Thermal degradation of aqueous amine/amino acid solutions in the presence and absence of CO₂

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Abstract. The stability to thermal degradation of aqueous solutions of methyldiethanolamine (MDEA) and their mixtures with glycine (Gly), in the absence and the presence of CO₂, was investigated by Gas chromatography-flame ionization detector (GC-FID). The results showed that the presence of CO₂ influenced significantly the degree of thermal degradation of these solutions. The investigated MDEA solutions were found less susceptible to thermal degradation in the absence of CO₂. However, in the presence of CO₂, the thermal degradation was more significant. The addition of glycine (Gly) to MDEA solution reduces the MDEA thermal degradation. It was concluded that MDEA + Gly amine/amino acid aqueous blend could be a potentially interesting absorbent for industrial CO₂ capture applications.

1. Introduction

The continued worldwide economic growth depends largely on the energy supply provided mainly by fossil fuel combustion, making it the most significant source of CO₂ emissions which is the largest contributor of all the greenhouse gases in the atmosphere responsible for climate change. Hence, Carbon capture is a necessary tool for alleviate the impact of fossil fuel combustion on global warming. Amine scrubbing is the most effective and widely used technology to capture CO₂ from stationary sources such as power plants. Monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA) are the most widely used amines for CO₂ absorption. MDEA is widely used in combination with Piperazine for natural gas treatment, in tail gas treating for selectively removing hydrogen sulphide (H₂S) from gas streams containing carbon dioxide[1, 2]. Amino acids are potential new solvents with several benefits over conventional amines in CO₂ capture. Amino acids have significantly lower vapour pressures than amines, resulting in reduced solvent make up. Furthermore, amino acids have greater resistance to oxidative degradation and lower toxicity than typical amine solvents [3-7] and have been proposed as alternatives to amines in recent years [4, 8]. Using novel solvents with superior CO₂ capture performance is a critical approach to reduce the cost of regeneration. Most solvent screening studies focused on CO₂ capacity [9] and CO₂ absorption rate[10-12] as CO₂ capacity and CO₂ absorption rate are directly related to the CO₂ absorber cost and solvent regeneration cost. However, thermal stability should also be a crucial criterion for solvent selection for natural and flue gas CO₂ capture. Regeneration of amines at high temperature, can degrade it following different mechanisms[13, 14].

In this work, MDEA aqueous solutions and blends of MDEA with glycine were evaluated for their thermal stability under laboratory conditions. The operating conditions were chosen to be relevant to those encountered in CO₂ stripping conditions in term of CO₂ loading of the solution and the heating temperature. It has been reported that CO₂ loading enhances amine thermal degradation (Lepaumier [13]). Hence, this work investigates the degradation of MDEA AND its mixtures with glycine under three different CO₂ loading. Degradation products were investigated by GC-FID. By analysing the products...
new insight is provided into the MDEA degradation with completely new degradation data for its blends with Glycine.

2. Material and methods

2.1. Chemicals

Aqueous amines solutions used in this work were prepared by gravimetric method using distilled water, methyl diethanolamine (MDEA, CAS no. 105-59-9) purchased from Sigma Aldrich and Glycine (Gly, CAS no56-40-6) purchased from Reidel De Haen. The purity of MDEA and Gly were both 99 %. The structures of these amines are represented in Figure 1. All amines/amino acids were used without further purification. An Adam precision balance model PW 214 with a precision of ±1 × 10−4 g was used to prepare the solutions and the uncertainties of the reported concentrations were calculated to be less than 0.01 wt%.

![Figure 1. The structures of the amines investigated in this work.](image)

2.2. Thermal degradation

2.2.1. Degradation in the absence of CO2

In typical thermal degradation experimental runs in the absence of CO2, stainless steel tubes of 0.635 cm inside diameter having an internal volume of 10 ml were filled with amine/amino acids solutions and closed with two end caps. For each tested solution, three tubes were prepared and placed in an oven and maintained at 413 K. The test tubes were individually removed from the oven after the specified time (from 1 day to 60 days), cooled to avoid continued degradation and the content was transferred to screw-cap glass vials stored at 278 K until the analyses of the amine samples were performed.

2.2.2. Degradation in the presence of CO2

The degradation experiments involving CO2 were performed in the 250 ml stirred cell reactors. First, 150 ml of aqueous amine solution was introduced into the reactor and allowed to saturate under a constant CO2 partial pressure at 298.15 K. Once the equilibrium was reached indicated by a constant pH of the solution for at least 10 min, a 5 ml sample was withdrawn from the reactor and put in the degradation stainless tube described earlier. The tube was then put in the oven and set at a temperature of 413 K for periods of time varying from one day to 2 months. The Samples were withdrawn cooled down and rapidly analysed.

2.2.3. Sample analysis

2.2.4. Gas Chromatography Flame ionization detector (GC-FID)

An Agilent GC-FID (model 7890 A) equipped with an FID detector was used in this work. A chromatographic capillary column DB1 (nonpolar) having crosslinked with dimethylpolysiloxane as stationary phase and column dimension of 5 μm thickness × 0.53 mm id × 60 m length and supplied by Agilent technologies. The introduction of sample was done using an auto sampler/ auto injector (model G4513A). The reproducibility of the auto-injector volume was 0.3% relative standard deviation (RSD) in terms of area percent of the peaks. Identical GC-FID operating conditions were applied in all runs.
Table 1. GC FID method for quantification of the amine degradation

| Parameter                  | Value         |
|----------------------------|---------------|
| Initial temperature        | 100 °C        |
| Oven temperature ramp      | 15 °C/min     |
| Final temperature          | 180 °C        |
| Flow rate                  | 4.7 ml/min    |
| Injector temperature       | 250 °C        |
| Detector temperature       | 280 °C        |

3. Results

3.1. Amine loss Percentage

The stability to degradation of single MDEA and mixed MDEA + Gly aqueous solution was investigated at 413 K in the absence and presence of CO2. The initial concentrations of the solutions at 298 K were 1 moles/l for MDEA and (0.95+0.05) for mixed MDEA + glycine. The remaining amine concentration for each studied system and degradation condition was tracked by GC-FID analysis during the experiments (up to 60 days) and the percentages of amines loss at the end of this period are shown in Figure 2.

![Figure 2: Effect of process conditions on MDEA thermal degradation.](image)

![Figure 3: Effect of process conditions on MDEA + Gly degradation.](image)

3.2. Amine degradation first-order rate constant

Freeman and Rochelle [14] demonstrated that the loss of amine during degradation is generally well modelled by a first-order dependence on the amine concentration equation. The experimental amine concentration profiles obtained a long the experimental period were therefore modelled by an exponential equation where the amine concentration (\(C_{\text{Amine}}\)) is a function of the initial amine concentration (\(C_{0,\text{Amine}}\)), a first-order rate constant, \(k_1\), and time, \(t\), as follows:

\[
C_{\text{Amine}} = C_{0,\text{Amine}} \cdot e^{-k_1 \cdot t}
\]

First-order rate constants for the different studied systems were summarised in Table 2.

![Table 2: Thermal degradation first-order rate constants.](image)
4. Discussions

4.1. Effect of process conditions on degradation of single amine aqueous systems

The degree of degradation of MDEA was studied at a temperature of 140 °C and different CO₂ partial pressures of industrial interest for a period of times reaching 60 days. Based on the fact that amine degradation is usually a slow phenomenon as pointed out by Lepaumier et al [15], the conditions above were selected to accelerate amine degradation rates and therefore reducing the length of experiments.

4.2. Pure thermal degradation

Thermal degradation of MDEA and MDEA + Gly aqueous solutions were performed at a temperature of 413K. The thermal degradation results are presented in Figures 2 and 3 respectively. Both figures show that both solutions were vulnerable to thermal degradation but at different degrees. A comparison between the degradation of MDEA in the absence and presence of glycine is shown in Figure 4. From this figure, it is very clear that the MDEA + Gly is less vulnerable to thermal degradation compared to pure MDEA solution. The presence of Gly makes the solution more thermally stable. This finding is in good agreement with the results of Lepaumier et al.[15]. The kᵢ values for MDEA MDEA + Gly were estimated, assuming a first-order amine degradation behaviour and were found summarised in Table 2.

4.3. CO₂ effect on amine degradation

The influence of CO₂ loading on the degree of amine degradation was investigated by applying different CO₂ partial pressures and hence different loadings in the solutions. The degradation percentage of MDEA was found to increase with increasing CO₂ loading in the solution (Figure 5). A similar phenomena was reported by Supap et al. [16]. The degradation rate is a function of CO₂ concentration which in turn depends on the species concentrations in the solution. At high CO₂ loading in conventional CO₂-amines absorption, bicarbonate concentration increased as a result of carbamates reversion[9] and hence decreased the oxidative degradation rates[17].

4.4. Effect of process conditions on degradation of the aqueous MDEA + Gly blend

The degradation percentage of MDEA + Gly from their mixture can be compared to the results of single MDEA systems (Figure 4). The trends mentioned previously are similar, the thermal degradation in the presence of CO₂ is more important compared to thermal in the absence of CO₂, ie, the more CO₂ loading, the more severe is thermal degradation. Furthermore, the presence of glycine reduced considerably MDEA thermal degradation. A similar behaviour has been reported for blends of MDEA/Piperazine [18].
5. Conclusions
Thermal degradation experiments in the absence and in the presence of CO₂ for aqueous amine solutions of MDEA and MDEA + Gly were performed in order to evaluate their stability to degradation and their rate constants were estimated. Single amine and one blended system were investigated. It was found that MDEA + Gly are more resistant to thermal degradation than the conventional amine MDEA investigated in this work. The presence of CO₂ induced further thermal degradation in both solutions. The addition of Gly to MDEA solution also reduced the thermal degradation percentage. The use of the MDEA + Gly blend could be beneficial in a CO₂ absorption due to its minimized degradation. Future experimental studies concerning the identification of degradation products, elucidation of the degradation reaction mechanism and corrosiveness to other steels and stainless steels in different blend proportions of this mixture would be very interesting for the industry to optimize the operation conditions, minimize the amine degradation process and evaluate the process equipment life time.

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