

Study of Inhibition Efficiency of Model Volatile Corrosion Inhibitors in the Presence of n-Heptane

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ABSTRACT

Volatile corrosion inhibitors (VCIs), such as thiol- and amine- based formulations, can be used to mitigate top of the line corrosion (TLC) that occurs during transportation of wet gas via transmission pipeline. However, the presence of condensable hydrocarbons can compromise VCI inhibition efficiency. This phenomenon can be related to the higher solubility of VCIs in the hydrocarbon phase, compared to water, which leads to a deleterious partitioning effect. This partitioning can happen both in the bulk fluid at the bottom of the line, hindering the evaporation of VCIs, and in any condensed hydrocarbon phase at the top of the line, leading to a decrease in the availability of VCI molecules. The presence of condensable hydrocarbon can even lead to the VCI desorption from the steel surface. The inhibition efficiency of three VCI mixture combinations for TLC scenarios was studied in the presence and absence of n-heptane, as a representative liquid hydrocarbon phase. A mixture of thiols (decanethiol and hexanethiol) and two mixtures of thiol and amines (decanethiol and diethylamine/t-butylamine) were considered. In the presence of n-heptane, only the thiol mixture, where the molecules involved had different tail lengths, conferred high inhibition efficiency. This behavior was attributed to the superior inhibition efficiency provided by thiol-based molecules with a shorter carbon tail (hexanethiol) in the presence of n-heptane. It was further demonstrated that the decanethiol and amine mixtures did not provide any improved corrosion inhibition with n-heptane in the system.

Key words: VCI, n-heptane, thiols, amines, inhibitor mixtures.

INTRODUCTION

Top of the line corrosion (TLC) is a phenomenon encountered in the transportation of wet gas, where temperature differences between the pipelines and the surroundings lead to condensation of water and subsequent metal degradation. This kind of corrosion occurs due to the condensation of saturated vapors present in the unprocessed gas stream which collects on the internal surface of the cold pipe wall. The condensed liquid contains hydrocarbons and water. It forms a thin film and/or droplets of liquid on the pipeline. The condensed water phase can be, at least initially, very corrosive to typical pipeline (made of carbon steel), because it contains dissolved acid gases (such as carbon dioxide [CO₂] and hydrogen sulfide [H₂S]) and organic acids (such as acetic acid [CH₃COOH]).¹

The TLC corrosion mechanism is not different from what occurs in the bulk liquid phase.² However, TLC holds important specificities that make its mitigation difficult and the occurrence of localized corrosion likely. TLC depends on fluid temperature, flow regime, water condensation rate, CO₂/H₂S content, and organic acid concentration.¹ The rate of uniform corrosion rate is initially quite high but tends to decrease with time due to the release of ferrous ions in the condensed water and the consequent increase in pH. When saturation of ferrous ions in the condensed water is reached (depending on the system temperature), the precipitation of the corrosion product layer (FeCO₃) occurs. Thermodynamically, precipitation of FeCO₃ occurs once the saturation level ($S_{FeCO_3} = [Fe^{2+}][CO_3^{3-}]/K_{sp,FeCO_3}$) is above one.¹ In the mentioned equation, $K_{sp,FeCO_3}$ is the solubility product and a function of temperature and ionic strength. During the TLC process, freshly condensed water, free of iron ions, continues to dilute the existing electrolyte. Since the chemistry of the solution is continuously altered, the protectiveness of the FeCO₃ layer is constantly challenged as well and localized corrosion is inevitable, although its extent is variable.¹

In stratified flow regimes (that are favorable for TLC), conventional CO₂ corrosion inhibitors cannot be used to protect the top of the line since they will not reach the upper surface of the pipe.³ Therefore, volatile corrosion inhibitors (VCI) are used to mitigate corrosion of equipment parts exposed to the vapor phase.⁴ The mitigation provided by VCIs depends on the nature and surface charge of the metal, the type of aggressive media present, the molecular structure of the inhibitor, and the nature of its interaction with the metal surface.⁵ For instance, if the steel surface is charged positively (versus the potential of zero charge [PZC]), and if the VCI is a thiol, the interaction between the permanent dipole of the thiol head group (R-SH with negative charge on the sulfur [S] atom) and the steel surface should be favorable, leading to adsorption due to the electrostatic interaction.

Finding the correct balance between volatility and inhibition efficiency is complex. Determining the optimal functional group, that will define the adsorption mechanism, and the right length of the alkyl tail are also challenging. The most common VCIs contain functional groups such as amine, imine, amide, and thiol.

Based on the available literature (mainly performed at the Institute for Corrosion and Multiphase Technology),^{3,5,6} decanethiol is one of the most effective VCIs and can significantly reduce localized and uniform TLC of carbon steel under sweet and sour conditions. Under specific experimental conditions, decanethiol in particular, and other thiols such as hexanethiol, were shown to be more efficient than amines in reducing the corrosion rate. This is because the amines are almost all protonated in the pH range tested (3.8), therefore their vapor pressure, and consequently their concentration in the condensed water, are very low and cannot provide significant inhibition.⁷

One of many challenges associated with TLC mitigation is the interference of hydrocarbons with VCI inhibition. It has been shown that in the presence of n-heptane, decanethiol loses its inhibition efficiency and shows very poor persistency.^{3,6}

The aim of the present study is to compare the corrosion inhibition by different thiols in a water/n-heptane co-condensing environment. Moreover, the potential synergistic effect of VCI mixtures is also investigated in hydrocarbon containing environments.

EXPERIMENTAL PROCEDURE

Setup and test matrix

The specimens of a 1018 (UNS⁽¹⁾ G10180) steel with a ferritic-pearlitic microstructure were used for the experiments. The nominal composition of this steel is provided in Table 1.

Table 1
Nominal composition of UNS G10180 carbon steel samples

	C	Mn	P	S	Nb	Cr	Ni	Mo	Cu	Al	Si	V	Ti	Fe
Composition (wt%)	0.17	0.66	0.007	0.02	0.002	0.073	0.06	0.04	0.14	0.04	-	-	-	Bal

The steel specimens were machined into a cylindrical shape, with a diameter of 3.15 cm and 1.15 cm height. One of the faces and sides of the specimen were covered with Xylan® coating, leaving an exposed area of 7.79 cm². The exposed surface was polished up to #600 grit using silicon carbide (SiC) abrasive papers. They were then ultrasonically cleaned in isopropanol for 5 minutes, and dried.

The experimental setup was a 4 L glass cell especially designed for TLC experiments. Figure 1 depicts the schematic of the mentioned setup. 2.5 L of deionized (DI) water was poured into the glass cell and sparged with CO₂ for 2 hours to facilitate deoxygenation and electrolyte saturation. In the experiments that included n-heptane, the volume of DI water was reduced to 1.7 L and 0.8 L of n-heptane was added to the glass cell after the 2-hour period of CO₂ sparging. In this case, sparging was continued for another hour to purge any remaining oxygen from the system.

During CO₂ sparging, the solution was heated to 75 °C using a hot plate which led the gas temperature to reach to ~ 65 °C. The effect of the evaporation of the solution were minimized using a condenser on top of the glass cell setup (Figure 1). After the desired solution temperature was reached, 600 ppm_v of acetic acid and 400 ppm_v of each of the selected inhibitor(s) were added to the solution. The specimen (referred to as weight loss (WL) specimen in Figure 1) was subsequently inserted into the lid, being flush-mounted to its underside; thereby exposing its polished surface to the wet gas phase. To control the water condensation rate, the specimen was cooled to the temperature of 56 °C by circulating water through a heating/cooling system. The water condensation rate (WCR), with or without inhibitor, was 0.1±0.03 mL/m²/s under this condition. This rate was calculated by measuring the volume of the condensed water accumulated in the cup that was placed underneath the specimen during the experiment (see [Figure 1]). In the presence of n-heptane, all other conditions being the same, a significant amount of the heat transfer rate is used to condense the hydrocarbon, leading to a substantial decrease in the water condensation rate. Prior works in similar environments⁸ have shown that n-heptane condensation is roughly seven times higher than water. Under the experimental conditions of this study, it can be anticipated that the water condensation rate could be as low as 0.01 mL/m²/s in the presence of n-heptane. In addition, the partial pressure of CO₂, in the experiments with n-heptane, would also be lower than those without (~0.8 bar for pure water experiments vs. ~0.6 bar for the experiments with water

⁽¹⁾ UNS numbers are listed in Metals and Alloys in the Unified Numbering System, published by the Society of Automotive Engineers (SAE International) and cosponsored by ASTM International.

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and n-heptane, based on the gas temperature). These considerations point to the lower corrosiveness in environments containing n-heptane, as compared with the pure water systems.

The test matrix is summarized in Table 2. The temperature of the gas, the solution, and the steel specimen were monitored during the experiment. Each experiment was 3 days long. All chemical used in this study were of analytical grade.

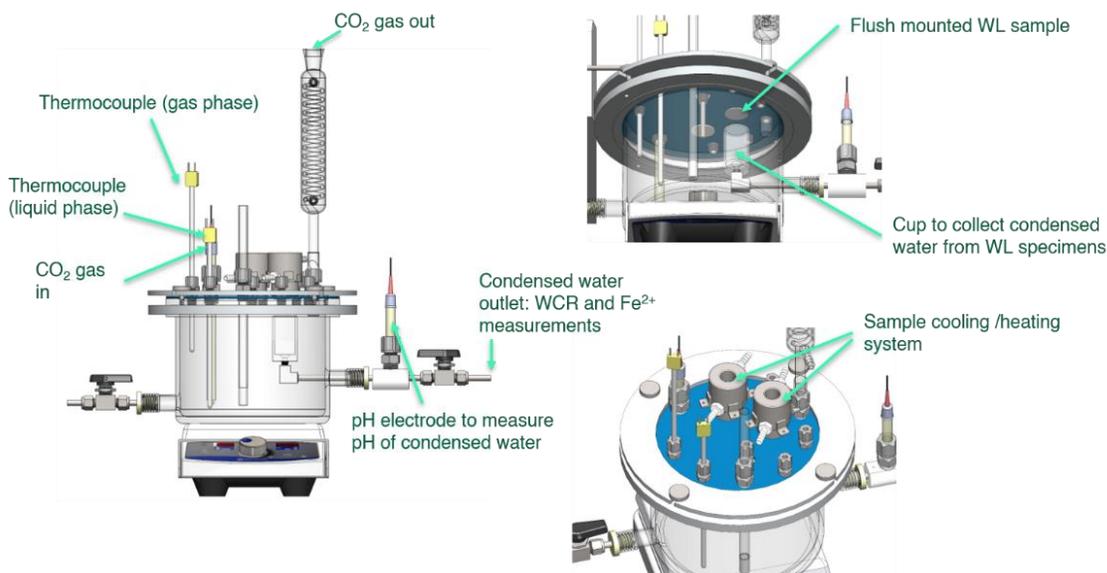


Figure 1: The glass cell setup for the TLC experiments.

**Table 2
Test matrix of glass cell experiments**

Test ID	Decanethiol (ppm _v)	Hexanethiol (ppm _v)	Diethylamine (ppm _v)	t-Butylamine (ppm _v)	n-Heptane (L)	Acetic acid (ppm _v)
B	0	0	0	0	0	600
B-Hep	0	0	0	0	0.8	600
D	400	0	0	0	0	600
D-Hep	400	0	0	0	0.8	600
H	0	400	0	0	0	600
H-Hep	0	400	0	0	0.8	600
D- H	400	400	0	0	0	600
D- H-Hep	400	400	0	0	0.8	600
D-Di	400	0	400	0	0	600
D-Di-Hep	400	0	400	0	0.8	600
D-t-B	400	0	0	400	0	600
D-t-B-Hep	400	0	0	400	0.8	600

* Acronyms: B: Blank, D: Decanethiol (C₁₀H₂₂S), H: Hexanethiol (C₆H₁₄S), Di: Diethylamine (C₄H₁₁N), t-B: t-Butylamine (C₄H₁₁N), Hep: n-Heptane (C₇H₁₆)

** All concentrations are based on total liquid volume.

Post characterization

After each experiment, the corrosion products on the corroded specimens were removed using Clarke solution, according to ASTM Standard G1-03.⁹ The specimens were then rinsed with DI water followed by isopropanol and subsequently dried with nitrogen (N₂). The corrosion rate was calculated using the

difference between the initial and the final weight of each specimen before the experiment and after the Clarke solution cleaning. The following equation was used:¹⁰

$$CR = 87600\Delta m/\rho At \quad (1)$$

In this equation CR is the corrosion rate (mm/y), Δm is the mass difference (g), ρ is the density of carbon steel (7.874 g/cm³), A is the exposed area (cm²), t is the immersion time (h), and 87600 is the conversion factor. In addition to the corrosion rate obtained from the weight loss measurements, the maximum penetration rate for each specimen was determined using the optical profilometry data of the maximum penetration depth and a simple proportion calculation. This maximum penetration rate can be used to quantify the extent of localized corrosion:

- if the maximum penetration rate is higher than the average corrosion rate, localized corrosion is likely occurring,
- if the maximum penetration rate is lower than the average corrosion rate, then the specimen suffers from uniform corrosion and the maximum penetration rate is just a representation of surface roughness.

After the corrosion tests (before and after Clarke solution cleaning), surfaces of the specimens were characterized using scanning electron microscopy (SEM, JEOL JSM-6090⁺), energy dispersive X-ray spectroscopy (EDS) and optical profilometry.

RESULTS

Values of corrosion and maximum penetration rates related to the first 6 TLC experiments (as described in Table 2) are plotted in Figure 2.

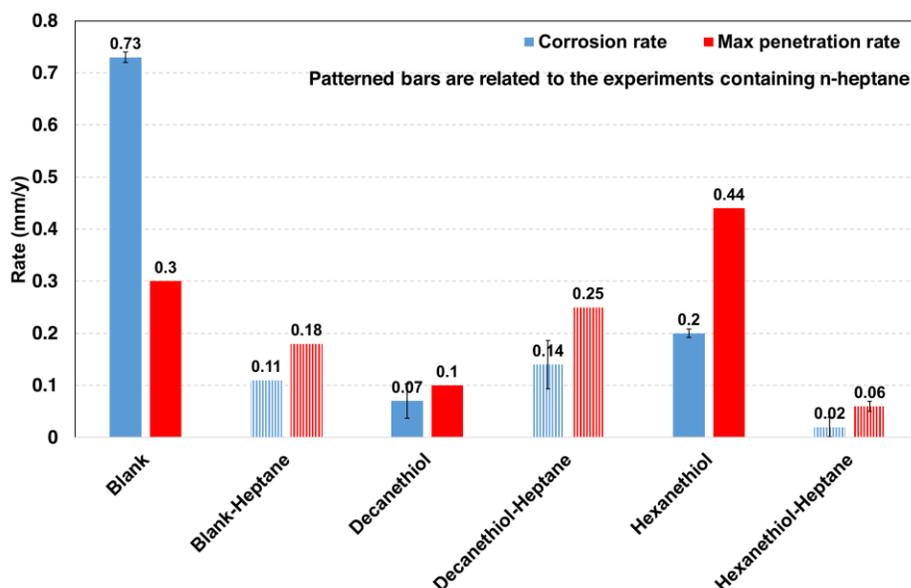


Figure 2: Results of corrosion rate for different TLC experiments (the error bars represent standard deviation).

Table 3 summarizes the results of inhibition efficiency (IE) for decanethiol and hexanethiol in the presence and absence of n-heptane. The IE was calculated using the following equation:

⁺ Trade name.

$$IE (\%) = \frac{CR (blank) - CR (inhibited)}{CR (blank)} \times 100 \quad (2)$$

Table 3
Inhibition efficiency for decanethiol and hexanethiol in the presence and absence of n-heptane

	Decanethiol	Decanethiol- Heptane	Hexanethiol	Hexanethiol- Heptane
IE (%)	90	0	72	82

Regarding the blank experiments (i.e., the experiments without inhibitors), the bar chart in Figure 2 shows that the presence of the hydrocarbon phase (n-heptane) decreases the average corrosion rate. However, this conclusion can be misleading. As mentioned above, the environment is significantly less corrosive in the presence of the hydrocarbon phase (lower WCR and lower pCO₂). The decrease in the average corrosion rate in the presence of a condensable hydrocarbon phase, such as n-heptane, can also be attributed to the change in the water wetting of the steel surface or to the change in the water chemistry of the system. In the following analysis, the experiments with inhibitors in water-only environments are compared to the blank experiment (water-only) while the experiments with inhibitors in water-heptane environments are compared to the blank-heptane experiment.

According to a study by Pojtanabuntoeng, et al.,⁸ in a hydrocarbon-free system, the corrosive condensed water wets the entire surface and the TLC rate increases with the water condensation rate. However, in the presence of n-heptane, which condenses at a rate seven times faster than water, n-heptane wets most of the surface resulting in the segregation of water droplets. In such scenarios, the change in the water droplet chemistry can lead to a rapid formation of FeCO₃. More importantly, the surface areas covered by the condensed n-heptane are protected from corrosion, while the areas wet by the aggressive condensed water experience localized corrosion at a relatively high rate.

The change in water wetting in the presence of n-heptane is reflected in the optical profilometry results shown in Figure 3. According to Figure 3 (b), in a water/n-heptane system, the areas of the surface that were wet by the condensed water can be recognized by a deeper corrosion attack compared to adjacent areas that were covered by n-heptane and therefore were not corroded. As expected, a larger fraction of the surface is covered by n-heptane. Note that, according to Figure 3 (a), in the absence of n-heptane, the surface experiences a more uniform mode of corrosion.

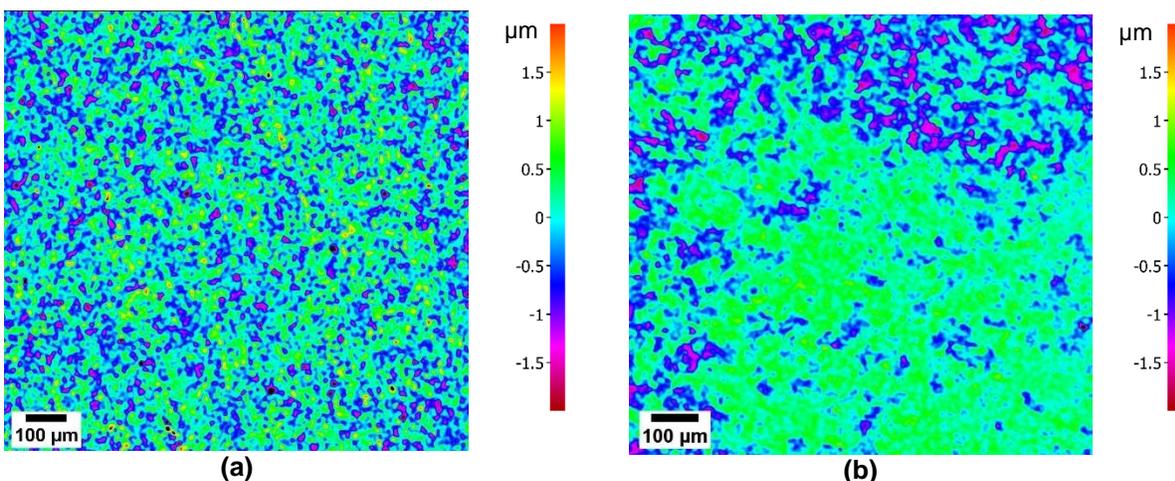


Figure 3: Optical profilometry analysis of the specimen after the blank experiment (a) without and (b) with n-heptane.

As shown in Figure 2 and Table 3, decanethiol is effective in decreasing the corrosion rate in the absence of the hydrocarbon phase. However, when n-heptane is added to the system, this inhibitor loses its inhibition efficiency. This is evidenced by the high corrosion rate under this condition (similar to the blank experiment with heptane). The maximum penetration rate, in the presence of decanethiol and heptane in the system, is higher than the value obtained in the blank-heptane experiment.

Hexanethiol, on the other hand, presents the opposite behavior. As depicted in Figure 2 and Table 3, the presence of this inhibitor results in a reduction in the corrosion rate when the hydrocarbon phase is present in the system. This is quite unexpected as this inhibitor did not perform as well as decanethiol in pure water condensation environments.

Figure 4 compares the SEM images and the optical profilometry data of the specimens tested with decanethiol and hexanethiol in the presence of n-heptane in the system. Figure 4 (a) shows that the surface of the specimen tested with decanethiol (in a water/n-heptane system) is covered by FeCO_3 , while the surface of the specimen tested with hexanethiol (under similar conditions) is free from any corrosion product. This difference can be due to a higher FeCO_3 supersaturation stemming from the higher corrosion rate in the experiment with decanethiol. According to the SEM image of the surface after Clarke solution cleaning (Figure 4 [b]), the FeCO_3 corrosion product layer does not seem to be protective. The analysis of the surface underneath this layer indicates the presence of iron carbide (Fe_3C) corrosion product residues. On the other hand, the surface of the specimen tested with hexanethiol clearly shows a less severe corrosion (Figure 4 [d]). Similarly, to the SEM images, the results of optical profilometry confirm that, under these experimental conditions, the localized corrosion is less deep when hexanethiol is used.

The different corrosion behavior of specimens with decanethiol and hexanethiol during co-condensation of water and n-heptane can be attributed to their solubility. The higher solubility of decanethiol in n-heptane compared to water leads to its partitioning in the hydrocarbon phase, both in the bottom solution and on the surface of the specimen. This partitioning results in the loss of inhibition efficiency. The same behavior has been reported by previous researchers.⁶ From the results obtained in the current study, it seems that due to the higher vapor pressure of hexanethiol compared to decanethiol and its higher molar concentration (at the same “ppm concentration” due to the smaller molar mass of hexanethiol compared to decanethiol [118.24 g/mol versus 174.3 g/mol]) a higher number of moles of hexanethiol will be present on the specimen surface, rendering it more oleophilic and leading to greater accumulation of n-heptane on the surface. This would result in a lower corrosion rate under this condition, driven by synergistic effect.

Therefore, even though decanethiol would provide a better protection efficiency in a hydrocarbon-free environment compared to hexanethiol, the abovementioned hypothesis can be postulated to explain the better protection efficiency conferred by hexanethiol in a co-condensing environment.

Nevertheless, the absolute reason behind this behavior by hexanethiol is still unclear and requires further investigation.

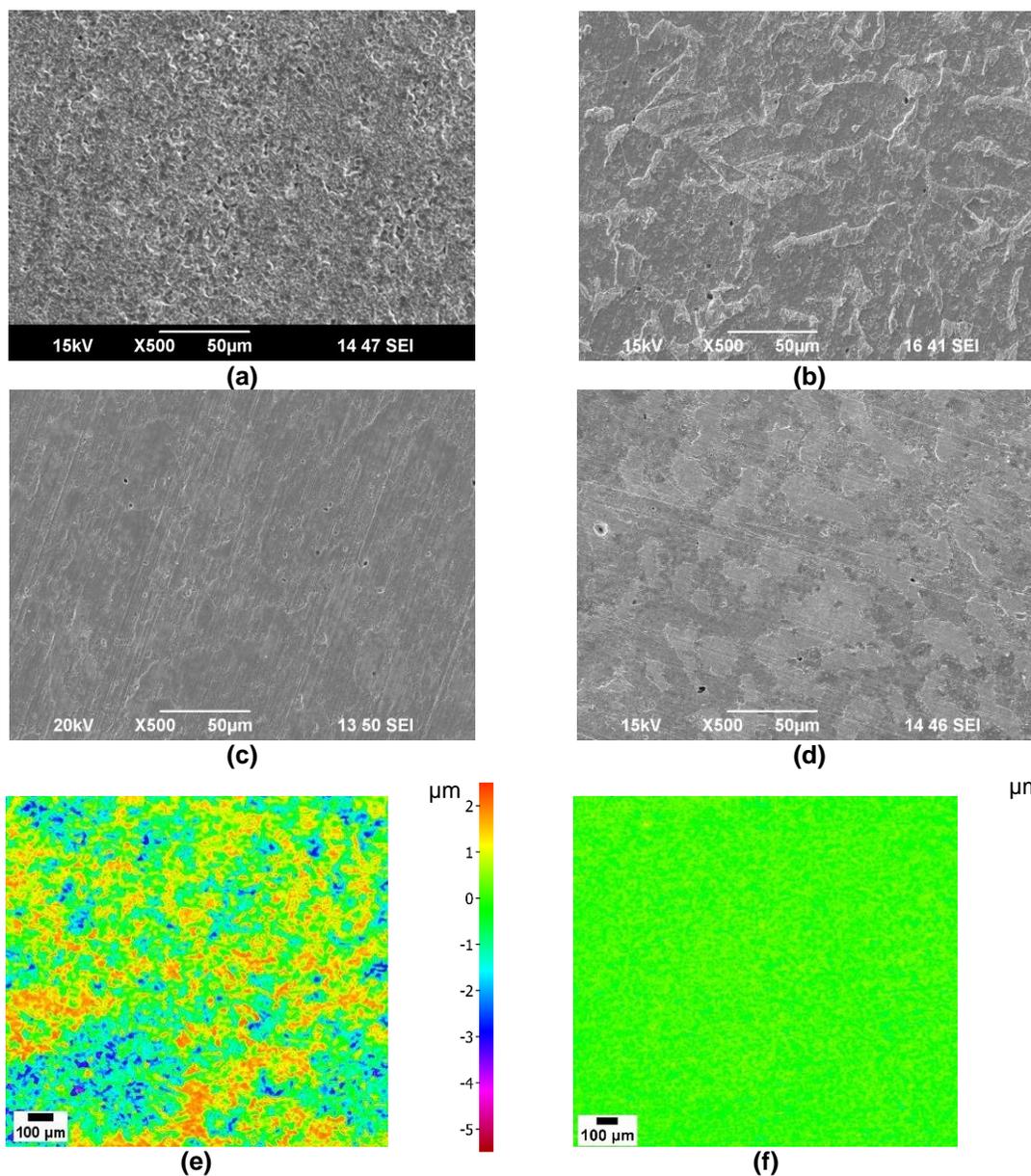


Figure 4: SEM images of the specimen tested with decanethiol (a) before and (b) after Clarke solution cleaning and with hexanethiol (c) before and (d) after Clarke solution cleaning. Optical profilometry analysis of the specimen tested with (e) decanethiol and (f) hexanethiol (both experiments contained n-heptane).

It is well known that commercial inhibitors are a made of several active compounds. Therefore, additional experiments were performed to investigate if a mixture of inhibitors could provide a synergistic effect in systems containing a condensable hydrocarbon phase. Figure 5 shows the corrosion rate and maximum penetration rate obtained from three different mixtures of inhibitors in environments with and without hydrocarbon (n-heptane). The results of the blank experiments are also included in this graph for comparison. The tested mixtures included decanethiol/hexanethiol, decanethiol/diethylamine and decanethiol/t-butylamine. Table 4 summarizes the results of inhibition efficiency for the mixture of inhibitors tested in this study in the presence and absence of n-heptane.

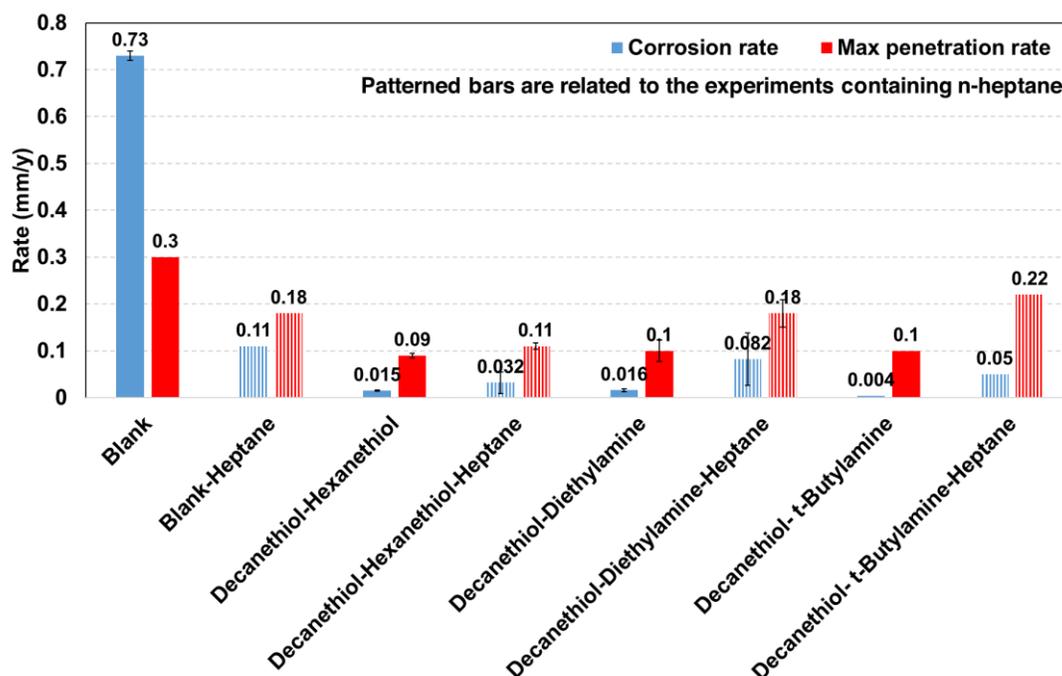


Figure 5: Results of corrosion rate for different TLC experiments with VCI mixtures (the error bars represent standard deviation).

**Table 4
Inhibition efficiency for various inhibitor mixtures tested in this study**

	Decanethiol-Hexanethiol	Decanethiol-Hexanethiol-Heptane	Decanethiol-Diethylamine	Decanethiol-Diethylamine-Heptane	Decanethiol-t-Butylamine	Decanethiol-t-Butylamine-Heptane
IE (%)	98	71	98	25	99	54

The results shown in Figure 5 and Table 4 indicate that when the specimen was tested with a mixture of two thiols (decanethiol and hexanethiol), notable corrosion mitigation was observed in the condensed water environment. Under this condition, both corrosion rate and the maximum penetration rate were significantly decreased. Indeed, in the absence of n-heptane, this mixture of inhibitors shows a lower corrosion rate compared to decanethiol. This can be due to the higher concentration of inhibitor in this experiment (400 ppm decanethiol and 400 ppm hexanethiol). Unlike decanethiol, the mentioned mixture does not lose its inhibition efficiency when exposed to co-condensing environments. This behavior is most probably due to the presence of hexanethiol in the mixture that, as mentioned earlier, provides a high inhibition efficiency in the presence of n-heptane.

Figure 6 depicts the surface of the specimens tested with a mixture of decanethiol and hexanethiol both in the presence and absence of n-heptane in the system. The two specimens show similar surfaces protected from corrosion with no accumulation of corrosion products (Figure 6 [a] and [c]). No sign of significant localized corrosion (Figure 6 [b] and [d]) were observed after cleaning with Clarke solution.

According to the results in Table 4, in the condensed water environment, the mixture of decanethiol and diethylamine and the mixture of decanethiol and t-butylamine show a remarkably high inhibition efficiency with a corrosion rate ≤ 0.01 mm/y. Under this condition, the maximum penetration rate for both mixtures is 0.1 mm/y, similar to that of the mixture of decanethiol and hexanethiol. While amines were previously shown to be ineffective in preventing corrosion under similar experimental conditions,⁷ the results of this

study show that their synergistic effect with decanethiol is promising. The corrosion rates obtained with these two mixtures are the lowest among all the cases studied here. This could be partly due to increase in pH of the condensed water as a result of amine protonation, which decreases the corrosion rate.

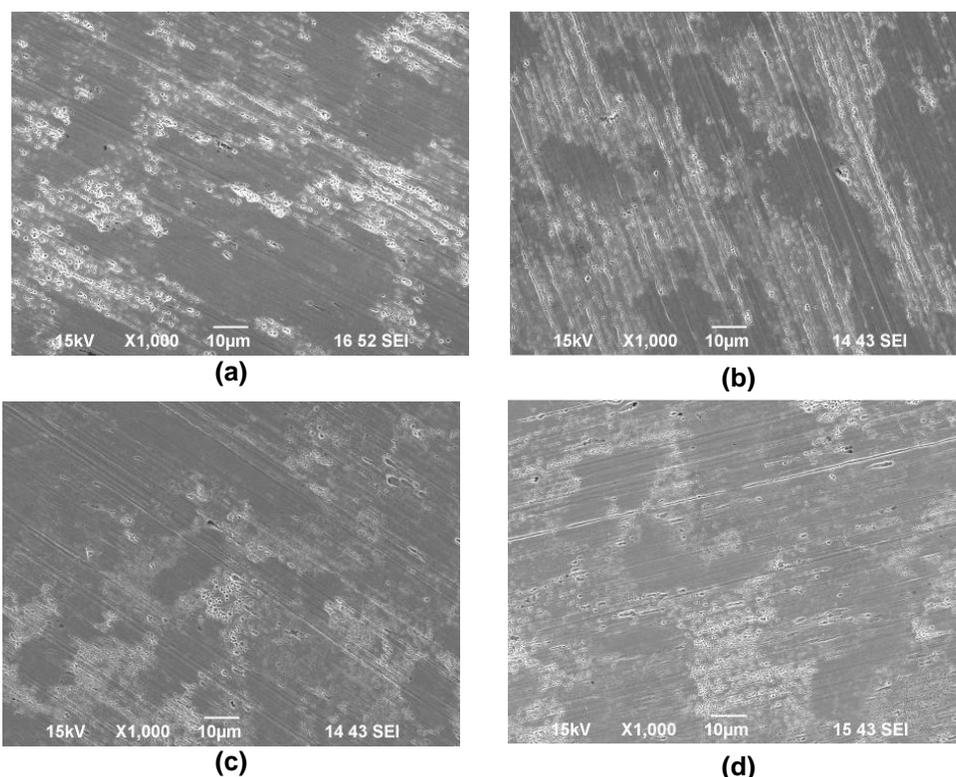


Figure 6: SEM image of the specimen after the experiment with decanethiol-hexanethiol (a) before and (b) after Clarke solution cleaning and with decanethiol-hexanethiol (with n-heptane) (c) before and (d) after Clarke solution cleaning.

SEM images of the surface of specimens tested with these mixtures confirm their high inhibition efficiency. According to the SEM images in Figure 7, no corrosion product and no localized corrosion are visible on the surface before or after cleaning with Clarke solution.

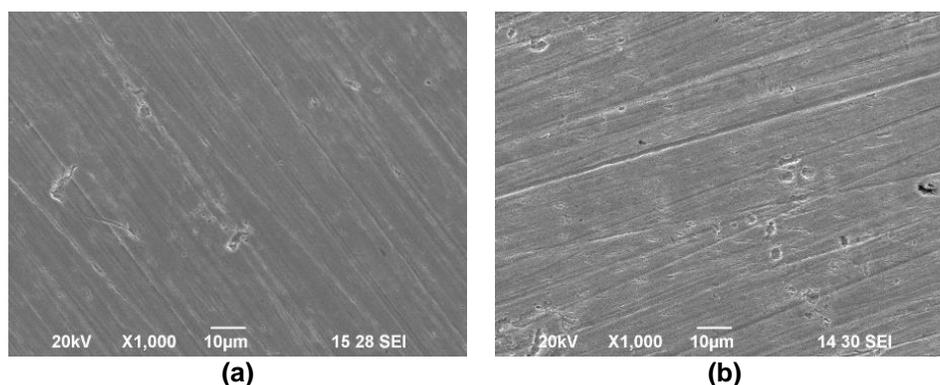


Figure 7: SEM image of the specimen after the experiment with decanethiol-diethylamine (a) before and (b) after Clarke solution cleaning.

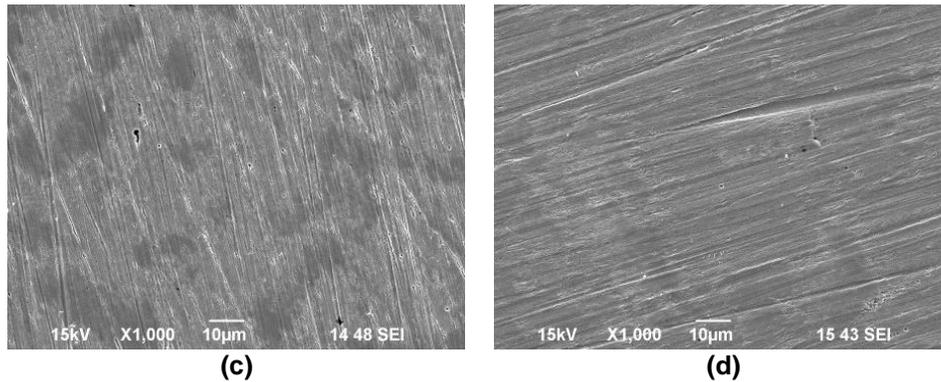


Figure 7 (Continued): SEM image of the specimen after the experiment with decanethiol-t-butylamine (c) before and (d) after Clarke solution cleaning.

Table 4 also shows that when the mixture of decanethiol and diethylamine and the mixture of decanethiol and t-butylamine were tested under co-condensation conditions, the inhibition efficiency was significantly reduced. More specifically, according to Figure 5, a maximum penetration rate of ~ 0.2 mm/y was observed. This rate is higher than the rate obtained after the experiments with the same mixtures but under water-only condensation condition (0.1 mm/y) and is similar to that of the blank-heptane experiment.

The SEM images of specimens tested under co-condensation conditions (Figure 8 [a] and [b]), that were taken after removing the corrosion product layer, show severe corrosion in both cases. This means that the mixtures of thiol and amines lose their inhibition efficiency in the presence of the hydrocarbon phase in the system. As explained earlier, a possible explanation is that the affinity between inhibitors (specifically decanethiol that is main responsible for inhibition) and steel is lower than the affinity between inhibitors and n-heptane, preventing adsorption of inhibitor on the steel surface. The optical profilometry maps of the tested surfaces in Figure 8 (c) and (d) confirm localized corrosion in both cases.

These results undermine the premise of the synergistic inhibiting effect of decanethiol and amines, in the presence of a condensable hydrocarbon phase. However, further experiments are needed to determine the inhibition efficiency of the mixture of hexanethiol and amines.

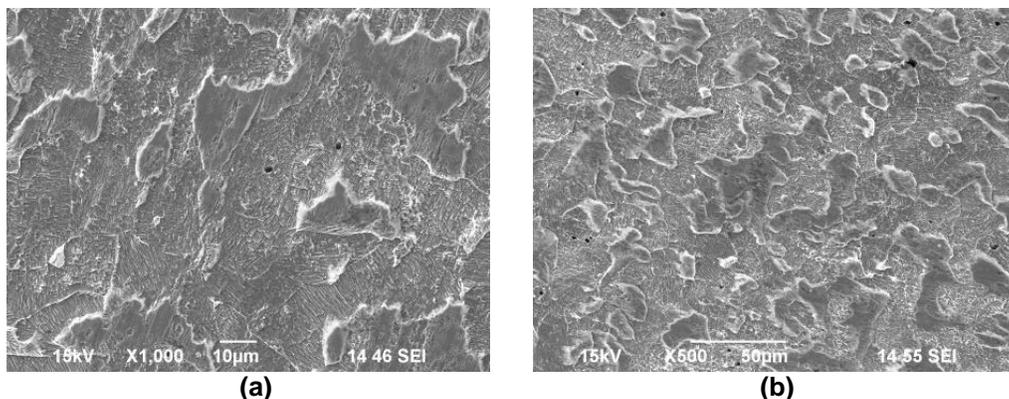


Figure 8: SEM image of the specimen after the experiment with (a) decanethiol-diethylamine and (b) decanethiol-t-butylamine (both experiments contained n-heptane, SEM images taken after Clarke solution cleaning).

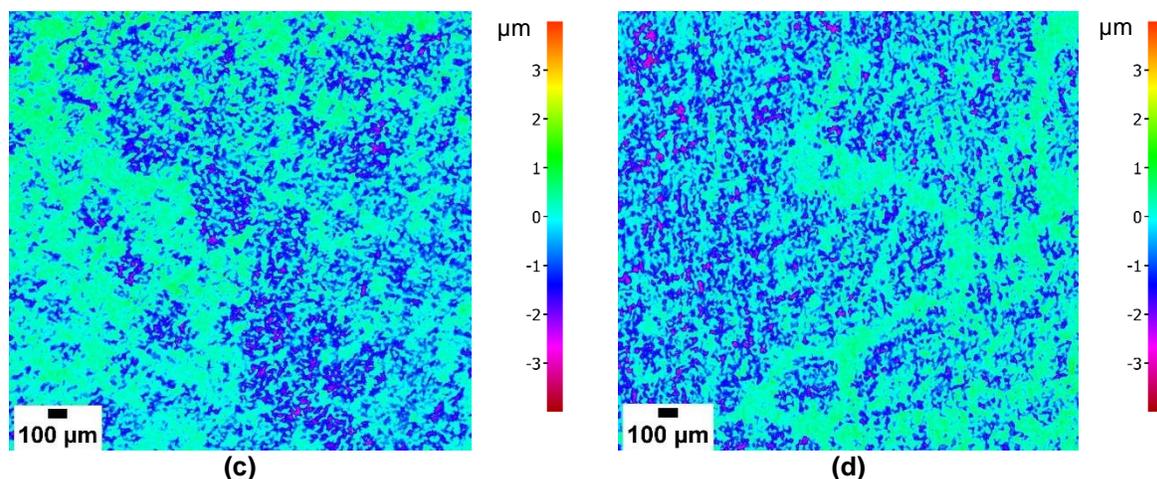


Figure 8 (Continued): Optical profilometry of the specimen after the test with (c) decanethiol-diethylamine, and (d) decanethiol-t-butylamine (both experiments contained n-heptane).

CONCLUSIONS

The following conclusions can be drawn from this study:

- The presence of a condensable hydrocarbon phase, such as n-heptane, interferes with the inhibition efficiency of the studied model VCIs and their mixtures, except for hexanethiol and decanethiol/hexanethiol mixture.
- Decanethiol provides 90% corrosion inhibition efficiency in the condensed water environment but loses its efficiency in co-condensation conditions (0% inhibition efficiency).
- The interference of n-heptane with the corrosion protection by VCIs (especially decanethiol) might be due to the higher solubility of these inhibitors in n-heptane compared to water, which leads to partitioning of the inhibitors in the hydrocarbon phase and therefore loss of corrosion inhibition.
- Hexanethiol provides a better corrosion inhibition in co-condensation scenarios with n-heptane (82% versus 72% inhibition efficiency). It seems that due to the higher vapor pressure of hexanethiol compared to decanethiol and its higher molar concentration (at the same “ppm concentration”) a higher number of moles of hexanethiol will be present on the specimen surface, rendering it more oleophilic and leading to greater accumulation of n-heptane on the surface. This would result in a lower corrosion rate under this condition.
- The mixture of thiols with different tail lengths provides corrosion inhibition efficiency higher than 70% in the presence and the absence of the hydrocarbon phase.
- The mixture of decanethiol and amines does not provide any improved corrosion protection for TLC scenarios in the presence of a condensable hydrocarbon phase.

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