

In Situ Atomic Force Microscopy Study of Microstructure Dependent Inhibitor Adsorption Mechanism on Carbon Steel

H. Wang, B. Brown, S. Nesic
Institute for Corrosion Multiphase Technology
Department of Chemical & Biomolecular Engineering, Ohio University
342 West State Street
Athens, OH 45701
USA

A. Pailleret
Sorbonne Université, CNRS, Laboratoire Interfaces et Systèmes Electrochimiques (LISE, UMR 8235)
4 place Jussieu, (case courrier 133)
Paris, 75005
France

ABSTRACT

Organic surfactant-type corrosion inhibitors are widely applied in the oil and gas industry considering their high efficiency at low ppm concentrations. The investigation of organic inhibitor adsorption and inhibition mechanisms on carbon steel has been limited by the difficulties with surface characterization techniques at a molecular level. Atomic force microscopy (AFM) can provide localized visual observation, and can also achieve characterization of mechanical properties of an inhibitor film, through friction and surface stiffness measurements in multiple operational modes. Reported research has systematically studied the frictional properties of self-assembled surfactant monolayers on mica using lateral force microscopy. However, there has been no such studies done on carbon steels. In the work reported herein, in situ AFM topography measurements in contact mode, in situ AFM friction imaging and in situ AFM phase imaging techniques have been applied to investigate the influence of different microstructures present in a ferritic-pearlitic carbon steel on inhibitor adsorption mechanisms as well as corrosion inhibition of CO₂ corrosion. AFM c friction images show a large friction contrast between inhibitor covered cementite structures and ferrite structures, while in the absence of inhibitor this friction contrast almost disappears, indicating the inhibitor adsorption induced this difference. AFM phase images indicate no preferential adsorption of inhibitor on cementite or ferrite structures. These results indicate that either the adhesion force of inhibitor molecules on the cementite structures could be much smaller than on ferrite structures, or the molecular orientations of inhibitor molecules adsorbed on the cementite and ferrite structures could be different. In either case, it is hypothesized that the carbide component of the steel microstructure directly influences inhibitor adsorption, which could decrease inhibitor efficiency in ferritic/pearlitic regions and areas where iron carbide is more prevalent.

Key words: corrosion inhibitors, quaternary ammonium, carbon steel, in-situ atomic force microscopy, CO₂ corrosion, molecular simulations

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INTRODUCTION

Corrosion resistant alloys (CRAs) are used for many pipeline and wellhead components associated with oil and gas production environments but may be considered too costly for longer crude oil and natural gas production lines. Mitigation of internal corrosion for these types of pipelines is normally carried out by batch treatment or continuous injection of corrosion inhibitors, especially the surfactant type of organic inhibitors, which are more economical than using a CRA.^{1, 2}

Current research regarding corrosion inhibition of carbon steel by organic corrosion inhibitors mainly focused on studying the influence of inhibitor concentration, solution pH and temperature on inhibition efficiency by weight loss measurement and electrochemical studies, involving for example potentiodynamic polarization and electrochemical impedance spectroscopy.^{3, 4} These studies were used to evaluate the inhibitor efficiency for a specific inhibitor under specific test conditions, but most neglected to address the mechanisms related to formation of an adsorbed layer on a metal surface or the nature/structure of this layer. Some publications have investigated the relationship between inhibitor structure and mitigation performance.⁵⁻⁹ However, a molecular level understanding of carbon steel/aqueous inhibitor solution interface properties was always impeded by the traditional electrochemical methods, which cannot obtain the localized adsorption properties of inhibitor layers.

Atomic force microscopy (AFM) has already been used to study the topography of a carbon steel surface in the presence of a corrosion inhibitor.^{7, 10} However, AFM was mainly used as a supportive technique only to verify the presence of inhibitor on carbon steel by use of topography images and measures decrease of surface roughness variation after adding the inhibitor, while the surface properties of adsorbed inhibitor film that include hardness, friction, adhesion, and structural orientations, which are more related to mitigation efficiency under pipe flow, have not been adequately characterized. These topographic studies alone could not provide insight into the correlation between inhibitor structure and corrosion inhibition mechanisms. However, although the application of AFM for the corrosion inhibitor field is relatively immature, there have already been a few studies characterizing mechanical properties of surfactant systems at a molecular level by AFM. Liu et al presented a systematic study of frictional properties of self-assembled double chain quaternary ammonium surfactant monolayers using lateral force microscopy.¹¹ By measuring the friction force on bare mica and on a surfactant monolayer covered mica, they found the frictional forces were greatly diminished with the addition of surfactant and the adsorbed surfactant film was found to have a viscoelastic nature as indicated by an observed plateau in friction force curves created by increasing the tip sliding velocity. Similar friction force measurements have also been adopted by Li et al to develop a mechanistic model for surfactant molecular orientations which fit into an observed super low friction regime.¹²

In the present study, in situ AFM topography measurements in contact mode, in situ AFM friction imaging and in situ AFM tapping mode phase imaging techniques have been applied to investigate the influence of different microstructures present in a ferritic-pearlitic carbon steel on inhibitor adsorption mechanisms as well as corrosion inhibition of CO₂ corrosion.

EXPERIMENTAL PROCEDURE

Materials and Solutions

In order to obtain the required types and purity of corrosion inhibitors, model compounds are routinely synthesized and characterized within our laboratory. The specific model compound used in this work have a polar head group, dimethylbenzylammonium, and a tetradecyl (-C₁₄H₂₉) hydrophobic tail, as shown in **Figure 1**. The shortened name for this structure is BDA-C14, corresponding to tetradecylbenzyltrimethylammonium, used in the form of its bromide salt.

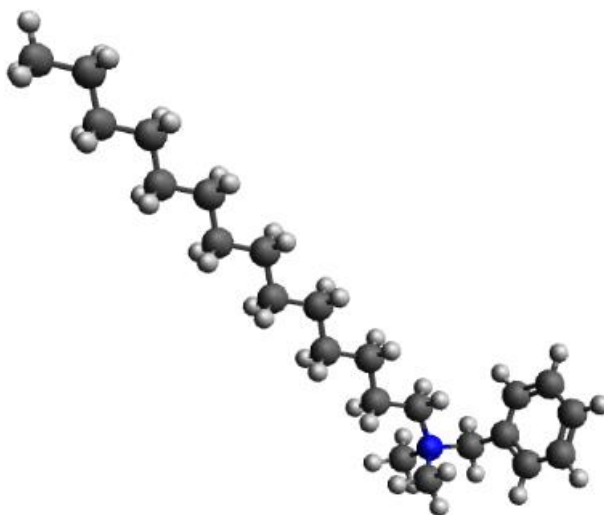


Figure 1. The molecular structure of tetradecylbenzyltrimethylammonium (BDA-C14)

Inhibitor concentration was selected based on its critical micelle concentration in a 1 wt.% NaCl electrolyte, specifically 100 ppm (2 CMC). The CMC of BDA-C14 was obtained by measuring changes in surface tension with concentration using the drop weight method.¹³ All solutions were prepared using deionized water with a conductivity of $18 \text{ M}\Omega \text{ cm}^{-1}$. The concentration of 2 CMC (100 ppm) was used in this work to obtain a full coverage film.

The steel specimen were machined from UNS G10180 carbon steel, and successively polished using 400, 600, 800, and 1200 grit silicon carbide abrasive papers followed by 9, 3, and $1 \mu\text{m}$ diamond particle loaded paste on a polishing cloth. The samples were then rinsed with acetone, ethanol and water and then dried in air.

In situ Contact Mode and Tapping Mode AFM Measurements

A commercial AFM (Molecular Imaging) was used to collect topography, friction, and phase images of the UNS G10180 steel surface in inhibitor solutions under an ambient CO_2 atmosphere by both contact mode and tapping mode consecutively in the same experiments. One V-shaped, silicon cantilever (HYDRA-ALL-G-50, AppNano) with standard normal spring constant of 0.049 N/m was used for both operation modes. The scan area was usually set as $10 \times 10 \mu\text{m}^2$ with the tip scanning at a speed of 8000 nm/s , and a resolution of 512 by 512 pixels was adopted for all AFM images.

During the contact mode AFM scanning, the cantilever bending (normal force) was kept at a constant value which is usually low enough to avoid removal of inhibitor film from the substrate surface. During operations both the height change and twisting of the cantilever were measured simultaneously and recorded as topography images and friction images, respectively.¹⁴

In order to avoid any lateral removal and shear effects at the tip-sample interface and retain the original adsorption morphology of the inhibitor film, tapping mode AFM was used.¹⁵ The phase image collected during tapping mode AFM operations records the phase lag of cantilever oscillation when the tip encounters a surface with different stiffness or hardness properties.^{16, 17} In this case, it was used for distinguishing soft inhibitor film and hard carbon steel substrate surfaces.

RESULTS

Comparison of Contact Mode AFM Topography and Friction Images- in the Presence of Inhibitor

Figure 2a and 2b show $30 \times 30 \mu\text{m}$ AFM topography and friction images of the adsorbed film structures on the UNS G1018 steel surface in the presence of 1 wt.% NaCl solutions with BDA-C14 inhibitor model

compound at 2 CMC. The topography image (**Figure 2a**) and friction image (**Figure 2b**) are obtained during the same line scan, but they show greatly different features. The surface topography resembles the originally polished surface in air, except for some features of slightly less deep polishing lines (the disappearance of the polishing lines over time is a sign of corrosion which occurred during the first few minutes of immersion before inhibitor adsorption. The fact that these lines did not appreciably change with time may be related to inhibitor adsorption. The friction image, however, shows several obvious lamellar structures in addition to the polishing lines seen in the topography image.

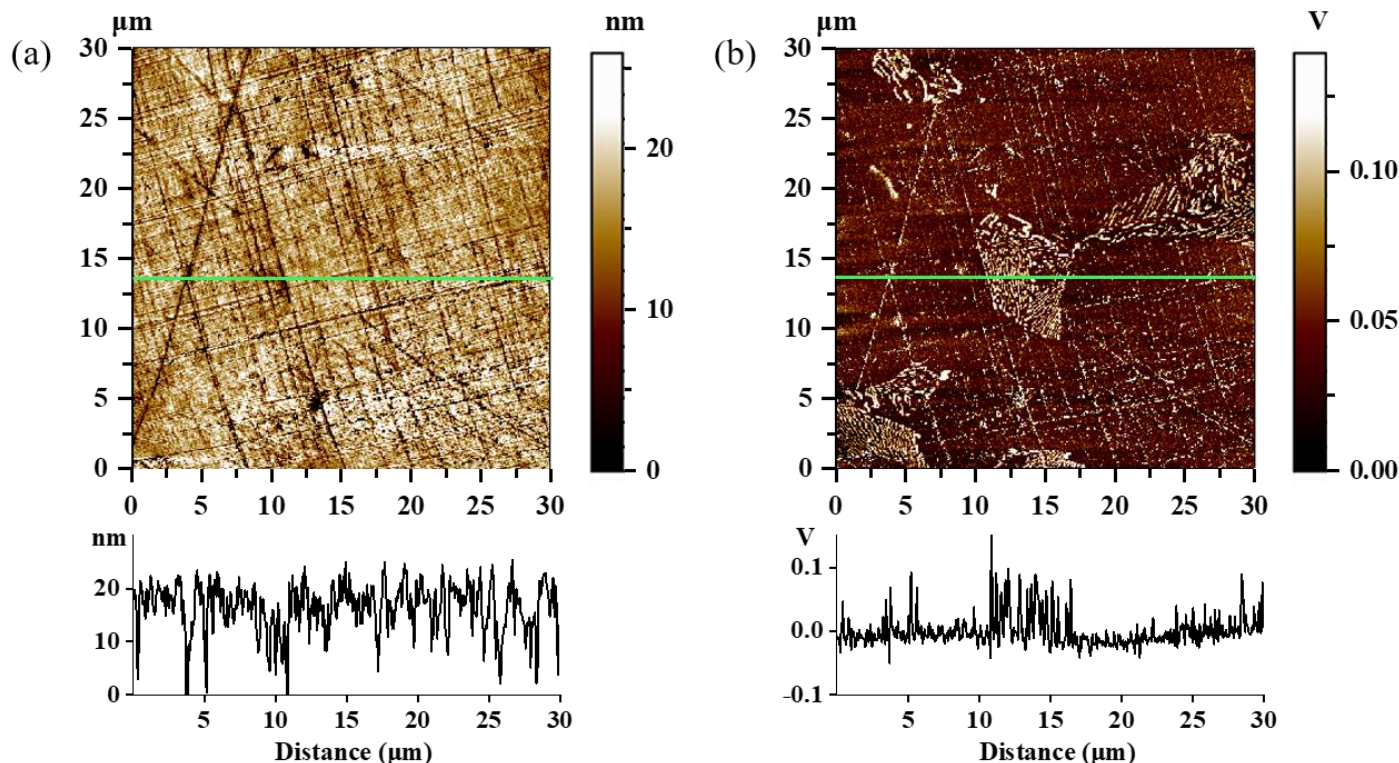


Figure 2. Contact mode AFM image of inhibitor film formed on UNS G1018 steel in a 2 CMC BDA-C14, 1 wt% NaCl solution: (a) topography image (b) friction image.

According to our previous studies related to the corrosion inhibition behavior of 1018 steel with the same inhibitor,¹⁸ these lamellar structures are cementite. The appearance of cementite can be caused by the ferrite preferentially corroding during the corrosion process. The 1018 steel is composed of a ferrite-pearlite microstructure, where pearlite consists of lamellar cementite structures filled with ferrite. As corrosion proceeds, the ferrite structure gradually dissolves while the cementite structure remains largely intact. A gradually increasing height difference between cementite and ferrite resulting from an expected corrosion phenomenon was detected by contact mode AFM topography images in our previous work.¹⁸ However, in **Figure 2b**, the cementite structures were only observed in friction images, while no such features emerged in topography images.

This situation has been repeatedly observed in multiple experiments **Figure 3a** and **3b** show two examples of small topographic contrast and large friction contrast obtained simultaneously on a same region of a 1018 steel sample in 2 CMC BDA-C14 inhibitor solution.