

The University of Texas at Austin
Department of Chemical Engineering

Dissertation Proposal

A Predictive Model for Aqueous Potassium Carbonate/Piperazine/Ethanolamine for
Carbon Dioxide Removal from Flue Gas

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Introduction

Carbon dioxide (CO₂) emissions from coal-fired power plants continue to contribute to the steady rise in atmospheric concentrations in greenhouse gases which are known to contribute to global warming. Over the past 40 years, observations at the Mauna Loa Observatory in Hawaii have shown an increase in CO₂ concentration levels by 18.8% [Keeling et al. (1995)]. As a result, CO₂ capture technologies continue to become one of the most important industrial and academic research areas.

CO₂ removal by reactive absorption/stripping using aqueous monoethanolamine (MEA) and other blended amine solvents has been established as a mature CO₂ capture technology. Figure 1 shows a typical counter-current absorber/stripper. Flue gas entering the absorber is counter-currently contacted with an aqueous amine solvent. CO₂ is absorbed into the aqueous amine solvent through a reversible chemical reaction to form a rich or loaded solvent (with respect to CO₂). Alkanolamine/CO₂ reactions are known to occur within the liquid boundary layer. Under some conditions, the reactions are nearly instantaneous as the concentration of the amine becomes depleted at the gas-liquid interface. To correctly predict these rates, we will need an accurate equilibrium model to account for the complexities of the mass transfer with fast chemical reaction as well as the speciation of the amines in the solution. The rich amine solution is then sent through a counter-current heat exchanger, where the solution is pre-heated by the lean amine solution before entering the stripper. In the stripper, heat is provided in the reboiler in the form of steam to reverse the chemical equilibrium between the amine and CO₂. The liberated CO₂ and water vapor then leaves the stripper for downstream processing and storage. The optimal amine solvent would depend on the residual CO₂ specification and the stripping energy costs associated with the heat of CO₂ absorption. The hot, lean amine solution is then sent back through the counter-current heat exchange where the solution is cooled before reaching the absorber.

The development of new solvents involving potassium carbonate (K₂CO₃) and piperazine (PZ) has shown potential as a new CO₂ capture process [Cullinane (2005)]. Cullinane found that solutions of K₂CO₃ and PZ have 1.5 – 3 times faster rates of CO₂ absorption and decrease levels in the heat of CO₂ absorption than equivalent solutions of MEA. This study also measured speciation at 40 to 60 °C and CO₂ solubility at 40 to 110 °C with a wide range of solution compositions in PZ/K₂CO₃. When Cullinane (2005) and Hilliard (2005) regressed this data with an

electrolyte-NRTL model they found that the apparent heat of CO₂ absorption was, unexpectedly, a significant function of temperature. As compared to other amines, researchers have shown that the heat of CO₂ absorption may not be a strong function of temperature [Mathonat et al. (1998)].

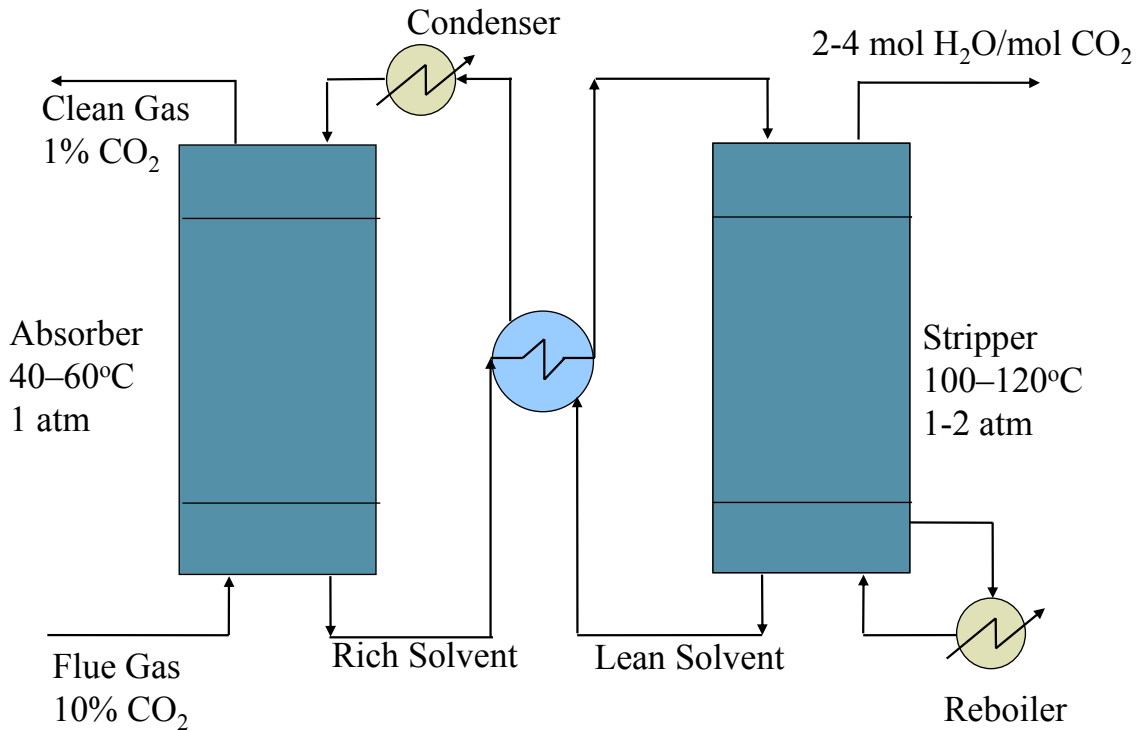


Figure 1. Schema of an Absorption/Stripping System for Removal of CO₂ from Flue Gas using Aqueous Alkanolamine Solutions.

In 2003, Dang and Rochelle reported absorption rates and equilibrium partial pressure of CO₂ with aqueous MEA/PZ to be 1.5 – 2.5 times greater than and 2 - 5 times smaller than with MEA alone, respectively. Okoye (2005) observed similar trends with 7 m MEA/2 m PZ (where m = mole of solute per kg of water) and determined that PZ would be an effective promoter to MEA.

This project proposes to expand upon previous work in the area of modeling amines and amine blends for the application of CO₂ capture via gas treating where a rigorous electrolyte-NRTL thermodynamic model is required for quantitative analysis of the solvent to describe: the driving forces for CO₂ mass transfer utilizing all available data types (e.g. CO₂ solubility, heat of CO₂ absorption, and NMR liquid speciation), speciation of the liquid phase where complex kinetic contributes to mass transfer enhanced by fast reactions, driving forces for amine mass transfer in terms

of volatilization, heats of absorption/desorption and the effective liquid heat capacity to size the counter-current heat exchange contributing to the additional heating requirements and vapor rates for the stripper. This project will focus on characterizing the system of chemical reactions at equilibrium to predict the capacity of the solvent, the heat of CO₂ absorption, and the concentration of reactive species for aqueous H₂O-K₂CO₃-PZ-MEA-CO₂ from the respective sub-component systems as shown in Figure 2.

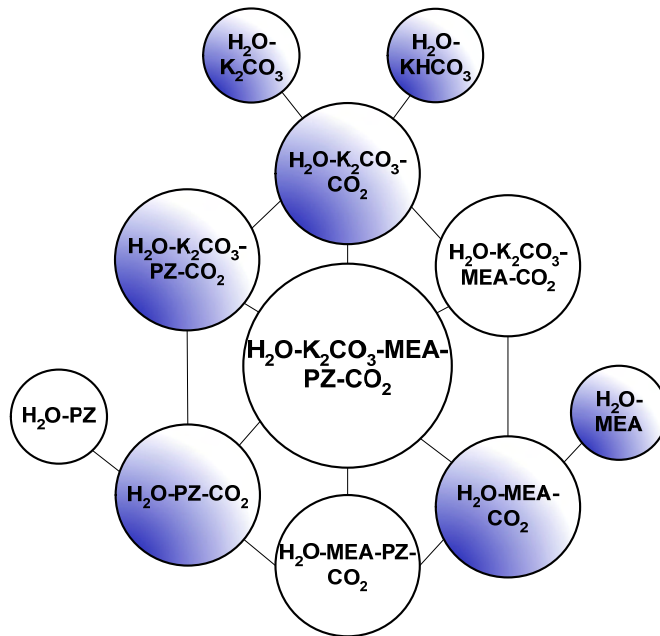


Figure 2. Thermodynamic Sub-Component System Tree. Shaded circles: Systems found in literature, Open circles: Systems proposed to study.

Part of this work will be a collaborative effort between The University of Texas at Austin (UT) and the Norwegian University of Science and Technology (NTNU) to generate data by independent methods to confirm the heat of absorption and CO₂ solubility at stripper conditions.

Research Objectives

Mixtures of aqueous potassium carbonate, piperazine, and monoethanolamine will be investigated to add additional thermodynamic data to sub-component systems in the following areas:

1. Additional CO₂ solubility data through vapor-liquid equilibrium (VLE) and total pressure measurements.

2. The determining the enthalpies of absorption of CO₂ in solutions of potassium carbonate, piperazine, and monoethanolamine.
3. To determine amine volatility through VLE measurements of the vapor phase utilizing a unique Fourier-Transform infrared (FT-IR) analysis technique.
4. Development of methods for quantifying solution and vapor speciation using acid-base titration and FT-IR analysis.
5. Predict thermodynamic characteristics of H₂O-K₂CO₃-PZ-MEA-CO₂ using a rigorous thermodynamic model of the sub-component systems.

Experimental Focus

This research will focus on the following conditions to quantify the rigorous thermodynamic model with respect to loading:

1. CO₂ Solubility (NTNU)
 - a. H₂O-K₂CO₃-PZ-CO₂: 80 – 120 °C, 3.6 – 6.0 m K⁺, 0.6 – 3.6 m PZ
 - b. H₂O-MEA-PZ-CO₂: 100 – 120 °C, 3.5 – 7.0 m MEA, 1.0 – 3.5 m PZ
2. Heat of CO₂ Absorption (NTNU)
 - a. H₂O-K₂CO₃-PZ-CO₂: 40 – 80 °C, 5.0 – 6.0 m K⁺, 1.2 – 2.5 m PZ
 - b. H₂O-MEA-PZ-CO₂: 40 – 80 °C, 7.0 m MEA, 2.0 m PZ
3. CO₂ Solubility/Amine Volatility (UT)
 - a. H₂O-MEA-PZ-CO₂: 25 – 80 °C, 3.5 – 7.0 m MEA, 1.0 – 3.5 m PZ
 - b. H₂O-PZ: 25 – 80 °C, 0.5 – 3.6 m PZ (supported by John McLees)
 - c. H₂O-MEA-PZ: 25 – 80 °C, 3.5 – 7.0 m MEA, 1.0 – 3.5 m PZ
 - d. H₂O-K₂CO₃-PZ-CO₂: 25 – 80 °C, 3.6 – 6.0 m K⁺, 0.6 – 3.6 m PZ
4. Total Pressure (UT)
 - a. H₂O-MEA-PZ-CO₂: 80 - 130 °C, 3.5 – 7.0 m MEA, 1.0 – 3.5 m PZ

Modeling Focus

Modeling for this research will focus on the thermodynamic regression of following systems:

1. Correct the reference state code associated with Cullinane's FORTRAN model [Cullinane (2005)] to emulate Aspen Plus.
2. H₂O-PZ
3. H₂O-MEA
4. H₂O-MEA-PZ

5. H₂O-K₂CO₃-PZ-CO₂
6. H₂O-MEA-CO₂
7. H₂O-MEA-PZ-CO₂

Beyond the scope of this work

The following topics will be considered beyond the scope of this research project:

1. High temperature amine volatility (> 80 °C)
2. Additional heat of CO₂ absorption measurements from NTNU
3. Solid solubility (measured and modeling)
4. Heat capacity measurements
5. Speciation for the H₂O-MEA-PZ system

Literature Review

Solvent Blends

The quest to develop a new solvent to maximize CO₂ capacity can be very laborious. A tremendous amount of experimental work has been done over the years to characterize new solvents with respect to different properties (solubility, absorption, capacity, amine volatility, etc.). Alkanolamines are among several solvents that have been investigated and current research is focus on designing a chemically stable, less corrosive solvent with fast reaction rates and low heats of absorption to minimize energy requirements for regeneration of the solvent.

Recently, there has been an increased interest in the use of mixed amine solvents in gas-treating processes. Blends comprising of primary, secondary, or tertiary amines have been suggested for the industrial gas-treating processes (Mandal et al., 2003). Using different blends of amines, researchers can tailor solvent properties associated with each amine to meet specific acid gas removal requirements (high capacity, fast reaction rates, etc.). Table 1 lists available VLE for amine blends with MEA.

While previous models have studied the rates of MEA blends [Dang and Rochelle (2003) and Okoye (2005)], to date, a rigorous thermodynamic model has not been developed for the MEA/PZ system. The motivation behind this work is to complete a comprehensive thermodynamic study for MEA/PZ where reliable data for the solubility of CO₂ in aqueous MEA/PZ at elevated temperatures between 80 and 120

°C could then serve as a standard for use in stripper modeling of vapor-liquid equilibrium in blended MEA/PZ solutions.

Table 1. VLE data for Various Blends of MEA.

Author	Solvent	MEA Concentration/m ^a	Amine Concentration/m ^a	Temperature/°C	P _{CO₂} /kPa
Austgen et al. (1991)	MEA + MDEA	3.04	3.04	40 80	0.1 - 300
Li and Shen (1992)	MEA + MDEA	1.40 4.21	1.44 2.88	40 60 80 100	1 - 2000
Murrieta-Guevara et al. (1992)	MEA + NMP	15 wt%	85 wt%	25 50 100	20 - 2200
Shen and Li (1992)	MEA + MDEA	2.81 5.61	0.72 2.16	40 60 80 100	2 - 1998
Murrieta-Guevara et al. (1993)	MEA + Sulfolane	15 wt% 30 wt%	85 wt% 70 wt%	30 - 100	2 - 2210
Dawodu and Meisen (1994)	MEA + MDEA	1.41 3.29	3.29 5.99	70 100 120 140 160 180	100 - 4000
Jou et al. (1994)	MEA + MDEA	0.35 0.70 2.34 4.68	1.20 2.40 3.24 3.42	25 40 80 120	0.001 - 19930
Song et al. (1996 and 1997)	MEA + EG	3.61 5.91	3.55 16.07	40 60	4.2 - 2513
Song et al. (1996 and 1997)	MEA + PEG	3.61 5.91	0.55 2.49	40 60	3.1 - 2270
Park et al. (2002)	MEA + AMP	1.17 2.34 4.68	1.60 3.21 4.01	40 60 80	0.7 - 345
Dang and Rochelle (2003)	MEA + PZ	0.43 2.27 2.94 5.62 7.11	0.00 0.72 1.77	40 60	0.0002 - 9.55
Okoye (2005)	MEA + PZ	7.00	2.00	40 60	0.051 - 36

a: m = mole/kg of H₂O, Methyl-diethanolamine (MDEA), N-methylpyrrolidone (NMP), Ethylene glycol (EG), Poly(ethylene glycol) (PEG), 2-amino-2-methyl-1-propanol (AMP)

In addition to PZ as a possible promoter with MEA, several researchers have demonstrated the potential of amine promoted K₂CO₃ solutions for CO₂ capture. Table 2 gives the available literature data for amine promoted K₂CO₃ systems.

Table 2. VLE data for Various Amine Promoted K₂CO₃ Systems.

Author	Solvent	K ₂ CO ₃ Concentration/m ^a	Amine Concentration/m ^a	Temperature/°C
Sanyal et al. (1988)	K ₂ CO ₃ + DEA	2.99	0.43	70
Tseng et al. (1988)	K ₂ CO ₃ + DEA	3.19 - 3.34	0.28 - 0.73	50 - 103
Rahimpour and Kashkooli (2004)	K ₂ CO ₃ + DEA	2.94	0.43	70
Cullinane and Rochelle (2005)	K ₂ CO ₃ + PZ	1.25 - 3.1	0.0 - 3.6	40 - 110

a: m = mole/kg of H₂O, Diethanolamine (DEA)

Cullinane (2005) reported equilibrium partial pressure of CO₂ as measured in a wetted-wall column in 0.6–3.6 m PZ and 2.5–6.2 m potassium ion (K⁺) from 40 – 110 °C. Cullinane (2005) suggested that additional measurements be carried out at high temperatures (80 – 120 °C) to account for amine volatility and to verify current CO₂ solubility in aqueous PZ and K⁺/PZ solutions.

Amine Volatility/Vapor Speciation

Currently, little information is available in literature concerning the vapor pressure of alkanolamines in blended or aqueous binary systems. For example, Park and Lee (1997) reported isobaric VLE measurements for MEA and water from 100 – 170 °C at atmospheric pressure where compositions of the liquid and gas phases were determined by gas chromatography. Unfortunately, there are no useful binary VLE data for systems with PZ available in literature. Cullinane (2005) and Hilliard (2005) predicted PZ volatility for 5 m K⁺/2.5 m PZ at 40 and 60 °C. Even though Cullinane

(2005) and Hilliard (2005) were able to represent the K^+/PZ VLE behavior deviating by 25 and 13 %, respectively. Predictions for the vapor pressure of PZ demonstrated that even though the two rigorous thermodynamic electrolyte-NRTL models were able to predict solubility of CO_2 ; there are apparent inconsistencies between the predictive capabilities for the vapor pressure of PZ due to a lack of available literature data, as shown by Figure 3.

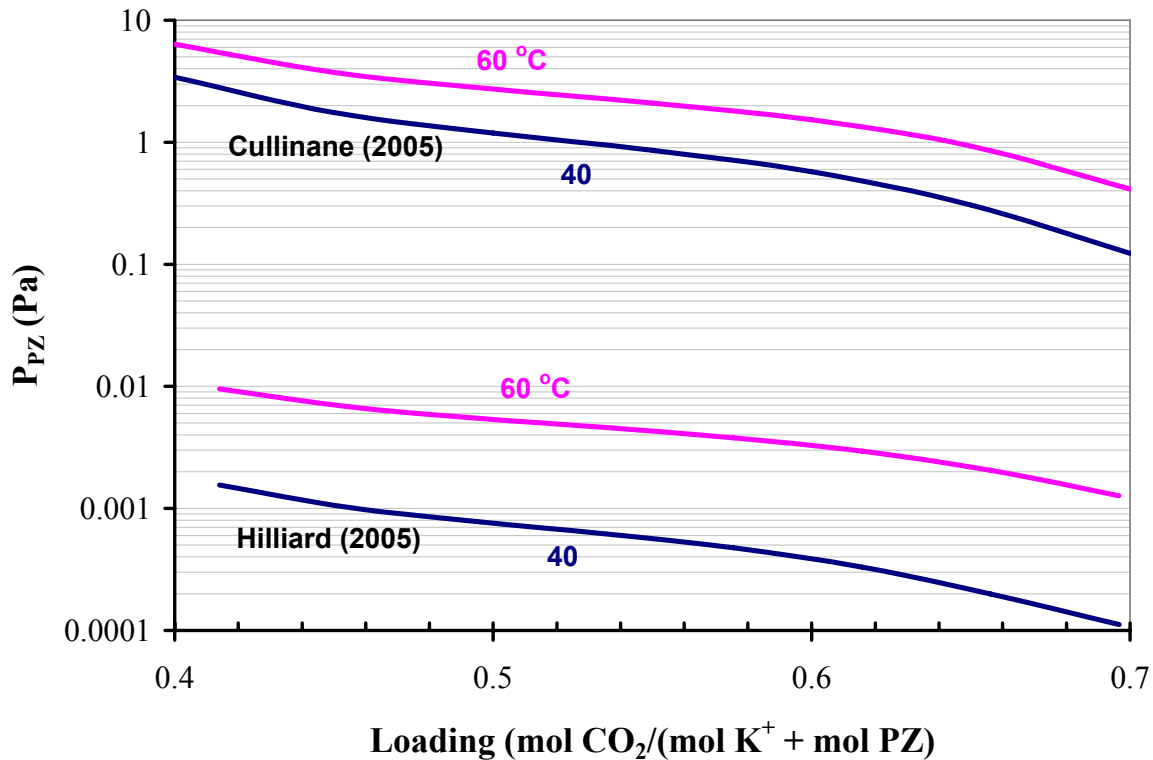


Figure 3. Predicted Piperazine Volatility from Cullinane (2005) and Hilliard (2005) for 5 m $K^+/2.5$ m PZ at 40 and 60 °C.

Researchers have been able to quantify vapor phase oxidative degradation products in aqueous MEA (Goff 2005) and solubility of CO_2 and H_2S in aqueous methyldiethanolamine (MDEA) (Rogers et al., 1998) using a unique Fourier-transform infrared (FTIR) technique to measure the vapor phase speciation in aqueous alkanolamine systems. Using this type of technique will allow us to measure the vapor phase partial pressure of PZ providing valuable information on the activity coefficient of PZ in the liquid phase and aid in estimating solvent losses in the design and optimization of separation equipment to predict the chemical and phase equilibrium behavior in absorber/stripper conditions.

Heat of CO₂ Absorption

The enthalpy of CO₂ absorption is an important physical property that is required in the design of acid gas removal plants. The enthalpy of CO₂ absorption is directly related to the energy requirements for the solvent regeneration, and it is desirable that the value be known as accurately as possible to avoid uneconomic over design. Although the enthalpy of CO₂ absorption may be estimated from a rigorous thermodynamic model using the Gibbs–Helmholtz equation to predict CO₂ solubility, the process of differentiation can magnify any errors in the solubility data and the resulting values are rarely more accurate than $\pm 10\%$. For this reason direct calorimetric measurements for the enthalpy of CO₂ absorption in the solvent are preferred. Table 3 lists current literature data for the enthalpy of CO₂ absorption from calorimetric measurements.

Table 3. Literature data for Enthalpy of CO₂ Absorption from Calorimetric Measurements.

Author	Solvent	1 st Amine Concentration/m ^a			2 nd Amine Concentration/m ^a		Temperature/°C	-ΔH _{abs} /kJ/(mole-CO ₂)
Kahrim and Mather (1980)	DEA	2.38	5.11	9.51			25 50 75	55.1 - 74.6
Christensen et al. (1986)	DGA	1.06	2.38	6.34	14.26		15 60 115 168	1.8 - 2.2
Merkley et al. (1987)	MDEA	2.10	5.59	12.58			15 60 115 168	47 - 66
Oscarson et al. (1989)	DEA	2.38	5.11	9.51			26 76 126	69 - 75
Mathonat et al. (1997)	MDEA	4.20					40 80 120	13 - 33
Mathonat et al. (1998)	MEA	7.00					40 80 120	20 - 83
Carson et al. (2000)	MEA	1.82	4.09	7.00			25	79.37 - 83.15
Carson et al. (2000)	DEA	1.06	2.38	4.07			25	68.17 - 71.15
Carson et al. (2000)	MDEA	0.93	2.10	3.59			25	47.42 - 50.56
Carson et al. (2000)	MEA + MDEA	1.74			3.43		25	72.93 - 75.79
Dallos et al. (2001)	TMBPA	0.28 - 2.29					25	44
Schafer et al. (2002)	MDEA + PZ	2.20	4.20		1.63		25 40	76.7 - 81.2

a: m = mole/kg of H₂O, Diglycolamine (DGA), Bis-(3-dimethylaminopropyl)amine (TMBPA)

In this work, we will use an isothermal heat flow calorimeter to measure the enthalpy of CO₂ absorption in a mixed solvent of K₂CO₃ + PZ + water and in a mixed amine solution of MEA + PZ + water.

Equilibrium Modeling

Understanding the thermodynamics of amine and blended amine systems is essential to their use as part of a CO₂ capture methodology. This includes the understanding of amine vaporization losses, CO₂ solubility, calorimetry, speciation, and solution phase behavior. The main objective of this study is to predict thermodynamic characteristics of H₂O-K₂CO₃-PZ-MEA-CO₂ using a rigorous thermodynamic model.

Several thermodynamic models have been developed and applied to the thermodynamic modeling of aqueous amine solutions. Kent and Eisenberg (1976) were the first to create an equilibrium model based on pseudo-equilibrium constants and Henry's Law, but the result was a model with only two adjustable parameters that could not predict speciation. Edwards et al. (1975, 1978) developed a model for the capture of carbon dioxide, hydrogen sulfide, sulfur dioxide, and hydrogen cyanide using an aqueous ammonia solution. Included in their work, they assembled chemical equilibrium and Henry's constants in water as a function of temperature. In 1981, Deshmukh and Mather developed a rigorous thermodynamic equilibrium model based on the extended Debye-Hückel theory where the activity coefficient equation had one term to account for electrostatic forces and the second adjustable term to account for short range interactions. More recently, Cullinane (2005) modified a stand-alone rigorous thermodynamic equilibrium/rate model for the H₂O-K₂CO₃-PZ-CO₂ system by utilizing the electrolyte-Nonrandom Two-Liquid (NRTL) theory developed by Chen and coworkers [Chen et al. (1979, 1982), Chen and Evans (1986), and Mock et al. (1986)] where the stand-alone FORTRAN code was first created by Austgen (1989) for the amine-water systems and then later modified by Bishnoi (2000), Dang (2001), and Freguia (2002).

For this work, we have chosen the electrolyte-NRTL model available as a property package in Aspen Plus®. The framework of Aspen Plus® was chosen for its wide use in process industries and academic institutions and provides a process environment framework for simulating multiple unit operations on a plant wide scale. Aspen Plus® also facilitates collaborative engineering by allowing different engineering groups to work together more effectively through electronically sharing information, and contains accurate and up-to-date physical properties databanks. Also, Aspen Plus® contains a built in data regression algorithm called the Data Regression System® (DRS). DRS allows for the simultaneous regression of multiple types of data sets to create a fundamental based thermodynamic model. The final reason for choosing the Aspen Plus® framework was the successful modeling of CO₂ capture technologies by utilizing the rigorous thermodynamic electrolyte-NRTL model within Aspen Plus® from previous authors [Austgen (1989) and Posey (1996)]. Based on the above reasons, we felt that the Aspen Plus® framework would be ideal environment to further the thermodynamic understanding of the H₂O-K₂CO₃-PZ-MEA-CO₂ system as part of a synergistic CO₂ capture methodology.

Experimental Methods and Design (NTNU)

The following section describes experimental methods and equipment that were used at the Norwegian University of Science and Technology to gather heat of absorption and CO₂ solubility data at stripper conditions (January - August 2005).

CO₂ Solubility – High Temperature VLE

The experimental apparatus used to study the solubility of CO₂ consisted of a vapor-liquid equilibrium apparatus with gas phase circulation operating at approximately 700 kPa using nitrogen (N₂) dilution as shown in Figure 4. The apparatus was designed to operate at pressures up to 700 kPa and temperatures up to 130 °C. The use of this apparatus to measure CO₂ solubility in amine solutions has previously been described by Ma'mun et al. (2005).

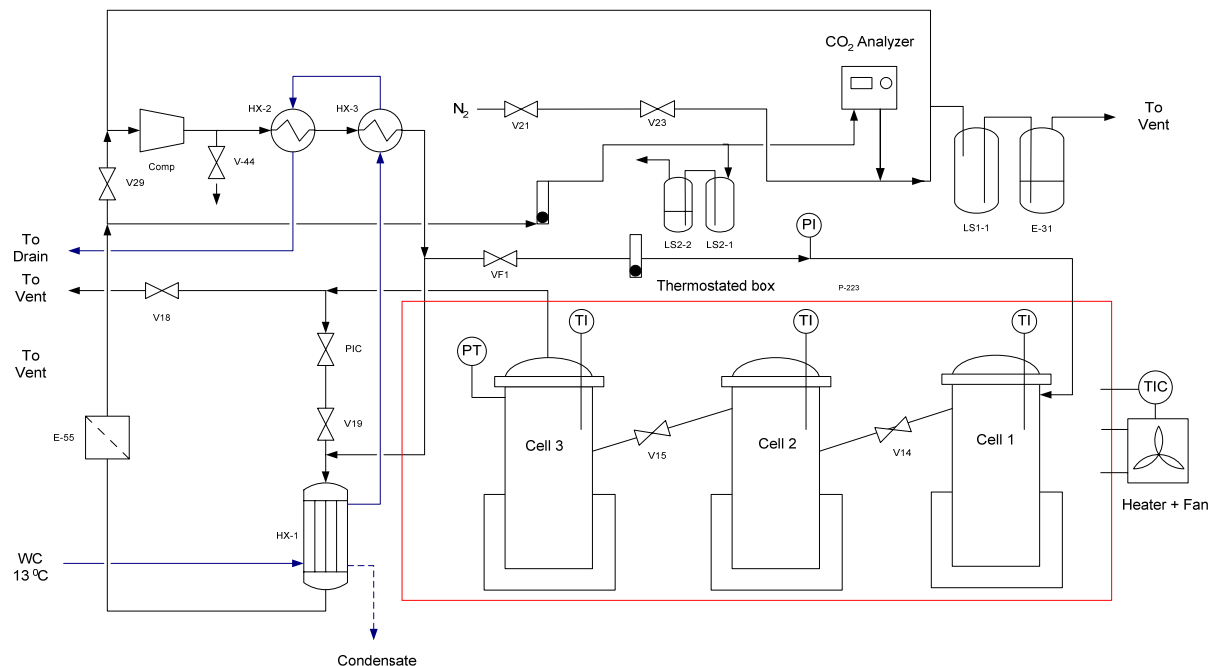


Figure 4. Process Flow Diagram for Solubility of CO₂ experiments, Vapor Phase.

During an experiment, three 300 cm³ stainless steel cylinders (cells 1, 2, and 3) containing 200/150/150 cm³, respectively, were filled with a known amount of preloaded sample solution. The cells were located within a thermostated box where the temperature of each cell was measured within ± 0.1 °C and controlled through the use of three separate oil baths. Initially, the cells were pressurized to 300 kPa to minimize vaporization of the loaded solution during the initial heating of the

apparatus. When the experimental temperature was reached, the system was then pressurized to 700 kPa and the vapor phase was then allowed to circulate. Equilibrium was obtained when the temperature, CO₂ concentration in the vapor phase, and the equilibrium pressure were constant. This process normally took two to three hours. When equilibrium was achieved, a 75 cm³ liquid sample was withdrawn from cell 3 into an evacuated sampling cylinder and then allowed to cool to ambient temperature before the sample was removed and analyzed.

Analytical Methods - CO₂ Solubility

CO₂ loading analysis was performed after each experiment by using two parallel liquid samples each titrated for CO₂ and total alkalinity using barium carbonate precipitation and a standard monotonic endpoint titration with 0.1 N sulfuric acid, respectively. The relative standard uncertainty in the loadings was $\pm 2\%$.

A vapor bleed stream from the main vapor phase recycle line was cooled to 13 °C with cooling water to allow water to condense. The stream was then sent to a Fisher-Rosemount nondispersive IR CO₂ analyzer to determine the volume percent of CO₂ in the vapor bleed stream consisting of N₂, CO₂, and small amount of H₂O. The IR analyzer was calibrated using CO₂/N₂ calibration gasses (0.5, 1, 5, 10, 20, and 35 mol %) with a relative standard uncertainty of $\pm 2\%$.

The concentration of amine in the vapor bleed stream was assumed to have condensed into the water condensate due to the low vapor pressure of the amine at 13 °C. The partial pressure of water after the condenser was assumed to be the vapor pressure of water at 13 °C. As noncondensable gasses, the amount of N₂ was assumed to be the same before and after the condenser. Thus, the partial pressure of CO₂ can be calculated from the following equation:

$$P_{CO_2} = y_{CO_2}^{IR} \left(P - P_{H_2O} + P_{H_2O}^{IR} - P_{PZ} + Ldg \cdot P_{PZ} \right) \quad (1)$$

where

P is the total pressure, kPa, $y_{CO_2}^{IR}$ is the volume percent of CO₂ from the IR analyzer, %, P_i is the partial pressure of component i , kPa, Ldg is the loading of the liquid condensate.

Through liquid analysis, it was found that the water condensate collected from the vapor bleed stream during the experiment contained trace amounts of dissolved CO₂ and amine. The CO₂ concentration in the condensate was estimated by a correlation of limited data from analyses of the condensate:

$$Ldg\left(\frac{\text{mol CO}_2}{\text{mol PZ}}\right) = 0.6913 + 0.0498 \cdot \ln(P_{\text{CO}_2}) - 0.0163 \cdot \left(\frac{\text{mol K}^+}{\text{mol PZ}}\right) \quad (2)$$

Enthalpies of CO₂ absorption

A ChemiSens CPA122 reaction calorimeter was used to take direct calorimetric measurements for determining the enthalpies of absorption of CO₂ as shown in Figure 5. The apparatus consisted of a two liter stainless steel calorimeter with a maximum 2000 rpm agitator designed to operate at pressures from 0.5 to 100 bar and over a temperature range from 30 to 200 °C. The instrument resolution has an accuracy of ± 0.1 W. A vacuum pump was used to evacuate the system to 0.25 - 0.5 bar prior to charging the vessel. The pressure in the reactor is measured by means of IDA transducer 330-50, working in the range of from 0 to 50 bar. A known amount of CO₂ was charged into two 2250 cm³ cylinders and placed into a thermostat container where the cylinder pressure and temperature were measured by a Tecsis GmbH pressure transducer with an accuracy of ± 0.3% of full scale and two K-type thermocouples with an accuracy of 0.1 °C, respectively. A mass flow controller from Bronkhorst calibrated for 1 NL/min of CO₂ was used to monitor the flowrate of CO₂ into the reaction calorimeter.

Before starting the experiment, the solution reservoir was flushed with N₂ filled with the experimental solution and weighed. The calorimeter was then evacuated to a pressure between 0.25 – 0.5 bar prior to charging the vessel. This procedure was completed twice to ensure proper evacuation and to prevent contamination of the experimental solution. Approximately 1 - 1.5 kg of the experimental solution was then transferred to the calorimeter where the apparatus was then sealed. The solution reservoir was weighed to determine the exact amount of solution transfer. The system was allowed to come to equilibrium at a desired temperature to obtain a baseline reading of the heat flow (Watts). On average, 0.26 moles of CO₂ was then feed into the calorimeter and allowed to come to equilibrium before the next amount of CO₂ was introduced and continued until the solution was saturated.

Analytical Methods - Enthalpies of CO₂ absorption

CO₂ loading analysis was preformed before each experiment by using two parallel liquid samples each titrated for CO₂ and total alkalinity using barium carbonate

precipitation and a standard monotonic endpoint titration with 0.1 N sulfuric acid, respectively. The relative standard uncertainty in the loadings was $\pm 2\%$.

The number of moles of CO₂ in the calorimeter was determined utilizing the Peng-Robinson Equation of State (PR). PR was used to calculate the number of moles of CO₂ that were fed into the calorimeter initially and the moles of CO₂ in the calorimeter gas phase at equilibrium. The number of moles of CO₂ that reacted could then be calculated. The heat flow through the calorimeter during the experiment could be integrated at each point to give the amount of heat that was absorbed by the thermostating liquid or the amount of heat released due to the net heat of absorption with CO₂.

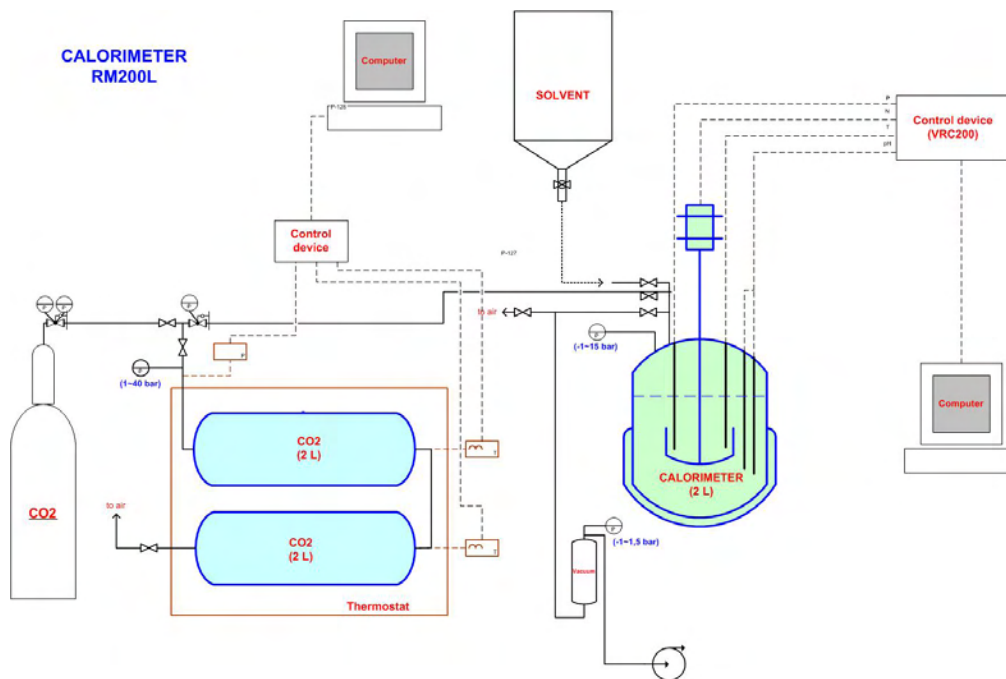


Figure 5. Process Flow Diagram for the Heat of CO₂ Absorption Experiments.

Preliminary Results (NTNU)

The following section describes experimental results measured at NTNU for the solubility and heat of absorption for CO₂ for solutions of loaded K₂CO₃/PZ with CO₂ (January - August 2005). Table 4 and 5 summarizes the range of experimental measurements.

Table 4. Summary of High Temperature VLE Measurements for K₂CO₃/PZ Solutions^{ab}.

K ⁺ (m ^a)	PZ (m)	Loading (α^b)	Temp. (°C)	P _{CO2} (bar)	Data Points
3.6 - 6.0	0.6 - 3.6	0.47 - 0.74	80 - 120	0.001 - 0.856	41

Table 5. Summary of CO₂ Heat of Absorption Measurements for K₂CO₃/PZ Solutions^{ab}.

K ⁺ (m ^a)	PZ (m)	Loading (α^b)	Temp. (°C)	ΔH_{abs} (kJ/mol-CO ₂)	Data Points
5.0 - 6.0	1.2 - 2.5	0.49 - 0.70	40 - 80	16.6 - 72.2	95

Figure 6 compares CO₂ solubility measurements based on Equation 1 to predictions as reported by Hilliard [2005] for the 6 m K⁺/1.2 m PZ system at 100 and 120 °C. Even though previous model predictions seem to over predict the new experimental data from this study by $\pm 30\%$ at 100 °C and $\pm 5\%$ at 120 °C, the data are in agreement within the error bounds associated with the loading measurements ($\pm 2\%$). Figure 7 compares CO₂ solubility for the full range of K⁺/PZ solutions at 100 °C to predictions reported by Hilliard [2005]. The over prediction discrepancy could be hypothesized as the result in an error in loading of the original experimental data set. Due to inconsistencies between the present work and previous CO₂ solubility predictions reported by Hilliard [2005], more experiments should be performed to reinforce the current measurements over similar conditions.

^a defined as mole/kg-H₂O

^b α is defined as mol CO₂/(mol MEA + 2 mol PZ)

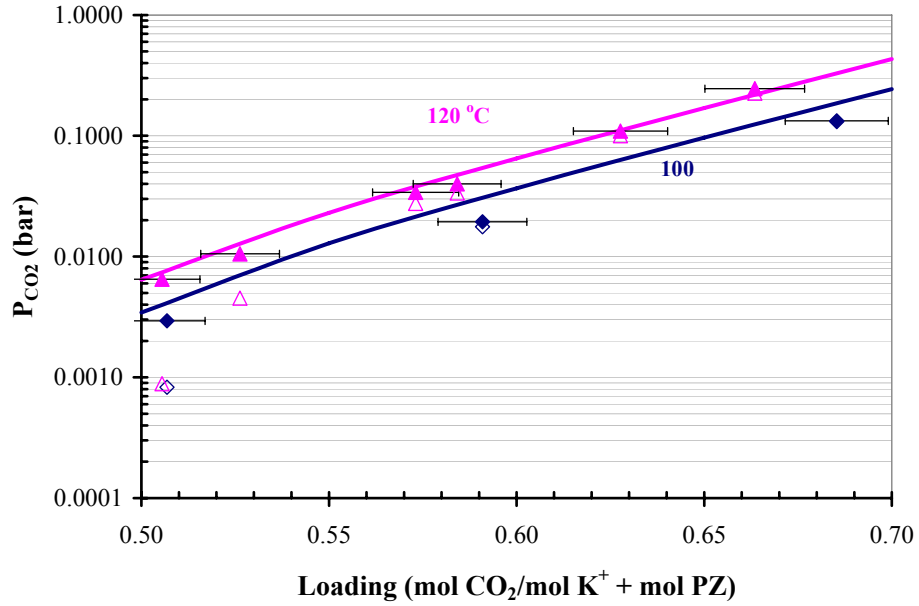


Figure 6. Comparison of experimental CO₂ solubility measurements to Hilliard [2005] predictions for the 6 m K⁺/1.2 m PZ system at 100 and 120 °C. Solid Points: Corrected for H₂O Condensate Loading, Open Points: Experimental Measurements, Lines: Hilliard [2005], Error bars = ± 2%.

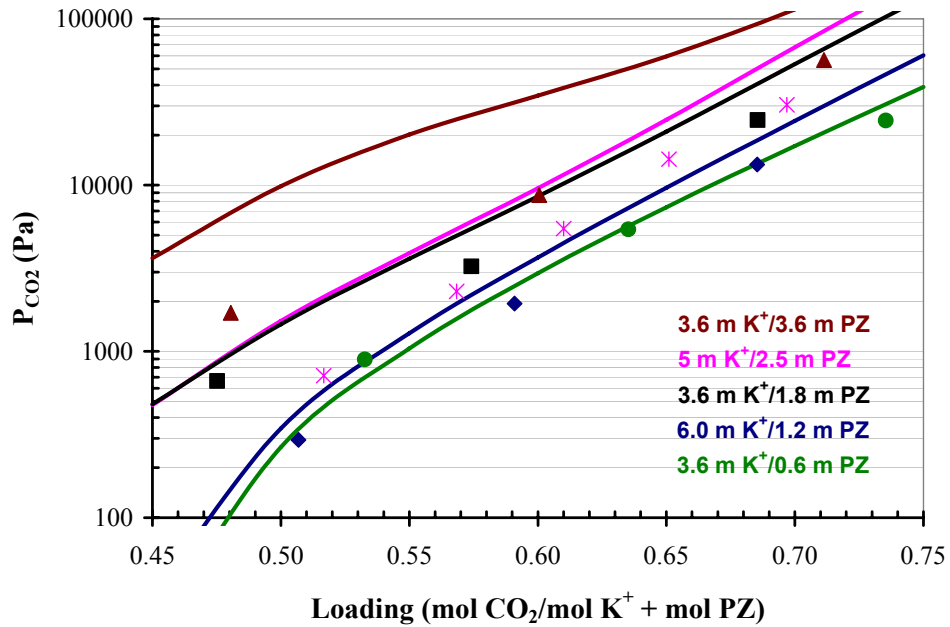


Figure 7. CO₂ solubility in K⁺/PZ solutions at 100 °C. Solid Points: Measurements Corrected for H₂O Condensate Loading, Lines: Predicted by Hilliard [2005].

Figure 8 compares the heat of CO₂ absorption measurements to predictions as reported by Hilliard [2005] through the evaluation of the Gibbs-Helmholtz equation based on the differentiation of the partial pressure of CO₂ for the 5 m K⁺/2.5 m PZ system at 80 °C. Figure 8 illustrates that the model predictions underestimate the temperature dependence within the experimental data from this study by ± 19.4 %, where the experimental data shows that enthalpy of absorption strongly depends on the loading of the amine solution with CO₂. It was also observed that enthalpy of absorption increases with temperature.

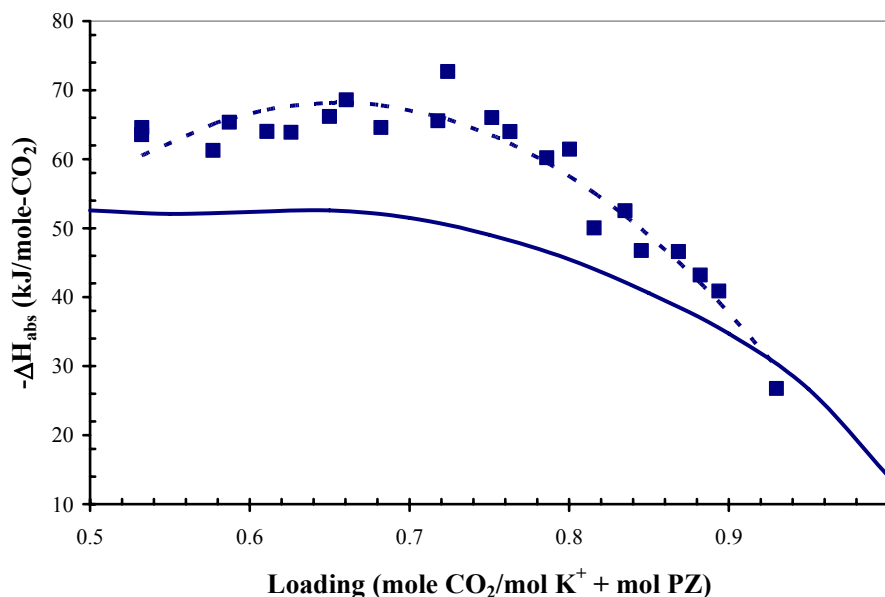


Figure 8. Comparison of experimental heat of CO₂ absorption measurements to Hilliard [2005] predictions for the 5 m K⁺/2.5 m PZ system at 80 °C. Solid Points: This work, Solid Line: Hilliard [2005].

Solubility and heat of absorption for CO₂ measurements were also carried out for solutions of loaded MEA/PZ with CO₂. Table 6 and 7 summarizes the range of experimental measurements.

Table 6. Summary of High Temperature VLE Measurements for MEA/PZ Solutions^{cd}.

MEA (m ^c)	PZ (m)	Loading (α ^d)	Temp. (°C)	P _{CO2} (kPa)	Data Points
3.5 - 7.0	1.0 - 3.5	0.19 - 0.43	100 - 120	2.5 - 213.3	44

^c defined as mole/kg-H₂O

^d α is defined as mol CO₂/(mol MEA + 2 mol PZ)

Table 7. Summary of CO₂ Heat of Absorption Measurements for MEA/PZ Solutions^{cd}.

MEA (m ^c)	PZ (m)	Loading (α^d)	Temp. (°C)	ΔH_{abs} (kJ/mol-CO ₂)	Data Points
7	2	0.02 - 0.59	40 - 80	34.4 - 81.2	42

Figure 9 gives the results for the experimental CO₂ solubility at 100 and 120 °C for 7 m MEA + 1, 2, and 3 m PZ, 30, respectively, as compared to 7 m MEA as reported by Jou et al. (1995). At the given temperature, the solvent exhibits a weak effect of PZ presented in the CO₂ solubility data, but illustrates an increase in capacity as the concentration of PZ increases.

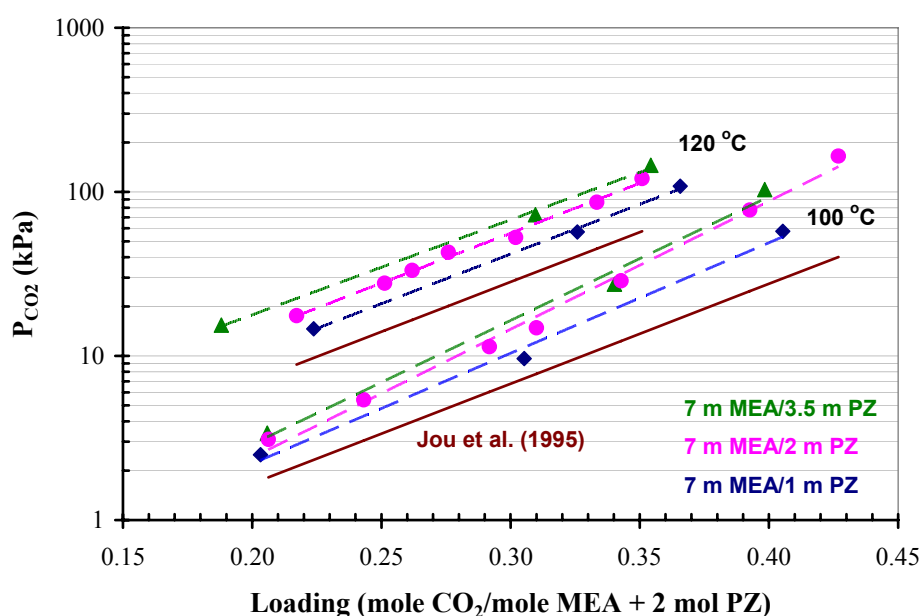


Figure 9. CO₂ solubility at 100 and 120 °C in 7 m MEA + 1, 2, and 3 m PZ, respectively, as compared to 7 m MEA as reported by Jou et al. (1995).

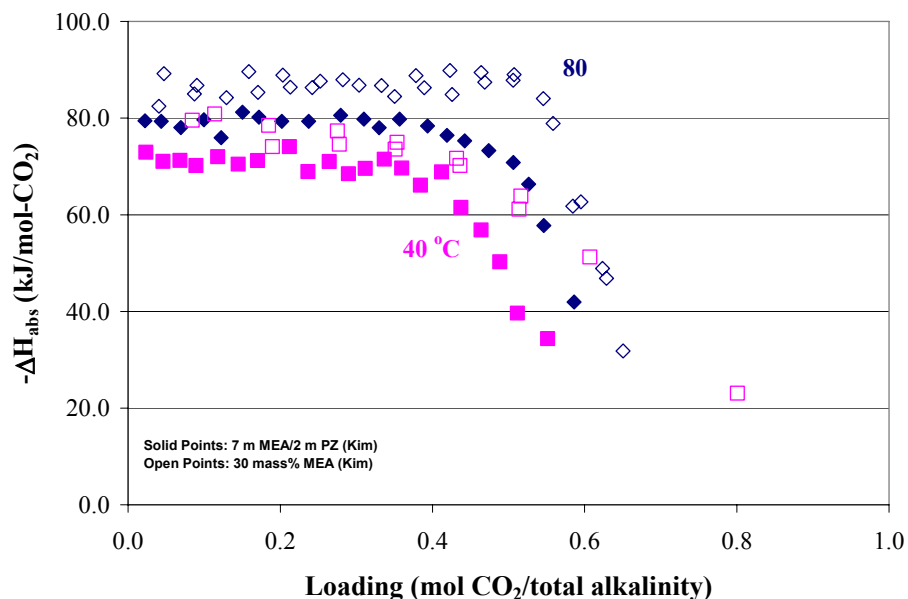


Figure 10. Comparison of experimental heat of CO₂ absorption measurements for the 7 m MEA/2 m PZ to 7 m MEA at 40 and 80 °C.

Future Work

To date, no studies in literature have shown the complete vapor phase speciation for VLE experiments. Researchers have been able to study CO₂ solubility in aqueous systems but have been unable to also study amine volatility due to the amine's low partial pressure with respect to H₂O. We have design two apparatus to quantify CO₂ solubility and amine volatility as described below.

Total Pressure Apparatus (UT)

We are currently building a total pressure apparatus to study CO₂ solubility consisting of a Parr stirred reactor designed to operate at pressures from 0.5 to 8 bar and over a temperature range from 30 to 120 °C as shown in Figure 11. A vacuum pump will be used to evacuate the system to 0.25 - 0.5 bar prior to charging the vessel. The pressure in the reactor will be measured by means of a Druck transducer PTX 610, working in the range of from 0 to 8 bar with an accuracy of ± 0.08% of full scale. The temperature will be measured by a platinum resistance thermometer, 1/10th class B, with an accuracy of ± 0.01 °C.

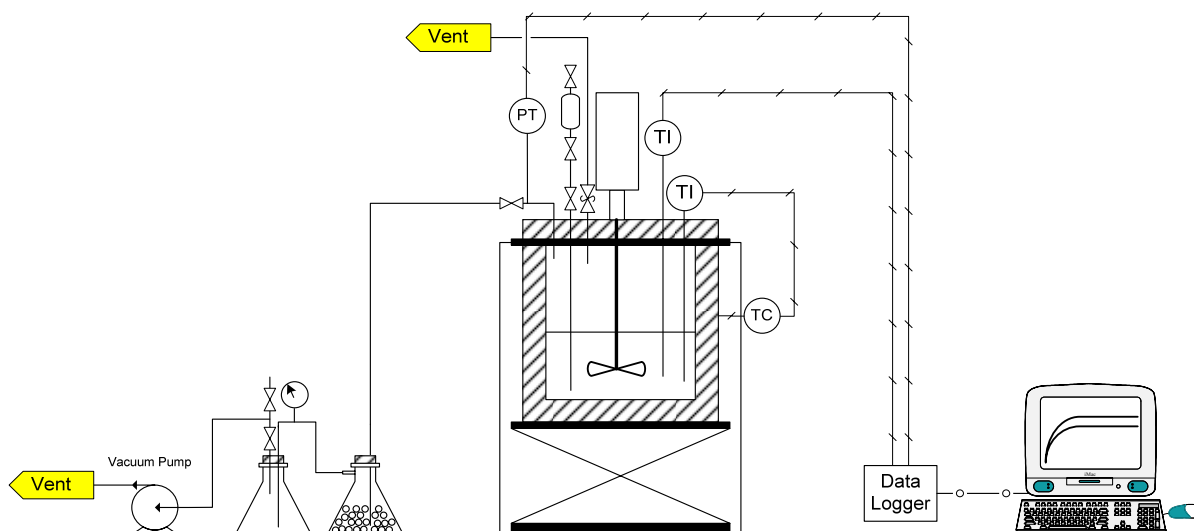


Figure 11. Process Flow Diagram for Total Pressure Experiments

Before starting the experiment, the Parr reactor will be evacuated to a pressure between 0.25 – 0.5 bar prior to charging the vessel. This procedure will be completed twice to ensure proper evacuation and to prevent contamination of the experimental solution. The solution reservoir will be flushed with N₂ filled with the experimental solution and weighed. Approximately ~150 cm³ of the experimental solution will then be transferred to the Parr reactor where the apparatus is then sealed. The solution reservoir will be weighed to determine the exact amount of solution transfer. The system will then be allowed to come to equilibrium, at a desired temperature, to obtain the total pressure. The CO₂ solubility will then be determined by the difference in total pressure from a loaded and unloaded solution. When equilibrium is achieved, a 25 cm³ liquid sample is then withdrawn from the equilibrium cell into an evacuated sampling cylinder and allowed to cool to ambient temperature before the sample is removed and analyzed. A CO₂ loading analysis will then be performed by analyzing for total carbon dioxide by acidic evolution into a Horiba PIR 2000 carbon dioxide analyzer and a standard monotonic endpoint titration with 0.1 N sulfuric acid, respectively.

VLE Apparatus for Vapor Speciation (UT)

The experimental apparatus described below will use a unique Fourier-transform infrared (FT-IR) technique to measure the vapor phase speciation of aqueous alkanolamine systems to improve the accuracy of VLE measurements.

We are in the process of designing an experimental apparatus to study vapor phase speciation consisting of a bubble column with gas phase circulation to the FT-IR as shown in Figure 12. The bubble column was designed to operate at atmospheric pressure and over a temperature range from 30 to 70 °C.

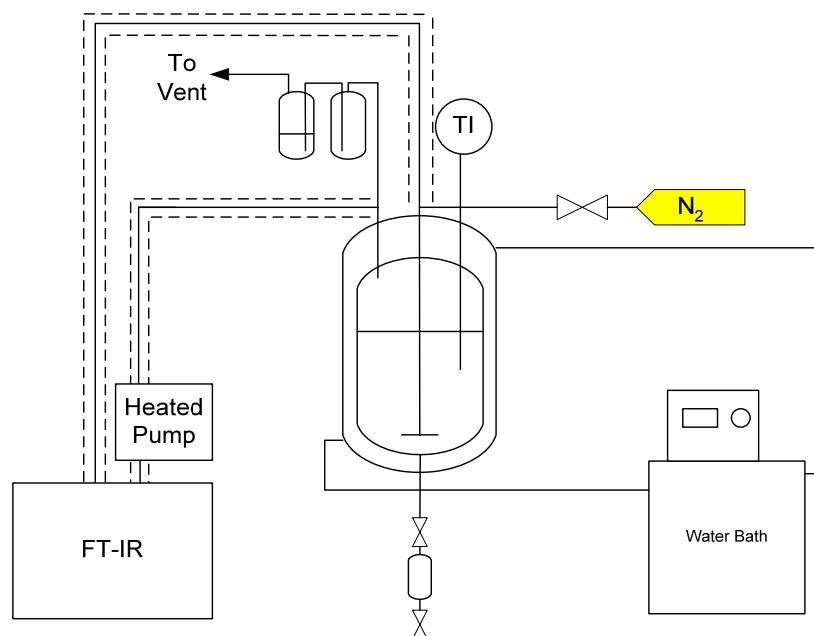


Figure 12. Process Flow Diagram for Vapor Phase Speciation Experiments

During an experiment, 3000 cm³ glass cylinder (bubble column) is filled with a known amount of preloaded sample solution ~2000 cm³. The column is located within a thermostated cylinder where the temperature of column will be measured within ± 0.1 °C and controlled through the use of a water bath. When the experimental temperature is reached, the wet vapor phase is then allowed to circulate, where the vapor stream passes into a heated sample line operated at approximately 180 °C before entering a Temet Gasmet™ DX-Series portable Fourier-Transform infrared spectrometer. The vapor stream is then analyzed to determine the volume percent of water, CO₂, and amine. The use of this device to measure oxidative degradation of aqueous MEA has previously been described by Goff [2005]. After analysis, the vapor stream is then circulated back to the bubble column through a second heated line operating at approximately 80 °C. Equilibrium is obtained when the temperature, CO₂ concentration in the vapor phase, and the equilibrium pressure are constant. When equilibrium is achieved, a 25 cm³ liquid sample is withdrawn from the bubble column into an evacuated sampling cylinder and then allowed to cool to ambient temperature before the sample is removed and

analyzed. A CO₂ loading analysis will then be performed by analyzing for total carbon dioxide by acidic evolution into a Horiba PIR 2000 carbon dioxide analyzer and a standard monotonic endpoint titration with 0.1 N sulfuric acid, respectively.

Scientific Contributions

This project encompasses several different disciplines and allows for contributions in the following fields:

- Vapor-Liquid Equilibrium: This project will produce reliable VLE measurements for amine volatility and CO₂ solubility over a broad range of temperature and solution loading.
- Enthalpy of CO₂ Absorption: This data will improve heats of reaction, the temperature dependence of binary interaction parameters used in thermodynamic modeling, and improve predictions for the heat capacity of the solution.
- Analytical Methods: This project is strongly dependent on analytical methods to characterize liquid and vapor phase compositions. The use of innovative techniques such as multi-component FT-IR analysis and acid-base titration will aid in quantifying solution compositions.
- Thermodynamic Modeling: Incorporating current literature covering amine vaporization losses, CO₂ solubility, calorimetry, speciation, and solution phase behavior into a comprehensive rigorous thermodynamic model, this project expects to provide a basis to all future modeling efforts in this area.

Timeline towards PhD

Table 8 presents a proposed timeline for completion of the research objectives. The target completion date is the summer of 2007.

Table 8. Projected Research Timeline

Spring 2005	• Begin solubility and heat of absorption for CO ₂ measurements at NTNU.
Summer 2005	• Complete high temperature solubility studies from 100 – 120 °C.
Fall 2005	• Admission to candidacy
	• Complete heat of CO ₂ absorption studies.
	• Build and benchmark total pressure and vapor speciation apparatus.
Spring 2006	• Begin low temperature VLE studies from 40 – 100 °C.
Fall 2006	• Complete low temperature VLE studies.
	• Begin thermodynamic model regression

- Spring 2006 • Begin to write dissertation
- Complete thermodynamic model
- Summer 2007 • Defend dissertation

Table 9 shows 28 hours of coursework completed for a MSE degree awarded May 21, 2005.

Table 9. Coursework Completed for MSE Degree.

Fall 2002	CHE 381N	Fluid Flow and Heat Transfer	B
	CHE 381P	Advanced Analysis for Chemical Engineers	B
	CHE 387K	Advanced Thermodynamics	B
	CHE 180C	Laboratory Safety	A
Spring 2003	CHE 387M	Mass Transfer	A
	CHE 398T	Supervised Teaching in Chemical Engineering (Plant Design)	A
Summer 2003	CH w391	Proton and C13 Spectroscopy	A
Fall 2003	M 384G	Regression Analysis	A
	C S 380S	Environmental Fluid Mechanics	A
Spring 2004	CHE 388K	Separations Processes	A

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