

Kinetics of the Oxidative Degradation of CO₂ Loaded and Concentrated Aqueous MEA-MDEA Blends during CO₂ Absorption from Flue Gas Streams

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A study of empirical kinetic models of the degradation of MEA and MDEA in MEA-MDEA-H₂O-O₂, MEA-MDEA-H₂O-CO₂, and MEA-MDEA-H₂O-O₂-CO₂ systems was conducted in a stirred cell reactor at temperatures in the range of 328–393 K, overall amine concentration of 7–9 mol/L, MEA/MDEA ratio (*r*) in the range of 2.5:1–9:1, CO₂ loading (α) in the range of 0.4 and 0.43 mol/mol total amine, and a CO₂ or O₂ pressure of 250 kPa. The results showed that higher total amine concentrations and temperatures resulted in higher rates of degradation, whereas higher CO₂ loadings had the opposite effect. The results, however, showed that the rates of degradation of MEA and MDEA in the MEA-MDEA-H₂O-CO₂ system were practically zero. On the other hand, both the MEA-MDEA-H₂O-O₂ and the MEA-MDEA-H₂O-CO₂-O₂ systems had rates greater than zero.

Introduction

The combustion, processing and upgrading of various fossil fuels has been identified as the major contributor to carbon dioxide (CO₂) emissions,¹ which constitutes the major fraction of greenhouse gases (GHG) blamed for global warming and climate change. Nearly 60% of CO₂ emissions emanate from power generation and other industrial point sources. Thus, flue gas effluents of medium to large point sources present a desirable control point for CO₂ mitigation because of their large scale and centralized locations.²

Chemical absorption (e.g., with amine-type absorbents) is well-suited for CO₂ recovery from dilute low-pressure flue gas streams representative of most large point sources, including power plants. The chemical reaction between CO₂ and amines greatly enhances the driving force for the separation, even at a low partial pressure of CO₂. A wide variety of alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA), di-2-propanolamine (DIPA), and methyldiethanolamine (MDEA) could be used industrially,³ but there are differences in performance in their reactivities or rates of CO₂ absorption. Primary and secondary amines such as MEA and DEA are very reactive and thus are able to effect a high volume of acid gas removal at a fast rate.⁴ However, they have a limitation that their 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%. In addition, the stripping of CO₂ from MEA or DEA requires a large amount of energy input as compared to MDEA.

Mixed amines have been reported to maximize the desirable qualities of individual amines.⁵ Thus, the specific goal with respect to the use of mixed amines is to have a solution consisting of tertiary and primary amines or tertiary plus secondary amines that in comparison with single amine systems retains much of the reactivity of primary or secondary amines at similar or reduced circulation rates but offers low regeneration costs similar to those of tertiary amines.⁴ Consequently, by blending a primary or secondary alkanolamine with a tertiary alkanolamine, bulk CO₂ removal is easily accomplished, while

regeneration energy costs are minimized. In addition, another degree of freedom (the amine concentration) is gained. The amine concentration can be altered to achieve precisely the desired separation for a given process.

Substantial reductions in energy requirements and modest reductions in circulation rates have been reported for amine blends relative to the corresponding single amine system of similar total amine concentration.⁶ Also, simulation studies have shown that for CO₂ loadings below 0.5 mol/mol amine, MDEA + MEA and MDEA + DEA blends containing 2 kmol/m³ of each amine produced equilibrium partial pressure of the amine blend that is intermediate between those of the corresponding single amine systems of equivalent total amine concentration.⁷ For higher CO₂ loadings, the equilibrium partial pressures in blended amine systems were less or comparable with those of single amine systems. Furthermore, experiments on CO₂ solubility in aqueous blends of MEA + MDEA and DEA + MDEA have confirmed that equilibrium solution loading is influenced mostly by the blended compositions under conditions typical of industrial regenerators.^{8,9}

The previous benefits can only lead to operational savings if the loss of amine due to its irreversible reaction (degradation) with CO₂ and/or O₂ (another component of flue gas) and/or catalyzed by corrosion inhibitors is less than or comparable with the loss in the corresponding single amine systems; otherwise, degradation in mixed amines system should be prevented or minimized. However, to obtain a good strategy for the prevention of degradation of mixed amines, a good understanding of the degradation process is necessary. This should involve the kinetics, product identification, stoichiometry, and mechanisms.

There is limited information on the degradation of mixed amines. Dawodu and Meisen⁴ conducted experiments on CO₂ (2.58 MPa) induced degradation of aqueous solutions of MDEA, MDEA + DEA, and MDEA + MEA at temperatures ranging from 120 to 180 °C in a stainless steel reactor. On the basis of their result, they concluded that the use of MDEA based blends for CO₂ removal would introduce degradation products at concentration levels unusual for MDEA plants. They also concluded that the rate of DEA makeup for the MDEA/DEA blends would be higher than the rate of MEA makeup for the MDEA/MEA blends to maintain the desired solution capacity. Also, it has been reported¹⁶ that the studies on the oxidative

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Table 1. Operating Conditions

MEA-MDEA-H ₂ O-O ₂ system			
temperature (K)	328	373	393
MEA concentration (mol/L)	5	6.3	5, 6.3, 7, 8.1
MDEA concentration (mol/L)	2	0.7	2, 0.7, 2, 0.9
O ₂ pressure (kPa)	250	250	250
MEA-MDEA-H ₂ O-CO ₂ system			
temperature (K)			393
MEA concentration (mol/L)			5, 7
MDEA concentration (mol/L)			2, 2
CO ₂ pressure (kPa)			250
MEA-MDEA-H ₂ O-O ₂ -CO ₂ system			
temperature (K)			393
MEA concentration (mol/L)			5, 7
MDEA concentration (mol/L)			2, 2
CO ₂ loading (mol/mol)			0.4, 0.43
O ₂ pressure (kPa)			250

degradation of 2.5 N different amine solutions (MEA, DEA, MDEA, and mixed MDEA/DEA) conducted by Kindrick et al.¹⁷ using a gas mixture of 50% CO₂ and 50% O₂ contacted with the amines at a rate of 100 mL/min at 353 K was limited to showing that MDEA had the best resistance and that DEA had the least resistance to O₂. In addition, a blend of MDEA and DEA has been reported to have a significantly better resistance to O₂ than DEA alone.¹⁶ Also, in our recent work,^{18,19} we identified most of the products, provided the stoichiometry, and elucidated a possible mechanism of the oxidative degradation of CO₂ loaded aqueous MEA-MDEA blends.

Thus, except for our earlier work^{18,19} as well as the modest work of Kindrick et al.,¹⁷ other studies have shown the individual contributions of either CO₂ or O₂ toward degradation of amine blends, whereas a typical flue gas stream contains both O₂ and CO₂ as well as corrosion inhibitors. Besides, none of these studies took into account all of the requirements (products, stoichiometry, mechanism, and kinetics) necessary to elucidate the complete nature of the degradation reactions, whereas these are all essential to obtain a good degradation prevention strategy for an aqueous mixed amine system such as the MEA-MDEA-H₂O system. This work is a continuation of our comprehensive study on the degradation of MEA-MDEA blends^{18,19}. It is specifically aimed at evaluating the kinetics of degradation of MEA-MDEA-H₂O-CO₂, MEA-MDEA-H₂O-O₂, and MEA-MDEA-H₂O-CO₂-O₂ systems under typical stripper and absorber conditions. This work is to study, for the first time, the effects of operating conditions on the kinetics of each alkanolamine in the oxidative degradation of concentrated CO₂ loaded aqueous MEA-MDEA blends during CO₂ absorption from flue gases. The results are presented and discussed in this paper.

Experimental Section

Equipment and Chemicals. The experiments were conducted in a semibatch mode using a 600 mL stainless steel reactor (model 4560, Parr Instrument Co., Moline, IL) equipped with an insulating Jacket, a Bourdon-type pressure gauge, a variable speed stirrer, and ports for introducing and withdrawing liquid and gas samples. The heat supplied to the reactor was controlled by a temperature indicator-controller system equipped with a J-type thermocouple. The temperature accuracy of the controller was within $\pm 0.1\%$. The operating temperatures were 328, 373, and 393 K. The O₂ partial pressures, CO₂ loadings, as well as the concentrations of the MEA-MDEA blends used in this study are given in Table 1. Analytical grade O₂ and CO₂ were used and were supplied by Praxair (Regina, SK, Canada). Concentrated MEA and MDEA (reagent grade, 99% purity) were obtained from Fisher scientific, Whitby, ON, Canada.

These solvents were diluted with distilled water to the desired concentrations. The 1 N hydrochloric acid, also obtained from Fischer Scientific, was used to establish the exact MEA and MDEA concentrations.

Typical Experimental Run. CO₂ or O₂ Induced Degradation of Aqueous MEA-MDEA (i.e., MEA-MDEA-H₂O-CO₂ or MEA-MDEA-H₂O-O₂ Systems). The experimental procedure for degradation studies was similar to the one described in our earlier work.^{18,19} Briefly, the water vapor pressures under various reaction conditions were determined earlier in the absence of O₂ or CO₂ pressures. For a typical experimental run, 450 mL of aqueous MEA/MDEA blends of the desired concentration was loaded into the reactor. The solvent was stirred at 500 rpm and heated to the desired temperature. O₂ or CO₂ was then fed into the vessel up to the desired reactor pressure (i.e., O₂ or CO₂ pressure + water vapor pressure) by opening the inlet valve of the O₂ or CO₂ cylinder tank set at a predetermined value. O₂ and CO₂ are soluble in aqueous amine blends. This resulted in an initial decline of O₂ or CO₂ in the reaction chamber. However, to maintain a constant pressure, the reaction chamber was boosted with extra O₂ or CO₂ supply as needed. Prior to the introduction of O₂ or CO₂ into the system, the pressure in the reactor was essentially the vapor pressure of H₂O. When O₂ or CO₂ was added, the pressure became the vapor pressure of H₂O + pressure of O₂/CO₂. Thus, there is a need to know the vapor pressure of H₂O to be exact about the pressure of O₂ or CO₂ introduced into the reactor.

In all the test runs, it was ensured that the desired O₂ or CO₂ pressure was maintained throughout the duration of the reaction. About 3 mL samples of the reaction mixture were removed from the reactor through the liquid sampling port at predetermined time intervals. Extra O₂ or CO₂ was also quickly added after each sampling to compensate for the loss of pressure during the sampling process and to maintain the constant pressure of the system. The reaction in each sample taken was quenched by quickly running cold water over the test tube containing the sample. Also, the reaction between aqueous MEA/MDEA blends and O₂ or CO₂ is exothermic. Thus, cooling water (flowing through the cooling coil) was employed to ensure reactor isothermality. For each run under each set of experimental conditions, an average of 15 samples was taken. Also, some of the runs were repeated to check the reproducibility of the runs.

O₂ Induced Degradation of Aqueous CO₂-Loaded MEA-MDEA (i.e., MEA-MDEA-H₂O-CO₂-O₂ System). For a typical experimental run, 450 mL of an aqueous MEA/MDEA blend of the desired concentration was loaded into the reactor. The solvent was stirred at 500 rpm, and CO₂ was then fed into the vessel up to the desired pressure by opening the CO₂ gas inlet valve of the CO₂ cylinder tank set at a predetermined value. The gas inlet valve was left open for about 12 h, after which about 3 mL of sample of the reaction mixture was withdrawn through the liquid sampling port of the reactor to determine the CO₂ loading in the sample using a Chittick CO₂ analyzer. The reactor content was then heated to the desired temperature, and CO₂ loading was again determined. O₂ was then fed into the vessel up to the desired pressure (O₂ pressure + water vapor pressure + CO₂ vapor pressure) by opening the O₂ gas inlet valve of the O₂ cylinder tank set at a predetermined value. Apart from the preloading of CO₂, the procedure was similar to that of O₂ induced degradation runs of the aqueous MEA-MDEA system. A schematic of the reactor used for the runs is available elsewhere.¹⁸

Analysis of the Products. Analysis of the samples was carried out using a high-performance liquid chromatograph

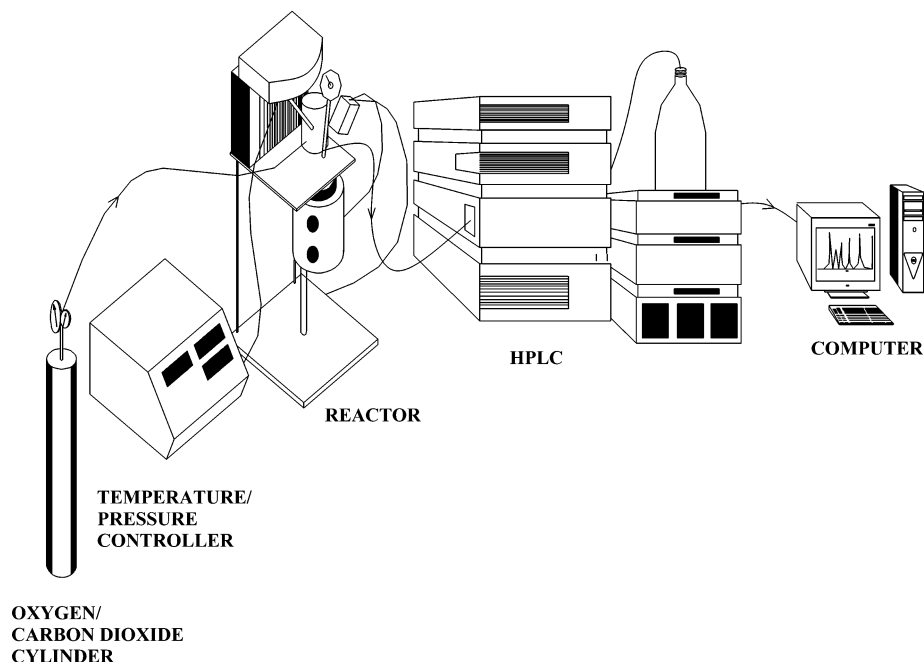


Figure 1. Schematic representation of the experimental setup.

(HPLC series 1100 supplied by Agilent Technologies Canada Inc., Mississauga, ON, L4W 5M2). A Shodex IC YK-421 column (length = 125 mm, internal diameter = 4.6 mm, and theoretical plates = 2500 minimum) packed with silica gel bonded with a carboxylic group and a Shodex IC YK-G guard column (length = 10 mm, internal diameter = 10 mm) were used in the HPLC for the separation of components. The mobile phase used with the column was 5 mM tartaric acid + 1 mM dipicolinic acid + 1.5 g/L boric acid dissolved in ultrapure water with the aid of an ultrasonic vibrator. The solvent (mobile phase) was passed through a 0.45 μm cellulose membrane filter prior to use in the column. The components in each sample (mostly MEA and MDEA) were identified by their retention time (based on an earlier calibration) using a refractive index (RI) detector. Prior to HPLC analysis, each sample was diluted with the mobile phase to 10 times its original volume to avoid column overload and to improve separation of the components. Several trials were done to select the optimum operating conditions for the HPLC, which are summarized as follows. An autoinjector (series 1100 supplied by Agilent Technologies Canada Inc., Mississauga, ON, L4W 5M2) containing a 100 μL syringe was used to automatically introduce samples into the HPLC column to give better reproducibility. A standard injection with an injection volume of 1 μL was used. The column maximum and minimum pressures were 400 and 0 bar, respectively, while the flow rate and the temperature were 1 mL/min and 318 K, respectively. For the refractive index detector (RID), an optical unit temperature of 318 K and a positive polarity were used. Each sample analysis took 15 min. MEA and MDEA concentrations were based on calibrations using standard MEA and MDEA. The error of the HPLC was less than $\pm 2\%$. Figure 1 shows the schematic of experimental setup including the analytical setup used for this study.

Determination of Concentrations of MEA and MDEA in Degraded Samples. Degradation of MEA and MDEA was measured in terms of reduction in MEA and MDEA concentrations over a period of time. This involved plotting of calibration curves for MEA and MDEA for which five known concentrations of pure MEA (ranging from 0.25 to 8 mol/L) and five known concentrations of pure MDEA (ranging from 0.25 to 4

mol/L) were, respectively, prepared. These pure samples were analyzed by HPLC using the same operating conditions described earlier. The HPLC was used to obtain the peak areas for these pure samples. Three injections were made for each concentration, and the average value of the peak areas were calculated. The concentrations of the pure samples were plotted against the corresponding average peak areas. For each degradation sample analyzed, the HPLC was used to obtain the peak areas of MEA and MDEA in the sample. The concentrations of MEA and MDEA were then calculated using the equations obtained from the calibration curves.

Results and Discussion

The concentrations of MEA and MDEA were plotted against time to represent the kinetic data. The slopes obtained on these concentration–time curves at suitably selected concentration values were used to represent the rate of reaction at those concentrations and times. Figure 2a–c shows typical concentration–time curves obtained for the O_2 , CO_2 , and O_2 – CO_2 systems, respectively. These curves (Figure 2a–c) were obtained by using an exponential curve fitting technique for our plotted experimental concentration versus time data. The equations of the curves as given in Figure 2a–c were differentiated at various experimental times to obtain the instantaneous rate of degradation of MEA and MDEA at different times. These were considered as the rates at these times. The instantaneous rate of MEA and MDEA were also plotted against time to evaluate the variation of the rate with different operating variables in all the systems. These are shown in Figures 3 and 4 for MEA–MDEA– H_2O – O_2 and MEA–MDEA– H_2O – O_2 – CO_2 systems, respectively.

MEA–MDEA– H_2O – O_2 System. Effect of Temperature. Figure 3a,b, respectively, illustrates the variation of the MEA and MDEA instantaneous rate of degradation with time for all our operating conditions. The effect of temperature was studied by comparing the plot obtained at 328 and 393 K using 7 mol/L (2 mol/L MDEA) total amine. The plots obtained at 373 and 393 K using 7 mol/L (10% MDEA) total amine were also compared. The figures show that the rates of degradation of

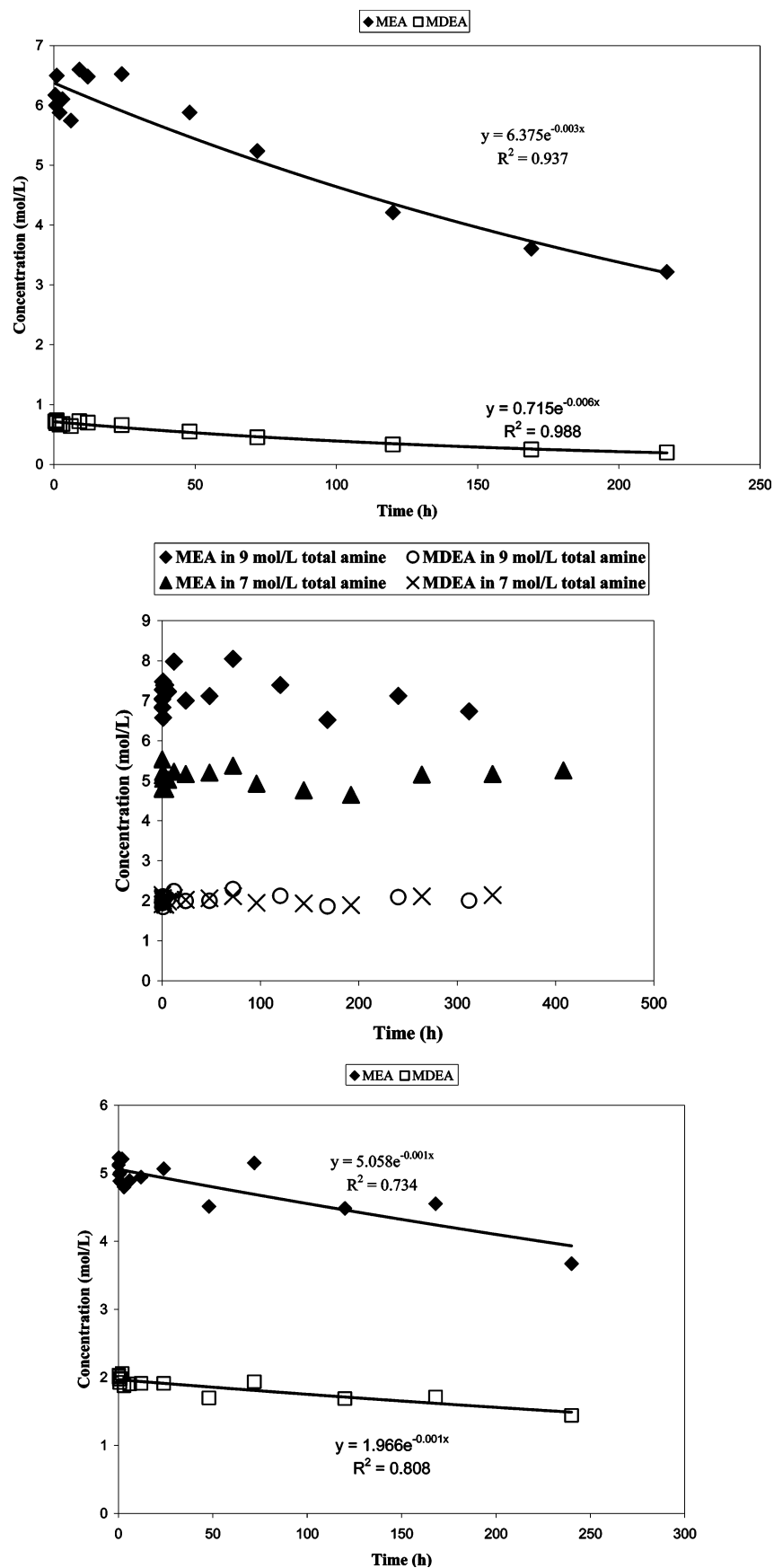


Figure 2. (a) Typical concentration-time curve for the MEA-MDEA-H₂O-O₂ system using 7 mol/L (0.7 mol/L MDEA) total amine concentration, 250 kPa O₂ at 393 K (120 °C). (b) Concentration-time curve for the MEA-MDEA-H₂O-CO₂ system using 7 and 9 mol/L (2 mol/L MDEA) total amine concentration, 250 kPa CO₂ at 393 K. (c) Typical concentration-time curve for the MEA-MDEA-H₂O-CO₂-O₂ system using 7 mol/L (2 mol/L MDEA) total amine concentration, 250 kPa O₂ pressure, 0.4 mol/mol CO₂ loading at 393 K.

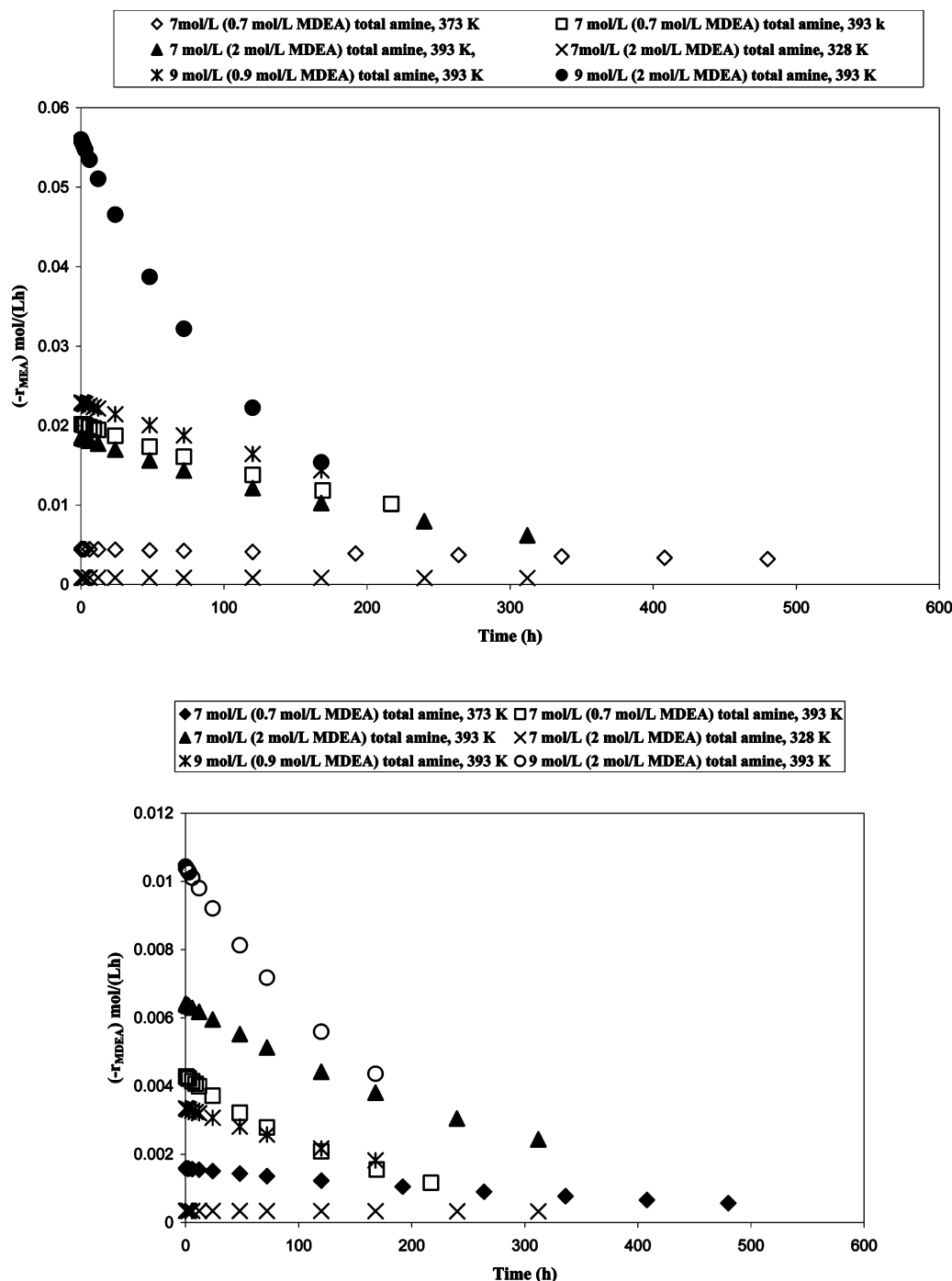


Figure 3. (a) Rate of degradation of MEA against time for the MEA-MDEA-H₂O-O₂ system at a constant O₂ pressure of 250 kPa. (b) Rate of degradation of MDEA against time for a MEA-MDEA-H₂O-O₂ system at constant O₂ pressure of 250 kPa.

MEA and MDEA were higher at higher temperatures (393 K) than at lower temperatures (373 and 328 K). This is expected because, at a higher temperature, more products can overcome the energy barrier required for their reaction with MEA and/or MDEA and, thus, result in higher rates of MEA and/or MDEA disappearance in the system. The overall rates of degradation of MEA and MDEA (i.e., $\Delta[\text{MEA}]/\Delta t$ and $\Delta[\text{MDEA}]/\Delta t$ (where $\Delta[\text{MEA}]$, $\Delta[\text{MDEA}]$, and Δt represent the overall change in MEA concentration, overall change in MDEA concentration, and the time taken to obtain the described concentration changes, respectively)) at 328 K when 7 mol/L total amine concentration with 2 mol/L MDEA was used were 0.0008 and 0.0003, whereas their overall rates at 393 K using the same MEA and MDEA concentrations were 0.0112 and 0.0041 mol/(L h), respectively.

For 7 mol/L total amine concentration with 0.7 mol/L MDEA, the overall rates of degradation at 373 K for MEA and MDEA were 0.0038 and 0.00099 mol/(L h), respectively. At 393 K, the overall rate for MEA increased to 0.0146, while that of MDEA increased to 0.0024 mol/(L h). Therefore, as expected, the overall rate of degradation also increased with temperature.

Effect of Total Amine Concentration. Results of the experiments conducted using 7 and 9 mol/L total amine concentrations with 0.7 and 0.9 mol/L (10 mol % MDEA) MDEA, 250 kPa O₂ at 393 K were compared to see how the total amine concentration affected the rates of MEA and MDEA degradation. The plot of the experimental rates of degradation of MEA and MDEA against time at these total amine concentrations (Figure 3a,b) shows that the degradation rates were

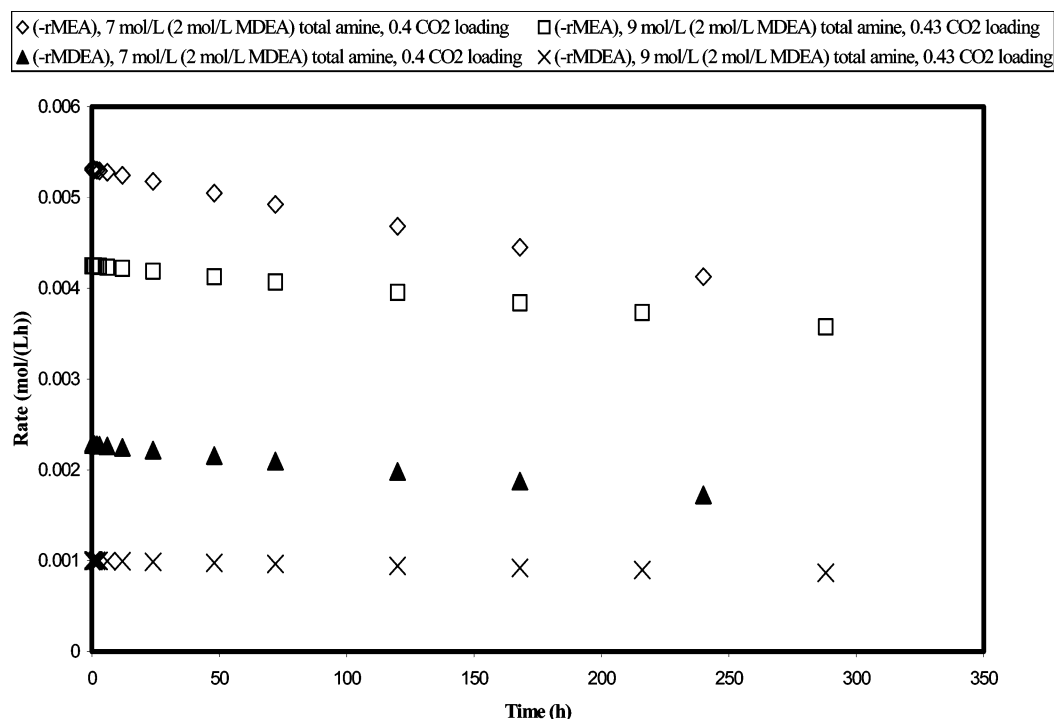


Figure 4. Rate of degradation of MEA and MDEA against time for the MEA-MDEA-H₂O-CO₂-O₂ system using a constant O₂ pressure of 250 kPa at 393 K.

higher at 9 mol/L than at 7 mol/L total amine concentration. This indicates that the rate of degradation increases with an increase in total amine concentration because more amine is available for reaction with O₂ and other products.

Although the number of degradation products observed at higher concentration was less as compared to those at lower total amine concentration, it should be noted that the number of degradation products cannot be used as a measure of the rates of disappearance of MEA and MDEA in the system because a lower number of products could be attributed to the limited relative concentration of O₂ at higher total amine concentration if most of the products observed at lower (7 mol/L) total amine concentrations were due to reactions that directly involved O₂. It could also be attributed to the formation of more intermediates than the final products at higher total amine concentrations. The overall rates of MEA and MDEA degradation at 7 mol/L total amine concentration were 0.0146 and 0.0024 mol/L h, respectively, whereas their overall rates at 9 mol/L total amine concentration were 0.0183 and 0.0025 mol/L h, respectively. There was an increase in the overall rates of degradation of MEA and MDEA when the total amine concentration was increased, but the increments were small as compared to the case with the temperature effect.

Effect of MEA/MDEA Ratio. The effect of the MEA/MDEA ratio on the rates of oxidative degradation of MEA and MDEA was studied using 7 and 9 mol/L total amine concentration at 393 K and 250 kPa O₂ pressure. For 7 mol/L total amine concentration, a change in the MEA/MDEA ratio from 9:1 to 2.5:1 leads to a decrease in the rate of MEA degradation with time and an increase in that of MDEA as can be seen in Figure 3a,b. This observation is reasonable because as more MDEA becomes available in the system, it increases its ability to participate in additional reactions. The overall rates of MEA and MDEA at this total amine concentration when the MEA/MDEA ratio was 9:1 were 0.0146 and 0.0024 mol/(L h), respectively. When the ratio of MEA/MDEA was reduced to 2.5:1 for the same total amine concentration, the overall rates of MEA and

MDEA were 0.0112 and 0.0041 mol/(L h), respectively. Thus, a lower MEA/MDEA ratio at this lower total amine concentration also resulted in a higher overall rate of degradation of MDEA and lower overall rate of degradation of MEA.

At higher total amine concentrations (9 mol/L), the rates of degradation of MEA and MDEA with time were higher at a lower MEA/MDEA ratio (3.5:1) than at a higher ratio (9:1) as is seen in Figure 3a,b. For this total amine concentration, when the MEA/MDEA ratio was 9:1, the overall rates of MEA and MDEA degradation were 0.0183 and 0.0025 mol/(L h), respectively, but when the MEA/MDEA ratio was decreased to 3.5:1, the overall rates of MEA and MDEA degradation were 0.0314 and 0.007 mol/(L h), showing that a decrease in the MEA/MDEA ratio in this system leads to a high degradation rate of MDEA. There appears to be a change of mechanism in the 9 mol/L total amine (3.5:1) as compared with the other operating conditions. It is not clear at this time what is responsible for this change.

MEA-MDEA-H₂O-CO₂ System. Effect of Total amine Concentration. The results from the experiments conducted using 7 and 9 mol/L (2 mol/L MDEA) total amine concentrations, 250 kPa CO₂ at 393 K were evaluated to study the effect of the change in initial MEA concentration, total amine concentration, and MEA/MDEA ratio on CO₂ induced degradation of MEA-MDEA blends. Figure 2b illustrates the variation of MEA and MDEA concentrations with time for this system. The figure shows that for both initial MEA and total amine concentrations as well as MEA/MDEA ratios considered, the decrease in MEA and MDEA concentrations with reaction time was negligible (approximately zero). Therefore, the rate of MEA and MDEA degradation for this CO₂ system alone could also be assumed to be negligible or zero irrespective of changes in the initial MEA concentration, total amine concentration, and MEA/MDEA ratio as can be seen in Figure 2b.

MEA-MDEA-H₂O-O₂-CO₂ System. Effect of Total Amine Concentration. The dependence of MEA and MDEA degradation rates on the total amine concentration for this system was

evaluated by comparing the results obtained from 7 mol/L (0.4 CO₂ loading, 2 mol/L MDEA) with those obtained from 9 mol/L (0.43 CO₂ loading, 2 mol/L MDEA) total amine concentrations at the same temperature and O₂ partial pressure (250 kPa and 393 K). Figure 4 illustrates how the rates of degradation of MEA and MDEA changed with time at the two concentrations. The figure shows that for both concentrations considered, the rates of MEA and MDEA versus reaction time were higher at lower total amine concentrations (7 mol/L) than at higher total amine concentrations. When 7 mol/L (2 mol/L MDEA) total amine concentration was used as the starting concentration, the overall rates of MEA and MDEA degradation were 0.0047 and 0.0020 mol/(L h), respectively, whereas, when 9 mol/L (2 mol/L MDEA) total amine concentration was used as the starting concentration, the overall rates of MEA and MDEA were 0.0039 and 0.0009 mol/(L h), respectively. This observation is attributed to the higher CO₂ loading used at higher total amine concentrations. The presence of CO₂ in the system reduces the solubility of O₂ in the amine. This implies that the higher the CO₂ loading, the slower the reactions of MEA and MDEA with O₂ are.

Conclusions

(1) In the MEA-MDEA-H₂O-O₂ systems, an increase in the total amine concentration resulted in an increase in the rate of degradation because of the higher reactivity of some of the products. (2) A change in the MEA-MDEA ratio affected the rate of degradation of both MEA and MDEA in a complex manner. (3) In the MEA-MDEA-H₂O-CO₂ systems, concentration-time curves for MEA and MDEA showed no significant CO₂ induced degradation of MEA and MDEA at both lower and higher total amine concentrations. (4) A higher CO₂ loading in the MEA-MDEA-H₂O-CO₂-O₂ system resulted in a reduction in the rate of MEA and MDEA degradation because of the ability of CO₂ to reduce the solubility of O₂ in the amine.

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