

Use of Quartz Crystal Microbalance in Study of Inhibitor Adsorption

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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. Quartz crystal microbalance (QCM) has been shown to be a powerful acoustic technique which can be effectively used to evaluate net mass adsorption of inhibitors, adsorption rates and kinetic coefficients. In the present study, calibration of QCM by electrochemical deposition of copper on gold-coated quartz crystal resonator was done to evaluate the minimum mass change that can be determined using these devices. Sensitivity coefficient was measured within 5% accuracy for QCM-D equipment vs. within 20% accuracy for oscillatory circuit based-QCM equipment. Also, a different oscillatory circuit based-QCM equipment was used with flow cell to investigate the adsorption of tetra-decyl-dimethyl-benzyl-ammonium (Q-C14) inhibitor model compound on gold-coated quartz crystal resonator. Analysis of experimental data indicated that the inhibitor was adsorbed on the gold surface within a few minutes and the net amount of inhibitor adsorbed depends upon the bulk inhibitor concentration. However, the rate of frequency change for adsorption and desorption processes did not vary much for two inhibitor concentrations (50 ppm(w) and 100 ppm(w)) used for this study. This calls for further investigation of inhibitor adsorption at different concentrations.

Keywords: QCM, organic inhibitor, inhibitor adsorption, mass calibration, Sauerbrey equation

INTRODUCTION

Corrosion is a material degradation process, mostly related to metals, after exposure to adverse environmental conditions.¹ It leads to huge economic losses, environmental damage and

possible risks to human life. According to a report published in 2016, economic losses due to corrosion were estimated to be US\$ 2.5 trillion which is approximately equivalent to 3.4% of the global Gross Domestic Product (2013).² Corrosion of carbon steel pipelines in oil and gas industry is a major contributor to corrosion related losses.² The majority of oil and gas transportation structures are made of low alloy carbon steel, which has poor resistance to corrosion. Hence, pipelines are often prone to internal corrosion in service environments. Any structural failure directly implies significant economic burdens and associated risk to the environment and human life. Therefore, corrosion as a process, becomes a key factor in structural design and material selection in energy applications.

The two main strategies to combat the problem of internal corrosion in upstream oil and gas pipelines are the use of corrosion resistant alloys and the addition of corrosion inhibitors to flow in mild steel pipelines. Corrosion resistant alloys (CRAs) are normally used in areas where inhibition of mild steels may not provide sufficient protection from corrosion related damages as the use of CRAs is typically not cost effective. Use of corrosion inhibitors is a comparatively cost effective corrosion mitigation method.^{3,4} A corrosion inhibitor (CI) is a chemical substance that, when added in small amounts, can diminish corrosion rates significantly in particular environments.¹ Development of CIs with high efficiency as well as persistency can yield huge advantages in saving corrosion costs.

Organic CIs are most widely used in the oil and gas industry. They are typically surfactant-type carbon-based compounds with a hydrophilic head group and a hydrophobic alkyl tail. It is a well-established fact that corrosion inhibition using organic CIs heavily relies on the mechanisms related to adsorption of molecules on a metal surface.^{3,5} However, the exact adsorption mechanisms are not yet clearly understood. Most of the research related to designing new inhibitor compounds has been based on trial and experimentation methods.¹ To design new CIs with increased efficiency, understanding their adsorption mechanisms is highly important. Many studies explain the process of corrosion inhibition using a “geometric blockage” model, which suggests the formation of a CI protective layer over the metal surface.^{3,6} This model suggests that CI’s work by forming a barrier layer between the metal surface and the water molecules, thus stopping corrosion by a blockage effect. The point of view of the “blockage model”, as discussed by Dominguez, *et al.*, contains intrinsic limitations that has hindered the development of a mechanistic model to satisfactorily describe and predict the effect of organic CIs on CO₂ corrosion of mild steel for many years.^{7,8} In 2016, Dominguez, *et al.*, has shown the ability to mechanistically model the influence of an inhibitor on mild steel corrosion and, in 2018, published results showing the influence of increasing the alkyl tail length of an inhibitor molecule on corrosion mechanisms by using this model.^{7,9} Although studies are becoming more mechanistic in nature, the current literature available in this field is dominated by purely qualitatively described inhibition mechanisms, which necessitates the continued development of more rigorous inhibition models to be used for corrosion prediction.⁴

With a broader purpose to understand inhibitor performance, it is important to address the adsorption mechanisms for CIs. Quantifying CI adsorption kinetics would develop this understanding further and enhance the use of this knowledge for field applications. QCM can be effectively used to study surface phenomena and evaluate net mass adsorption of inhibitors, as well as adsorption rates and kinetic coefficients. Moreover, the recent advances in this technology (QCM with dissipation monitoring) allows characterization of the structure and the viscoelastic properties of the adsorbed layer.^{10,11} This technique has been widely used in the fields of protein adsorption and air quality monitoring but has been minimally applied in corrosion

related research.^{11–13} To use QCM effectively and accurately, it is very important to understand the fundamentals and working principles of this technique and efficiently apply those to CI containing systems. With an effort to quantify the operating boundaries of the equipment with repeatability, reproducibility, sensitivity and accuracy as key parameters, mass calibration of an electrochemical quartz crystal microbalance (EQCM) was conducted using electrodeposition of copper on gold-coated quartz crystal resonators (QCRs).

This paper consists of two parts. The first part focuses on mass calibration experiments conducted using copper electrodeposition on two different types of QCM equipment. Apart from comparing the mass sensitivities for these two QCM, the focus was also to accurately define the electrochemically and piezoelectrically active area of a resonator and define the correct methodology to conduct mass calibration of a QCM. The second part of the paper reports on the experimental results for corrosion inhibitor adsorption on gold-coated QCR, conducted using an oscillatory circuit based-QCM setup equipped with a flow cell.

EQUIPMENT

Experiments presented in this paper were done on different QCM equipment. So, for the quick reference and the ease of reading, this section is added. For the first part of this paper on the mass calibration of QCM, experimental methodology and results obtained using Stanford Research Systems* (SRS QCM200 – shown in Figure 1a, referred to as QCM system 1) and AW Sensors† (AWS X1 - shown in Figure 1b, referred to as QCM system 2) are compared and summarized. QCM system 1 consists of a QCM200 digital controller, QCM25 crystal oscillator and crystal holder. QCM system 2 consists of a X1 controller and an electrochemical cell. The second part of this paper is focused on measurement of inhibitor adsorption, and a lab-made QCM setup (oscillatory circuit based) (as shown in Figure 2, referred to as QCM system 3) was used.

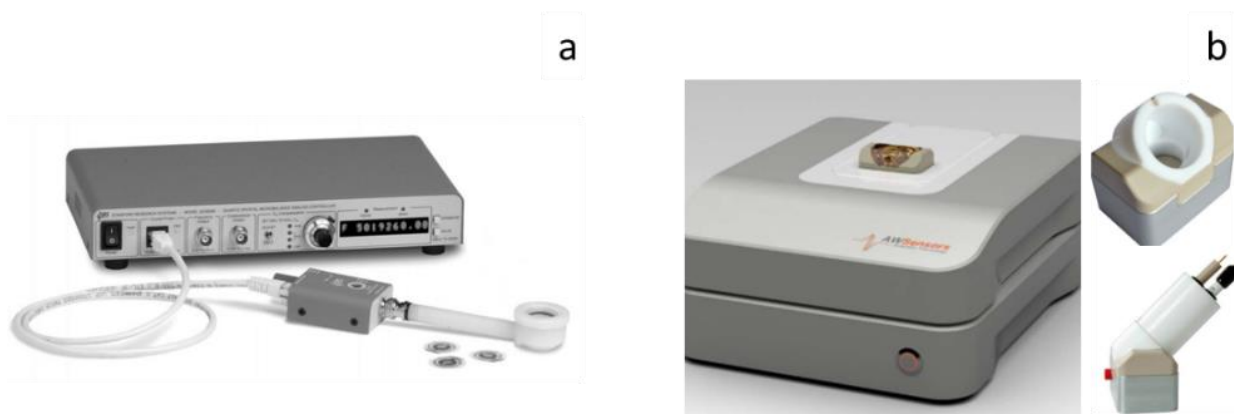


Figure 1: (a) The QCM200 setup consisting of digital controller, crystal oscillator and crystal holder.^{14,15} (Equipment based at ICMT, Ohio University and referred to as QCM system 1.) (b) The AWS X1 from AW sensors, setup consisting of controller and electrochemical cell.¹⁶ (Equipment based at LISE, Sorbonne University and referred to as QCM system 2.)

* Trade Name

† Trade Name

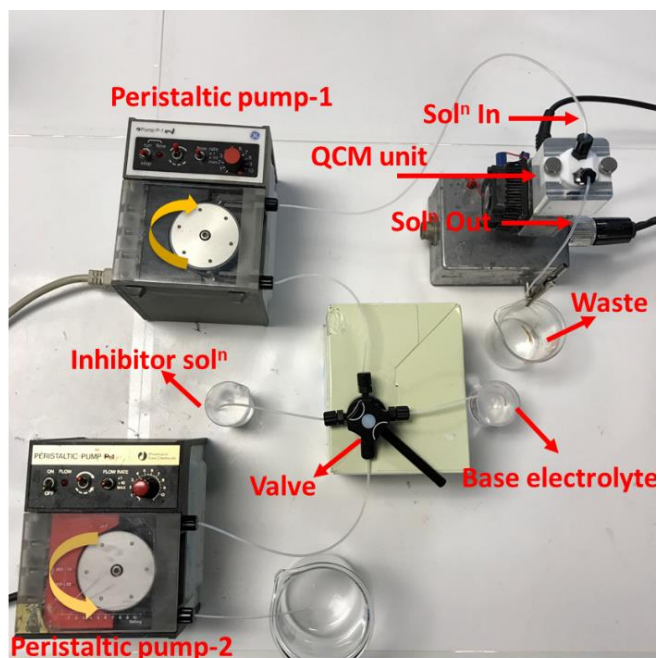


Figure 2: QCM setup equipped with flow cell used for inhibitor (Q-C14) adsorption. (Equipment based at LISE, Sorbonne University and referred to as QCM system 3.)

MASS CALIBRATION OF QCM

Methodology

The correct procedure for mass calibration was established and is as follows:

1. Calculate mass change using Faraday's law; variables: applied current (I) and time (t).

$$\Delta m_{Faraday} = \frac{I \cdot t \cdot M_w}{F \cdot n'} \quad (1)$$

where,

- $\Delta m_{Faraday}$ – mass deposited, g
- I – applied current, A
- t – time interval, s
- M_w – molar mass of substance, g mol⁻¹
- F – Faraday constant, 96485.3 C mol⁻¹
- n' – no. of electrons exchanged, $n'=2$

2. Evaluate piezoelectrically and electrochemically active area based on cell design and crystal configuration; A and A' respectively (measured in cm²).
3. Normalized electrochemically deposited mass based on Faradic calculations.

$$\Delta m_F = \frac{I \cdot t \cdot M_w}{F \cdot n'} * \left(\frac{A}{A'} \right) \quad (2)$$

where,

- Δm_F – normalized electrochemically deposited mass, g
- A' – electrochemically active area, cm²
- A – piezoelectrically active area, cm² (area of overlap between two electrodes)

4. Evaluate validity of Sauerbrey's equation; Δf vs. time.

5. Mass sensed by QCM (based on Sauerbrey's equation)^{10,17,18}

$$\Delta m_{QCM} = - \left(\frac{\left(\frac{\Delta f_{mass}}{n} \right)}{C_f} \right) * A \quad (3)$$

where,

$$C_f = -2f_o^2 (\mu_q \rho_q)^{-\frac{1}{2}} \quad (4)$$

μ_q - shear modulus for quartz crystal ($2.947 \times 10^{11} \text{ g cm}^{-1} \text{ s}^{-2}$)

ρ_q - density of quartz crystal (2.648 g/cm^3)

n - number of overtones

✓ In air, theoretical value of C_f for 5 MHz AT-cut quartz crystal is $56.6 \text{ Hz cm}^2 \mu\text{g}^{-1}$

✓ In air, theoretical value of C_f for 9 MHz AT-cut quartz crystal is $183.4 \text{ Hz cm}^2 \mu\text{g}^{-1}$

6. Compare equations (2) and (3) to get the experimental mass sensitivity value, C_f .

Electrochemically and piezoelectrically active area:

One key parameter that plays an important role in data analysis in the mass calibration procedures for the QCM is to evaluate the exact piezoelectric and electrochemically active areas. So, to shed clarity on this aspect, the two areas for three different QCR configurations and cell designs used (Figure 3) are explained in this section.

Figure 3 schematically shows the 3 different QCR configurations and the side view representation of their position in the experimental cells. The top part is in contact with electrolyte (represented here by sea green color, Figure 3) and this wetted electrode area will be referred to as the electrochemically active area (A'). The area of overlap between gold electrodes on two sides of quartz crystal is defined as the piezoelectrically active area (A). The solid boundaries on the top part and dashed boundaries on the bottom part are representative of experimental cell walls, in contact with the electrolyte and in air, respectively. A and A' is estimated and associated to the different configurations in the following part.

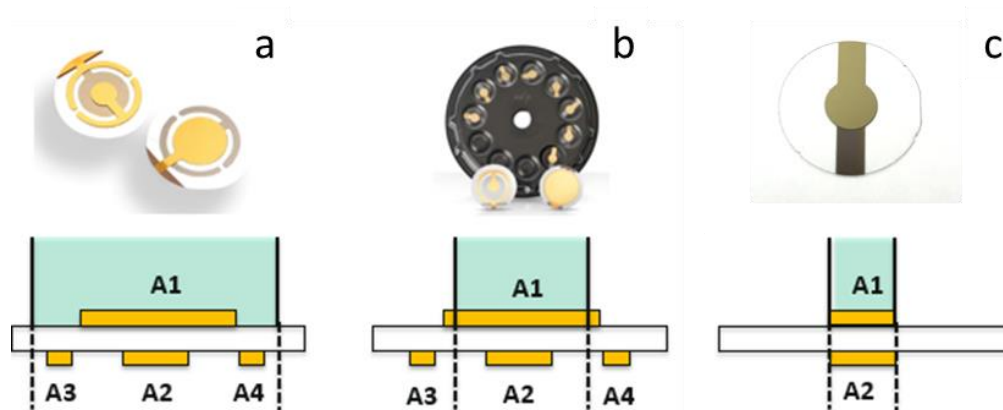


Figure 3: Different QCR configurations and schematic for QCR in experimental cell design. (a) Wrapped around configuration for QCM system 1.¹⁴ (b) Wrapped around configuration for QCM system 2.¹⁹ (c) Keyhole configuration for QCM system 3.