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Addition of potassium iodide reduces oxidative degradation of monoethanolamine (MEA)

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ABSTRACT

We introduce the addition of stable salts to aqueous MEA as a way of inhibiting oxidative degradation reactions. We performed oxidative degradation studies in aqueous MEA containing sodium chloride (NaCl) and potassium iodide (KI). These "salted amine solvents" have been shortened to SAS. The 2.0 % wt. and 1.0 %wt. KI SAS show remarkable oxidative degradation behavior. Loss of alkalinity after 42 days of oxidative degradation experiments with the 1.0 %wt. KI SAS was of 4%, whereas that of aqueous MEA was of 40% after only 21 days. We evaluated how the addition of stable salts impacts CO_2 solubility, viscosity, and thermal degradation and corrosion behavior and verify negligible deviations from aqueous MEA. Thus, addition of stable salts affects oxidative degradation phenomena without deranging CO_2 solubility or mass transfer rates. With the promising inhibition behavior of KI on MEA degradation, this work presents the initial steps towards making it a commercially viable degradation inhibitor.

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1. Introduction

The use of aqueous amine solvents for CO_2 absorption is the state-of-the-art technology for post-combustion CO_2 capture (Rochelle, 2016). Amine scrubbing is at the forefront of greenhouse gas control techniques for climate change mitigation. However, this is still a very capital-intensive process, and cutting costs is an essential step for large scale deployment (Bui et al., 2018). The expenses associated with amine degradation have been estimated as making up close to 10% of the total cost of CO_2 capture via amine scrubbing (Vega et al., 2014). Oxidative degradation is the most significative degradation pathway for amine loss experienced in industrial CO_2 capture applications (Lepaumier et al., 2011; Vega et al., 2014). Finding a suitable inhibitor for oxidative degradation in aqueous amine solvents is crucial for reducing costs and increasing the feasibility of CO_2 capture technologies.

Degradation is as much an operational as an economic problem, bringing forth operational interruptions, incurring in solvent and plant replacement costs, and increasing emissions, which impacts the environmental footprint of the process. The benchmark solvent for amine-based flue gas scrubbing, monoethanolamine (MEA), is known for its tendency to undergo rapid and uncontrollable oxida-

* Corresponding author. E-mail address: hanna.knuutila@ntnu.no (H.K. Knuutila). tive degradation. Experience from pilot campaigns with MEA proves that degradation is often the reason for ending a campaign (Dhingra et al., 2017).

Mechanistically, oxidative degradation is not as well understood as the thermal degradation pathways within the process, and different routes for the formation of a multitude of identifiable degradation compounds have been suggested (Lepaumier et al., 2009a, 2009b; Vevelstad et al., 2016, 2011). It is commonly accepted that the initial step of the oxidative degradation mechanism is a radical reaction, where the amine reacts with dissolved oxygen originating from the flue gas. Such radical reactions are assumed to be catalyzed by dissolved metals such as iron and copper, which have proven to increase degradation rates in laboratory scale studies (Blachly and Ravner, 1963; Goff, 2005; Sexton and Rochelle, 2009). In the initial reaction step, volatile ammonia and organic acids such as formic, acetic and oxalic acid are formed. These acids can react further with one another or with other amine molecules to create further degradation compounds, and are also known to give rise to corrosion of the construction material (Rooney and DuPart, 2000).

As a means of tackling the issues of degradation and corrosion in CO_2 capture plants, a plethora of degradation inhibitors have been suggested. There are typically three categories of oxidative degradation inhibitors for amine solutions:

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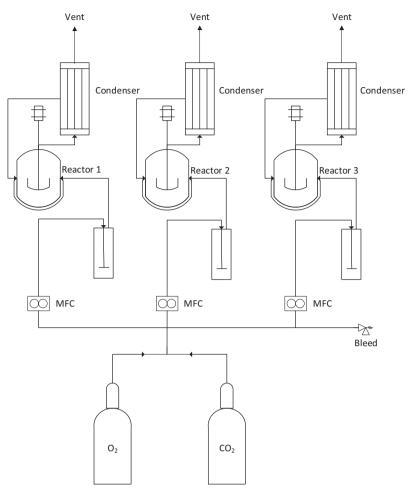


Fig. 1. Schematic of oxidative degradation Setup 1.

- Oxygen or peroxide scavengers;
- Chelating agents;

- Stable salts.

The first approach to finding degradation inhibitors was published in 1964, when Blachly and Ravner tested ethylenediaminetetraacetic acid (EDTA) as a chelating agent for inhibiting the reaction between amine and metals by forming chelate complexes with metal ions. They also successfully proposed bicine as an efficient peroxide scavenger, which proved to be an excellent degradation inhibitor in metal-free solutions (Blachly and Ravner, 1964). Their findings have since been employed for aiding CO₂ separation in nuclear submarines (Blachly and Ravner, 1966, 1965), and EDTA has remained an attractive inhibitor, being thoroughly tested by many researchers (Chi and Rochelle, 2002; Goff and Rochelle, 2006; Lee et al., 2012; Sexton and Rochelle, 2009; Supap et al., 2011). More recently, a number of other chelating agents and oxygen/peroxide scavengers have been assessed in Fytianos et al. (2016).

One big issue with these two categories of inhibitors is that these materials lose effect with time and require replenishing throughout the process. On the other hand, Goff and Rochelle (2006) tested a range of heat stable salts as degradation inhibitors including potassium chloride (KCl), potassium bromide (KBr) and potassium formate (CHKO₂) in concentrations between 10 and 1000 mM, observing a small decrease of ammonia formation rate with both KBr and CHKO₂. The great advantage of salt addition, compared to scavenging additives, is that these salts simply change the properties of the solvent without getting exhausted with time. As such, their need for replenishing is minimal. Another significant advantage of employing stable salts for reduction of amine degradability is their toxicity when compared to many suggested degradation inhibitors, such as reactive vanadium or copper salts. Halide containing stable salts were already pointed out as inhibitors for the oxidative degradation of organic acids by Lee and Rochelle (1987). Their work proved that iodide (I⁻) worked as a powerful scavenger for sulfate (SO₄²⁻), inhibiting its oxidation of the organic acid (Cl⁻ < Br⁻ < I⁻). A recently published patent also identifies iodide as an effective oxidative degradation inhibitor in the context of organic acids (Sjostrom et al., 2020).

In this study, we have analyzed the effects of adding two stable inorganic salts to aqueous monoethanolamine (MEA) solvents. These salts are sodium chloride (NaCl) and potassium iodide (KI). The 30 %wt. MEA (*aq.*) with added salts have been denominated "salted amine solvents", or simply SAS. Their effects have been evaluated in terms of changes in CO₂ solubility both at 40 and 120 °C, shifts in viscosity of loaded and unloaded solvents, and overall effects on oxidative degradation, thermal degradation, and corrosion phenomena in loaded MEA solutions. Our results show that oxidative degradation is inhibited with addition of both salts, and that the salts do not seem to be consumed through the course of our experiments (i.e., their activity in inhibiting amine loss is not lost with time). In the case of potassium iodide, this is achieved without a significant gain in viscosity. Additionally, in neither case is there a significative loss of CO₂ solubility nor an increase in thermal degradation or corrosion phenomena. These results are encouraging for the use of potassium iodide as an oxidative degradation inhibitor in the context of aqueous amine scrubbing.

2. Materials and methods

2.1. Chemicals

Monoethanolamine ("MEA", CAS: 141-43-5, purity \geq 99.0%), ferrous sulfate heptahydrate (FeSO₄·7H₂O, CAS: 7782-63-0, purity \geq 99.0%) and potassium iodide (KI, CAS: 7681-11-0, purity \geq 99.0%) were purchased from Merck Life Science/Sigma Aldrich Norway, and sodium chloride (NaCl, CAS: 7647-14-5) was purchased at a local grocery store and was of the brand JOZO. Oxygen (O₂, N5.0) and carbon dioxide (CO₂, N5.0) gases were purchased from AGA, and deionized water was obtained from a local water purification system at NTNU.

2.2. Oxidative degradation experiments

2.2.1. Setup 1 (three parallel reactors)

Oxidative degradation experiments were performed at absorber conditions in custom made open, water bath-heated, doublejacketed glass reactors (approximately 250 mL) as shown in Fig. 1. The reactor temperature was maintained at 60 °C and the water bath-cooled Graham condensers at 5 °C. Each reactor was filled with 200 mL of the gravimetrically prepared solvent mixture, which was pre-loaded to 0.4 mol of CO₂ per mol MEA and contained 0.5 mM iron sulfate (FeSO₄·7H₂O). A mixture of 98% oxygen (O₂) and 2% carbon dioxide (CO₂) gas was sparged through the solutions at a rate of 60 mL min⁻¹ from Alicat mass flow controllers and through Pyrex[®] glass gas distribution tubes of porosity grade 1, under constant magnetic stirring for the total experimental time of three-six weeks. Empty gas wash bottles were used as safety solvent traps between the mass flow controllers and the gas distribution tubes in case of power outage. Sampling was performed on days 3, 7, 10, 14 and 17 (as well as 21, 28 and 35 for the sixweek experiment), through a septum on top of each reactor. Each experiment was performed in two or three parallels, and the data presented in this work is given as the average values, with the standard deviation of the sample average as uncertainty. Experiments were primarily conducted in Setup 1, but validation was done with Setup 2, against published data for MEA stability.

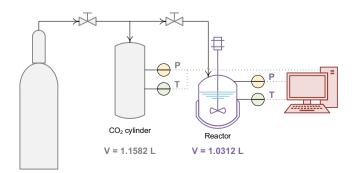


Fig. 2. Schematic of the vapor-liquid equilibrium setup.

2.2.2. Setup 2 (single reactor)

1 L 30 %wt. MEA (*aq.*) with 2.0 %wt. KI, preloaded with 0.4 mol_{CO2} mol_{MEA}⁻¹ and FeSO₄ (1 mM), was added to an open batch setup described in Vevelstad et al. (2016). The setup belongs to SINTEF Industry and consists of a double-jacketed, water-bath heated glass reactor, kept at 55 °C, with a double water-cooled Graham condenser, continuous magnetic stirring and sparging with water-saturated gas (98% O₂; 0.350 L min⁻¹ and 2% CO₂; 7.5 mL min⁻¹). A recycle gas stream (50 L h⁻¹) is bubbled through the solution for increased mass transfer from gas to liquid phase. This is precisely the same apparatus employed by Vevelstad et al. (2016). The experiment was performed for three weeks with regular sampling and the results were compared to that of 30 %wt MEA without addition of iron as given in Vevelstad et al. (2016).

2.2.3. Thermal degradation experiments

Thermal degradation experiments were performed in accordance with Eide-Haugmo et al. (2011) in stainless steel 316 cylinders with diameters of 0.5 in. and volumes of approximately 11 mL equipped with Swagelok[®] end caps. The cylinders were filled with 8 mL of the solution, which was pre-loaded to 0.4 mol_{CO2} mol_{MEA}^{-1} and kept at 135 °C for up to five weeks. Each sampling involved the removal of two metal cylinders per experiment and the analyses of their contents, meaning that the sample taken after three weeks was kept uninterruptedly at 135 °C for three weeks, etc. The cylinders were weighed on a Mettler-Toledo ME204 analytical scale (taring range 0-220 g and readability 0.0001 g) prior to the filling with solution, as well as after the sample was removed, before and after the cylinders were washed with sulfuric acid (H₂SO₄, 0.1 M) to remove iron carbamate (FeCO₃) and other corrosion products from the stainless steel surface. The solutions were analyzed for amine concentration by titration, and CO₂ loading was verified by TIC procedures and sent for ICP-MS analysis.

2.3. Vapor-liquid equilibrium experiments

A schematic drawing of the VLE apparatus employed in this work is shown in Fig. 2. This apparatus and its standard operating procedure are the same as used in past studies by our group (Bernhardsen et al., 2019; Hartono et al., 2017). What follows is a quick recapitulation of what has been reported previously.

The setup consists essentially of a steel cylinder containing pressurized CO₂ and a stirred glass autoclave coupled to a Julabo temperature controller. Fresh solution containing water, amine and salt is prepared gravimetrically and fed to the reactor. This reactor is then vacuumed, so that the vapor phase in the autoclave should consist only of solvent molecules in equilibrium with the liquid phase. The temperature controller is set to its designed setpoint and the stirrer is turned on to approximately 500 rpm. After this setpoint is reached and enough time is given for temperature and pressure to reach equilibrium both inside the CO₂ cylinder and the reactor, the valve connecting these two equipments is opened. Gas flows from the cylinder to the autoclave. Once enough CO₂ is injected, the valve is closed. Once again, one must wait until temperature and pressure reach an equilibrium in both equipments. If required, the CO₂ cylinder must be refilled. A new injection is made when temperature and pressure are stable again, and this cycle is repeated until the autoclave reaches its maximum safe pressure of 600 kPa.

The volume comprised between the two valves and the CO_2 cylinder shown in Fig. 2 has been previously calibrated, and so has the volume comprised between the second valve and the autoclave. The volume of the liquid phase is considered constant throughout the experiment, being estimated by knowledge of the amount of solvent fed to the reactor plus its density, here assumed to be the same density of aqueous MEA 30 %wt. at 40 °C as

obtained by Amundsen et al. (2009). With volumes, temperatures and pressures for both the cylinder and the vapor phase of the autoclave before and after each injection, mass balance calculations can be performed to evaluate CO₂ loadings versus total pressure. In our work, the Peng-Robinson equation of state has been chosen for estimating the molar quantity of CO₂ at all times.

This methodology does not allow for the direct evaluation of CO_2 partial pressures, though these can be obtained by subtraction if one assumes that the solvent vapor pressure is kept constant throughout the experiment. After the procedure is finished, the solvent left in the reactor is titrated so that one can compare if the loading calculated by mass balance is consistent with the loading evaluated analytically. A match of ±3% between these final loading values is considered sufficient for validating our methodology. Additionally, our data is reported in the Appendix with confidence intervals obtained by following the procedure outlined by Wanderley et al. (2020).

2.4. Viscosity experiments

All viscosity experiments carried in this work were undertaken at 25 °C in an Anton Paar MCR rheometer with a double gap measuring cell (Evjen et al., 2019; Hartono et al., 2014; Skylogianni et al., 2019). This apparatus operates at atmospheric pressures. The double gap cell is filled with about 3.6 mL of solvent and semi-closed, so that there is little contact between the solution and the surrounding air and chemical stability can be assumed (i.e. there is negligible loss of CO₂ to the atmosphere even in loaded solutions). Once the liquid is enclosed, a rotor is set in motion. The shear rates in the standard operational procedure vary between 10 and 1000 s⁻¹. A computer connected to the equipment records shear stress versus shear rate values, producing the dynamic viscosity as the slope between these two variables. Hartono et al. (2014) have reported confidence intervals of ±2% for the dynamic viscosities obtained with this procedure, an interval that we assume to be valid for our data as well.

The loaded solvents evaluated in the Section 3.4 were obtained by preparing a fresh solution, loading part of it with CO_2 up to values above 0.5 mol_{CO2} mol_{MEA}⁻¹ and then mixing loaded and fresh solvent in different proportions. After these partially loaded solutions are prepared, they are analytically titrated through the methods explained in Section 2.5. The values reported for the loadings are the values obtained analytically.

2.5. Analytical methods

The concentration of amine in the solutions was determined by titration with sulfuric acid (H₂SO₄, 0.1 M), a procedure with an uncertainty of $\leq 2\%$ according to Ma'mun et al. (2005). The concentration of CO₂ was determined by Total Inorganic Carbon (TIC) analysis, on a Shimadzu TOC-L_{CPH} analyzer, also with an uncertainty of $\leq 2\%$. For all the samples, the concentration of amine is back calculated to the solution without CO₂ and corrected for loss of water assuming a linear loss of water throughout the experiment, as the total mass of the solution is only known for the start and end solutions. The CO₂ loadings reported in this study are simply the ratios between CO₂ and amine concentrations obtained by these two methods.

Inductively coupled plasma mass spectrometry (ICP-MS) analyses were performed on a High Resolution Inductive coupled plasma ELEMENT 2 from Thermo Electronics. The samples were diluted in purified water (18.2 m Ω) from a Merck Millipore ICW-3000TM Water Purification System and digested with HNO₃ prior to analysis. The results were verified against certified reference material and the relative standard deviation (RSD) 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 2.0 %wt. KI SAS oxidative degradation experiments. The instrument used was a Thermo Scientific™ Dionex[™] ICS-5000 IC system, connected to an ICW-3000 Millipore water purification system and equipped with an ASRS300 suppressor (2 mm), a carbonate removal device and conductivity detection. The column was an IonPac AS15 2 \times 250 mm with an AG15 guard column 2 \times 50 mm and column temperature 30 °C. An eluent generator provided a KOH gradient with the profile 13 mM for 10 min, then an increase to 45 mM between 10 and 15 min, kept at 45 mM from 15 to 49 min, then 13 mM for the remaining time. The total run time for each analysis is 60 min. Quantification of iodide concentrations were performed based on calibration in a concentration range of 0-116 ppm of iodide in the form of KI and dilution of the fresh and degraded samples to the corresponding concentration range. Peak areas were used for calculating iodide concentration.

3. Results and discussion

3.1. Oxidative degradation

The addition of both NaCl and KI reduce the oxidative degradability of aqueous 30 %wt. MEA significantly, as shown in Fig. 3. Of the two, KI is the strongest inhibitor of oxidative degradation. Whereas 30 %wt. MEA (aq.) experiences a loss of $40 \pm 4\%$ alkalinity after three weeks under the conditions applied in this work (assumed to directly correlate to the concentration of MEA), the addition of NaCl to the solvent results in a loss of alkalinity of only $24 \pm 5\%$, and the addition of KI reduces this loss to as little as 4 ± 1 %. This shows that the increase of salinity of the solvent has a positive effect in terms of degradability, making MEA less degradable under oxidative conditions. As no significant difference in stability was seen neither between the 2.0 %wt. and 7.5 %wt. NaCl SAS , nor between the 1.0 and 2.0 %wt. KI SAS, it can be inferred that, if the salt employed possesses certain properties, its concentration is of less importance. Moreover, a SAS with 15 %wt. NaCl was tested in the same setup. Although oxidative stability was in the same range as the two other NaCl SAS, the reproducibility of the parallels was low, and that data is not reported in this study. An important factor behind these effects might be that we are approaching a saturation limit of the NaCl in solution, especially if water is lost or

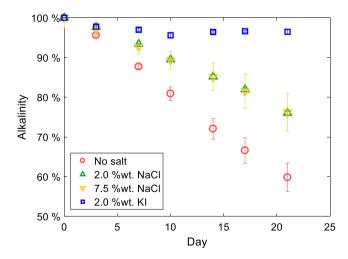


Fig. 3. Amine conservation during the oxidative degradation experiments in Setup 1 with 30 wt%. MEA (*aq*.), with and without salt addition. Absolute amine concentrations back-calculated to CO_2 -free solution, measured and corrected by titration and TIC analysis. Error bars represent standard error of the 2 or 3 parallel experiments.

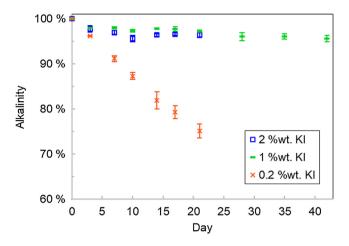


Fig. 4. Oxidative degradation of 30 %wt. MEA (*aq.*) in Setup 1 with different concentrations of KI added. Absolute amine concentrations back-calculated to CO_2 -free solution, measured and corrected by titration and TIC analysis. Error bars represent standard error of the 2 or 3 parallel experiments.

degradation compounds are formed, thus influencing the solubility of the salt. A reduction in KI concentration to 0.2 %wt. gave much more oxidative degradation than the higher concentrations of KI as can be seen in Fig. 4.

As Fig. 4 shows, the degradation inhibition is equally strong with 1.0 %wt. KI as it is with 2.0 %wt. Upon decreasing the concentration to 0.2 %wt. KI, there is a slight degradation inhibition observed, similar to that of the NaCl SAS shown in Fig. 3. It should be noted that also for the 0.2 %wt. KI SAS there is no plateau in the degradation curve and the rate of degradation is steady throughout the experiment. To investigate whether the inhibition effect would wear off with the 1.0 %wt. KI case, if the KI is indeed consumed by the reaction, the 1.0 %wt. KI experiment was run twice as long as the other experiments. After six weeks, no significant amine loss was observed.

In the case of all the KI SAS, it was observed that the typical yellow/orange coloration, characteristic of iron-containing solutions faded away in the course of the three weeks of experiment, while a red precipitate accumulated on the reactor walls. This effect was less visible in the 0.2 %wt. KI SAS than in 2.0 and 1.0 %wt., but still evident. We therefore hypothesize that KI reduces the solubility of iron oxide in 30 %wt. MEA (*aq.*), promoting its precipitation. For this reason, 2.0 %wt. KI SAS was also studied in another oxidative

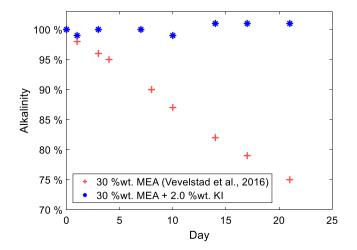


Fig. 5. Validation of oxidative degradation of 2.0 %wt. KI SAS with iron against 30 % wt. MEA (*aq.*) without iron from Vevelstad et al. (2016) in Setup 2.

degradation setup and compared to literature data for pure 30 % wt. MEA (*aq.*, without iron) from Vevelstad et al (2016). The results and comparison are given in Fig. 5. As the literature shows significant degradation of MEA (~25% loss after three weeks) even in the absence of iron, the fact that no significant amine loss was seen in the 2.0 %wt. KI SAS confirms that salting out of metal from the solution is not the only effect causing the solvent to be more stable under oxidative conditions.

Additionally, anion exchange chromatography showed no loss of iodide through the duration of the 21 days of oxidative degradation experiments in the 2 %wt KI case, which indicates that iodide is not being consumed while it inhibits the degradation reactions. The results of this analysis can be viewed in the Appendix.

Since both oxidative degradation setups used in these experiments use continuous agitation of the liquid, both by magnetic stirring (~200 rpm) and bubbling the gas into the solution, mass transfer from gas to liquid phase should not be the limiting factor for whether degradation takes place or not. Setup 2 has the advantage of recycling the gas phase and thereby enhancing the total gas flow into the liquid phase, making mass transfer of oxygen as high as possible throughout the experiment.

We would like to address the hypothesis that the salts might shield the amine from being degraded by being themselves oxidized instead, thus being "sacrificed" for the amine. If the salts are being consumed during the oxidation process, this will decrease their value as inhibitors because of the subsequent need for replenishing. This hypothesis is particularly interesting in elucidating the good performance of potassium iodide, which is known for being readily oxidized (Altshuller et al., 1959).

Fig. 6 shows the amount of amine degradation avoided by employing the SAS. There are three important things to notice in this image. The first one is that the degradation avoided with the use of potassium iodide does not reach a maximum, or a plateau, in the course of the 21 days of oxidation experiments. Such a plateau would have been expected in case of KI consumption, as eventually one would observe iodide depletion in the solvent. For comparison, a plateau does start to appear for the NaCl SAS, though very incipiently. Incidentally, the second point of notice is that, if salt was indeed being consumed in this reaction, one would expect to see different curves for 2.0 %wt. and 7.5 %wt. NaCl – which clearly have very distinct amounts of "reactants". Finally, the SAS prepared in these experiments have very small molar amounts of NaCl and KI. Let us suppose that KI reacts with oxygen in a 1:1 mo-

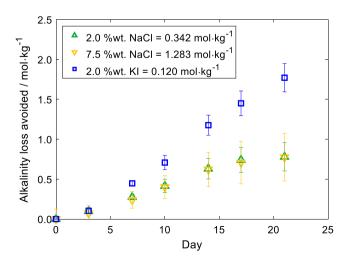


Fig. 6. Avoidance of oxidative degradation brought by the addition of inorganic salts to aqueous 30 %wt. MEA. Error bars represent standard deviations of calculated values with sets of parallel experiments.

lar basis, shielding MEA that would otherwise react with oxygen following an assumed 1:1 stoichiometry. By the end of day 21, having avoided the loss of almost 2 mol kg⁻¹ MEA in the SAS containing 2.0 %wt. KI, one could expect to have instead lost 2 mol kg^{-1} KI. However, this SAS contains merely 0.120 mol kg⁻¹ of KI. If potassium iodide is indeed being consumed by oxygen, it is doing so in a basis far below 1:1 and indeed experiencing no reduction in inhibition capacity, as the lack of a plateau demonstrates. For these three reasons, we do not believe that salt consumption explains the differences in degradation behaviors alone, though it might certainly contribute with them to some extent. Contrary to the previous studies of halides as degradation inhibitors (Lee and Rochelle, 1987), we cannot see that it is a scavenging effect that is seen in these experiments, as the degradation rate is stable over time and iodide concentration is preserved. Conversely, our results agree with the observation by Siostrom et al. (2020) that iodide is not consumed in this process.

The mechanism through which potassium iodide inhibits oxidative organic acid degradation is not very well understood. Both Lee and Rochelle (1987) and Sjostrom et al. (2020) suggest a direct mechanism through which, for example in the context of limestone scrubbing, iodide is oxidized to iodine by reacting with SO_4^{2-} and then reduced back to iodide after reacting with excess sulfite (SO_3^{2-}) (Lee and Rochelle, 1987). Conversely, iodide could also react with some of the metal ions in solution, preventing their activity in catalyzing oxidative degradation reactions (Sjostrom et al., 2020), which could also explain its application in inhibiting corrosion phenomena (Khadom et al., 2018). At any rate, the equilibrium between oxidation and reduction reactions in the solvent would enable iodide to be constantly regenerated in solution without being consumed. There might also exist other effects through which stable salts such as potassium iodide inhibit oxidative degradation. It might be, as Goff and Rochelle (2006) suggest, that these salts are effective simply through salting-out of O₂. A reduction of dissolved oxygen concentrations will surely decrease oxidative degradation rates, explaining the observed phenomena. It could also be that the increase in ionic strength of the solvent upon salt addition affects its molecular structure (Marcus, 2012, 2009a). promoting the creation of rigid solvation shells that are disadvantageous for many radical reaction mechanisms (Marcus, 1964; Marcus et al., 1954). These two phenomena could explain inhibition even when using stable salts that are not known for being easily oxidized.

Whether the degradation inhibition effect seen in the NaCl SAS experiments is sufficient to justify its implementation as a degradation inhibitor on a commercial scale can be discussed. This relatively small effect can possibly be explained by salting out of oxygen, achieving a lower oxygen solubility, although using the Schumpe parameters (Weisenberger and Schumpe, 1996) predicted in Buvik et al. (2020) to calculate the solubility of oxygen in loaded MEA, the relative contributions of NaCl and KI to the salting out of gases is very small compared to that of MEAH⁺ and MEACOO⁻. The fact that iron oxide-like precipitates were not observed in the NaCl SAS also suggests that there is a different inhibition effect taking place here than in KI SAS.

On the process level fears that iodide will be lost upon conventional thermal reclaiming of the spent solvent should be mitigated by the facts that (1) implementation of potassium iodide as a degradation inhibitor could perhaps reduce the need for thermal reclamation to one fourth of the frequency of its current requirement and (2) methodologies for recovery of iodide are known to literature (Sjostrom et al., 2020). At any rate, a feasibility study shall be carried out in the future to evaluate how easy it is to implement these iodide recovery techniques. Since cases of increased foaming upon inhibitor addition in MEA have been observed (Thitakamol and Veawab, 2008), this should therefore be investigated in future tests of KI as a degradation inhibitor.

It will be, of course, crucial to test KI as a degradation inhibitor under more realistic conditions before it should be implemented in the CO₂ capture process. Previous studies of degradation inhibitors have shown that certain inhibitors are only efficient at absorber conditions and lose their properties when tested in a cyclic system (Nielsen, 2018; Voice and Rochelle, 2014). This will therefore be an important next step towards the potential commercialization of the KI inhibitor. However, before testing KI inhibitor on cyclic CO₂ capture systems, one should assess SAS's impact on the vapor–liquid equilibrium (VLE), the viscosity, thermal degradation, and corrosion tendency to ensure that the SAS does not render the solvents unfeasible for CO₂ capture process applications. Results from these tests will be discussed before concluding remarks.

3.2. Thermal degradation

The thermal stability of aqueous MEA with and without added NaCl or KI have no significant difference, as can be seen in Fig. 7. After 5 weeks in stainless steel cylinders at 135 °C, all the four tested solutions had amine/alkalinity losses between 22 and 25%, regardless of the type of salt and salt concentration.

ICP-MS analysis of the end samples in the thermal degradation study shows comparable concentrations of iron (Fe), nickel (Ni), chromium (Cr) and molybdenum (Mo) in all the SAS solutions, as in aqueous 30 %wt. MEA without salt addition (Fig. 8). Only the 7.5 %wt. NaCl SAS shows a significantly higher iron concentration than the other solutions. This indicates that the 2.0 %wt. SAS solutions do not influence the corrosivity of MEA. As a comparison, a cylinder that contained just deionized water was also subjected to thermal degradation conditions for five weeks, and close to no dissolved metals could be detected by ICP-MS.

The cylinders were weighed both after rinsing with water and after 24 h soaking in 0.1 M H_2SO_4 , so that the cylinder mass loss could be used to assess corrosivity in addition to ICP-MS data. The absolute mass losses during the experimental period are very low (<0.05% at most). This is due to the relative total mass of the cylinders of about 170 g. A mass loss due to corrosion in <5 weeks is therefore relatively small, but still a statistically significant difference could be observed between the different salt solutions.

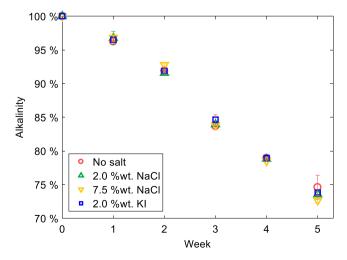


Fig. 7. Amine loss over time in the five-week thermal degradation experiments with 30 wt% MEA (*aq.*), respectively with and without salt addition, at 135 °C. The concentrations given are corrected to CO₂-free solution and error bars represent the standard error of the two parallel samples.

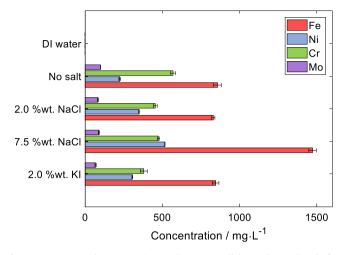


Fig. 8. Average metal concentration in the two parallel samples analyzed after 5 weeks of thermal degradation by ICP-MS. Error bars represent the average relative standard deviation of the analyses.

Fig. 9 shows that the lowest cylinder mass losses are seen in those that contained 30 %wt. MEA with 2.0 %wt. KI, while the highest losses are in those containing 7.5 %wt. NaCl, despite the statistical significance of these measurements being low. According to this test, all solutions seem to induce the same degree of cylinder destruction as salt-free MEA, something that confirms the ICP-MS results. Since this method is sensitive to corrosion-unrelated causes of cylinder loss, such as chipping, it is not a perfect indication of corrosion and shows a relatively high uncertainty.

3.3. Vapor-liquid equilibrium

Fig. 10 shows a comparison between the vapor–liquid equilibria (VLE) of unsalted 30 %wt. MEA with that of SAS both at 40 °C and at 120 °C. The data referring to the unsalted solvent comes from Wanderley et al. (2020). Though the curves shown in Fig. 10 are for CO₂ partial pressure (p_{CO2}) versus loadings (α), we must reinforce that the methodology described in Section 2.3 is able to produce only total pressure versus loading, meaning that the CO₂ partial pressures have to be estimated from the original data set.

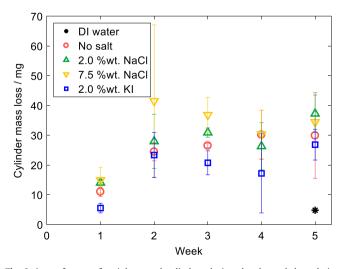


Fig. 9. Loss of mass of stainless-steel cylinders during the thermal degradation experiments with 30 wt% MEA (*aq.*), as well as a set of end-sample cylinders containing only deionized water. Error bars represent the standard error of the two cylinders used for each time of sampling for each solution. The total cylinder mass without solution is 170 g.

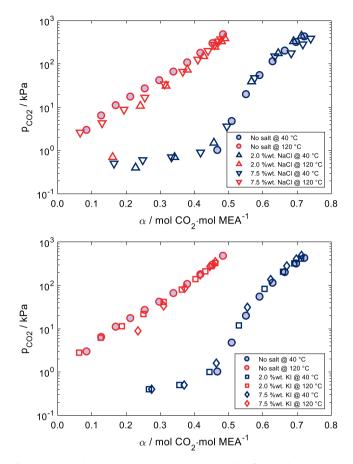


Fig. 10. Estimated CO_2 partial pressure versus CO_2 loading for salted 30 %wt. MEA compared to the VLE for the unsalted amine obtained from Wanderley et al. (Wanderley et al., 2020).

As a result, some data points referring to lower CO_2 partial pressures have to be eliminated since their values end up being smaller than the inherent propagated uncertainties of ±0.34 kPa. Complete disclosure of the total pressures and loadings measured throughout our experiments, together with their uncertainties, can be found in the Appendix to this study.

Once we account for the uncertainties, which are particularly meaningful for the lower CO₂ partial pressure data points, what results from Fig. 10 is nearly an overlap between the VLE curves for the unsalted 30 %wt. MEA (aq.) and the SAS. It is even unclear whether the SAS experience a loss of CO₂ solubility or not. Looking at the blue scattered data points, both for solutions with NaCl and KI, it seems that a small shift in equilibrium towards less CO₂ conversion might be observed with the SAS at 40 °C. As such, both the blue \triangle and \bigtriangledown data points and the blue \Box and \Diamond data points are slightly to the left of the curves for unsalted MEA in top and bottom images alike. There are three outlying points for the SAS with 7.5 %wt. NaCl at 40 °C (uppermost blue \bigtriangledown markers at the top image). In this experiment, we observed precipitation of white solids at high CO₂ pressures, likely of sodium bicarbonate (NaHCO₃). This demonstrates a clear risk of employing too concentrated SAS for CO₂ absorption. At 120 °C, on the other hand, there are indications of a slight *increase* in CO_2 solubility for the SAS, with both the red \triangle and \bigtriangledown data points and the red \Box and \diamondsuit data points falling a bit to the right of the curves for unsalted MEA.

These contradictory small shifts in equilibrium at 40 °C and at 120 °C could imply a very small reduction in cyclic capacity for the SAS. However, it is difficult to interpret Fig. 10 as anything but an overlap of VLEs curves. It appears to us that, other than

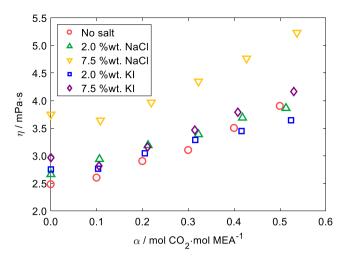


Fig. 11. Viscosity versus CO_2 loading for salted 30 %wt. MEA compared to that for the unsalted amine obtained from Amundsen et al. (Amundsen et al., 2009) at 25 °C.

the caveat of precipitation issues at high NaCl concentrations, one can conclude an insignificant shift in absorption capacity when employing the SAS.

3.4. Viscosity

Fig. 11 shows how the viscosities of SAS increase with loading at 25 °C when compared to that of unsalted 30 %wt. MEA as measured by Amundsen et al. (2009). Once again, the full data set together with its uncertainties is found in the Appendix to this study.

As expected, the addition of inorganic salts promotes an increase in solvent viscosity. This seems to happen both with NaCl, which is structure-making at 25 °C, and with KI, which is structure-breaking (Marcus, 2009b). However, NaCl does indeed increase the viscosity of aqueous MEA more than KI. This is particularly evident in the SAS with 7.5 %wt. salt, wherein the 7.5 %wt. NaCl SAS (yellow \bigtriangledown markers) clearly has the highest viscosity at all loadings while that of the 7.5 %wt. KI SAS (purple \diamondsuit markers) almost overlaps with both the 2.0 %wt. SAS. This might be a consequence of the SAS with KI having lower ionic strength than the SAS with NaCl on account of KI having higher molecular mass than NaCl. KI has a molecular mass of 166.00 g mol⁻¹ compared to 58.44 g mol⁻¹ of NaCl, meaning that the ionic strength of the unloaded NaCl SAS is almost three times as big as that of the unloaded KI SAS. As shown by Esteves et al. (2001), higher viscosities might be attributed to higher ionic strengths.

The viscosity of the SAS with 2.0 %wt. salt is very similar to that of aqueous MEA, and there appears to be even a crossing-over for both 2.0 %wt. NaCl and KI SAS at around $\alpha \approx 0.4$ and 0.5 mol $_{CO2}$ mol_{MEA}⁻¹ respectively (see where the yellow \triangle markers and blue \Box markers overlap with the red stars in Fig. 4). This is a very interesting behavior. In fact, except for the 7.5 %wt. NaCl SAS, the viscosities of the SAS apparently increase less steeply with loading than that of aqueous 30 %wt. MEA. To our knowledge, there is no explanation for this observed behavior in the Debye-Hückel theory (Esteves et al., 2001), which suggests that such phenomena might be attributed to unexpected solute–solute interaction between the inorganic salt electrolytes and the products of the MEA–CO₂ reaction.

In other words, the impact of mixing both inorganic salts to aqueous 30 %wt. MEA (*aq*.) on solvent viscosity is not nearly as noticeable as one would expect. This is good, as it signalizes that transport phenomena in SAS will probably not be significantly depressed due to the addition of salts.

4. Conclusion

The increase in oxidative stability upon addition of just 1.0 %wt. potassium iodide is remarkable. With the KI SAS system we have achieved an oxidative stability comparable to tertiary and sterically hindered amines under the given conditions. Both the tested salts give an increased stability and, based on the salt concentration tested, the type of salt seems to matter much more than its concentration. Regarding thermal stability, no significant difference is observed between the SAS and fresh, salt-free MEA, and in terms of corrosivity the ICP-MS results indicate that the 2.0 % wt. SAS solutions are comparable to salt-free MEA. However, the higher concentration of dissolved iron in the 7.5 %wt. NaCl SAS hints towards a higher corrosion potential when using this formulation.

The addition of stable salts has little effect on the vapor–liquid equilibrium between CO_2 and the solvent (except for the 7.5 %wt. NaCl SAS case, where precipitation was observed at 40 °C). It also has an almost negligible impact on the viscosity of loaded and unloaded solvents at 25 °C, with the potential of becoming completely negligible at higher temperatures. In other words, the reduction of CO_2 physical solubility, the shift in chemical equilibria and the increase in viscosity should not be a cause of concern regarding the SAS.

The nature of the phenomena behind this reduction in degradation potential with potassium iodide is yet to be properly understood. Future studies are required to assess if there is indeed no salt depletion during the oxidation of the solvent. The KI SAS is a promising degradation inhibitor for absorption-based CO_2 capture based on the current results. However, to further validate its applicability, testing in cyclic systems and pilots is needed.

CRediT authorship contribution statement

Vanja Buvik: Conceptualization, Methodology, Investigation, Writing - original draft, Writing - review & editing. **Ricardo R. Wanderley:** Conceptualization, Methodology, Investigation, Writing - original draft, Writing - review & editing. **Hanna K. Knuutila:** Conceptualization, Writing - review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cesx.2021.100096.

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