

Thiols as Volatile Corrosion Inhibitors for Top of the Line Corrosion

Z. Belarbi

Institute for Corrosion and Multiphase
Technology
Ohio University
342 West State Street
Athens, OH 45701

F. Farelas

Institute for Corrosion and Multiphase
Technology
Ohio University
342 West State Street
Athens, OH 45701

M. Singer

Institute for Corrosion and Multiphase
Technology
Ohio University
342 West State Street
Athens, OH 45701

T.N. Vu

Institute for Corrosion and Multiphase
Technology
Ohio University
342 West State Street
Athens, OH 45701

D. Young

Institute for Corrosion and Multiphase
Technology
Ohio University
342 West State Street
Athens, OH 45701

S. Nesic

Institute for Corrosion and Multiphase
Technology
Ohio University
342 West State Street
Athens, OH 45701

ABSTRACT

The effectiveness of hexanethiol, decanethiol and 11-mercaptoundecanoic acid for CO₂ corrosion inhibition of carbon steel exposed to top of the line conditions has been investigated. Weight loss measurements were used to measure the corrosion rate in the absence and presence of these volatile inhibitor compounds. After the experiments, steel surfaces were characterized by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). In addition, surface characterization of adsorbed decanethiol molecules on carbon steel was performed using X-ray photoelectron spectroscopy (XPS). The results suggest the formation of an adsorbed inhibitor film on the steel surface, leading to a decrease in corrosion rate. Persistency experiments were also performed to evaluate the residence time for inhibitors adsorbed on carbon steel. Among the inhibitors tested, decanethiol showed very good corrosion inhibition properties as well as high persistency.

©2017 by NACE International.

Requests for permission to publish this manuscript in any form, in part or in whole, must be in writing to

NACE International, Publications Division, 15835 Park Ten Place, Houston, Texas 77084.

The material presented and the views expressed in this paper are solely those of the author(s) and are not necessarily endorsed by the Association.

Keywords: CO₂ corrosion, top of the line, inhibition, decanethiol, XPS

INTRODUCTION

Top-of-line corrosion (TLC) is a phenomenon of global importance in the oil and gas industry, being problematic for both offshore and onshore fields. In stratified flow regimes, conventional CO₂ corrosion inhibitors cannot be used to protect the top of the line since the inhibitor does not reach the upper surface of the pipe; only the lower surface that is in contact with the liquid phase is effectively protected against corrosion. Therefore, the condensation of wet gas can result in the development of a highly corrosive environment, leading to failure, release of hydrocarbons, environmental damage, risk to life, and costly repairs for damaged pipelines. To combat TLC, Gunaltun, *et al.*,^[1] recommended batch treatment or treatment by continuous injection, with a commercial inhibitor comprising *N*-methyldiethanolamine in order to neutralize the acidity of the corrosive aqueous medium. Belarbi *et al.*^[2], have studied the role of amines in the mitigation of CO₂ Top of the Line Corrosion. It was found that morpholine and diethylamine did not fully protect the steel specimen exposed to the TLC conditions; they only slightly reduce the pH of the condensed water.^[2] Volatile corrosion inhibitors (VCIs) are one of the modern technologies used to manage corrosion for the benefit of the global economy. The importance and relevance of VCIs are evidenced by the existence of several patents, as well as recent publication of comprehensive reviews thereof.^[3, 4] A literature search revealed that alkanethiols have been used as corrosion inhibitors for copper^[5] and iron^[6, 7]; 11-mercaptoundecanoic acid is used as corrosion inhibitor for copper coated by dopamine in 3.5 wt.% NaCl.^[8] It is also used as a corrosion inhibitor for stainless steel in a phosphate buffer containing 0.16 M NaCl.^[9] However, no work has been reported in the literature related to TLC inhibition mechanisms using alkanethiols in conditions that simulate those encountered in the oil and gas industry.

In this paper, research on alkanethiols as novel volatile corrosion inhibitors is presented. The emphasis in this work was placed on better understanding of the TLC inhibition mechanism by alkanethiols in CO₂ environments, and identifying the type of chemical or physical bonds likely to form between the alkanethiols and the carbon steel surface.

EXPERIMENTAL PROCEDURE

Materials and Chemicals

Hexanethiol, decanethiol, and 11-mercaptoundecanoic acid used in this research were acquired from Sigma-Aldrich⁽¹⁾. Specimens used in the weight loss experiments were made of an API⁽²⁾ 5L X65 carbon steel with a tempered martensite microstructure; its chemical composition is given in Table 1.

⁽¹⁾ Trade name.

⁽²⁾ American Petroleum Institute (API), 1220 L St. NW, Washington, DC 20005.

Table 1. Composition (wt.%) of API⁽²⁾ 5L X65 carbon steel.

Element	C	Nb	Mn	P	S	Ti	V	Ni	Fe
X65	0.05	0.03	1.51	0.004	<0.001	0.01	0.04	0.04	balance

Weight loss measurements

The experimental setup used for evaluating the efficacy of VCIs under TLC conditions is shown in

Figure 1. Weight loss samples were used to measure the corrosion rate at the top of the line. The bulk aqueous phase comprised of a 1 wt.% NaCl electrolyte, sparged with CO₂ for 2 hours to facilitate deoxygenation and ensure saturation. Carbon steel X65 samples (exposed area = 7.917 cm²) were mechanically polished using silicon carbide paper (600 grit), cleaned with isopropanol in an ultrasonic bath, and dried at room temperature before introduction into the glass cell. A pH probe was used to measure the pH of the bottom solution before and after adding the VCI. In order to have a gas temperature of 65°C, the bottom solution was heated to 72°C. A weight loss specimen was flush-mounted at the top of the experimental setup, controlling its temperature at 32°C using a cooling coil. Corrosion rate of the specimen at the top (TLC rate) with and without the addition of inhibitors was measured following the ASTM⁽³⁾ G1 standard. [10] Consequently, measurements of TLC rates were performed in the condensed water phase, containing dissolved CO₂ and inhibitor. The detailed TLC experimental matrix for the experimental work is shown in Table 2.

The average corrosion rate is determined by:

$$CR = (K * W) / (A * t * \rho) \quad (1)$$

Where:

CR : corrosion rate in mm y⁻¹
 K : conversion factor $8.76 \times 10^4 = 24 \text{ h/d} * 365 \text{ d/y} * 10 \text{ mm/cm}$
 W : weight loss in g
 A : area in cm²
 t : time of exposure in h
 ρ : density of steel, 7.87 g/cm³

The residence time experiments for decanethiol and 11-MUA (dilution test) was evaluated by renewing the solution at a flow rate of 1.7 L/min (Figure 2). A borescope was used to observe the condensation process *in situ* during the dilution test.

⁽³⁾ American Society for Testing and Materials (ASTM), 100 Barr Harbor Drive, West Conshohocken, PA, 19428-2959.

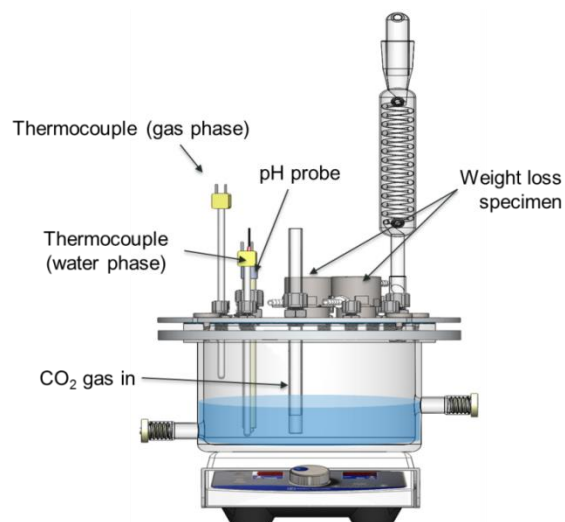


Figure 1. Experimental setup for evaluating efficacy of VCI candidates for TLC.

Table 2. Test matrix for TLC inhibition with thiols.

Total pressure (bar)	1
pCO ₂ (bar)	0.66
Solution	1 wt.% NaCl
Solution temperature at the bottom	74 ± 2°C
Gas temperature	65 ± 2°C
Sample temperature	32 ± 2°C
Calculated water condensation rate (ml/m ² /s)	0.6
Working electrode	X65 carbon steel
hexanethiol (ppm _v)	100, 400
decanethiol (ppm _v)	100, 400
11-mercaptoundecanoic acid (ppm _v)	100

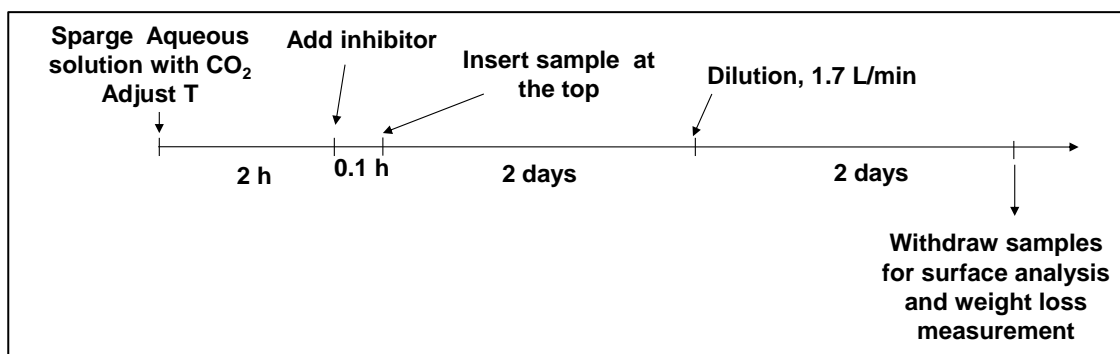


Figure 2. Experimental procedure for establishing residence time of thiols.

Surface analysis

Surface analysis of the exposed electrode was performed with a JEOL JSM-6090 LV scanning electron microscope (SEM) and an EDAX energy dispersive X-ray spectroscopy (EDS) system. Imaging was performed at an accelerating voltage of 15 kV using a secondary electron detector (SEI). The X-ray photoelectron spectroscopy (XPS) analyses were performed with a VG Scientific ESCALAB MKII spectrometer using an Al K α X-ray source (1486.6 eV). The instrumental resolution was 1.2 eV with a slit width of 0.6 cm. Samples were maintained at ambient temperature (25°C) at a pressure of 5×10^{-9} mbar. The following XPS regions were recorded: Fe 2p, O 1s, C 1s, and S 2p. In order to verify the reproducibility of results, XPS analysis was done on six different spots on each sample.

RESULTS AND DISCUSSION

Efficacy of thiols as volatile corrosion inhibitors for TLC

The TLC rate obtained by WL and surface images taken after the tests are shown in Figure 3 and Figure 4. The results show that under the baseline conditions, the X65 carbon steel specimen was corroded at a TLC rate of 1.0 mm y^{-1} and its surface was fully covered by a corrosion product (Figure 5). EDS analysis detected Fe and C, which suggested the likely presence of a residual iron carbide layer. In the presence of decanethiol and 11-mercaptoundecanoic acid the corrosion rate decreased to reach a value lower than 0.03 mm y^{-1} . No corrosion was apparent (Figure 4, Figure 7 and Figure 8), and the grooves due to specimen polishing remain clearly visible after 2 days of exposure to TLC conditions. The surface of the carbon steel was fully protected. In the presence of hexanethiol, the TLC rate was 10 times lower than the baseline test (0.1 mm y^{-1}). Under these conditions the steel surface was only partially protected, as can be observed by the black areas where corrosion occurred (Figure 4). The SEM images and EDS analyses (Figure 6) confirmed this conclusion, showing alternating corroded and protected areas.

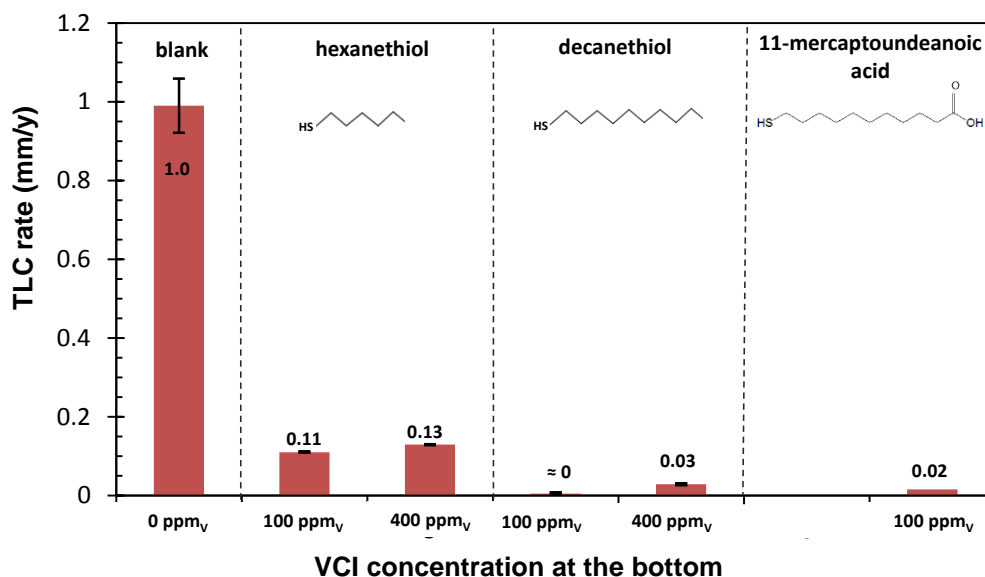


Figure 3. Corrosion rate by weight loss measurement of the uninhibited and inhibited TLC specimens ($\text{WCR} = 0.6 \text{ mL/m}^2/\text{s}$). Note: VCI candidate concentrations on x-axes are the injected concentration for the bottom solution.

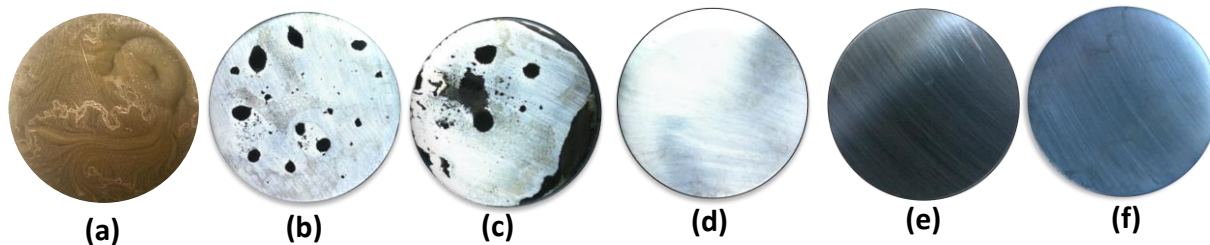


Figure 4. Visual images of sample exposed to corrosion in the co-condensation of water ($WCR = 0.6 \text{ mL/m}^2/\text{s}$) in the presence of a) no inhibitor; b) 100 ppm_V hexanethiol; c) 400 ppm_V hexanethiol; d) 100 ppm_V decanethiol; e) 400 ppm_V decanethiol; f) 100 ppm_V 11-mercaptoundecanoic acid after 2 days.

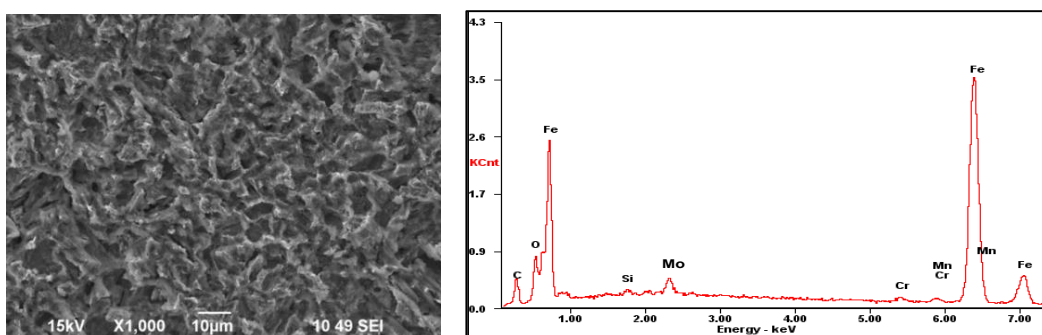


Figure 5. SEM image and EDS analysis of the blank sample after 2 days.

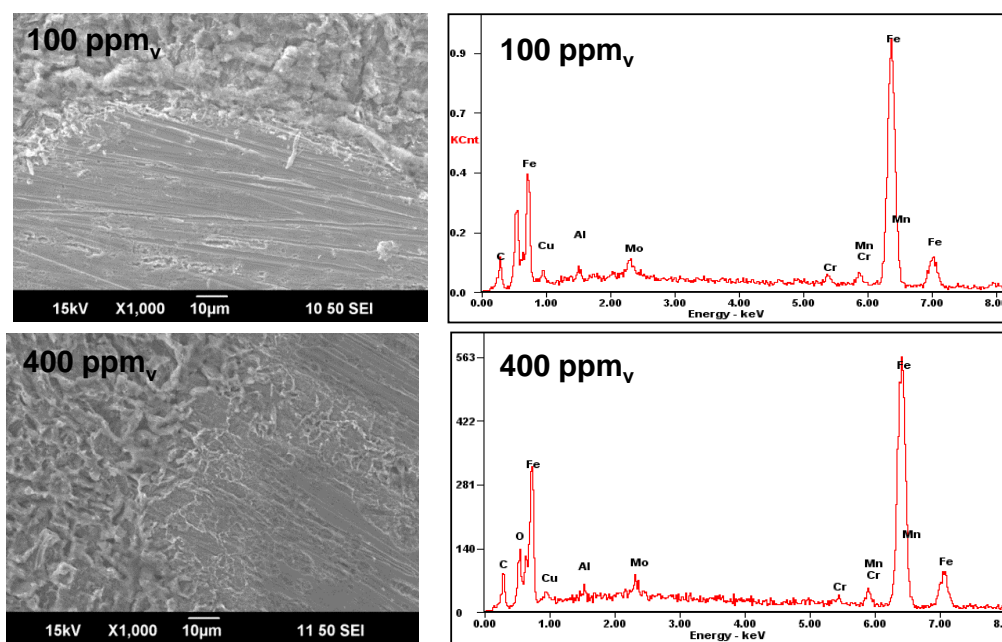


Figure 6. SEM images and EDS analysis of the sample in the presence of hexanethiol after 2 days.

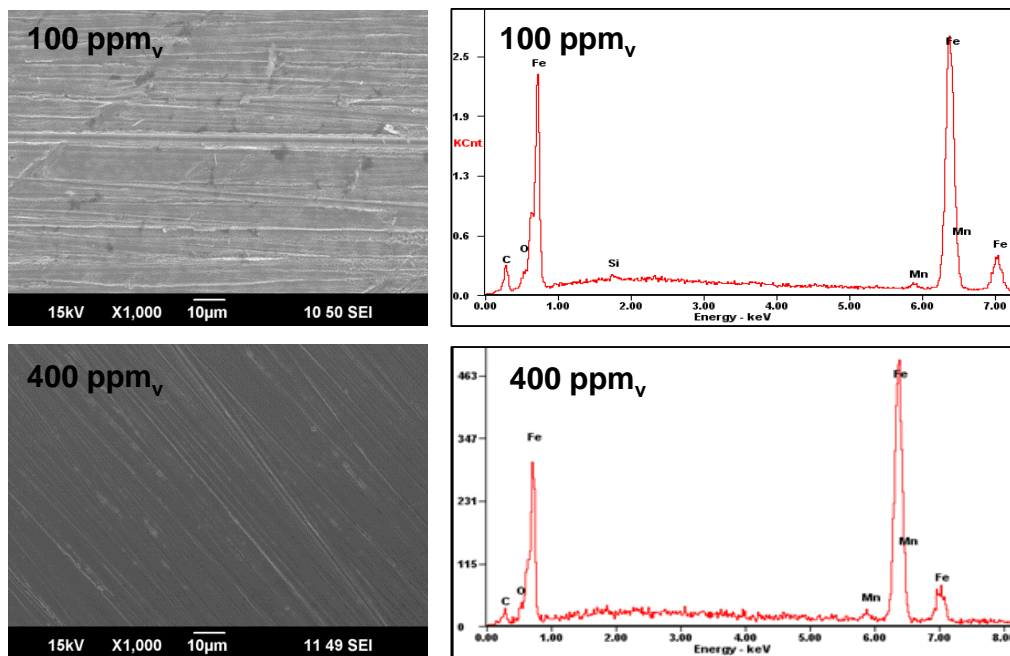


Figure 7. SEM images and EDS analysis of the sample in the presence of decanethiol after 2 days.

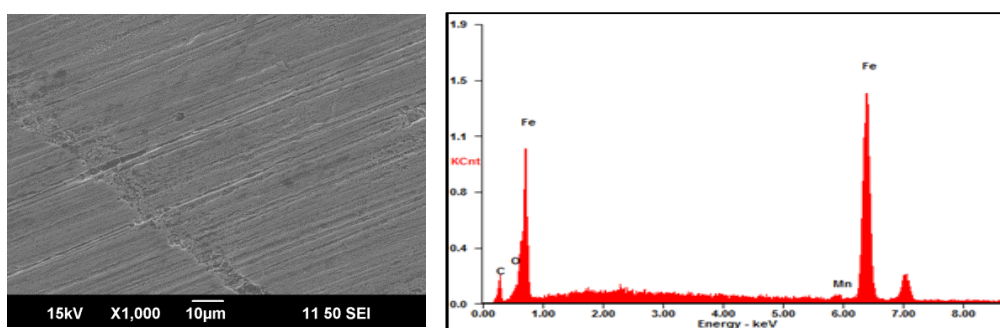


Figure 8. SEM images and EDS analysis of the sample in the presence of 100 ppm of 11-mercaptoundecanoic acid after 2 days.

Investigation of the interaction between thiol and the steel surface using X-ray photoelectron spectroscopy (XPS)

To further characterize the inhibitor films adsorbed on the steel surface to determine whether they were physisorbed or chemisorbed, XPS analyses were performed on a freshly polished carbon steel and on carbon steel surfaces after 2 days of exposure to the condensed water in the presence of 400 ppm_v of decanethiol. Figure 9 shows the XPS spectra of the carbon steel both as freshly polished and exposed to TLC conditions. In the absence and presence of decanethiol, two binding energies of 707.1 eV Fe 2p_{3/2} and 720.2 eV Fe 2p_{1/2} were observed. The splitting energy between Fe 2p_{3/2} and Fe 2p_{1/2} is equal to 13.1 eV, corresponding to the components of the Fe 2p of metallic iron.^[11] The peaks around 710 eV Fe 2p_{3/2} and 724 eV Fe 2p_{1/2} correspond to the Fe 2p signatures of oxidized iron species [11]; reported literature values^[11] have assigned the Fe 2p_{3/2} peak to Fe₂O₃ (710.8-710.9 eV) and Fe₃O₄ (708.2-710.4 eV). From the shape of the spectra and line positions in Figure 9, it appears that the steel surface is composed of a mixture of metallic and oxidized iron (FeO). The proportions of iron

oxides and iron are the same for the bare steel specimen and the steel specimen treated with decanethiol, as suggested by the Fe 2p peak positions and intensities. In order to corroborate the presence of oxides on the steel surface the O1s binding energy peak was analyzed. The O 1s core level of iron containing surfaces can be resolved into five components that are located at 530.2 eV (Fe_2O_3 and Fe_3O_4), 531.2 eV for $(\text{Fe}(\text{OH})_x)$, 532.1 eV (H_2O), 533.1 eV (C-O-C) and 534.4 eV ($\text{O}=\text{C}-\text{O}$)^[11]. As already suspected from the analysis of the Fe 2p peak, the bare electrode clearly exhibits an FeO component (530.4 eV) and experimental data overlap the fit. In the presence of decanethiol, the overall O 1s spectra was deconvoluted into two peaks with binding energies of 530.4 eV and 532 eV, reflecting the presence of an FeO component and oxidized sulfur (S-O) on the steel surface, respectively. Pirlot, *et al.*,^[11] have shown that Fe substrates react with pure *n*-dodecanethiol, leading to surface modification. Two types of iron substrates, polished and electrochemically reduced, were reacted with pure *n*-dodecanethiol and characterized by X-ray photoelectron spectroscopy. It was found that the electrochemically reduced surfaces, rich in the less stable $\text{Fe}(\text{OH})_x$ and presenting a lower oxide film thickness, lead to modified surfaces of better quality in terms of possessing a well-controlled interface between the grafted molecule and the iron substrate. The C 1s binding energy spectra were composed of two peaks at 286 eV and 289-290.5 eV. It is common to observe carbon containing contaminants, such as the peak observed at 286 eV, solely associated with sample handling. This peak is generally used as an energy reference. The intensity of the peak at 286 eV increased in the presence of inhibitor; therefore, the presence of C-C bonding could be related to the inhibitor alkyl tail. The second peak at 289-290.5 eV ($\text{O}-\text{C}=\text{C}$) is an artifact. There is no binding energy peak belonging to C1s at 286 eV^[12], meaning no presence of iron carbide at the steel surface. For the bare steel surface, there is no comparable binding energy peak assignable to sulfur in this range. However, the XPS spectrum of the steel electrode exposed to TLC conditions shows obvious binding energy peaks at 164 eV and 169 eV, which are assigned to S 2p of the free thiol and oxidized sulfur (sulfate or sulfite), respectively. There is no binding energy peak belonging to Fe-S at 162.1 eV, meaning no chemisorption of decanethiol on the steel surface.^[13] The binding energy peak belonging to oxidized sulfur can be postulated to mean that decanethiol on the steel surface is unstable in air. All of these results support the physisorption of decanethiol on the steel surface. Figure 10 shows the possible interactions between the steel surface, assuming that it is positively charged, and thiols.^[14, 15, 16] It has been reported in the literature^[2] that the steel surface is positively charged in acid environments, based on potential of zero charge measurements; therefore, the adsorption of anions or molecules possessing permanent dipole is considered likely. The chemical structure of thiols plays a significant role and determines their effectiveness as corrosion inhibitors. The inhibiting efficacy of thiols depends on the inductive effect of various functional groups related to the sulfur atom. Evans^[17] discussed the influence of substituents on the protective effect of organic inhibitors. The sulfur atom (heteroatom) possesses a free electron pair which can establish Van der Waals secondary bonding interactions with the steel surface Figure 10. Therefore, thiols can easily desorb because they do not form a primary chemical bond.

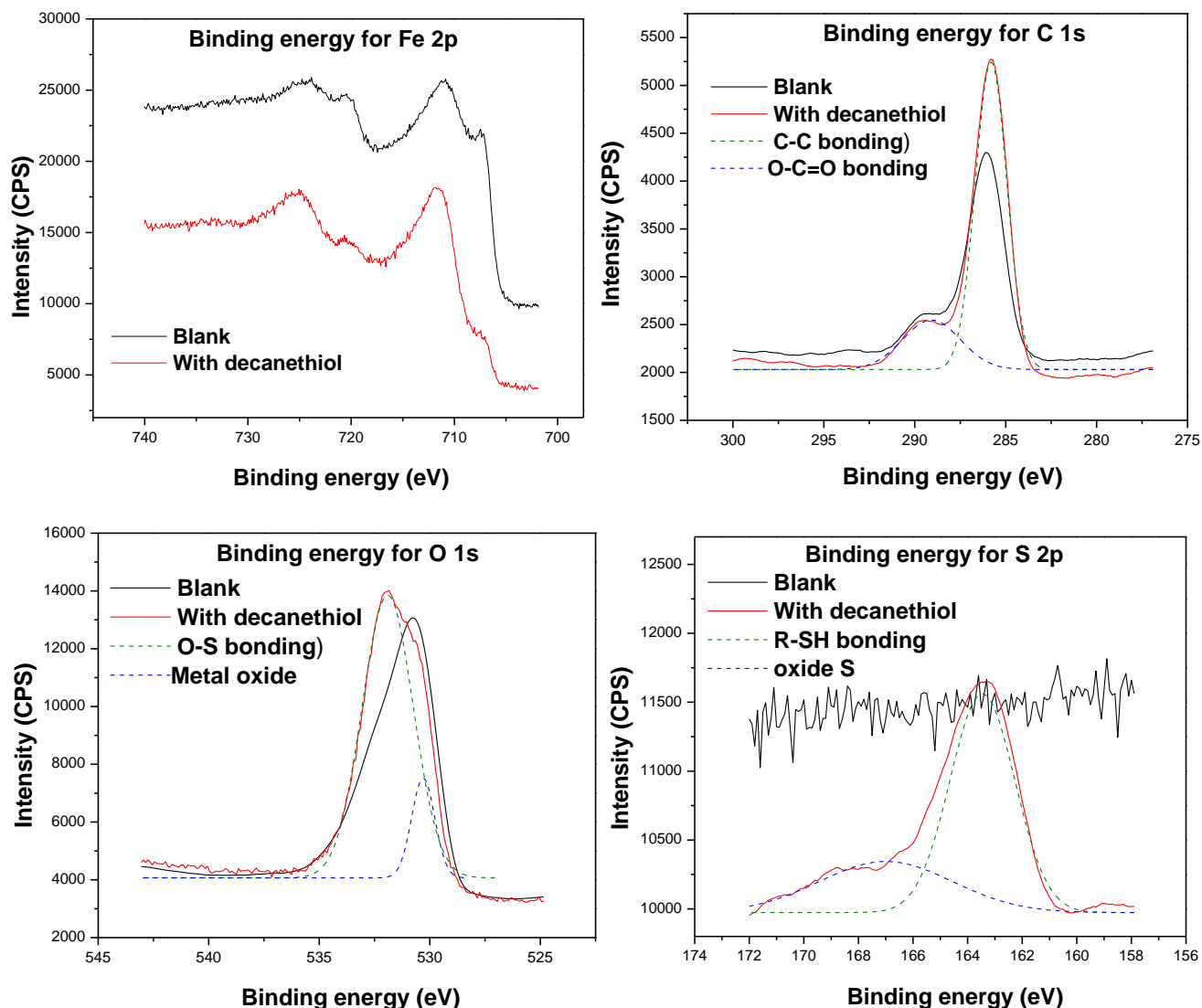


Figure 9. XPS spectra of bare steel (blank) and steel electrode exposed to TLC conditions after 2 days in the presence of 400 ppm_v of decanethiol

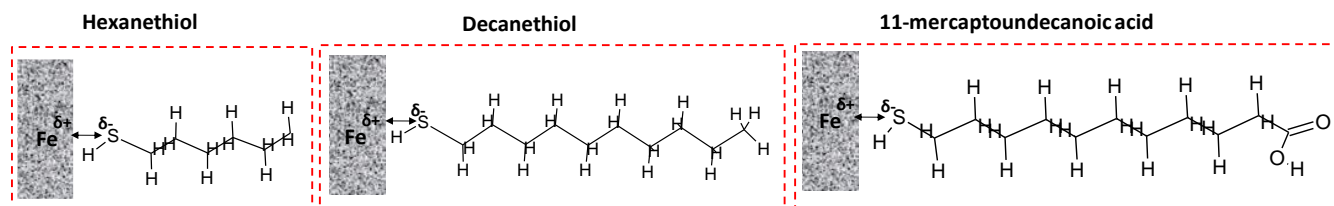


Figure 10. Possible interactions between thiols groups and metal surface. [14, 15, 16]

(\longleftrightarrow): Van der Waals bonding.

Identification of residence time (persistency test) of thiols

Figure 11 shows the condensation behavior of water with time in the presence of 11-mercaptoundecanoic acid. Before and after dilution the surface looks practically the same. No corroded surface was observed with time. Corrosion rates obtained by weight loss are shown in Figure 12. In the presence of 11-mercaptoundecanoic acid and decanethiol, corrosion rates are very low, 0.04mm y^{-1} for decanethiol and 0.01 mm y^{-1} for 11-mercaptoundecanoic acid. The surface of the specimen was fully protected and no corrosion products were observed after 4 days (Figure 13), indicating a good persistency of the tested thiols. The good persistency of thiols observed in this research could be due to their low association by hydrogen bonding and their lower solubility in water. Thiol is a sulfur analogue of alcohol, but the smaller difference in electronegativity between the sulfur atom and the hydrogen atom makes the S-H bond less polarized than the O-H bond, leading to a diminished propensity to form hydrogen bonds ^[18]. In other words, “inhibitor/steel” affinity is stronger than for “inhibitor/water. The SEM images and EDS analysis of the specimen surface (Figure 14) confirmed this conclusion, showing a protected area.

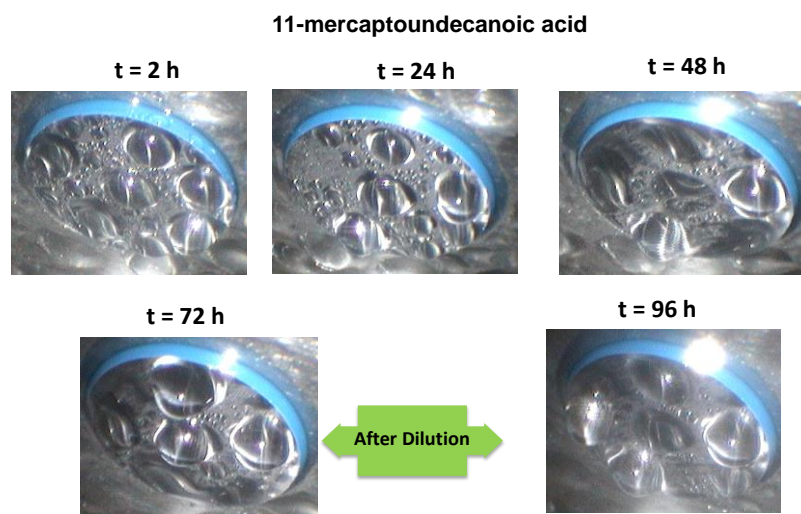


Figure 11. Samples exposed to corrosion with co-condensation of water, in the presence of 11-mercaptoundecanoic acid.

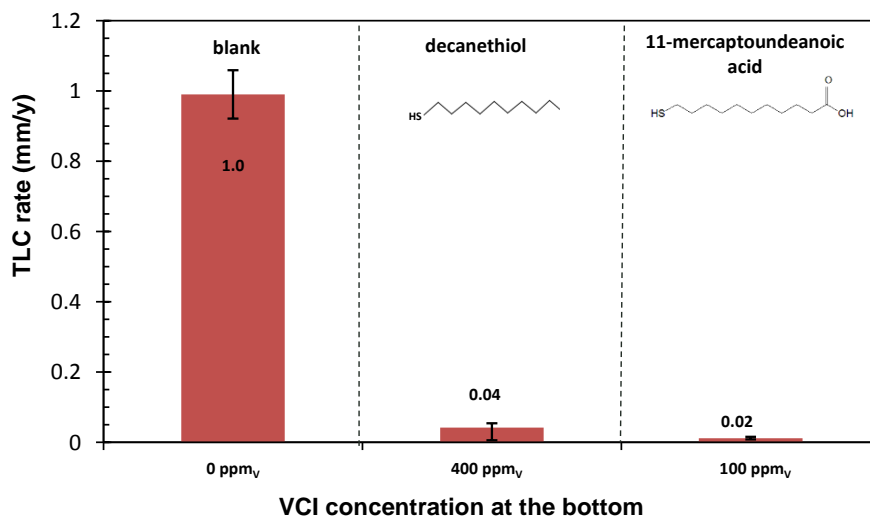


Figure 12. Corrosion rate by weight loss measurement of the uninhibited and inhibited TLC specimens ($WCR = 0.6 \text{ mL/m}^2/\text{s}$). Note: VCI candidate concentrations on x-axes are the injected concentration for the bottom solution.

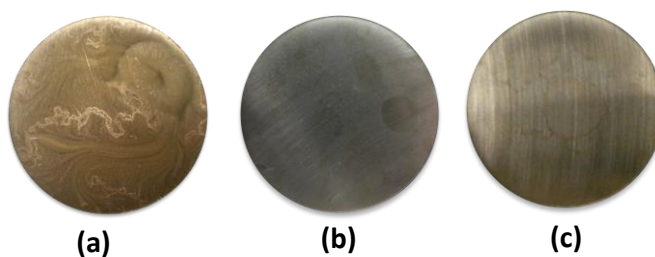


Figure 13. Visual images of sample exposed to corrosion in the co-condensation of water ($WCR = 0.6 \text{ mL/m}^2/\text{s}$) in the presence of a) no inhibitor; b) 400 ppm_v decanethiol; c) 100 ppm_v 11-mercaptoundecanoic acid after dilution test.

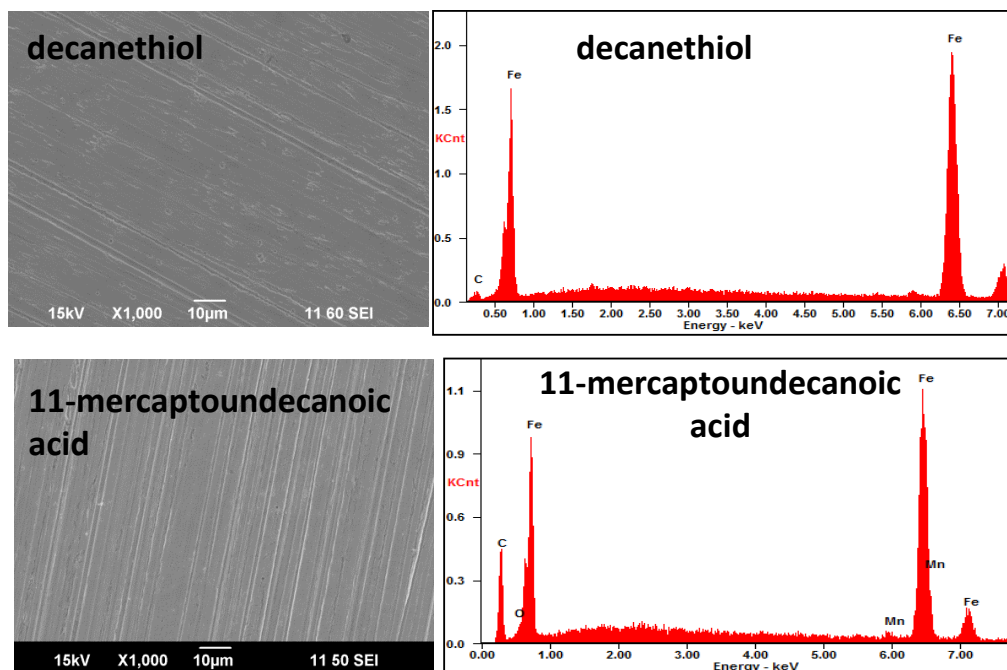


Figure 14. SEM images and EDS analysis of the sample in the presence of thiols after dilution test.

CONCLUSIONS

In this work, the weight loss method was used to study the TLC inhibition mechanism in the presence of hexanethiol, decanethiol and 11-mercaptoundecanoic acid in a CO₂ environment and acidic pH. The mechanisms were investigated by studying their interaction with the steel surface. As a result of this study, the following conclusions were drawn:

- With the same added amount (100 ppm_v), decanethiol and 11-mercaptoundecanoic acid provided a better protection against TLC than hexanethiol.
- XPS analysis suggests physisorption of decanethiol on the steel surface as no primary chemical bond formed between metal and sulfur (Fe-S bond) could be identified.
- The inhibitor films of decanethiol and 11-mercaptoundecanoic acid are characterized by a high hydrophobicity which provides an excellent barrier against corrosive species from attacking the underlying carbon steel substrate.

ACKNOWLEDGMENTS

The authors would like to thank the following companies for their financial support: Apache, BHP Billiton, BP, Chevron, ConocoPhillips, MI-SWACO, PETRONAS, PTTEP, Woodside and Talisman. The authors are grateful to Prof. David Ingram of the “Edwards accelerator Laboratory– Ohio University” for his help on *ex situ* XPS experiments. Also, the technical support from the lab’s staff at Institute for corrosion and multiphase technology by Mr. Alexi Barxias, Mr. Cody Shafer and Mr. Phil Bullington is highly appreciated.

BIBLIOGRAPHY

- [1] Y. M. Gunaltun and A. Belghazi, "Control of top of line corrosion by chemical treatment," in *Corrosion/2001, paper no. 01033*, Houston, TX: NACE 2001.
- [2] Z. Belarbi, F. Farel, M. Singer and S. Nesic, "Role of amines in the mitigation of CO₂ Top of the Line Corrosion," *Corrosion*, vol. 72, no. 10, pp. 1300-1310, 2016.
- [3] R. Inzunza, B. Valdez and M. Schorr, "Corrosion inhibitor patents in industrial applications – A review," *Recent Patents on Corrosion Science*, vol. 3, pp. 71-78, 2013.
- [4] V. Saji, "A review on recent patents in corrosion inhibitors," *Recent Patents on Corrosion Science*, vol. 2, pp. 6-12, 2010.
- [5] V. Feng, W. K. Teo, K. S. Siow, Z. Gao, K. L. Tan and A. K. Hsieh, "Corrosion protection of copper by a self-assembled monolayer of alkanethiol," *Journal of the Electrochemical Society*, vol. 144, no. 1, pp. 55-64, 1997.
- [6] V. Jovancicevic, Y. S. Ahn, J. Dougherty and B. Alink, "CO₂ corrosion inhibition by sulfur-containing organic compounds," in *Corrosion/2000, paper no. 00007*, Houston, TX: NACE, 2000.
- [7] T. S. M. Ehteshamzadeh, "Synergistic effect of 1-dodecanethiol upon inhibition of Schiff bases on carbon steel corrosion in sulphuric acid media," *Anti-Corrosion Methods and Materials*, vol. 53, pp. 147-152, 2006.
- [8] Y. Chen, S. Chen and Y. Lei, "Surface Structure and Anti-Corrosion Properties of Copper Treated by a Dopamine-Assisted 11-Mercaptoundecanoic Acid Film," *Corrosion*, vol. 68, pp. 747-753, 2012.
- [9] H. Dadafarin, E. Konkov and S. Omanovic, "Electrochemical Functionalization of a 316L Stainless Steel Surface with a 11-mercaptoundecanoic Acid Monolayer: Stability Studies," *International Journal of Electrochemical science*, vol. 8, pp. 369 - 389, 2013.
- [10] "Standard practice for preparing cleaning and evaluating corrosion test specimens," *ASTM-G1*, pp. 15-21, 1999.
- [11] C. Pirlot, J. Delhalle, J. Pireaux and Z. Mekhalif, "Surface modification of polycrystalline iron surfaces by n-dodecanethiol: an XPS investigation," *Surface and Coatings Technology*, vol. 138, pp. 166-172, 2001.
- [12] E. Park, J. Zhang, S. Thomson, O. Ostrovski and R. Howe, "Characterization of Phases Formed in the Iron Carbide Process by X-Ray Diffraction, Mossbauer, X-Ray Photoelectron Spectroscopy, and Raman Spectroscopy Analyses," *Metallurgical And*

- [13] H. Zhang, C. Romero and S. Baldelli, "Preparation of Alkanethiol Monolayers on Mild Steel Surfaces Studied with Sum Frequency Generation and electrochemistry," *The Journal of Physical Chemistry B*, vol. 109, pp. 15520-15530, 2005.
- [14] A. Shiri, M. Etman and F. Dabosi, "Thiol compounds as corrosion inhibitors of carbon steel (XC 38) in sodium chloride medium," *Werkstoffe und Korrosion*, vol. 43, pp. 406-414, 1992.
- [15] D. Lavrich, S. M. Wetterer, L. S. Bernasek and G. Scoles, "Physisorption and chemisorption of alkanethiols and alkyl aulfides on Au(111)," *Journal of Physical Chemistry B*, vol. 102, pp. 3456-3465, 1998.
- [16] M. Hines, J. Todd and P. Guyotsionnest, "Conformation of alkanethiols on au, ag(111), and pt(111) electrodes – a vibrational spectroscopy study," *Langmuir*, vol. 11, pp. 493-497, 1995.
- [17] B. Sanyal, "Organic compounds as corrosion inhbitors in diffrenent environments- a review," *Progress in Organic Coatings*, vol. 9 , pp. 165 - 236, 1981.
- [18] J. Coply, C. S. Marvel and E. Ginsberg, "Hydrogen Bonding by S-H. VII: Aryl Mercaptans," vol. 61, pp. 3161-3162, 1939.