Investigation of Degradation Inhibitors on CO₂ Capture Process

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Abstract

In this study we have used sodium sulfite (Na₂SO₃), potassium sodium tartrate tetrahydrate (KNaC₄H₄O₆.4H₂O), ethylenediaminetetraacetic acid (EDTA), and hydroxylamine (NH₂OH) to effectively inhibit O₂-SO₂ induced degradation of amines such as monoethanolamine (MEA) during CO₂ capture from flue gases (i.e. the degradation systems of MEA-O₂-SO₂-H₂O-CO₂). The ranges of experimental conditions were such as to duplicate the extremes normally encountered in a typical CO₂ capture process in a coal fired power plant. MEA concentration, O₂ concentration, SO₂ concentration, CO₂ concentration and degradation temperature were respectively in the range of 3 – 7 kmol/m³, 6 – 100%, 0 – 196 ppm, 0 – 0.52 loading, and 393K. There were optimum concentrations of these inhibitors that best prevented the degradation; namely, 0.05, 0.01, 0.0025, and 0.025 kmol/m³ respectively for Na₂SO₃, NaKC₄H₄O₆.4H₂O, EDTA, and NH₂OH. Outside these concentrations the inhibitors were not very effective. The blend of Na₂SO₃-KNaC₄H₄O₆.4H₂O was the most effective inhibitor either in the absence or presence of CO₂. Based on the evaluation of the inhibition mechanisms, Na₂SO₃ works as an O₂ and SO₂ scavenger, while KNaC₄H₄O₆.4H₂O, EDTA, and NH₂OH function as radical scavengers. It was also observed that CO₂ alone works on the basis of the salting out effect whereby CO₂ goes into the aqueous amine solution in preference to O₂ and SO₂.

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Introduction

The degradation of amine often occurs during carbon dioxide (CO₂) capture operation from industrial gas streams such as fossil fuel fired flue gases. Reactive flue gas contaminants specifically oxygen (O₂) and sulfur dioxide (SO₂) can introduce considerable amine deterioration during the absorption process. The degradation is known to severely affect the absorption plant by reducing the CO₂ absorption capacity of the amine and inducing corrosion and foaming problems due to accumulation of the degradation products. Since, the long-term solution for amine degradation done of preventing contact of amine with O₂ and SO₂ is a very difficult process, a less complicated technique such as the use of effective chemicals to prevent amine degradation becomes more attractive.

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because of its simplicity and instant effect. A useful guideline has been given for selection of an effective inhibitor.

For an inhibitor to work effectively, it must scavenge O$_2$ at ambient temperature and should have more favourable kinetics than the partial oxidation reactions involved in the degradation [1]. Consequent upon the test and confirmation of severity of oxidative degradation of various amines, it was recommended to use O$_2$ scavengers such as sulfites, hydroxylamine, and hydrazine to reduce O$_2$ to ppm level in amine systems [2]. An undisclosed commercial corrosion inhibitor which also acted as O$_2$ scavenger was also reported to control the level of bis(2-hydroxyethyl) glycine (bicine), an oxidative degradation product in a commercial methyldiethanolamine (MDEA)-based gas treating unit [3]. Ethylenediaminetetraacetic acid (EDTA) and sodium sulfite (Na$_2$SO$_3$) and formaldehyde were respectively tested in iron and copper catalyzed MEA oxidative degradation system with and without CO$_2$ [4], [5]. No inhibitor has so far been tested or developed for the case of SO$_2$ induced or combined O$_2$ and SO$_2$ induced degradation of any amine.

This study proposes to use sodium sulfite (Na$_2$SO$_3$), potassium sodium tartrate tetrahydrate (KNaC$_4$H$_4$O$_6$.4H$_2$O), ethylenediaminetetraacetic acid (EDTA), and hydroxylamine (NH$_2$OH), and their blends as effective inhibitors for O$_2$-SO$_2$- induced amine degradation during CO$_2$ capture from flue gases. The MEA was used at a typical concentration of 5 kmol/m$^3$. The inhibitor concentration was used in the range between 0–1 kmol/m$^3$. The simulated flue gas contained 6% O$_2$ and varied SO$_2$ concentrations in the range of 0-196 ppm. CO$_2$ loading varied between 0-0.33 mole CO$_2$/mole MEA was used. Samples degraded at 393 K were analyzed for MEA concentration change using the HPLC technique. The degradation rate information derived from the experiments was then used to evaluate the potential of the chemicals as inhibitors.

Experiments

Equipment and Chemicals

The selected inhibitors were evaluated using a 600 ml stainless-steel magnetic stirred reactor (model 5523, Parr Instrument Co., Moline, IL). The speed of the stirrer and the solution temperature were both controlled by a temperature-speed controller (Model 4836, Parr Instrument Co., Moline, IL). Simulated gas containing 6% O$_2$ (N$_2$ balance) with 0 – 196 ppm SO$_2$ were used (Praxair, Regina, Saskatchewan, Canada). Concentrated MEA solution with 99%+ purity was used to prepare aqueous MEA solutions with the desired concentration by diluting with dionized water. Standard hydrochloric acid of 1 kmol/m$^3$ (HCl) with methyl orange indicator was used to determine the exact MEA concentration by volumetric titration techniques. Reagent grade inhibitors were used as obtained and introduced into the solvent by dissolving a predetermined weight into the known MEA solutions. All chemicals were purchased from Fisher Scientific (Nepean, Ontario, Canada). Solution analysis was carried out by using a high performance liquid chromatograph (HPLC) equipped with a refractive index detector (RID), an on-line degasser, and an autosampler (model 1100/G1315B/G1322A/G1313A, Agilent Technologies Canada, Mississauga, Ontario, Canada). The system mobile phase was 0.05 kmol/m$^3$ potassium dihydrogen phosphate (KH$_2$PO$_4$). Details of HPLC procedure followed our previous work [6].

Experimental procedures

For non CO$_2$-loaded runs, 450 ml of 5 kmol/m$^3$ MEA solution with or without inhibitors was transferred into the reactor vessel which was subsequently assembled with the reactor head. After insertion of the reactor into the furnace, connections to the magnetic drive motor and the speed-temperature controller were made. Simultaneously, the MEA solution was stirred at the speed of 500 ppm and heated to the desired temperature. A few minutes was allowed to stabilize the temperature after it had reached the set-point. At this stage, the pressure gauge showed mostly water vapor pressure. The solution was then pressurized with an additional predetermined 250 kPa of a desired feed gas of O$_2$-SO$_2$/N$_2$ mixture from the appropriate gas cylinder. The total pressure of the reactor was therefore the sum of water vapor pressure and 250 kPa feed gas pressure. In order to maintain the isothermicity of the system, the solenoid valve regulated water cooling system was available to remove heat from the initial reaction of MEA and the feed gas. It was also required in case of temperature overshoots. Sampling process was done at predetermined intervals of times by opening the liquid sampling valve. Sample of 2.5 ml drawn into a 5 ml-sampling
bottle was quickly cooled down by running cold water over the bottle to prevent further degradation. Boosting an equivalent amount of feed gas pressure to that lost during the sampling process was also done to keep the system pressure constant throughout the experiment. The HPLC technique with MEA standard calibration was subsequently used to determine MEA concentration of all the samples. MEA concentration-time data were subsequently converted to degradation rate-time plots.

For CO₂-loaded experiments, prior to heating the solution, 250 kPa of CO₂ pressure was fed into MEA solution. Feeding time ranged from 0 – 0.35 h for CO₂ loading in the range of 0 – 0.33 mol CO₂/mol MEA. After this step, sample was withdrawn through the liquid sampling valve to determine the CO₂ loading using the aqueous HCl volumetric titration and CO₂ displacement technique described in our previous work [7]. The mixture was then heated to the desired temperature and the CO₂ loading was once again determined and recorded. Additional 250 kPa O₂-SO₂/N₂ pressure was introduced into the system. The combination of water vapor pressure, CO₂ vapor pressure, and 250 kPa pressure of O₂-SO₂/N₂ was taken as the total reactor pressure. The rest of the procedure was then carried out following those explained for non CO₂ loaded runs.

Determination of degradation rate

A predetermined MEA calibration curve plotted between various MEA concentrations and their corresponding HPLC peak areas was used to calculate MEA concentration in all degraded samples. The accuracy of the curve was within 2% AAD. To obtain degradation rate of each run, MEA concentrations calibrated from the MEA standard curve were plotted against their corresponding degradation times. Exponential function was used to fit the concentration-time data so that the degradation rate at each point of the curve could be calculated. The averaged degradation rate taken from all points was used throughout this study to evaluate effectiveness of the inhibitors.

Results and Discussion

Determination of optimum concentrations of Na₂SO₃, KNaC₄H₄O₆.4H₂O, EDTA, and NH₂OH

Figure 1 shows effect of Na₂SO₃ concentration on averaged MEA degradation rate. Na₂SO₃ of 0.05 kmol/m³ was initially added to 5 kmol/m³ MEA solution. The spiked amine was subjected to degradation condition of simulated flue gas containing 6%O₂ balanced with N₂ and 393 K temperature. At this concentration, averaged MEA degradation rate was measured at 4.10 \times 10^{-5} \text{ kmol/m}³\text{.h}. The rate was much slower than that of the base run carried out earlier in the absence of Na₂SO₃ measured at 4.89 \times 10^{-4} \text{ kmol/m}³\text{.h}. The percent inhibition of Na₂SO₃ at 0.05 kmol/m³ calculated by comparing its degradation rate with that of the base run was 91%. A further experiment conducted using a higher Na₂SO₃ concentration of 0.1 kmol/m³ yielded the opposite effect, as also shown in Figure 1. Averaged degradation rate was measured at 6.56 \times 10^{-4} \text{ kmol/m}³\text{.h} which was faster than that measured for the base run. A higher degradation rate of 1.28 \times 10^{-3} \text{ kmol/m}³\text{.h} was even observed when Na₂SO₃ concentration was increased to 0.3 kmol/m³. Since, Na₂SO₃ of 0.05 kmol/m³ only reduced the degradation rate. It was further tested with a more realistic system in which simulated flue gas stream contained SO₂. Figure 2 shows effect of Na₂SO₃ on MEA degradation rate when 6 and 196 ppm SO₂ was present in the feed gas. Without Na₂SO₃, the rates of degradation were respectively found for runs with 6 and 196 ppm as 4.74 \times 10^{-4} and 7.60 \times 10^{-4} \text{ kmol/m}³\text{.h}. For 6 ppm SO₂ system, the rate decreased drastically to 1.43 \times 10^{-4} \text{ kmol/m}³\text{.h} when Na₂SO₃ was present. The run containing 196 ppm SO₂ with the inhibitor also resulted in a slower degradation rate measured to be 1.14 \times 10^{-4} \text{ kmol/m}³\text{.h}. This indicates a strong inhibition effect of Na₂SO₃ in minimizing the degradation of MEA by both O₂ and SO₂ as long as the appropriate concentration is used. Percent inhibitions of Na₂SO₃ in 6 and 196 ppm SO₂ systems were respectively found to be 70 and 85%.

A similar procedure was used for the remaining inhibitors. The only exception was that simulated feed gas stream with 6 ppm SO₂ was applied right away to determine the optimum concentrations of KNaC₄H₄O₆.4H₂O, EDTA, and NH₂OH. Figure 3 shows effect of KNaC₄H₄O₆.4H₂O concentration on MEA degradation rate using 6 ppm SO₂, 6%O₂, 5 kmol/m³ MEA, and 393 K temperature as degradation conditions. The inhibitor concentration used ranged from 0 - 0.3 kmol/m³. Concentration of 0.005 kmol/m³.h was found ineffective resulting in increased degradation.
rate valued at $5.71 \times 10^{-4}$ whereas the base run’s was only $4.74 \times 10^{-4}$ kmol/m$^3$.h. The remaining concentrations of 0.01, 0.06, 0.1, and 0.3 kmol/m$^3$ all reduced the degradation rate of MEA solvent to $2.58 \times 10^{-5}$, $1.02 \times 10^{-4}$, $8.04 \times 10^{-5}$, and $1.88 \times 10^{-4}$ kmol/m$^3$.h. Based on these experiments, 0.01 kmol/m$^3$ was found as the optimum concentration of KNaC$_4$H$_4$O$_6$.4H$_2$O producing the maximum inhibition effect of as high as 95% for the O$_2$-SO$_2$ induced degradation of MEA. The optimum concentration also worked effectively when 196 ppm SO$_2$ was present in the simulated gas reactant. As also shown in Figure 3, 91% inhibition was achieved when 0.01 kmol/m$^3$ KNaC$_4$H$_4$O$_6$.4H$_2$O was added to 5 kmol/m$^3$ MEA solution. The degradation rate obtained with this inhibitor concentration was $6.48 \times 10^{-5}$ kmol/m$^3$ as compared to $7.60 \times 10^{-4}$ kmol/m$^3$ of the comparable run conducted without this inhibitor.

Figure 1. Averaged MEA degradation rate and Na$_2$SO$_3$ concentrations (5 kmol/m$^3$ MEA, 6% O$_2$, 393 K)

Figure 2. Averaged MEA degradation rate at Na$_2$SO$_3$ optimum concentration with various SO$_2$ concentrations (5 kmol/m$^3$ MEA, 6% O$_2$, 393 K)

Figure 3. Averaged MEA degradation rate of various concentrations of KNaC$_4$H$_4$O$_6$.4H$_2$O in the presence of 6 and 196 ppm SO$_2$ (5 kmol/m$^3$ MEA, 6% O$_2$, 393 K)
EDTA concentrations used were varied between 0 and 0.1 kmol/m$^3$. Figure 4 shows averaged MEA degradation rate of various EDTA concentrations. It was clear that spiking of 0.00125 and 0.0025 kmol/m$^3$ to MEA solution respectively slowed down the degradation rate from $4.74 \times 10^{-4}$ to $3.41 \times 10^{-4}$ and $1.44 \times 10^{-3}$ kmol/m$^3$. Higher concentrations, namely 0.005 and 0.1 kmol/m$^3$ both gave negative effect in which at these concentrations, they increased the degradation rate respectively to $5.29 \times 10^{-4}$ and $1.48 \times 10^{-3}$ kmol/m$^3$.h. In summary, the optimum concentration of EDTA to reduce the degradation rate of MEA was 0.0025 kmol/m$^3$, and this provided an inhibition efficiency of 68%. The same effect was obtained with the 196 ppm SO$_2$ system in which the optimum concentration of EDTA determined earlier reduced the degradation rate from $7.60 \times 10^{-4}$ to $8.93 \times 10^{-3}$ kmol/m$^3$.h. The inhibition efficiency of EDTA for this system was 88%.

![Figure 4. Averaged MEA degradation rate of various concentrations of EDTA in the presence of 6 and 196 ppm SO$_2$ (5 kmol/m$^3$, 6% O$_2$, 393 K)](image)

The degradation system of 5 kmol/m$^3$ MEA, 6% O$_2$, 6 ppm SO$_2$, and 393 K was also used for optimum concentration determination of NH$_2$OH. Figure 5 illustrates the concentration effect of NH$_2$OH using an averaged degradation rate of MEA. The addition of 0.025 kmol/m$^3$ NH$_2$OH into the MEA solution resulted in $5.96 \times 10^{-5}$ kmol/m$^3$.h averaged MEA degradation rate. At this concentration, the degradation rate was decreased by 87% when compared to the base run (without inhibitor). The use of higher concentrations of NH$_2$OH at 0.5 and 1 kmol/m$^3$ of MEA were also found to respectively reduce the degradation to $3.76 \times 10^{-4}$ and $2.14 \times 10^{-4}$ kmol/m$^3$.h. However, these concentrations were not as effective as 0.025 kmol/m$^3$ since they only resulted in 21 and 55% degradation inhibition. The optimum concentration of NH$_2$OH found to be most effective in inhibiting O$_2$-SO$_2$ induced MEA degradation was 0.025 kmol/m$^3$.

![Figure 5. Averaged MEA degradation rate of various concentrations of NH$_2$OH (5 kmol/m$^3$ MEA, 6% O$_2$,6 ppm SO$_2$, 393 K)](image)
Blended inhibitors

It was decided to also evaluate blended inhibitors. The blend combination was chosen based on the initial proposal of inhibiting mechanisms. Consequently, the inhibitor compounds in this study were categorized as either \( \text{O}_2\text{-SO}_2 \) or radical (i.e. hydroxyl and MEA radicals) scavengers. Our aim was to determine if the inhibiting effect of these scavengers could be enhanced if they were combined using their optimum concentrations found earlier. Since, \( \text{Na}_2\text{SO}_3 \) was more of a \( \text{O}_2\text{-SO}_2 \) scavenger, the blend formulation was therefore based on this compound mixed with each one of the radical scavengers (e.g. \( \text{KNaC}_4\text{H}_4\text{O}_6\cdot4\text{H}_2\text{O}, \text{EDTA}, \) and \( \text{NH}_2\text{OH} \)). To test our theory, blends of \( \text{Na}_2\text{SO}_3/\text{KNaC}_4\text{H}_4\text{O}_6\cdot4\text{H}_2\text{O} \) (0.05:0.01 molar ratio) and \( \text{Na}_2\text{SO}_3/\text{EDTA} \) (0.05:0.0025 molar ratio) were initially chosen for test.

To test the blend formulations, a more aggressive condition with 196 ppm \( \text{SO}_2 \) was used to conduct the degradation experiments while the rest of the degradation parameters remained the same as used with the 6 ppm \( \text{SO}_2 \) runs. Figure 6 shows the average MEA degradation rate for the system using blends of \( \text{Na}_2\text{SO}_3/\text{KNaC}_4\text{H}_4\text{O}_6\cdot4\text{H}_2\text{O} \) and \( \text{Na}_2\text{SO}_3/\text{EDTA} \). Rates of runs without these blends and with their individual compounds are also included for comparison. As shown in Figure 6, \( \text{Na}_2\text{SO}_3/\text{KNaC}_4\text{H}_4\text{O}_6\cdot4\text{H}_2\text{O} \) blend could minimize MEA degradation effect by decreasing its rate from \( 7.60 \times 10^{-4} \) to \( 1.44 \times 10^{-5} \) kmol/m\(^3\).h. This was the only blend formulation to work more effectively (98% inhibition) than the individual \( \text{Na}_2\text{SO}_3 \) and \( \text{KNaC}_4\text{H}_4\text{O}_6\cdot4\text{H}_2\text{O} \) components in which their percent inhibition were respectively only 85 and 91%. On the other hand, the formulated \( \text{Na}_2\text{SO}_3/\text{EDTA} \) could not produce the same effect in which its individual compounds performed better in preventing MEA to degrade. It is clear that \( \text{Na}_2\text{SO}_3 \) blended with \( \text{KNaC}_4\text{H}_4\text{O}_6\cdot4\text{H}_2\text{O} \) results in a synergy, and the inhibitive effect of the blend is enhanced. However, the same effect was cancelled if the blend formulation was \( \text{Na}_2\text{SO}_3 \) and \( \text{EDTA} \).

To be more realistic, the evaluation of the effect of inhibitors for amine degradation must be evaluated in the presence to \( \text{CO}_2 \). Our previous experience also shows that \( \text{CO}_2 \) alone could slow down the degradation of MEA. This is due to the fact that \( \text{CO}_2 \) is more soluble in MEA solution than \( \text{O}_2 \) and \( \text{SO}_2 \). This lowers the solubility of the latter components (i.e. degradation inducing species), thus reducing the MEA degradation rate. In non-\( \text{CO}_2 \) loaded system, our previous results have identified the blend of 0.05 kmol/m\(^3\) \( \text{Na}_2\text{SO}_3 \) and 0.01 kmol/m\(^3\) \( \text{KNaC}_4\text{H}_4\text{O}_6\cdot4\text{H}_2\text{O} \) to be the most effective among the inhibitors tested. It was decided to test this formulation also in \( \text{CO}_2 \) loaded environment. To evaluate this blend in the presence of \( \text{CO}_2 \), 5 kmol/m\(^3\) MEA was initially spiked with \( \text{Na}_2\text{SO}_3 \) and \( \text{KNaC}_4\text{H}_4\text{O}_6\cdot4\text{H}_2\text{O} \) with the respective concentrations of 0.05 and 0.01 kmol/m\(^3\) (5 to 1 ratio). The solution was later loaded with 0.33 \( \text{CO}_2 \) loading. It was subsequently degraded by feed gas containing 196 ppm \( \text{SO}_2 \), 6% \( \text{O}_2 \), at 393 K. The average MEA degradation rate measured was found at \( 1.57 \times 10^{-4} \) kmol/m\(^3\).h. As shown in Figure 7, MEA was...
degraded more slowly than that of the based run carried out with neither inhibitor nor CO\textsubscript{2} having 7.60 \times 10^{-4} kmol/m\textsuperscript{3}.h degradation rate (used as a basis for inhibitive percentage calculation). The rate was also slower than that of run with CO\textsubscript{2} alone of comparable loading found to be 4.40 \times 10^{-4} kmol/m\textsuperscript{3}.h. The inhibition efficiency of the blended Na\textsubscript{2}SO\textsubscript{3} and KNaC\textsubscript{4}H\textsubscript{4}O\textsubscript{6}.4H\textsubscript{2}O with 0.05 to 0.01 molar ratio was calculated as 79% whereas CO\textsubscript{2} alone only produced 42% inhibition effect.

Further experiments were conducted to determine if changing blend concentration or molar ratio of Na\textsubscript{2}SO\textsubscript{3} and KNaC\textsubscript{4}H\textsubscript{4}O\textsubscript{6}.4H\textsubscript{2}O by changing either concentration of Na\textsubscript{2}SO\textsubscript{3} or KNaC\textsubscript{4}H\textsubscript{4}O\textsubscript{6}.4H\textsubscript{2}O or both would affect the inhibitive power of the blend in CO\textsubscript{2} environment. Since, KNaC\textsubscript{4}H\textsubscript{4}O\textsubscript{6}.4H\textsubscript{2}O was found the most effective compared to Na\textsubscript{2}SO\textsubscript{3} if used individually in non CO\textsubscript{2} loaded-196 ppm SO\textsubscript{2} system. It was decided to initially change only the molar concentration of KNaC\textsubscript{4}H\textsubscript{4}O\textsubscript{6}.4H\textsubscript{2}O from 0.01 to 0.015 and then 0.025 kmol/m\textsuperscript{3} while Na\textsubscript{2}SO\textsubscript{3} concentration was kept at its optimum concentration of 0.05 kmol/m\textsuperscript{3}. The run conditions were kept the same as used with the original blend concentration (e.g. 196 ppm SO\textsubscript{2}, 0.33 CO\textsubscript{2} loading, and 393 K). It is clear from Figure 7 that changing ratio of Na\textsubscript{2}SO\textsubscript{3} and KNaC\textsubscript{4}H\textsubscript{4}O\textsubscript{6}.4H\textsubscript{2}O from 5 : 1 (0.05 to 0.01 molar ratio) to 3.3 : 1 (0.05 to 0.015 molar ratio) boosted up the inhibitive power of the blend. The MEA degradation rate was reduced further to 8.24 \times 10^{-5} kmol/m\textsuperscript{3}.h accounting for 89% inhibition. Further increase of KNaC\textsubscript{4}H\textsubscript{4}O\textsubscript{6}.4H\textsubscript{2}O to 0.025 kmol/m\textsuperscript{3} (ratio 2 : 1 or 0.05 to 0.025 molar ratio) did not produce any additional inhibition to the blend. In fact, it reduced the inhibition effect of the original blend (e.g. 0.05 : 0.01 molar ratio) from 79 to 63%. An increase in the molar concentration of Na\textsubscript{2}SO\textsubscript{3} of the blend was also studied. In this test, Na\textsubscript{2}SO\textsubscript{3} concentration was increased from 0.05 to 0.075 kmol/m\textsuperscript{3}. This concentration was then mixed with 0.015 kmol/m\textsuperscript{3} KNaC\textsubscript{4}H\textsubscript{4}O\textsubscript{6}.4H\textsubscript{2}O previously determined as it was capable of increasing the inhibitive power of the blend formulation. As also shown in Figure 7, the blend of 0.075 kmol/m\textsuperscript{3} Na\textsubscript{2}SO\textsubscript{3} and 0.015 kmol/m\textsuperscript{3} KNaC\textsubscript{4}H\textsubscript{4}O\textsubscript{6}.4H\textsubscript{2}O (5 : 1 ratio) resulted in an adverse effect. Therefore, it is clear that determining the formulated ingredient concentration is the major key in obtaining the most effective blend of these two inhibitors. Thus, the appropriate molar concentrations of Na\textsubscript{2}SO\textsubscript{3} and KNaC\textsubscript{4}H\textsubscript{4}O\textsubscript{6}.4H\textsubscript{2}O in the blend must be carefully selected so that the blend could work as an anti-oxidant rather exhibit pro-oxidative properties.

![Figure 7. Effect of inhibitors in the presence of CO2 (5 kmol/m3, 6% O2, 196 ppm SO2, 0.33 CO2 loading, 393 K)](image)

It must be noted that CO\textsubscript{2} affected the performance of all inhibitors by decreasing the inhibitive power against O\textsubscript{2}-SO\textsubscript{2} induced degradation. Their effectiveness could not compete with the effect respectively obtained from Na\textsubscript{2}SO\textsubscript{3}, KNaC\textsubscript{4}H\textsubscript{4}O\textsubscript{6}.4H\textsubscript{2}O, EDTA, and blended Na\textsubscript{2}SO\textsubscript{3}/KNaC\textsubscript{4}H\textsubscript{4}O\textsubscript{6}.4H\textsubscript{2}O in non-CO\textsubscript{2} loaded environment. The inhibition efficiencies of Na\textsubscript{2}SO\textsubscript{3}, KNaC\textsubscript{4}H\textsubscript{4}O\textsubscript{6}.4H\textsubscript{2}O, EDTA, and blended Na\textsubscript{2}SO\textsubscript{3}/KNaC\textsubscript{4}H\textsubscript{4}O\textsubscript{6}.4H\textsubscript{2}O obtained in non-CO\textsubscript{2} runs were 85, 91, 88, and 98%, and these reduced respectively to 50, 83, 69, and 79% when used in the CO\textsubscript{2} loaded system. A hypothesis is that CO\textsubscript{2} is also acidic similar to SO\textsubscript{2} and could react with the inhibitors. The amount of CO\textsubscript{2} could become less as it can be partially consumed in the reactions, thus allowing O\textsubscript{2} and SO\textsubscript{2} to
induce more MEA degradation. Although, the inhibitors still exist in the solution, the maximum protection would not be achieved, simply because part of their optimum concentrations were also consumed by CO₂ thereby resulting in a less than optimum concentrations/ratios being available for degradation prevention.

Conclusions

1. Na₂SO₃, KNaC₄H₄O₆.4H₂O, EDTA, and NH₂OH at the optimum concentration of 0.05, 0.01, 0.0025, and 0.025 kmol/m³ were respectively found to be the most effective in minimizing the degradation of MEA in the presence of O₂ and SO₂. Outside these optimum concentrations they resulted in adverse effects of accelerating the MEA degradation rate.

2. In MEA-H₂O-O₂-SO₂ system, the blend Na₂SO₃/KNaC₄H₄O₆.4H₂O was found to enhance the inhibitive effect by working more effectively than their individual compounds. On the other hand, Na₂SO₃/EDTA blend did not perform better than either single Na₂SO₃ or EDTA only giving 41% degradation protection.

3. In the presence of CO₂, the inhibitors: Na₂SO₃, KNaC₄H₄O₆.4H₂O, EDTA, and blended Na₂SO₃/KNaC₄H₄O₆.4H₂O (0.05:0.015 ratio) still worked effectively resulting in reduced degradation rate of MEA while blended Na₂SO₃/KNaC₄H₄O₆.4H₂O (0.075:0.015 ratio) gave the opposite effect.

4. The inhibitive power of Na₂SO₃, KNaC₄H₄O₆.4H₂O, EDTA, and blended Na₂SO₃/KNaC₄H₄O₆.4H₂O were decreased when CO₂ was present in MEA solution.

5. In any environment (e.g. CO₂ loaded and non-CO₂ loaded), the blend of Na₂SO₃/KNaC₄H₄O₆.4H₂O was the most effective inhibitor.

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