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Carbon dioxide capture with concentrated, aqueous piperazine

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Abstract

Concentrated, aqueous piperazine (PZ) has been investigated as a novel amine solvent for carbon dioxide (CO₂) absorption. The CO₂ absorption rate with aqueous PZ is more than double that of 7 m MEA and volatility at 40 °C ranges from 10 to 19 ppm. Thermal degradation is negligible in concentrated PZ solutions up to a temperature of 150°C, a significant advantage over MEA systems. Oxidative degradation of concentrated PZ solutions is appreciable in the presence of copper (4 mM), but negligible in the presence of chromium (0.6 mM), nickel (0.25 mM), iron (0.25 mM), and vanadium (0.1 mM). Initial system modeling suggests that 8 m PZ will use 5 to 10 % less energy than 7 m MEA. The fast kinetics and low degradation rates suggest that concentrated PZ has the potential to be a preferred solvent for CO₂ capture.

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1. Introduction

The increase in the anthropogenic carbon dioxide (CO₂) concentration in the atmosphere over the past few decades is known to be part of the cause of global warming. A large impact on CO₂ emissions can be made by targeting large point sources such as coal-fired power plants. Amine based absorption and stripping systems have been studied for CO₂ capture from coal-fired power plants and have shown the most promise for effective CO₂ control. Traditional amines such as monoethanolamine (MEA) and amine blends such as potassium carbonate/piperazine (PZ) and methyldiethanolamine (MDEA)/PZ have been investigated extensively for this application [1-3].

PZ is a diamine that has previously been studied as a promoter for amine systems to improve kinetics, such as MDEA/PZ or MEA/PZ blends. The concentration of PZ when used as a promoter has been between low, between 0.5 to 2.5 m PZ, because PZ is not highly soluble. Given the nature and magnitude of absorption/stripping systems, any possibility of precipitation ruled out PZ for use at concentrations above its room temperature solubility. Additionally, the boiling point of PZ (146.5°C) is lower than that of MEA (170°C), indicating the possibility for higher volatility. Recent work has indicated that the volatility of PZ is comparable to that of MEA due to the non-ideality of PZ in solution. Increasing the concentration of PZ in solution allows for increased solvent capacity and faster kinetics.

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PZ has been studied as a solvent for absorption/stripping systems for the removal of CO₂ from the flue gas of coal-fired power plants. The current work examines solid solubility, oxidative degradation, and thermal degradation of concentrated aqueous PZ solutions. Additionally, extensive work on the kinetics of the absorption of CO₂ into PZ is reported. Finally, preliminary modeling work indicates that stripper performance with a concentrated PZ solvent is comparable to MEA systems.

2. Materials and methods

2.1 Solution preparation

Aqueous piperazine solutions were created by heating anhydrous piperazine (99% pure, Fluka) with water until the solid crystals melted into a solution. The warm solution was transferred to a glass cylinder with a CO₂ gas sparger and the cylinder was placed on a scale. The scale was used to gravimetrically add CO₂ to achieve the desired loading.

2.2 CO₂ loading through total inorganic carbon (TIC)

The concentration of CO₂ in solution was determined by total inorganic carbon analysis [2]. The sample is diluted and then acidified in 30 wt% phosphoric acid to release aqueous CO₂, carbamate, and bicarbonate species as gaseous CO₂. The CO₂ is carried through an infrared analyzer with nitrogen. The resulting analyzer peaks are integrated and correlated to CO₂ concentrations using a 1000 ppm K₂CO₃/KHCO₃ standard inorganic carbon solution. CO₂ loading is reported as moles CO₂/mole alkalinity or moles CO₂/equiv PZ, where 2 moles alkalinity/mole PZ is the conversion factor.

2.3 Amine titration

The concentration of piperazine in solution was determined using acid titration [2]. An automatic Titrando series titrator with automatic equivalence point detection was used (Metrohm USA). The 300X diluted sample was titrated with 0.1 N H₂SO₄ to a pH of 2.4. The amount of acid needed to reach the equivalence point at a pH of 3.9 was used to calculate the total amine concentration in solution.

2.4 Viscosity measurements

Viscosity was measured using a Physica MCR 300 cone and plate rheometer (Anton Paar). The apparatus allows for precise temperature control for measuring viscosity at temperatures ranging from 20 to 70°C. To determine viscosity, the angular speed of the top disk (cone) is increased from 100 to 1000 s⁻¹ over a period of 100 seconds and the shear stress exerted by the solution is measured every 10 seconds. Reported viscosities are averages of these 10 individual measurements.

2.5 Oxidative degradation

Oxidative degradation experiments were performed in a low gas flow agitated reactor fed with 100 mL/min of a saturated 98%/2% O₂/CO₂ gas mixture [4]. The reactor is a 500-mL jacketed reactor is filled with 350 mL of solvent. The jacket contains circulated water maintained at 55°C. The reactor is agitated at 1400 rpm to increase the mass transfer of oxygen into the solution. The reactor is operated continuously for 3-5 weeks, depending on the experiment. Liquid samples are taken every two days and water is added to maintain the water balance on the reactor contents. The liquid samples were analyzed for PZ and degradation products by cation and anion chromatography.

2.6 Vapor-liquid equilibrium
CO₂ solubility and amine volatility were measured in a batch equilibrium cell with gas recycle through a hot gas FTIR [2]. The cell was a jacketed, glass reactor where temperature is controlled within 1°C. The inlet gas is sparged from the bottom of the reactor and there is additional mechanical agitation to enhance mass transfer. The gas in the headspace of the reactor is continuously sampled by an FT-IR. The gas leaves the reactor and passes through a mist eliminator and into a sample line heated to 180°C. The heated gas stream is then analyzed by the multi-component FTIR analyzer.

2.7 Thermal degradation

Thermal bombs were constructed from 1/4 or 3/8-inch stainless steel tubing with two Swagelok® end caps [5]. Bombs were filled with 2 or 10 mL of PZ solution, sealed, and placed in forced convention ovens at various temperatures. Bombs were removed from the ovens each week and the contents were analyzed for degradation products, remaining amine concentration, and CO₂ loading. Amine losses are reported as a fraction of the initial amine that is remaining after the indicated time period as analyzed using cation ion chromatography (IC).

2.8 Wetted-wall column operation

The wetted wall column counter-currently contacts an aqueous piperazine solution with a saturated N₂/CO₂ stream on the surface of a stainless steel rod with a known surface area [3, 6]. The wetted wall column can either perform absorption or desorption of CO₂ depending on the inlet CO₂ partial pressure of gas phase. By bracketing CO₂ partial pressures that result in absorption and desorption, the equilibrium partial pressure of the solution can be determined.

The gas flow rate entering the wetted wall column is controlled via mass flow controllers. Inlet and outlet CO₂ concentrations are measured by Horiba CO₂ analyzers. As Equation 1 shows, the calculated CO₂ flux divided by the CO₂ partial pressure driving force provides an overall mass transfer coefficient for the experiment (Kₐ). The overall mass transfer coefficient is related to the liquid and gas phase mass transfer coefficients via a series resistance relationship shown in Equation 2.

\[
\text{Flux} = K_G \left( P_{\text{CO}_2, \text{bulk}} - P_{\text{CO}_2}^* \right)
\]

\[
\frac{1}{K_G} = \frac{1}{K_g} + \frac{1}{K_g'}
\]

The gas phase mass transfer coefficient, kₐ, is correlated to experimental conditions and is a strong function of the geometry of the apparatus. The liquid film mass transfer coefficient, kₐ', quantifies how fast the solution will absorb or desorb CO₂.

3. Results

3.1 Solid solubility

The solid solubility of PZ was studied over a range of PZ concentration, CO₂ loading, and temperature. Solutions were prepared to cover the desired solution properties and were allowed to equilibrate at each condition with stirring before solubility observations were made. The transition temperature of 8 and 10 m PZ solutions over a range of CO₂ loading is shown in Figure 1. The transition temperature is the temperature at which a liquid solution will first precipitate when cooled slowly. The approximate temperature ramp for all transitions was 1°C every 5 minutes. The two dashed lines at rich loadings in Figure 1 represent soluble PZ solutions indicating that the solubility envelope extends at least this far. The transition temperature of unloaded PZ solutions ranging from 1.0 to 40 m PZ is shown in Figure 2.
The data from this study shows a eutectic point around 60 wt% PZ that was observed in the other data sources as well [2, 7]. For 8 m PZ, a CO₂ loading of approximately 0.25 mol CO₂/mol alkalinity is required to maintain a liquid solution without precipitation at room temperature (20 °C). In addition, the solubility of PZ at 20°C is 14 wt% PZ, which corresponds to 1.9 m PZ.

### 3.2 Viscosity

The viscosity of aqueous PZ solutions has been measured from 0.20 to 0.45 moles CO₂/mole alkalinity, 2 m PZ to 20 m PZ, and 25°C to 60°C. The viscosity of 8 and 10 m PZ is compared with other amines in Figure 3. The amine concentration is plotted in units of moles alkalinity per kg of water in order to compare mono- and diamines on the same basis. All of the viscosities are at 40°C and at the rich loading of the system (0.3 mol CO₂/mol alkalinity for MDEA and MDEA/PZ; 0.4 mol CO₂/mol alkalinity for PZ and DGA; 0.5 mol CO₂/mol alkalinity for MEA).

Comparison of the viscosity on this basis shows how the amine basic groups affect overall viscosity. As the concentration of basic groups increases, the viscosity increases in a linear direction. The viscosity of 8 m PZ is higher than that of 7 m MEA, but as compared to 60 wt % DGA®, the viscosity of PZ is lower for a higher alkalinity. DGA® solutions at 60 wt % are successfully used in natural gas treating [8].

### 3.3 Oxidative degradation
Heavy metals are known to catalyze the oxidative degradation of amines [11]. The results of oxidative degradation of concentrated PZ in the presence of several dissolved metals are shown in Table 1. The experiments simulated four scenarios: (1) leaching of stainless steel metals, (2) addition of a copper-based corrosion inhibitor, (3) addition of a vanadium-based corrosion inhibitor (low concentration), and (4) addition of a copper-based corrosion inhibitor and proprietary inhibitor “A”.

Table 1: Oxidative Degradation of PZ and MEA at 55°C (100 ml min of 98% O2/2% CO2, 350 mL solution)

<table>
<thead>
<tr>
<th>Case</th>
<th>Solution (m)</th>
<th>Heavy Metals</th>
<th>Rate of Formation (mM/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Formate</td>
</tr>
<tr>
<td>-</td>
<td>7 MEA</td>
<td>1.0 Fe</td>
<td>0.29</td>
</tr>
<tr>
<td>1</td>
<td>10 PZ</td>
<td>0.6 Fe2+, 0.25 Cr3+, 0.25 Ni2+</td>
<td>0.005</td>
</tr>
<tr>
<td>2</td>
<td>10 PZ</td>
<td>4.0 Cu2+</td>
<td>0.14</td>
</tr>
<tr>
<td>3</td>
<td>8 PZ</td>
<td>0.1 Fe2+, 0.1 V4+</td>
<td>0.006</td>
</tr>
<tr>
<td>4</td>
<td>8 PZ</td>
<td>4.0 Cu2+, 0.1 Fe2+, 100 “A”</td>
<td>0.011</td>
</tr>
</tbody>
</table>

Oxidative degradation of concentrated PZ was found to be four times slower than that of MEA in the presence of stainless steel metals (Fe2+, Cr3+, and Ni2+) and a low concentration of vanadium. As with MEA solutions, PZ was determined to be highly susceptible to oxidative degradation in the presence of Cu2+ [12]. The primary degradation products were found to be ethylenediamine (EDA), formate, oxalate, and N-formylpiperazine, the amide of formate and PZ (denoted as Formamide in the table). The N-formylpiperazine concentration was not measured directly, but inferred from formate production through the basic reversal of the N-formylpiperazine formation reaction. Also, as with MEA, Inhibitor “A” was able to vastly reduce this degradation to levels comparable with the stainless steel and vanadium cases [12].

3.4 Thermal degradation

Thermal degradation was investigated in PZ solutions at slightly above stripper temperature (135°C) and much higher than stripper temperatures (150°C and 175°C). The thermal degradation results are shown in Table 2. Experiments ranged from 4 to 12 weeks in length.

PZ thermal degradation was determined to be negligible at 135 and 150°C as compared to 7 m MEA. At 175°C, 32% of the PZ was degraded in 4 weeks. EDA was observed as a thermal degradation product at 175°C but not at lower temperatures. Addition of 5.0 mM Cu2+/0.1 mM Fe2+, 5.0 mM Cu2+/0.1 mM Fe2+/100 mM Inhibitor “A”, and 0.6 mM Cr3+/0.25 mM Fe2+/0.25 mM Ni2+ did not affect degradation rates at 175°C.

Table 2: Thermal Degradation of PZ and MEA [5]

<table>
<thead>
<tr>
<th>Solvent</th>
<th>CO2 Loading (mol/mol alkalinity)</th>
<th>Temperature (°C)</th>
<th>Amine Loss (% per week)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7 m MEA</td>
<td>0.4</td>
<td>135</td>
<td>5.3%</td>
</tr>
<tr>
<td>10 m PZ</td>
<td>0.3</td>
<td>135</td>
<td>0.25%</td>
</tr>
<tr>
<td>7 m MEA</td>
<td>0.4</td>
<td>150</td>
<td>11%</td>
</tr>
<tr>
<td>10 m PZ</td>
<td>0.3</td>
<td>150</td>
<td>0.8%</td>
</tr>
<tr>
<td>8 m PZ</td>
<td>0.3</td>
<td>175</td>
<td>8.0%</td>
</tr>
</tbody>
</table>

3.5 CO2 solubility

The measured solubility of CO2 in 2 m to 8 m PZ solutions is in given in Figure 4 and compared to previous studies [2, 13].
The CO$_2$ solubility of concentrated, aqueous PZ solutions follows the trends found previously for lower concentration PZ solutions at 40 and 60°C. CO$_2$ solubility is known to not be a strong function of amine concentration and this is confirmed for high concentration PZ solutions [2]. At 40°C, 8 m PZ provides a working capacity of 0.73 moles/kg (PZ+H$_2$O), which is calculated based on a change in the equilibrium CO$_2$ partial pressure from 7.5 kPa (loading of 0.415 mol CO$_2$/mol alkalinity) to 0.75 kPa (0.33 mol CO$_2$/mol alkalinity). For 7 m MEA at 40°C, the working capacity is 0.43 moles CO$_2$/kg (MEA+H$_2$O) based on a change in the equilibrium partial pressure of CO$_2$ from 5 kPa (0.53 mol CO$_2$/mol alkalinity) to 0.5 kPa (0.45 mol CO$_2$/mol alkalinity). The selected range of CO$_2$ loading for the 8 m PZ solution falls within the solubility envelope established in Figure 1 and 2.

### 3.6 Kinetics of CO$_2$ absorption in PZ solutions

The kinetics of the CO$_2$ absorption into concentrated aqueous PZ was studied in a wetted wall column. The measured liquid-side mass transfer coefficient based on a gas side driving force, $k_g^*$, is shown compared to 7 m MEA in Figure 5 for 40°C and 60°C. Data at 60°C are plotted versus the equilibrium partial pressure of CO$_2$ if the solution were at 40°C for comparison purposes.

As demonstrated in Figure 5, the normalized flux, $k_g^*$, for 8 m PZ is 2 to 3 times greater than for 7 m MEA. For example, at 40°C and an equilibrium CO$_2$ partial pressure of 500 Pa, the $k_g^*$ for 8 m PZ and 7 m MEA are $1.98 \times 10^{-6}$ and $7.66 \times 10^{-7}$ mol/s-Pa-m$^2$, respectively. This demonstrates that the kinetic rate of concentrated PZ is over twice as fast as MEA at 40°C. The same trend is observed for the data at 60°C.

### 3.7 Volatility of PZ solutions

The volatility of PZ was measured in the equilibrium cell with hot gas FTIR. The volatility of 8 m PZ solutions is compared to that of 5 m PZ and 7 m MEA in Figure 6. The volatility of each solution is normalized by the PZ concentration for comparison purposes.

At 40°C, the normalized volatility of PZ solutions is the same as the normalized volatility of MEA solutions. It was anticipated that PZ would have a higher volatility than MEA because the boiling point of PZ, 146°C, is lower than that of MEA, 170°C. However, the volatility of PZ is comparable at 40°C. Initial modeling of PZ systems demonstrates this effect as a greatly reduced activity coefficient for PZ [2]. At 40°C, PZ volatility varies from 10 to 19 ppm at atmospheric pressure.
3.8 Estimated energy requirement

Thermodynamic models for MEA and PZ were developed by Hilliard, and the PZ model was modified for concentrated solutions [2]. The stripper section of an absorber/stripper system for CO₂ removal was simulated for 8 m PZ and compared with 7 m MEA. These simulations included a simple stripper with CO₂ compression to 5 MPa, a 5°C cold side temperature approach for the cross heat exchanger, and a 10°C approach for the reboiler. For all cases, 15 m of CMR NO-2P packing was used with an 80% approach to flood. The rich stream for each case assumed a P*subscript=CO2 at the absorber temperature of 40°C. One PZ case assumed a higher P*subscript=CO2 due to the faster rates of PZ expected in the absorber. Equivalent work, W_eq, is calculated as shown in equation 3 using the stripper reboiler duty, Q, total pumping work, W_pump, and total CO₂ compression work to achieve 50 atm, W_comp.

\[
W_{eq} = 0.75 \frac{Q}{T_{reboiler}} + W_{pump} + W_{comp}
\]

Eqn. 3

Each system was simulated at their optimum lean loadings and the baseline system, 7 m MEA, had an equivalent work of 36.1 kJ/mol CO₂, as shown in Figure 7. The two 8 m PZ systems modeled at a 5.0 or 7.5 kPa rich equilibrium CO₂ partial pressure had minimum equivalent works of 33.5 kJ/mol CO₂ and 32.6 kJ/mol CO₂, respectively. The PZ system with the lower rich P*subscript=CO2, 5 kPa, was less efficient than the system with 7.5 kPa P*subscript=CO2, but was better than the 7 m MEA case with an equivalent rich loading. The increased capacity of PZ improved its performance over the baseline, despite a lower ΔH_{abs}.
4. Conclusions

Concentrated, aqueous solutions of PZ have shown promise for improved solvent performance in absorption/stripping systems for CO₂ capture. For 8 m PZ, a CO₂ loading of approximately 0.25 mol CO₂/mol alkalinity is required to maintain a liquid solution without precipitation at room temperature (20°C). Additionally, the solubility of PZ at 20°C is approximately 14 wt% PZ, or 1.9 m PZ. The volatility of 8 m PZ systems was found to be between 10.2 and 18.7 ppm PZ at 40°C, which is comparable to 7 m MEA solutions.

Oxidative degradation of concentrated PZ has been shown to be four times slower than 7 m MEA in the presence of the combination of Fe²⁺, Cr³⁺, and Ni²⁺ and Fe²⁺ and V⁴⁺. In the presence of copper-based corrosion inhibitors, oxidative degradation is an issue but can be drastically reduced with the use of Inhibitor “A”. Concentrated PZ is resistant to thermal degradation up to 150°C but does degrade at 175°C, losing 32% of the PZ over 2 weeks. The resistance of PZ to thermal degradation allows for the possibility of higher pressure strippers to improve energy performance.

Kinetic measurements have shown that the rate of CO₂ absorption into 8 m PZ is more than twice that of 7 m MEA at 40°C and nearly double at 60°C. The working capacity of an 8 m PZ solution is 0.73 mol CO₂/(kg PZ + H₂O), nearly double that of 7 m MEA. Initial modeling of the stripper section indicate that the equivalent work required for stripping of an 8 m PZ solution will be approximately 5-10% lower than that of 7 m MEA.

The rapid rate of CO₂ absorption, low degradation rate, and low predicted equivalent work indicate that 8 m PZ solutions are an attractive option for CO₂ capture in absorption/stripping systems.

5. Acknowledgements

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