

Adsorption of Model Inhibitor Compound Characterized Using Quartz Crystal Microbalance with Dissipation Monitoring

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ABSTRACT

Although inhibitor adsorption and inhibition mechanisms have been studied extensively using various electrochemical techniques, these electrochemical techniques only provide an indirect estimate of inhibitor adsorption. In the present study, a QCM with dissipation monitoring (QCM-D) was used to investigate the adsorption on gold coated quartz crystal resonator (QCR) of a model corrosion inhibitor (CI) compound at different bulk inhibitor concentrations. In a first step, the classical Sauerbrey's equation was used to analyze the normalized frequency change data for estimation of adsorbed mass. Normalized frequency change was also analyzed in conjunction with dissipation change using small load approximation (SLA) model to establish the nature of adsorbed layer and to qualify the validity of Sauerbrey's equation. In context of the bulk inhibitor concentrations tested (50 ppm(w) and 100 ppm(w) of CI in 1wt.% NaCl solution) in this study, the adsorbed layer behaves as a rigid mass. A conscious effort is made to state and validate the assumptions for the analysis of experimental results.

Keywords: Corrosion inhibitor, inhibitor adsorption, inhibition, Sauerbrey equation, QCM, QCM-D

INTRODUCTION

Oil and gas transportation pipelines are often prone to internal corrosion in service environments. Two main strategies used to combat the problem of internal corrosion in pipelines involve the use of corrosion inhibitors (CIs) and more corrosion resistant alloys. Corrosion mitigation using inhibitors is a favorable choice because of better economic feasibility.¹⁻⁴ Among all the types of corrosion inhibitors, organic corrosion inhibitors are most widely used in the industry.

Organic corrosion inhibitors are typically surfactant-type organic molecules with a hydrophilic head group and a hydrophobic alkyl tail. Corrosion inhibition using organic CIs relies on the mechanisms related to the adsorption of inhibitor molecules on a metal surface.^{2,4} However, the exact adsorption mechanisms are not yet clearly understood. So, in designing CIs with improved efficiency and to have a better understanding of underlying inhibition mechanisms, it becomes extremely important to study and quantify

adsorption mechanisms. Various studies focusing on electrochemical experiments have been performed in the past but due to the intrinsic limitations of traditional electrochemical techniques, there is a lack of molecular level understanding of electrode/electrolyte interfacial properties such as adsorbed layer thickness, orientation of adsorbed inhibitor molecules etc. in the presence of corrosion inhibitor.⁵⁻⁷

Adsorption of CIs is a surface phenomenon happening at the electrode/electrolyte interface. Quartz crystal microbalance (QCM) is a powerful surface acoustic sensor that can be effectively used to study surface reactivity.⁸ With recent advances in technology, a QCM-D (QCM with dissipation monitoring and measurements at multiple overtones) can now be used to delve into the territory of characterizing the mechanical properties of the adsorbed layer.⁹ QCM-D as a tool has found an extensive application in the field of protein adsorption but has been minimally applied in corrosion inhibition research. This project makes a conscious effort to borrow the learnings from a different field of science, learn, understand, and develop a tool for corrosion related research.

With this motivation, a QCM-D equipped with a flow control unit was used for better understanding of an electrode/electrolyte interface to understand the nature of the adsorbed layer and quantify the adsorbed layer thickness for a model inhibitor compound, tetradecyldimethylbenzylammonium (BDA-C14), on a noble substrate (gold for QCM-D) in 1 wt.% NaCl solution. In this paper, adsorption experiments are discussed for BDA-C14 at two inhibitor concentrations (50 ppm(w) and 100 ppm(w)). Based on the frequency change and dissipation change vs. time, experimental results are discussed for qualitative indications and quantitative analysis primarily for the adsorbed layer thickness.

EXPERIMENTAL PROCEDURE

Model corrosion inhibitors such as quaternary ammonium-based compounds and imidazolines with different alkyl tail lengths have been synthesized in-house for multiple research projects at the ICMT.¹⁰⁻¹² The rationale of using lab synthesized model compounds was to decrease the number of unknowns in the experiments because it is understood that commercial CI packages contain certain formulations which are trade secrets.^{1,2} For this study, the adsorption behavior of BDA-C14 has been tested since it has already been well characterized.¹⁰⁻¹² BDA-C14 is a quaternary ammonium type model inhibitor compound with alkyl tail having fourteen carbons as shown in Figure 1. Test conditions for this experiment are presented in Table 1.

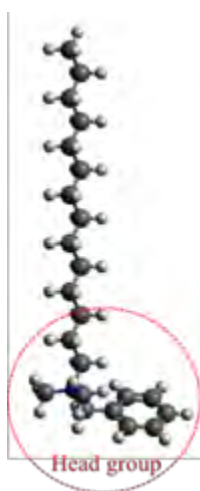
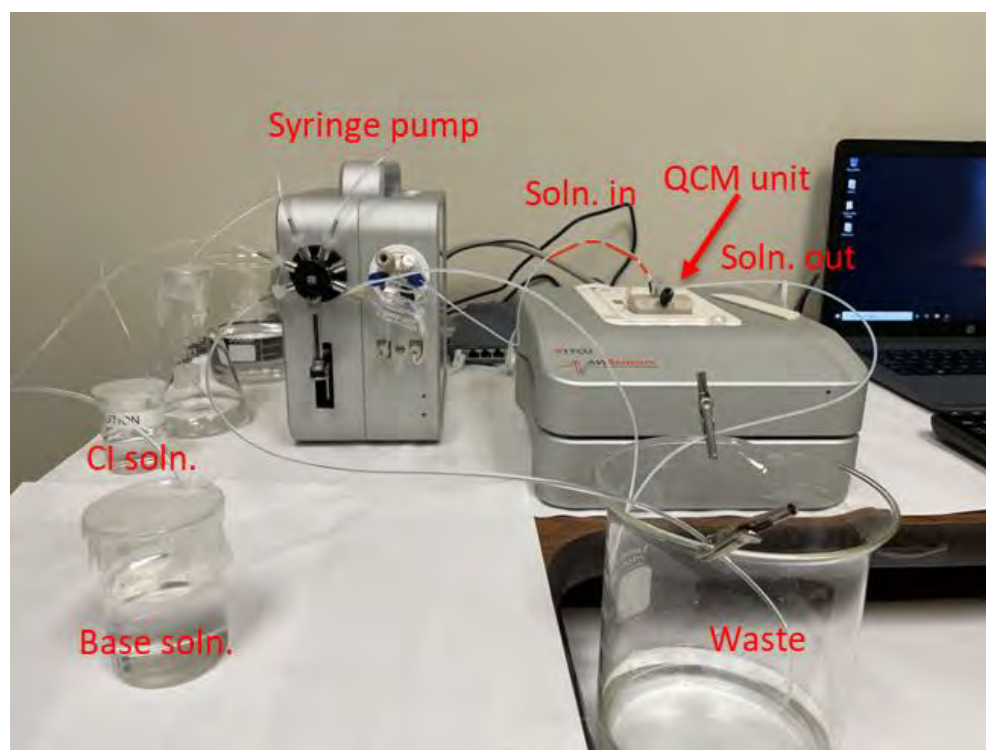


Figure 1: BDA-C14; a quaternary ammonium-type corrosion inhibitor.¹³

Table 1: Test matrix for inhibitor adsorption on gold coated QCR.

Parameter	Value
Base Electrolyte	1 wt. % NaCl in deionized water
Inhibitor Solution	50 ppm(w) & 100 ppm(w) BDA-C14 in base electrolyte
Substrate/QCR	5 MHz, wrapped around configuration ¹² , Au/Ti, polished
Operating overtones	n=1, 3, 5, 7, 9, 11 and 13
Flow rate	0.05 mL/minute

The QCM-D unit used for this study monitors frequency change and dissipation change at multiple overtones simultaneously (n=1, 3, 5, 7, 9, 11 and 13).^{14,15} AT-cut gold coated, polished quartz crystals with a fundamental resonance frequency of ~5 MHz were used as the substrates.[§] Figure 2 shows the QCM-D experimental setup that was used for inhibitor adsorption experiments. Firstly, base electrolyte solution (base solution) without any inhibitor was pumped through the QCM unit cell at a constant flow rate to get a baseline frequency response against which any change in frequency due to mass adsorption was measured. Then, the valve at the syringe pump was switched to flow inhibitor solution (CI solution) through the QCM cell while the change in frequency and dissipation values were measured with respect to time. Experimental data is represented in terms of frequency change and dissipation change with respect to time.

**Figure 2: QCM-D setup with flow control unit used for inhibitor (BDA-C14) adsorption.**

[§] purchased from Advanced Wave Sensors S.L., (Paterna, Spain).

METHODOLOGY

Recorded frequency change and dissipation change can be analyzed in two ways:

1. **Qualitative indications:** Based on certain signatures in frequency and dissipation change data recorded with respect to time, some preliminary predictions can be made about the nature of adsorbed mass (rigid or viscoelastic). Figure 3 suggests that:

- For no mass deposit, there is no change observed with respect to time for normalized frequency change and dissipation change. This is often referred to as baseline in QCM experiments. Obtaining a stable baseline is equally important in any QCM based measurements as any change due to an adsorption/desorption process is measured with respect to a stable baseline.
- For a rigid mass deposit, dissipation change with respect to time is small or negligible and there is no split in dissipation change values at multiple overtones. Net frequency change for such cases can be used directly for estimation of adsorbed mass using Sauerbrey's equation.
- For a viscoelastic mass, dissipation change with respect to time cannot be neglected anymore and hence should be part of any quantitative analysis. The validity of Sauerbrey's equation would no longer hold for calculation of net adsorbed mass at the surface of the QCR. In addition to net dissipation change, there is also an obvious split observed in the frequency change and dissipation change values measured at different overtones which can be related to the mechanical properties of adsorbed layer. Consideration of the magnitude of dissipation is necessary to make any conclusions.

2. **Quantitative analysis:** To estimate the adsorbed layer thickness and mechanical properties of the adsorbed layer, different models can be used to analyze QCM-D data such as Sauerbrey's model (applicable for rigid films only), small load approximation (SLA) model, and Voigt based viscoelastic model.^{8,16–18} For the results analyzed in this paper, Sauerbrey's model and SLA model were used.

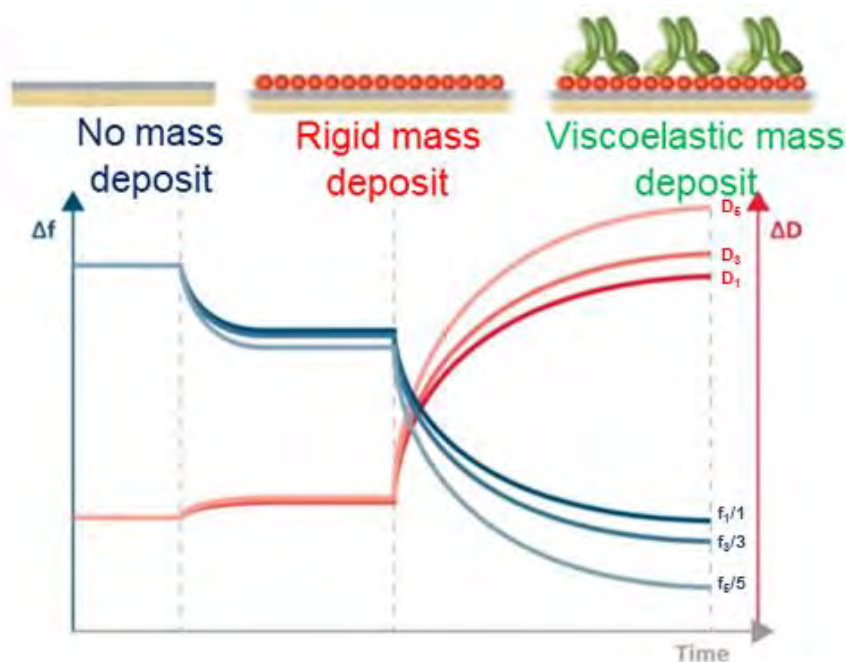


Figure 3: Schematic of frequency and dissipation response using QCM-D at multiple harmonics for rigid and viscoelastic mass deposit.⁹