Importance of Location for Addition of Surfactant Inhibitors in Corrosion Experiments

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The use of organic surfactant corrosion inhibitors provides an economical and effective way for internal corrosion control of oil and gas production and transportation pipelines. Corrosion inhibition measurements using electrochemical techniques can be used to evaluate the efficacy of corrosion inhibitors based on steady-state corrosion rates. The corrosion behavior with respect to time can further be utilized to quantify the adsorption kinetics of inhibitor molecules on metal and can further be integrated into the development of corrosion prediction tools. However, corrosion rate measurements can be very sensitive to experimental methodology in the presence of corrosion inhibitors in the test solution, and repeatability is often difficult to achieve if a robust methodology is not followed meticulously. In this study, the importance of the location of inhibitor addition in lab-scale corrosion experimentation is discussed.

KEY WORDS: corrosion rate, inhibitor addition, organic corrosion inhibitors, surface tension

INTRODUCTION

C orrosion is a major concern for the safety and durability of various metallic structures and components, and corrosion inhibitors are widely used to mitigate corrosion risk.¹⁻² Inhibitors, more specifically organic corrosion inhibitors, are typically surfactant-type molecules with a hydrophilic head group and a hydrophobic tail. Corrosion inhibition using organic corrosion inhibitors relies on the adsorption of inhibitor molecules on the metal surface that reduces the reaction rate between the metal and the corrosive environment.³ Electrochemical measurements are often used in lab-scale testing of corrosion inhibitors to understand the adsorption mechanisms and evaluate the corrosion rates measured using linear polarization resistance (LPR) technique, corrosion inhibition efficiency can be calculated using Equation (1):⁴

$$\label{eq:link} \text{Inhibition efficiency} \ (\%) = \frac{(CR)_0 - (CR)_i}{(CR)_0 - (CR)_{SSC}} \times \ 100\% \tag{1}$$

where $(CR)_0$ is the steady-state corrosion rate with no inhibitor (before inhibitor injection), $(CR)_i$ is the inhibited steady state corrosion rate, and $(CR)_{SSC}$ is the lowest corrosion rate achievable with a given inhibitor at surface saturation concentration (SSC).

Corrosion inhibition measurements at different bulk inhibitor concentrations using electrochemical techniques is an indirect way to estimate the metal's SSC at given environmental conditions. SSC is defined as the minimum inhibitor concentration at which the maximum corrosion inhibition efficiency is achieved, when increasing the bulk inhibitor concentration further does not lead to any significant decrease in steady-state corrosion rates.⁵ More details on metal SSC are described elsewhere.^{4,6}

This corrosion inhibition efficiency at steady state calculated using Equation (1) has also been reported as a measure of inhibitor surface coverage (θ) assuming a "geometric blockage" model of corrosion inhibition.⁴ This type of analysis has also been extended to analyze the transient behavior of the inhibitor adsorption process to estimate kinetic adsorption/ desorption constants and to be integrated with corrosion prediction models.⁷⁻⁸ The key point is the first step to this analysis, which is to determine the metal SSC for the specific inhibitor. It should also be understood that the effectiveness of inhibitors is influenced by several factors, including the method of inhibitor application.

In lab corrosion inhibition experiments, inhibitor injection is a commonly used method to introduce inhibitors into a corrosive environment. Upon addition to the test solution, the inhibitor molecules can undergo partitioning: some may remain in the test solution, some can adsorb onto the metal surface, a portion may migrate to the gas/solution interface, and others may contribute to the formation of micelles.⁵ As the adsorption onto the metal surface directly affects the inhibition performance, electrochemical corrosion rate measurements would shed light on the metal adsorption part. Additionally, as the inhibitor molecules in question belong to the surfactant type, their adsorption at the gas/solution interface would lead to a decrease in the surface tension of the gas/solution interface. Therefore, measuring the surface tension provides insights into the extent of inhibitor molecule adsorption at the gas/solution interface.

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The influence of the inhibitor addition method in corrosion inhibition experiments is often overlooked, despite its potential impact on inhibitor performance. This study aims to address this gap by investigating the different methods of inhibitor addition, specifically focusing on the location of inhibitor addition (directly into the solution phase vs. addition at the gas/solution interface), in lab corrosion inhibition experiments with a prime focus to determine the metal SSC.

EXPERIMENTAL PROCEDURES

2.1 | Corrosion Rate Measurement

In the present work, model corrosion inhibitors such as quaternary ammonium-based compounds and imidazolines with different alkyl tail lengths have been synthesized in the lab as reported elsewhere.⁵ The rationale for using lab-synthesized model compounds was to decrease the number of unknowns in the experimental design because it is understood that commercial corrosion inhibitor packages contain formulations that are trade secrets and difficult to account for and control.¹ For this study, a quaternary ammonium-type corrosion inhibitor, tetradecyldimethylbenzylammoniumbromide (BDA-C14), is tested. LPR corrosion rate measurements were conducted at different inhibitor concentrations in separate tests to measure the steady-state corrosion rates and calculate corrosion inhibition efficiencies. The final objective was to establish the metal SSC for the BDA-C14 model inhibitor compound from corrosion rate measurements.

Corrosion experiments were conducted using a typical three-electrode glass cell setup. The working electrode was an API 5L X65 rotating cylindrical electrode with a rotating speed of 1,000 rpm, a saturated Ag/AgCl electrode was used as a reference electrode, and a platinum-covered titanium mesh was used as a counter electrode. For each experiment, the working electrode was polished with emery paper using 80, 120, 400, and 600 grit and then ultrasonically cleaned in isopropyl alcohol and dried with a nitrogen gas stream.

A 2 L glass cell setup was filled with 1 wt% aqueous NaCl solution. The test solution was sparged continuously with 1 bar CO₂ for 60 min to remove any dissolved oxygen before introducing the working electrode and the sparging continued for the entire duration of tests. The temperature was maintained at 30±1°C and the pH of the solution was adjusted to 4.00±0.01 using a nitrogen-sparged, deoxygenated NaOH solution. A deoxygenated inhibitor solution was prepared containing a predetermined amount of corrosion inhibitor that would be needed to achieve the required bulk inhibitor concentration, which was then added to a glass cell after 20 min of exposure in test solution at the open-circuit potential (OCP) (also sometimes referred to as precorrosion). The inhibitor was added using a long needle inserted through a septum on the glass cell lid so that it would be injected into the solution approximately at the height of the working electrode. This methodology of inhibitor injection was meticulously maintained for all electrochemical experiments as it is believed to have a considerable effect on the repeatability of corrosion inhibition measurements. Corrosion rates were then measured using LPR technique every 20 min by scanning from -5 mV_{OCP} to +5 mV_{OCP} at 0.125 mV/s until the steady-state corrosion rates were achieved in different tests with different bulk inhibitor concentrations (5 ppm(w), 10 ppm(w), 25 ppm(w), 37.5 ppm(w), and 50 ppm(w)). For accurate calculation of corrosion rates using LPR, solution resistance was measured at each step using potentiostatic electrochemical impedance spectroscopy and subtracted from the measured polarization resistance values. The B value of 26 mV/decade was used to convert corrected polarization resistance to corrosion rates. The corrosion inhibition experiments conducted in this study were compared to the corrosion inhibition measurements previously reported by Moradighadi, et al.,⁵ for the BDA-C14 model inhibitor compound. The sole distinction between the two sets of experiments lies in the method of inhibitor addition, specifically the injection of the inhibitor into the solution phase in the present study vs. the inhibitor addition at the gas/solution interface for previously reported measurements.⁵

2.2 | Surface Tension Measurement

Surface tension measurements were performed to supplement the corrosion rate measurements and to understand the effect of the location of inhibitor addition on the adsorption of inhibitor molecules at the gas/solution interface. Solutions with the desired bulk inhibitor concentration were prepared in two ways. In the first approach, a concentrated solution of the inhibitor was carefully injected directly into a 1 wt% NaCl solution using a pipette. This method was chosen to ensure precise control over the final concentration of the inhibitor in the solution. Subsequently, the solution was thoroughly mixed using a glass rod, aiming to closely replicate the conditions observed during electrochemical measurements when the inhibitor was injected directly into the solution. In the second approach, the necessary quantity of the concentrated inhibitor solution was added drop by drop onto the gas/solution interface. This was done to investigate any potential variations in surface tension measurements that may arise from this specific mode of introducing the inhibitor. Surface tension measurements at the gas/solution interface were conducted using a semiautomatic Krüss K20[†] tensiometer with the Du Noüy ring method. An elaborate cleaning practice using acetone, deionized water, and propane flame was followed meticulously to avoid the contamination of the Du Noüy ring by inhibitor molecules between the measurements. All of the reported measurements were repeated at least three times.

RESULTS AND DISCUSSION

3.1 | Corrosion Rate Measurements

The key goal of this study was to understand the influence of the inhibitor addition on steady-state corrosion rates and evaluate the metal SSC value for the BDA-C14 model inhibitor compound in experimental conditions. After 20 min of exposure in the test solution at the OCP (precorrosion), the inhibitor solution was injected directly into the glass cell in the solution phase using a long needle. Figure 1 shows experimental results. It is shown that for inhibitor concentrations of 5 ppm(w) there was a significant decrease of the corrosion rate, which was even more pronounced at 10 ppm(w). Above 10 ppm(w) and up to 50 ppm(w), there is no significant difference in the measured corrosion rates. Hence, metal SSC for BDA-C14 inhibitor added directly into the solution phase way lies somewhere between 5 ppm(w) and 10 ppm(w).

However, it has been reported by Moradighadi, et al.,⁵ previously that the metal SSC for the same inhibitor molecule (BDA-C14) and the same experimental conditions, lies between 25 ppm(w) and 50 ppm(w), see Figure 2. The only difference between that series of experiments and the present one is the location of inhibitor addition; they did it at the gas/solution interface and in the present study it was injected directly into the solution with a needle and a syringe.⁵ In addition to the

[†] Trade name.



FIGURE 1. Electrochemical corrosion rate measurements with respect to time to determine metal SSC of BDA-C14 model inhibitor compound in 1 wt% aqueous NaCl solution, 1 bar CO_2 , pH 4, and 30°C. Inhibitor addition in the solution phase.



FIGURE 2. Difference in steady-state corrosion rates and transient corrosion behavior due to location of inhibitor addition for BDA-C14 model inhibitor compound in 1 wt% NaCl aqueous solution, 1 bar CO_2 , pH 4, and 30°C. For two curves referred as 25 ppm and 50 ppm, inhibitor addition was in the solution phase. For two curves referred to as 25 ppm* and 50 ppm*, inhibitor addition was at the gas/solution interface and are reproduced from results presented by Moradighadi, et al., for comparison.⁵

difference in the measured steady state corrosion rates, the transient behavior observed is also different. There is a sudden decrease in corrosion rate observed when the inhibitor is injected into the solution vs. a gradual decrease in corrosion rates reported previously for inhibitor addition at the gas/ solution interface, refer to Figure 2 for comparison.⁵

The schematic of two scenarios of inhibitor addition is shown in Figure 3. This difference in corrosion behavior can be explained as follows. When inhibitor molecules are added to the test solution, they partition between the gas/solution interface, solution phase, and steel electrode surface. Let us examine how this partitioning happened for the two different ways of inhibitor addition.

Case 1: When inhibitor was added at gas/solution interface (Figure 3[a]), a large share of the inhibitor molecules



FIGURE 3. Schematic showing two cases based on location of inhibitor addition for electrochemical corrosion rate measurements. (a) Inhibitor addition at gas/solution interface and (b) inhibitor addition in solution phase.

remained adsorbed there initially. Hence, for adsorption onto a steel electrode surface to happen, inhibitor molecules had to first desorb from gas/solution interface and migrate through the liquid phase for final adsorption on a steel electrode surface. The desorption of inhibitor molecules from gas/solution interface to the solution phase has a kinetic barrier and is rather slow.⁹⁻¹⁰ Due to this kinetic barrier for desorption of inhibitor molecules from gas/solution interface, inhibitor molecules stayed longer at gas/solution interface and a lower concentration of inhibitor molecules was available in bulk solution for adsorption and inhibition at the steel surface. This explains the slower decrease in corrosion rates and higher steady state corrosion values reported by Moradighadi, et al.,⁵ who added the inhibitor at the gas/solution interface. In a perfect steady state scenario, one can imagine that a true steady state would be reached and inhibited corrosion rates would be the same, irrespective of where the inhibitor was added, at the gas/ solution interface, or injected directly into the solution. However, this is not what the experimental results show, indicating that the time required to achieve this equilibration is indeed very long or that it cannot be achieved when the inhibitor is added at the gas/liquid interface, probably because of some sort of hysteresis.

Case 2: When inhibitor addition was done directly by injection into the solution (Figure 3[b]). In this case, the adsorption of the inhibitor on the metal electrode surface proceeded rapidly. This is because a higher concentration of inhibitor molecules was present in the solution and available for adsorption on a steel electrode surface and for providing protection against corrosion. Hence, adding inhibitor directly in the solution phase helped in reaching the steady state much faster as compared to a gas/solution interface addition and explains the lower steady-state corrosion rates in current study vs. previously reported values.⁵

When the inhibitor is added at the gas/solution interface (Figure 3[a]), upon injection, some of the inhibitor solution can permeate the gas/solution interface, mix with the bulk solution and thereby become accessible more readily to the metal surface for adsorption. The result is a reduction in corrosion rates,

SCIENCE SECTION



FIGURE 4. Surface tension measurements of BDA-C14 model inhibitor compound in 1 wt% aqueous NaCl solution. Error bars show the standard deviation values obtained.

as illustrated by corrosion rate curves in Figure 2 (25 ppm* and 50 ppm*). However, we must also acknowledge that this is not the whole story and emphasize the significance of adsorption occurring at the gas/solution interface. The sudden decrease in corrosion rates was observed when the inhibitor was injected directly into the solution, as opposed to the relatively gradual decrease when the same inhibitor molecules added at the gas/ solution interface (Figure 2), at the same concentrations and under the same experimental conditions, suggests differences in the availability of inhibitor molecules for adsorption at the metal surface (i.e., the working electrode).

It is therefore thought that the direct method of injection of inhibitor into the solution is more representative of the practical situation in the field and is also a more reproducible way to conduct lab experiments with inhibitor addition. Based on this methodology, SSC for the BDA-C14 model inhibitor compound on mild steel was re-established and it lies between 5 ppm(w) and 10 ppm(w) at the given experimental conditions. As the rate of adsorption determines the rate of decrease in corrosion rates, the results presented in this study are also consistent with previously reported quartz crystal microbalance measurements and suggest that the adsorption step happens rather fast—within minutes and does not take hours, as previously thought.¹¹⁻¹² Similar observations related to the kinetics of adsorption of BDA-C14 inhibitor molecules were made by Wang, et al., using atomic force microscopy.¹³

3.2 | Surface Tension Measurements

In the *Corrosion Rate Measurements* section, the argument regarding slower adsorption kinetics on the steel surface when the inhibitor is added at the gas/solution interface was based on the premise that a larger portion of inhibitor molecules would remain adsorbed at the gas/solution interface for a long time, due to the kinetic barrier in desorption.⁹⁻¹⁰ However, this hypothesis requires further verification and confirmation. This hypothesis was tested by conducting surface tension measurements for inhibitor solutions prepared in two different ways, as explained earlier in the *Surface Tension Measurement* section. BDA-C14 is a surfactant molecule that reduces the gas-solution surface tension proportional to inhibitor concentration until a point, where the gas/solution interface is saturated. This means that for our hypothesis to hold, the measured surface tension for a thoroughly mixed inhibitor solution prepared by direct injection of the inhibitor should be higher than that for the solution prepared by inhibitor addition at the gas/solution interface. Figure 4 shows the surface tension measurement results. The findings indicate that, when the inhibitor is added at the gas/solution interface, more inhibitor molecules remain at the interface, leading to lower surface tension values. One could argue that, over an extended period, the surface tension measurements would become equivalent in both cases once a "true" equilibrium is reached between all surfaces and bulk concentration, regardless of the location of inhibitor addition. However, the surface tension measurements strongly align with the corrosion inhibition measurements, suggesting that the desorption of inhibitor molecules from the gas/solution interface is a very slow process, thus providing further evidence in support of our hypothesis.

CONCLUSION

> This paper presents a systematic study that highlights the importance of the location of inhibitor addition in lab-scale corrosion inhibition experiments. The experimental methodology favored in this study-by direct injection into the solution, is robust, helps in conducting repeatable corrosion inhibition experiments which is otherwise very difficult, and more importantly, is better suited when interpreting corrosion inhibition results in terms of inhibitor adsorption on the metal electrode surface. This is because when the inhibitor is injected directly into the solution phase, this excludes an extra slow desorption step of inhibitor molecules from the gas/solution interface into the solution, which might play a significant role and cause delays in corrosion inhibition response. It was proven with confidence that for the tested model inhibitor compound (BDA-C14), direct inhibitor injection in solution phase leads to lower steady-state corrosion rates and faster adsorption kinetics as compared to addition at the gas/solution interface.

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