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Thermal Degradation of Piperazine Blends with Diamines

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Abstract

Concentrated, aqueous piperazine (PZ) has been developed as an attractive solvent for use in CO\textsubscript{2} capture for coal-fired power plants because of its low degradation rate, high CO\textsubscript{2} capacity, and high CO\textsubscript{2} absorption rate, but its use may be limited by precipitation of solids at low and high CO\textsubscript{2} loading. In this work we examine the effects of blending diamines, such as hexamethylenediamine (HMDA), 1,4-diaminobutane (DAB), or bis(aminoethyl)ether (BAE), with PZ on thermal degradation of the amine. The presence of the diamine does not catalyze the thermal degradation of piperazine and appears to degrade independently of piperazine; in particular, HMDA and BAE appear to have thermal degradation rates that are competitive with piperazine.

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Keywords: Thermal Degradation; Piperazine; Diamines; Solvent Management

1. Introduction

1.1. Motivation

PZ is considered to be a “state of the art” solvent for use in CO\textsubscript{2} capture from flue gas, with high absorption rate, high working capacity, and negligible oxidative and thermal degradation compared to other solvents [1]. However, it has a limited solubility window somewhat close to its operating range and may cause precipitation issues and problems for plant operations [2]. One option to widen the solubility window of the PZ solvent is to blend it with another amine that maintains the desirable properties of PZ.

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1.2. Scope / Amines Tested

This paper discusses the thermal degradation of PZ solvents when blended with linear diamines such as 1,4-diaminobutane (DAB), 2-(2-aminoethoxy)ethanamine (BAE), and hexamethylenediamine (HMDA) (Figure 1). Li and Du discuss the CO₂ mass transfer and CO₂ vapor-liquid equilibrium of the PZ blended with DAB, BAE, and HMDA [3] and mass transfer, thermodynamics, and degradation of a blend of PZ with aminoethylpiperazine (AEP) [4] respectively. Additionally, Sherman [5] discusses the properties of a blend of PZ and 2-methylpiperazine (2-MPZ).

![Structures of the amines used in this study.](image)

1.3. First-Order Degradation Rate Models

Thermal degradation was modeled using rate model that assumes first order kinetics in the concentration of the degrading amine. An Arrhenius relationship was used to determine the activation energy. This model can represent thermal degradation reasonably well and is a useful method to compare thermal degradation rates of one amine system to another [2].

1.4. Maximum Stripper Temperature

Higher amine regeneration temperature generally results in reduced energy usage for carbon capture plants using aqueous amine solvents due to the greater efficiency of thermal compression over mechanical compression. Higher temperatures, however, result in increased thermal degradation rates. Davis determined that the optimum temperature to balance energy usage and amine loss was 121 °C for monoethanolamine (MEA) [6]. The thermal degradation rate at this temperature was estimated to be 2.9*10⁻⁸ sec⁻¹. Freeman extended this work to cover other amines and defined the maximum stripper temperature to be the temperature at which the first order rate constant for thermal degradation is equal to 2.9*10⁻⁸ sec⁻¹.

2. Experimental

2.1. Solution Preparation and Experimental Approach

Solutions were prepared gravimetrically. The solution was then loaded into a gas-washing bottle and sparged with CO₂; the amount of CO₂ added was measured gravimetrically. 7 ml of the loaded solution was placed inside sealed stainless-steel ½” OD Swagelok® cylinders with a volume of 10 ml. The sealed cylinders were placed in convection ovens operating at set temperature. Cylinders were removed periodically and their contents analyzed to determine degradation rates.
2.2. Analytical Tools – Cation Chromatography

A Dionex ICS-2100 chromatograph was used to quantify parent amines and determine the presence of other amine byproducts. The methods used are similar to those by Freeman [2]. Samples were diluted by a factor of 10000 (mass) in 18.2 umho analytical grade water. A 4x50 mm CG17 guard column and a 4x250 mm CS17 analytical column were connected in series and used to carry out the separation. The mobile phase consisted of 18.2 umho analytical grade water spiked with a gradient of methanesulfonic acid. Ion suppression was used to improve the signal/noise ratio.

2.3. Analytical Tools – Anion Chromatography

A Dionex ICS-3000 chromatograph was used to determine anions in the samples, such as total formate. The methods used are essentially similar to those by Freeman [2]. Samples were diluted to a ratio of at least 1:1 in concentrated NaOH solution and left standing for at least 24 hours to allow for hydrolysis, and then were diluted by a factor of 100 (mass) in 18.2 umho analytical grade water. A 4x50 mm AS15 guard column and a 4x250 mm AS15 analytical column were connected in series to carry out the separation. The mobile phase consisted of 18.2 umho analytical grade water spiked with a gradient of potassium hydroxide. Ion suppression was used to improve the signal/noise ratio.

2.4. Analytical Tools – Total Alkalinity

A Metrohm Titrando 836 potentiometric autotitrator was used to measure the alkalinity of the sample. This technique measures the concentration of amino groups able to accept protons. Samples were diluted by a factor of 300 (mass) in 18.2 umho analytical grade water. 0.2N H$_2$SO$_4$ was used as the titrant. The amount of H$_2$SO$_4$ added to the sample to reach a pH of 3.9 (corresponding to total protonation of the amino groups in the sample) was used to determine the alkalinity. The methods used are essentially similar to those by Freeman [2].

2.5. Analytical Tools – Total Inorganic Carbon

A Horiba IR detector was used to analyze the CO$_2$ content in the sample. Samples were diluted anywhere from 25X to 100X and injected into the sump of a column containing 30 wt % phosphoric acid, evolving all of the CO$_2$ present in the sample. Nitrogen is bubbled through the sump of the column. The N$_2$/CO$_2$ mixture is then dehydrated before being analyzed by the IR detector. The methods used are essentially similar to those by Freeman [2].

3. Results and Analysis

3.1. Degradation Rates of Diamines in Comparison to PZ

8 m DAB at an initial loading of 0.4 mol CO$_2$/mol alkalinity and 8 m BAE at an initial loading of 0.4 mol CO$_2$/mol alkalinity were degraded at 175 °C. The first-order degradation rate constants, along with data from the degradation of 8 m HMDA at an initial loading of 0.3 mol CO$_2$/mol alkalinity and of 8 m PZ at an initial loading of 0.3 mol CO$_2$/mol alkalinity [2], are summarized in Table 1.

The thermal degradation rate of DAB is much greater than the thermal degradation rate of BAE or HMDA, though the initial rate of degradation for all three amines appears to be greater than PZ. The activation energy of PZ (180 kJ/mol) is used to estimate the maximum stripper temperature for these...
amines; for DAB, however, an activation energy of 140 kJ/mol was estimated based on additional degradation experiments carried at 135 °C. Only the data points taken after 7 days were used to determine the thermal degradation rate constant of DAB at 175 °C.

Table 1. Summary of Degradation Rates of Piperazine and Various Diamines, PZ, and HMDA data from Freeman [2].

<table>
<thead>
<tr>
<th>Amine System</th>
<th>Degradation Rate, 1/sec (measured at 175 °C)</th>
<th>Maximum Stripper Temperature, degrees C</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 m PZ, α=0.3</td>
<td>1.3*10^-7</td>
<td>163</td>
</tr>
<tr>
<td>8 m HMDA, α=0.3</td>
<td>1.9*10^-7</td>
<td>160</td>
</tr>
<tr>
<td>8 m BAE, α=0.4</td>
<td>2.0*10^-7</td>
<td>158</td>
</tr>
<tr>
<td>8 m DAB, α=0.4</td>
<td>27.2*10^-7</td>
<td>127</td>
</tr>
</tbody>
</table>

3.2. Degradation Behavior of Diamines: Mechanisms & Byproducts

The dominant degradation mechanism of DAB is likely by ring closing to form pyrrolidine (Pyr) and ammonia (Figure 2). The concentrations of Pyr and DAB are plotted as functions of time (Figure 3) and appear to reach a kinetic equilibrium after about two weeks at 175 °C. Like DAB, BAE can also ring close, forming ammonia and morpholine (Mor); however, Mor was not observed to be a significant byproduct of degraded BAE.

Formate generation was studied in degraded DAB and BAE. Along with HMDA, the linear diamines appear to generate less formate than PZ (Figure 4). The data for PZ and HMDA are from Freeman [2].

![Figure 2. Generic S_N2 Reaction Scheme (top) and proposed mechanism of formation of Pyrrolodine (Pyr) from 1,4-diaminobutane (DAB) (bottom) (Image)](image)

3.3. Degradation Rates and Behavior of Piperazine-Diamine Blends

6 m PZ/2 m HMDA at an initial loading of 0.4 mol CO₂/mol alkalinity, 6 m PZ/2 m BAE at an initial loading of 0.35, and 6 m PZ/2 m DAB at an initial loading of 0.4 were thermally degraded at 175 °C. The PZ/HMDA degradation data are reported as a function of total amine concentration only as both PZ and HMDA have identical retention times with the analytical methods used in the experiment (Table 2). The total formate was measured for both PZ/HMDA and PZ/DAB. Pyr was also measured in PZ/DAB. Pyr is a significant product in the degradation of PZ/DAB, and formate (measured as total formate) is a significant product in the thermal degradation of PZ/DAB and PZ/HMDA (Figures 5 and 6).
Total alkalinity and dissolved CO$_2$ were measured for the amine blends. Both sets of data suggest that the loading of the amine remained relatively constant throughout the duration of the experiment. The decrease in alkalinity and CO$_2$ concentration is likely due to the formation of ureas, formate salts, and amides (Figures 7 and 8). In PZ/DAB degradation, formate salts accounted for about 20% of the lost alkalinity; in PZ/HMDA degradation, formate salts accounted for nearly 50% of the lost alkalinity.

3.4. Comparison with Other PZ Blends

Table 2 compares the thermal degradation of the PZ-diamine blends with other PZ blends, including PZ/methyldiethanolamine (MDEA) and PZ/2-amino-2-methyl-1-propanol (AMP). The thermal degradation of PZ/BAE and PZ/HMDA is unique as the thermal degradation rate of PZ in the blend is nearly identical to that of concentrated PZ. Both PZ/MDEA and AMP/PZ experience higher rates of thermal degradation. In the case of PZ/MDEA, the PZ can attack the methyl group of protonated MDEA, forming 1-methylpiperazine and diethanolamine (DEA). Both DEA and AMP degrade via the carbamate polymerization pathway, and the intermediate oxazolidinone degradation products of both amines are rapidly attacked by PZ [5, 6].

First-order rate models were used to estimate thermal degradation rates. Two sets of values are presented: thermal degradation rates with respect to the individual parent amines that constitute the blend, and the thermal degradation rate with respect to the total parent amine. Maximum stripper T for PZ/DAB, PZ/HMDA, and PZ/BAE are calculated on the basis of total amine thermal degradation rate; the activation energy for these blends is estimated to be the same as 8 m PZ (180 kJ/mol) [2]. These data are summarized in Table 2. Data for all other amine blends are sourced from Freeman [2].
Figure 5. Parent amine concentrations and principal thermal degradation byproducts in the thermal degradation of 6 m PZ/2 m DAB initially at 0.4 mol CO$_2$/mol alkalinity at 175 °C.

Figure 6. Parent amine concentrations and principal thermal degradation byproducts in the thermal degradation of 6 m PZ/2 m HMDA initially at 0.4 mol CO$_2$/mol alkalinity at 175 °C.

Figure 7. Total alkalinity and CO$_2$ loading trends thermal degradation of 6 m PZ/2 m DAB initially at 0.4 mol CO$_2$/mol alkalinity at 175 °C.

Figure 8. Total alkalinity and CO$_2$ loading trends thermal degradation of 6 m PZ/2 m HMDA initially at 0.4 mol CO$_2$/mol alkalinity at 175 °C.
Table 2. Degradation rate of PZ blends. PZ, PZ/MDEA, 2-MPZ, PZ/2-MPZ, and PZ/AMP data from Freeman [2]; PZ/AEP data from Du [4]

<table>
<thead>
<tr>
<th>Amine System</th>
<th>PZ Degradation Rate (1/sec)</th>
<th>Other Amine Degradation Rate (1/sec)</th>
<th>Total Amine Degradation Rate (1/sec)</th>
<th>Experimental Degradation T (°C)</th>
<th>Maximum Stripper T (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 m PZ, α=0.3</td>
<td>--</td>
<td>--</td>
<td>1.3*10^-7</td>
<td>175</td>
<td>163</td>
</tr>
<tr>
<td>6 m PZ / 2 m BAE, α=0.35</td>
<td>1.3*10^-7</td>
<td>1.3*10^-7</td>
<td>1.3*10^-7</td>
<td>175</td>
<td>162</td>
</tr>
<tr>
<td>6 m PZ / 2 m HMDA, α=0.4</td>
<td>n/a</td>
<td>n/a</td>
<td>1.4*10^-7</td>
<td>175</td>
<td>161</td>
</tr>
<tr>
<td>5 m PZ / 2 m AEP, α=0.3</td>
<td>1.6*10^-7</td>
<td>3.9*10^-7</td>
<td>2.0*10^-7</td>
<td>175</td>
<td>156</td>
</tr>
<tr>
<td>6 m PZ / 2 m DAB, α=0.4</td>
<td>1.6*10^-7</td>
<td>1.7*10^-6</td>
<td>2.4*10^-7</td>
<td>175</td>
<td>156</td>
</tr>
<tr>
<td>4 m PZ / 4 m 2-MPZ, α=0.3</td>
<td>n/a</td>
<td>n/a</td>
<td>1.6*10^-8</td>
<td>150</td>
<td>156</td>
</tr>
<tr>
<td>8 m 2-MPZ, α=0.3</td>
<td>--</td>
<td>2.5*10^-8</td>
<td>2.5*10^-8</td>
<td>150</td>
<td>151</td>
</tr>
<tr>
<td>2 m PZ / 7 m MDEA, α=0.1</td>
<td>4.9*10^-7</td>
<td>4.2*10^-8</td>
<td>6.1*10^-8</td>
<td>150</td>
<td>138</td>
</tr>
<tr>
<td>6 m PZ / 4 m AMP, α=0.4</td>
<td>9.2*10^-8</td>
<td>2.5*10^-7</td>
<td>1.4*10^-7</td>
<td>150</td>
<td>134</td>
</tr>
</tbody>
</table>

4. Conclusions

1. The thermal degradation rate of bis(aminoethyl)ether (BAE) is nearly identical to hexamethylenediamine (HMDA) and about 50% higher than piperazine (PZ). The “maximum stripper temperature” of HMDA and BAE is 160 and 158 °C, respectively.
2. The thermal degradation rate of 1,4-diaminoutane (DAB) is much greater than PZ, with a maximum stripper temperature of 127 °C.
3. DAB likely thermally degrades via a S_N2 mechanism, forming pyrrolidine as its majority byproduct. This mechanism does not appear to be dominant in BAE degradation.
4. PZ blends with BAE, DAB, and HMDA do not appear to increase the degradation rate of PZ significantly. Maximum stripper temperature for the 6 m PZ/2 m diamine is 162 °C for BAE, 161 °C for HMDA, and 156 °C for DAB.
5. Formate salts appear to be significant thermal degradation byproducts for DAB, BAE and blends of PZ with DAB, BAE, and HMDA.

Acknowledgements

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References


