

Calorimetric Study of CO₂ Absorption into Amine Solutions

Muhammad Usman Idrees

Chemical Engineering
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Supervisor: Hallvard Fjøsne Svendsen, IKP

DECLARATION

I declare that this is an independent work according to the exam regulations of the Norwegian University of Science and Technology

Date and signature:

A handwritten signature in blue ink, appearing to be 'M. S. H. H. H.', written over a dotted line.

Tuesday, June 21, 2011

Abstract

To date, fossil fuels are the main source of energy which causes green house gas (GHG) emissions. Major component of these GHG is carbon dioxide (CO_2). Carbon dioxide capture from an efficient power plant and other industrial processes using solvents is a developed technology but it reduces the overall efficiency of the process mainly due to energy needed to desorb chemically bound CO_2 with the solvent. This energy is used to provide by low pressure steam flow inside the tubes of reboiler of a stripping column in a CO_2 capture plant. This heating energy is same as that release during absorption stage. This heat of absorption and pumping energy requirement for a CO_2 capture plant depends on the type of solvent and its physical properties (viscosity, density etc). Sometimes activators like piperazine use along with solvent which increases the reactivity of solution. Hence solvent selection is the most important step during process design and development stage.

Heat of absorption of CO_2 with different solvents was measured in this work in a commercially available reaction calorimeter CPA-122 of ChemiSens as a function of temperature and loading over the temperature range from 40 to 80 °C. This method was developed and validated by Kim (2009). Studied absorbent systems are 5 % by weight ammonia aqueous solution, 0.8 M piperazine, blend of 5 % weight of ammonia and 0.8 M piperazine, blend of 5 % weight of ammonia and 0.4 M piperazine (PZ) and blend of 2.5 % weight of ammonia and 0.8 M piperazine. Experimental heats of absorption of CO_2 with these systems are compared with other systems as well.

The heat of absorption of CO_2 with 5% by weight aqueous NH_3 is estimated to be 70 kJ/mol CO_2 and with 0.8 M PZ is estimated to be 75 kJ/mol CO_2 at low loading interval (less than 0.5 mol CO_2 /mol amine) at 40 °C. Heat of absorption decreases for aqueous ammonia solution while increases for the case of PZ with increasing temperature at a specific loading less than 0.5 mol CO_2 /mol amine. Heat of absorption of CO_2 with blend of these two solutions is also measured which reveals that it is similar to that of heat of absorption of CO_2 with 5% by weight aqueous NH_3 solution at 40 °C and 60 °C while it is also similar up to loading of 0.35 mol CO_2 /mol amine at 80 °C. Hence PZ has almost negligible effect on heat of absorption in blends. This may be due to low concentration of PZ (0.4 M & 0.8 M).

Preface

Thanks God Almighty who make me able to do this task. The work presented in this report has been performed at Norwegian University of Science & Technology (NTNU), Trondheim between January 2011 and June 2011. This thirty credit project is a part of my 4th semester at NTNU. My supervisor throughout this project has been **Prof. Hallvard F. Svendsen**. I deem it as my privilege to express my sincerest gratitude and heartfelt thankfulness to him for his resources, cooperation, guidance and continuous support right from the first semester. I also want to pay my gratitude to **Inna Kim, Ardi Hartono** and **Jinzhao Liu** for their help and discussions during this work.

I am thankful to **Chemical Engineering department of NTNU & SINTEF** to facilitate me to complete my masters by providing every possible facility and make me feel at home. I also want to pay my gratitude to **Government of Norway** for free education of quality for international students.

I also want to pay my thanks to my parents, brothers, friends and all teachers who teach me to date for their support.

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Nomenclature

ppm	parts per million
f_i^{\wedge}	Fugacity of individual specie (Pa)
$\Delta H_s = \Delta H_{abs}$	Heat of absorption (kJ/mol CO ₂)
R	Universal gas constant (8.314J/mol. K)
T	Temperature (K)
n_{CO_2}	CO ₂ absorbed
Q_{total}	Heat (J)
α	CO ₂ loading (mol CO ₂ /mol amine)

Chapter 1 INTRODUCTION

1.1. Background

Economic stability and development depend upon the availability of secure and reliable energy at affordable price. To date, fossil fuel is the main source of energy which causes green house gas (GHG) emissions. It is a need of the hour to mitigate these emissions, including those related to energy production and consumption. Major component of these GHG is carbon dioxide (CO₂). The atmospheric concentration of CO₂ rose from 280 ppm in 1800 to 370 ppm in 2000, mainly due to the consumption of fossil fuels [1]. The two-year decrease in Norwegian greenhouse gas emissions was followed by a new increase in 2010, when the emissions amounted to 53.7 million tonnes CO₂ equivalents. This is 4.8 per cent more than in 2009. Higher metal production and more transport have contributed most to the increase [2].

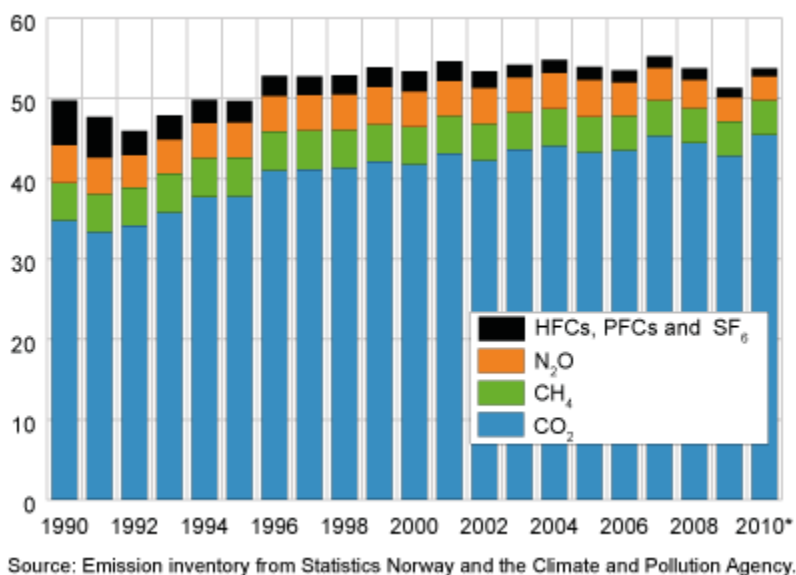


Figure 1.1: Emissions of GHG. 1990-2010* Million tones CO₂ equivalents (2011 © Statistics Norway) [2]

These are some of the results found in the new, preliminary emission figures estimated by Statistics Norway in cooperation with the Climate and Pollution Agency as shown in figure 1.1 [2].

Power generation, cement production, refineries, iron and steel industry, petrochemical industry, oil and gas processing units are the major stationary sources of CO₂. Approximately 69% of all CO₂ emissions are energy related, and about 60% of all GHG emissions can be attributed to energy supply and energy use. Electricity production is currently responsible for 32% of total global fossil-fuel use and 41% of energy-related CO₂ emissions. Improving the efficiency of electricity production offers a significant opportunity to reduce the world's dependence on fossil fuels, and to help combat climate change. This is also a key enabling step for carbon dioxide capture and storage (CCS), as capture and storage only makes sense for highly efficient plants [4, 5].

The total Norwegian greenhouse gas emissions were 2.5 million tonnes higher in 2010 than in 2009. This increase should be regarded in relation to the emission reductions in 2008 and 2009, caused by the financial crisis. Increased economic activity in 2010 contributed to higher emissions from manufacturing industries and transport. There were only minor changes from 2009 to 2010 in emissions from agriculture and oil and gas-related activities as shown in figure 1.2 [2].

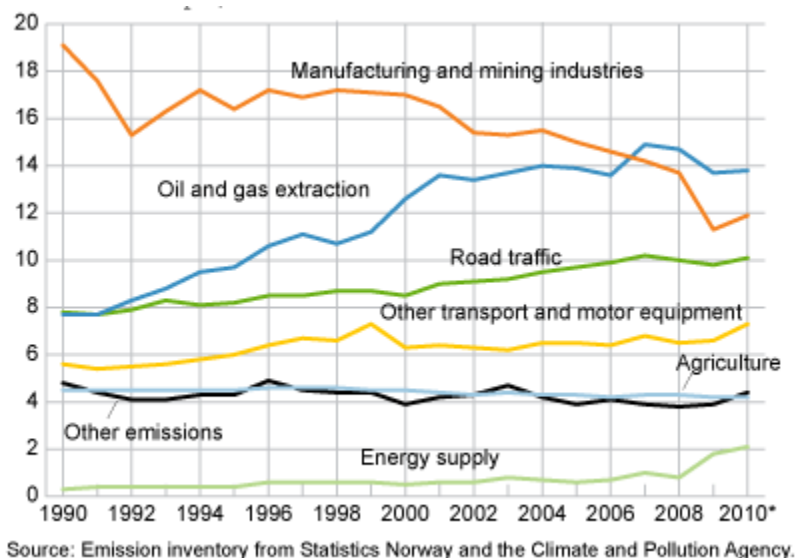


Figure 1.2: Emissions of GHG. 1990-2010* Million tones CO₂ equivalents (2011 © Statistics Norway) [3]

1.1.1. Available Processes

There are different processes available for CO₂ capture:

- Capture from industrial processes e.g., natural gas sweetening & in ammonia production process
- Post combustion capture
- Pre combustion capture
- Oxy fuel combustion capture

Figure 1.3 shows these processes.

In post combustion flue gas is available at atmospheric pressure having CO₂ 3-15% by volume. Pre-combustion CO₂ capture involves initial fuel catalytic conversion steps of steam reforming (endothermic reaction) and water gas shift (exothermic). In steam reforming fuel converted to a mixture of CO and H₂ while in water gas shift CO is converted to CO₂. Hence a mixture of CO₂ and H₂ is obtained at high pressure and high concentration of CO₂ (15-60% by volume on dry

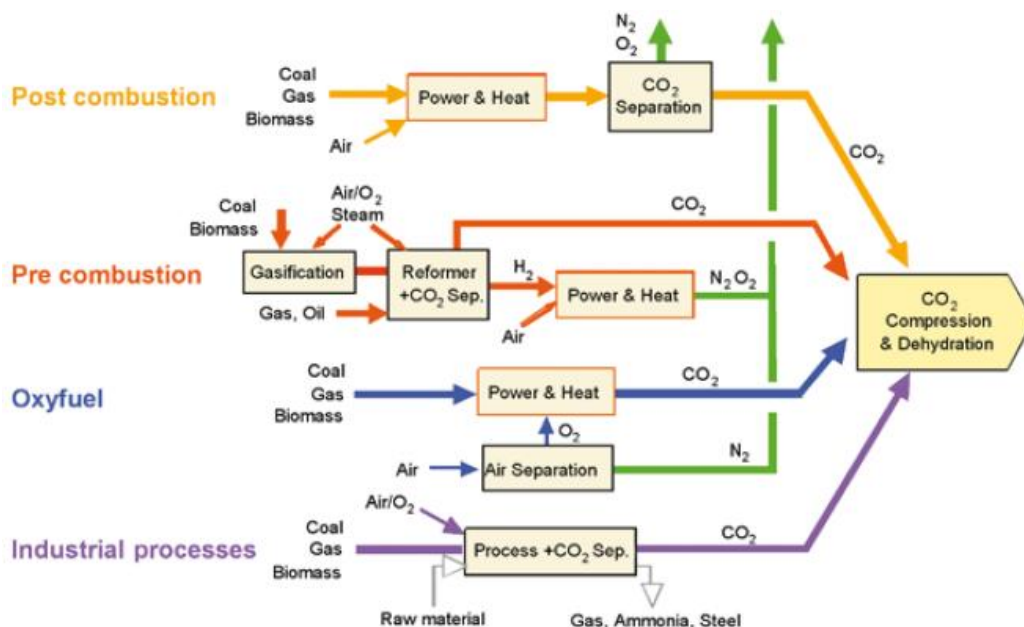


Figure 1.3: Overview of CO₂ capture systems [5]

basis) that makes separation easy. In oxy fuel combustion system, oxygen is used for combustion. Oxygen is separated from air by cryogenic distillation. Flue gas contains water vapors and CO₂ (more than 80 % by volume). Water can be removed by cooling and then by compressing the flue gas to high pressure to facilitate separation.

Post combustion and pre-combustion CO₂ capture are economically feasible if favorable CO₂ tax is applied. These technologies are well understood and used in selected commercial applications. Oxy-fuel combustion is in demonstration phase for CO₂ coming from boilers while in R & D stage for gas turbine systems. Present CO₂ capture systems are energy intensive and significantly reduce the overall efficiency of fossil fuel based power plants and other industrial processes. Increased fuel requirements, generation of solid waste and other environmental impacts are other issues. All of these CO₂ capture systems require involve the separation of CO₂, H₂ or O₂ from a bulk gas stream (such as flue gas, synthesis gas, air or raw natural gas). These separation steps can be accomplished by means of absorption using physical or chemical solvents, membranes, adsorbents, or by cryogenic separation. To date, chemical absorbent processes are preferred technology due to their high capture efficiency, selectivity, low energy and cost as compared to other existing post combustion CO₂ capture technologies [5, 6].

Total energy required in operation of a CO₂ capture plant consists of thermal energy required to regenerate absorbent, electrical energy required by pumps and flue gas blower and liquefaction/compression of separated CO₂ for geological storage. Absorbent selection is a critical task as different absorbents required different heat of desorption for chemically bound CO₂ and for producing sufficient steam for stripping in the upper part of the desorber [6]. Furthermore viscosity and loading capacity of an absorbent play important role as it affects lean amine flow rate requirement and hence pumping energy.

A typical absorption process is shown in figure 1.4. Flue gases after cooling to 40-80 °C contacted in an absorber with amine solution. Amine solution chemically bound with CO₂ (Rich amine) pumped to stripper via Lean/Rich exchanger. In stripper, regeneration of amine takes place at round 2 bar & 110-125 °C depending upon the type of absorbent. Lean amine is then pumped back to absorber via exchanging heat in Lean/Rich exchanger and a cooler.

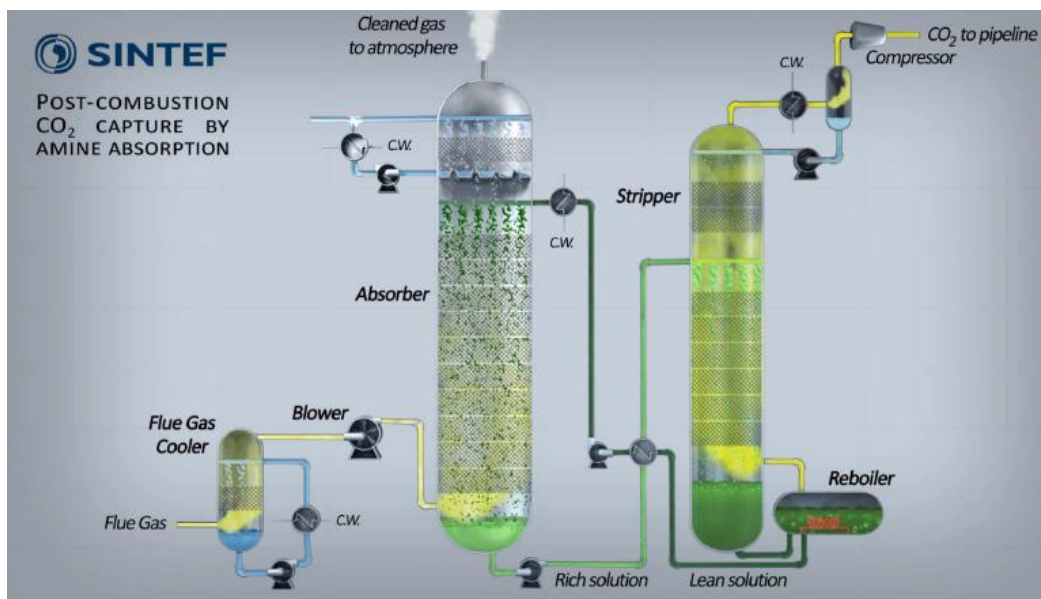


Figure 1.4: Process flow diagram (PFD) of CO₂ capture process using chemical absorbent [7]

‘To meet global emissions reduction goals at lowest cost, extensive deployment of CCS is required. Figure 1.5 shows that around 100 large-scale CCS projects will be needed by 2020, and over 3 000 by 2050. This represents a significant scale-up from the five large-scale CCS projects that are in operation today’ [8].

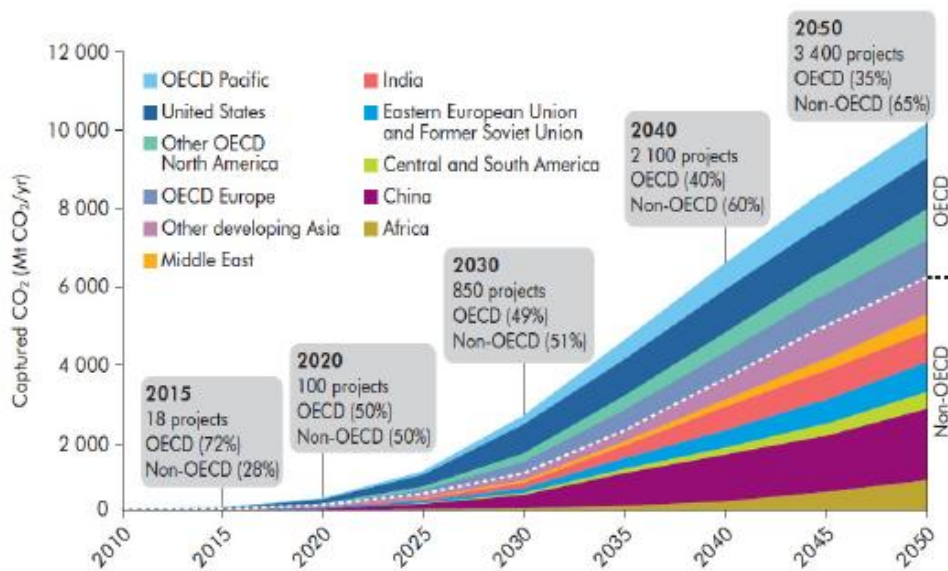


Figure 1.5: CCS deployment by region 2010-2050[8]

1.1.2. Solvents

Some of the commercial processes available based upon chemical solvent are as following [7]:

Process name	Solvent	Licensors
aMDEA	MDEA + Piperazine	BASF
ADIP, ADIP X	DIPA, DIPA + MDEA	Shell
Amine Guard II	MDEA	UOP LLC
Fluor Econamine FG, Econamine FG+	MEA	Fluor
Amine Guard FS	MEA	UOP LLC
Kerr McGee	MEA	ABB Lummus

1.1.3. Heat of absorption

Heat of absorption is directly related to the energy used for the regeneration of the solvent. However other important properties should be also taken into account when selecting a new solvent. For example, tertiary amines like MDEA and DEEA show the lowest heats of absorption indicating that less energy may be needed to reverse the chemical reaction for these amines in the stripper. However, tertiary amines are known to have low reaction rate with CO₂. Besides, their low biodegradability makes these solvents less environmentally friendly. Potassium carbonate solutions are more environmentally friendly and precipitation should be taken into account when using this chemical [14].

An ideal solvent system is that which gives the overall lowest cost of CO₂ capture with the least environmental impact. Solvent properties (viscosity, density, molecular weight etc) are directly related to the process parameters there should be a set of optimal process design and operating conditions for each solvent [14].

1.2 Scope of work

Solvent selection is a vital step as it directly relates regeneration energy (reversal of heat of absorption) required which accounts for over more than half of the operational cost (OPEX). Hence it is desirable that enthalpy of absorption must be low. The objective of this work is to measure heat of absorption of CO₂ for different absorbents both single and mixed at different temperatures that will be helpful in selection and characterization of absorbent for CO₂ capture

processes. Heat of absorption of CO₂ with different solvents was measured in this work in a commercially available reaction calorimeter CPA-122 of ChemiSens as a function of temperature and loading over the temperature range from 40 to 80 °C. Studied absorbent systems are 5 % by weight ammonia aqueous solution, 0.8 M piperazine, mixture of 5 % weight of ammonia and 0.8 M piperazine, mixture of 5 % weight of ammonia and 0.4 M piperazine and mixture of 2.5 % weight of ammonia and 0.8 M piperazine. Experimental heats of absorption of CO₂ with these systems are compared.

Chapter 2 **EXPERIMENTAL SETUP & PROCEDURE**

2.1 Calorimetry and calorimeters

“Calorimetry is a technique used to determine amount of heat generated or consumed in processes which may either chemical reactions or physical transitions. Measuring devices in which an exactly known amount of heat is input into a sample, or abstracted from it, and the temperature change in the sample is measured, are referred as calorimeters” [6].

2.1.1 Classification of calorimeters

Depending upon kind of heat-generating or heat consuming process, physical state of sample and conditions (temperature, pressure and atmosphere) under which calorimeter is to be used, a great variety of calorimeters has been developed. Primarily calorimeters classification depends upon following:

1. The principle of measurement
2. The mode of operation
3. The construction principle

The individual groups of primary criteria comprise the following secondary criteria:

1. The principle of measurement

- a) Heat-compensating principle:** Determination of the energy (power) required for compensating the heat (heat flow rate) to be measured.
- b) Heat-accumulating principle:** Measurement of the temperature change caused by the heat to be measured.
- c) Heat-exchanging principle:** Measurement of the temperature difference between sample and surroundings caused by the heat (heat flow rate) to be measured.

2. The mode of operation

- a) **Static:** This type of calorimeter may be isothermal, isoperibol and adiabatic in operation.
- b) **Dynamic:** This includes scanning of surroundings, isoperibol scanning and adiabatic scanning.

3. The construction principle

- a) Single measurement principle
- b) Twin or differential measuring principle

Most of the calorimeters can be classified by means of these criteria. Not all secondary criteria from the three groups can be combined. As the heat to be measured (first) appears as a heat flow to be exchanged, there are always temperature gradients in calorimetric measuring systems so that, for example, an ideally isothermal state cannot be established. In addition, temperature differences always occur between sample and the environment so that there are undesired heat leaks which must be taken into account as a correction i.e., there are no ideal adiabatic operating conditions [9].

Calorimeters used for the measurement of heat of absorption of acid gases in amines are isothermal flow calorimeter, differential flow calorimeter, adiabatic flow calorimeter and reaction calorimeter [6]. In the present work, reaction calorimeter is used.

Heat of absorption can also be estimated from phase equilibrium data by application of following thermodynamic relation:

$$\left[\frac{\partial \ln f_i^{\wedge}}{\partial (1/T)} \right]_{P,x} = \frac{\Delta H_s}{R}$$

When using above equation, uncertainties in gas solubility data result in an increase in an uncertainty heat of absorption. If the solubility data are accurate to ± 2 -3%, this results in enthalpy values that are ± 20 -30-%. So the calculation of fugacity coefficient and its inclusion is not considered justified and a simplified form of above equation, equating partial pressures and fugacities, is used. No temperature dependency can be observed from such calculations, because the plots of CO₂ partial pressure versus 1/T are considered linear [11].

2.1.2 Reaction calorimeter

Reaction calorimeters are calorimeters of sufficient scale such that production plant conditions can be mimicked. Several types of reaction calorimeters are available commercially. Reactor calorimeters from ChemiSens were used for measuring heats of absorption of acid gases with amine solutions by Kierzkowska-Pawlak and Zarzycki (2002), Inna Kim (2009), Feng Qin (2009) and in this work.

ChemiSens has developed calorimeters with measurement of the enthalpy difference between the inlet and outlet of the jacket. The scheme of the calorimeter is presented in the figure-2.1.

The CPA-122 reaction calorimeter of 2 liter volume is used in this work. The ChemiSens TC200 circulator is used to control the reactor temperature of the CPA 122 system by pumping the thermostating liquid through the reactor jacket. TC200 which is a cascade control loop (control loop within a control loop: reactor temperature control loop which is an outer or primary loop feeds the circulator control loop which is secondary or inner loop) adjust the temperature of the liquid in the jacket and controls the temperature of the reactor. The reactor temperature control loop feeds the circulator control loop with the difference between reactor temperature set point and jacket set temperature. The temperature of the thermostating liquid is controlled by the direct heating/cooling in the TC200 circulator. Cascade control with CPA 122 system suppresses powerful overshoots from the control circuits.

The thermal power, generated in the reactor, is measured according to heat balance:

$$HB = \frac{dM}{dt} C_p (T_{out} - T_{in})$$

Where $(T_{out} - T_{in})$ is the measured temperature difference between the outlet and inlet of the thermostating liquid in the jacket. The flow rate (dM/dt) and the heat capacity (C_p) are system properties of the CPA-122 [6, 10].

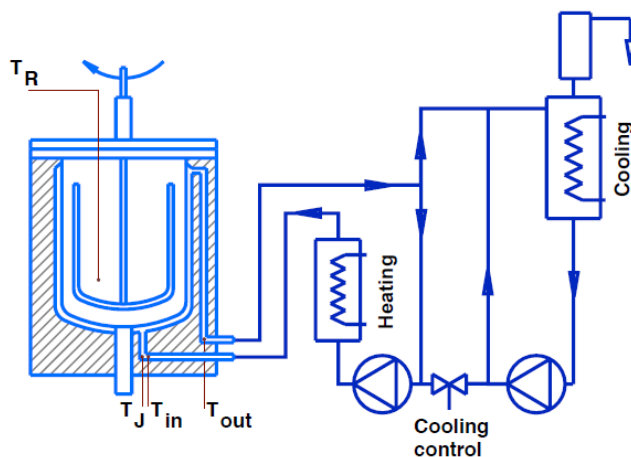


Figure-2.1: Reaction calorimeter of ChemiSens

2.2. Experimental procedure

2.2.1 Chemicals

The chemicals used in this work CO₂ (AGA, $\geq 99.99\%$ pure), aqueous ammonia (Merck, 25% minimum) and Piperazine (Sigma-Aldrich, 99%) were used without any further purification. Ammonia solutions were prepared by diluting 25 wt% aqueous ammonia, and the exact concentrations were found by titration with sulfuric acid after the solutions charged into reactor.

2.2.2. Procedure

The reaction calorimeter CPA-122 used in this work is a mechanically stirred reactor of 2 liter volume. Operation pressure of the reactor is -1 to 100 barg at temperatures from -20 °C to 200 °C. The system provides a measure of the heat flow in real time.

The calorimetric studies involved measurements of the gas phase pressure in the CO₂ storage cylinders and heat generation rate with respect to the time during semi-batch isothermal absorption of CO₂. The system continuously measures heat production rate, reactor temperature, stirring speed, system pressure, and other parameters.



Figure 2.2: Photograph of experimental arrangement

All operating conditions are recorded as function of time. The experimental set-up is shown in figure 2.3.

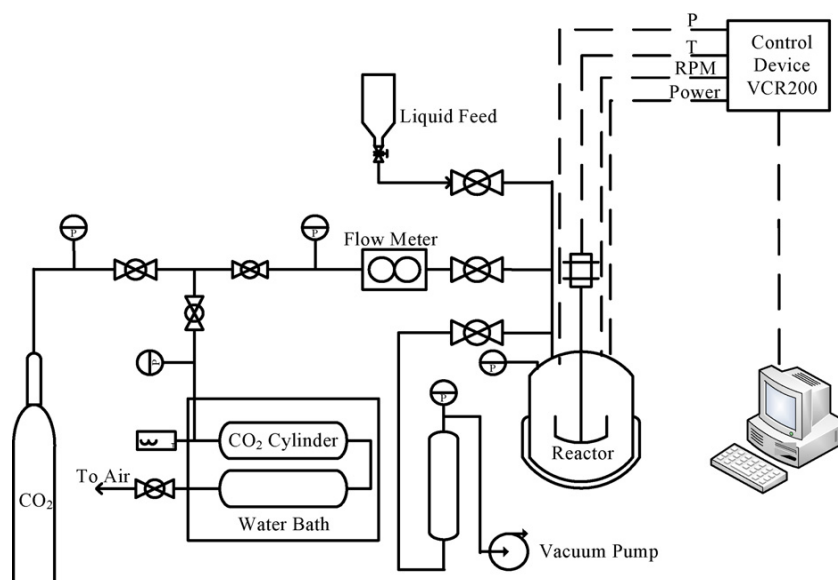


Figure 2.3: Experimental setup

Before filling the feed bottle, with solution, it was flushed with nitrogen. To avoid any inert gas in the reactor and to prevent contamination of reactants, before transferring the amine solution into reaction vessel, vacuum is created (around -0.95 to -1 barg). Turn on the circulation unit, control box and PC. Launch the InTouch window viewer program on PC. Check the pressure in the CO₂ cylinders. Add CO₂ if necessary (max. possible P about 20 barg). Charge the reaction vessel which is already vacuumed with solution of around 1.2-1.5 litres. Due to the volatility of ammonia/ ammonia & Piperazine solution, a sample was used to take for titration in order to determine the exact concentration at the time of charging. Using HMI, set the desire temperature, turn on stirring at a certain RPM and data logging must be started afterwards. The solution was heated to the set temperature. The system was considered to be at equilibrium when no change in the reactor temperature (within ± 0.01 °C) or pressure (within ± 0.01 bar) was observed, and also when no heat transfer to or from the reaction system from the thermostating media took place, $\Delta T = (T_{in}^{jacket} - T_{out}^{jacket}) = const.$ After the system reached equilibrium, an amount of CO₂ monitored by pressure difference in the CO₂ cylinders, was fed to the reactor through the mass flow controller. This difference in pressure for ammonia / ammonia & piperazine solution was around 1-1.5 bar and for 0.8 M piperazine solution it was around 0.4-0.45 bar. The system was then allowed to reach a new equilibrium before next loading sequence could take place. The experiments were conducted in isothermal mode while the pressure in the reactor before and after the reaction and the amount of heat added or removed to the system by the thermostating media to keep the system at constant temperature were recorded. Normally 10 to 12 points used to take in one experiments or till no more CO₂ could enter the reactor at set CO₂ feed pressures. The amount of CO₂ fed to the reactor was calculated from the pressure difference in the CO₂ storage cylinders before and after each feeding of CO₂ using the Peng-Robinson equation of state.

After finishing the experiment stop logging and cool down the reactor contents to around 40 °C. Open reactor vent valve slowly while fume hood must be top of it and then drain the reactor contents to a specified waste liquid storage drum. It is better to prepare the reactor for next experiment immediately by first cleaning with two times a bit warm tap water and then with distilled water so it can be dry overnight.

2.2.3. Uncertainties and experimental problems

There are three main uncertainties:

- the calculation of the molar amount of CO₂ added into the reactor from the storage cylinder
- the molar amount of CO₂ remaining in the gas phase of the reactor after each stage
- the heat power flow curve integration.

Peng-Robinson equation of state was used to calculate the molar amount of CO₂ added in each loading interval which can be calculated by the integration of the mass flow controller reading at the same time as a comparison reference. Based on the difference between both of these two methods, the estimated uncertainty of CO₂ addition was about $\pm 1.2\%$ [11].

The heats of absorption per molar CO₂ were calculated by the ratio of the heat released during a loading process (Q_{total}) and the amount of CO₂ absorbed (n_{CO_2}). The total uncertainty can be expressed as following [11]:

$$\frac{\delta \Delta H_{\text{abs}}}{\Delta H_{\text{abs}}} = \sqrt{\left(\frac{\delta Q_{\text{total}}}{Q_{\text{total}}} \right)^2 + \left(\frac{\delta n_{\text{CO}_2}}{n_{\text{CO}_2}} \right)^2}$$

On the other hand, another important source of the total uncertainty is the heat flux calculation which was mainly from determining the baseline in Fig. 2.4. It was assumed that the heat flux curve is integrated by the trapezoidal method and the baseline changes linearly [11]. Another source of uncertainty is the partial pressure of NH₃.

At lower CO₂ loading levels during the absorption process of CO₂ in aqueous NH₃, the total pressure in the reactor before and after CO₂ addition dropped around 0-0.04 bar; for the same process of CO₂ in PZ solution, the total pressure dropped around 0-0.01 bar. Considering the pressure change for pure CO₂ in the cylinder was about 1-2 bar, the volume of the cylinder (about 4 L) and the volume of the gas in the reactor (about 0.8 L), the changing of CO₂ pressure in the gas phase of the reactor could be disregarded. The addition of CO₂ could be assumed to be totally absorbed in the solution.

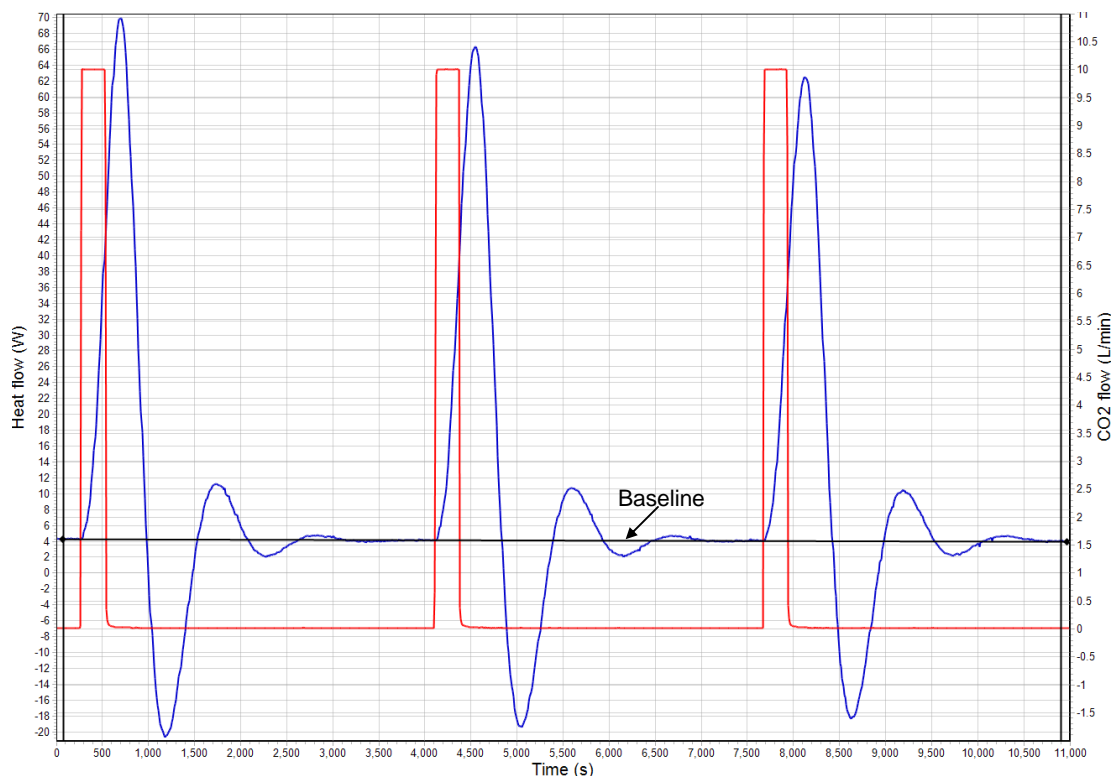


Figure 2.4: Heat of absorption of CO₂ with 5wt% aqueous NH₃

At higher loading levels (>0.5 mol CO₂/mol Am), the NH₃ partial pressures over the solution are low enough and cannot be detected even at 80°C according to Goppert and Maurer (1988). And the PZ partial pressure in gas-phase was much lower than NH₃ at the same condition and also could certainly be ignored. The total pressure change resulting from NH₃ and PZ gas-phase partial pressure is thus very small, comparing with the large amount of CO₂ added, the uncertainty caused by NH₃ partial pressure changing with CO₂ loading is negligible.

Problem which most encountered during experiments is the temperature control of reaction mixture. Sharp and irregular fluctuations in temperature were appeared during last week of February. It took time to identify exact problem and rectification of this was done by replacing an electric rely and control card. During first week of April there was ± 0.05 offset in reactor temperature. Tuning of control parameters tried but of no avail. Temperature sensor replaced and connection of heaters checked few found broken but rectified. At the moment this problem still persists (May 19, 2011) and it took 2-3 hours for settling to set-point but with said offset.

Chapter 3 HEAT OF ABSORPTION MEASUREMENTS

3.1. Related prior work

The temperature dependency of the heat of absorption is often neglected assuming a constant value both for absorber and desorber conditions (Kohl and Nielsen, 1997). However, experimental data from the literature and from this work show that there is difference between the heats of absorption at different temperatures [12].

The impact of acid gas loading on the heat of absorption is also often neglected. It may be explained by the fact that nearly all experimenters until now reported integral heats of absorption data where the effect of loading may not be seen. Kim et al. (2009) presented data on these variations and Bullin et al. (2007) show that knowledge of the effects of acid gas loading and other parameters on the heat of absorption can be used to more accurately predict and improve calculations in designing and operating amine sweetening facilities [12].

Experimental data from different authors agree that the heat of absorption increases with temperature, while the absorption capacity at high temperature is much lower than at low temperature. Higher pressure results in higher absorption capacity of the solution, since more CO₂ may be dissolved at higher pressures [12, 14].

Table 3.1: Prior work using reaction calorimeter [6, 12, and 13]

References	Calorimeter	Solvent	Temperature (°C)
Kierzkowska-Pawlak and Zarzycki (2002)[14]	CPA-102 (250 cm ³) reaction calorimeter	MDEA (10, 20, 30 wt%), Water	20, 40, 60
Kim and Svendsen (2007)	CPA-122 (2 liter) reaction calorimeter	MEA (30% by wt.), AEEA (30% by wt.)	40, 80, 120

Kim and Svendsen (2009)	CPA-122 (2 liter) reaction calorimeter	MEA(7molal)+Piperazine(3.5molal),water MEA(7molal)+ Piperazine (2molal),water DEEA(32wt%)+MAPA(8wt%),water DEEA(37wt%)+MAPA(3wt%),water MDEA(25wt%)+MAPA(15wt%),water Piperazine: 2 M aqueous solution	40, 80, 120
Qin & Svendsen (2009)	CPA-122 (2 liter) reaction calorimeter	2.5 wt. % aqueous NH ₃ 10 wt. % aqueous ammonium carbonate	35, 40, 60, 80

Kim (2009) used reaction calorimeter CPA-122 for measuring enthalpies of absorption of CO₂ with different solvents over a temperatures range of from 40 to 120 °C. Different from experimental data from other sources, heats of absorption measured in this work are differential both in temperature and loading. Experiments show that enthalpy of absorption depends on the solvent type, acid gas loading and temperature. Heats of absorption of CO₂ with single amine solvents and amine blends at 40 °C (absorber conditions) are compared in figure 3.1 and 3.2 with 30 wt% MEA solution [12].

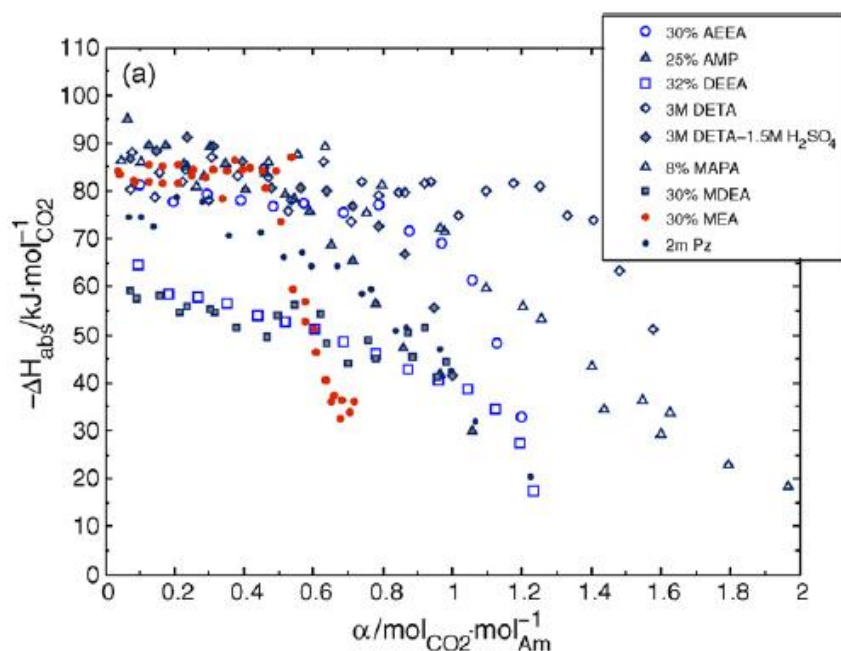


Figure 3.1: Heat of absorption of CO₂ with single amine solution 40 °C [13]

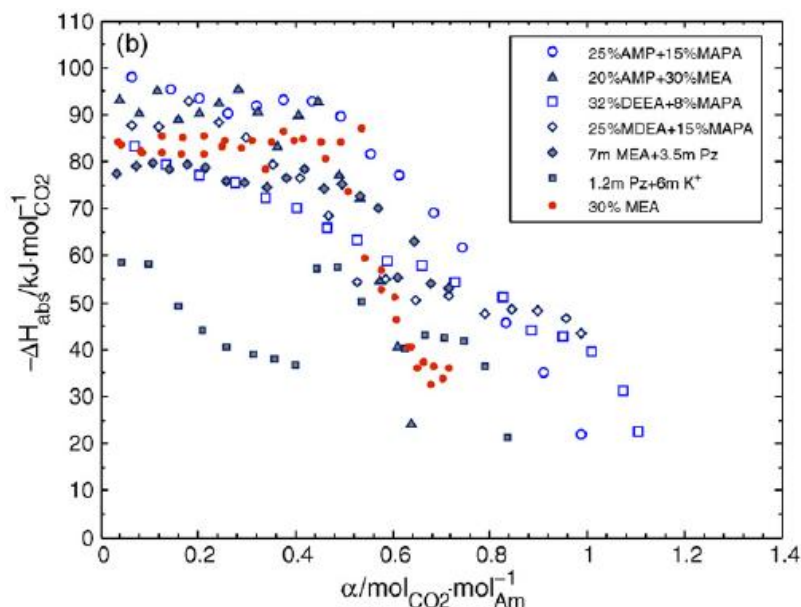


Figure 3.2: Heat of absorption of CO₂ with mixed amine solution 40 °C [12]

Tertiary amines, MDEA and DEEA, give the lowest heats of absorption. Piperazine, having two secondary amine groups, show heat of absorption similar to that of a secondary amine like DEA. All other single amines containing a primary amino-group in the molecule, gave heats of absorption close to that of MEA. Absorption capacity of the single amine solvents increase with the number of amine groups in the molecule. Among all tested amines, MEA showed the lowest absorption capacity. In the mixture of amines, the dependency of the heat of absorption on loading is affected by the composition of the solvent as shown in figure 3.2 [12].

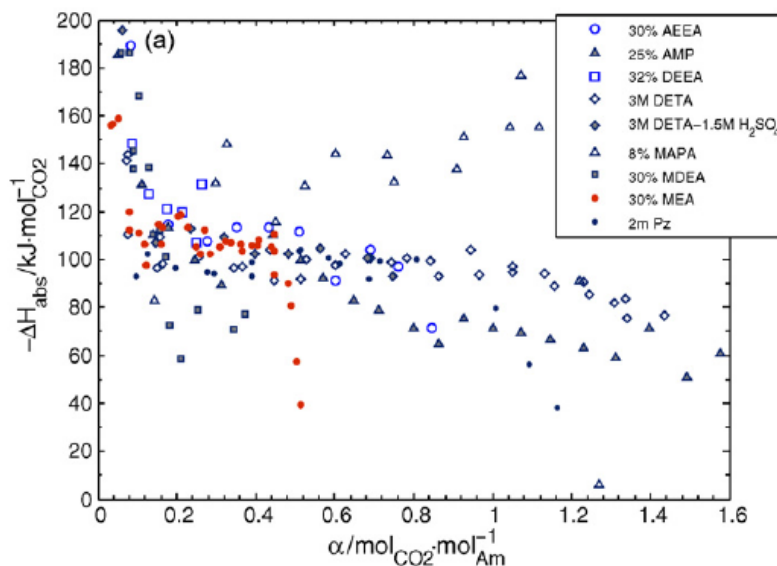


Figure 3.3: Heat of absorption of CO₂ with single amine solution 120 °C [12]

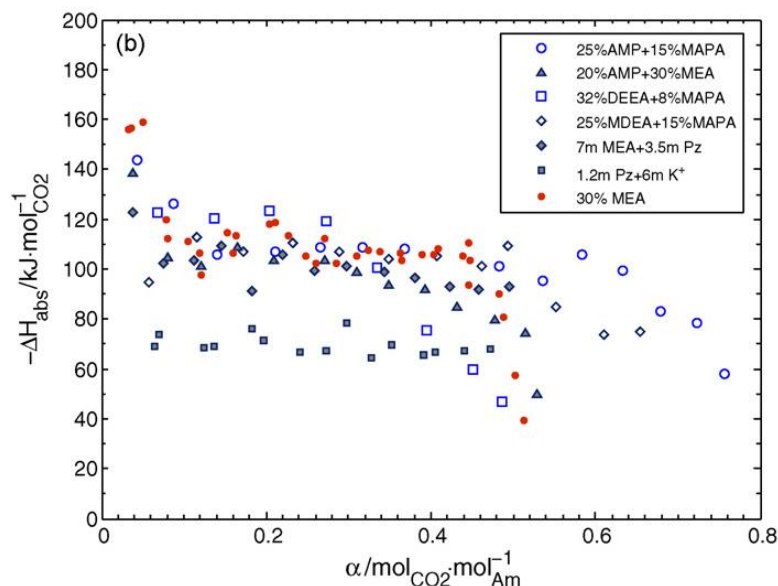


Figure 3.4: Heat of absorption of CO₂ with mixed amine solution 120 °C [12]

Heats of absorption of the same solvents at 120 °C (desorber conditions) are shown in figure 3.3 and 3.4. It may be seen from figure 3.3 & 3.4 that all systems, except the Pz–K⁺ mixtures, gave comparable heats of absorption [12].

Feng et al. (2009) used the same reaction calorimeter (CPA-122) as that of Kim et al. (2009) to determine the enthalpies of absorption of CO₂ in aqueous ammonia at temperatures of 35–80 °C as shown in figures 3.5, 3.6 & 3.7 [13].

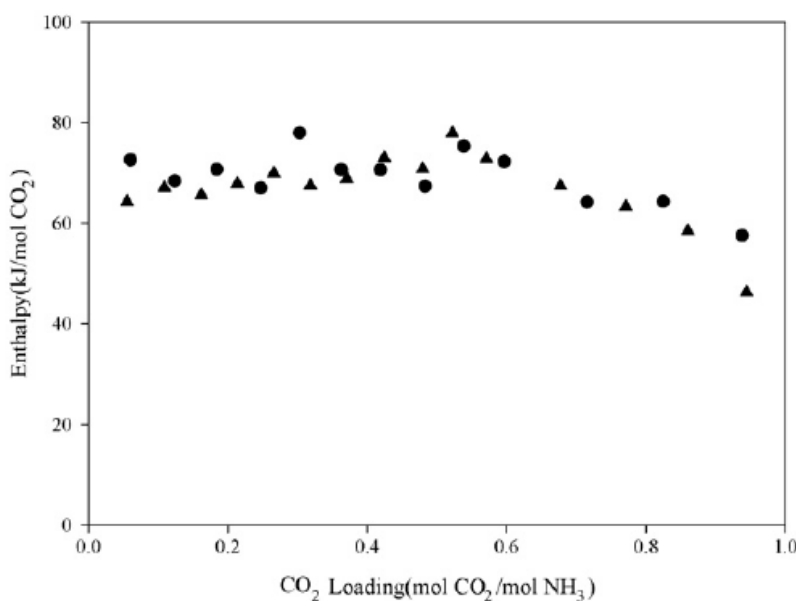


Figure 3.5: Enthalpy of absorption of CO₂ in ~ 2.5 wt. % aqueous ammonia solution at 40 °C for two runs [13]

The heat of absorption of CO₂ with 2.5 wt% aqueous ammonia solution was found to be about 70 kJ/mol CO₂, which is lower than that with MEA (around 85 kJ/mol) at 35 and 40 °C. The value slightly decreases with increased loading, but not to as low a value as expected by the carbonate–bicarbonate reaction (26.88 kJ/mol). The enthalpy of absorption of CO₂ in aqueous ammonia at 60 and 80 °C decreases at first, then increases with loadings between 0.2 mol CO₂/molNH₃ and 0.6 mol CO₂/molNH₃, and then decreases again figure 3.6 & 3.7 [13].

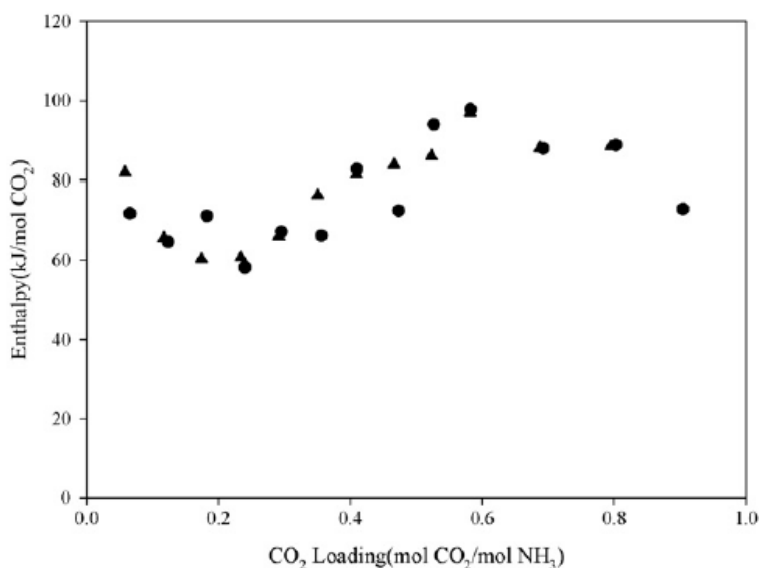


Figure 3.6: Enthalpy of absorption of CO₂ in ~ 2.5 wt. % aqueous ammonia solution at 60 °C for two runs [13]

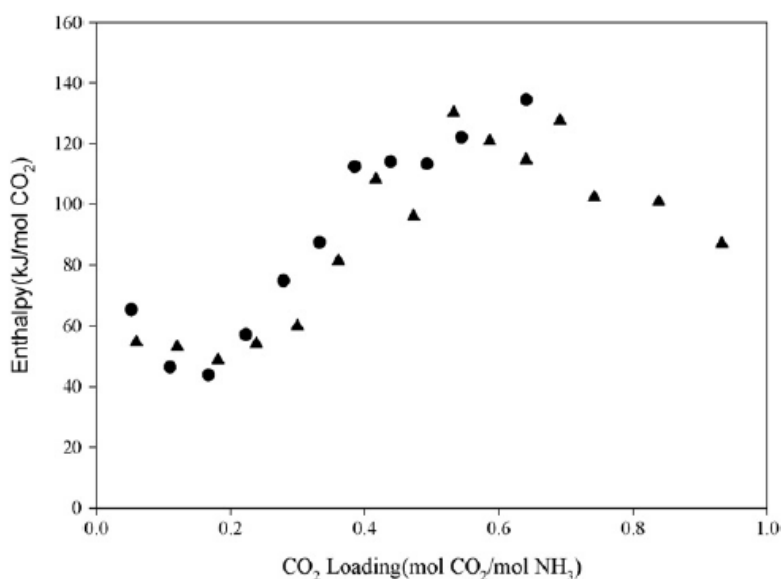


Figure 3.7: Enthalpy of absorption of CO₂ in ~ 2.5 wt. % aqueous ammonia solution at 80 °C for two runs [13]

The heats of absorption are directly related to the extent of the various reactions with CO₂ and can be assessed from the species variation in the liquid phase [13].

3.2. Experimental results & discussions

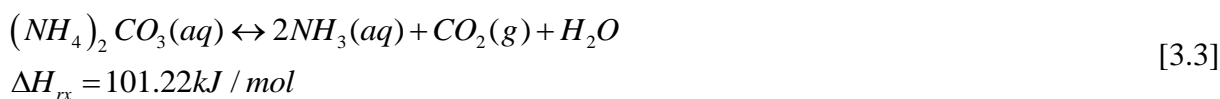
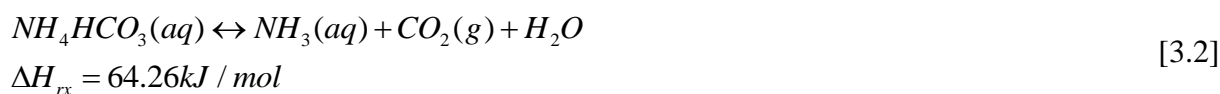
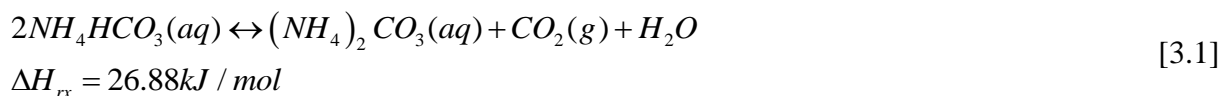
Experimental data are presented below as plots of semi-differential heats of absorption, ΔH_{abs} , as function of loading and temperature. Full tables with the data points are provided in Appendix.

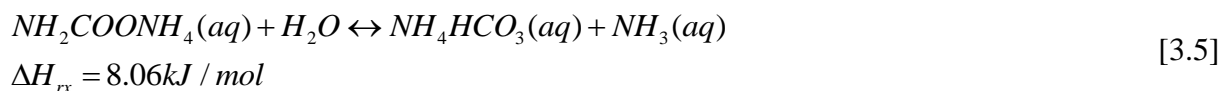
3.2.1. Single solvent systems

3.2.1.1. Aqueous ammonia solution (5% by wt.)

Aqueous ammonia solution has certain advantages over MEA due to its high loading capacity, no thermal and oxidative degradation, less regeneration energy requirement, system scrub Sox and NO_x as well and most importantly ammonia is cheap [13]. The differential enthalpies of absorption of CO₂ with 5 wt. % aqueous ammonia solution were measured in this work at 40, 60 & 80 °C. The results are compared in figure 3.8(a, b, c, d). The data is presented in tabulated form in appendix. The experimental data show that enthalpy of absorption depends both on loading and temperature. ‘This is a fact that is very often overlooked or ignored in simulators, most probably because o lack of good data’ [6].

When CO₂ reacts with aqueous ammonia solution a mixture of ammonium carbonate, bicarbonate and carbamate is produced at lower loadings as shown in following reaction equations (Kohl & Nielsen 1997):





The total reaction can be described by equation [3.2]. First of all reaction [3.4] occurs then $\text{NH}_2\text{COONH}_4$ has an irreversible reaction [3.5] in the reaction mixture while reactions [3.1] & [3.3] occur simultaneously.

Reaction [3.1] is the preferred path to absorb and regenerate CO_2 because it has lowest energy requirement. Experimental results as shown in figures 3.8 (a, b, c) suggest that this reaction does not occur even when the loading reaches 0.45-0.5 mol CO_2 / mol NH_3 which indicate this reaction occurs at higher loadings. At 40 °C heat of absorption, seems to be constant till loading 0.45 mol CO_2 / mol NH_3 as shown figure 3.8(a) having value of 75 kJ/mole CO_2 and then start decreasing with constant slope at higher loadings. Similarly, at 60 °C heat of absorption, seems to be a bit vary till loading 0.45 mol CO_2 / mol NH_3 as shown figure 3.8(b) having value of 70-75 kJ/mole CO_2 and then start decreasing at higher loadings. At 80 °C heat of absorption remains constant (65 kJ/mole CO_2) up to loading of 0.35 mol CO_2 / mol NH_3 then increased to 70 kJ/mole CO_2 for further loading up to 0.5 mol CO_2 / mol NH_3 and then for higher loading it decreases as shown in figure 3.8(c).

The reason for the high enthalpy of absorption than the preferred reaction [3.1] is that, even with higher loadings than 0.45 mol CO_2 / mol NH_3 , there is still a lot of free ammonia in the solution, which means that reaction between ammonium carbonate and CO_2 is not the dominant one. At higher loadings enthalpy of absorption decreases as carbonate and carbamate start reacting with CO_2 with a lower reaction heat [13].

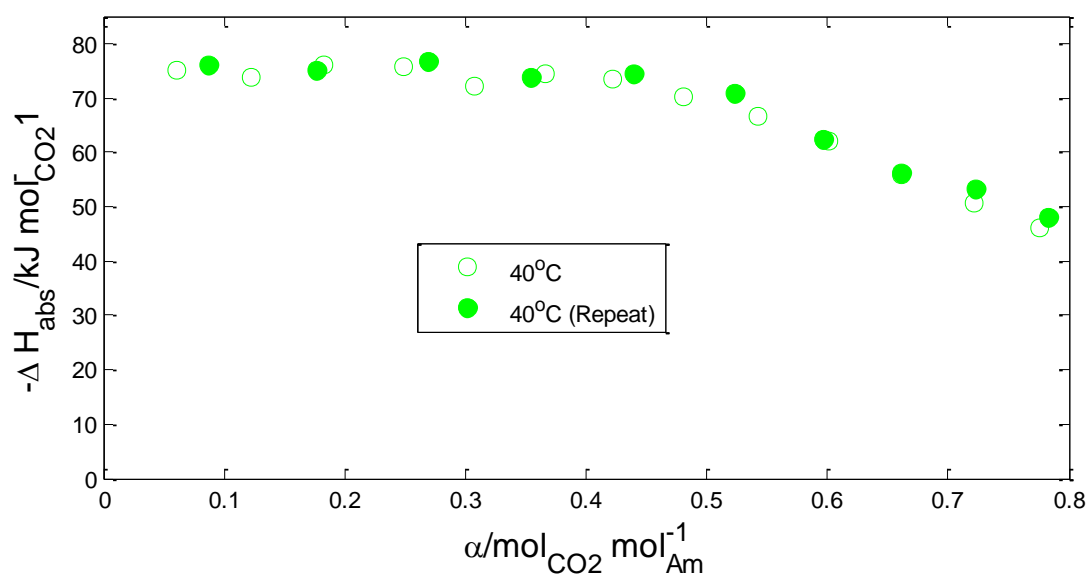


Figure 3.8(a): Experimental heat of absorption and repeatability of CO₂ with 5 wt. % aqueous ammonia solution at 40 °C

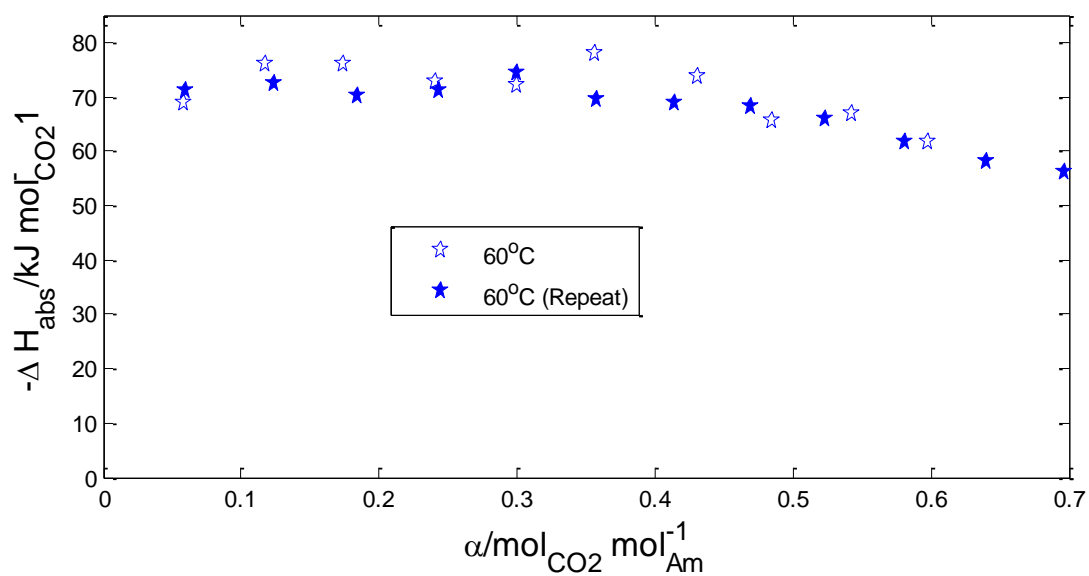


Figure 3.8(b): Experimental heat of absorption and repeatability of CO₂ with 5 wt. % aqueous ammonia solution at 60 °C.

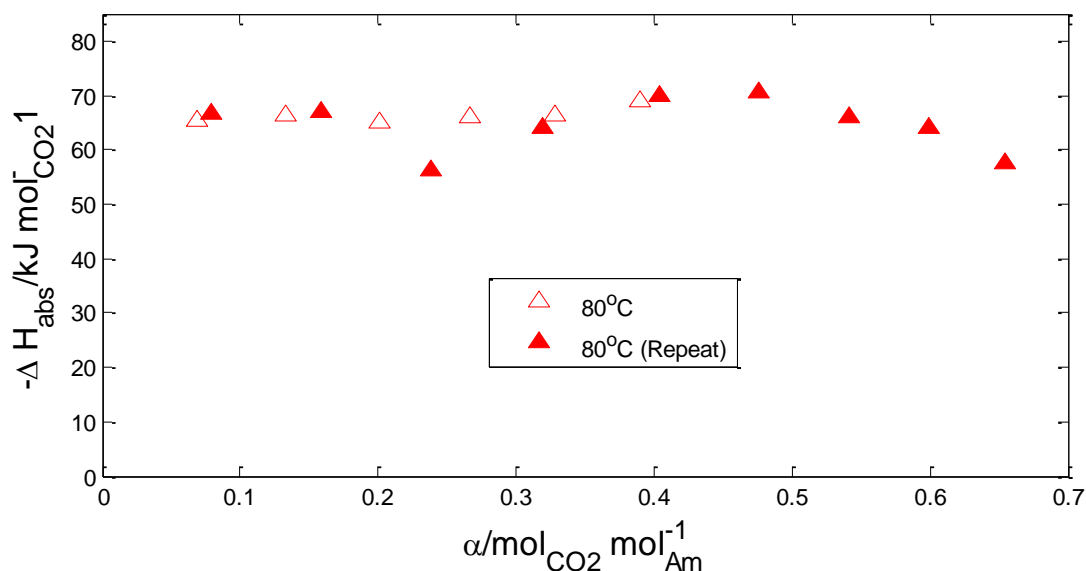


Figure 3.8(c): Experimental heat of absorption and repeatability of CO₂ with 5 wt. % aqueous ammonia solution at 80 °C

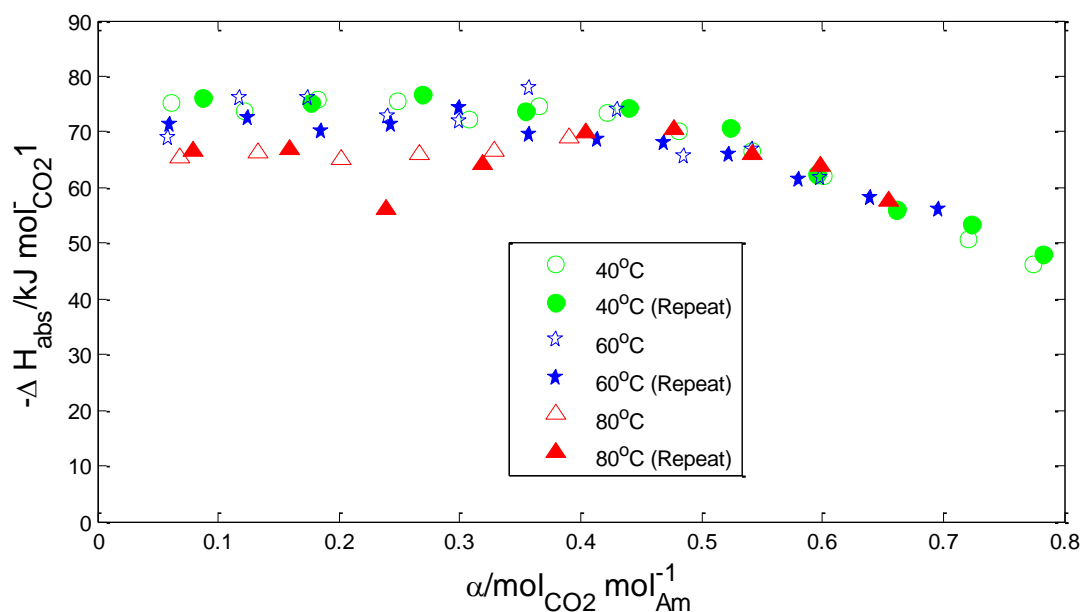


Figure 3.8(d): Experimental heat of absorption and repeatability of CO₂ with 5 wt. % aqueous ammonia solution at different temperatures.

At low loading interval (<0.5), the heat of absorption is around 65-75 kJ/mol CO_2 at each temperature that is similar to reaction of heat of reactions [3.4] & [3.5]. Thus experimental

results strongly proved that the reaction heat of CO₂ in aqueous NH₃ is mainly contributed by the formation of NH₂COONH₄ at the beginning of the absorption process.

For the reaction heat remain stable at low CO₂ loading interval (<0.5), it proved that free NH₃ in the solution is enough for the reaction of CO₂ with NH₃ during the whole low loading interval (<0.5) at each temperature, so that the reaction heat value is stable. And the reaction heat decreasing gradually at high loading interval (>0.5) indicated that with the increasing of the loading after 0.5, the free NH₃ in the solution started to reduce. Therefore instead of reaction [3.4], the effect of reaction [3.1] to the reaction heat became to be more and more important, so the reaction heat decreased significantly. However, there is still free NH₃ in the solution (Holmes et al., 1998), when the CO₂ loading is higher than 0.5, so the reaction heat reduced not as fast as MEA which shown in Figure 3.

Overall this system is showing opposite behavior as compared to MEA, MDEA, piperazine etc as differential heat of absorption is less at higher temperature (80 °C) as compared to lower temperature (40 °C) for same loading. This is true up to loading of 0.45 mol CO₂ / mol NH₃ and at higher loadings it become similar at all temperatures 40-80 °C as shown in figure 3.8(e). Probable reason is hydrolysis of ammonium carbamate i.e. reaction [3.5] which is an irreversible reaction and extent of which increases as temperature increases. When loading increases from 0.5 mol CO₂ / mol NH₃ reaction [3.1] become more prominent as compared to reaction [3.4] due to decrease in available free NH₃ in the reaction mixture. Hence the effect of hydrolysis of ammonium carbamate on heat of absorption becomes less significant as compared to low loading. All these discussions are validating experimental results as shown in figure 3.8(e).

It was observed that a white crystalline solid form in the pulsation line of reactor pressure sensor, reactor pressure gauge and in all lines in contact with the gas phase. This occurs due to reaction of CO₂ with ammonia in gas phase at elevated temperature during long period of time (10-15 hours).

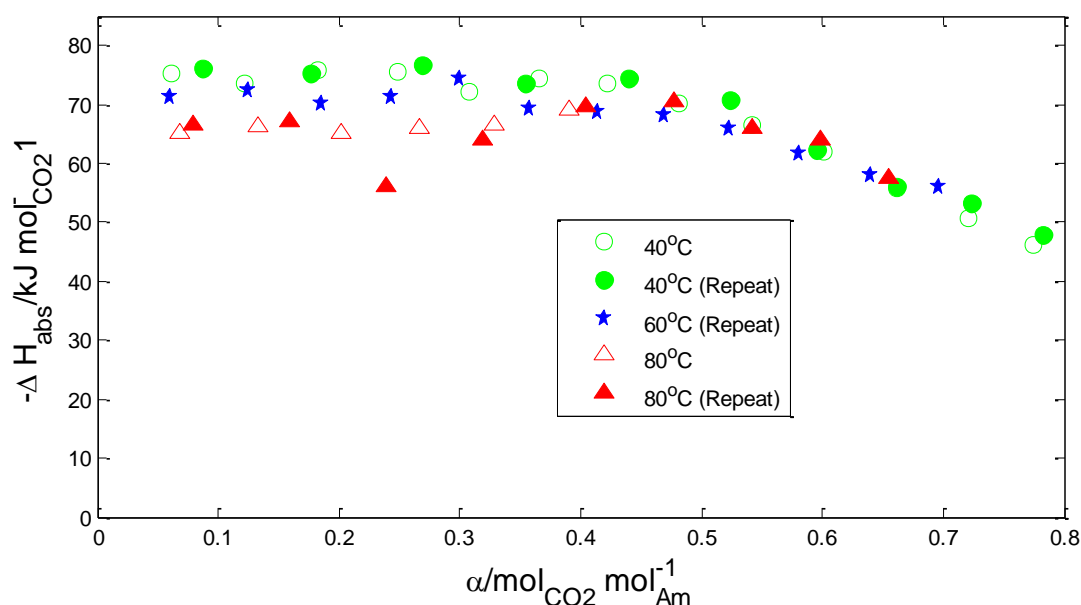
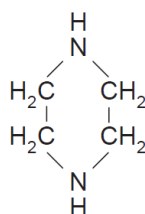


Figure 3.8(e): Experimental heat of absorption and repeatability of CO₂ with 5 wt. % aqueous ammonia solution at different temperatures.

3.2.1.2. Aqueous solution of piperazine (0.8 M)

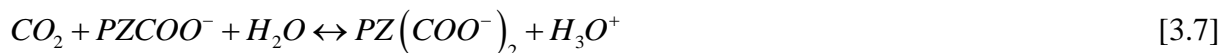
Piperazine is a cyclic amine with the following structure:



There are only few studies dealing with single aqueous piperazine solutions. This might seem logical due to the fact that, in industry, piperazine is only used in combination with other amines rather than as a stand-alone solvent, but information on the kinetics of the individual components of a solvent with CO₂ is essential for a better understanding of the mechanism and working principle of the absorption process of CO₂ in blends of alkanolamine solutions. Inna Kim (2009) experimentally found differential heat of absorption of 2 M piperazine aqueous solution. Moreover, in rigorous flux models all these reaction kinetics are required input parameters [Versteeg and Van Swaaij, 1988a]. Once experimentally observed fluxes of CO₂ into aqueous

piperazine solutions can be understood and simulated accurately, it is possible to theoretically predict the behavior of blends of piperazine with other amines [16].

In aqueous environment, piperazine can react with CO₂ to form many different reaction products.



Overall rate of absorption is solely influenced by reaction [3.6] ^[12]. Initially PZ, H₂O and CO₂ react to form $PZCOO^-$ & H_3O^+ according to this reaction that mainly determine heat of reaction. As the absorption process going on, the CO₂ loading of solution increased so PZ decreased and generation of $PZCOO^-$ stimulate reaction [3.7] to occur. Piperazine has lower heat of absorption than MEA at all temperatures and absorption capacity is much higher than MEA [4]. Heat of absorption of CO₂ with 0.8 M piperazine solution is measured in this work at 40, 60 and 80 °C and compared with the results obtain by Inna Kim (2009). The results are compared in figure 3.9 (a, b, c, d). The data is presented in tabulated form in appendix.

At 40 °C , enthalpy of absorption remains constant (70 kJ/mole CO₂) up to loading of 0.4 mol CO₂ / mol PZ, then decreases with a constant slop up to loading of 1 mol CO₂ / mol PZ and then decreases more sharply as shown in figure 3.9 (a).

At 60 °C, enthalpy of absorption increases from 70 to 75 kJ/mole CO₂ during initial loading up to 0.2 mol CO₂ / mol PZ then remains constant (70 kJ/mole CO₂) up to loading of 0.55 mol CO₂ / mol PZ, then increases to 75 kJ/mole CO₂ and at loading higher than that of 0.6-0.65 mol CO₂ / mol PZ decreases sharply as shown in figure 3.9 (c). Repeatability is not good at 60 °C.

At 80 °C, enthalpy of absorption remains constant (75 kJ/mole CO₂) up to loading of 0.2 mol CO₂ / mol PZ, then increases to 90 kJ/mole CO₂ for loading up to 0.35 mol CO₂ / mol PZ, then decreases to 75 kJ/mole CO₂ for loading up to 0.55 mol CO₂ / mol PZ and then again increase to 85 kJ/mole CO₂ for loading up to 0.7 mol CO₂ / mol PZ and for further increase in loading it decreases as shown in figure 3.9 (d).

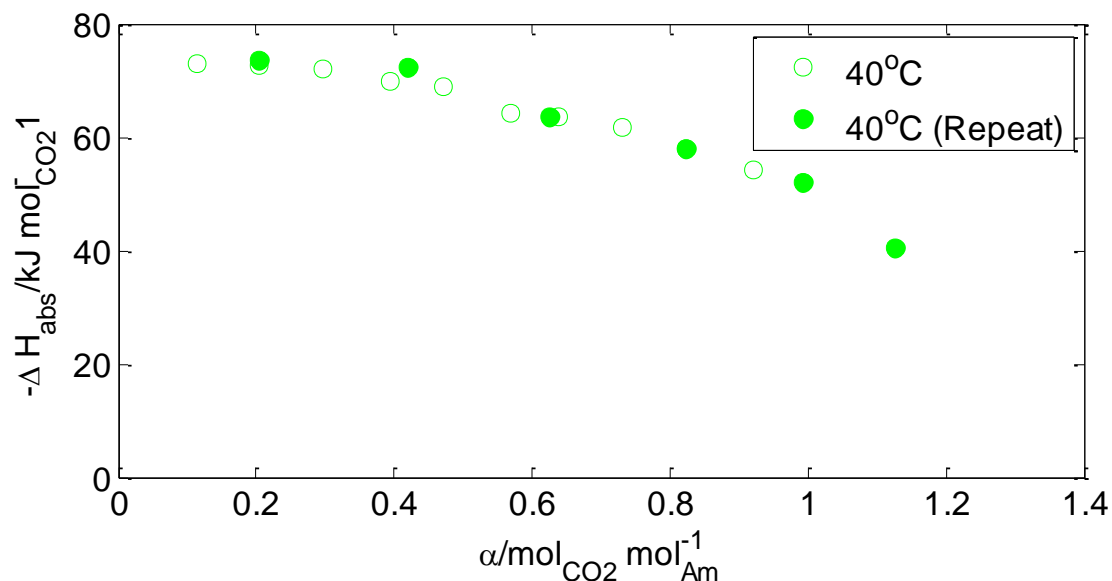


Figure 3.9 (a): Experimental heat of absorption and repeatability of CO₂ with 0.8 M Piperazine solution at 40 °C.

The comparison of 0.8 M and 2 M PZ solutions at 40 °C as shown in Figure 3.9(b) that the concentration of PZ solution has no big effect on the reaction heat. This implies that the reaction of PZ with CO₂ at different PZ concentration give almost the same distribution of reaction products.

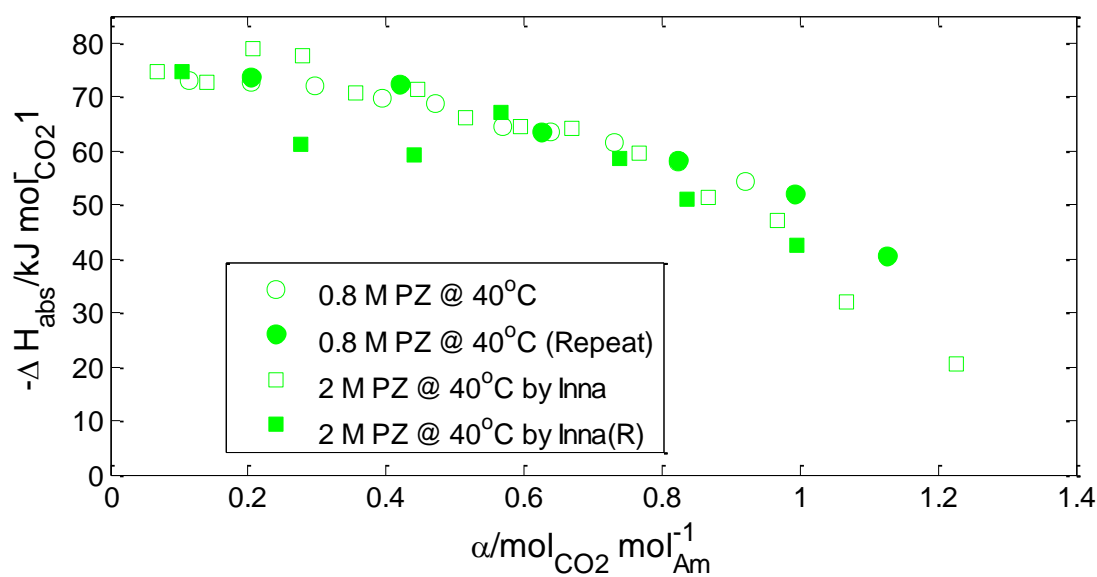


Figure 3.9 (b): Experimental heat of absorption and repeatability of CO₂ with 2 M Piperazine solution at 40 °C by Inna Kim (2009).

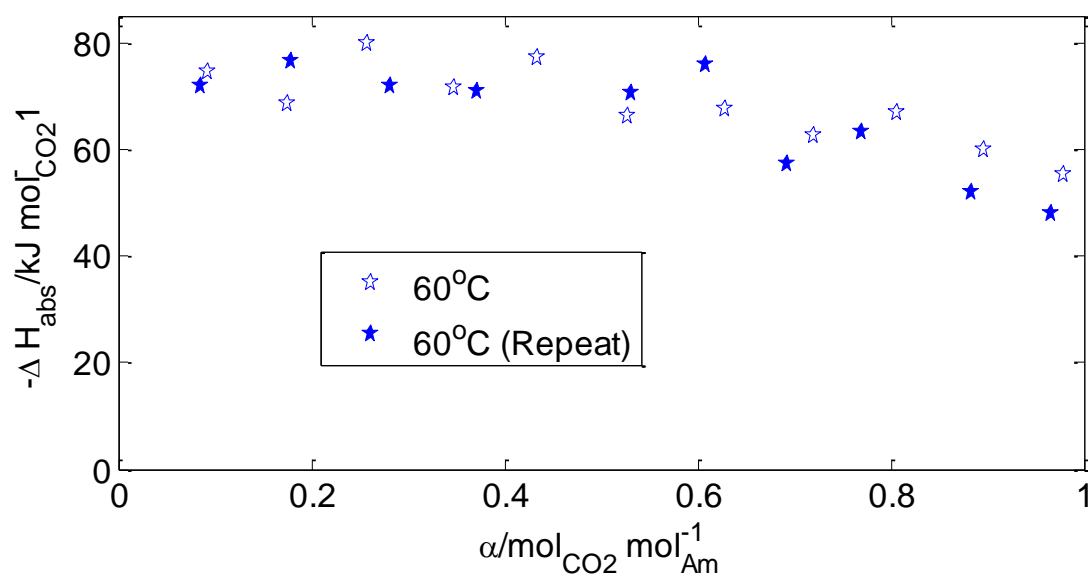


Figure 3.9 (c): Experimental heat of absorption and repeatability of CO₂ with 0.8 M Piperazine solution at 60 °C.

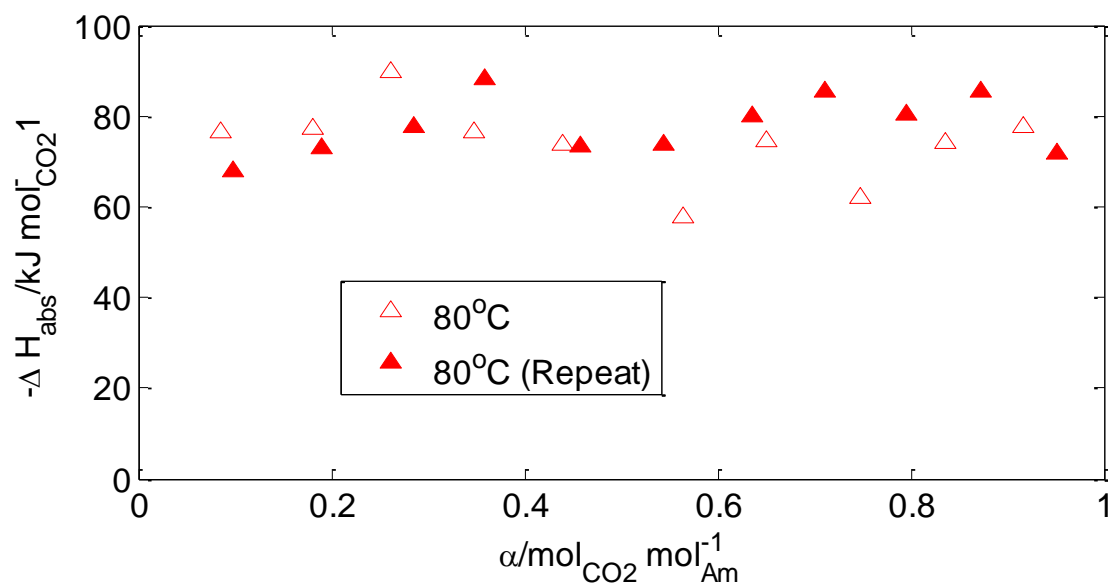


Figure 3.9 (d): Experimental heat of absorption and repeatability of CO₂ with 0.8 M Piperazine solution at 80 °C.

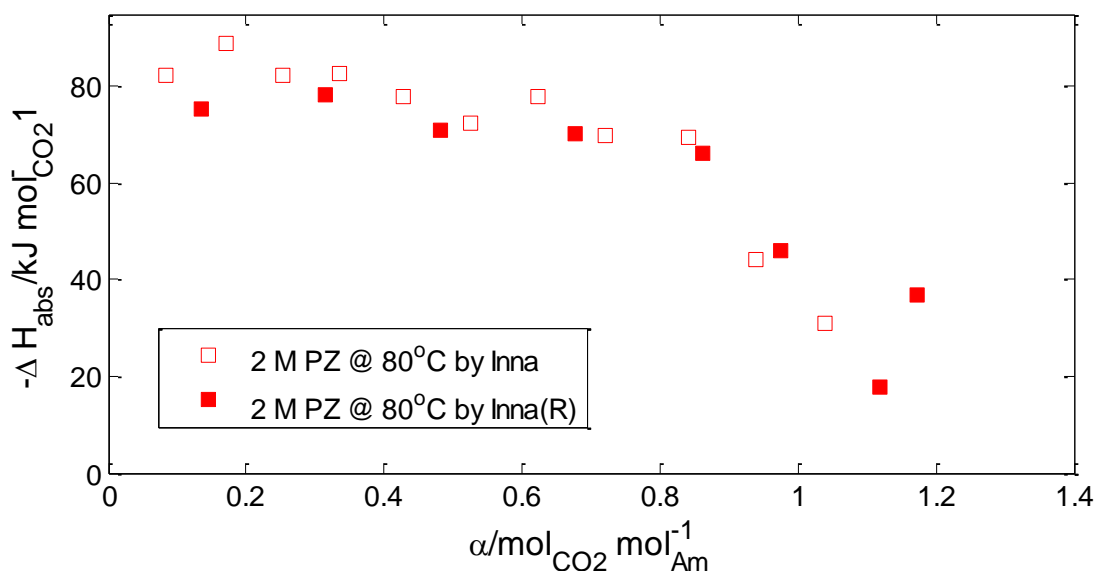


Figure 3.9 (e): Experimental heat of absorption and repeatability of CO₂ with 2 M Piperazine solution at 80 °C by Inna Kim (2009).

The comparison of 0.8 M and 2 M PZ solutions at 80 °C as shown in Figure 3.9(f) which shows there is variation in both. This implies that the reaction of PZ with CO₂ at different PZ concentration gives some different distribution of reaction products.

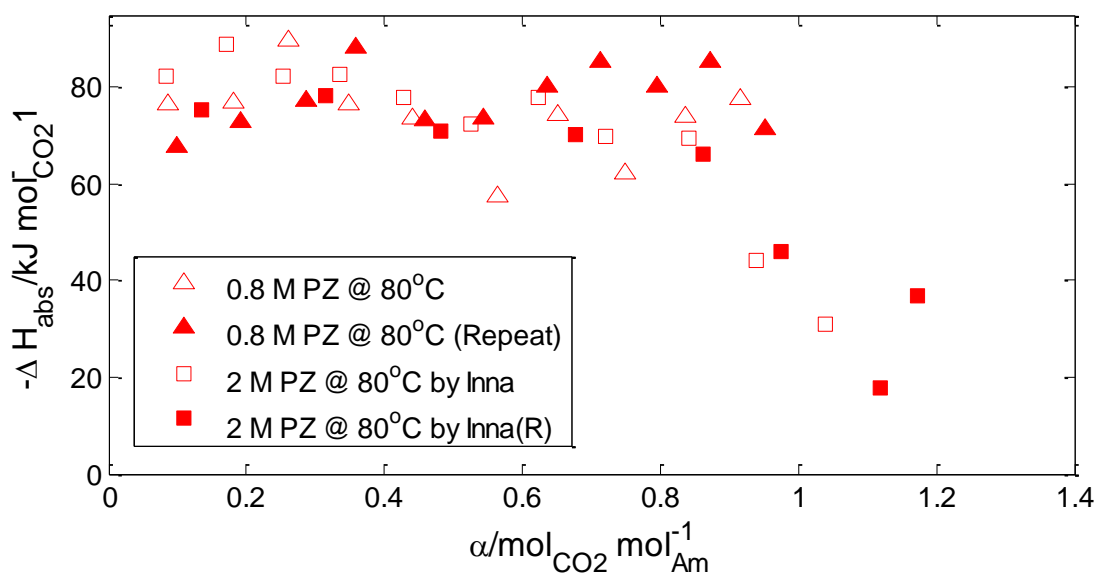


Figure 3.9 (f): Experimental heat of absorption and repeatability of CO₂ with 0.8 M Piperazine solution at 80 °C.

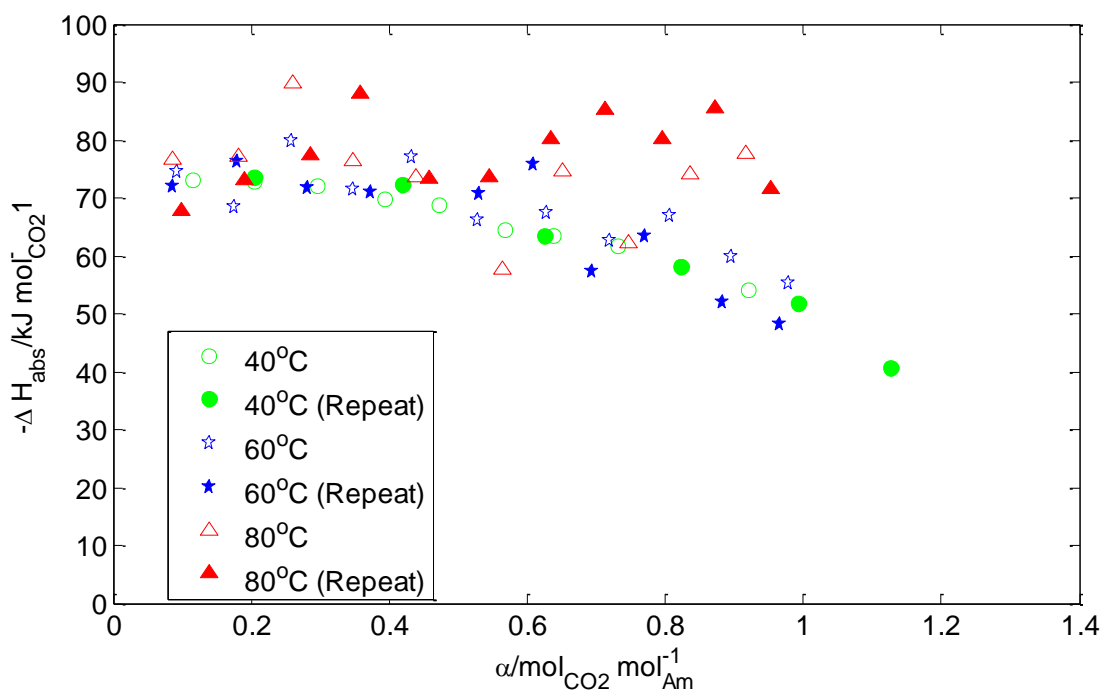


Figure 3.9 (g): Experimental heat of absorption and repeatability of CO₂ with 0.8 M Piperazine solution at different temperatures.

Overall differential heat of absorption is increases with temperature as shown in figure 3.9 (g) which is clearly opposite to that of what found for the case of 5% by weight aqueous solution of ammonia where heat of absorption decreases with increasing temperature of solution in the calorimeter for any specific loading less than 0.5 mol CO₂ / mol NH₃. The reaction heats of CO₂ in 0.8 M PZ have no big difference at 40 °C and 60 °C under full loading conditions. And with the temperature up to 80 °C, the reaction heats at low CO₂ loading interval (less than 0.5 mol CO₂/mol PZ) were little higher than 40 °C and 60 °C values, but at high loading (greater than 0.5 mol CO₂/mol PZ) were significantly higher. At high temperature, reaction [3.6] is more prominent even at high loading. Meanwhile, the rise in temperature also change the equilibrium constant of reversible reactions of CO₂ with PZ solution and consequently, to a certain extent, increase in the total reaction heat. This phenomenon could also be verified in Kim's results (2009).

3.2.2. Blends

3.2.2.1. Aqueous solution of 5% wt. NH₃ & 0.8 M piperazine

Recent interest and developments in the bulk removal of CO₂, owing to the Kyoto agreement, involve the addition of an activator (usually a primary or secondary amine) to an aqueous N-methyldiethanolamine (MDEA) solution particularly for natural gas sweetening. The reason for the use of such a blend is related to the relatively high rate of reaction of CO₂ with the activator combined with the advantages of MDEA concerning regeneration and stoichiometric loading capacity, which leads to higher rates of absorption in the absorber column while maintaining a low heat of regeneration in the stripper section [16].

The use of piperazine (PZ) activated aqueous MDEA solutions was patented by BASF as it proved to be successful when applied in the bulk removal of CO₂ in ammonia plants [Appl et al., 1982]. Since then, several studies have reported on the characteristics and performance of piperazine activated blends [16]:

- PZ activated aqueous MDEA solutions [Bishnoi and Rochelle, 2002a,b, Liu et al., 1999, Xu et al., 1992, 1998, Zhang et al., 2001, 2003]
- PZ activated aqueous AMP solutions [Seo and Hong, 2000, Sun et al., 2005]
- PZ activated aqueous MEA solutions [Dang and Rochelle, 2003]
- PZ activated aqueous K₂CO₃ solutions [Cullinane and Rochelle, 2004, 2005]

Heat of absorption of CO₂ in aqueous solution of ammonia activated by piperazine is studied in this work.

In the initial stage of the absorption process for the mixed solution, PZ had a much faster reaction rate with CO₂ than NH₃, over the low loading interval when there was still free PZ in mixed solution.

At 40 °C, heat of absorption of CO₂ with remains constant (75-78 kJ/mol of CO₂) up to loading of 0.3 mol CO₂/mol of NH₃ & PZ and then it decreases with increase in loading as shown in figure 3.10 (a).

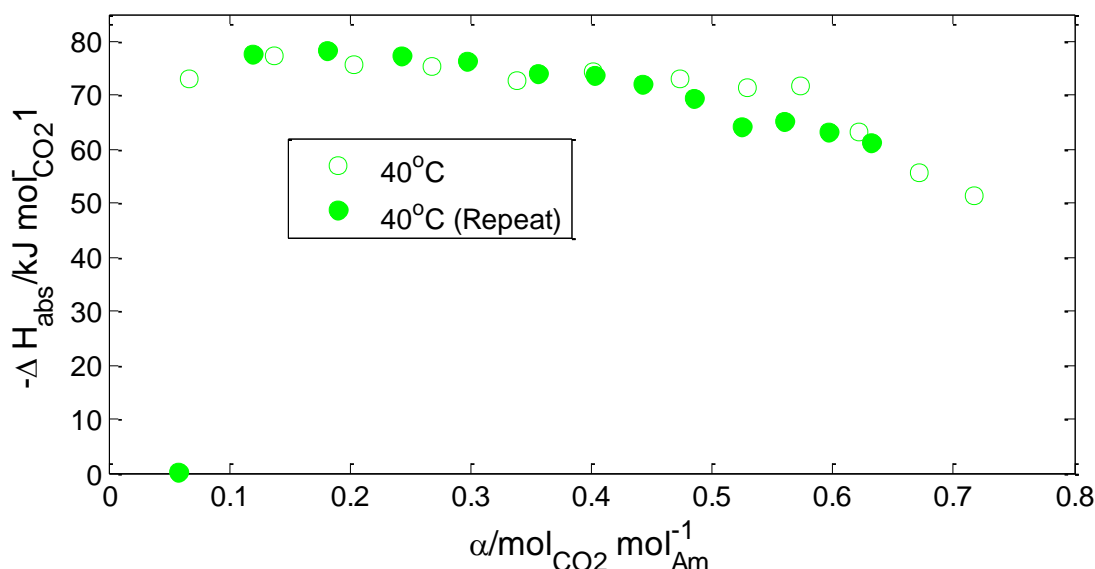


Figure 3.10 (a): Experimental heat of absorption and repeatability of CO₂ with 5% wt. NH₃ & 0.8 M Piperazine solution at 40 °C.

At 60 °C, heat of absorption of CO₂ with remains constant (72 kJ/mol of CO₂) up to loading of 0.35 mol CO₂/mol of NH₃ & PZ and then it decreases with increase in loading as shown in figure 3.10 (b).

At 80 °C, heat of absorption of CO₂ with remains constant (65 kJ/mol of CO₂) up to loading of 0.55 mol CO₂/mol of NH₃ & PZ as shown in figure 3.10 (c). It was observed that a white crystalline solid form in the pulsation line of reactor pressure sensor, reactor pressure gauge and in all lines in contact with the gas phase. This occurs due to reaction of CO₂ with ammonia in gas phase at elevated temperature during long period of time (overnight or 10-15 hours).

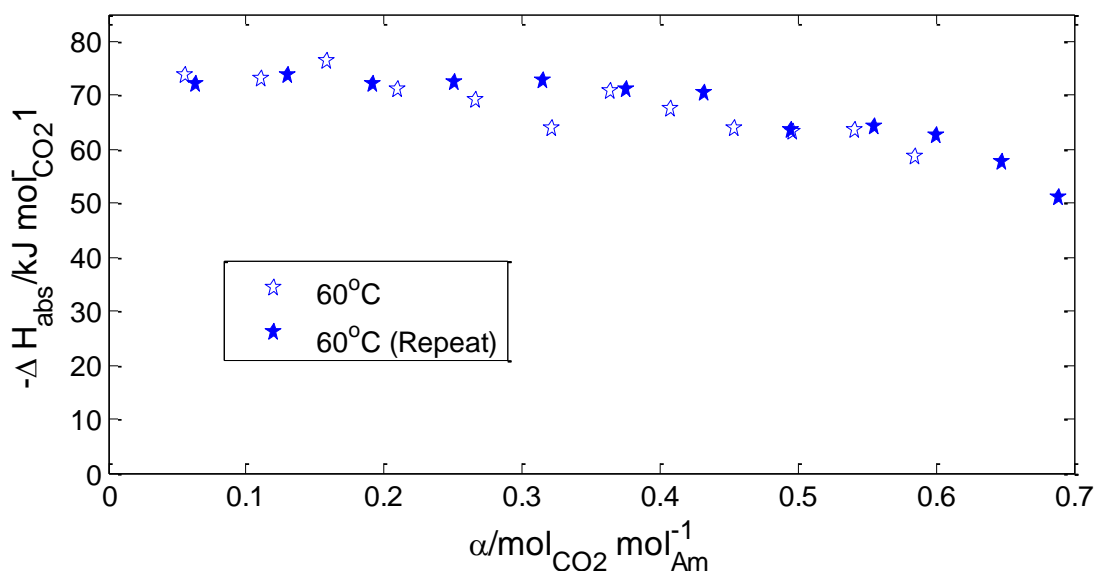


Figure 3.10 (b): Experimental heat of absorption and repeatability of CO₂ with 5% wt. NH₃ & 0.8 M Piperazine solution at 60 °C.

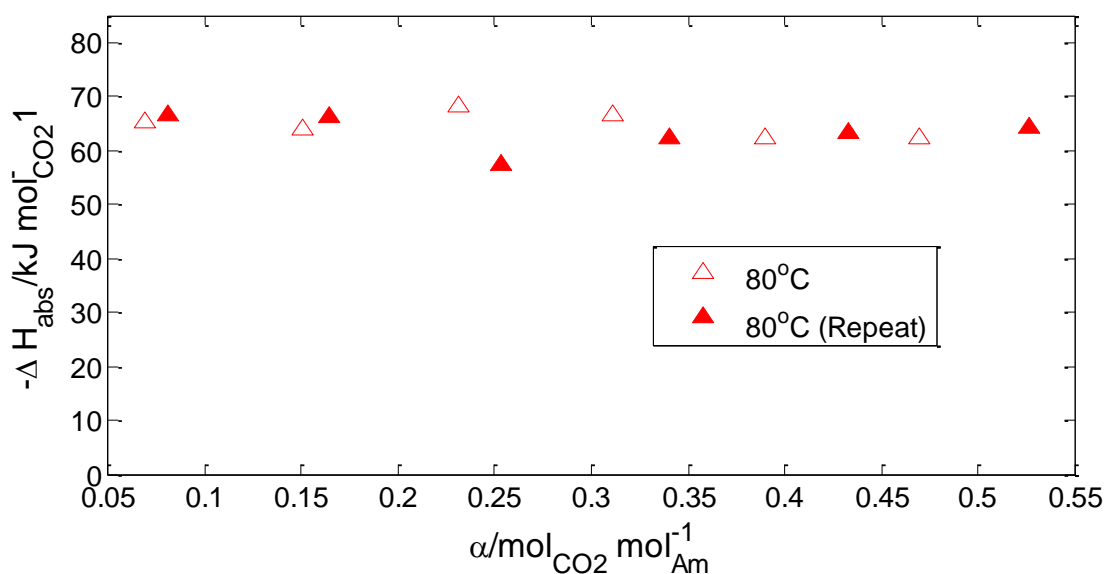


Figure 3.10 (c): Experimental heat of absorption and repeatability of CO₂ with 5% wt. NH₃ & 0.8 M Piperazine solution at 80 °C.

Overall this system is showing opposite behavior as compared to MEA, MDEA, piperazine etc as differential heat of absorption is less at higher temperature (80 °C) as compared to lower

temperature (40 °C) for same loading. This is true up to loading of 0.55 mol CO₂ / mol NH₃ and at higher loadings heat of absorption becomes similar at all temperatures 40-80 °C as shown in figure 3.10 (d).

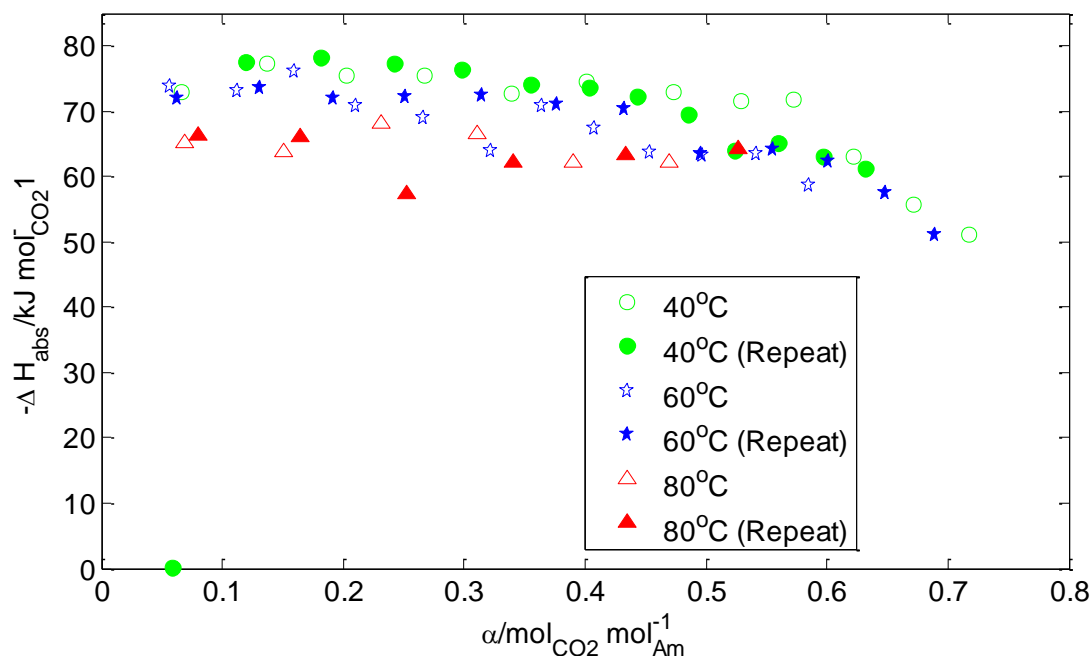


Figure 3.10 (d): Experimental heat of absorption and repeatability of CO₂ with 5% wt. NH₃ & 0.8 M Piperazine solution at 80 °C.

3.2.2.2. Aqueous solution of 5% wt. NH₃ & 0.4 M piperazine

In two experiments, 0.4 M aqueous piperazine solution used instead of 0.8 M and results are shown in figure 3.11(a). At 40 °C, heat of absorption of CO₂ with this type of mixture remains constant (75 kJ/mol CO₂) up to loading of 0.45 mol CO₂ / mol of NH₃ & PZ and for higher loadings it decreases as shown in figure 3.11(a). At 60 °C, heat of absorption of CO₂ with this type of mixture remains constant (72 kJ/mol CO₂) up to loading of 0.35 mol CO₂ / mol of NH₃ & PZ and for higher loadings it decreases as shown in figure 3.11(a). There is no significant effect on heat of absorption of CO₂ whether use 0.8 M or 0.4 M piperazine solution in the blend of it with 5% (by weight) ammonia aqueous solution both at 40 °C & 60 °C as shown in figure 3.11(b) & (c).

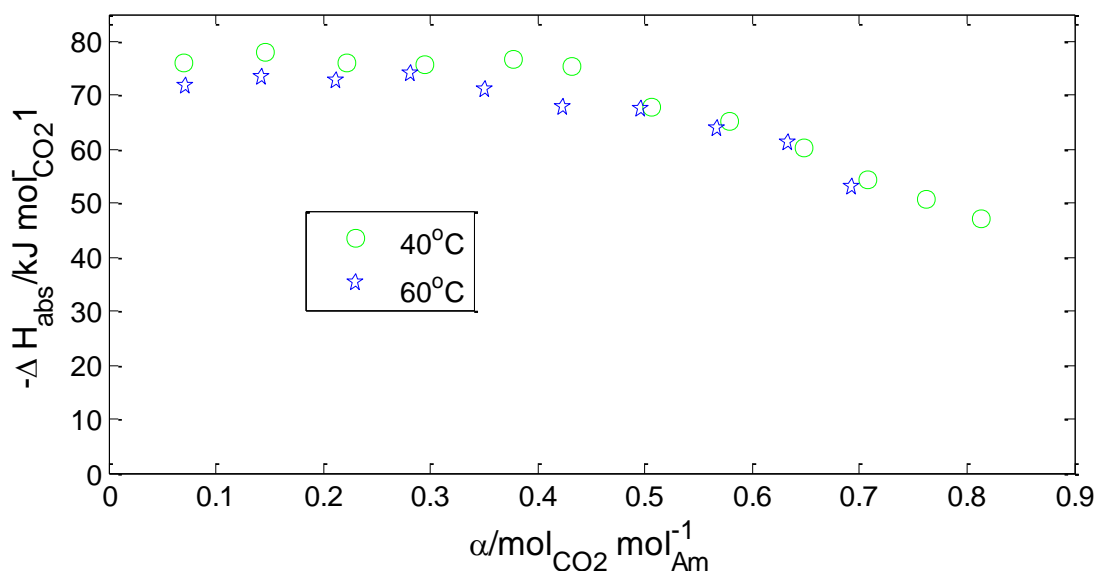


Figure 3.11(a): Experimental heat of absorption of CO₂ with 5% wt. NH₃ & 0.4 M Piperazine solution at 40 °C & 60 °C.

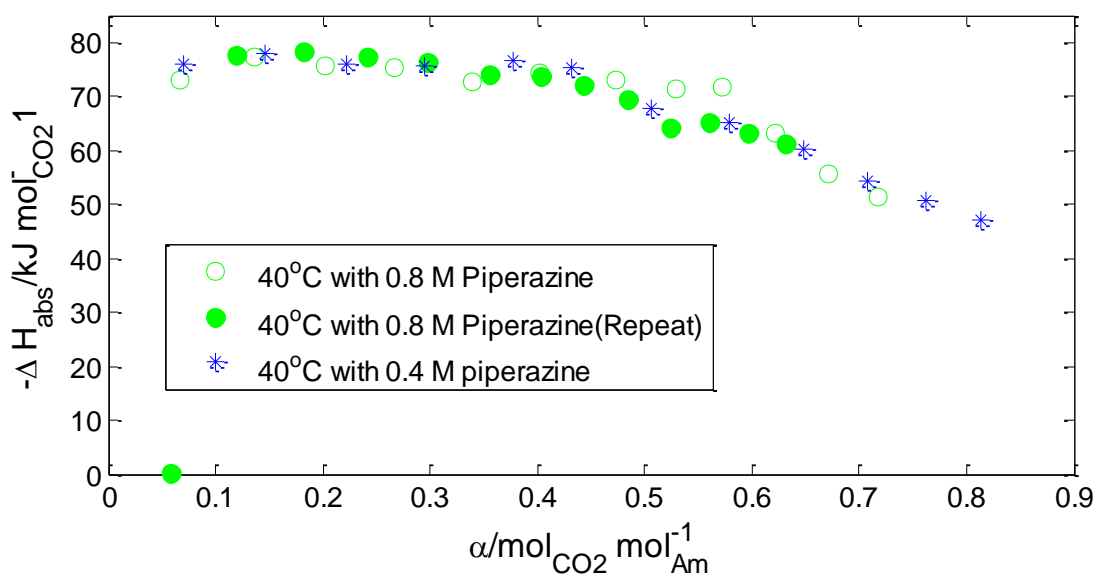


Figure 3.11(b): Comparison of experimental heat of absorption of CO₂ with (5% wt. NH₃ & 0.8 M Piperazine) & (5% wt. NH₃ & 0.4 M Piperazine) solutions at 40 °C.

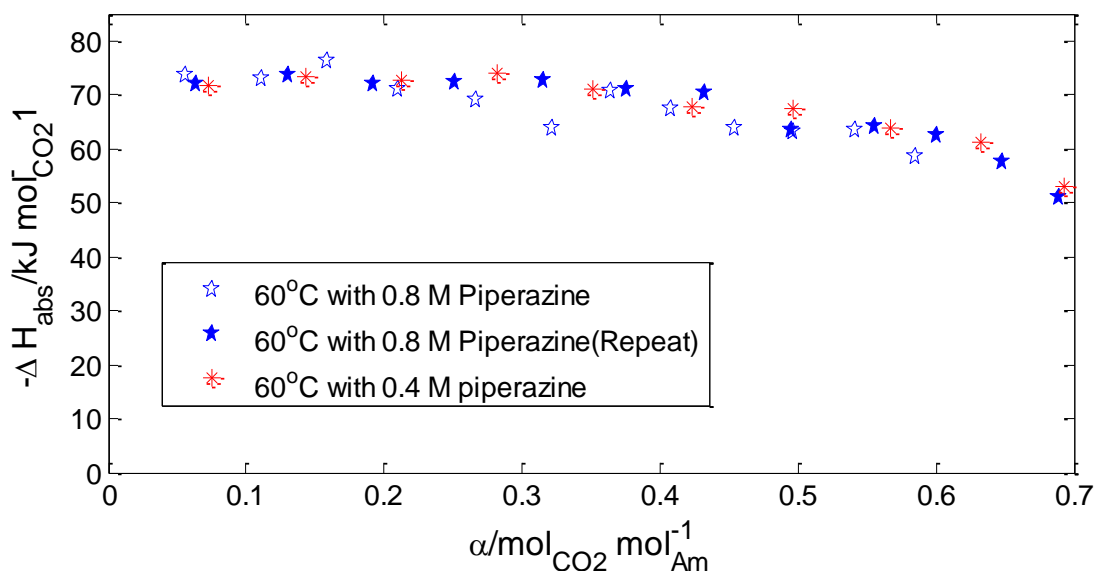


Figure 3.11(c): Comparison of experimental heat of absorption of CO₂ with (5% wt. NH₃ & 0.8 M Piperazine) & (5% wt. NH₃ & 0.4 M Piperazine) solutions at 60 °C.

3.2.2.3. Aqueous solution of 2.5% wt. NH₃ & 0.8 M piperazine

At 40 °C heat of absorption of CO₂ with a blend of 2.5% (by weight) aqueous solution of ammonia & 0.8 M aqueous piperazine solution remains almost constant (78 kJ/mol of CO₂) for loading up to 0.35 mol CO₂ / (mol of NH₃ & PZ) then it decreases for higher loadings as shown in figure 3.12.

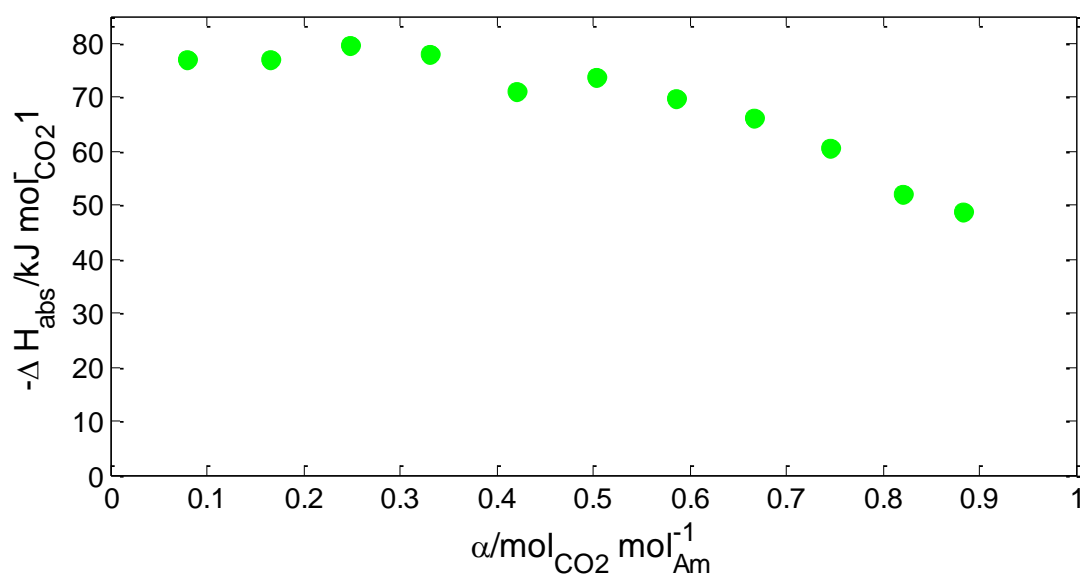


Figure 3.12: Experimental heat of absorption of CO₂ with 2.5% wt. NH₃ & 0.8 M Piperazine solution at 40 °C.

Chapter 4 COMPARISONS

4.1. Single solvent systems

At 40 °C, heat of absorption of aqueous NH₃ and piperazine solution is found significantly higher than MDEA for all loadings while lower than MEA at low loading interval (less than 0.5 mol CO₂/mol amine) and higher than MEA for loading greater than 0.5 mol CO₂/mol amine. The decline in differential heat of absorption is significant for MEA as compared to piperazine as piperazine has two amino groups (MEA has one amino group) so more reaction sites. Decline in heat of absorption of CO₂ with aqueous ammonia is a middle case of two extreme cases of MEA and piperazine. All these can be observed in figure 4.1.

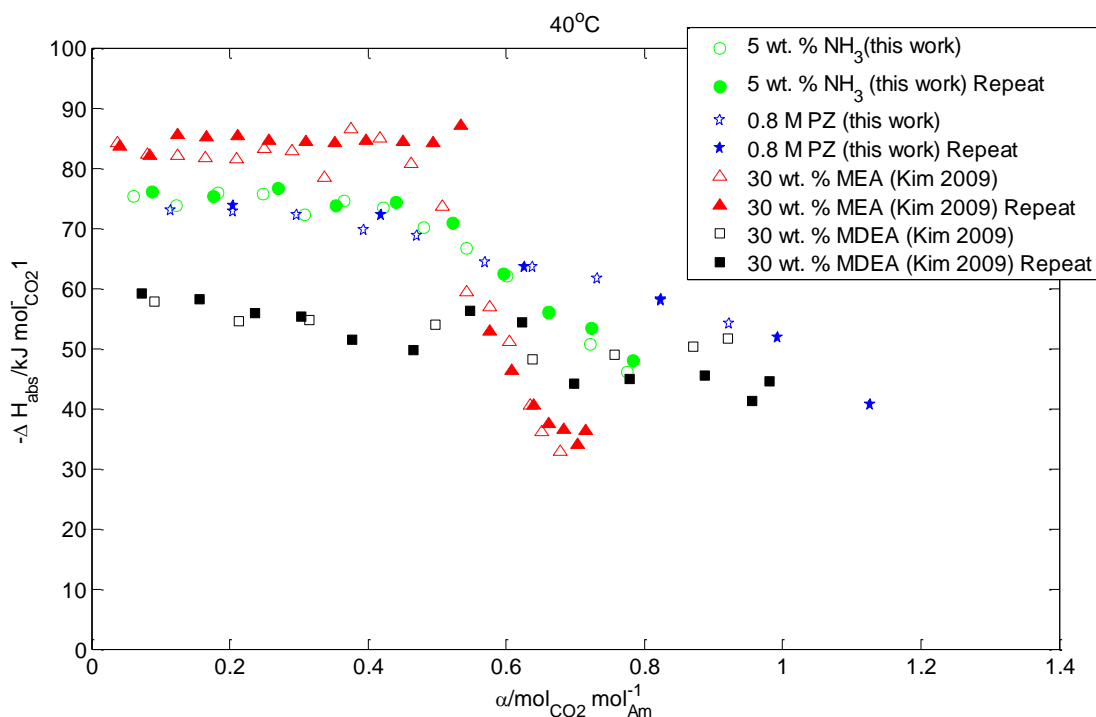


Figure 4.1: Heat of absorption of CO₂ with single solvent systems at 40 °C

At 80 °C, heat of absorption of aqueous NH₃ and piperazine is lesser than MEA up to loading of 0.55 and for higher loadings MEA has lower values. MDEA has higher values of enthalpy of absorption than NH₃ up to loading of 0.3 and for higher loadings reverse is true as shown in figure 4.2.

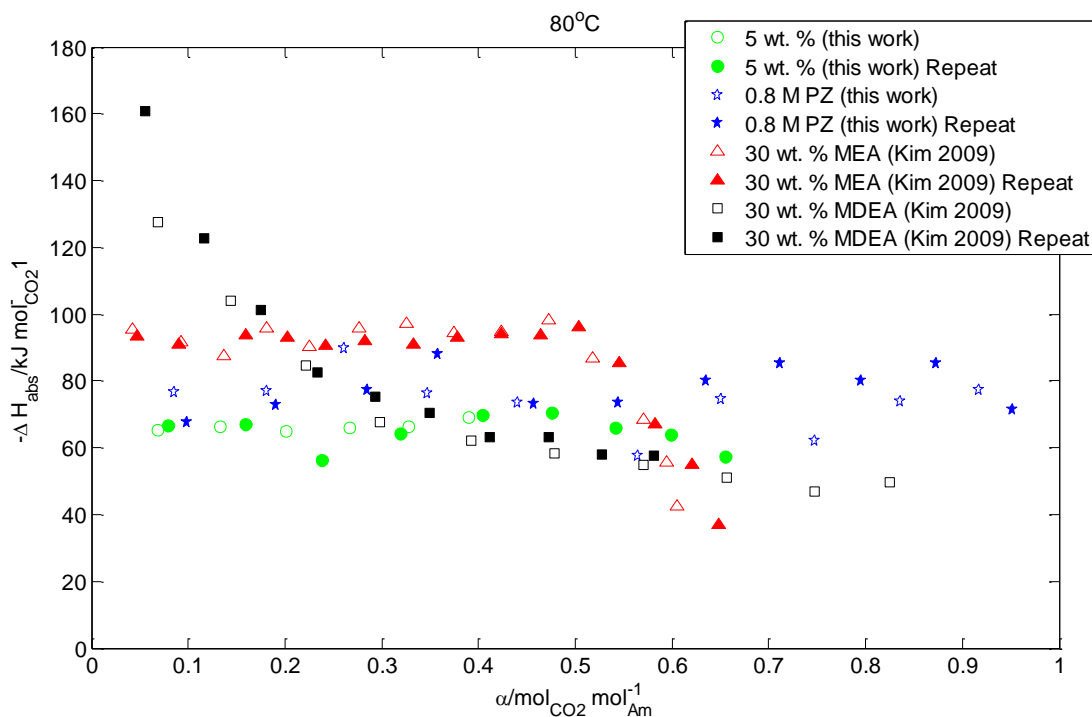


Figure 4.2: Heat of absorption of CO₂ with single solvent systems at 80 °C

4.2. Effect of PZ

Blending a small amount of PZ did not have a significant effect on the heat of absorption of CO₂ in aqueous NH₃. The effect of temperature on the heat of absorption of mixed solution also show no big difference with individual aqueous ammonia as shown in figures 4.3 (a), (b) and (c).

CO₂ would firstly reacts with PZ, the heat of absorption of CO₂ in mixed solution is mainly contributed by the reaction of CO₂ with PZ at the beginning of the absorption process, and since the absorption heats of NH₃ and PZ over low loading interval are probably the same base on the experimental data by this work as shown in figures 4.3 (a), (b) and (c), that's why the value of the absorption heat was not only consistent with the results of individual PZ solution but also showed nearly the same results as that of obtained for the case of aqueous NH₃.

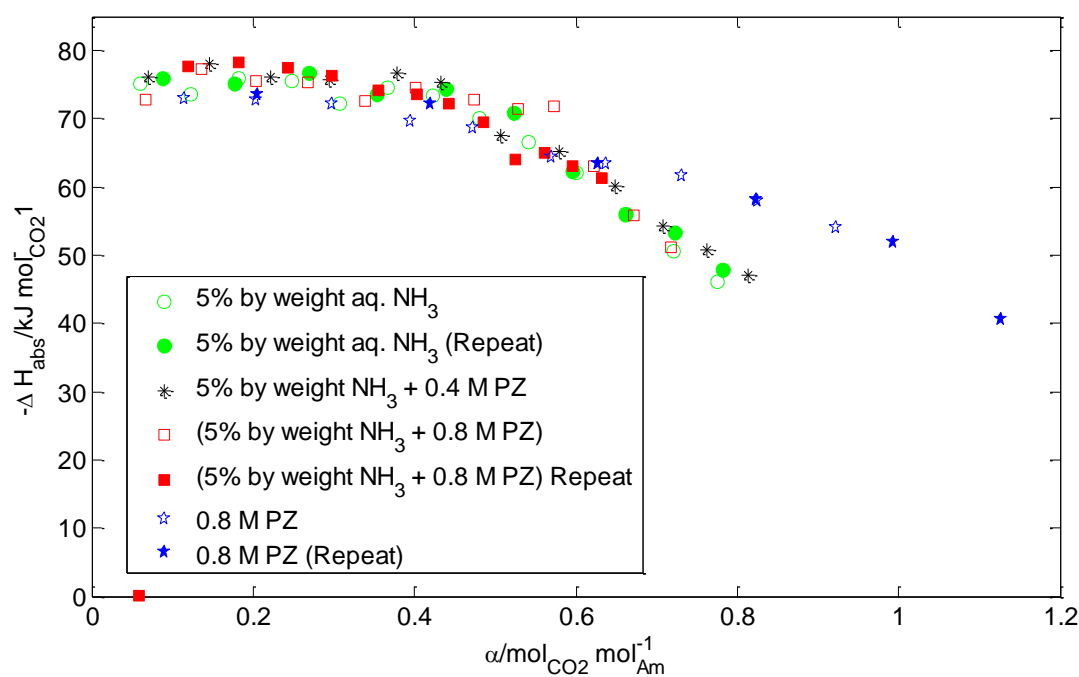


Figure 4.3(a): Effect of piperazine concentration on heat of absorption of CO₂ at 40 °C

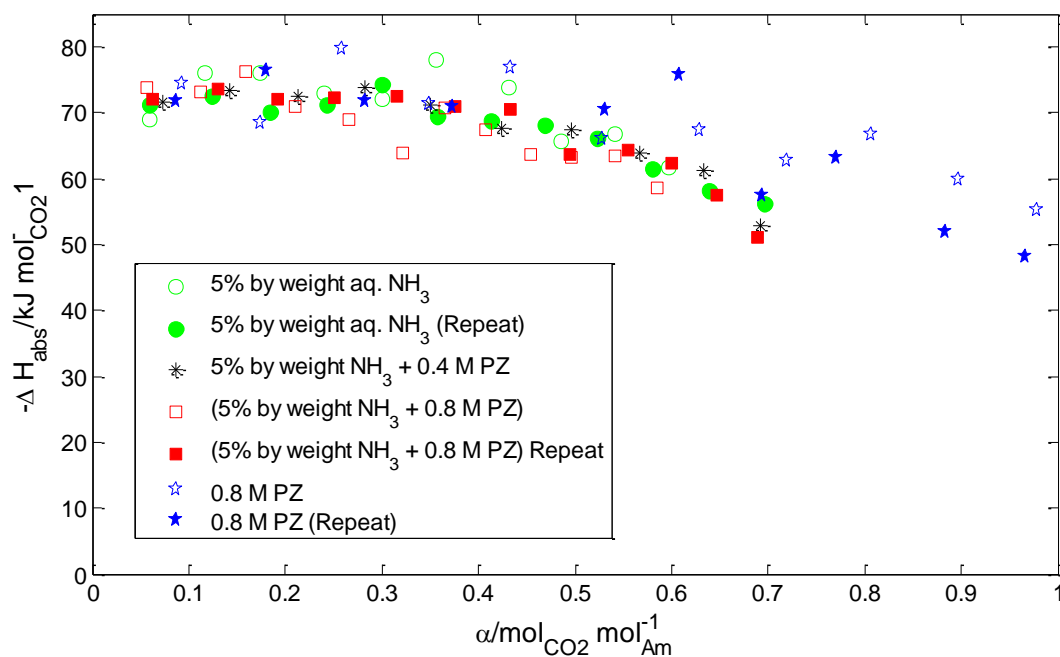


Figure 4.3(b): Effect of piperazine concentration on heat of absorption of CO₂ at 60 °C

After the first stage of absorption process, the free PZ in blend start decreasing, the reaction of CO₂ with PZ would not account for a large proportion of the overall reactions. At the same time, there is still a lot of free NH₃ in the blend, so CO₂ reaction with NH₃ become prominent and hence the heat of absorption trend continues to follow the trend of aqueous NH₃ which can clearly seen in figures 4.3 (a), (b) and (c).

This inference in can also be verified by comparison of heat of absorption of CO₂ with (7m MEA+2m PZ) blended solution with individual solution of 7m MEA aqueous solution and 2m PZ aqueous solution as shown in figure 3.5.

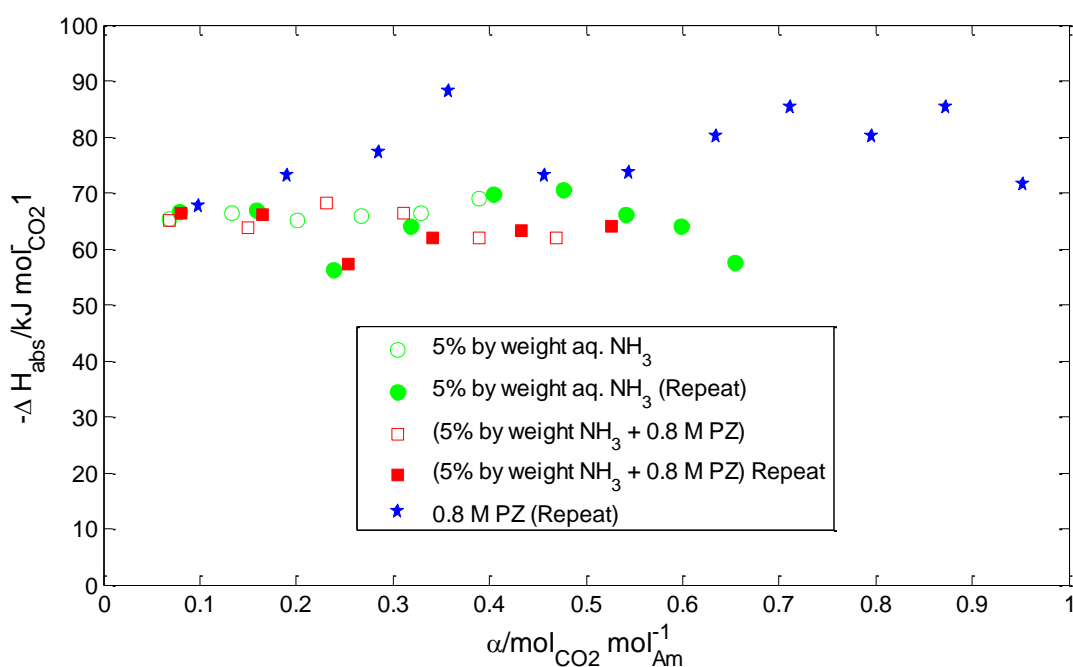


Figure 4.3(c): Effect of piperazine concentration on heat of absorption of CO₂ at 80 °C

4.3. Blends

Heat of absorption of CO₂ in blend of 5 % by weight NH₃ solution & 0.8 M PZ solution at 40 °C is similar to that of with MEA and PZ blended solutions and significantly higher than the blends of K₂CO₃ and PZ solutions over the entire loading as shown in figure 4.4(a).

The comparison of heat of absorption of CO₂ in blend of 5 % by weight NH₃ solution & 0.8 M PZ solution at 80 °C is significant different than what at 40 °C as shown in figure 4.4(b).

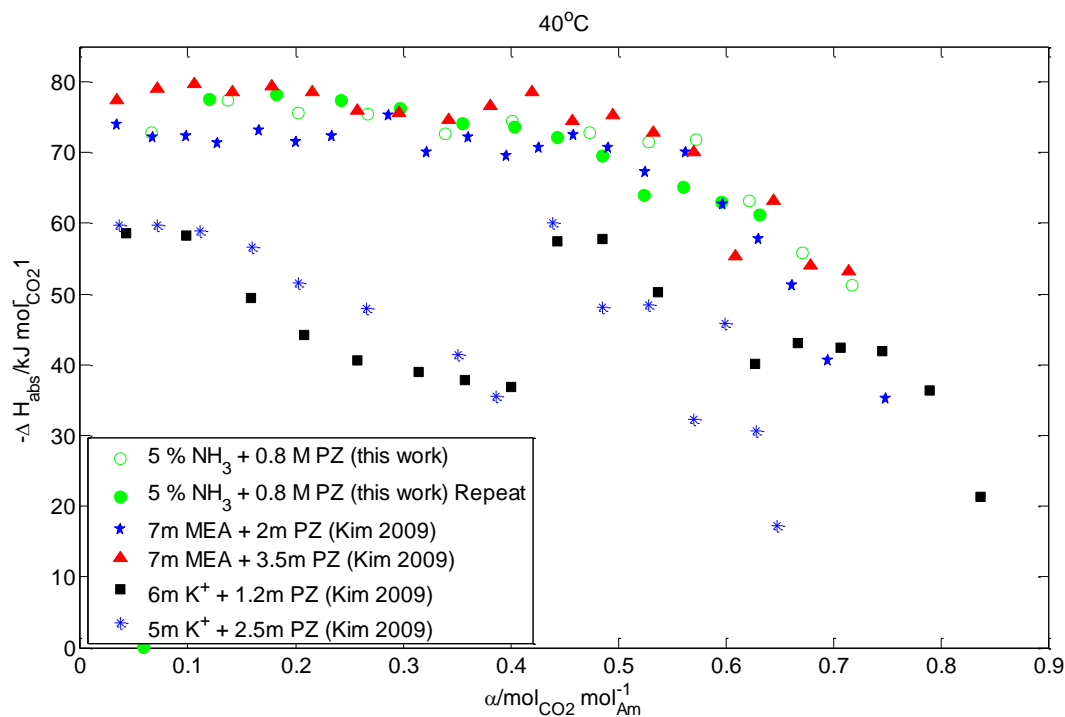


Figure 4.4(a): Heat of absorption of different blends at 40 °C

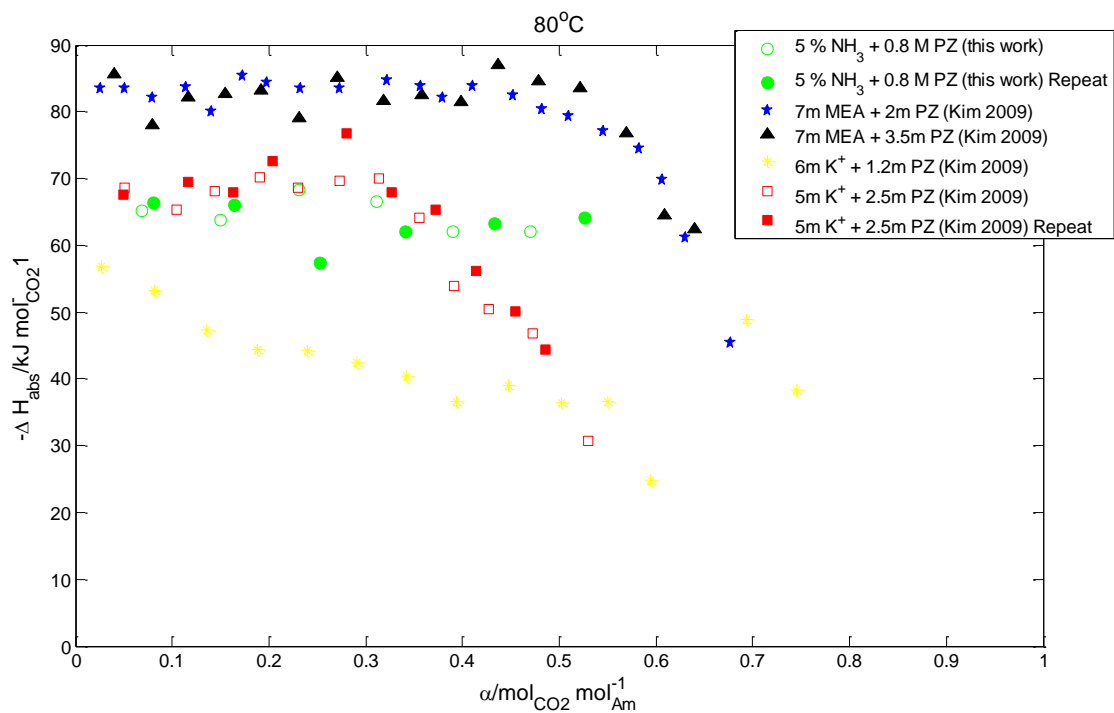


Figure 4.4(b): Heat of absorption of different blends at 80 °C

Heat of absorption of CO₂ in blend of 5 % by weight NH₃ solution & 0.8 M PZ solution at 80 °C is lesser than that of with MEA and PZ blended solutions, higher than the blend of 6m K₂CO₃ and 2m PZ solutions and somewhat similar to that of blend of 5m K₂CO₃ and 3.5m PZ solutions up to loading of 0.5 mol CO₂/mol of amine as shown in figure 4.4(b).

Conclusion

The heat of absorption of CO₂ with 5% by weight aqueous NH₃ is estimated to be 70 kJ/mol CO₂ and with 0.8 M PZ is estimated to be 75 kJ/mol CO₂ at low loading interval (less than 0.5 mol CO₂/mol amine) at 40 °C. Heat of absorption decreases for aqueous ammonia solution while increases for the case of PZ with increasing temperature at a specific loading less than 0.5 mol CO₂/mol amine. Heat of absorption of CO₂ with blend of these two solutions is also measured which reveals that it is similar to that of heat of absorption of CO₂ with 5% by weight aqueous NH₃ solution at 40 °C and 60 °C while it is also similar up to loading of 0.35 mol CO₂/mol amine at 80 °C. Hence PZ has almost negligible effect on heat of absorption in blends. This may be due to low concentration of PZ (0.4 M & 0.8 M).

At 40 °C, for loading up to 0.55 mol CO₂/mol amine, heat of absorption of CO₂ is lesser for 5% by weight aqueous solution of NH₃ as compared to 30% by weight MEA, greater than 0.8 M PZ and 30% by weight MDEA while at 80 °C it is lesser than both 30% by weight MEA & 0.8 M PZ but it is far greater when compared with 30% by weight MDEA up to loading of 0.3 mol CO₂/mol amine.

At 40 °C, for loading up to 0.45 mol CO₂/mol amine, blends of NH₃ & PZ (5% by weight NH₃ + 0.8 M PZ & 5% by weight NH₃ + 0.8 M PZ) has similar values of differential heat of absorption as that of blends of MEA & PZ (7m MEA + 2m PZ & 7m MEA + 3.5m PZ) while much higher values compared to blends of K₂CO₃ with PZ (6m K₂CO₃ + 1.3m PZ & 5m K₂CO₃ + 3.5m PZ).

At 80 °C, for loading up to 0.40 mol CO₂/mol amine, blends of NH₃ & PZ (5% by weight NH₃ + 0.8 M PZ & 5% by weight NH₃ + 0.8 M PZ) has lesser values of differential heat of absorption as that of blends of MEA & PZ (7m MEA + 2m PZ & 7m MEA + 3.5m PZ) and blend of potassium carbonate (5m K₂CO₃ + 3.5m PZ). Blend (6m K₂CO₃ + 2.5m PZ) has lesser values of differential heat of absorption up to loading of 0.5 mol CO₂/mol amine.

Future work

Piperazine's affect in its blend with aqueous ammonia solution should be studied in more detail with varying concentration of piperazine from low to high. Heat of absorption is function of both temperature & loading but in simulators very often a constant value is used in models (Kim 2009). Therefore a thermodynamic model must be developed for accurate prediction of heat of absorption of CO₂ in aqueous ammonia, piperazine and blend of these two. It may be a good idea for cross checking to take sample of the reaction mixture at the end of experiment, analyze for CO₂, total alkalinity and found loading and compare this with the calculated loading.

As far as calorimeter is concern, it requires complete diagnosis for temperature control problem by manufacturer but first open reactor top and confirms that stirrer is still intact or not.

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Appendix

Loading	Enthalpy	Loading	Enthalpy
mole CO ₂ /mole amine	KJ/mol CO ₂	mole CO ₂ /mole amine	KJ/mol CO ₂
5% by weight aqueous NH ₃			
40 °C		40 °C (Repeat)	
0.0607	74876.60	0.0880	76453.43
0.1225	73656.27	0.1769	75383.79
0.1826	75840.38	0.2697	76466.17
0.2483	75373.08	0.3540	73645.72
0.3080	72186.95	0.4400	74197.50
0.3662	74376.04	0.5234	70958.92
0.4223	73624.06	0.5961	64014.47
0.4810	69992.69	0.6616	56406.45
0.5422	66516.62	0.7231	54650.38
0.6012	62544.54	0.7830	47404.22
0.6611	57712.79		
0.7209	51378.33		
0.7751	46359.72		
5% by weight aqueous NH ₃			
60 °C		60 °C (Repeat)	
0.0588	69520.15	0.0601	71740.25
0.1170	76554.15	0.1240	71242.55
0.1737	76276.21	0.1849	69300.46
0.2409	71951.45	0.2433	71869.68

0.3002	72154.72	0.3001	74851.72
0.3568	77017.12	0.3577	69195.91
0.4308	73789.59	0.4138	69079.90
0.4854	67375.02	0.4694	68217.81
0.5421	67774.05	0.5230	67932.11
0.5977	61086.95	0.5810	61672.87
		0.6397	59457.39
		0.6966	56668.87
5% by weight aqueous NH ₃			
80 °C		80 °C (Repeat)	
0.0681	64795.72	0.0792	67332.11
0.1329	66935.81	0.1593	67500.70
0.2015	65589.66	0.2385	56261.52
0.2666	65015.89	0.3193	64537.37
0.3285	66016.97	0.4045	77600.42
0.3900	68657.45	0.4764	71014.23
		0.5414	66571.82
		0.5983	65685.84
		0.6542	57447.11
0.8 M Piperazine			
40 °C		40 °C (Repeat)	
0.115	72944.04	0.205	73656.96
0.204	72765.56	0.420	72250.1

0.297	72150.43	0.627	63521.12
0.394	69705.16	0.824	58112.07
0.472	68796.73	0.993	51875.07
0.569	64366.3	1.127	40582.73
0.637	63529.91		
0.732	61682.96		
0.824	57978.73		
0.922	54150.91		

0.8 M Piperazine

60 °C		60 °C (Repeat)	
0.0931	74525.94	0.0860	71971.20
0.1744	68552.19	0.1792	76398.43
0.2579	79820.49	0.2818	71886.49
0.3479	71451.17	0.3721	70987.58
0.4332	77048.85	0.5310	70643.82
0.5273	66230.23	0.6076	75921.13
0.6282	67547.49	0.6935	57409.97
0.7197	62750.44	0.7702	63347.77
0.8067	66847.51	0.8832	52001.56
0.8963	59879.99	0.9659	48133.44
0.9787	55353.18		

0.8 M Piperazine

80 °C		80 °C (Repeat)	
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0.0860	76550.29	0.0983	67660.82
0.1814	77008.60	0.1905	72988.45
0.2606	89687.52	0.2853	77365.31
0.3476	76365.87	0.3583	88056.20
0.4397	73541.04	0.4575	73202.81
0.5640	57480.85	0.5439	73602.15
0.6511	74437.73	0.6351	80040.76
0.7476	62043.10	0.7118	85233.20
0.8362	74035.14	0.7955	80241.90
0.9166	77532.61	0.8723	85407.07
		0.9521	71497.90

5% by weight aqueous NH₃ + 0.8 M Piperazine

40 °C		40 °C (Repeat)	
0.0663	72896.39	0.0583	0.21
0.1366	77323.21	0.1201	77592.77
0.2029	75578.88	0.1818	78177.15
0.2673	75409.74	0.2427	77398.54
0.3388	72680.28	0.2978	76327.59
0.4016	74483.84	0.3553	74122.79
0.4733	72886.29	0.4035	73659.66
0.5289	71498.98	0.4432	72190.75
0.5729	71767.81	0.4854	69530.85
0.6219	63154.99	0.5243	64053.85
0.6716	55781.62	0.5606	65089.97

0.718	51224.72	0.5967	63078.84
		0.632	61226.56

5% by weight aqueous NH₃ + 0.8 M Piperazine

60 °C		60 °C (Repeat)	
0.0631	72060.55	0.0560	73777.95
0.1307	73640.96	0.1117	73129.66
0.1920	72068.06	0.1589	76208.74
0.2510	72345.72	0.2100	70918.40
0.3150	72572.41	0.2660	69084.70
0.3760	70997.01	0.3218	63891.59
0.4322	70503.28	0.3645	70776.92
0.4952	63629.34	0.4077	67350.83
0.5551	64248.04	0.4534	63769.97
0.6008	62436.43	0.4968	63215.48
0.6476	57518.58	0.5412	63463.71
0.6889	51042.74	0.5847	58653.79

5% by weight aqueous NH₃ + 0.8 M Piperazine

80 °C		80 °C (Repeat)	
0.0685	65177.57	0.0805	66381.40
0.1505	63864.43	0.1644	66105.67
0.2314	68218.78	0.2530	57374.08
0.3112	66488.19	0.3408	62049.54
0.3899	62074.44	0.4332	63249.42

0.4696	62072.07	0.5268	64115.25
5% by weight aqueous NH ₃ + 0.4 M Piperazine			
40 °C		60 °C	
0.0703	76084.92	0.0726	71681.98
0.1459	78060.22	0.1430	73404.90
0.2218	76057.40	0.2126	72563.10
0.2947	75733.42	0.2818	73842.80
0.3781	76708.51	0.3509	71173.17
0.4323	75289.60	0.4235	67702.79
0.5066	67612.25	0.4960	67379.81
0.5791	65272.47	0.5669	63870.59
0.6479	60188.37	0.6331	61284.21
0.7075	54373.26	0.6924	52878.14
0.7615	50765.32		
0.8134	47050.13		
2.5% by weight aqueous NH ₃ + 0.8 M Piperazine			
40 °C			
0.0805	76871.03		
0.1654	76917.64		
0.2486	79523.28		
0.3310	78001.68		
0.4209	71078.39		
0.5029	73838.61		

0.5854	69855.09
0.6674	66110.82
0.7450	60475.23
0.8203	52167.46
0.8841	48833.72

