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MDEA/Piperazine as a solvent for CO₂ capture

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Abstract

The solvent blend methyl-diethanolamine/piperazine (MDEA/PZ) has been investigated as an alternative for CO₂ capture from coal-fired power plants. MDEA/PZ offers advantages over monoethanolamine (MEA) and MDEA alone because of its resistance to thermal and oxidative degradation at typical absorption/stripping conditions. We measured thermal degradation rates of MDEA and PZ of -7 ± 20 mmolal/day and -9 ± 5 mmolal/day, respectively, in a loaded 7 m MDEA/2 m PZ solvent blend at 120°C. At 135°C, the PZ degradation rate in the loaded solvent blend is -44 ± 2 mmolal/day, which follows the appearance of unidentified diamine compounds. When sparged with 98% O₂ at 55°C, 7 m MDEA/2 m PZ with 1 mM Fe²⁺ produced 0.011 ± 0.001 mmoles formate/L-hr. At the same conditions, 7 m MDEA produced 0.024 ± 0.007 mmoles formate/L-hr. We determined that the resistance to oxidative degradation follows the order: MDEA/PZ > MDEA > PZ. The formation of amides in oxidatively degraded samples can be as much as twice the amount of formate produced. In the absence of PZ, MDEA forms amides at an order of magnitude greater rate. The volatility of MDEA in 7 m MDEA/2 m PZ at 40 and 60°C with low CO₂ loading is 6 to 11 ppm and 19 to 30 ppm, respectively. PZ activity decreases by nearly an order of magnitude in the solvent blend as loading of CO₂ is increased to a one-to-one ratio with PZ, giving a PZ volatility at 40°C of 2 to 16 ppm. We calculated a CO₂ capacity of approximately 0.75 moles CO₂/kg amine+water, as compared to a capacity of 0.5 moles CO₂/kg amine+water for MEA under comparable conditions in an absorber/stripper configuration.

© 2009 Elsevier Ltd. Open access under [CC BY-NC-ND license](http://creativecommons.org/licenses/by-nc-nd/3.0/).*Keywords:* methyl-diethanolamine; piperazine; formate; CO₂ capacity.

1. Introduction

The aqueous solvent methyldiethanolamine (MDEA)/piperazine (PZ) has been investigated as an alternative to aqueous monoethanolamine (MEA) and aqueous K^+ /PZ for CO_2 capture from coal-fired flue gases. This is an attractive solvent because it has greater capacity and lower equivalent work for CO_2 removal than MEA. MDEA/PZ has been successfully used for years in the natural gas industry for removal of CO_2 and hydrogen sulfide (H_2S). A full understanding of its resistance to degradation and vapor-liquid equilibrium (VLE) behavior is needed to design effective CO_2 capture systems. As a tertiary amine, MDEA does not form a carbamate and is not susceptible to carbamate polymerization processes that the primary and secondary amines undergo.

We have investigated the thermal and oxidative degradation of the MDEA/PZ solvent blend and compared our results to those for MEA and PZ under similar experimental conditions. We have also investigated the solubility of CO_2 in the MDEA/PZ solvent, and measured the equilibrium partial pressure of MDEA, PZ, and CO_2 in the solvent in a reactor configured with a closed loop measuring system. These measurements allowed us to determine volatility and activity of the amines, and the capacity of this solvent blend for CO_2 capture in flue gas.

2. Degradation Studies

2.1 Thermal Degradation Background

Degradation studies were performed to determine the resistance of the MDEA/PZ blend to thermal and oxidative degradation. Thermal degradation of monoethanolamine (MEA) has been studied at length. It probably degrades through the formation of an oxazolidone from MEA-carbamate. Less is known about the thermal degradation mechanisms which occur with MDEA.

Dawodu and Meisen [1] studied the thermal degradation of CO_2 loaded aqueous blends including MDEA, MDEA + diethanolamine (DEA), and MDEA + MEA using GC and GC/MS techniques. They identified up to fifteen degradation products, and the rate of amine degradation followed the order MDEA < MEA < DEA. Reza and Trejo [2] conducted short-term (90 hours), high temperature (200°C) thermal degradation studies of blended solutions of MDEA, DEA and 2-amino-2-methyl-1-propanol (AMP) loaded with CO_2 and, in some cases, H_2S . In summary, the authors found that MDEA is more resistant to degradation than DEA and AMP in the presence of acid gases. Using similar equipment and methods described for our studies, Freeman [3] found that PZ does not thermally degrade up to 150°C.

2.2 Thermal Degradation Data

In our studies, the thermal degradation of the MDEA/PZ solvent blend was investigated at 100°C to 135°C, which spans the range of practical stripper temperatures for CO_2 capture using aqueous alkanolamines. Experiments were performed with the blended system (7 m MDEA/2 m PZ) and with 7 m MDEA at a CO_2 loading of 0.1 to 0.2 moles CO_2 /mole alkalinity. Solvents were prepared using gravimetric loading to achieve 0.1 to 0.3 moles CO_2 /mole alkalinity in each tested solvent. A single experiment was conducted on the 7 m MDEA/2 m PZ system with the addition of 1 mM Fe^{2+} to investigate catalytic effects of this metal on the thermal degradation process.

The thermal degradation studies were performed using reusable 10 cm³ (nominal size) bombs constructed with stainless steel Swagelok® materials. The basic setup for each experiment entailed placing approximately 10 grams of CO_2 -loaded solvent in a bomb, placing the bomb in a temperature-controlled oven for periods of up to nine weeks, and removing the bombs from the oven(s) over time, recovering the degraded amine solutions for analysis. Solutions were loaded using a gravimetric method with $\geq 99.99\%$ CO_2 , and confirmed using a total inorganic carbon (TIC) analyzer (Horiba Model PIR-2000 infrared analyzer) with nitrogen purge. CO_2 concentrations were confirmed in a subset of degraded samples and generally did not vary more than five percent after eight weeks of degradation. The MDEA used in these studies was supplied by Huntsman Chemical (95 to 99.99%) and the PZ supplied by Acros Organics (anhydrous at 99%).

Cation analyses were performed to determine the amount of MDEA and PZ remaining in each solvent sample using a Dionex Ion Chromatograph with a polystyrene-based cation exchange resin column (Dionex IonPac CS17, 4 mm X 250 mm), a Dionex CD25 conductivity detector, CRSR 300 anion suppressor, and ultrapure deionized water with 55 mM methanesulfonic acid (MSA) as the liquid eluent. The separation method developed for cation analysis utilized a linear gradient of MSA eluent and ultrapure water.

Table 1 summarizes the key conditions for the thermal degradation experiments reported in this paper, and the degradation rates and uncertainties of MDEA and PZ (mmolal/day) based on linear regressions of the data for each compound (MDEA and PZ) using peak areas from the cation chromatograph. The chromatograms for each analysis exhibited unknown compound peaks eluting immediately after PZ, indicating the probable appearance of diamine compounds resulting from PZ degradation.

Estimates of the total concentration (based on the calibration curve for PZ) and rate of appearance of those diamine unknowns were made and presented in Table 1.

Table 1 – Thermal Degradation Rates – Average MDEA/PZ Loss and Diamine Appearance Rates

Solvent	Temp (°C)	Duration (Days)	MDEA Deg Rate (mmolal/day)		PZ Deg Rate (mmolal/day)		Diamine Appearance Rate (mmolal/day)	
			$\alpha = 0.1$	$\alpha = 0.2$	$\alpha = 0.1$	$\alpha = 0.2$	$\alpha = 0.1$	$\alpha = 0.2$
CO ₂ Loading (mol/mol alk)			$\alpha = 0.1$	$\alpha = 0.2$	$\alpha = 0.1$	$\alpha = 0.2$	$\alpha = 0.1$	$\alpha = 0.2$
7m MDEA	100	63	-6 ± 6	-18 ± 52	NA	NA	NA	NA
	120	63	-0.3 ± 11	-31 ± 16	NA	NA	NA	NA
7m MDEA/2m PZ	100	54	-3 ± 13	-19 ± 4	-2 ± 4	-6 ± 1	1 ± 2	2 ± 2
	120	54	-11 ± 11	-7 ± 20	-7 ± 3	-9 ± 5	2 ± 2	5 ± 2
7m MDEA/2m PZ 1mM Fe ²⁺	100	42	NA	3 ± 13	NA	-2 ± 5	NA	2 ± 3
	120	49	NA	-18 ± 20	NA	-11 ± 10	NA	12 ± 3
7m MDEA/2m PZ	135	42	-9 ± 8	-30 ± 15	-31 ± 3	-44 ± 2	20 ± 4	16 ± 6

In the 7 m MDEA/2 m PZ solvent, MDEA degradation rates generally ranged from immeasurable to -30 ± 15 mmolal/day, while PZ degradation rates ranged from -2 ± 4 mmolal/day to -44 ± 2 mmolal/day. The magnitude of the errors in comparison to the absolute values of the degradation rates suggest that the degradation rates of MDEA and PZ are nearly zero or immeasurable within the time periods studied using cation chromatography. In general, amine degradation rates were greater at higher temperatures (120°C than 135°C) and higher loadings. The greatest extent of MDEA and PZ thermal degradation in the blended solvent experiments occurred at a temperature of 135°C and a loading of 0.2 moles CO₂/mole alkalinity. However, given the error in the regressed degradation rates, we conclude that the catalytic effect of Fe²⁺ on MDEA degradation is undetectable over the time frames studied (63 days maximum). When 7 m MDEA was studied alone, its degradation rates were comparable to the rates of MDEA loss in the blended system at 120°C, but lower when compared to the rates at 100°C. The unknown diamine appearance rates were generally of the same magnitude as the PZ degradation rates up to a temperature of 120 °C. Diamine appearance rates measured at 135°C were approximately three to ten times as great as the rates measured at 120°C, and up to twenty times as great as the rates measured at 100°C. The energy of activation of the appearance of unknown diamine compounds is approximately 114 kJ/mol for all loading conditions. We conclude that there is a one-to-one relationship between moles of PZ degraded and moles diamine unknowns appearing with time in the blended solvent system.

3. Oxidative Degradation

3.1 Oxidative Degradation Background

Typical temperatures in an absorber configuration will be in the range of 45°C to 55°C, and it is of interest to understand how much oxidative degradation of alkanolamine solvents occurs at these conditions. Some of the first oxidative degradation studies on alkanolamines were performed by the Girdler Corporation (Kindrick *et al.*) [4] in 1950. The authors screened several alkanolamines for use in CO₂ scrubbing and reported that 50 wt % MDEA exhibited higher resistance to oxidation than other amines screened in the study. Blends of 50 wt % MDEA and MEA and DGA lost less than 4% by weight of free amine. Rooney [5] performed oxidative degradation screening studies on loaded and unloaded alkanolamines. In particular, Rooney looked at the formation of heat stable salts including acetate, formate, glycolate, and oxalate, and concluded that measuring the formation of heat stable salts would be a helpful predictive factor in determining the role of oxygen in the formation of these compounds in an amine plant. Experiments were conducted at 180°F (82°C) for a period of 28 days in stirred reactors, and samples withdrawn weekly for ion chromatography analysis. In these studies, acetate, formate, and glycolate were detected in 30 wt % and 50 wt % solvents after seven days. Greater than 100 ppm of formate was formed in the 30 wt % amine solution at 82°C after only seven days.

3.2 Oxidative Degradation Data

We conducted oxidative degradation studies using an enclosed jacketed glass reactor. Approximately 375 ml of solvent was placed in the reactor and degraded for ten to fourteen days. The jacket-side of the reactor was filled and circulated with a Lauda E100 water bath maintained at 55°C. Solvent samples were retrieved from the reactor at two-day intervals and analyzed using a Dionex Ion Chromatograph for cations (same as above), and a separate Dionex ICS 3000 Ion Chromatograph and conductivity detector with KOH eluent for anions. We used a polystyrene-based anion exchange resin column for separations (Dionex IonPac AS15) to measure the formation of heat stable salts including formate and glycolate. We also performed NaOH treatment of an aliquot of each sample for a period of 24 hours to reverse the formation of amides through hydrolysis back to the heat stable salt and amine.

Table 2 presents formate production rates measured in four experiments conducted in 7 m MDEA and the 7 m MDEA/2 m PZ. Loading was in the range of 0.10 to 0.30 moles CO₂/moles alkalinity. Figure 1 is a plot of formate concentration with time for the four experiments listed in Table 2. Linear regressions of the formate concentrations were performed to generate formate production rates in each experiment. The rate of production of formate in 7 m MDEA (0.024 ± 0.007 mmole/L-hr) was approximately twice the rate observed in three experiments conducted with 7 m MDEA/2 m PZ and various metals, suggesting that PZ inhibits the oxidation of MDEA in the solvent blend. The presence of the corrosion inhibitor, 5 mM Cu²⁺, did not appreciably increase the production of formate in 7 m MDEA/2 m PZ with other metals. We also observed that the addition of chromium and nickel did not appreciably increase the production of formate. Glycolate eluted from the anion column at approximately 19 minutes with 7 m MDEA/2 m PZ. We estimate the glycolate concentration to be less than 1 ppm in the 7 m MDEA/2 m PZ solvent blend after 14 days, resulting in a formation rate of less than 0.0001 mmol/L-hr. In contrast to these results, Sexton [6] reported formate production rates of 0.39 mmole/L-hr in 7 m MEA, which is approximately twenty-five times the rate of formate production in the 7 m MDEA/2 m PZ solvent blends.

Table 2 - Oxidative Degradation Studies - Formate Production, 55°C, 98% CO₂/2% O₂
375 ml Solvent, Agitated 1400 rpm

Expt No.	Solvent	CO ₂ Loading (mol/mol alk)	Duration (Days)	Production Rate (mmol/L-hr)	
				Formate	**Amide
1	7 m MDEA, 1 mM Fe ²⁺	0.10	14	0.024 ± 0.007	0.165 ± 0.095
2	7 m MDEA/2 m PZ, 1 mM Fe ²⁺	0.30	14	0.011 ± 0.001	0.010 ± 0.001
3	7 m MDEA/2 m PZ 0.1 mM Fe ²⁺ , 0.6 mM Cr ³⁺ , 0.1 mM Ni ²⁺	0.24	10	0.012 ± 0.003	0.027 ± 0.009
4	*7 m MDEA/2 m PZ 0.1 mM Fe ²⁺ , 5 mM Cu ²⁺	0.23	10	0.0159 ± 0.006	0.018 ± 0.004

* Glycolate production rate is <0.0001 mmol/L-hr.

** Calculated as difference between formate production with and without hydrolysis of amide by NaOH.

When we reversed the formation of amide in the degraded solvent through treatment of samples with NaOH, we found that the amount of measurable formate (Table 2) increased by a factor of 2 to 3 with 7 m MDEA/2 m PZ, and by an order of magnitude with 7 m MDEA. Sexton [6] reported that in MEA studies, degradation products other than formate can be present in greater quantities than the formate, but are undetectable through standard anion chromatography methods.

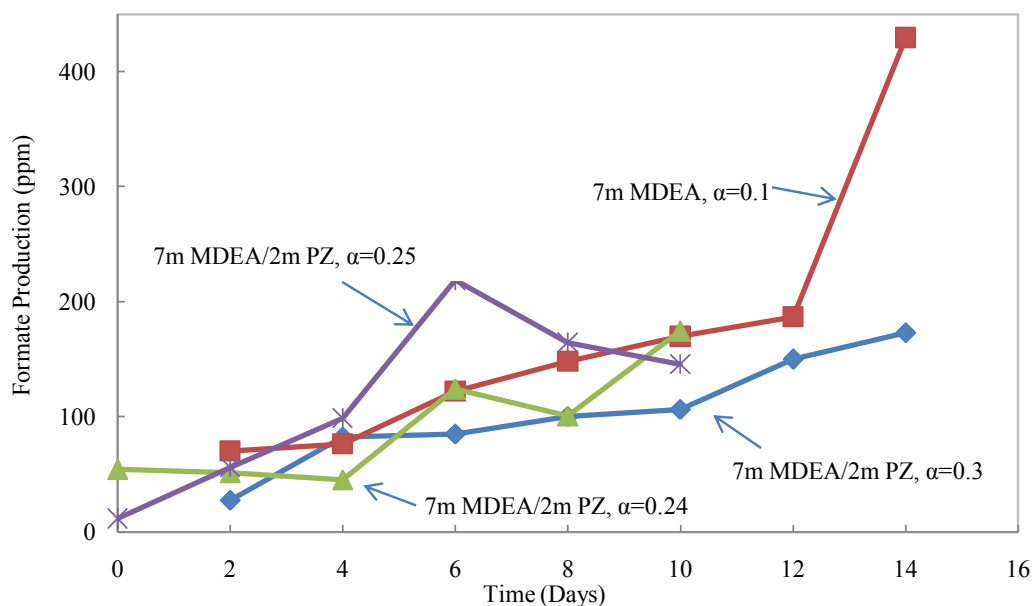


Figure 1: Formate Production, 55°C, 350 mL reactor, 100 mL/min

This work confirms the work of previous groups investigating the oxidative degradation of alternatives to MEA. We conclude that the resistance to oxidative degradation follows the order: MDEA/PZ>MDEA>MEA. In an oxidative degradation study with 50 wt % MDEA and no metals, Rooney reported a formate production rate of 0.008 ± 0.001 mmole/L-hr, which is within our reported range for the 7 m MDEA/2 m PZ blend, but an order of magnitude below the range we are reporting for the 7 m MDEA system with 1 mM Fe^{2+} ; the presence of 1 mM Fe^{2+} in the solvent in our experiment may have catalyzed the oxidative degradation of MDEA. We also conclude that the greater formation of amides in the 7 m MDEA solvent experiment when compared to all experiments conducted with MDEA/PZ is indicative of greater formation of amides through the carboxylic acid pathway in the oxidative degradation of MDEA when PZ is not present. Rooney [5] reported the formation of other carboxylic acids including acetate and glycolate at concentrations comparable to those for formate. We did not see appreciable amounts of glycolate in our studies.

4. Volatility

Amine losses in CO_2 scrubbing systems occur through volatilization in the stripper and absorber units. The degree to which these losses occur directly affects amine management system requirements. Using a semi-batch reactor apparatus and Fourier Transform Infrared (FTIR) spectrometer maintained at 180°C , we performed volatility measurements on loaded MDEA/PZ in an agitated environment by the method of Hilliard [7]. The reactor was sparged with a pre-saturated gas consisting of 98% O_2 and 2% CO_2 . Measurements of gas-phase amine concentrations were made with the FTIR at temperatures of 40°C and 60°C with 0.0, 0.5, and 1 moles CO_2 /mole PZ. From the amine concentrations and the assumption that solution behavior adheres to a modified Raoult's Law, we also calculated amine activities.

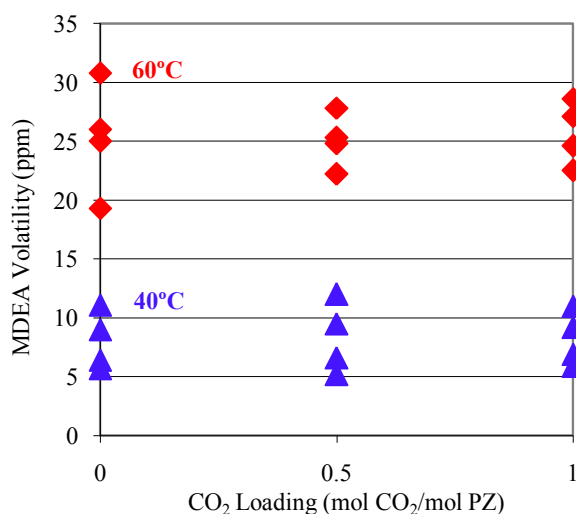


Figure 2: MDEA Volatility for MDEA-PZ Blends (2.7m-8.7m MDEA /0.4m-2.6m PZ)



At 1 atm and 60°C , the PZ volatility was 8 to 66 ppm at 0 to 1 mole CO_2 /mole PZ. At the low end of the loading range, the volatility of PZ was greater than MDEA, but slightly lower at the high end. Figure 3 presents the activity of PZ as measured from solubility data generated in the experiments described above. The activity of PZ decreases linearly with loading at both 40°C and 60°C in each of the solvent blends. We attribute this behavior to the reduction in free PZ in the solvent blend as loading increased. In most cases, the activity of the PZ is greater at 60°C for the corresponding MDEA/PZ blend and loading condition. With 8 m MDEA/1.2 m PZ at a loading of 0.5 moles CO_2 /mole PZ, the estimated PZ volatility is 6 ppm at 1 atm.

5. CO_2 Solubility and Capacity

Figure 4 presents measurements of CO_2 solubility in MDEA/PZ solvents. Bishnoi [8] used our wetted wall column to generate data for 4 M MDEA/0.6 M PZ (7.7 m/1.2 m) at 40 and 70°C . Recently we have measured CO_2 solubility with the hot gas FTIR at the same time as amine volatility. We have also collected CO_2 equilibrium partial pressure data at 40°C and 60°C over a 7 m MDEA/2 m PZ solvent blend with the wetted wall column (Figure 4). The equilibrium partial pressure of CO_2 increases two orders of magnitude over a low loading range (0.01 to 0.07 moles CO_2 /mole alkalinity) at 70°C . Over a higher

Figure 2 presents the volatility (ppm at 1 atm) for MDEA in various MDEA/PZ solvent blends at 40°C and 60°C over the range of tested loading. At 40°C , the gas-phase MDEA was 6 to 11 ppm, with little or no increase when the loading was increased from 0.0 to 1.0 moles CO_2 /mole PZ. The gas-phase MDEA concentration increased to 19 to 30 ppm for all the MDEA/PZ blends at 60°C , but was generally unchanged over the range of loading. The MDEA volatility results follow an anticipated relationship with loading and PZ concentration. The formation of the PZ-carbamate (Reaction 1) is more favorable than the formation of bicarbonate from MDEA (Reaction 2). Thus, only after the amount of CO_2 in the solvent exceeds the amount of PZ will the MDEA actively react with CO_2 , resulting in a reduction in the amount of free MDEA in solution and a lower partial pressure of MDEA in the gas phase. Given the maximum loading conducted in our experiments (1 mole CO_2 /mole PZ), we did not anticipate a significant decrease in MDEA volatility.

loading range (0.025 to 0.25 moles CO₂/mole alkalinity), the partial pressure of CO₂ increases by two and one-half orders of magnitude to approximately 9 kPa at 40°C. Using 7.7 m MDEA/1.2 m PZ in an absorption/stripping system, a lean loading of 0.1 moles CO₂/mole alkalinity would give a CO₂ partial pressure of 0.7 kPa at 40°C, which is well below anticipated conditions at the lean end of an absorber (~1.2 kPa for 90% CO₂ removal). With a rich loading of 0.25 moles CO₂/mole alkalinity at 40°C, the corresponding equilibrium CO₂ partial pressure is 7 kPa, which provides a sufficient driving force for CO₂ absorption (CO₂ at 12 kPa). At these conditions, the working capacity is 0.75 moles CO₂/(kg amine + water) compared to 0.5 moles CO₂/(kg amine + water) for 7 m MEA (rich and lean loading of 0.55 and 0.45 moles CO₂/mole alkalinity). The heat of CO₂ absorption of the blended solvent is about 75 kJ/mol, compared to about 84 kJ/mol for 7 m MEA. The closeness in values is a result of the fact that the PZ and MEA form carbamates in the primary reaction with CO₂.

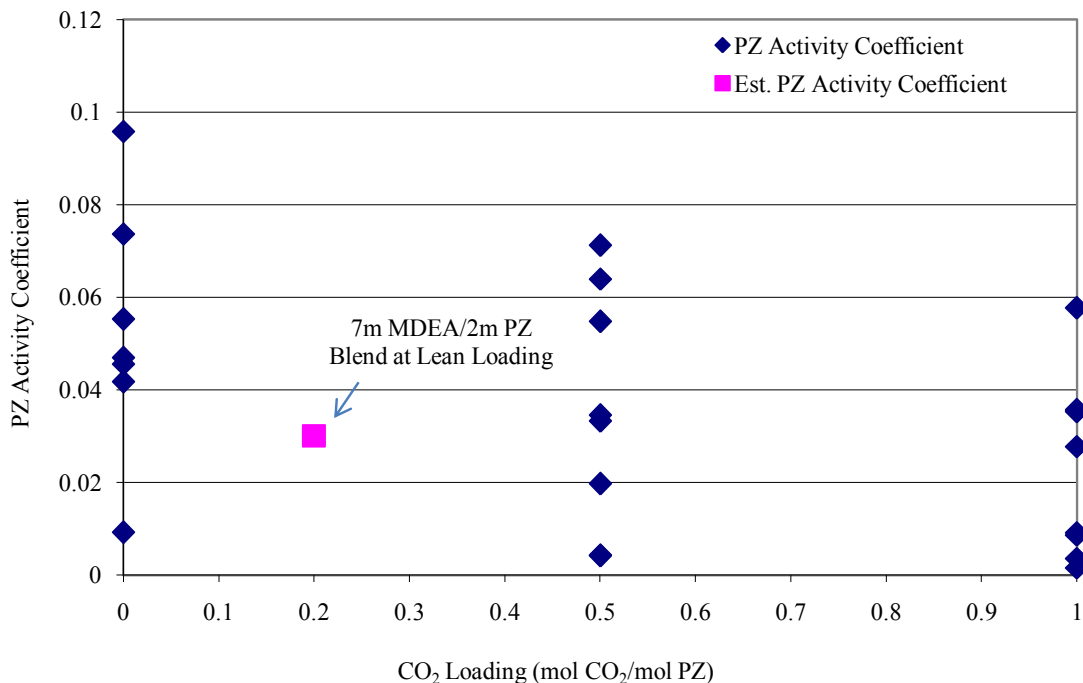


Figure 3: PZ Volatility in MDEA-PZ Blends at 40-70°C (2.7m-8.7m MDEA / 0.4m-2.6m PZ)

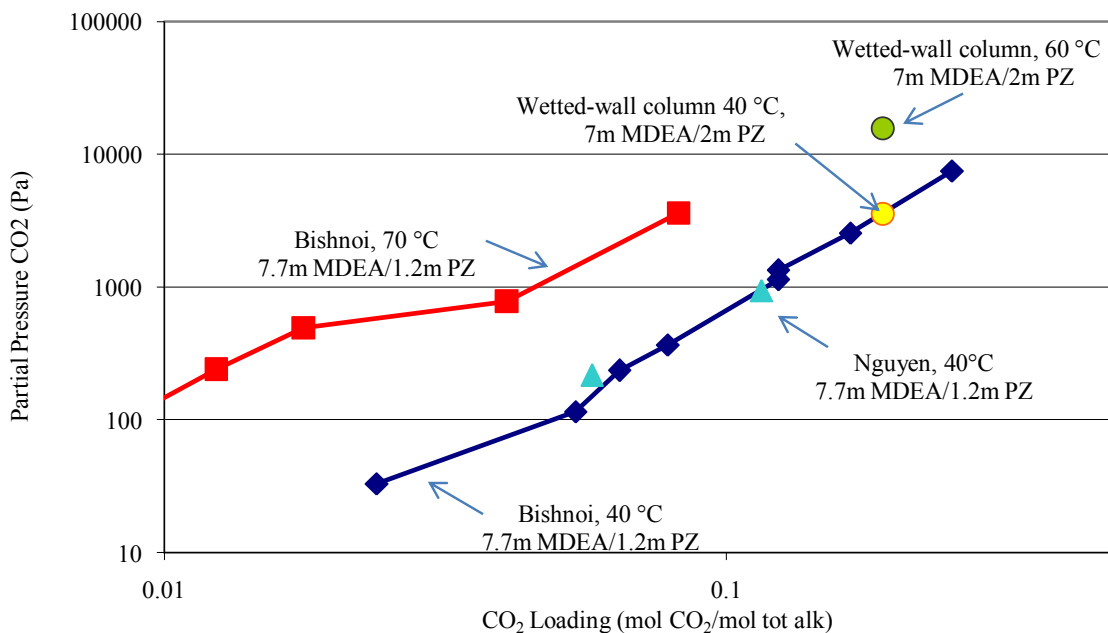


Figure 4: CO₂ Solubility for MDEA-PZ Blend

6. Conclusions

The MDEA/PZ solvent blend provides greater stability than MEA (30 to 50 wt %) when tested at conditions pertinent to CO₂ scrubbing in flue gas. We found that a 7 m MDEA/2 m PZ blend was resistant to thermal degradation up to 120°C at a loading of 0.2 moles CO₂/mole alkalinity, with the highest measured total degradation rates -30 ± 15 mmolal/day for MDEA and -44 ± 2 mmolal/day for PZ at 135°C. The presence of PZ in the MDEA/PZ solvent blend may inhibit the thermal degradation of MDEA. At comparable conditions, MEA degrades at a rate of -20 mmolal/day. Formate production rates in oxidative degradation experiments conducted at 55°C were in the range of 0.010 to 0.016 mmoles formate/L-hr, as compared to formate production rates in MEA under comparable conditions (0.39 mmole/L-hr). Formate production in solvents adhered to the following order: MEA>MDEA>MDEA/PZ. Amide production rates are roughly twice the formate production rates in the MDEA/PZ solvent blend.

The volatility of MDEA in the MDEA/PZ solvent does not change over a range of loading at typical absorber conditions (40°C to 60°C) as long as the predominant reactions involve PZ. The PZ activity in this solvent decreased with loading and temperature over the loading range 0.0 to 1.0 moles CO₂/mole PZ, which we anticipated due to the fast reaction which results in the formation of a PZ-carbamate species. The volatility of PZ for the 8 m MDEA/1.2 m PZ solvent blend was measured as 8 to 66 ppm at 1 atm. We calculated a capacity of 0.75 moles CO₂/kg amine + water, which compares favorably to a value of 0.5 moles CO₂/kg amine + water for a 7 m MEA solvent.

7. Acknowledgements

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