

## **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]. Tandler 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.

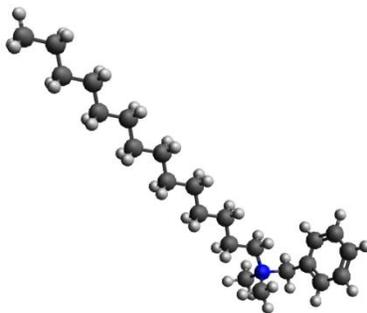
Prior research [11] using a mechanistic approach to model the effects of surfactant-type organic corrosion inhibitors has shown a direct relationship between a longer alkyl tail length on inhibitor molecules and corrosion mitigation efficiency. This study used synthesized versions of a quaternary ammonium 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<sup>†</sup> 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

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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 nm  $\pm$  0.1nm. 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.

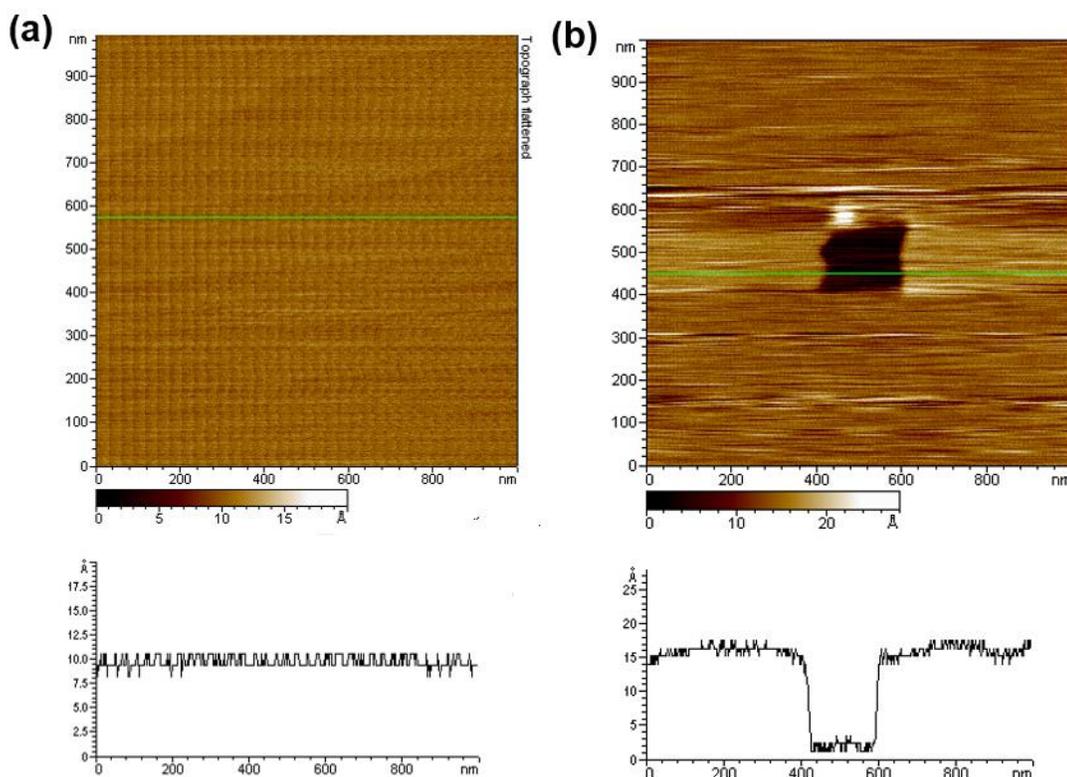


Figure 2. Contact mode AFM topography image of inhibitor film formed on mica at 2 CMC Q-C14 in 1 wt% NaCl solution: (a) 0 contact force, (b) 24nN contact force.

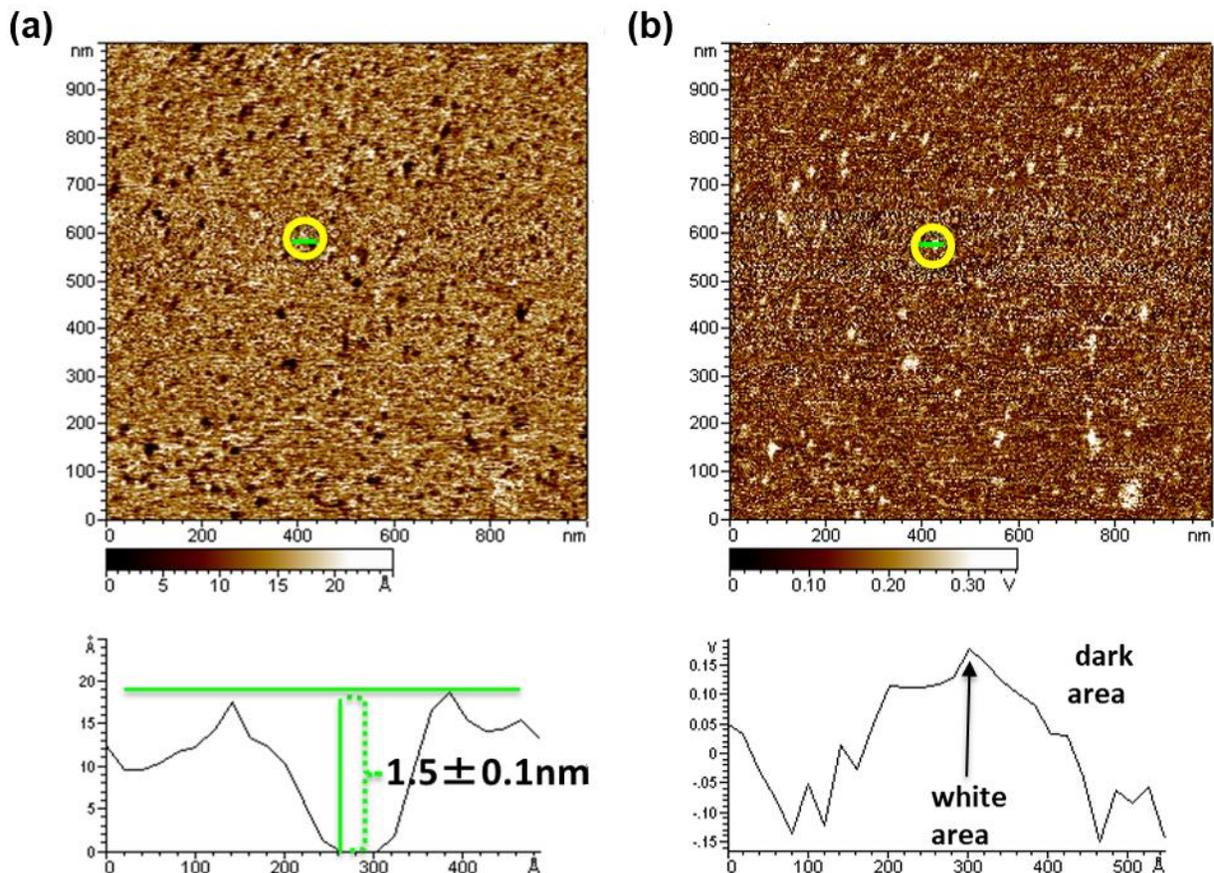
## Tapping mode AFM imaging

**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  $1.5 \pm 0.1$ 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 is 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].

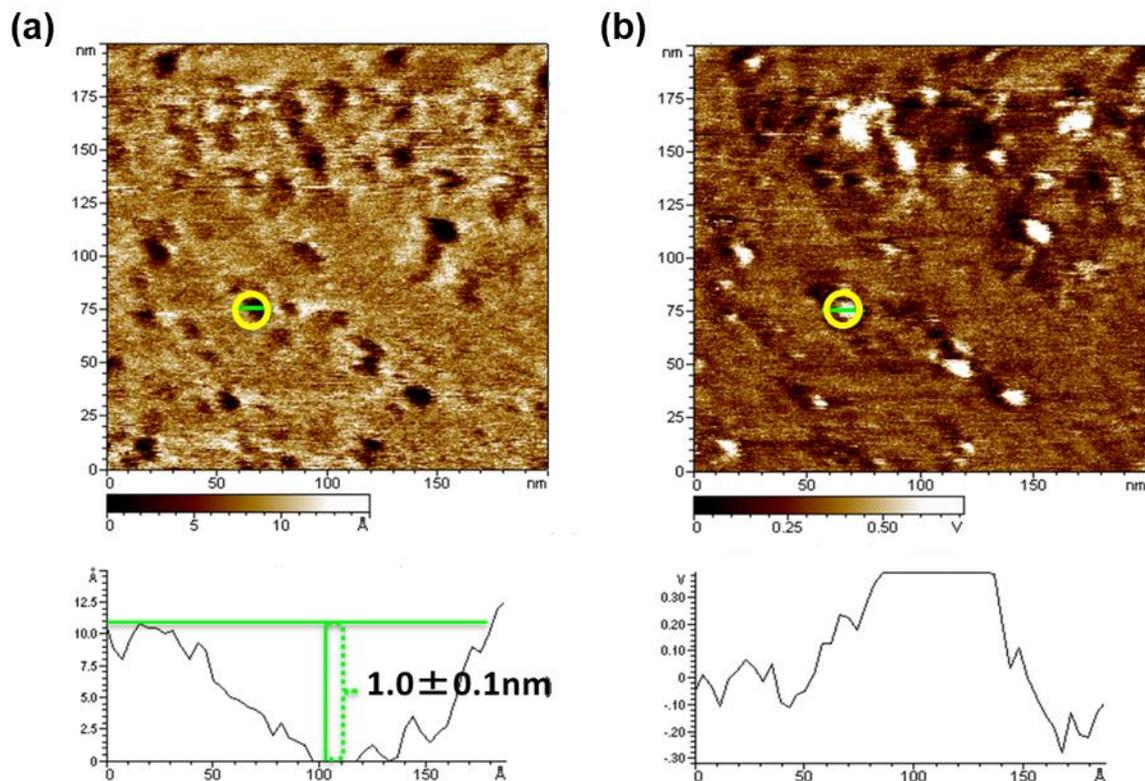
$$A = A_{max} \times \sin(\omega t + \varphi) \quad (1)$$

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.



**Figure 3.** TMAFM images of inhibitor films formed on mica at 2 CMC Q-C14+1 wt% NaCl after 15 hours immersion-scan size 1000um: (a) topography image, (b) phase image

**Figure 4** shows zoom in (scan size 200 um compared with 1000 um in **Figure 3**) TMAFM images of the adsorbed film structures on mica surface from a 1wt% NaCl solution with 2 CMC Q-C14 inhibitor after immersion for 15 hours. At a larger view with a scanned area of  $0.5 \times 0.5 \mu\text{m}^2$ , it can be seen more clearly that the inhibitor film is a porous layer rather than a uniform tightly packed layer. Holes are irregularly distributed on the inhibitor film. Lower spots (exposed mica in the holes) in the AFM topography images correspond to the hard phase. The measured depth of hole varies from 1 to 1.5 nm, indicating the thickness of adsorbed film may not be uniform.

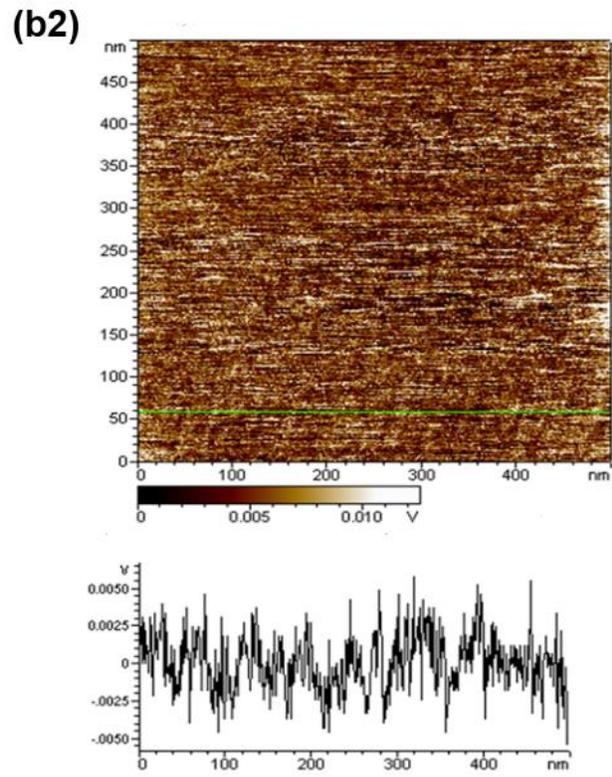
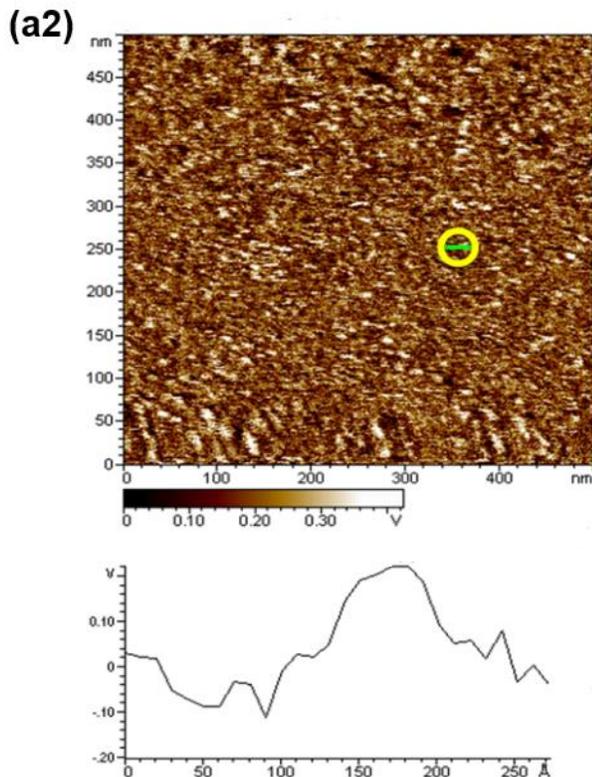
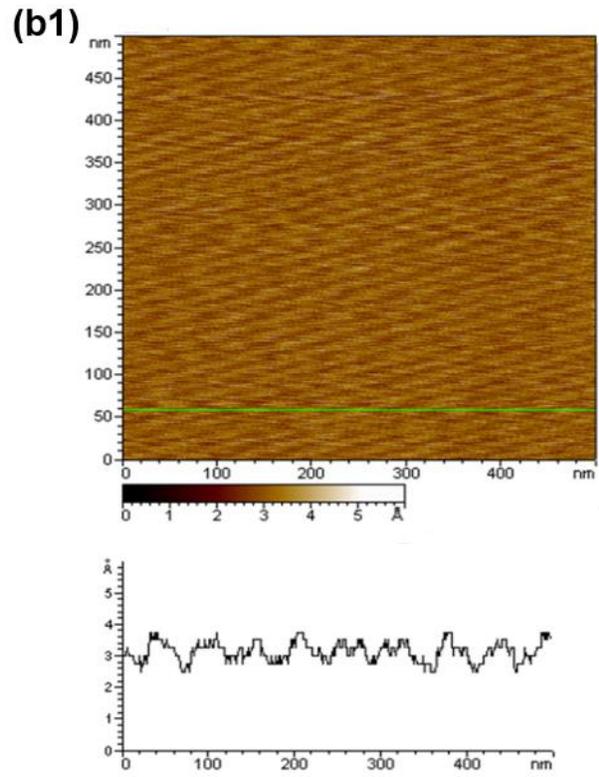
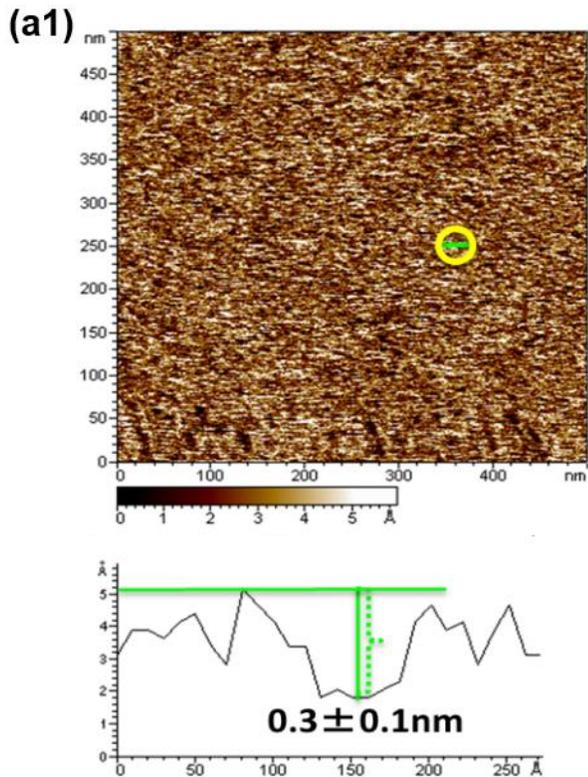


**Figure 4. TMAFM images of inhibitor films formed on mica at 2 CMC Q-C14 + 1 wt% NaCl after 15 hours immersion-scan size 200  $\mu$ m: (a) topography image, (b) phase image.**

### Contact vs tapping in the same condition

In order to obtain a direct comparison between the effect of different AFM operating modes on image quality, both AFM tapping mode and contact mode have been performed in situ in the same experiment, whereas the contact mode image was collected right after the tapping mode image, as shown in **Figure 5**. **Figure 5a1** shows tapping mode topography image of the adsorbed film structures on mica surface from a 1wt% NaCl solution with Q-C14 inhibitor at 2 CMC after immersion 6 hours, while **Figure 5b1** shows the contact mode topography image which has been obtained immediately after the tapping mode image. Small black holes can be observed on the inhibitor film from the tapping mode topography image (**Figure 5 a1**), while the contact mode topography image (**Figure 5 b1**) shows a uniform featureless layer.

Same comparison can be found on the tapping mode phase image and contact mode friction image. The interpretation of height contrast is a bit hard because the depth of black holes is quite small under this immersion time. When the change of surface roughness is too small to be detected by topography image, the phase image can distinguish more clearly from soft area and hard regions. Plenty of exposed hard mica microdomains can be found on the tapping mode phase image (**Figure 5 a2**), shown as bright spots, while on the contact mode friction image (**Figure 5 b2**) no features can be observed. These comparisons revealed that for the same soft inhibitor film surface, the tapping mode imaging technique is more suitable and can better retain the original surface topography features, whereas the contact mode imaging could distort the delicate surface by the larger lateral forces used. The sweeping motion of the AFM tip during contact mode measurements on the soft surface may make the surface smoother than its real morphology.



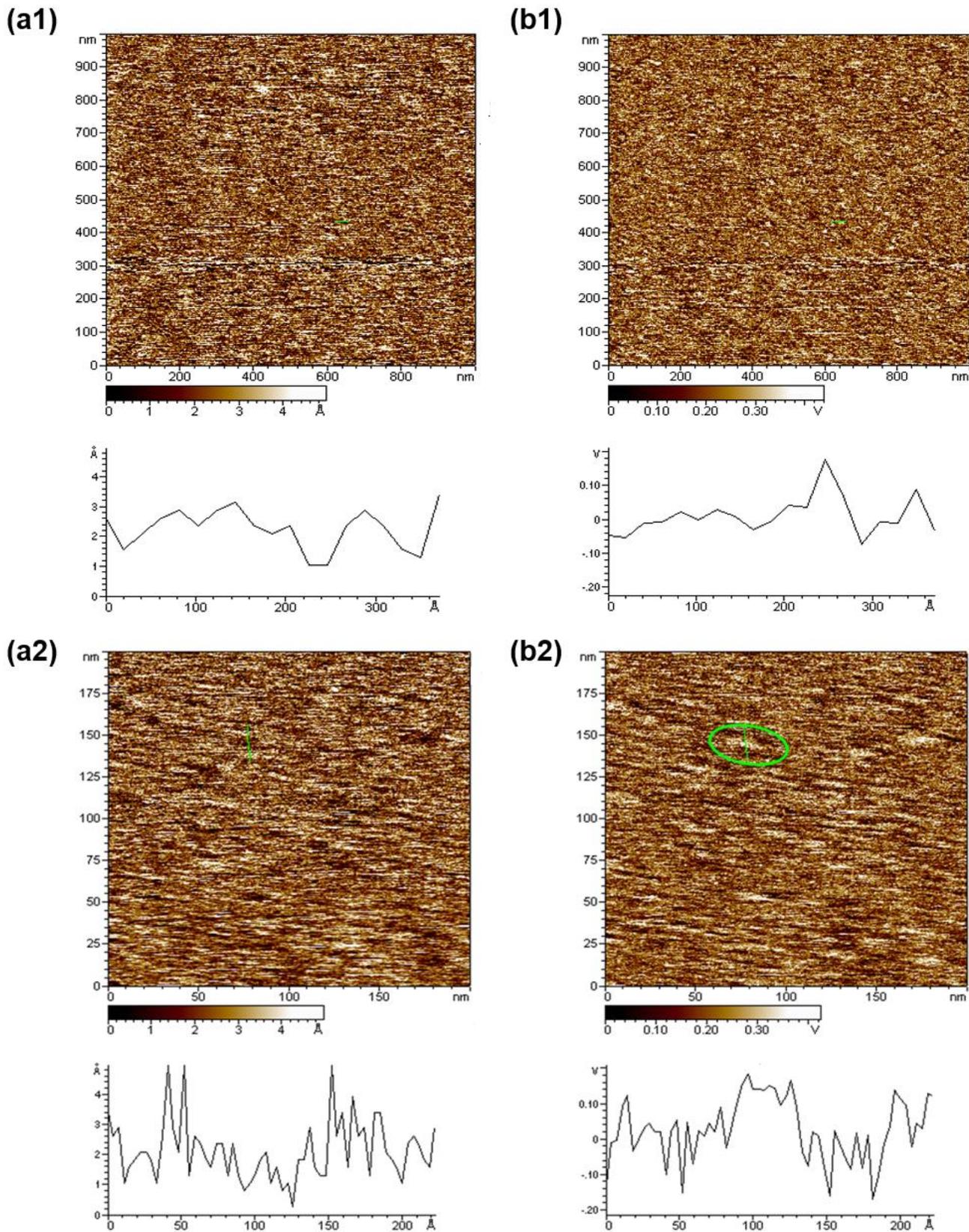
**Figure 5. Comparison between TMAFM images and contact mode AFM images of inhibitor films formed on mica at 2 CMC Q-C14 in 1 wt% NaCl after 6 hours immersion-scan size 200  $\mu\text{m}$ : (a1) tapping mode topography image (b1) contact mode topography image (a2) tapping mode phase image (b2) contact mode friction image.**

## Adsorption kinetics and molecular orientation investigated by tapping mode AFM: A real time monitoring of Q-C14 adsorption morphology evolution on mica

In order to investigate the adsorption kinetics and molecular orientations of Q-C14 inhibitor, a real time monitoring of the evolution of inhibitor film morphology has been performed by AFM tapping mode imaging.

**Figure 6** shows TMAFM images of the adsorbed film structures on mica surface from 1wt% NaCl solution with 2 CMC Q-C14 inhibitor after immersion for 20 minutes. It is hard to see any special microdomains with height contrast on the inhibitor film at this moment from the topographical image (**Figure 6 a1**). As discussed above, in order to minimize the interaction between the tip and the surface using TMAFM, a cantilever is forced to oscillate with the probing tip at a given amplitude [20]. The energy stored in the oscillating system allows the tip to touch the surface only at its lowest point of each vibrational cycle [21]. Therefore, imaging of soft samples with tapping mode should not suffer from plastic deformations introduced by the tip as in contact mode [22], which means the nearly featureless image indicates an uniformly adsorbed film after 20 minutes immersion. Considering the great potential of phase imaging as an additional tool for characterizing surface properties, the phase difference (**Figure 6 b1**) has also been measured to find out if there are any domains of defects on the inhibitor film. Using a 1  $\mu\text{m}$  by 1  $\mu\text{m}$  scanning size, no obvious contrast in phase and a uniform film has been observed.

However, using a 200 nm by 200 nm scanning range (**Figure 6 a2** and **b2**) at the same condition, bright microdomains of exposed mica surface were captured in the phase image (**Figure 6 b2**), indicating the defects already exist after only 20 minutes immersion time. However, on the topography image (**Figure 6 a2**) it is still hard to distinguish holes, which implies the depth of defects on the inhibitor film was too small to be detected at this moment. According to the discussion in the last section, the depth of microdomain defects are thought to equal to the inhibitor film thickness when a measured 'hole' in the TMAFM topography corresponds to a measured 'harder material' in the measured TMAFM phase. This negligible thickness of inhibitor film may indicate that the inhibitor molecules have adsorbed flatly on the mica surface with alkyl chains lying down at 20 minutes-immersion time. It is suggested by Weiss et al. [23] that the alkyl chains of alkylammonium ions could lie flat on the mica surface when the charge density of substrate is low and that the length of chains would influence the molecular orientation. The existence of phase difference in the image indicates that the lying down molecules are not very tightly packed as there are gaps with exposed mica surface between molecules, which provided phase contrast.

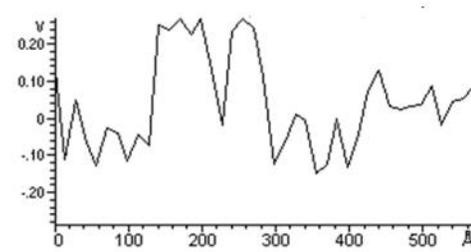
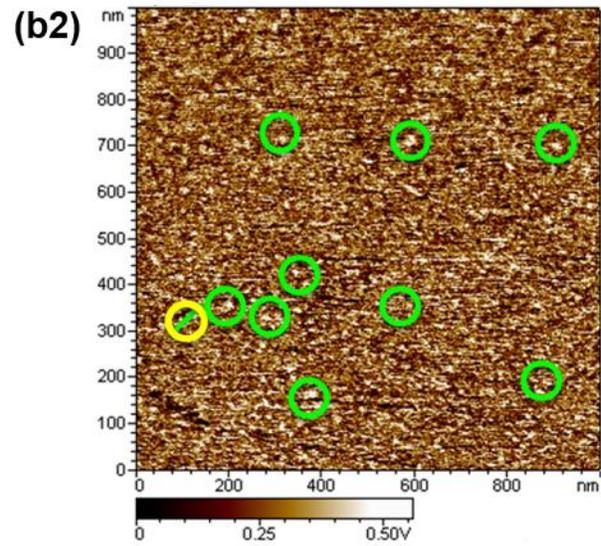
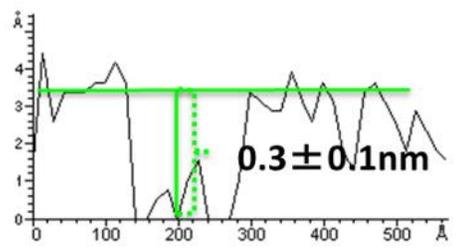
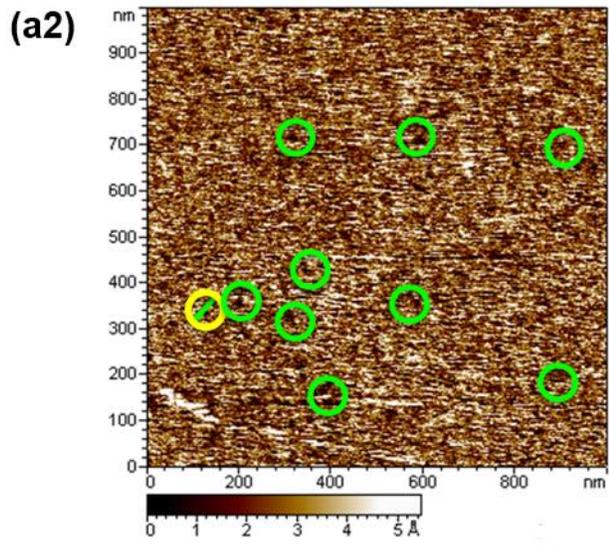
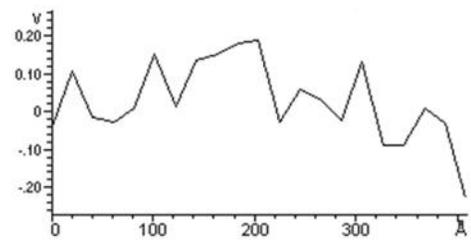
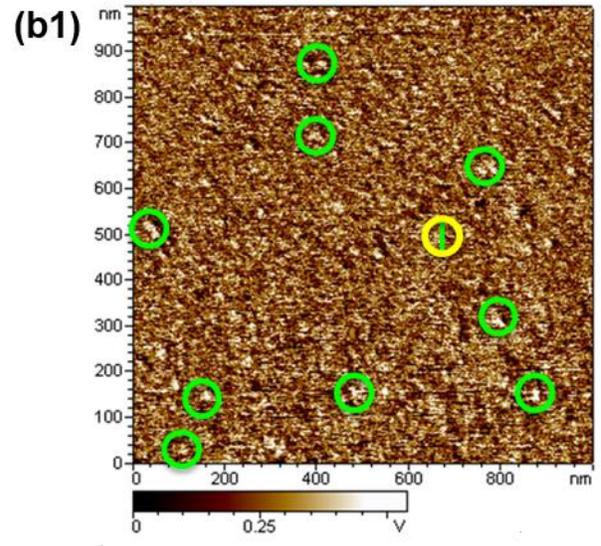
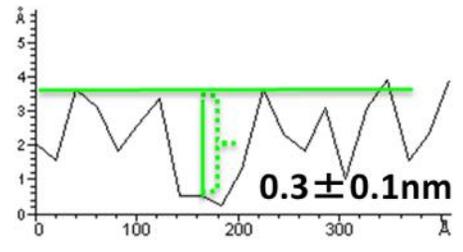
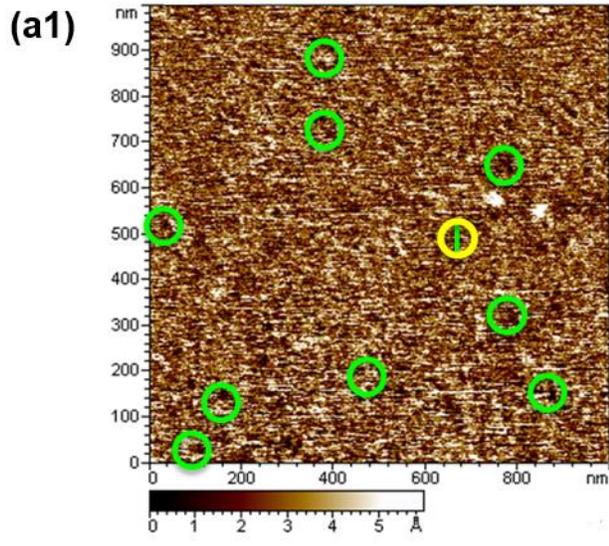


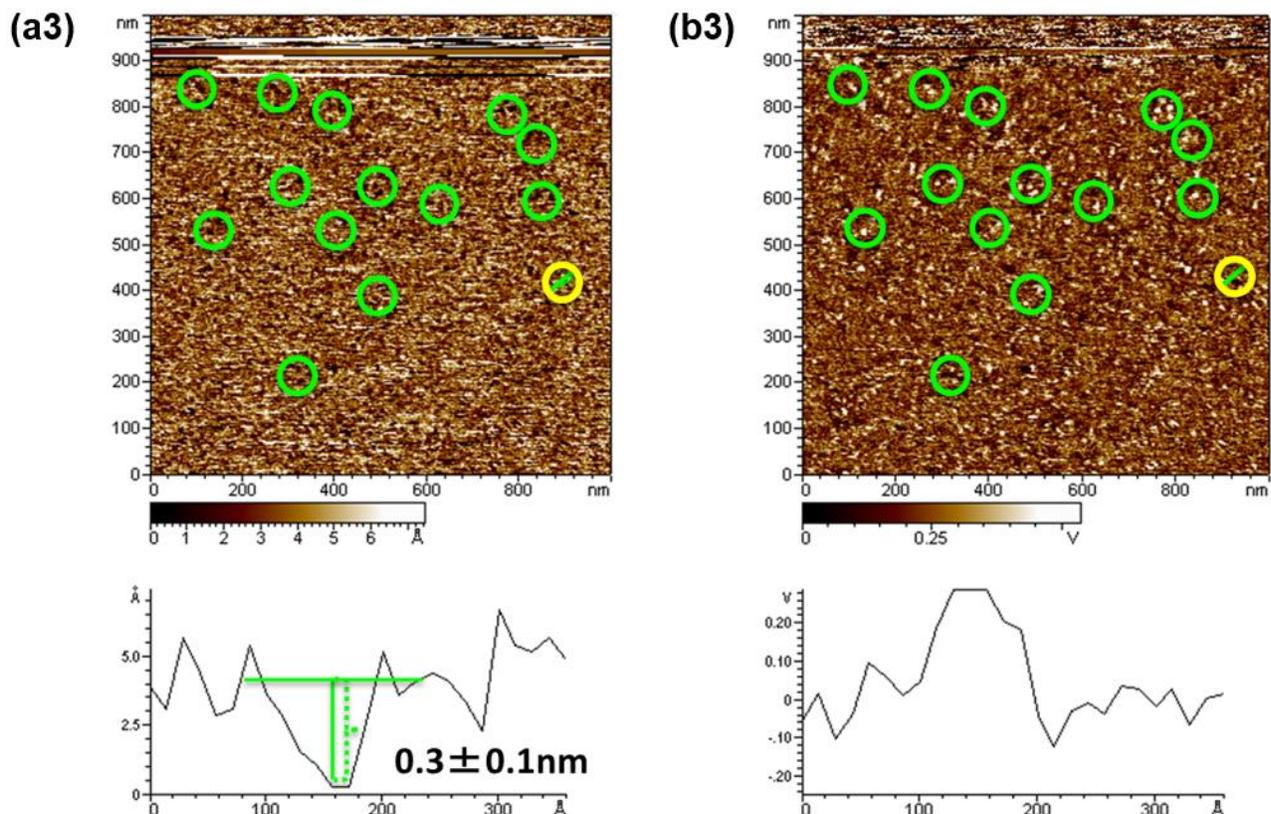
**Figure 6. TMAFM images of inhibitor films formed on mica at 2 CMC Q-C14 in 1 wt% NaCl solution after 20 minutes immersion: (a1) scan size 1 μm, topography image, (b1) scan size 1 μm phase image (a2) scan size 200 nm, topography image, (b2) scan size 200 nm, phase image.**

**Figure 7** shows TMAFM images of the adsorbed film structures on mica surface from 1wt% NaCl solutions with 2 CMC Q-C14 inhibitor after immersion 1 hour, 3 hours, and 6 hours. These images are representative of images obtained from at least three macroscopically separated regions on several different samples and exhibit the typical behavior of inhibitor film structures vs time. Since the contrast between bright and dark colors in a phase image are more distinct than the contrast between dark and darker colors in a topographical image, the phase images were used to determine locations which were confirmed as holes by the topographical images. At 1 hour immersion, some bright spots can be observed on the phase image (**Figure 7 b1**), while black holes are not so easy to be detected from height contrast. By using these bright spots on the phase image as reference locations, black holes were found in the corresponding positions on the topography image. The appearance of these black domains suggests that at 1-hour immersion, the integral film formed within 20 minutes starts to become porous with relatively sparse defects. From the section analysis, the depth of holes (the thickness of the film), was estimated to be  $0.3 \pm 0.1 \text{ nm}$ , which is much less than one molecule length (the length of the Q-C14 molecule is  $1.64 \text{ nm}$ , calculated as mentioned above), revealing that these molecules may adsorb slightly tilted on the mica surface. This slightly tilted orientation can occur when the substrate surface has a medium charge density [23]. As freshly cleaved mica surface is hydrophilic, it is reasonable to assume that Q-C14 molecules adsorbed by their head group and the alkyl chains became directed towards the solution.

After 3 hours immersion, as shown in **Figure 7 a2** and **b2**, more holes and bright spots can be observed, indicating that with an increase of immersion time, the number of defects on inhibitor film increases. The depth measured from topography profile (**Figure 7 a2**) doesn't change compared with the depth of holes at 1 hour immersion, implying that the film thickness and slightly tilted molecule geometry doesn't change.

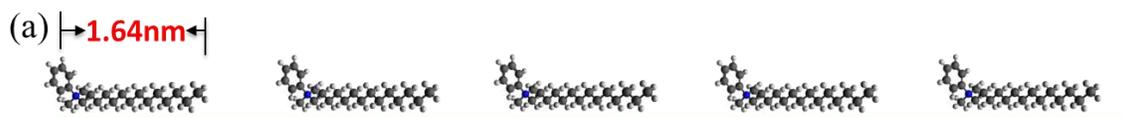
However, at 6 hours, as observed from **Figure 7 b3**, the bright spots on phase image become quite obvious and more dense. If using these white spots as reference positions, the corresponding black holes on topography image (**Figure 7 a3**) with the depth of around  $0.3 \text{ nm} \pm 0.1 \text{ nm}$  can be found. Apparently as immersion time increases, the number of holes on the inhibitor film gradually increased. Small and dense holes were all over the surface after 6 hours immersion.

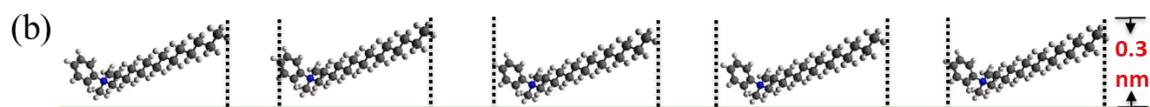




**Figure 7. TMAFM images of inhibitor films formed on mica at 2 CMC Q-C14+1 wt% NaCl after 1 hour immersion: (a1- a3) 1 hour, 3 hours, 6 hours immersion, topography image, (b1-b3) 1 hour, 3 hours, 6 hours immersion, phase image.**

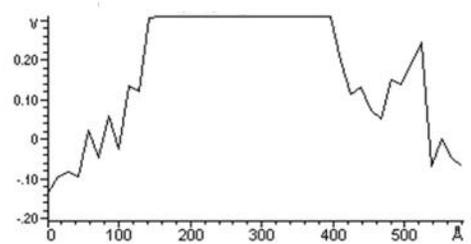
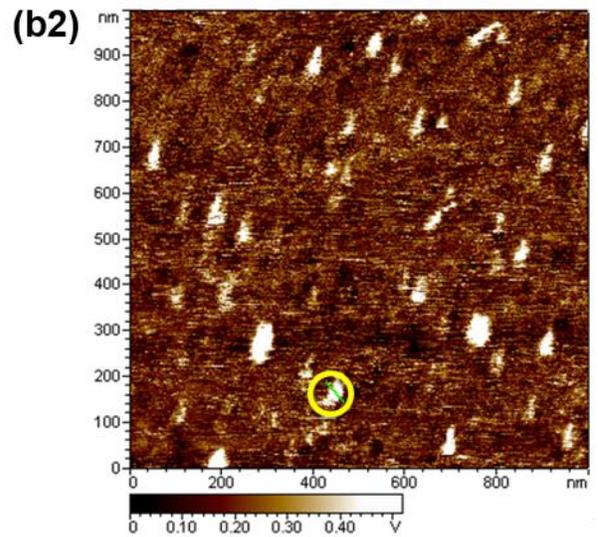
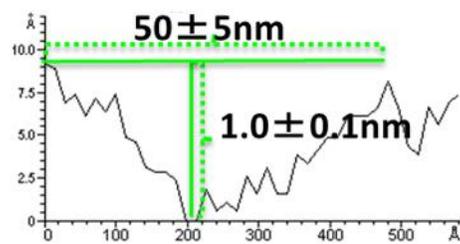
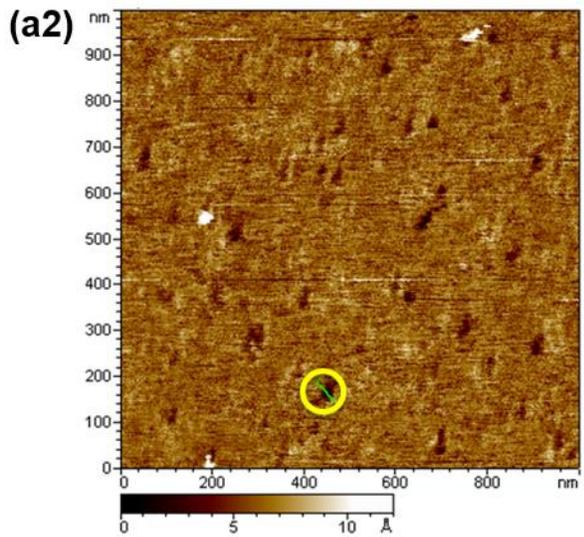
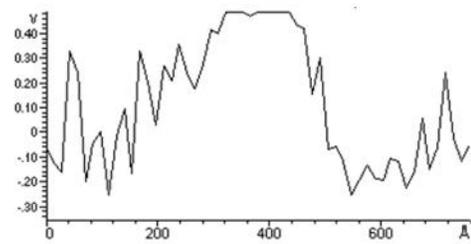
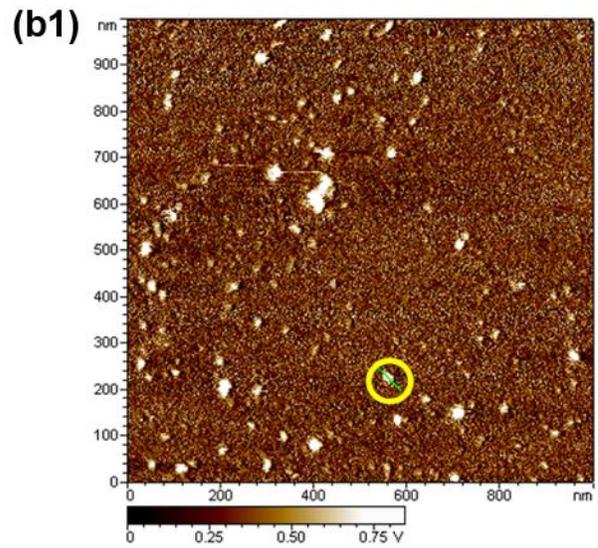
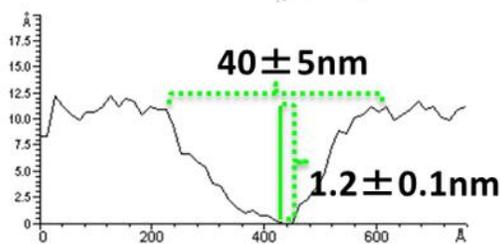
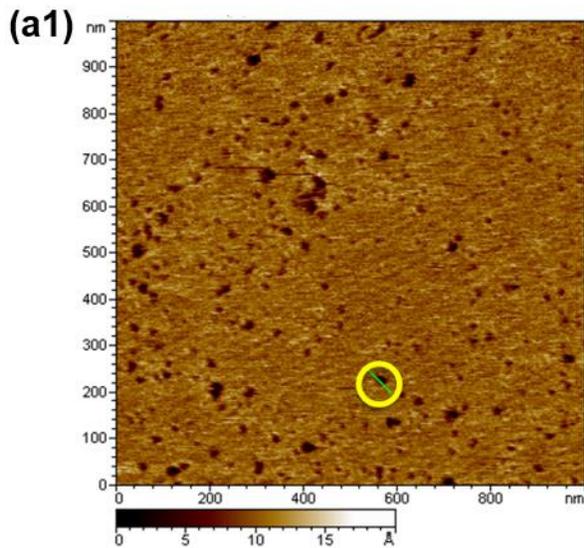
As discussed above, inhibitor molecules diffuse randomly in solution and can adsorb lying flatly on the mica substrate in the initial stage, displayed as an integral featureless layer (**Figure 6**). The lying-down configuration is observed because this configuration is energetically favorable with strong tail-surface interactions. However, as the adsorption time increased from 1 hour to 6 hours, the orientations of molecules changed from lying down to slightly tilted on the mica surface, indicating the randomly adsorbed molecules are gradually standing up. The standing up of molecules is driven by lateral hydrophobic interactions between alkyl tails. Since the energy penalty for a molecule to stand-up is large, the molecules are kinetically trapped in the lying-down configurations to some extent so that this standing up process is quite slow. After 6 hours adsorption the tilted angle is only  $10.54^\circ$ , as can be calculated from the film thickness and molecule length ( $\arcsin 0.3 / 1.64$ ). This adsorption and self-assembly process is illustrated in **Scheme 1**. As can be seen from Scheme 1b, there are empty spaces between slightly tilted molecules, which can be detected as microdomains by TMAFM with height contrast (black holes) and phase contrast (bright spots). These holes are quite shallow because the molecules are in the original stage of standing up and the tilted angles are very small.





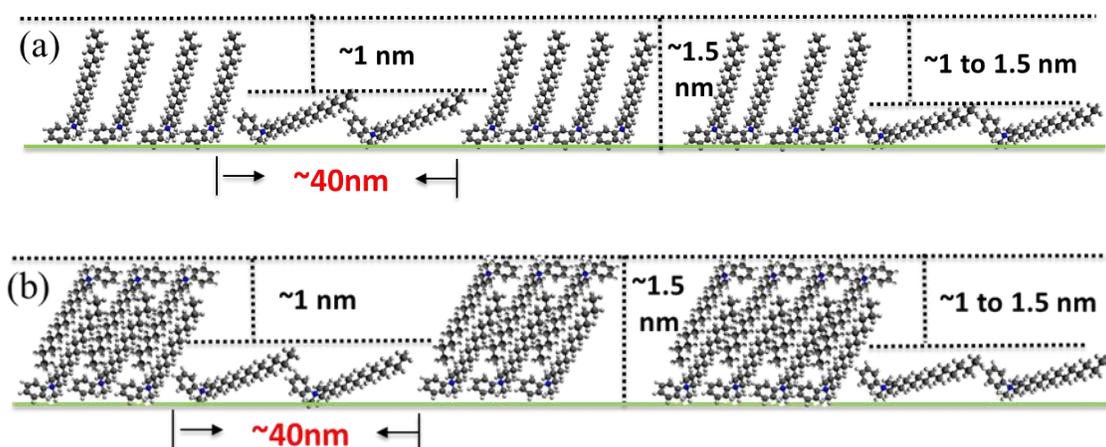
**Scheme 1.** Schematic diagram of evolution mechanisms of Q-C14 inhibitor molecular orientation during adsorption process on mica: (a) after adsorption 20 minutes; (b) after adsorption 6 hours

**Figure 8** shows TMAFM images of the adsorbed film structures on mica surface from 1wt% NaCl solutions with Q-C14 inhibitor at 2 CMC after immersion 14 hours and 20 hours. As observed from **Figure 8 a1** and **b1**, the holes on inhibitor film have changed greatly after immersion 14 hours. The depth of holes increased until  $1.2 \text{ nm} \pm 0.1 \text{ nm}$ , while before immersion 6 hours the depth is about  $0.3 \text{ nm} \pm 0.1 \text{ nm}$ . The diameter of holes increased to about 40 nm and the number of holes has decreased. After immersion 20 hours, as can be seen from **Figure 8 a2** and **b2**, the distribution of holes on inhibitor film is similar as in 14 hours. There are larger, deeper and fewer holes dispersed on the film randomly. The film structure and molecular configurations seem to stabilize after 14 hours immersion.



**Figure 8. TMAFM images of inhibitor films formed on mica at 2 CMC Q-C14+1 wt% NaCl after: (a1) 14 hours immersion, topography image (b1) 14 hours immersion, phase image (a2) 20 hours immersion, topography image (b2) 20 hours immersion, phase image.**

The increased depth of holes, i.e. the increased height difference between adsorbed inhibitor molecules and underneath mica surface, indicates the inhibitor molecules may stand up more vertically at 14 and 20 hours immersion compared to the configuration at 6 hours. Because the film thickness of  $1.2 \text{ nm} \pm 0.1 \text{ nm}$  is still slightly smaller than the length of a single molecule, these molecules are proposed to adsorb onto mica surface in monolayer with highly tilted geometry rather than an upright standing orientation. Also after a long immersion time, the inhibitor in the bulk solution may re-adsorb in the empty spaces and therefore the density of holes decreases. Considering the diameter of holes (around  $40 \text{ nm}$ ) is much larger than molecule length, it is assumed that patchy aggregation and islands formation would occur during the standing up process [24], as illustrated in **Scheme 2a**. The gaps between inhibitor aggregates would be detected as large and deep holes by AFM height image (**Figure 8 a1** and **a2**). The depths of holes vary from  $1$  to  $1.5 \pm 0.1 \text{ nm}$  because there are different height contrasts. Inhibitor molecules from the bulk solution could adsorb again on the empty spaces (**Scheme 2a**) after these big holes formed and then start the standing up process like previous molecules did. The height differences exist between inhibitor film surface and mica surface, and may originate from highly tilted molecules with newly adsorbed less tilted molecules as displayed in **Scheme 2a**. Another possibility is the formation of tilted bilayers (**Scheme 2b**). Similarly, new adsorption may occur during the standing up process of bilayer molecules, which would be indicated by multiple holes with various depths. Until now, a discontinuous film with porous appearance and randomly distributed defects was formed. The initial adsorption was dominated by the electrostatic interactions between polar head and negative mica surface, and then alkyl tails lie flat because the strong tail-surface interaction which influences the adsorbed configuration. With time, the hydrophobic interaction between tails drives the molecules into a standing up configuration, where finally close-packed islands of highly tilted molecules form. This self-assembled film structure formed after 14 hours is considered to be more thermodynamically stable.



**Scheme 2.** Schematic diagram of possible evolution mechanisms of Q-C14 inhibitor molecular orientations after adsorption 14-20 hours on mica: (a) possible mechanism I, (b) possible mechanism II.

## Summary of Results

The results of Q-C14 inhibitor indicates the formation of a porous film during a fast lying down initial adsorption and a slow standing up self-assembly process. This new finding of inhibitor adsorption mechanism on mica give us inspiration on how to better understand the corrosion behavior in the presence of inhibitor and how it can alter the nature of electrochemical reactions by adsorbing on metal-water interfaces.

From previous research, it can be concluded that inhibition efficiency will increase with the inhibitor concentration, and that a surface saturation concentration can be determined where it is assumed the first monolayer of inhibitor is formed on the metal surface [11]. Beyond that concentration, slight changes in inhibition efficiency may occur with increasing inhibitor concentration, but will never achieve 100%;

indicating that the corrosion rate never reduces to 0 (zero). With the small corrosion rates observed under inhibitor protection at a saturated concentration, it is hard to determine which parts of the surface corrode and which do not. But now with a porous film observed by use of the tapping mode AFM, it can be speculated that these holes can be where the corrosion are happening. So it can be imagined that some empty places may exist between adsorbed inhibitor molecules on a metal surface and the corrosion may occur there. However, is it not widely observed that corrosion inhibitors cause localized corrosion, so there must be more to the explanation. If the holes are dynamic, as some molecules from the bulk move to fill the existing holes other molecules may desorb from the surface to maintain an equilibrium with the concentration of inhibitor in the solution. This would result in uniform corrosion with very low corrosion rate.

There is still the question of why measured corrosion rates in experiments usually need several hours to decrease to a steady value after adding inhibitor. This may be explained by the extended period of time necessary for self-assembly of molecules into a tighter, more upright orientation before greatly influencing the measured corrosion rates. Further research will be needed to explore this phenomenon using TMAFM on a corroding metal surface.

## CONCLUSIONS

Based on TMAFM imaging and the proposed adsorption mechanism, it can be concluded that:

- The adsorption morphology of Q-C14 inhibitor on mica develops a porous film.
- As for the adsorption kinetics and molecular orientation, initially Q-C14 inhibitor adsorbs flatly on a mica surface within a few minutes, then follows a self-assembly process with molecules standing up slowly, forming small islands of molecules with intermittent holes between 0 – 6 hours.
- As molecules continue to stand up, interactions between the tails influence the observed structure. Larger and fewer holes can be observed on the film. Under the tested conditions, the adsorption morphology seemed to stabilize after 14 hours of immersion.
- The defects observed with inhibitor film formation on mica are believed to occur similarly on mild steel and influence the measured corrosion inhibition efficiency.

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## REFERENCES

- [1] J. Woodward, I. Doudevski, H. Sikes, D.J.T.J.o.P.C.B. Schwartz, Kinetics of self-assembled monolayer growth explored via submonolayer coverage of incomplete films, 101 (1997) 7535-7541.
- [2] D. Schwartz, S. Steinberg, J. Israelachvili, J.J.P.r.l. Zasadzinski, Growth of a self-assembled monolayer by fractal aggregation, 69 (1992) 3354.
- [3] M. Jaschke, H.-J. Butt, H. Gaub, S. Manne, Surfactant aggregates at a metal surface, Langmuir, 13 (1997) 1381-1384.
- [4] Y. Martin, C.C. Williams, H.K. Wickramasinghe, Atomic force microscope–force mapping and profiling on a sub 100-Å scale, Journal of Applied Physics, 61 (1987) 4723-4729.
- [5] P. James, M. Antognozzi, J. Tamayo, T. McMaster, J. Newton, M. Miles, Interpretation of contrast in tapping mode AFM and shear force microscopy. A study of nafion, Langmuir, 17 (2001) 349-360.

- [6] I. Schmitz, M. Schreiner, G. Friedbacher, M.J.A.c. Grasserbauer, Tapping-mode AFM in comparison to contact-mode AFM as a tool for in situ investigations of surface reactions with reference to glass corrosion, 69 (1997) 1012-1018.
- [7] P. Leclère, R. Lazzaroni, J.-L. Brédas, J.M. Yu, P. Dubois, R. Jérôme, Microdomain morphology analysis of block copolymers by atomic force microscopy with phase detection imaging, *Langmuir*, 12 (1996) 4317-4320.
- [8] J. Cleveland, B. Anczykowski, A. Schmid, V. Elings, Energy dissipation in tapping-mode atomic force microscopy, *Applied physics letters*, 72 (1998) 2613-2615.
- [9] J. Tamayo, R. García, Relationship between phase shift and energy dissipation in tapping-mode scanning force microscopy, *Applied physics letters*, 73 (1998) 2926-2928.
- [10] X. Chen, C. Roberts, J. Zhang, M. Davies, S. Tendler, Phase contrast and attraction–repulsion transition in tapping mode atomic force microscopy, *Surface science*, 519 (2002) L593-L598.
- [11] J.D. Olivo, D. Young, B. Brown, S. Nestic, Effect of corrosion inhibitor alkyl tail length on the electrochemical process underlying CO<sub>2</sub> corrosion of mild steel, in: *NACE Corrosion Conference*, 2018.
- [12] N. Moradighadi, S. Lewis, Effect of Alkyl Tail Length on CMC and Mitigation Efficiency Using Model Quaternary Ammonium Corrosion Inhibitors, in: *NACE Corrosion conference*, 2019.
- [13] J.D. Olivo, B. Brown, S. Nestic, Modeling of corrosion mechanisms in the presence of quaternary ammonium chloride and imidazoline corrosion inhibitors, in: *NACE/2016*, NACE International, Houston, Texas, 2016, pp. 1.
- [14] J.D. Olivo, D. Young, B. Brown, S. Nestic, Effect of Corrosion Inhibitor Alkyl Tail Length on the Electrochemical Process Governing CO<sub>2</sub> Corrosion of Mild Steel, *Corrosion*, 75 (2019) 137-139.
- [15] H. Wang, B. Brown, S. Nestic, A. Pailleret, Investigation of Organic Inhibitor on Mild Steel using In Situ Atomic Force Microscopy and Electrochemical Measurement, in: *CORROSION 2020*, NACE International, 2020.
- [16] Y. Wang, R. Song, Y. Li, J. Shen, Understanding tapping-mode atomic force microscopy data on the surface of soft block copolymers, *Surface science*, 530 (2003) 136-148.
- [17] F.E. Ala'a, M.F.J.J.o.c. Paige, i. science, The influence of salinity on surfactant miscibility in mixed dipalmitoylphosphatidylcholine–perfluorooctadecanoic acid monolayer films, 353 (2011) 210-219.
- [18] Y. Xiong, B. Brown, B. Kinsella, S. Nestic, A. Pailleret, AFM studies of the adhesion properties of surfactant corrosion inhibitor films, in: *NACE-International Corrosion Conference Series*, 2013.
- [19] E. Nagao, J.A. Dvorak, Phase imaging by atomic force microscopy: analysis of living homoiothermic vertebrate cells, *Biophysical journal*, 76 (1999) 3289-3297.
- [20] R. Godehardt, W. Lebek, R. Adhikari, M. Rosenthal, C. Martin, S. Frangov, G.H. Michler, Optimum topographical and morphological information in AFM tapping mode investigation of multicomponent polyethylene, *European polymer journal*, 40 (2004) 917-926.
- [21] I. Schmitz, M. Schreiner, G. Friedbacher, M. Grasserbauer, Phase imaging as an extension to tapping mode AFM for the identification of material properties on humidity-sensitive surfaces, *Applied Surface Science*, 115 (1997) 190-198.
- [22] B. Bhushan, J.N. Israelachvili, U. Landman, Nanotribology: friction, wear and lubrication at the atomic scale, *Nature*, 374 (1995) 607-616.
- [23] A. Weiss, Organic derivatives of mica-type layer-silicates, *Angewandte Chemie International Edition in English*, 2 (1963) 134-144.
- [24] S. Sharma, X. Ko, Y. Kurapati, H. Singh, S. Nešić, Adsorption Behavior of Organic Corrosion Inhibitors on Metal Surfaces—Some New Insights from Molecular Simulations, *Corrosion*, 75 (2019) 90-105.