

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

Maryam Eslami
Institute for Corrosion and Multiphase Technology, Ohio University
342 West State St.
Athens, Ohio 45701
United States

Marc Singer
Institute for Corrosion and Multiphase Technology, Ohio University
342 West State St.
Athens, Ohio 45701
United States

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 ($S_{FeCO_3} = [Fe^{2+}][CO_3^{2-}]/K_{sp,FeCO_3}$) 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.

© 2022 Association for Materials Protection and Performance (AMPP). All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means (electronic, mechanical, photocopying, recording, or otherwise) without the prior written permission of AMPP.

Positions and opinions advanced in this work are those of the author(s) and not necessarily those of AMPP. Responsibility for the content of the work lies solely with the author(s).

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.

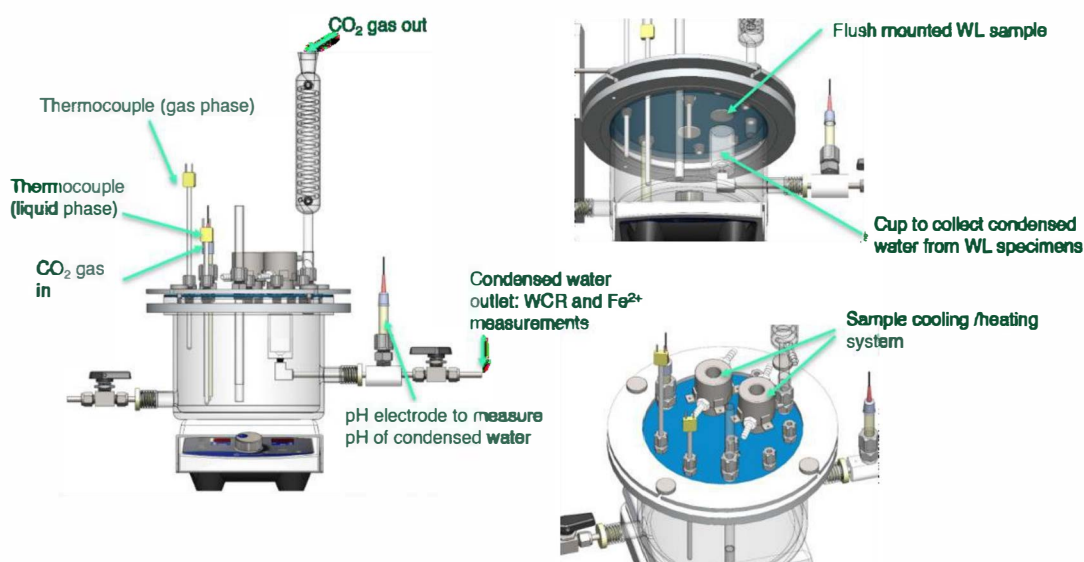


Figure 1: The glass cell setup for the TLC experiments.

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

© 2022 Association for Materials Protection and Performance (AMPP). All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means (electronic, mechanical, photocopying, recording, or otherwise) without the prior written permission of AMPP.

Positions and opinions advanced in this work are those of the author(s) and not necessarily those of AMPP. Responsibility for the content of the work lies solely with the author(s).