INTRODUCTION OF POTASSIUM IODIDE AS AN INHIBITOR FOR OXIDATIVE DEGRADATION OF AMINES

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Abstract

Oxidative degradation of amines for CO_2 capture is a challenge that has yet to be overcome. This work presents the potential of using potassium iodide as a stable inhibitor, potentially without the need for replenishment in the capture process. The experimental results prove that the addition of only 1wt% potassium iodide to a 30 wt% ethanolamine (aq.) solution significantly reduces amine loss at absorber conditions, even if the amine solution already is degraded. 3-Aminopropanol seems to be equally stabilized under oxidative conditions as ethanolamine. Thermal stability and corrosivity as well as viscosity, density and vapour liquid equilibrium properties seem unaltered by the addition of a small amount of salt. The results presented here show why potassium iodide should further be evaluated as an inhibitor for oxidative degradation of amines.

Keywords: amine scrubbing, stability, inhibition

1. Introduction

Amine scrubbing is a popular choice for carbon capture and storage (CCS) as it is one of the most mature technologies for CO_2 capture and delivers storage quality carbon dioxide (CO_2) streams (<99%). A challenge faced within the technology is amine degradation, giving rise to cost issues such as solvent replacement, corrosion of equipment, interruption of operation and increased potential of emissions due to formation of volatile degradation compounds. With the currently existing knowledge about degradation, this issue is fortunately not a showstopper in the process but finding a means of stopping it will increase the amine solvent's lifetime and decrease the overall cost the capture process.

Degradation reactions inside a CO_2 capture facility are usually divided into those induced by oxidation reactions in the absorber column and those induced by the high temperatures in the reboiler and the desorber column. The conditions in the system are complex, with the presence of multiple gas species, including flue gas contaminants, as well as taking place inside metal equipment, potentially supplying catalytic surfaces and sources of corrosion products that dissolve into the liquid amine.

Ethanolamine (MEA) is one of the most widely studied amines for CO_2 capture, with an abundance of degradation products identified and many degradation mechanisms suggested.[1-3] Of the degradation compounds observed in pilot scale tests using ethanolamine, products of oxidative degradation tend to be found in higher abundance than thermal degradation products.[4] Many of the oxidative degradation compounds are acidic and therefore known to give rise to corrosion[5], providing corrosion products to the solution that in turn catalyse the degradation reactions[6].

Oxidative degradation inhibitors have been widely studied and commercially available solvent blends.[6-10] A downside to many studied degradation and corrosion inhibitors is their single-use nature, making replenishment of the inhibitor necessary, as well as removal of used inhibitor.[11] Other disadvantages associated with additives to the solvent are foaming or cross-reactions between solvent molecules and the inhibitor molecules.[12, 13] In Buvik et al. 2021[14] we first introduced potassium iodide (KI) as an for oxidative degradation of MEA. Sodium chloride was also considered as a degradation inhibitor in that work but deemed too inefficient to successfully be implemented in commercial CCS plants. KI is however still being thoroughly studied and will be tested under different conditions and with different amines and blends in the upcoming months.

At TCCS-11 we want to present experimental results indicating that KI could be of use as an oxidation inhibitor for industrial CO_2 capture including the results given here and in Buvik et al. 2021[14], as well as further experimental testing of the inhibitor with other amine solvents.

2. Materials and methods

2.1. Chemicals

Ethanolamine (MEA, CAS: 141-43-5, purity ≥99.0%), 3-aminopropanol (AP, CAS: 156-87-6, 99%), ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$, CAS: 7782-63-0, purity ≥ 99.0%) and potassium iodide (KI, CAS: 7681-11-0, purity ≥ 99.0%) were purchased from Merck Life Science/Sigma Aldrich Norway. Oxygen (O_2, N5.0), carbon dioxide (CO_2, N5.0) and synthetic air (79% N_2, 21% O_2) were purchased from AGA, and deionized water was obtained from a local water purification system at NTNU.

2.2. Oxidative degradation experiments

Oxidative degradation experiments were done at simulated absorber conditions in open, water bath-heated, double-jacketed glass reactors (approximately 250 mL) as shown in Figure 1. The temperature of the reactors was maintained at 60 °C and the water bath-cooled Graham condensers at 5 °C. Each reactor was filled with 200 mL of the 30 wt% (*aq.*) amine solution, which was pre-loaded to 0.4 mol of CO_2 per mol amine and contained 0.5 mM iron sulfate ($FeSO_4 \cdot 7H_2O$). Also, solutions of pre-used 30wt% MEA (*aq.*) were prepared from two pilot campaigns where degradation of the amine had been observed, these are denominated Pilot A and B, for the sake of simplicity. Pre-degraded MEA solutions were corrected to contain 30wt% MEA (assuming all alkalinity of pre-degraded solution being present as MEA) and 0.4 mol CO_2 per mol MEA, as well as added 0.5 mM $FeSO_4$. These were run with and without the addition of 2wt% KI under the same conditions as fresh MEA.
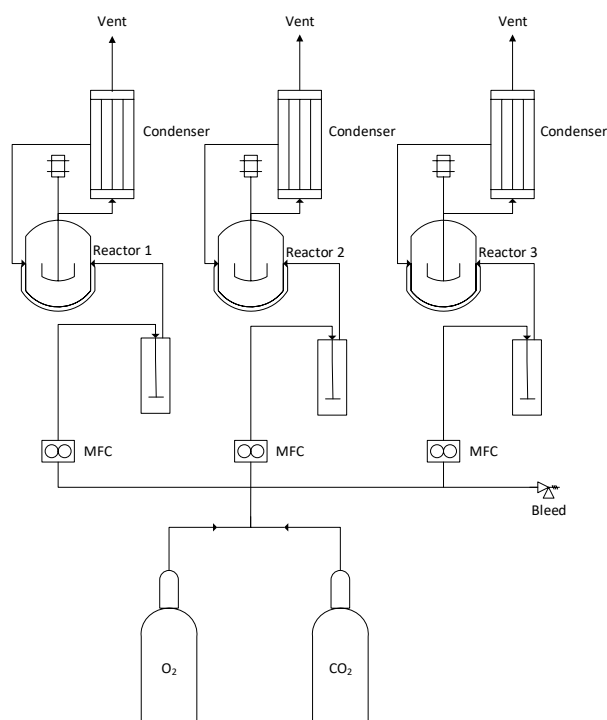

Figure 1: Schematic of oxidative degradation setup.

A mixture of O_2 and CO_2 gas was sparged through the solutions from Alicat mass flow controllers (MFC) and through Pyrex® glass gas distribution tubes (porosity grade 1), under constant magnetic stirring for the total experimental time of three weeks. Gas wash bottles were used between the mass flow controllers and the gas distribution tubes in case of power outage. Sampling from the liquid phase was performed through a septum on top of each reactor. Each experiment was run in three identical parallels, and the data presented in this work is given as the average of the three, with the standard deviation of the sample average given as the uncertainty. Uncertainty within each analytical method is given in the description of each method and comes in addition to the standard deviation of the sample average.

2.3. Thermal degradation experiments

Thermal degradation experiments were performed following Eide-Haugmo et al. (2011)[15] in 316 stainless steel cylinders with diameters of 0.5 inch and volumes of 11 mL. Each cylinder was equipped with Swagelok® end caps. The cylinders were filled with 8 mL of the solution, pre-loaded to 0.4 mol CO_2 per mol MEA, and kept at 135 °C for up to five weeks. For each sampling two metal cylinders per experiment were sacrificed and their contents analysed, meaning that every experiment consisted of 10 cylinders (2 identical samples per week).

2.4. Analytical methods

More thorough descriptions of all analytical procedures can be found in Buvik et al. 2021[16].

Titration with sulfuric acid was used to measure the concentration of amine in the solutions, according to Ma'mun et al. (2006)[17]. This procedure has an uncertainty of $\leq 2\%$. For all samples, the amine concentration is back calculated to the solution without CO_2 and corrected for evaporation of water and degradation products, assuming a linear loss throughout the experiment, as the total mass of the solution is only known for the start and end solutions.

A Shimadzu TOC-L$_{CPH}$ analyzer equipped with an auto sample injector (ASI) was used for the quantification of CO_2 loading as total inorganic carbon (TIC).

Inductively coupled plasma mass spectrometry (ICP-MS) analyses were performed on a High Resolution Inductive coupled plasma ELEMENT 2 from Thermo Electronics. The results were verified against certified reference material and the relative standard deviation for three scans of a sample varies from sample to sample.

Anion exchange ion chromatography (IC) was used to quantify the iodide concentration in the oxidative degradation experiment with 30 wt% MEA and 1.0 wt% KI. This was performed on a Thermo Scientific™ ion chromatographic system.

3. Results and discussion

3.1. Stability of 30wt% MEA (aq.) with and without salt addition

As can be seen in Figure 2, 30 wt% MEA (*aq.*) linearly loses alkalinity, resulting in a loss of as much as $60 \pm 4\%$ after three weeks. Upon addition of 2.0 wt% KI, this loss is reduced to $4 \pm 1\%$. KI was therefore further considered for use as an oxidative degradation inhibitor for industrial CO_2 capture. In Buvik et al. 2021[16] we also studied sodium chloride as a potential stable salt for degradation inhibition, but its effect ($24 \pm 3\%$ loss in alkalinity after 21 days) was deemed insufficient for commercial applications and will therefore not be described in detail in this short paper.
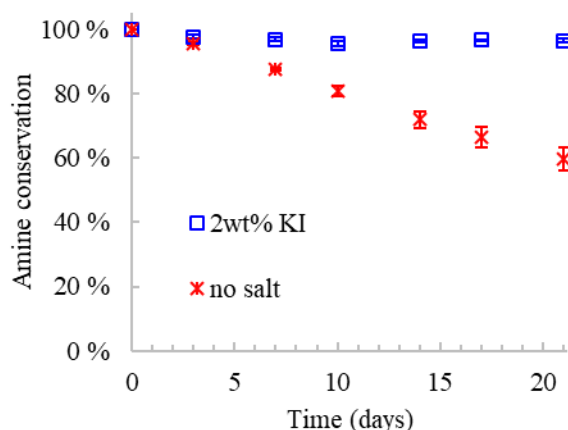
Figure 2: Loss of alkalinity of MEA with and without the addition of KI over the course of the 21 days at 60 °C, 0.5 mM of Fe^{2+} added and 60 mL min^{-1} O₂ (98%) and CO₂ (2%) added per 200 mL liquid.

The addition of KI inhibitor is not just positive for the amines oxidative stability in fresh MEA solutions, but also when added into already degraded solutions, as shown in Figure 3.
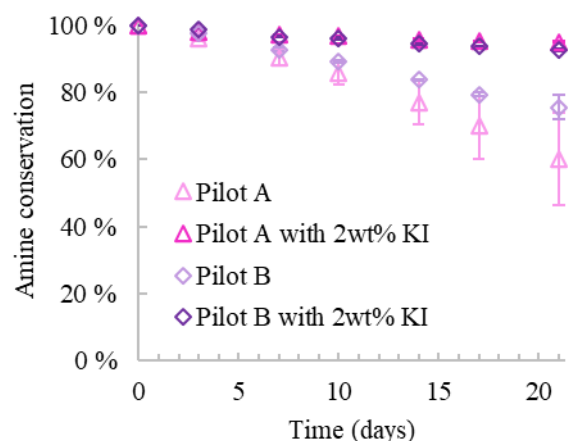

Figure 3: The oxidative stability of pre-used 30wt% MEA (*aq.*) from two pilot scale campaigns, with and without addition of the KI inhibitor.

3.2. The effect of KI concentration on 30wt% MEA (aq.) stability

To assess the concentration of KI necessary to stabilize 30 wt% MEA (*aq.*), two additional sets of experiments were run with 1.0 and 0.2 wt% KI addition to the solvent. As Figure 4 shows, the addition of only 1.0 wt% KI is as effective as 2.0 wt%, but when reduing the concentration to 0.2 wt% the effect is drastically reduced. In the case of 1.0 wt% the experiments were rund for additional three weeks, to investigate whether the degradation inhibition effect decreases with time. The degradation inhibition did not decrease throughout the six weeks under highly oxidative conditions for the 1.0 wt% KI case, where the loss of alkalinity was only 4 ± 1% at the end. The 0.2 wt% KI solution had lost 25 ± 2% alkalinity after three weeks. This indicates that the minimum concentration of KI needed for inhibiting degradation of MEA is ≤ 1.0 wt% and > 0.2 wt%.
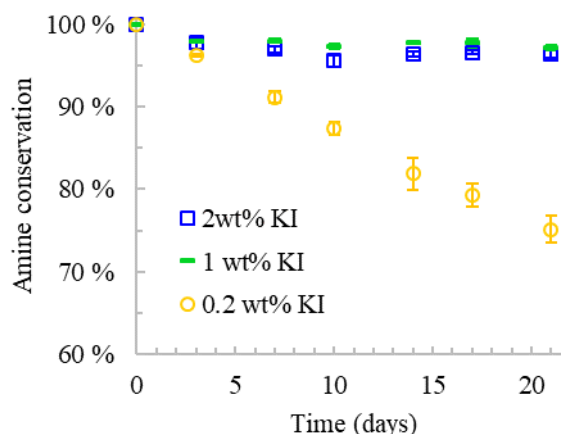

Figure 4: The effect of addition of different concentrations of KI in 30wt% MEA (aq.) under oxidative conditions of 60 °C, with 0.5 mM of Fe^{2+} added and 60 mL min^{-1} O₂ (98%) and CO₂ (2%) added per 200 mL liquid.

Anion chromatographic testing of the concentration in the solution before and after the experiment the 2.0 wt% KI case, showed no difference in the iodide concentration. This, and the linear rate of loss of alkalinity in the 0.2 wt% KI case, suggest that the inhibition effect is not caused by a single-reaction of the iodide with oxygen or that it acts as a scavenger that is used by the oxidant, rather that the stabilization originates from other physical effects. This eliminates the need for inhibitor replenishment in the CO₂ capture process, which is a highly desirable property of the system. It is still unsure whether the iodide oxidized and then is reduced and that this could be the cause of the unchanging iodide concentration and continuous inhibition.[18] Foaming was not observed with any of the 30 wt% MEA (*aq.*) systems, with or without added KI or NaCl.
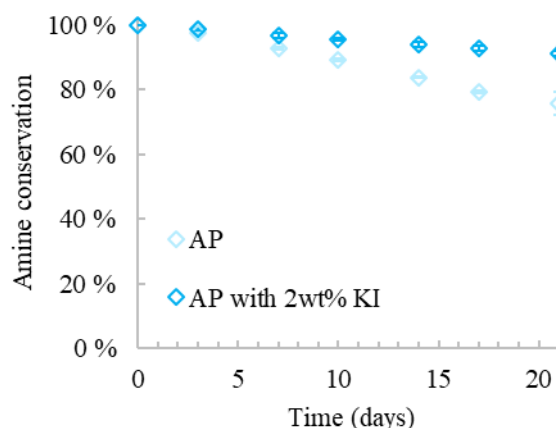
3.3. The effect of KI on 30wt% AP (aq.) stability

Figure 5: Oxidative stability of 30wt% AP (aq.), with and without the addition of 2wt% KI inhibitor.

Also aqueous aminopropanol (AP) is stabilized under oxidative conditions in the presence of the KI inhibitor, as seen in Figure 5, giving reason to suspect that the inhibition effect is independent of the amine in use.

3.4. Effect of KI addition on other properties of the 30 wt% MEA (aq.) solution

Thermal and oxidative degradation mechanisms are independent of one another, so to assure that the addition of salt does not decrease the thermal stability of the amine solution, a set of thermal degradation experiments were performed. The amine loss, given as loss of alkalinity, is shown in Figure 6. It is evident that the addition of KI neither has a positive nor negative effect on the 30 wt% MEA (aq.). seeing as oxidative degradation being the dominating degradation pathway in large scale CO_2 capture by amine scrubbing, the fact the thermal degradation is not inhibited is acceptable.
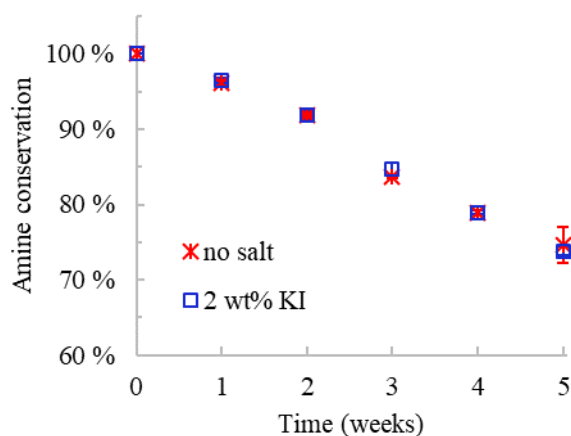

Figure 6: Thermal degradation of 30 wt% MEA (aq.) with and without addition of KI, at 135 °C in 316 cylinders.

The end samples, those degraded at 135 °C for 5 weeks, were analysed by ICP-MS to determine the content of dissolved metals from the 316 stainless-steel cylinders. the addition of 2 wt% KI to 30 wt% MEA (aq.) does not seem to increase the amount of dissolved metals in the solution, on the contrary, the concentration of nickel is lower in the solution containing KI than in that without, as can be seen in Figure 7. This indicates that KI does in fact not increase the corrosivity of the MEA solution.
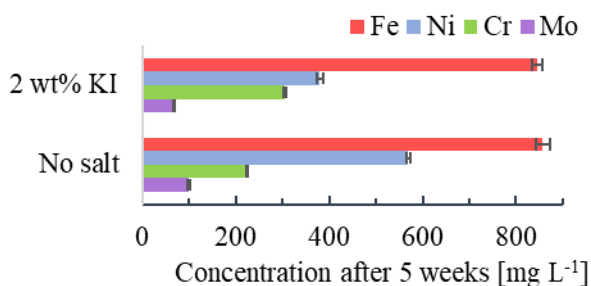

Figure 7: Concentration of metals in the thermally degraded (in closed 316SS cylinders at 135 °C) solutions of 30 wt% MEA (*aq.*) with and without KI.

Furthermore, the viscosity, density and the vapour liquid equilibrium (VLE) properties of MEA with and without 2 wt% KI were studied. None of these properties showed any significant deviations between the two solutions.

3.5. Finalizing remarks and planned work

The inhibition effect seen by KI in MEA seems independent of the presence of degradation products in the solvent. The stabilization of AP shows that KI does not only stabilize MEA and gives reason to expect a similarly positive effect on more amines. The mechanism of inhibition given by KI is still unclear, but it can be expected that an analogous process as suggested in the patent of Sjostrom et al. from 2020[19] takes place also in this place. This includes direct oxidation of iodide to iodine in contact with the oxidizing species in the solution, then a reversed reaction by contact with slightly reducing agents also present. We have, in agreement with Sjostrom et al. not observed that iodide is consumed throughout the process, further supporting this hypothesis.

It can be assumed removing heat stable salts (HSS) from the solvent in the reclaimer will also remove the KI inhibitor. MEA is, however, lost at only a fraction of the rate with inhibitor compared to without. This would mean that the need for reclaiming to keep HSS concentrations in the solvent low enough would also reduce. Despite KI being relatively costly, the lower loss of solvent and lower reclaiming frequency could make up the cost of inhibitor replenishment. Anyhow, the possibility of recovering the salt from the reclamation waste should be evaluated.

The experimental setup, supplying a constant bubbling flow of 98% O_2, as well as continuous agitation by magnetic stirring may not be directly translatable to the conditions in a CO_2 capture facility. It can be argued that the degradation mechanisms must differ a lot to those that are likely to occur under industrial conditions, but these experiments do provide an extremely harsh oxidative environment, under which compounds sensitive to oxidation will degrade. We argue that this alone is indeed a valuable primary tool to assess the stability of an amine before performing cyclic absorption/desorption testing with temperature swing. Testing at cyclic conditions will be the next step in the inhibitor development.

Acknowledgements

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