

KINETIC STUDY OF SO₂ AND O₂ INDUCED DEGRADATION OF AQUEOUS MEA

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Abstract

A kinetic study was conducted to evaluate the contributions of sulfur dioxide (SO₂) and oxygen (O₂) to the degradation of monoethanolamine (MEA) during CO₂ capture from power plant flue gas streams. The study was performed in a 600 mL semi-batch autoclave reactor using aqueous MEA concentrations in the range of 3-7 mol/L at temperatures ranging from 328–413 K and a constant gas pressure of 250 kPa. The aqueous MEA was contacted with SO₂/O₂/N₂ gas mixtures of SO₂ concentration in the range of 6-196 ppm and O₂ concentration in the range of 6-100 mol%. The effects of CO₂ and a corrosion inhibitor (NaVO₃) were also evaluated. The results showed that both SO₂ and O₂ were detrimental as they accelerated the rate of MEA degradation. NaVO₃ also accelerated the MEA degradation rate whereas CO₂ had the opposite effect. A new kinetic model was formulated to account for the presence of O₂ and the option of the presence or absence of SO₂ in the flue gas stream.

Introduction

One of the most effective and widely used techniques to capture CO₂ from low-pressure flue gas streams [1,2] from large point sources such as power plants is chemical absorption using alkanolamine solutions. The most widely used alkanolamines for this process include monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA) with MEA being the most widely studied because it is very reactive and thus is able to effect a high volume of acid gas removal at a fast rate.

One of the major disadvantages of using MEA is its high energy requirement for CO₂ regeneration relative to DEA and MDEA [4]. The other major setback is that MEA has a limitation that its maximum CO₂ loading capacity based on stoichiometry is about 50% unlike tertiary amines such as MDEA, which have an equilibrium CO₂ loading capacity that approaches 100%. Furthermore, MEA undergoes degradation when exposed to coal fired power plant flue gas composed of CO₂, fly ash, O₂, N₂, SO₂ and NO_x [2, 4, 5]. Fly ash is the fine particulates in flue gas consisting of inorganic oxides such as SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, Na₂O, K₂O and P₂O₅. Considerable efforts have been focused on the O₂ induced degradation of MEA [6-8]. SO₂ can also react with MEA to form HSS such as isothiocyanatoethane and tetrahydrothiophene that cannot be reclaimed [2, 9]. Thus, while there is substantial information on O₂ induced MEA degradation, the information on the effects of SO₂, NO_x and fly ash on MEA degradation is scant. This kinetic study is aimed at evaluating the contributions of SO₂ and O₂

individually and in combination to MEA degradation when aqueous MEA is used for the capture of CO₂ from coal-fired power plant flue gas streams.

Experimental

The degradation studies were carried out under well-defined laboratory conditions. However, we have attempted to use operating conditions that are close to what obtains in real life. For example, the ranges of operating conditions included the following: MEA concentration in the range of 3-7 mol/L, temperature in the range of 330-403 K reflecting the extremes of absorber and stripper temperatures, SO₂ concentration in the range of 6-200 ppm (representing typical concentrations of polished and unpolished flue gas streams) and O₂ concentrations ranging from 6-100% [1,2]. The case of O₂ concentration greater than 6% was used for comparison only. The only parameter that was not fully reflective of real life situation either in the absorber or stripper was the pressure which was higher in order to obtain results within reasonable time frames.

Equipment. Studies of SO₂ and O₂ induced degradation of aqueous MEA were conducted in a rotary type 600 mL stainless steel semi batch autoclave reactor (model Parr 5500, obtained from Parr Instrument Co., Moline, Illinois) which consisted of a variable speed impeller, cooling coils, a gas feed port, a liquid sampling port, a thermo well and a pressure gauge. The heat supplied to the reactor was controlled by a temperature and impeller speed controller system (model Parr 4836, also supplied by Parr Instrument Co., Moline, Illinois) equipped with a J-typed thermocouple. The temperature accuracy for the controller was about ± 0.1 %.

Chemicals and gases. Reagent grade MEA (99% purity) obtained from Fischer Scientific, Whitby, Ontario was used for the studies. The MEA was diluted with deionized water to the desired concentration and used for this work. 1 mol/L hydrochloric acid, also obtained from Fischer Scientific, was used to establish the exact concentration of MEA. Three analytical grade gas mixtures composed respectively of 6 ppm SO₂, 11 ppm SO₂ and 196 ppm SO₂ each with 6% O₂ and balance N₂ were also used. These were supplied by Praxair, Regina, Canada. Also, 21% (balance N₂) and 100% analytical grade O₂, also supplied by Praxair, Regina, Canada were also used in this investigation. *Typical experimental run:* Four systems were evaluated for the degradation of MEA. The first system (MEA-H₂O-O₂) was to establish the contribution of O₂ alone to the degradation of MEA in the absence of CO₂. The second system (MEA-H₂O-O₂-SO₂) evaluated the contribution of both SO₂ and O₂ to MEA degradation in the absence of CO₂. The third (MEA-H₂O-O₂-CO₂) and fourth systems (MEA-H₂O-O₂-SO₂-CO₂) respectively evaluated the first two systems in the presence of CO₂.

Analysis of reaction samples. The samples of MEA withdrawn from the reactor were analyzed using a High Performance Liquid Chromatography (HPLC) technique. The

HPLC analytical instrument (model 1100/G1315B/G1322A supplied by Agilent Technologies, Mississauga, Ontario, Canada) was equipped with an online degasser and a refractive index detector (RID). A Shodex YK-421 column packed with a weak carboxyl-coated silica exchanger (Showa Denko, Tokyo, Japan) was used.

The mobile phase was a mixture of 0.024 mol/L Boric acid (H_3BO_3), 0.001 mol/L 2,6- Pyridine carboxylic acid ($C_7H_5NO_4$) and 0.005 mol/L L-tartaric acid ($C_4H_6O_6$). These were mixed in 1 L of nanopure water to ensure that there was absolute sterility within the column. The resulting solution was degassed in an ultrasonic water bath for 3 h and filtered using a 0.20 μm nylon membrane filter before being fed into the HPLC. All chemicals for the mobile phase were of reagent grade and purchased from Sigma-Aldrich, Mississauga, Ontario, Canada, with the exception of the L-tartaric acid, which was purchased from Fisher Scientific, Neopean, Ontario, Canada. Prior to the analysis, the degraded MEA samples were diluted with nanopure water to the ratio 1:60 and filtered with 0.20 μm nylon membrane filter. The exact concentration of fresh aqueous MEA and each of the reacted samples were determined by interpolation from a standard MEA calibration curve, which was obtained by titrating known concentrations of MEA against 1 N HCl using 0.5 wt% methyl orange solution as indicator. The error of the HPLC was estimated to be less than $\pm 2\%$.

Results and Discussion

The instantaneous rates of degradation were evaluated as slopes of the concentration–time curves by differentiating the respective curves at the desired time. The effects of operating variables were then evaluated as a function of the rate-time plots in terms of the values of the parameters of the rate equation.

A model was developed in order to account for a situation where the concentration of SO_2 in the flue gas stream could be zero or negligible as in a natural gas-fired power plant flue gas stream. The model is of the form:

$$-r_{MEA} = k_o e^{-E/RT} [MEA]^n [CO_2]^m \{ [SO_2]^p + [O_2]^s \} \quad (1)$$

A non-linear regression package (NLREG) was used for parameter estimation. The estimated parameters are shown in Table 1. The order of the reaction with respect to the concentrations of MEA, O_2 and SO_2 are positive, an indication that an increase in their concentration leads to an increase in the rate of MEA degradation, while the negative order with respect to CO_2 is an indication of its degradation inhibition effect on MEA degradation.

The absolute average deviations of the rates predicted by model 1 and rates of a power law model from those obtained experimentally were calculated, and found to be 14.4 and 5%, respectively. These values indicate good predictive ability of the models as shown in the parity chart in Figure 1.

Table 1. Estimates of Parameters of Rate Model

| Kinetic Parameters | Estimates |
|--------------------|-----------|
| E_a (KJ/mol) | 45.3 |
| k_0 | 0.00745 |
| n (MEA) | 1.91 |
| m (CO_2) | -0.33 |
| p (SO_2) | 3.42 |
| s (O_2) | 2.78 |

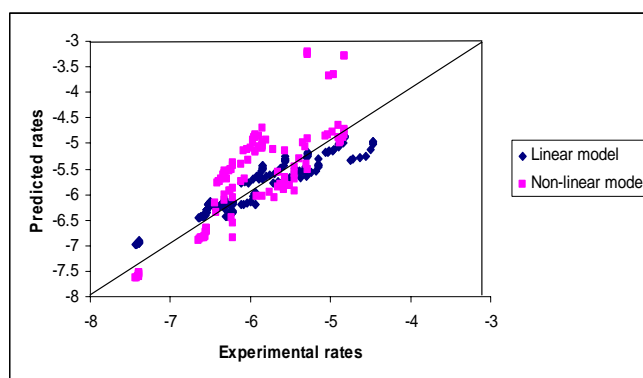


Figure 1. Parity chart for comparing the MEA degradation rates obtained from model 1 and power law model with those from experiment.

Conclusions

An increase in the concentrations of SO_2 and O_2 in the gas phase and MEA in the liquid phase resulted in an increase in MEA degradation whereas an increase in CO_2 loading in the liquid phase produced an inhibition effect to MEA degradation.

The presence of a corrosion inhibitor ($NaVO_3$) was detrimental to MEA and acted as catalyst to accelerate MEA degradation.

A kinetic model has been formulated to predict MEA degradation rate during CO_2 capture from power plant flue gas streams. This general model allows the SO_2 and/or O_2 concentration in the flue gas stream to be zero or greater than zero.

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