

Residual Analysis Assay for Thiol-Based Volatile Corrosion Inhibitor Quantification in Top-Of-Line Corrosion Environments

Mariana Costa Folena, José Antônio da Cunha
Ponciano Gomes
LabCorr/UFRJ
Centro de Tecnologia - UFRJ, Rio de Janeiro
21941-972
Brazil

Hanan Alshareef Farhat
The Corrosion Center
Qatar Environment & Energy Research Institute
Hamad Bin Khalifa University
Doha, 34110
Qatar

Iain Manfield
Astbury Centre for Structural Molecular Biology
Faculty of Biological Science
University of Leeds
LS2 9JT
United Kingdom

Joshua Owen, Anne Neville, Richard Barker
Institute of Functional Surfaces (iFS)
School of Mechanical Engineering
University of Leeds
LS2 9JT
United Kingdom

ABSTRACT

Carbon dioxide (CO₂) Top of Line Corrosion (TLC) poses a significant problem in oil and gas fields, resulting in both economic losses and health and safety issues. The use of conventional corrosion inhibitors does not typically ensure effective protection against this particular type of corrosion, limiting the working lifetime of carbon steel pipelines. The main chemistry of inhibitors used for such application relies on volatile chemicals that can be transported through the vapor phase to reach the top of the pipeline. Studies have shown that alkanethiol compounds may form self-assembled monolayers in acid environments with good efficiency in mitigating steel corrosion. Recently, long chain thiols (> C₆) have been investigated as potential volatile corrosion inhibitors (VCIs), demonstrating good efficiency. This work seeks to evaluate the efficiency, mechanism and bulk-vapor partitioning behavior of volatile thiol corrosion inhibitors through the implementation of a biochemical technique which targets sulphhydryl groups, coupled with a miniature electrode configuration for real time, *in situ* electrochemical TLC measurements. The proposed assay results in a rapid, cost effective screening technique that can monitor thiol-based chemistries that are partitioned in the condensate. The implementation of these methods enables the performance and mechanisms of volatile inhibitors to be better characterized and understood, shedding new light on their behavior, whilst also facilitating more effective optimization of their dose rate.

Key words: top-of-line corrosion; corrosion inhibitor; VCI; electrochemistry

INTRODUCTION

Top of line corrosion (TLC) is a degradation mechanism predominantly encountered in the oil and gas industry. Initiation of TLC requires a stratified flow regime with wet gas transportation and the existence of a significant temperature gradient between the hot fluid inside the pipeline and the colder external environment.^{1,2,3} This temperature difference results in the condensation of water vapor, present in the gas phase, onto the cooler, upper internal section of the pipeline. The condensed water can be particularly aggressive as it lacks dissolved salts (e.g. bicarbonates), some of which are able to buffer the bulk electrolyte, increasing the pH and suppressing corrosivity.^{4,5,6} The absence of such salts typically results in a very low pH condensate (<pH 4), often containing dissolved acidic gases, such as carbon dioxide (CO₂) and hydrogen sulfide (H₂S), and also acetic acid (HAc), which can cause severe degradation, particularly in the form of localized corrosion.⁵

Despite the prevalence of TLC for decades within the oil and gas industry, the underlying mechanisms still remain unclear, limiting the success of mitigation techniques applied to control TLC rates. In hydrocarbon transportation via pipelines, the most common method of internal corrosion control is through the deployment of corrosion inhibitors (or surfactants). In this context, many of the organic chemistries that successfully control corrosion of steel in 'bulk fluids', typical of oilfield environments, fail to suppress corrosion at the metal-condensate interface. This is attributed to the low volatility of the chemistries used, which means that once they are injected into the bulk oil and/or water phase, they remain at the 'bottom' of the line and cannot be effectively transported to the top of the line.^{7,8} For this reason, TLC is one of the most challenging corrosion processes facing the industry. Consequently, there is a clear need to develop an understanding of the underlying mechanisms of TLC and its inhibition.

One branch of chemistries which have recently attracted interest as potential vapor corrosion inhibitors (VCIs) for suppressing TLC, and have been proven to be largely successful in laboratory experiments, are alkanethiols.^{9,10} In 2017, Belarbi *et al.*,¹⁰ evaluated two different alkanethiols and a carboxyl-containing thiol (hexanethiol, decanethiol and 11-mercaptoundecanoic acid) for TLC inhibition of carbon steel in CO₂-saturated conditions. In their study, it was identified that the longest chain molecule (11-mercaptoundecanoic acid) was more effective, reducing the general top-of-line corrosion rate of carbon steel from 1 mm/year to less than 0.03 mm/year, maintaining its efficiency during the 2 day exposure test. The long chain thiols and 11-mercaptoundecanoic acid also showed strong persistency, attributable to the compounds' hydrophobicity and affinity for the steel surface. In a subsequent study by Belarbi *et al.*,⁹ the influence of different water condensation rates (WCRs), monoethylene glycol (MEG), H₂S, and hydrocarbons on the inhibition efficiency decanethiol were evaluated. Decanethiol was shown to inhibit TLC irrespective of the WCRs evaluated and remained highly efficient in the presence of MEG and traces of H₂S.

Thiols have found wider application for corrosion inhibition outside of the field of TLC, notably as corrosion inhibitors for copper in acid solution.^{11,12} However, substantially less information exists in the open literature regarding its inhibition of carbon steel corrosion. A handful of studies have been completed, which have shown, for example, high inhibition efficiencies of 2,5-bis(nthienyl)-1,3,4-thiadiazoles (n-TTH) when used to protect mild steel in 1 M hydrochloric acid solution¹³ and of 4-amino-5-phenyl-4H-1, 2, 4-triazole- 3-thiol (APTT) in 2.5 M sulfuric acid solutions.¹⁴ Furthermore, despite its presence as a sulfur synergist in many fully formulated oilfield inhibitor chemistries,^{11,15,16} few studies have reported on the performance of thiols in aqueous CO₂-containing conditions, thus limiting the mechanistic understanding of their behavior as corrosion inhibitors in these environments. Additionally, no studies have been performed in order quantify the amount of VCI which partitions to the water condensate phase, and effectively protects the steel from corrosion.

This paper focuses on the understanding of one particular thiol, namely 2-mercaptoethanol (2-ME), and its inhibition mechanism and efficiency of general TLC in CO₂ containing environments. Through the

implementation of a biochemical technique, which targets sulphydryl groups, coupled with a miniature electrode configuration for real time, *in-situ* electrochemical TLC measurements, the 2-ME was thoroughly evaluated in TLC conditions. An advantage of using low-molecular weight mercaptoalcohols, such as 2-ME, is that they have high solubility in water, ethanol, and hydrocarbons, thus serving as a corrosion inhibitor across a range of fluids. Furthermore, 2-ME also has a high volatility, which raises the possibility of using it as a potential VCI. A rapid screening technique using a bio-chemical DTNB assay is optimised and utilised to measure the concentration of the volatile inhibitor within the condensate, enabling determination of the extent to which this chemical is able to reach and partition into the fluid at the top of the line, providing new insights into the inhibition process.

EXPERIMENTAL PROCEDURE

Top of Line Corrosion Rig and Method

A laboratory-scale TLC rig previously developed by De Carvalho *et al.*,¹⁷ was used in this study, with the schematic drawing provided in Figure 1. The setup consists of a 2 L glass beaker, placed on a hot plate to control solution temperature, and a bespoke lid that contained an internal channelled matrix, allowing flow of refrigerant to cool the surface of the TLC specimens, housed within the lid, to required temperatures. Slots machined into the channelled lid enabled three steel specimens to be inserted, simulating the 12 o'clock position of a horizontal 6 inch (152.4 mm) diameter pipeline.^{17,18} Mass loss tests, using mass loss coupons, and electrochemical measurements, using a miniaturized electrode, were utilised in this study to measure TLC rates. A full description of the rig assembly, and its validation as a robust TLC test method, can be found in previous published papers.^{17,18}

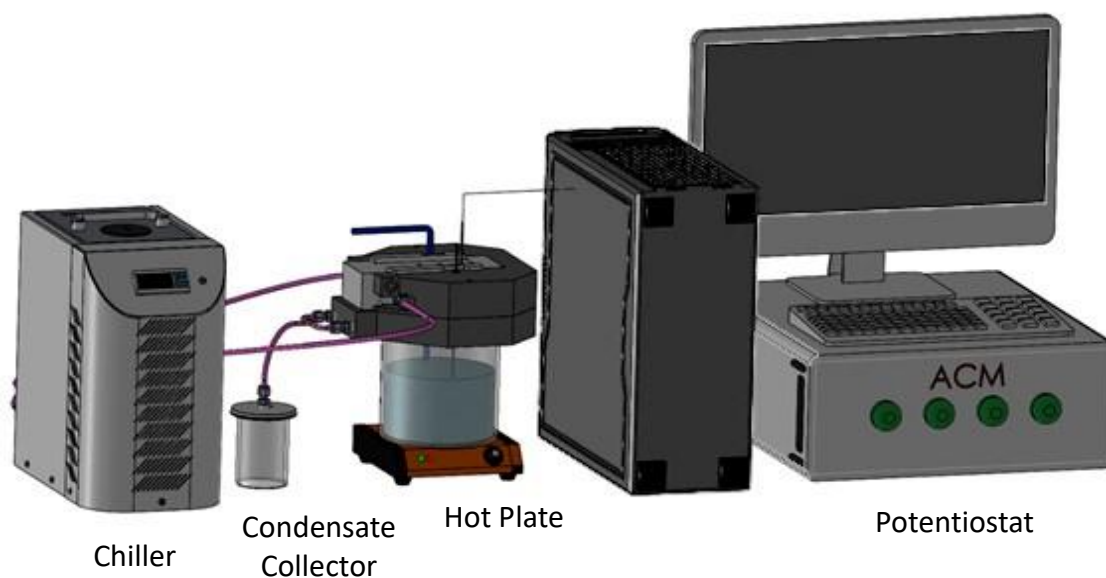


Figure 1: Top-of-line corrosion setup schematic diagram of the entire TLC experimental setup (modified from Folena *et al.*,)¹⁸.

Test Conditions

© 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).

To complete TLC experiments, and evaluate the performance of a corrosion inhibitor, tests were performed for a total of 20 h in a 2 L, CO₂-saturated, deionised water solution containing 3.5 wt.% of sodium chloride (NaCl). Based on previous TLC tests¹⁸ a gas temperature of 70°C and external temperature (achieved through the application of a chiller) of -10°C were chosen as initial test conditions. These conditions resulted in a WCR of 0.81 mL/m²·s and coupon surface temperature of 42.5°C.¹⁸ These initial conditions were chosen because the process of condensate droplet renewal was one of the fastest studied by Carvalho *et al.*,¹⁷ and Folena *et al.*,¹⁸ hence producing a relatively high corrosion rate to enable the performance of the inhibitor to be robustly evaluated. Secondly, stable electrochemical responses using the miniature electrode configuration, were obtained in these conditions.^{17,18} To achieve the required conditions, CO₂ was bubbled into the 3.5 wt.% NaCl solution for a minimum period of 12 h, before heating the bulk solution to 80°C using a hot plate, resulting in a gas temperature of 70°C. The cooling flow through the lid was started once fitted onto the beaker. In the experiments where corrosion inhibitor was applied, test specimens were pre-corroded for 4 h prior to addition of 20 ppm_v of 2-ME, directly into the bulk solution.

Test specimen materials, preparation and configuration of the miniature electrodes

Mass loss coupons and electrochemical test specimens (shown in Figure 2) were used in order to obtain both integrated and real-time corrosion rate data, respectively. The mass loss specimens consisted of cylindrical coupons, 10 mm in diameter and 6 mm thick, with an exposed area to the vapour phase of 0.785 cm². All test specimens were manufactured from the same API 5L¹⁹ X65 carbon steel stock bar, which possessed a ferritic-pearlitic microstructure and chemical composition as shown in Table 1.

The electrochemical tests were performed by using previously developed solid state miniature electrodes which allows electrochemical tests to be performed in condensation systems.^{17,18} The working electrode consisted of a 1 mm diameter cylindrical pin, with an exposed area to the vapour phase of 0.00785 cm². The reference electrode and auxiliary electrode consisted of 1 mm thick Hastelloy® C-276†(UNS N10276) wires, individually isolated and assembled as shown in Figure 2. A full description of the miniature three-electrode setup, used to monitor the changes in corrosion rate throughout the course of the present experiments, can be found in two previous papers by the authors.^{17,18}

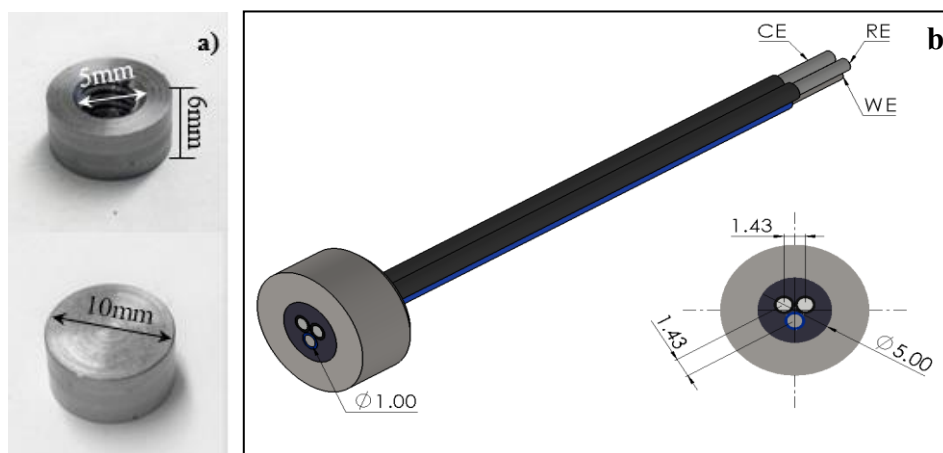


Figure 2: a) Mass loss specimens; both reverse side and test side and b) developed miniature electrodes consisting of two UNS N10276 wires as reference and counter electrodes and an X65 steel wire working electrode, isolated and flush mounted inside a larger X65 specimen (modified from Folena *et al.*)¹⁸.

† Trade name

Table 1:
Chemical Composition of API 5L¹⁹ X65 steel

Elements	C	Si	Mn	P	S	Cr	Ni
wt.%	0.18	0.17	0.64	0.015	0.013	0.04	0.03
Elements	Mo	Al	Cu	Co	Ti	V	Fe
wt.%	<0.002	0.017	0.013	0.018	0.002	<0.001	Balance

Electrochemical measurements

Electrochemical measurements were performed using the miniature three-electrode setup in conjunction with a computer-controlled potentiostat. Three electrochemical techniques were implemented in total, linear polarisation resistance (LPR) and electrochemical impedance spectroscopy (EIS) were employed to determine the *in situ* corrosion rate of the X65 carbon steel specimens. LPR measurements were performed every 20 minutes by polarising the sample from -15 mV vs the open circuit potential (OCP) to +15 mV vs OCP at a scan rate of 0.25 mV/s to obtain a polarisation resistance (R_p). The solution resistance (R_s) was determined over the course of the experiment by completing EIS measurements every 2 hours. These measurements were performed at an amplitude of ± 15 mV vs OCP and frequency range from 20 kHz to 0.1 Hz, resulting in 50 measurements (10 measurements per frequency decade), and were performed to obtain R_s values and further calculation of charge transfer resistance (R_{ct}).

The value of R_p was corrected for R_s ($\Omega \cdot \text{cm}^2$) and ultimately used to determine the corrosion rate with time using the Stern-Geary relationship in conjunction with Faraday's Law. For tests performed in the 4 different WCRs the average of R_s values were $5.6 \pm 0.9 \Omega \cdot \text{cm}^2$.

After completion of each 20 h experiment, Tafel plots were completed by performing individual cathodic and anodic sweeps (on separate test specimens), scanning from OCP to -150mV vs. OCP for the cathodic branch, and from OCP to +150mV vs. OCP for the anodic branch, at a scan rate of 0.5 mV/s. From the polarization curves produced, it was possible to determine the anodic (β_a) and cathodic (β_c) Tafel constants in mV by measuring their respective gradient over regions where linearity was observed (on an E vs log(i) plot).

From the polarisation curves produced, it was possible to determine the anodic (β_a) and cathodic (β_c) Tafel constants in mV/decade by measuring their respective gradient over regions where linearity was observed (on an E vs log(i) plot). Then determine the Stern-Geary coefficient (B), for each experiment, and ultimately the corrosion current density (i_{corr}) (Equation (1)):

$$i_{corr} = \frac{B}{R_{ct}} = \frac{1}{R_{ct}} \frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c)} \quad (1)$$

where B is the Stern-Geary coefficient, β_a is the magnitude of the anodic Tafel constant, and β_c is the magnitude of the cathodic Tafel constant (determined in separate experiments).

The value of corrosion current density (i_{corr}) was then used in conjunction with Faraday's Law and an appropriate conversion factor to obtain the corrosion rate in mm/year, as shown in the Equation (2), which was converted into a rate of thickness loss in mm/year, in accordance to ASTM G102.²⁰

$$V_c = K \frac{i_{corr} M_{Fe}}{nF\rho} \quad (2)$$