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Ethylated Amine Role in the Inhibition of Top of Line Corrosion in Marginally Sour Environments

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Abstract

Carbon steel pipelines used in oil and gas transportation suffer from top of line corrosion (TLC). This persistent issue endangers the safety of the pipeline network. Corrosion at 10-2 o'clock position could occur as a result of the condensation process of water vapor containing CO_2 and H2S acidic gases. Due to the difficulty of reaching inhibitors to the top of the pipeline, this type of corrosion represents a big challenge to the oil and gas industry. The injection of corrosion inhibitors is a typical method for corrosion mitigation. The conventional corrosion inhibitors employ in the petroleum industry are non-volatile liquids, and they hardly reach to the top of the pipeline where the condensed water which contains corrosive species, for instance, CO_2 and H_2S is accumulated. Rendering this mitigation technique unable to prevent the TLC, therefore, TLC is a major challenge in the oil and gas industry. This study details the work carried out to develop an inhibitor performance and presents a novel volatile corrosion inhibitor that prevents the TLC in marginally sour environments. An innovative glass cell setup was designed and applied in the study, to simulate the TLC process in conditions similar to field experience and to improve the experimental data quality. Weight loss measurement technique was conducted to find the TLC rates in the presence and the absence of the volatile corrosion inhibitor. The gas-phase concentrations of H_2S started from 0.015 of up to 0.15 mbar. . Upon injection of the inhibitor, the results showed that the developed inhibitor could effectively mitigate and reduce the corrosion rate at the top of the pipe which suggests its potential application in the oil and gas industry.

Keywords: Corrosion inhibitor, top of the line corrosion, inhibitor, ethoxylated amines.

1. Introduction

Since most oil and gas fields are located in remote areas, for economic reasons, carbon steel pipelines are commonly employed to transport large volumes of crude oil and gas to storage facilities, refineries and treatment plants. Maintaining transmission pipeline integrity represents one of the crucial challenges facing oil and gas companies **[1-3].**

When unprocessed wet natural gas is extracted from the oil well, it consists of a combination of oil, gas, brine, and solid [4] . The presence of brine in mixture with various dissolved acidic gases such as CO_2 and H_2S results in serious corrosion problems to the internal surface of oil and gas pipelines. Corrosion issues arise when these gases manifest themselves through different mechanisms, some of which are severe and difficult to control. One of these corrosion types is a top of line corrosion (TLC) and it is the most recently discovered type of corrosion, as it was first recognized in the 1990s **[5-7]**.

The specific case of TLC occurs at the upper part of wet gas pipelines as a result of the condensation process of water vapor in the gas phase containing dissolved acidic gases. Condensation occurs when temperature differences exist between the gas inside the pipeline and the external environments. When the flow regime is stratified and lacks effective thermal insulation, saturated water vapor condenses on the cooler inside surface at the top of the pipeline and forms small water droplets saturated with aggressive acidic gases and lead to severe corrosion problems **[8].**

In stratified flow regimes, non-volatile liquid inhibitors cannot reach to the upper part of the pipeline and remain at the bottom of the pipe. This leads to the formation of a protective layer around the lower surface of the pipe and effectively inhibits corrosion development. However, the top part of the pipe will be susceptible to corrosion.

Therefore, for TLC mitigation, there is no means to use conventional inhibitors unless the inhibitor proposes some volatile properties and able to evaporate then condense at the top of the pipe together with the water.

Researches have been conducted to develop volatile corrosion inhibitors (VCIs) and an acceptable protection level was achieved **[9]**. VCIs are complex mixtures of several compounds in particular ratios that are capable to vaporize and condense on a metallic surface to mitigate the TLC of carbon steel pipelines which are exposed to the corrosive environment **[10]**. A wide range of VICs have been used in oil and gas transportation to minimize the TLC, for example, triethylenetetramine, methoxypropylamine, pyridine salts, methyldiethanolamine (MDEA), and mono ethylene glycol (MEG) **[11, 12]**.

In the oil transportation fields, there are two main categories of TLC: sweet and sour corrosion, depending on whether TLC is dominated by CO_2 or H_2S. Sweet corrosion refers to the corrosion that occurs in the presence of CO_2, whilst sour corrosion is associated with the presence of H_2S.

However, the specifics of the corrosion mechanism in the marginally CO_2/H_2S environments can be quite different compared to a CO_2-dominated environment. A limited amount of studies have focused on the understanding and control of TLC in a marginally CO_2/H_2S environment. Therefore, the focus of this paper is to investigate the performance and efficacy of VICs in marginally sour environments since it represents the real-life for many oil and gas fields.

2. Mechanism of inhibition

The corrosion inhibition mechanism involves the adsorption of the long hydrocarbon chain, of non-ionic surfactants, to the electrode surface through hydrophilic interactions of oxygen, nitrogen, and sulfur atoms Furthermore, the hydrocarbon chains modify their conformation and reduce the contact area to minimize the interactions between the molecules themselves or with water molecules **[13]**.

Miksic et al [**14**] and Putilova et al **[15]** proposed in their studies that the optimum corrosion inhibition is mainly influenced by two properties of VCIs, the inhibitor functional groups, which are responsible for the adsorption, thickness and the adsorbed film inhibition efficiency, and the VCIs hydrophobic properties, which maintain the pH at the interface between the metal and the inhibitor on the alkaline side.

Balezin et al. [**16**] suggested an inhibition mechanism which is shown in خطأ! لم يتم العثور على مصدر المرجع. The adsorption on the metallic surface is attributed to the functional group R1 that is linked to the nucleolus group R_0. Moreover, the thickness and the protective efficacy of the adsorbed film are determined by R_2 which is also linked to the nucleolus group R_0.

Ethoxylateamines are non-ionic surfactants which are formed from the reaction between the aliphatic amine and ethylene oxide gas. As a result of their high water solubility, ethoxylateamines act as wetting agents, solubilizers and play a vital role in the film-forming of corrosion inhibitors formulation **[17]**. The film coats the metal surfaces and forms a barrier between the metal surface and the corrosive medium. This film works as an auxiliary film-former and surfactant together with other film-forming agents **[18]**.

Various aliphatic amines extracted from animal fats are appropriate components for ethoxylation reactions such as tallow amines. The latter consists of eighteen-carbon compounds and it is solid at room temperature and poorly soluble in water. Ethoxylation of tallow amines converts them into a liquid state and enhances their solubility. The higher degree of ethoxylation results in higher solubility of the component in aqueous solvents **[13]**.

There are two possible ways by which volatile inhibitors transfer to the metal surface. First, before inhibitors reach the metal surface, they are dissociated then saturate the air layer next to the metal surface with the protective groups. Secondly, without prior dissociating, the VCIs molecules are dissociated once they rest on the metallic surface [**19**].

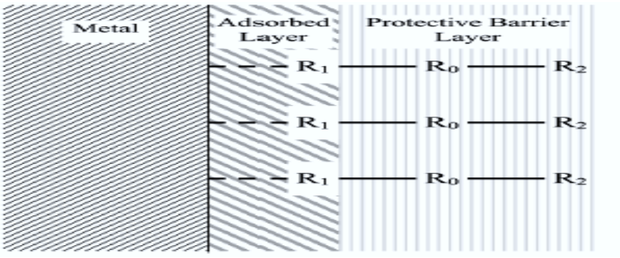


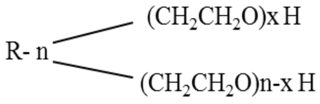
Figure. 1 Schematic representation of the inhibition mechanism of a corrosion inhibitor [**17**].

3. Material and experiment

Inhibitor Development and Materials

The inhibitor consisted of a volatile compound of a conventional gas pipeline corrosion inhibitor, (morpholine which has a chemical formula of $O(CH_2CH2)_2NH$) blended with different concentrations of volatile ethoxylated amine. The ability of the inhibitor to prevent TLC in slightly sour environments was evaluated by conducting numerous corrosion tests.

To determine the inhibitive performance of the investigated inhibitor, weight loss corrosion measurements were performed for the test coupons. The measurements were carried out with and without the addition of inhibitor and according to the ASTM standards [20]. The H_2S concentrations in the gas-phase started from 0.015 to 0.15 mbar Table 1 lists the test matrix for the TLC experimental work. The ethoxylated amine is represented by the following formula:



$$R\text{-}\,n \begin{cases} (CH_2CH_2O)x\,H \\ (CH_2CH_2O)n\text{-}x\,H \end{cases}$$

where R denotes the alkyl radical, n is the number of moles of ethylene oxide. API 5L X65 carbon steel is the steel used to made test coupons for weight loss measurements. The chemical composition of carbon steel is provided in Table 2. 1% wt of NaCl was dissolved in deionized water then was saturated with CO_2.

4. Experimental Setup and Procedures

Two of one-liter glass cell setups were used to assess the efficacy of the inhibitor under TLC conditions in Figure. 2.

Since the condensed water has a very low conductivity and due to the discontinuity of the water phase over time especially under a low condensation rate **[21]**, it is very challenging to implement electrochemical measurements in TLC conditions. Thus, the mass loss technique was used in this instance to measure the time-averaged corrosion rates. The coupon samples were polished by 300, 600 and 1200 grit sandpapers then rinsed in deionized water and isopropanol and air-dried before mounted to the glass cell lid. In all the conducted experiments, the bottom solution was deionized water containing 1 wt % NaCl

Table 1 Test matrix for Top of Line Corrosion in CO_2/H_2S environments.

Total pressure, bar	1
The partial pressure of CO_2, bar	0.85
NaCl	1 wt%
Solution temperature at the bottom	72±1°C
Gas temperature	60±1°C
Sample temperature	32±1°C
Water condensation rate, $mL/m^2/s$	1.34 ±0.122
Inhibitor concentrations, ppm/vol	0-500
The partial pressure of H_2S, mbar	0-0.15
Test Duration	24 hours

Table 2 Chemical composition of weight loss steel samples **[21].**

marginally sour environments at atmospheric pressure. A schematic diagram of the experimental setup is illustrated in

Element	**C**	**Nb**	**Mn**	**P**
	0.13	0.03	1.16	0.01
Element	**Ti**	**V**	**Ni**	**Fe**
	0.01	0.04	0.04	balance

To achieve condensation conditions, cooling coil of copper was placed around each test coupon then water circulated inside it to reach the desired sample holder temperature. A hot plate was employed to attain a satisfactory temperature and to heat the bottom solution.

The condensed water volume, the test duration volume, and the exposed surface area of the test coupons were measured, and the condensation rate of water was calculated.

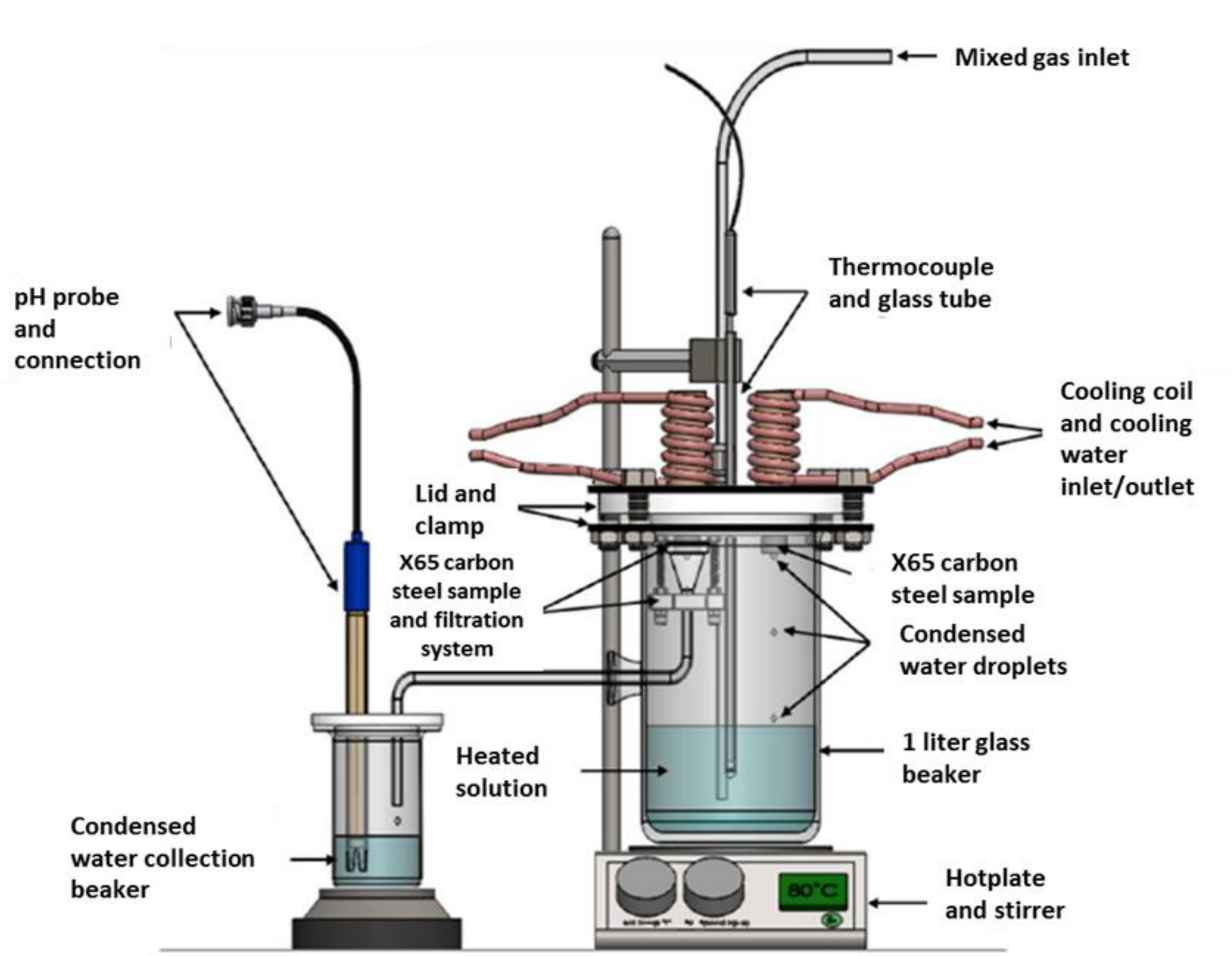


Figure. 2 Schematic of the glass cell experimental set up used in experiments

Once the experiment was finished, the coupons were removed from the system, rinsed with deionized water and isopropanol, and air-dried. Test coupons were then reweighed before the corrosion product was removed using Clarke's solution (1000 ml of Hydrochloric acid, 20 grams of Antimony trioxide (Sb_2O_3) and 50 grams of Stannous chloride($SnCl_2$) **[20]**. Coupons were then weighed for a final time to find out the mass of corrosion products if formed on the steel surface.

The used test coupon was a cylindrical coupon of 1.2 cm thickness and 2.2 cm diameter with a 3.8 cm2 area was exposed to the test solution To measure the surface temperature of the coupon, a hole of 2 mm diameter was drilled through the center of the sample holder up to 1 mm of the coupon for a temperature probe to be inserted. A drop of oil was placed into the bottom of the hole to provide consistent surface temperature readings. To avoid any galvanic effect resulting from the direct contact, the sides, and the top of the samples, the sample holder, and the specimens were coated on the sides and top with Teflon paint hence only one surface was exposed to the test solution.

The bulk aqueous fluid was composed of deionized water deoxygenated two hours prior to starting the experiment by purging with nitrogen gas. Subsequently, by using a rotameter, CO_2 and H_2S gases were mixed to reach the required concentration of H_2S, as shown in Figure 3, and the solution was then transferred to the test cell. A colorimetric gas detector tube was used to measure the concentration of H_2S in the gas phase regularly during the experiment to confirm that the concentration remains constant.

To treat the gas coming out of the system and remove the H_2S gas, a carbon scrubber was used. A schematic illustration of the overall setup of TLC testing is shown in Figure 3.

The condensed water was collected in a collection cup which was directly placed below one of the test samples and diverted immediately into a sealed collection vessel. The collected condensed water was maintained at the same temperature as the sample surface to determine the condensation rate and the pH of the condensed water.

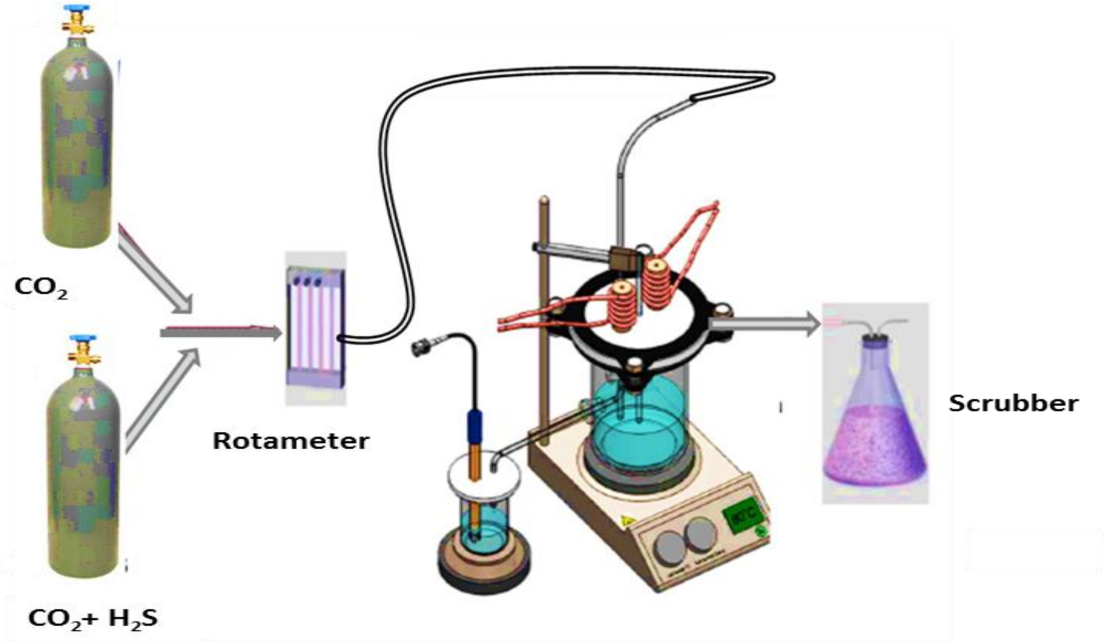


Figure. 3 Schematic of the overall set up for the TLC used in experiments.

5. Results

The corrosion protection efficacy of ethoxylated amines at the top of wet gas pipelines in marginally sour environments was tested. In order to achieve the inhibitor evaluation, a rig of two glass cells was used as shown in Figure 2. The results obtained are listed in Tables 3-7 and are presented in Figure 4. The percentage inhibition efficiency (IE%) of the inhibitor to mitigate the TLC in sour marginally environments was determined by using the equation below:

$$IE\% = \left(\frac{CR_u - CR_i}{CR_u}\right) * 100\%$$

where CR_u and CR_i are the calculated TLC rates in the absence and presence of the corrosion inhibitor respectively. To assess the H_2S partial pressure effect on the TLC rates, mass loss experiments were carried out at a constant condensation rate of 1.34 ml/m^2.s and in the presence of various inhibitor concentrations for 24 hours.

H_2S Partial pressure of 0 mbar:

Table 3 presents the data for the top line corrosion rates of the steel sample in free H_2S concentrations. It was found that the general corrosion rate of the steel under the environment containing CO_2 only was 1.82 mm/y. Nevertheless, with the addition of 50 ppm of the inhibitor (ethoxylated amine), the corrosion rate was reduced to 1.42 mm/y. When the inhibitor concentration was raised to 100 ppm, no significant variation was observed in the general TLC rate of the coupon sample. With the increase of the inhibitor concentration to 500 ppm, the protection efficiency was improved for more than 50%.

Table 3 H_2S concentration of 0 mbar

Dose rate of the inhibitor (ppm/vol)	Corrosion Rate (mm/y)	IE %
blank	1.82	-
50	1.42	22
100	1.33	27
150	1.16	36
250	1.04	43
500	0.83	51

H_2S partial pressure of 0.015 mbar:

The test matrix related to the experiments at H_2S partial pressure of 0.015 mbar was summarized in Table 4. The result showed that the uninhibited corrosion rate was relatively high at 1.44 mm/y. When 50 ppm of corrosion inhibitor was added, the TLC rate reduced to approximately 1.04 mm/y and about 24% protection. Consequently, the test was repeated with 100, 150, 250 and 500 ppm inhibitor dose rate. At 100 ppm, the inhibitor minimized the TLC rate to the value of 0.92 mm/y. At 150 ppm, the reduction in corrosion rapidly decreased and the corrosion rate became approximately 0.82 mm/y. At a dose rate of 250 ppm, the inhibited TLC rate further reduced to less than 0.7 mm/y. Finally, at the end of the test, when the 500 ppm of inhibitor was added, the corrosion rate reached its minimum value of about 0.66 mm/y which equates to more than 55% corrosion protection.

Table 4 H_2S concentration of 0.015 mbar

Dose rate of the inhibitor (ppm/vol)	Corrosion Rate (mm/y)	IE %
blank	1.44	----
50	1.04	24
100	0.92	35
150	0.82	42
250	0.7	49
500	0.61	55

H_2S partial pressure of 0.03 mbar

Table 5 summarizes the entire series of experiments performed at 0.03 mbar H2S partial pressure with various corrosion inhibitor concentrations. It was found that when 50 ppm of inhibitor was added, the TLC reduced from 1.32 to 0.95 mm/y which produced an increase in the percentage of protection up to 28%. The corrosion rate was further decreased from 0.95 mm/y to 0.26 mm/y when 100 ppm of the inhibitor was applied. At the end of the test, 500 ppm of the inhibitor was added, the TLC rate was reduced considerably to 0.55 mm/y and the protection percentage increased to approximately 58%.

Table 5 H_2S concentration of 0.03 mbar

Dose rate of the inhibitor (ppm/vol)	Corrosion Rate (mm/y)	IE %
blank	1.32	-
50	0.95	28
100	0.82	38
150	0.75	43
250	0.64	51
500	0.55	58

H_2S partial pressure of 0.08 mbar

In all the tests conducted under 0.08 mbar, the TLC rate decreased as the corrosion inhibitor dose rate increased as presented in Table 6. The TLC rate was reduced from 0.72 mm/y at 0 ppm to less than 0.27 mm/y at 500 ppm. Interestingly, the inhibitor resulted in about 62 % corrosion protection when 500 ppm of the inhibitor was added.

Table 6 H_2S concentration of 0.08 mbar

Dose rate of the inhibitor (ppm/vol)	Corrosion Rate (mm/y)	IE %
blank	0.72	----
50	0.48	33
100	0.44	39
150	0.38	46
250	0.33	54
500	0.27	62

H_2S partial pressure of 0.15 mbar

The TLC rates obtained under pH_2S of 0.15 mbar conditions are shown in Table 7 below. The result showed that under no presence of the corrosion inhibitor, the coupon sample was corroded at a rate of 0.65 mm/y. From the table, it is clear that as the corrosion inhibitor concentration increases, the TLC rate decreases. For example, when 50 ppm of the inhibitor was added, the TLC rate minimized and reached a value of 0.4 mm/y. Further increase of the inhibitor concentration to 100 ppm led to a reduction in the corrosion rate to be 0.35 mm/y. The TLC rate was decreased significantly to 0.22 mm/y at the dose rate of 500 ppm. In other words, the addition of 500 ppm, inhibitor demonstrates an inhibitive effect on the top of line corrosion at the given experiment environment.

Table 7 H_2S concentration of 0.15 mbar

Dose rate of the inhibitor (ppm/vol)	Corrosion Rate (mm/yr)	IE %
blank	0.65	---
50	0.4	38
100	0.35	46
150	0.32	51
250	0.27	58
500	0.22	66

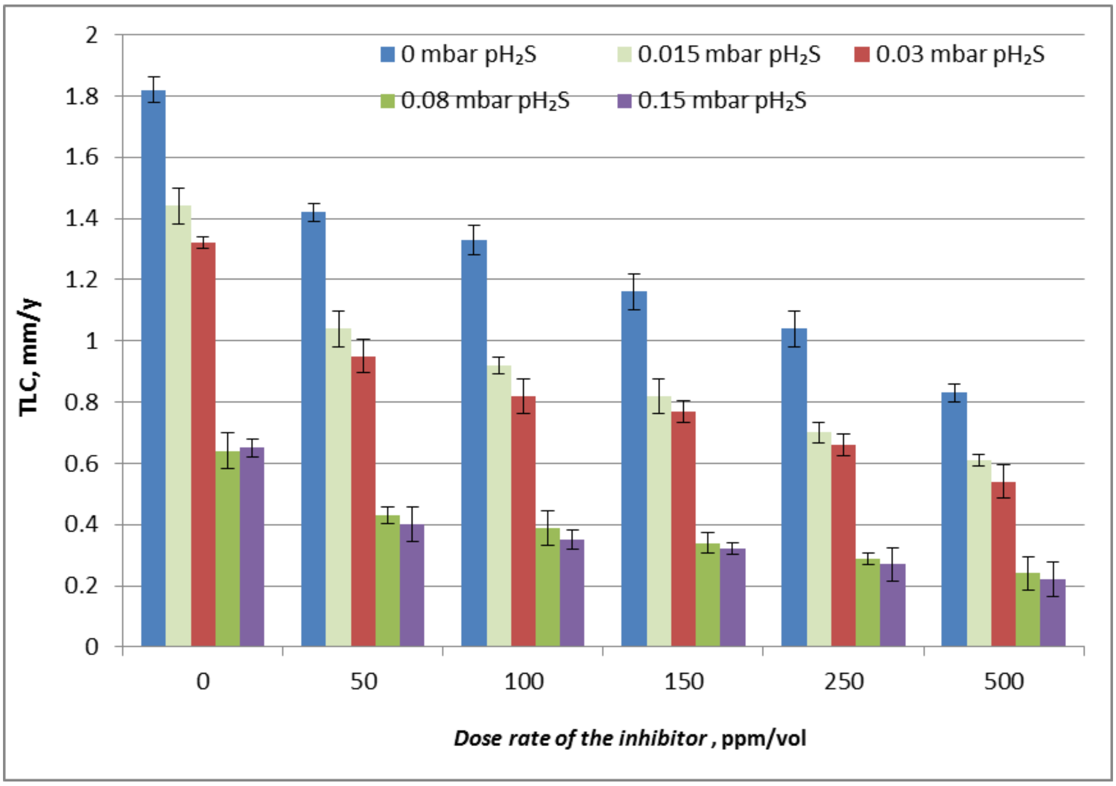


Figure .4 Top of line corrosion rates versus corrosion inhibitor dose rates at varying H_2S partial pressures.

6. Discussion

A volatile corrosion inhibitor was modified in this work. Besides, a new apparatus was designed and manufactured for this research, which allows for the investigation of TLC in conditions similar to the real oil field conditions. Importantly, the volatile inhibitor was required to have a sufficiently low boiling temperature to ensure it is fully present in the vapor phase. Across all of the experiments which have been conducted at different H_2S partial pressures and for all the dosage rates of the corrosion inhibitor, one distinct trend was observed in the corrosion rate response. The top line corrosion rates decreased with increasing corrosion inhibitor concentrations, as shown in Tables 3-7 and Figure 4.

In sour environments, it is possible to hypothesize that when the evaporated amine dissolves in the condensed water at the top of the line, it may increase the pH of the solution, which leads to decreasing the corrosion rate **[22]**. To confirm this hypothesis, the condensed water was drained to a liquid collector funnel which was at a position directly below one of the samples and collected into a closed collection cup, then the pH of the condensed water was in situ measured. Figure 5 and Figure 6 show the pH measurements at 0 and 0.15 mbar H_2S partial pressure respectively.

The results reveal that the protection efficiency level creased by increasing the pH of the solution. For example, at pH_2S of 0.15 mbar, the average pH of the condensed water increased from 4.3 in the absence of inhibitor to 4.8 after the addition of 500 ppm of the inhibitor.

Interestingly, it was observed that the highest corrosion protection efficiency was obtained at the highest pH_2S of 0.15 mbar, at which the corrosion inhibitor provided excellent corrosion protection. For example, at the dose rate of 50 ppm of the inhibitor, the TLC rate reduced from 0.65 to 0.4 mm/y and as the dosage increased to 500 ppm the corrosion dropped to be less than 0.22 mm/y. This indicates that at high pH_2S partial pressure, the inhibitor successfully migrated from the aqueous phase to the vapor phase and easily condensed on the sample. At these conditions, the H_2S can be combined with the amine to form stable products and forms a protective barrier on the steel surface providing protective properties to the metal, leading to a decrease in the corrosion rate.

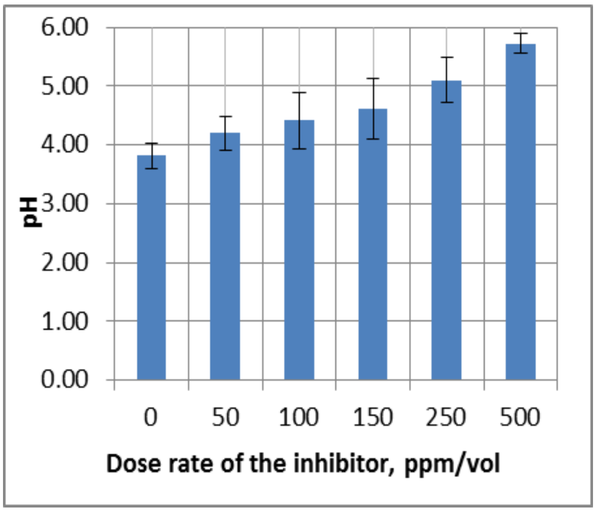


Figure. 5 pH measurements at the condensed water as a function of the dose rate at no presence of H_2S and condensation rate of 1.34 $mL/m^2/s$

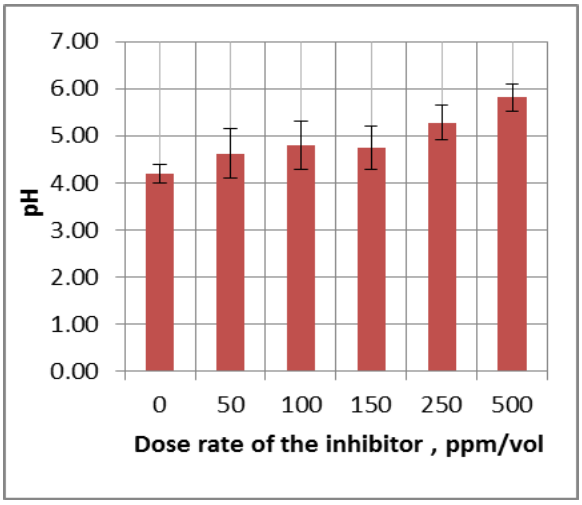


Figure 6.pH measurements at the condensed water as a function of the dose rate at pH_2S of 0.15 mbar and water condensation rate of 1.34 $mL/m^2/s$

7. Conclusions

In this research, weight loss measurements were successfully performed to test the efficacy of a volatile inhibitor and to aid the understanding of corrosion inhibition mechanism of the top of the line in marginally sour conditions. The developed test methodology provides a reasonably simple and quick procedure to evaluate volatile inhibitor efficiency in mitigating a TLC in marginally H_2S environments.

Based on the obtained results, the inhibitor (ethoxylated amines) could effectively mitigate the top of the line and significantly reduce the corrosion when the volatile inhibitor was injected and applied in a small apparatus. Moreover, acceptable inhibition efficiencies were achieved in the laboratory under the selected conditions.

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