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## Low Toxic Corrosion Inhibitors for Amine-based CO<sub>2</sub> Capture Process

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### Abstract

This work evaluated inhibition performance of a low toxic corrosion inhibitor, namely sodium thiosulfate, on carbon steel in 5.0 kmol/m<sup>3</sup> monoethanolamine (MEA) solution at 80°C and 0.55 mol/mol CO<sub>2</sub> loading. Effects of corrosion inhibitor concentration and process contaminants, including formate and chloride, on inhibition performance were studied. The results show that sodium thiosulfate significantly reduced corrosion rate with an inhibition efficiency of up to 94% in short term exposure tests, but did not perform well in long term exposure tests due to the instability of passive film. Its inhibition efficiency was not affected by the presence of chloride and formate.

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### 1. Introduction

Corrosion in amine-based carbon dioxide (CO<sub>2</sub>) capture processes is one of the most serious operational problems affecting safety and process economics [1]. Both uniform and localized corrosion can be found within the process due to elevated temperature, high CO<sub>2</sub> loading in solution, CO<sub>2</sub> gas flashing, high solution velocity and the presence of contaminants and degradation products in the solution. Several corrosion mitigation methods, such as use of corrosion-resistant materials of construction, proper process and equipment design, and corrosion inhibitor, are commonly recommended to be applied alone or in combination. The use of corrosion inhibitor is the most economical and flexible compared to other methods since it can be applied to the existing process without requiring any major process modification [1-3]. To date, a number of chemicals have been patented as corrosion inhibitors for

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amine-based acid gas treating plants. However, the effective ones including vanadium are toxic heavy metals. Their usage is restricted owing to more stringent environmental regulations particularly in the last few decades which consequently made their disposal and handling costly and difficult. This led to a shift in trend towards the use of low toxic corrosion inhibitors. The objective of this work is therefore to evaluate an corrosion inhibitor that are non-heavy metals and less toxic than conventional corrosion inhibitors and CO<sub>2</sub> absorption solvents while effective in corrosion inhibition.

## 2. Experiments

In this work, the inhibition performance of sodium thiosulfate was experimentally evaluated in a three-electrode corrosion cell using electrochemical techniques including cyclic potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). A series of corrosion experiments were carried out using 5.0 kmol/m<sup>3</sup> monoethanolamine (MEA) solution saturated with CO<sub>2</sub> at 80°C. Carbon steel 1018 was used as the test specimens. The sodium thiosulfate was also tested in a weight loss corrosion cell for 28 days. Surface analysis by SEM and XRD was also carried out to identify types of corrosion and corrosion products.

## 3. Result and Discussion

### 3.1. Electrochemical behavior

#### 3.1.1 Absence of process contaminants

Corrosion rates of carbon steel in the sodium thiosulfate inhibited MEA systems with no process contaminant were in the range of 0.26 - 0.38 mmpy when the corrosion inhibitor concentrations were 250 –10000 ppm with corresponding corrosion inhibition efficiencies of 91-94% (Fig. 1). From the potentiodynamic polarization analysis (Fig. 2), two different behaviors depending on the concentration of corrosion inhibitor can be observed. When the corrosion inhibitor concentration was 250 or 500 ppm, the metal was in active state. The anodic current densities were higher and the cathodic current densities were lower than the uninhibited condition. At higher corrosion inhibitor concentrations (1000 – 10000 ppm), the metal was in passive state. The passive film was unstable and black. This could be a result of the adsorption of thiosulfate (S<sub>2</sub>O<sub>3</sub><sup>2-</sup>) ions. The corrosion inhibition was anodic in nature. No trend between corrosion rate and corrosion inhibitor concentration was found. No pitting tendency was induced by the presence of sodium thiosulfate at any concentration.

Polarization resistances (R<sub>p</sub>) obtained from the impedance analysis of the sodium thiosulfate inhibited MEA systems were in the range of 174–995 ohm-cm<sup>2</sup> (Fig. 1). A relationship between R<sub>p</sub> and concentration of corrosion inhibitor could be observed. In addition to a semicircular loop characteristic of charge transfer kinetics at the interface, the low frequency end (the right end of X axis) of the spectrum was marked by linearity (diffusion tail) suggesting a passive film formation over the metal surface. This might be due to the adsorption of thiosulfate molecules (S<sub>2</sub>O<sub>3</sub><sup>2-</sup>) which limits the diffusion of corrosive species across the interface. At a corrosion inhibitor concentration of 250 or 500 ppm, it can be observed that the diffusion tail was not as pronounced (Fig. 1) as in higher concentrations (1000 – 10000 ppm).

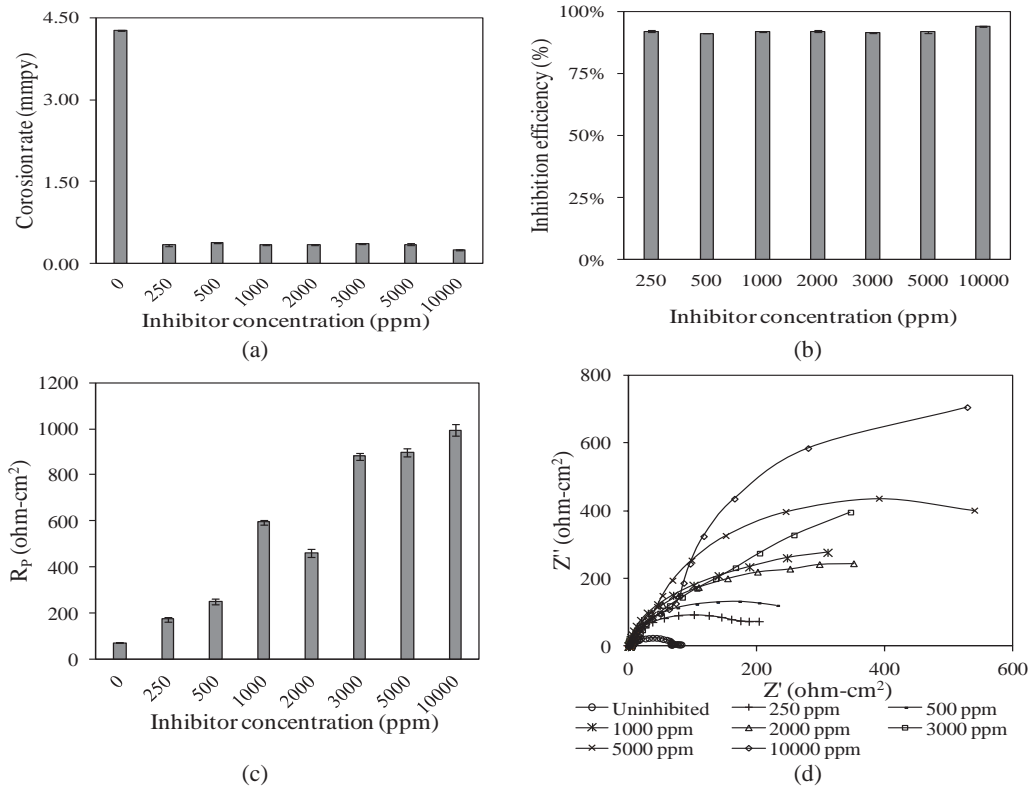


Fig. 1. Corrosion behavior of sodium thiosulfate inhibited MEA solutions (5.0 kmol/m<sup>3</sup> MEA, 80°C, 0.55 mol/mol CO<sub>2</sub> loading, no process contaminant) (a) Corrosion rate, (b) Inhibition efficiencies, (c) Polarization resistance, and (d) Impedance behavior

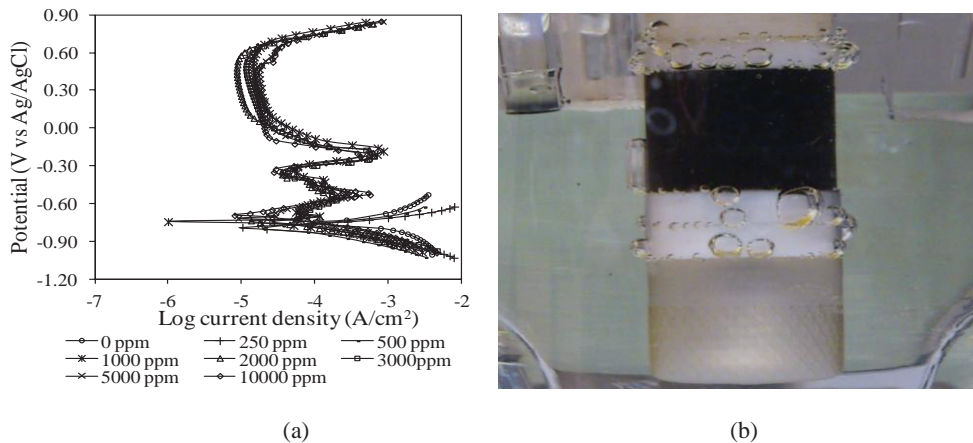


Fig. 2. (a) Polarization behavior of sodium thiosulfate inhibited MEA solutions (5.0 kmol/m<sup>3</sup> MEA, 80°C, 0.55 mol/mol CO<sub>2</sub> loading, 1000 ppm sodium thiosulfate with no process contaminant), and (b) Working electrode after stable open circuit potential

### 3.1.2 Presence of process contaminants

In the presence of chloride and formate, the corrosion rate of the sodium thiosulfate inhibited MEA system was reduced to a value of 0.05 and 0.07 mmpy compared to the 'No contaminant' corrosion rate of 0.35 mmpy (Fig. 3). Corrosion inhibition efficiency in the presence of chloride and formate was 99%. But from the potentiodynamic polarization behavior (Fig. 3), it can be observed that, even though the metal tends to passivate at lower anodic current densities compared to 'No contaminant' condition, the passive layer was highly unstable. As the initial passive layer breaks down, an increase in anodic current densities were observed which was followed by a repassivation. This cycle repeats without the formation of a stable passive layer throughout the anodic polarization suggesting that the passive layer may not be protective in presence of process contaminant. No pitting tendency was induced by the presence of process contaminants.

Polarization resistances ( $R_p$ ) obtained from the impedance analysis in the presence of chloride and formate were 889 and 974 ohm-cm<sup>2</sup> respectively, which was higher than the 'No contaminant' condition (594 ohm-cm<sup>2</sup>) (Fig. 3). This was in agreement with the lower corrosion rates obtained from potentiodynamic polarization analysis. Impedance behavior in the presence and absence of the process contaminants were similar in trend characterized by the presence of a diffusion tail suggesting that the metal is in passive state. The unstable nature of the passive layer in the presence of process contaminants could not be predicted mainly because the impedance analysis is carried out at the equilibrium potential of the metal unlike potentiodynamic polarization.

### 3.2. Weight loss behavior

In the MEA solution inhibited by sodium thiosulfate, loose corrosion product could be visually observed during the removal of specimen. From SEM images (Fig. 4), two distinct types of corrosion products were visible; loose and bulk corrosion product on the outer surface and relatively fine and intact corrosion product beneath that. Large quantity of sulfur (29%) was characterized by EDS analysis (Fig. 4) suggesting the presence of sulfur based corrosion product on the surface. Sodium thiosulfate can potentially decompose into hydrogen sulfide (H<sub>2</sub>S) at the tested condition which implies that the corrosion product can be speculated to be iron sulfide based on the EDS results. However, based on XRD results (Fig. 4), Fe<sub>3</sub>O<sub>4</sub> was characterized to be the primary component of the surface layer along with the presence of Fe. So iron sulfide might be present in an amorphous phase. The corrosion product was less protective in nature as the corrosion inhibition efficiency was only around 10%.

## 4. Conclusion

Sodium thiosulfate is an effective corrosion inhibitor in a short term exposure with an inhibition efficiency of 91-94% at a concentration range of 250-10000 ppm. However it can be ineffective in a long term exposure due to the instability of its passive film. Its performance is not deteriorated by the presence of chloride and formate.

## Acknowledgements

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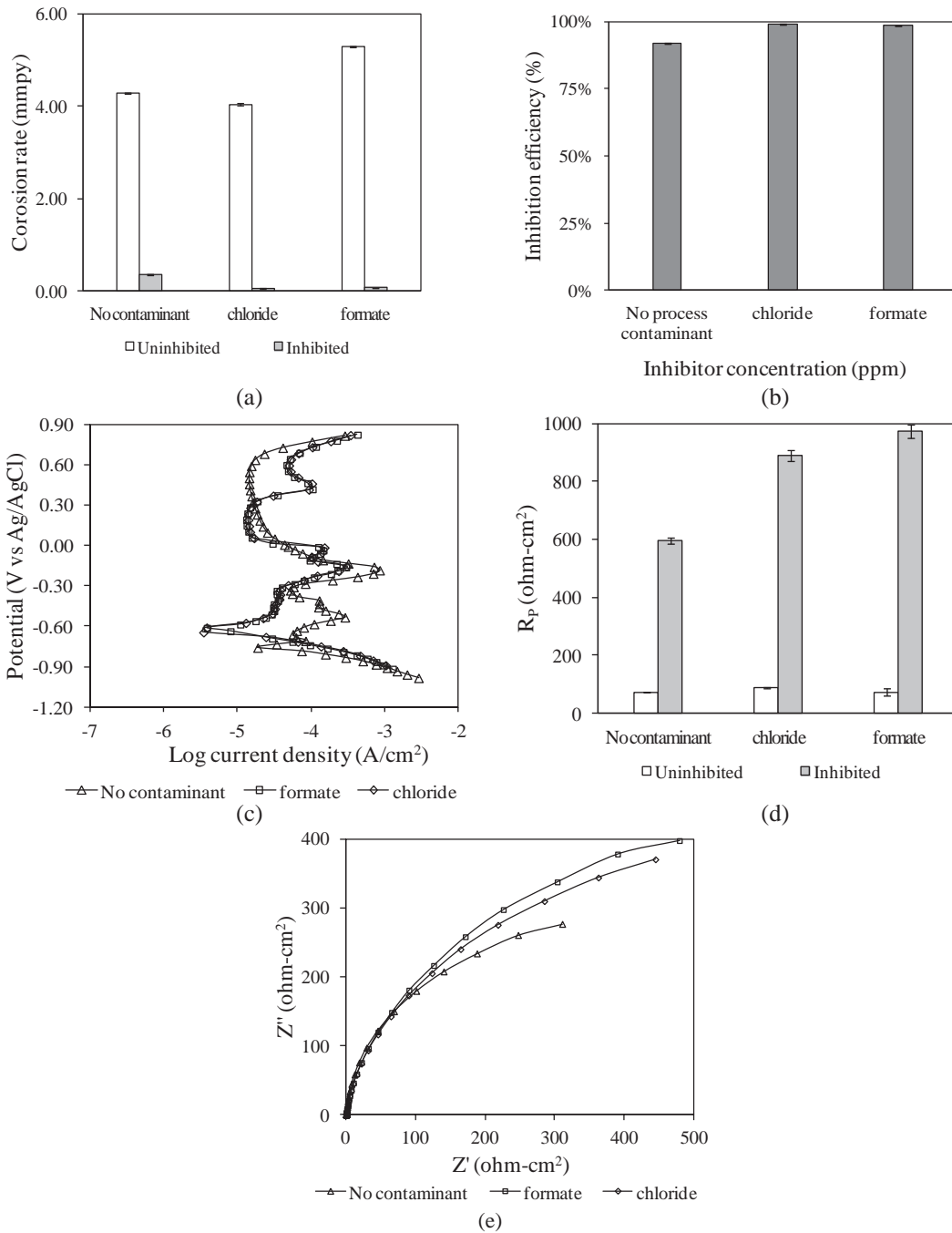


Fig. 3. Corrosion behavior of inhibited MEA solutions with and without process contaminants (5.0 kmol/m<sup>3</sup> MEA, 80°C, 0.55 mol/mol CO<sub>2</sub> loading, 1000 ppm sodium thiosulfate) (a) Corrosion rate (b) Inhibition efficiencies (c) Polarization behavior (d) Polarization resistance (e) Impedance behavior

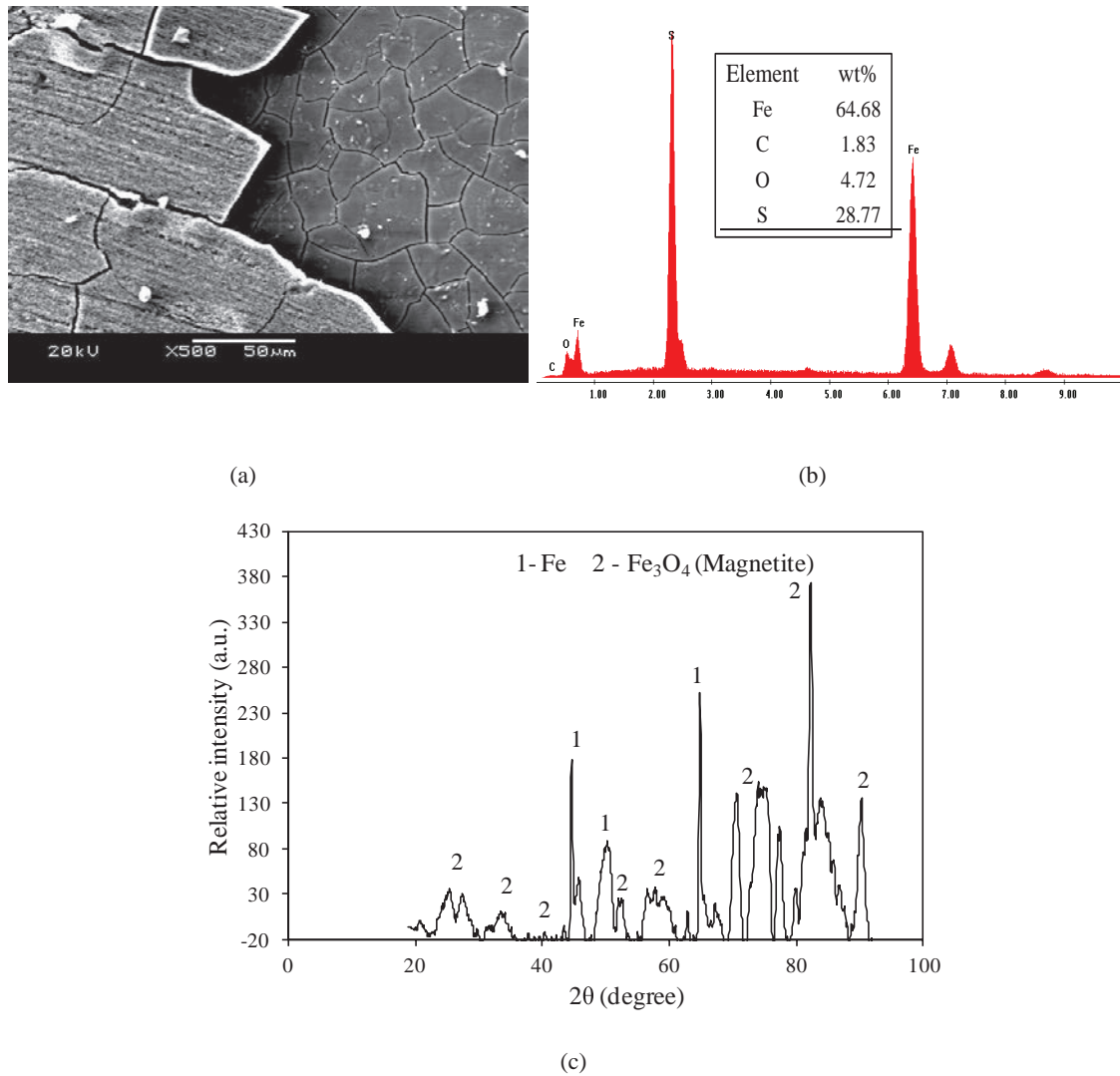


Fig. 4. Surface analysis of tested specimen after 28 days ( $5.0 \text{ kmol/m}^3$  MEA,  $80^\circ\text{C}$  and  $0.55 \text{ mol/mol CO}_2$  loading, 1000 ppm sodium thiosulfate) (a) SEM images (500X Magnification) (b) EDS spectra (c) XRD spectra

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