

Investigation of Inhibitor Adsorption Mechanism by in Situ Tapping Mode Atomic Force Microscopy

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ABSTRACT

Inhibition of internal corrosion is essential for assuring asset integrity of oil and gas transportation pipelines. Among the various types of inhibitors, the organic corrosion inhibitors are the most widely used in oilfield applications. Consequently, it is necessary to understand the adsorption mechanism and corrosion inhibition capabilities of organic inhibitors. Although the corrosion inhibition mechanisms of organic inhibitors have been extensively investigated by electrochemistry analysis, the adsorption modes and film properties of corrosion inhibitors have rarely been studied due to the limitation of localized surface characterization techniques. The application of atomic force microscopy (AFM) technique can achieve direct monitoring of microscopic inhibitor adsorption behaviors and compensate the deficiencies in traditional electrochemical measurements. Some previous research have studied the adsorption kinetics and growth mechanism of surfactant layers on mica surface with ex-situ AFM, which may bring distortion on the obtained layer structures due to the removal of inhibitor solutions. In this present study, in situ tapping mode AFM have been used to investigate the adsorption kinetics and molecular orientations of a tetra-decyl-dimethyl-benzyl-ammonium (Q-C14) inhibitor model compound on mica surface as a fundamental study. Analysis of AFM data indicated that Q-C14 inhibitor forms a porous film on mica surface. It is proposed that Q-C14 inhibitor molecules adsorb flatly on mica surface within a few minutes. With the increase of immersion time, inhibitor molecules stand up slowly, forming small and dense holes on the film between 0 to 6 hours. Molecular patches formed at longer exposure time, which led to the appearance of large holes on the film. The adsorption morphology seemed to stabilize after 14 hours of immersion. This fundamental research can provide insights on studying the relationship between inhibitor surface coverage and inhibition efficiency.

Key words: Tapping mode AFM, organic inhibitor, adsorption kinetics, molecular orientation

INTRODUCTION

Organic surfactants are commonly applied as corrosion inhibitors for mild steel in a typical service environment for the oil and gas industry. They are usually adsorption type inhibitors (e.g. amines, amides, and imidazolines) combined into an inhibitor package which is designed to form a protective barrier on the steel surface to mitigate corrosion. Because these are so widely used, it is crucial to understand the adsorption mechanisms and corrosion inhibition capabilities for the application of organic inhibitors. In addition to the conventional electrochemical techniques used, multiple advanced tools have been developed to investigate the adsorption properties for organic inhibitors. Atomic force microscopy (AFM) is one of the most powerful surface characterization techniques which has been shown to help with inhibitor adsorption research.

AFM can be operated in various modes to satisfy different imaging requirements. By recording cantilever deflections during scanning across the substrate surface with a sharp tip (~ 20 nm radius of curvature), AFM images can be generated to depict substrate surface topography. Based on the interaction force between tip and sample, AFM operation modes are generally classified as hard contact modes, pre-contact modes, non-contact modes, intermittent tapping modes, torsional resonance mode, and peak force tapping mode, etc. The surface hardness of substrate is one important standard for selecting appropriate AFM operation modes in order to obtain high-quality images without distortion. In previous AFM research with organic surfactants and corrosion inhibitors, multiple operation modes have been conducted for achieving different research objectives. *Ex-situ* hard contact mode has been widely applied in the investigation of surfactant adsorption kinetics. Woodward et al. [1] studied the self-assembled monolayer (SAM) deposition of octadecyl phosphonic acid (OPA) on mica substrate with contact mode AFM. They found the growth mechanism is composed of nucleation, growth, coalescence of dense sub-monolayer islands, and it took more than 16 hours for this acid to achieve maximum surface coverage. While in Schwartz et al.'s contact mode AFM work [2], the growth mechanism of self-assembled layer formed by octadecyl trichlorosilane (OTS) molecules is also patchy aggregation and islands formation. However, a complete monolayer can be developed within 5 minutes, indicating a much faster adsorption kinetics than the OPA acids. The *ex-situ* contact mode is suitable for adsorption kinetics studies because it can retain and capture the surface morphology change within short time by eliminating the difficulties of laser adjustment in liquid. However, with this method the detailed feature of molecular orientations in liquid is lost due to the removal of solution in *ex situ* operations. In addition, the high lateral force in hard contact mode can damage the soft inhibitor film and make it inappropriate for in situ imaging of inhibitor film topography.

In order to avoid these problems involved in hard contact mode imaging, several soft operation modes, such as pre-contact mode, non-contact mode, and tapping mode, are applied in the inhibitor adsorption research. The pre-contact mode relies on a repulsive force between the tip and the inhibitor film, which means the constant force is set just below the film penetration force during image acquisition. The force distance curve is sufficiently steep at this point to ensure good imaging contrast without altering the structure of the adsorbed molecules. Gaub et al. [3] investigated the adsorption of surfactant on gold surface with different AFM operation modes. They observed meandering cylindrical micelles on gold surface with a soft precontact mode, while with hard contact mode, the surface morphology looked like pure gold substrate because the surfactants were wiped away or deformed. However, it is difficult to apply this method when the penetration force of film is too small. For non-contact mode, the cantilever vibrates above the sample surface, and the distance between the tip and the sample is usually several nanometers [4]. The force between the tip and the sample is van der Waals attraction. In the non-contact mode, there is no damage to the surface of the sample and the lateral force is the smallest, but the resolution is low and the scanning speed is slow. Also, in order to avoid being stuck to the water film on the sample surface, it is often used to scan hydrophobic surfaces and soft samples.

Another soft operation mode is intermittent tapping mode. In standard tapping-mode scanning force microscopy (TMSFM), the tip intermittently contacts the surface, resulting in a minimization of the

destructive lateral forces compared to conventional contact mode in which the probe slides across the surface[5] , so the irreversible destruction on soft surface and weak adsorption of molecules can be eliminated. Schmitz et al. [6] compared the different effects of contact and tapping mode on image quality. They found that the contact mode tip would wipe away the glass corrosion products, and even caused plastic deformations of the weathered glass surface. However, for tapping mode, the tip instantly taps on the surface and there is no constant contact force. Therefore, the lateral forces are excluded and vertical compressive forces become intermittent, which helps retain the original morphology of silicate residues. The added advantage of tapping mode is that it has a phase image which can differentiate between areas with different properties regardless of their topographical nature [7-9]. Tendler et al.'s work [10] with the partial adsorption of ethyldimyristoylphosphatidylcholine (EDMPC) on mica shows that the phase image gives a clearer contrast between adsorbed structures and substrates compared with the topography image. The phase images in Antognozzi et al's work shows detailed structure for cations forms of Nafion, while topography images are quite blurry.

Although tapping mode AFM (TMAFM) has multiple advantages in the imaging of soft inhibitor film, limited related research has been performed due to the difficulty of tapping mode operations in aqueous solutions. Some current in situ tapping mode research adopted a method that the tip moved through only one drop of solution on the substrate, which may have huge difference in the self-assembly of inhibitor molecules with the fully immersed samples. In this work, an *in-situ* TMAFM technique was applied to study the molecular orientations and adsorption kinetics of a model inhibitor molecule.

Prior research [11] using a mechanistic approach to model the effects of surfactant-type organic corrosion inhibitors has shown a direct relationship between a longer alkyl tail length on inhibitor molecules and corrosion mitigation efficiency. This study used synthesized versions of a quaternary ammonium compound with alkyl tails containing 4 to 16 carbon atoms. A quaternary ammonium-type inhibitor was used in this prior research due to controversy in the literature whether this compound could be defined as having "anodic" or "uniform" inhibition properties. Additional research[12] using the same model compounds has shown a further relationship between the alkyl tail length of these model inhibitors and their measured critical micelle concentration values and measured inhibition efficiency. By using a pure, well defined surfactant-type organic corrosion inhibitor in research, the mechanisms of corrosion mitigation can be better understood and eventually modeled. In this work, a model quaternary ammonium inhibitor with an alkyl tail containing 14 carbon atoms was used.

EXPERIMENTAL PROCEDURE

Materials and solutions

Mica substrate was first used to develop the AFM techniques for studying the adsorption structure and measuring surface coverage. Mica has layer structure of aluminum, silicon, oxygen, and potassium. It can be mechanically cleaved to produce clean, atomically flat surfaces. The roughness of mica surface is only around 0.2 nm. A mica surface in an aqueous solution can produce strong electrostatic interaction which is favorable for the adsorption of a nitrogen-based inhibitor. Before every test the mica will be cleaved to have a fresh surface.

The model compounds used in this work consisted of a polar head group, dimethylbenzylammonium, and a hydrophobic tail: Tetradecyl ($-C_{14}H_{17}$) [13], as shown in Figure 1 (black spheres represent carbon, white spheres represent hydrogen, and the blue sphere is nitrogen). The synthesis and characterization of this compound is described in detail in previous publication [14].

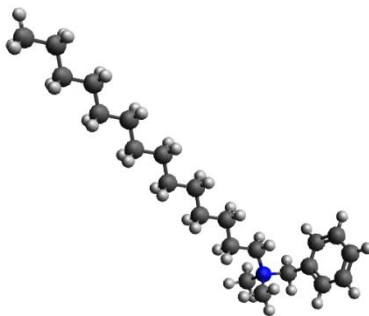


Figure 1: The molecular microstructure of tetradecylbenzyltrimethylammonium (Q-C14).

Based on previous research [11, 15], 2 CMC (100ppm) of inhibitor Q-C14 is a saturation concentration beyond which a complete film will be formed on mica surface. In this current work, the bulk inhibitor concentration was selected as 2 CMC for the convenience and reliability of film structure investigation. Solutions of 1 wt% NaCl containing Q-C14 were prepared using deionized water with a conductivity of $18 \text{ M}\Omega\cdot\text{cm}^{-1}$.

AFM measurements

TMAFM images, as well as AFM phase images, were obtained with a commercial Keysight[†] Scanning Probe Microscope system equipped with a fluid cell attachment and triangular silicon cantilevers with a nominal spring constant 0.38 N/m. Measurements were made at the mica-aqueous solution interface in order to analyze the inhibitor film structure. The scan rate was set to 200 nm/s for optimized imaging on mica, and the scan area was $1 \mu\text{m}^2$. A resolution of 256 by 256 pixels was adopted for all AFM images. The resonance frequency, which is usually around 25 KHz in liquid, would be tuned every time before experiment. The drive frequency is set as 0.1 KHz less than the resonance frequency.

Tapping-mode atomic force microscopy (TMAFM) measures topography by tapping the surface with an oscillating probe tip at a drive frequency so that the tip makes contact with the sample only for short duration[16]. In each oscillation cycle the topography and phase images presented were recorded. The oscillation amplitude, i.e. the height is kept at a constant set point value and is used as a feedback signal to measure topographic variations of the sample surface. The phase lag of the cantilever oscillation, relative to the signal sent to the cantilever piezo driver, is simultaneously monitored and converted as phase image, which is a relatively new AFM technique. This phase shift is very sensitive to local variations in the surface properties.

Tapping mode imaging in liquid is a challenge work because tip oscillation in liquid usually cause instability of laser and then bring all kinds of defects on the images. The parameter settings such as the set point amplitude need to be adjusted at all times to minimize these deficiencies.

RESULTS AND DISCUSSION

Comparison of adsorption morphology of Q-C14 on mica by contact mode AFM and tapping mode AFM

Figure 2a and 2b show $1 \mu\text{m}$ by $1 \mu\text{m}$ contact mode AFM images of the adsorbed film structures on mica surface developed in a 1wt% NaCl solution with 2 CMC of Q-C14 inhibitor over 15 hours. For contact mode, a constant force on the order of $\sim 1 \text{ nN}$ or less is applied to the tip to acquire the image, which is corresponding to the steep repulsive part of the force curves when the tip is in direct contact with metal surfaces. The adhesion of surfactant molecules to the solid substrate is weak and the tip may scrape away the adsorbed film from the surface. Given that the uniform and featureless image cannot be able

[†] Trade Name

to distinguish from mica surface and a flat layer, it is necessary to perform scratching tests to verify the exact adsorption structures.

As shown in **Figure 2b**, an AFM scratching technique was adopted [17, 18] in order to investigate the exact layer structure and also measure film thickness at 2CMC concentration, in which a small area of film (200 by 200nm) was removed from the underlying mica substrate by repeated scanning at a high operating force until a square hole with stable depth was created. Subsequently the height difference between mica substrate and untouched film surface was measured by calculating the difference on surface profile between hole bottom and undamaged film surface. This procedure has been described in detail elsewhere [18]. When the force is large enough to remove the inhibitor molecules, a hole can be observed on the center of topography image (**Figure 2b**). When the force is increased further, the depth of the hole didn't increase, which means the film has been completely removed under 24 nN operating force. Considering mica is a hard surface, previous research[18] shows that even 60nN operating force cannot scratch mica. Therefore, the scratching depth in **Figure 2b** must be the inhibitor film thickness. After measurement, the film thickness of Q-C14 inhibitor on mica at 2CMC concentration was around $1.5 \text{ nm} \pm 0.1 \text{ nm}$. The molecular length of Q-C14 inhibitor can be calculated as 1.64 nm, which is just above the measured film thickness, indicating the adsorption of a tilted monolayer. Multiple scratching tests under the same 24 nN normal force were repeated at different areas on mica surface providing consistent film thickness results.

A lot of film properties information, such as film thickness and adhesion forces, have been obtained through this scratching technique. This provided information about the adhesiveness of an inhibitor film on carbon steel, and whether the film was a monolayer or bilayer. In previous research, the conclusions were obtained through indirect analysis of the AFM data. In order to directly observe the inhibitor film structure, TMAFM imaging technique was developed and adopted in this work.

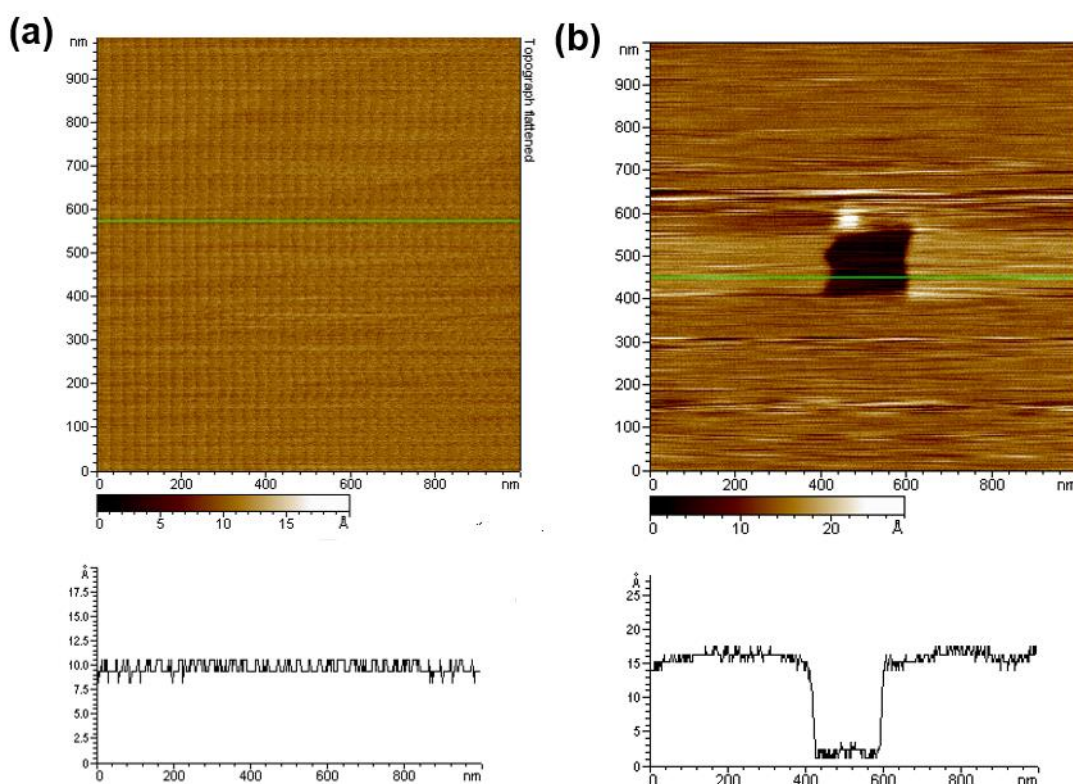


Figure 2. Contact mode AFM topography image of inhibitor film formed on mica at 2 CMC Q-C14 in 1 wt% NaCl solution: (a) 0 contact force, (b) 24nN contact force.

Tapping mode AFM imaging

Figure 3 shows the in situ TMAFM images of the adsorbed film structures on mica surface in a 1wt% NaCl solution with Q-C14 inhibitor at 2 CMC after immersion 15 hours. The tapping AFM images of film surface are still uniform as observed with contact mode. However, many black domain structures appear randomly on the surface. These black microdomains with a pinhole shape correspond to lower positions on the inhibitor film surface as shown in AFM topography image (**Figure 3a**). The topography profile (**Figure 3a**) indicates that the domain depth is about $1.5 \pm 0.1\text{nm}$, which is equal to the film thickness measurement in contact mode AFM scratching tests (**Figure 2b**). This depth value implies that these black microdomains could be defects in the inhibitor film. During the film formation process, multiple defects may occur which exist as empty holes. During TMAFM imaging, the tip would scan across both the film surface and the exposed mica surface, which provide a height contrast showing up as a black hole. The depth of each hole should be the height difference between inhibitor film surface and underneath exposed mica surface, which is thought to be equal to the thickness of inhibitor film.

In order to obtain more detailed evidence for the existence of these defects in the inhibitor film, the determination of phase attribution becomes the predominant task. As mentioned in the methodology section, tapping mode phase image reflects the variation of the surface property. The image indicates that the surface property is certainly different from that of contact mode measured surface (approximately bare mica surface) in **Figure 2a**. As observed from the phase image in **Figure 3b**, there exist multiple bright microdomains in exactly the same locations corresponding to the black holes in topography images (**Figure 3a**). More specifically, the phase image profile shows an obvious contrast of measured phase shift between the bright microdomain and surrounding area. In TMAFM, cantilever oscillation is a sinusoidal waveform with a fixed frequency, which has an alternating voltage amplitude that changes with surface topography as the cantilever's piezo driver maintains a very low contact force with the surface, and a phase signal which shifts as the surface stiffness varies, as displayed by Equation 1. The phase shift can be considered as a 'delay' in the oscillation of the cantilever relative to the signal sent to the cantilever's piezo driver as it moves up and down in and out of contact with the sample. This phase lag is used as a basis for phase image generation[19].

$$A = A_{max} \times \sin(\omega t + \varphi) \quad (1)$$

It is generally accepted [11,12], the brighter domains in a phase image correspond to a harder material as the interaction between the tip and surface is dominated by a repulsive force. The positive shift of the phase in the bright microdomains in **Figure 3b** indicates that these domains are harder in property than the surrounding surface. This is consistent with the properties of corresponding black holes in topography images because the exposed mica surfaces in the holes are indeed a harder phase than the surrounding soft inhibitor film. Therefore, AFM topography and phase images illustrate that Q-14 inhibitor forms a porous film on a mica surface.