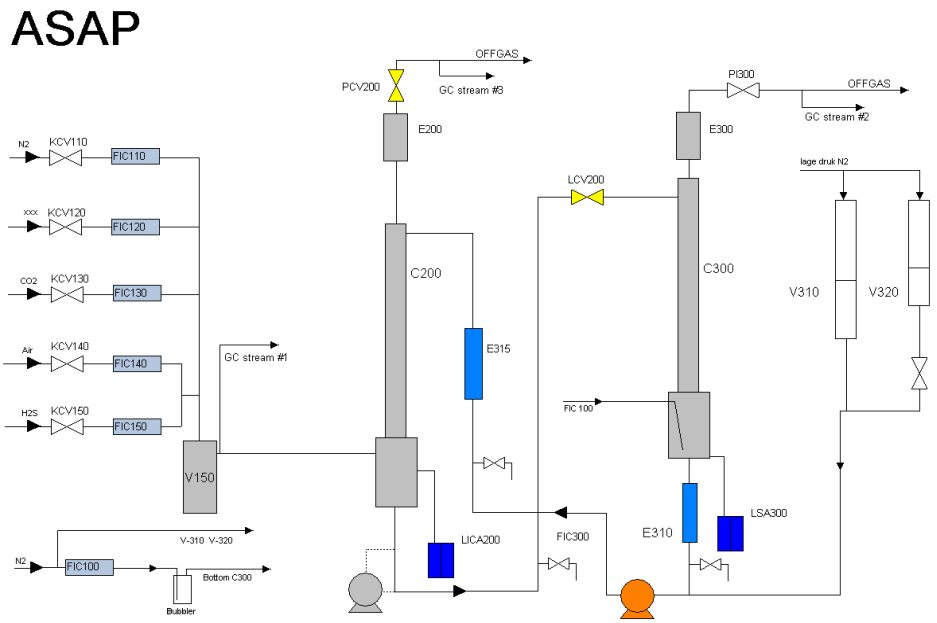

Figure 2, Simplified process flow scheme of pilot plant unit ASAP.

8.4. Experimental Procedure

In a typical experiment the inlet gas flow rate, temperature and pressure is already fixed. The absorber and regenerator pressure and temperature are also fixed. In this study absorption was done at 40°C, 1.3bar and regeneration at 120ºC, 2.0-2.2bar. The temperature of lean and rich solvent is known and kept constant (at respectively 40 and 100°C). To find the optimum solvent flow rate first the over stripping (higher then optimal reboiler duty (E310)) conditions were applied and CO_2 recovery from top of absorber is monitored. Once the CO_2 recovery reached 100%, the solvent flow rate is lowered in order to achieve CO_2 recovery at top of the absorber of 99% to 97%. Typically, the minimization of solvent flow rate should maximize CO_2 loading (mole CO_2/kg solvent) and reduce desorption energy requirements per amount of CO_2 captured. Once the solvent flow rate is obtained the energy requirement is further minimized by reducing the energy input until 90% CO_2 is recovered. Subsequently the solvent flow rate is adjusted again by

increasing or decreasing with maximally some 10%-15%. This solvent flow rate optimization helps to identify if further improvement in CO_2 recovery can be achieved at the lowest energy requirement. In the situation that CO_2 recovery increases with an increase in solvent flow rate it is then desired to reduce energy requirement until 90% CO_2 recovery is obtained.

8.5. Results

In this study, some of the main parameters affecting the capture process were pre determined by extensive validation of the experiments (not reported here) in this pilot plant and prior to this study. These parameters were adopted from existing operating procedures and are reported in Table 3.

Table 3, Process parameters which were kept constant in the pilot plant tests.

Parameter	**Experiment Value**
CO_2 at Inlet (vol%)	5 and 10
Flue gas flow rate (nL/h)	645 (5% CO_2 inlet Conc.) and 400 (10% CO_2 inlet Conc.)
Flue gas inlet temp.(°C)	37±1
Stripper pressure (bara)	2.00
Solvent concentration (wt%)	38.65 (AMP+HMDA) and 51 (New Solvent)
Lean solvent temerature (°C)	40±1

In this study as explained earlier, some of the main parameters affecting the capture process will be varied as an initial step towards an optimization of the process. Starting from the baseline conditions the following process parameters were varied:

- The solvent circulation rate (kg/h).
- Reboiler duty (Watt).

The energy requirement in the stripper (MJ/kg CO_2 removed) was used as an indicator when investigating the effect of the above parameters. The energy requirement was calculated from the heat required in the reboiler, mass rate of CO_2 regenerated and the system heat loss. The energy requirement (MJ/kg CO_2 removed) was chosen as the main parameter to evaluate different solvent performance in this pilot plant tests, as it is an indicative for operating costs.
Experiments were performed in the ASAP unit for aqueous solution of 26.74 wt% AMP + 11.91 wt% HMDA and the New Solvent-blend at 51 wt% concentration. Two different combinations of CO_2 inlet concentrations and inlet gas flow rate in the feed gas were chosen, a feed gas flow rate of 630 Nm3/h at 5 vol% CO_2 and 400 Nm^3/h at 10 vol% CO_2.

Table 4, Summary of pilot plant tests for the 26.74 wt % AMP + 11.91 wt % HMDA solvent; main input and results.

	Parameter							
Input	CO_2 at Inlet (vol%)	**5.01**	**5.01**	**5.01**	**10.02**	**10.03**	**10.03**	**10.03**
	Solvent flow rate (kg/h)	0.60	0.60	0.63	0.70	0.73	0.73	0.73
	Flue gas (nL/h)	644.46	644.74	644.68	399.66	399.69	399.74	399.56
	Flue gas inlet temp.(°C)	36.66	36.68	36.63	36.98	37.22	37.06	37.16
	Stripper pressure (bara)	2.11	2.16	2.10	2.11	2.21	2.20	2.22
Results	CO_2 at outlet regenerator (nL/h)	29.42	29.45	27.55	36.31	34.93	33.96	31.54
	CO_2 capture (mole CO_2/kg amine)	2.19	2.19	1.94	2.32	2.14	2.08	1.93
	CO_2 recovery from absorber (%)	**99.71**	**99.63**	**90.80**	**99.87**	**99.17**	**88.02**	**87.48**
	Solvent concentration (wt%)	38.65	38.65	38.65	38.65	38.65	38.65	38.65
	Rich loading (mole CO_2/mole amine)	0.48	0.51	0.47	0.48	0.49	0.50	0.51
	Lean loading (mole CO_2/mole amine)	0.05	0.07	0.14	0.05	0.06	0.16	0.16
	Cyclic loading (mole CO_2/mole amine)	0.43	0.44	0.33	0.42	0.43	0.33	0.34
	Rebolier duty (Watt)	87.84	71.37	76.86	87.84	76.86	79.61	81.25
	Energy requirement (MJ/kg CO_2)	**5.44**	**4.07**	**3.62**	**4.41**	**3.43**	**3.08**	**3.41**
	Flue gas outlet temperature (°C)	63.50	48.24	47.01	54.97	49.68	47.12	47.22
	Lean solvent temerature (°C)	40.57	40.66	40.79	40.92	41.08	41.02	40.95
	Reboiler temperature (°C)	122.94	123.60	121.63	122.81	123.35	121.46	122.02

Table 5, Summary of pilot plant tests for the 51 wt % New Solvent; main input and results.

	Parameter									
Input	CO_2 at Inlet (vol%)	**5**	**5**	**5**	**5**	**5**	**10**	**10**	**10**	**10**
	Solvent flow rate (kg/h)	0.50	0.50	0.50	0.50	0.48	0.50	0.55	0.55	0.57
	Flue gas (nL/h)	644	645	644	645	645	400	400	400	400
	Flue gas inlet temp.(°C)	37	37	37	37	37	37	37	37	37
	Stripper pressure (bara)	2.06	2.07	2.07	2.07	2.06	2.05	2.06	2.08	2.13
Results	CO_2 at outlet regenerator (nL/h)	30.28	30.17	29.00	29.01	27.96	37.78	36.23	35.58	33.02
	CO_2 capture (mole CO_2/kg amine)	2.70	2.69	2.60	2.58	2.60	3.38	2.95	2.87	2.59
	CO_2 recovery from absorber (%)	**100**	**100**	**99**	**98**	**93**	**100**	**100**	**98**	**89**
	Solvent concentration (wt%)	51	51	51	51	51	51	51	51	51
	Rich loading (mole CO_2/mole amine)	0.84	0.82	0.82	0.89	0.91	0.93	0.90	0.97	0.95
	Lean loading (mole CO_2/mole amine)	0.04	0.06	0.10	0.15	0.22	0.01	0.05	0.15	0.20
	Cyclic loading (mole CO_2/mole amine)	0.80	0.76	0.72	0.74	0.69	0.92	0.84	0.81	0.75
	Reboiler duty (watt)	82.35	76.86	71.37	65.88	60.39	109.80	82.35	68.63	60.39
	Energy requirement (MJ/kg CO_2)	**3.62**	**3.30**	**3.09**	**2.74**	**2.48**	**4.24**	**3.03**	**2.38**	**2.26**
	Flue gas outlet temerature (°C)	47	48	45	46	45	75	49	47	46
	Lean solvent temerature (°C)	40	40	40	40	40	40	40	40	40
	Reboiler temperature (°C)	121	121	120	119	117	122	121	119	117

Table 4 and 5 shows the experimental input and results from each test. It should be noticed that the approximate minimum solvent flow rate (kg/h) was already determined for each solvent before starting the experiments (see experiment procedure). Hence, the solvent flow rate (kg/h) is not varied much during the experiments.

8.6. CO_2 recovery and energy requirement

Figure 3, shows the energy requirement (MJ/kg CO_2) variation on the CO_2 lean loading (mole CO_2/mole amine) for 26.74 wt% AMP + 11.91 wt% HMDA and for 51 wt% New solvent. The results indicate that the reboiler heat duty is inverse to the lean CO_2 loading. For instance the energy requirement reduces from 3.43 to 3.08 MJ/kg CO_2 for AMP+HMDA as lean loading increases from 0.055 to 0.16 mole CO_2 / mole amine. A similar effect was noticed for the New Solvent as its energy requirement reduces from 4.23 to 2.55 MJ/kg CO_2 as its lean loading increases from 0.006 to 0.19 mole CO_2/mole amine, illustrating that the reduction in solvent regeneration efficiency at lower energy input. Figure 3 also shows that energy requirement indicate a nonlinear correlation with the lean loading obtained.

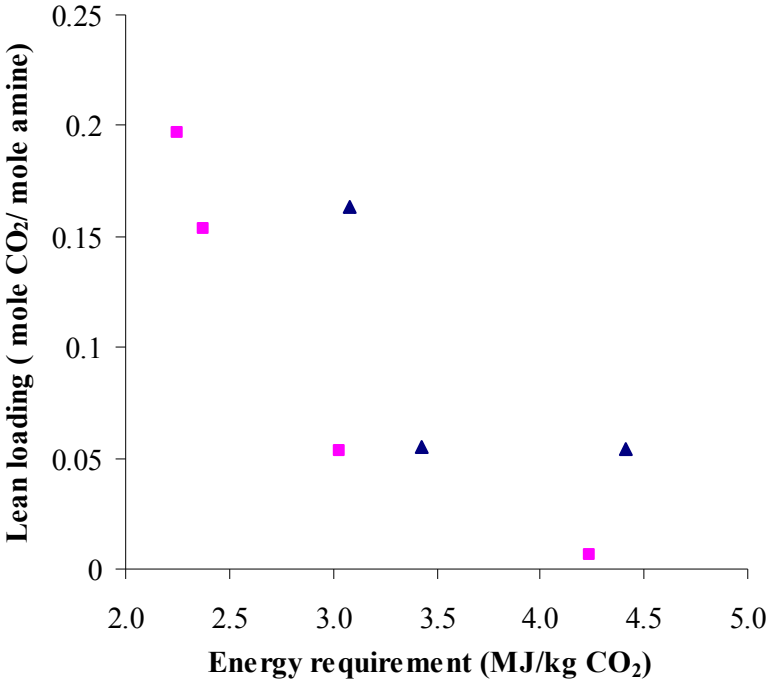

Figure 3, Effect of energy requirement (MJ/kgCO_2) on CO_2 lean loading (mole CO_2/mole amine) for ▲26.74 wt% AMP + 11.91 wt% HMDA and ■51 wt% New Solvent at 10 vol% inlet CO_2 concentration, CO_2 recovery range approximate 89 to 99%.

It should be noticed that for the New Solvent the lean loading is more sensitive to the energy input at lean loading lower than 0.05 mole CO_2/mole amine. Nevertheless, a significant additional heat is required to achieve a further reduction in lean loading below 0.05 mole CO_2/mole amine. For AMP+HMDA the addition of more heat did not result in a noticeable reduction of the lean loading below 0.05. Hence, regenerating the solvent to these low loading represents an unfavourable operating region that consumes excessive energy. For lean loadings above 0.05 mole CO_2/mole amine the energy requirement is less sensitive to the change in lean loading, implicating that only a small amount of additional heat duty is required to achieve a substantial reduction in lean-CO_2 loading, thus presenting a favourable operating condition. This effect is directly related to the vapour liquid equilibrium data.

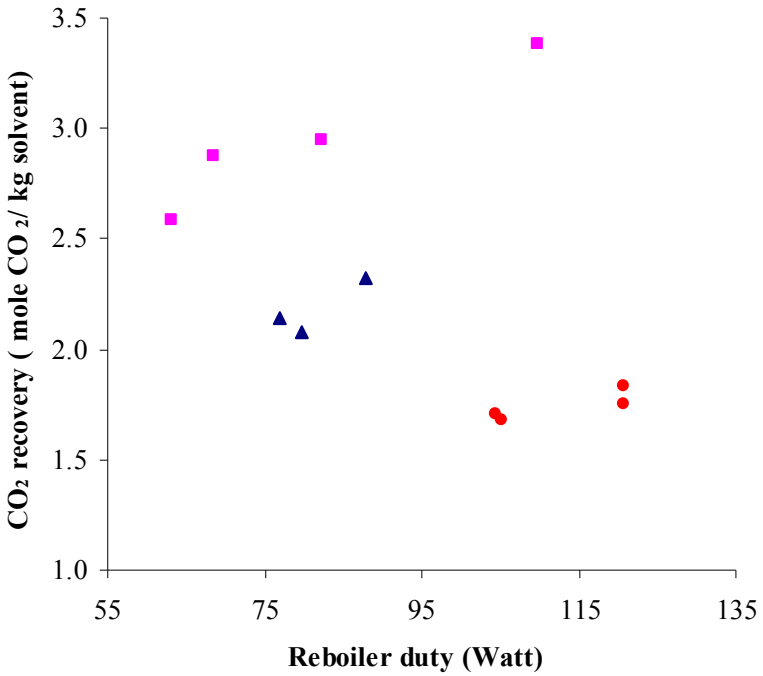

Figure 4, Effect of reboiler duty (Watt) on CO_2 recovery (mole CO_2/kg solvent) for ● 31 wt% MEA, ▲ 26.74 wt% AMP + 11.91 wt% HMDA and ■ 51 wt% New Solvent at 10 vol% inlet CO_2 concentration, CO_2 recovery range approximate 89 to 99%.

The operating CO_2 partial pressure at the reboiler is limited to an extremely low equilibrium CO_2 partial pressure for a very lean solution. The operating CO_2 partial pressure cannot be easily reduced further to achieve an even slight reduction in lean CO_2 loading without a penalty of excessive energy input, required to generate

the required considerable increase in the amount of water vapour leaving the regeneration column.

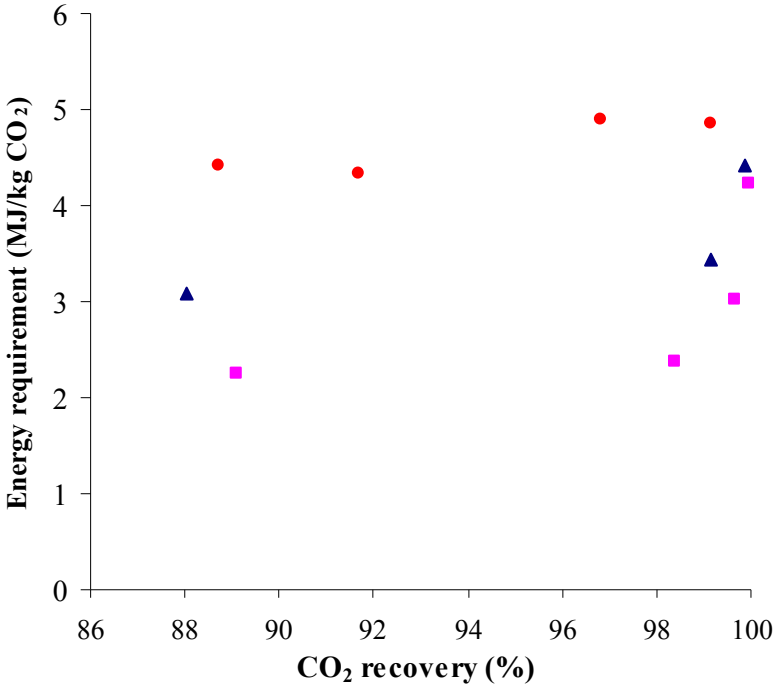

Figure 5, Effect of CO_2 recovery (%) on energy requirement (MJ/kgCO_2) for ● 31 wt% MEA, ▲26.74 wt% AMP + 11.91 wt% HMDA and ■ 51 wt% New Solvent at 10 vol% inlet CO_2 concentration, CO_2 recovery range approximate 89 to 99%.

Comparing the solvent energy requirement (MJ/kg CO_2) with CO_2 recovery shows that New Solvent can reach much higher CO_2 recovery (mole CO_2/kg solvent) when compared to AMP+HMDA and MEA (see Figure 4). Figure 5 shows the effect of CO_2 recovery (%) on energy requirement (MJ/kg CO_2). It should be noticed that the New Solvent can recover more CO_2 (mole CO_2/kg solvent) when compared to AMP+HMDA and MEA at much lower energy input. It is interesting to notice that for New solvent the energy requirement is only slightly increased 2.26 to 2.38 (MJ/kg CO_2) for CO_2 recovery from 89 to 99 %. Further increase in CO_2 recovery from 98% to 100% increases the energy requirement up to 3.03 (MJ/kg CO_2). Similar behaviour can be noticed for AMP+HMDA where the energy requirement is only slightly increased from 3.08 to 3.43 (MJ/kg CO_2) for CO_2 recovery increase from 88 to 99 %. Further increase in energy requirement does not affect much on CO_2 recovery for AMP+HMDA (see Table 4 and Figure 5). It is clear from the test results that both solvents are more energy efficient when compared to MEA and are suitable for recovery levels as high as 99%.

8.7. Solvent Evaluation

A further evaluation of the solvents performance at both CO_2 inlet concentration 5 and 10 vol% was done by measuring the required solvent circulation rate for a fixed CO_2 removal fraction of 99% recovery. It should be noticed that the values presented in this evaluation are based on those tests which achieved the lowest energy requirement for 99% CO_2 recovery from the absorber. Figures 6 (a) & 6 (b) show the resulting solvent circulation rate (kg/h) and cyclic loading (mole CO_2/mole amine) for the (26.74 wt% AMP + 11.91 wt% HMDA) solvent and the 51 wt% New Solvent and, for comparison, the 31 wt% MEA solvent at 5 and 10 vol% CO_2 inlet concentration respectively. Figure 6 (a) illustrates clearly that the 51 wt% New Solvent can achieve much higher cyclic loadings of 0.7 mole CO_2/mole amine at lowest solvent circulation rate 0.5 kg/h.

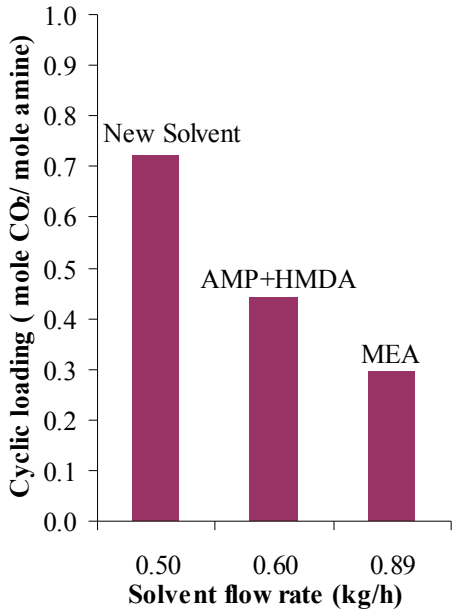

Figure 6 (a), 5 vol% inlet CO_2 conc.

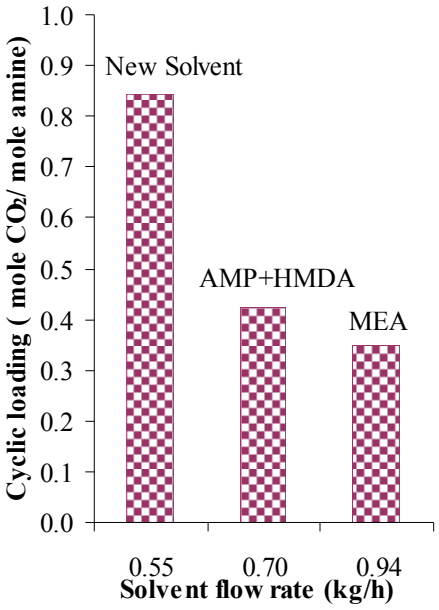

Figure 6 (b), 10 vol% inlet CO_2 conc.

Effect of solvent flow rate (kg/h) on cyclic loading (mole CO_2/mole amine)for 31 wt% MEA, 26.74 wt% AMP + 11.91 wt% HMDA and 51 wt% New Solvent at 99% CO_2 recovery .

From Figure 6 (b) it can be noticed that the increase in CO_2 inlet concentration to 10 vol% increases the required cyclic loading for the New Solvent up to 0.84 mole CO_2/mole amine with an optimum solvent flow rate of 0.55 kg/h. For AMP+HMDA at 5 vol% CO_2 inlet concentration a higher cyclic loading of 0.44 mole CO_2/mole amine was found when compared to that of MEA. Which can be explained by the lower solvent circulation rate (0.6 kg/h) of AMP+HMDA was

found in comparison with MEA, see Figure 6(a). At 10 vol% CO_2 inlet concentration an optimum solvent circulation rate of 0.70 kg/h was found for AMP+HMDA. Taking into account that the cyclic loadings are almost identical, this is in line with the increased total CO_2 recovery task (in mole/h) when comparing the 5 vol% CO_2, 645 nL/h with the 10 vol% 400 nL/h conditions. For the New Solvent, however, the cyclic loading increased significantly, when going from the 5 to 10 vol% CO_2 inlet concentration, Therefore, only a small increase in the required solvent circulation rate (from 0.50 to 0.55 kg/h) was observed.

Figures 7 (a) and 7 (b) show that the New Solvent obtains the highest CO_2 recovery 2.6 and 2.95 mole CO_2/ kg solvent for 5 and 10 vol% CO_2 inlet concentration. For AMP+HMDA solvent CO_2 recovery of 2.19 and 2.32 mole CO_2/ kg solvent was achieved at 5 and 10 vol% CO_2 inlet concentration respectively. New solvent and AMP+HMDA were found to have less energy requirement (MJ/Kg solvent) compared to MEA, as can be seen from Figure 8 (a) and 8 (b). It is interesting to notice that New solvent energy requirement was found to be same of 3.09 and 3.03 MJ/Kg solvent at 5 and 10 vol% CO_2 inlet concentration respectively.

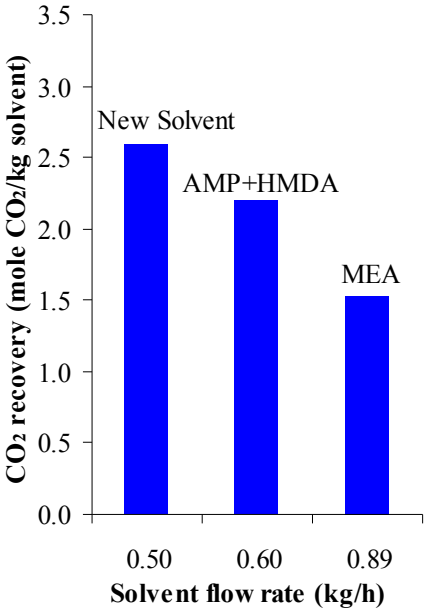

Figure 7 (a), 5 vol% inlet CO_2 conc.

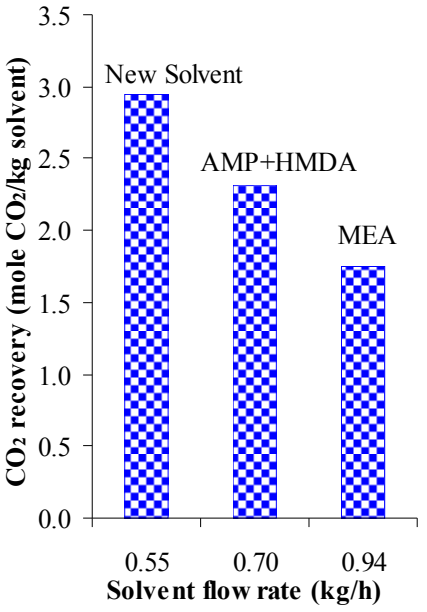

Figure 7 (b), 10 vol% inlet CO_2 conc.

Effect of solvent flow rate (kg/h) on CO_2 recovery (mole CO_2/kg solvent) for 31 wt% MEA, 26.74 wt% AMP + 11.91 wt% HMDA and 51 wt% New Solvent at 99% CO_2 recovery.

Whereas, AMP+HMDA energy requirement was increased from 4.07 to 4.41 MJ/Kg solvent for 5 to 10 vol% CO_2 inlet concentration respectively. This could be

due to the higher lean loading for AMP+HMDA at 5 vol% CO_2 inlet concentration case. These results already suggest that the benefit of the use of New Solvent as absorption liquid could be substantial.

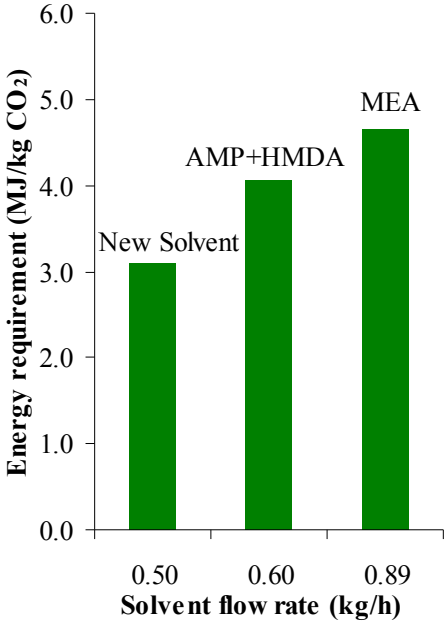

Figure 8 (a), 5 vol% inlet CO_2 conc.

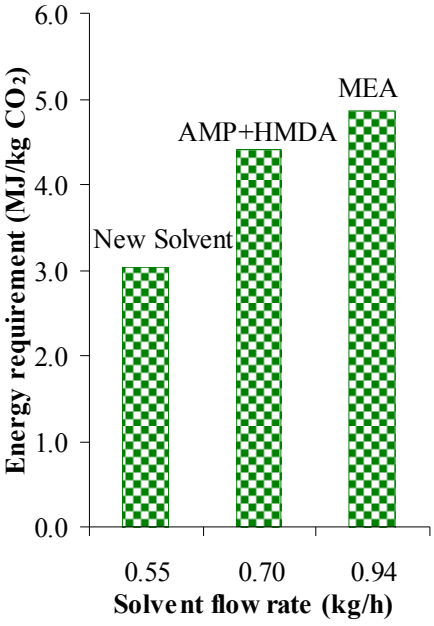

Figure 8 (b), 10 vol% inlet CO_2 conc.

Effect of solvent flow rate (kg/h) on energy requirement (MJ/kg CO_2) for 31 wt% MEA, 26.74 wt% AMP + 11.91 wt% HMDA and 51 wt% New Solvent at 99% CO_2 recovery.

Table 6, shows the comparison of the energy requirement for the AMP+HMDA – solvent and the New Solvent with the more conventional solvents as 31 wt% MEA and 30 wt% AMP + 5 wt% Pz for the gas streams containing 5 vol% inlet CO_2 concentration and at 90% (±3%) CO_2 recovery. For 10 vol% inlet CO_2 concentration and at 90% (±3%) CO_2 recovery 31 wt% MEA and 35.6 wt% AMP was chosen for comparison with New Solvent and AMP+HMDA - solvent. The New Solvent clearly shows that it requires the lowest energy requirement for both CO_2 inlet concentrations, reducing the energy requirement (according to the experimental results above) with almost 50% in comparison with the 31 wt% MEA solvent. Also the value obtained for the energy requirement for the New Solvent is not much different for both CO_2 inlet concentrations and not very sensitive to the CO_2 recovery fraction (see Figure 5) in the range up to 99%. Furthermore, it is interesting to notice that the energy requirement for the 26.74 wt% AMP + 11.91 wt% HMDA solvent is comparable (and even slightly lower) with the same of 30 wt% AMP + 5 wt% Pz solvent at 5 vol% inlet CO_2 concentration.

Table 6, Comparison of solvents energy requirement at 90% (± 3 %) CO_2 recovery.

Solvent	CO_2 inlet Conc.	Flue gas flow rate	Solvent flow rate	CO_2 recovery	Cyclic loading	Energy requirement
	vol%	nL/h	kg/h	%	mole CO_2 /mole amine	MJ/kg CO_2
MEA 31 wt%(*)	5	645	0.90	91	0.29	4.80
AMP 30 wt% + Pz 5 wt%(*)	5	645	0.63	90	0.51	3.87
New Solvent 51 wt%	5	645	0.48	93	0.84	2.48
AMP 26.74 wt% + HMDA 11.91 wt%	5	645	0.63	91	0.44	3.62
MEA 31 wt%(*)	10	400	0.91	89	0.34	4.33
AMP 35.6 wt%(*)	10	400	1.07	90	0.37	3.91
New Solvent 51 wt%	10	400	0.57	89	0.80	2.26
AMP 26.74 wt% + HMDA 1.91 wt%	10	400	0.73	88	0.46	3.41

(*)In-house data Shell Global Solutions, Amsterdam.

8.8. Conclusion

In this study two new, promising amine based solvent systems were successfully tested in a continuously operated pilot plant in order to prove the operability of the solvent system and to obtain information on the required solvent flow rates and energy requirements for regeneration of the solvent. It has been shown that the solvent formulations studied, which were identified as 'promising' during earlier solvent screening, indeed have the potential to reduce the reboiler energy requirements by 20-50% in comparison with a 31 wt% MEA solution as reference solvent. Since, additionally, corrosiveness and evaporative losses compare favourably, these solvents may form attractive alternatives to existing absorption systems. The pilot plant tests are considered to be reasonably representative for large scale operation but these has to be further investigated.

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Appendix A

Table a, Dissociation constant (pKa) of solvents tested in screening experiments in Chapter 4 and 5. Estimated pKa values are from ACD/pKa PhysChem software at 20°C and literature pKa values are taken from Perrin, 1965.

Solvent	Estimated pKa	Literature pKa	Literature Temp. °C
Diethanolamine (DEA)	8.7		
Diisopropanolamine (DIPA)	9.0		
2-Amino-2-methyl-1propanol (AMP)	9.2		
Methylenediethaloamine (MDEA)	9.0	8.5	25.0
Monoethanolamine (MEA)	9.2	9.6	20.0
3-Amino-1-proponaol	9.9	10.0	20.0
4-Amino-1-butanol	10.3	10.4	20.0
5-Amino-1-pentanol	10.5	10.5	23.0
6-Amino-1-hexanol	10.6	10.6	21.0
7-Amino-1-heptanol	10.6		
Ethylamine	10.6	10.7	25.0
Propylamine	10.7	10.7	25.0
Butylamine	10.7	10.6	25.0
n-Pentylamine	10.7		
Hexylamine	10.7		
Ethylenediamine	9.9	10.1	20.0
1-3 Diamino propane	10.4	10.6	20.0
1,4-Diaminobutane	10.7	10.8	20.0
Hexadimethylenediamine	10.9	11.0	20.0
1,7-diaminoheptane	10.9		
1,3-Propanediamine, N,N,N',N'-tetramethyl	9.9		
1,6-Hexanediamine, N,N'-dimethyl	11.1		
Sec-butylamine	10.7	10.6	25.0
Iso-butylamine	10.7	10.5	25.0
1,2-diamino propane	9.6		
3-amino 2- propanol	9.3		

2-amino-1-butanol	9.2		
N-(2-Hydroxyethyl) ethylenediamine	9.6		
N,N'-Bis(2-hydroxyethyl) ethylenediamine	9.4		
N-propylethylenediamine	10.3		
Diethylenetriamine	10.0		
Triethylenetetramine	10.1		
Tetraethylene pentamine	10.1		
Tris (2-aminoethyl) amine	10.0		
3,3'-Iminobis(N,N-dimethylpropylamine)	10.4		
N-(2-aminoethyl)1-3-propane diamine	10.5		
Piperazine	9.9	9.7	25.0
1-Methyl piperazine	9.7		
Trans piperazine, 2-5 dimethyl	10.0	9.7	25.0
2-Methyl piperazine	9.7		
N-ethylpiperazine	9.7		
2-(1-Piperazinyl)ethylamine	10.1		
2-(1-Piperazinyl)ethanol	15.0		
Piperidine	11.2	11.3	20.0
2-Methylpiperidine	11.3		
4-Amino piperidine	10.7		
Pyridine	5.3		
2-Methylpyridine	6.2		
2,5 Lutidine	6.2		
2-Pyridylamine	5.5		
Pyrazine	1.0		
2-methylpyrazine	1.3		
2,5 Dimethyl pyrazine	2.0		
Aminopyrazine	3.0		
DABCO	8.2		
Azetidine	11.3		

Publications and Presentations

Journal publications

Singh P., da Silva E. F., Brilman D. W. F., 2011, Determination of the molecular structural effects on the carbamate stability for various amine based solvents by using ab Initio Method.

Singh P., van Swaaij W. P. M., Brilman D. W. F., 2011, Kinetics study of carbon dioxide absorption in aqueous solutions of 1,6 Hexamethyldiamine (HMDA) and 1,6 Hexamethyldiamine, N,N' di-methyl (HMDA, N,N'). Chemical Engineering Science *(submitted)*

Singh P., Brilman D. W. F., Groeneveld M. J., 2011, Evaluation of CO_2 solubility in potential aqueous amine based solvents at low CO_2 partial pressure. International Journal of Greenhouse Gas Control, Vol 5 (1), pp 61-68

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Conference presentations

Two poster presentation at The Greenhouse Gas Control Technologies Conference-10, Amsterdam, The Netherlands, 19^{th} –23^{rd} Sept. 2010

Poster presentation at The Greenhouse Gas Control Technologies Conference-9, Washington DC, U.S.A., 16^{th} –24^{th} Nov. 2008

Poster presentation at Netherlands Process Technology Symposium-8, Veldhoven, The Netherlands, 28^{th} Oct. 2008

Presentation at European Congress of Chemical Engineering-6, Copenhagen, Denmark, 17th -21st Sept. 2007

Presentation at The Greenhouse Gas Control Technologies Conference-8, Trondheim, Norway, June 2006

Presentation at 2nd CATO Day, Utrecht, The Netherlands, June 2006

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Prachi

Global warming is a well known, worldwide concern, most probably caused by increasing concentrations of CO_2 and other greenhouse gases in the earth's atmosphere, due to human activities. Carbon Capture and Storage (CCS) offers the opportunity to reduce the CO_2 emissions associated with the use of fossil fuels. Carbon dioxide capture with a regenerable solvent is considered to be a mature technology, since it is successfully applied as CO_2 removal technology in industrial applications. In order to make this technology more economical for post-combustion capture, especially in the power-sector, more research is required to identify solvents which require less energy and lead to lower solvent loss- and corrosion rates in this application. In this thesis an improved understanding of the interaction between amine structure and CO_2 capture properties was developed, as well as a few potential solvents for post-combustion CO_2 capture. This work is expected to benefit the development of even better solvents for CO_2 capture in the future.

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