Octadecanethiol as Corrosion Inhibitor for Zinc and Patterned Zinc-Copper in Humidified Air with Formic Acid

Mattias Forslund, Christofer Leygraf,* Per M. Claesson, and Jishan Pan*.

Division of Surface and Corrosion Science, Department of Chemistry, School of Chemical Science and Engineering, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden

The corrosion inhibition efficiency of octadecanethiol (ODT) for zinc and a zinc-copper patterned sample (Zn-Cu) has been explored during exposure in an atmosphere that mimics indoor atmospheric corrosion containing humidified air (80% relative humidity at 20°C) and formic acid (around 100 ppb). The corrosion kinetics were monitored in situ with infrared reflection absorption spectroscopy, and the local nature of corrosion effects post-analyzed with complementary scanning electron microscopy, atomic force microscopy and confocal Raman spectroscopy. ODT shows initially a corrosion inhibiting ability both on zinc and on Zn-Cu. This ability decreases with time due to local removal of ODT, which causes micro-galvanic effects that eventually result in corrosion rates that exceed those for the uncovered samples. On bare and ODT-covered samples, the presence of a copper-zinc junction results in both accelerated corrosion and in structurally more developed corrosion products. Overall, the results suggest that ODT can function as a temporary corrosion inhibitor in representative indoor environments on zinc and zinc with zinc-copper junctions.

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It is nowadays well established that carboxylic acids, such as formic1–10 or acetic acids,11,12 may cause corrosion of several metals, including copper, nickel and zinc, in a variety of indoor atmospheric environments.13–15 Such acids are generated through out-gassing of organic constituents from, e.g., wood,16,17 paper,18,19 and paint,13 followed by gradual oxidation to carboxylic acids. The corrosion effects they cause may decrease the quality and performance of electronic materials,12 military equipment,16 and deteriorate our cultural heritage.13 A common situation is the simultaneous exposure of two metals in electrical contact. The galvanic corrosion that follows leads to an accelerated corrosion of the less noble metal. Both zinc and copper are important engineering materials widely used in everyday life. Brass is a copper-zinc alloy that has improved machinability compared to unalloyed copper. The corrosion of brass is more complex than unalloyed copper due to possible galvanic effects that favor selective zinc dissolution, which leads to dealloying of a copper-rich matrix.17 Micro-galvanic effects are established between local anodes and local cathodes on the surface, whereby the galvanic corrosion kinetics are dependent on the electrochemical potential difference and the area ratio between the anode and cathode.18

In order to explore the mechanism of micro-galvanic corrosion effects, well-defined Zn-Cu patterned samples were studied previously during exposure to humidified air with addition of formic acid.18 It was found that the micro-galvanic effects observed on the patterned sample not only resulted in accelerated corrosion kinetics but also in structurally more developed corrosion products with characteristic hemispherical features not seen on pure zinc or copper metals.

In this paper we present data on micro-galvanic effects on the Zn-Cu patterned sample in presence of an adsorbed layer of octadecanethiol (CH₃(CH₂)₁₇SH, hereafter referred to as ODT), which acts as a corrosion inhibitor on the patterned sample. ODT forms self-assembled monolayers on both copper19–21 and zinc22 through direct bonding between sulfur in the thiil group and zinc or copper atoms of the substrate. ODT is in solid form at room temperature, and its bonding between sulfur in the thiol group and zinc or copper atoms is involved in the inhibition and galvanic corrosion processes. Through in situ near-surface analysis, the development of corrosion products has been monitored by means of infrared reflection absorption spectroscopy (IRAS), providing information of both the kinetics and the chemical changes as a function of time. The exposed samples have also been post-analyzed by means of scanning electron microscopy (SEM, global surface morphology), atomic force microscopy (AFM, local surface morphology), and confocal Raman micro-spectroscopy (CRM, local chemical composition) to provide complementary information to the IRAS-data. Issues that were investigated in this study include the inhibition efficiency of ODT on zinc and the Zn-Cu patterned sample as a model system, competing effects between corrosion inhibition by ODT and corrosion acceleration due to galvanic effects, and the nature of corrosion products formed without and with ODT as corrosion inhibitor. It should be added that the exposure condition used for this model system, humidified air (80%) with addition of formic acid (around 100 volume parts per billion, ppb), mimics representative indoor atmospheric corrosion on copper and zinc with an acceleration factor in the range from 10 to 100.

Experimental

Sample preparation.— The zinc samples were made from as-rolled polycrystalline zinc foil (Goodfellow, 99.7% purity, 1 mm thickness), and cut into pieces sized 1 × 1 cm. The samples were wet ground with SiC paper in steps, from 800 mesh down to 2400 mesh, followed by diamond paste polishing (6 μm and 1 μm) in ethanol (Merck, Germany, 99.9%). All samples were then sonicated in ethanol for 5 minutes in order to remove residual diamond particles.

The preparation of the Zn-Cu patterned samples has been described previously.18 The copper islands on the zinc substrate have a thickness of 0.1 μm, an area of 10 × 10 μm, and spacing between the islands of 10 or 20 μm. The patterned samples were immersed in 5 wt% amidosulphuric acid (H₂NSO₄, Sigma-Aldrich, hereafter referred to as ASA) for 2 s prior to use.18 For consistency, the same immersion in ASA was also performed on the pure zinc samples. Between each step the sample was rinsed with ethanol and dried by means of a gentle nitrogen jet.
Deposition of ODT.— The ODT layer on zinc and Zn-Cu was formed as previously reported for the case of pure copper. Both sample types were immersed in ethanol solution containing 1 mM ODT (Sigma-Aldrich, > 95%) for two hours to allow a self-assembled monolayer (SAM) to form. The solution was purged with dry nitrogen gas for half an hour before immersion to reduce oxygen interference during the ODT deposition. The ODT-coated samples were finally rinsed with ethanol and dried by a nitrogen jet prior to use.

In situ IRAS measurements.— In situ IRAS measurements were performed during exposure of pure zinc and Zn-Cu samples with and without ODT. In situ IRAS spectra were recorded repeatedly using a Digilab FTS 40 Pro FTIR spectrometer equipped with a liquid nitrogen cooled mercury cadmium telluride (MCT) detector. The instrumental setup has been described in detail elsewhere. The IRAS data were obtained by reflecting a p-polarized IR beam having an angle of 78° against the sample surface normal. All IRAS spectra were recorded using 1024 scans in the wavenumber range from 400 to 4000 cm⁻¹, with 4 cm⁻¹ resolution. The spectra were background subtracted, i.e. the reflection, R, monitored during the exposure was normalized with the reflection of the background, R₀, monitored before exposure. The difference between R and R₀ is mainly due to changes in surface chemistry during exposure, and the amplitude of the spectra in this work has been expressed in absorbance units [log(R/R₀)].

Corrosive air generation.— The air was dried and filtered, resulting in a CO₂-concentration of less than 20 ppm. To obtain humidified air with addition of formic acid, one stream of the dried air (1.1 L/min) was passed through a heated glass container with Milli-Q water (18.2 MΩ cm), whereas the second air stream (0.1 L/min) was passed through a Dreschel bottle containing a permeation tube of formic acid (Vici Metronics). These two streams were mixed in a container before entering the IRAS chamber, resulting in a flow rate of 4 cm/s, a temperature of 20.5 ± 1.0 °C, a relative humidity (RH) of 80 ± 3% and a formic acid concentration of 94.3 ± 0.4 ppb (hereafter referred to as air with 80% RH and 94 ppb, respectively).

Microscopic surface analysis.— SEM, AFM, and CRM were used to analyze the morphology, distribution and composition of the corrosion products formed on the samples after the exposure. Overview SEM images were obtained using a tabletop Hitachi TM-1000 equipped with energy dispersive spectroscopy (EDS) utilizing an acceleration voltage of 15 keV. An Agilent 5500 AFM was employed to image the detailed morphology of corrosion products and surface potential using the SCM-PIT probes from Bruker Corp. The surface potential measurement was performed on a partially ODT covered Zn surface. The in situ IRAS results from the different types of samples are given below.

Identification of zinc corrosion products.— The in situ IRAS spectra in Fig. 1 represent the overall absorbance observed on pure zinc and Zn-Cu patterned samples, with and without an adsorbed ODT layer, obtained during the exposure to humidified air with formic acid. The spectra cover the wavenumber range from 1250 to 1750 cm⁻¹, and display the time dependent evolution of infrared bands assigned to the symmetric vibration mode, v₁(COO) at around 1340 cm⁻¹, the CH bending mode, δ(CH) at around 1380 cm⁻¹, and the asymmetric vibration mode, v₃(COO) at around 1610 cm⁻¹. The peak at 1680 cm⁻¹ observed on both ODT-covered samples is assigned to the carboxyl band, υ(C = O), of pyrrolsolvated formic acid. The exact peak positions changed somewhat with time, in particular for the Zn-Cu patterned samples. Differences in peak positions at given exposure times are exemplified in Fig. 1, showing that the peak positions of both v₁(COO) and v₃(COO) for zinc and ODT-covered zinc are located at different wave numbers. More detailed analyzes of the IRAS-results from the different types of samples are given below.

Zinc.— The v₃(COO) vibration band of formate formed on pure zinc was observed at 1630 cm⁻¹ in dry air, but at 1620 cm⁻¹ in humid air, and remained relatively constant over exposure time, Fig. 1A. This difference reflects molecular alternations around the formate ion in humid air compared to dry air, e.g., H-bonding to H₂O. The non-symmetrical shape of the v₃(COO) peak, being steeper on the high wavenumber side, and having a tail on the low wavenumber side, suggests an additional zinc formate structure that contributes to the absorbance at lower wavenumbers (~1605 cm⁻¹).

In all, the IRAS data suggest the formation of at least one zinc formate compound. In this formic acid will dissolve in the water adlayer and dissociate according to:

\[
HCOOH \rightarrow H^+ + HCOO^- \tag{1}
\]

As a result, the water adlayer becomes an electrolyte that promotes electrochemical reactions, including the anodic dissolution of zinc and the cathodic reduction of oxygen and/or protons:

\[
Zn \rightarrow Zn^{2+} + 2e^- \tag{2}
\]

\[
O_2 + 2H_2O + 4e^- \rightarrow 4 OH^- \tag{3}
\]

\[
O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{4}
\]

\[
2H^+ + 2e^- \rightarrow H_2 \tag{5}
\]

The anodic reaction leads to increased zinc ion concentration in the aqueous adlayer, while the cathodic reaction consumes protons and thus promotes the dissociation of formic acid. Zinc formate will form and precipitate on the metal surface when the concentration of Zn²⁺ and HCOO⁻ ions is high enough in the aqueous adlayer:

\[
Zn^{2+} + 2HCOO^- \rightarrow Zn(HCOO)_2 \tag{6}
\]

which may lead to the formation of a hydroxy complex at higher pH:

\[
5Zn^{2+} + 8OH^- + 2HCOO^- \rightarrow Zn_{5}OH_8(HCOO)_2 \tag{7}
\]

The overall result is indicating a fairly uniform formation of zinc hydroxy formate as the main corrosion product on zinc, as also previously detected by IRAS and confocal Raman microspectroscopy.

ODT-covered zinc.— The shape of the v₃(COO) peak observed on the ODT-covered zinc is somewhat different from that observed on bare zinc. The main peak is centered at around 1605 cm⁻¹, with slightly lower wavenumber than on bare zinc, and the tail is at slightly higher wavenumbers, Fig. 1B. The peak position of the v₁(COO) vibration on the ODT-covered zinc is also shifted to lower wavenumber compared to bare zinc, as shown in Fig. 2. Although it is difficult to precisely determine the identity of the zinc formates formed, the shifts in the positions of these vibration bands indicate the influence of the...
Figure 1. In situ IRAS spectra of pure zinc (A), ODT-covered zinc (B), Zn-Cu patterned sample (C), and ODT-covered Zn-Cu patterned sample (D). Spectra were collected every two hours during exposure to humidified air (80% RH) containing formic acid (94 ppb). The peaks at around 1340, 1380, 1610 and 1680 cm$^{-1}$ are assigned to vs(COO), $\delta$(CH), vas(COO) and v(C=O), respectively. The v(C=O) peak was only observed on the ODT-covered samples, and the splitting of the vas(COO) peak was only observed on the Zn-Cu patterned samples.

Figure 2. A comparison of in situ IRAS spectra for zinc (solid line) and ODT-covered zinc (dashed line) after 25 hours and 45 hours, respectively, exposure to humid air (80% RH) containing 94 ppb formic acid. The shifts in the symmetric and asymmetric vibration bands are indicated with brackets. The spectra are offset for clarity and the absorbance values are in arbitrary units.

ODT-layer on the chemical structure of the corrosion products. This reflects differences in surface conditions during the exposure of zinc without and with ODT.

The peak at 1680 cm$^{-1}$ observed on ODT-covered zinc (Fig. 2) together with a peak observed around 2920 cm$^{-1}$ (not shown here) are assigned to physisorbed or solvated formic acid (HCOOH).4,29 Fig. 1B shows that there is a continuous growth with exposure time of both the peaks from formic acid (1680 cm$^{-1}$) and from zinc formate (1605 cm$^{-1}$). The presence and increasing amount of formic acid are probably due to the continuous supply (gas flow) and slow consumption of formic acid in the adlayer. This suggests that there is a decrease in pH of the adlayer due to the dissociation of formic acid.

The presence of formic acid and likely low pH of the aqueous adlayer affect the reaction between zinc and formate ions, and alter the nature of the corrosion products formed as compared to bare zinc.

Zn-Cu patterned sample.— The dominant peak of the $\nu_{as}$(COO) vibration detected at around 1605 cm$^{-1}$ at the beginning of the exposure is close to that observed on ODT-covered zinc, Fig. 1C. It shifts slightly toward lower wavenumber during the first 6 hours and then toward higher wavenumber during prolonged exposure, approaching 1640 cm$^{-1}$ after one week of exposure. Similar to the previously discussed samples, it originates from hydrated zinc hydroxy formate (Reaction 7). The fact that the peak undergoes shifts reflects that its identity may alter during exposure. In addition, the $\nu_{as}$(COO) vibration also includes a weaker peak at around 1560 cm$^{-1}$ during longer exposure times, resulting in a broader width of the $\nu_{as}$(COO) vibration for the Zn-Cu patterned sample than for pure zinc without or with
ODT, see Fig. 1. This suggests the formation of various forms of zinc formate (Reaction 6), based on complementary CRM measurements as discussed later.

Upon drying of the exposed sample in dry air, a shift of the dominating $v_{\text{as}}$(COO) vibration was observed toward 1660 cm$^{-1}$, similar to that on bare zinc. However, the weak peak remained at around 1560 cm$^{-1}$. These are further indications of more than one zinc formate compound being formed as result of corrosion on the Zn-Cu patterned sample, one with more loosely and one with more strongly bound water. Possible compounds include anhydrous zinc formate, hydrated zinc formate and hydrated zinc hydroxy formate, as discussed below.

**ODT-covered Zn-Cu patterned sample.**— The main peak of the $v_{\text{as}}$(COO) vibration for the ODT-covered zinc-copper pattern sample is centered between 1600 and 1610 cm$^{-1}$ during the first 20 hours of exposure, similar to that observed on ODT-covered zinc, Fig. 1D. With prolonged exposure the $v_{\text{as}}$(COO) vibration undergoes both a shift and a splitting, Fig. 1D. As explained above, the results from ODT-covered Zn-Cu suggest that the corrosion products consist of different variants of zinc formates. Similar to ODT-covered zinc, a peak grows at 1680 cm$^{-1}$, assigned to physisorbed and solvated formic acid.

In all, the results suggest the formation of zinc formates on the Cu-Zn patterned samples not observed on pure zinc. Their identity will be further discussed in the next section based on complementary CRM measurements.

**Distribution and local identification of zinc corrosion products on ODT-covered samples.**— The distribution of corrosion products and local analysis of ODT-covered samples after different exposures by means of SEM, AFM and CRM are presented next through selected results shown in Figs. 3–5.

Backscattered electron mode SEM (BS-SEM) images in Fig. 3 display the distribution and morphology of corrosion products formed on ODT-covered zinc (Fig. 3A) and on ODT-covered Zn-Cu patterned samples (Figs. 3B-3D). After 15 hours of exposure there are clearly seen randomly distributed corrosion products on ODT-covered zinc, Fig. 3A. The same exposure times result in higher density of corrosion products on the ODT-covered patterned sample. The light gray background in Fig. 3B and 3C corresponds to the zinc substrate, while the darker ordered arrays are the copper squares, visible in the BS-SEM images. As revealed by energy-dispersive spectroscopy (EDS) the
Figure 5. Optical microscopy images taken with the CRM instrument displaying the corrosion products formed on an ODT-covered Zn-Cu patterned sample exposed for 0 hours (A), 15 hours (B), and 125 hours (C and D) to humid air (80% RH) containing 94 ppb formic acid. The images are shown in gray scale, and the copper squares are colored for clarity. The green dots with black crosses indicate the analyzed areas where the spectra in Fig. 6 were acquired.

Figure 6. CRM spectra of the corrosion products formed on the ODT-covered Zn-Cu patterned sample exposed to humid air (80% RH) containing 94 ppb formic acid for 125 hours. The spectra were offset for clarity. The lower spectrum suggests predominant zinc formate in the granular corrosion products (marked in Fig. 5C), and the upper spectrum suggests predominant zinc hydroxy formate in extended thicker corrosion products (marked in Fig. 5D).
Figure 7. (A) The absorbance of the $v_{\text{as}}$(COO) band as a function of time for zinc (dashed gray line), Zn-Cu patterned sample (dashed black line), ODT-covered zinc (gray line), and ODT-covered Zn-Cu patterned sample (black line), exposed to humid air (80% RH) containing 94 ppb formic acid. The lines are based on average values from at least duplicate measurements and the error bars represent standard deviations. For comparison, the values of the patterned samples were normalized with respect to the zinc area. The arrow indicates the intercept of the lines for zinc and ODT-covered patterned samples. The graphs in (B and C) are data for a longer exposure of the ODT-covered zinc and Zn-Cu patterned samples, respectively.

Kinetics of growth of zinc corrosion products.— The kinetics of growth of zinc corrosion products formed on the different samples have been determined by following the growth of absorbance of the strongest $v_{\text{as}}$(COO) vibration over time, as summarized in Fig. 7. The monitoring of the absorbance of this peak has turned out to be a good measure of the amount of zinc carboxylate formed.\(^{11}\)

The growth rates of the corrosion product formation on pure zinc can be divided into two regions, i.e., before and after $\sim 2$ h of exposure, Fig. 7A. Up to 2 hours, the corrosion products build up and successively become more protective, while after 2 hours the growth rate is slower and more constant.

The corrosion product formation is considerably slower on ODT-covered zinc compared to bare zinc in the beginning of the exposure, Fig. 7, obviously due to the inhibiting effect of the ODT-layer. There is a considerable scattering in data, which is most likely related to differences in the quality of the ODT-layer. The corrosion product formation rate appears to increase slowly up to 10 hours, and then becomes more constant. Eventually the amount of corrosion products exceeds that of bare zinc.

The Zn-Cu patterned sample exhibits the highest corrosion product formation rate among the four types of investigated samples. As discussed in detail in a previous paper, the high zinc formate formation rate is a result of galvanic corrosion effects of zinc adjacent to the copper squares.\(^{18}\)

The ODT-covered Zn-Cu patterned sample exhibits a low corrosion product formation rate during the initial 6 hours, where it is almost ten times lower than the rate observed for the bare patterned sample. This demonstrates a pronounced inhibition effect of the ODT-layer despite the zinc-copper galvanic coupling. However, after the initial period the corrosion product formation rate increases significantly, Fig. 7C, and exceeds that of bare zinc after about 9 hours. This change of the corrosion rate suggests that the protection by the ODT-layer is partly lost, and the galvanic acceleration effect dominates over the inhibiting effect of the ODT-layer.

In all, the results show clearly that the ODT-layer has a corrosion inhibiting effect. However, the inhibition effect is limited to a shorter period. After that, the galvanic acceleration effect is gradually increasing, especially for the Zn-Cu patterned sample.

Discussion

In what follows we will discuss the possible corrosion inhibition of ODT on zinc and on the Zn-Cu patterned sample. We will also address important chemical differences between samples covered by ODT and uncoated samples.

Corrosion inhibiting ability of ODT on zinc.— SAMs with thiol as the anchoring head group have frequently been reported to act as corrosion inhibitors for copper and silver, and it is believed that they can find applications for temporary corrosion protection in, e.g., electrical contacts or connectors, which require the application of an ultrathin protective film.\(^{30}\) It is clear that the quality of the monolayer depends
strongly on the way in which the thiol group anchors to the underlying substrate. When applied on gold, the absence of any oxide results in a strong gold-sulfur bonding with reproducible and well-ordered monolayer films. Copper or silver, on the other hand, may form oxides during handling and application of the film, and the resulting SAM may lose corrosion inhibiting performance during oxidation in, e.g., air. Hence, when applied to less noble and oxide-forming metals, such as iron and zinc, it is expected that the SAM bonds less well with a concomitant loss in corrosion inhibiting performance. Nevertheless, under favorable conditions, ODT on zinc has been reported to form a well-ordered monolayer with demonstrated corrosion inhibiting ability. The adsorption of thiol on oxide-covered metals involves the ability of the thiol to reduce the thin metal oxide and form a metal-sulfur bond.

Under the current exposure conditions, humidified air with additions of about 100 ppb of formic acid, ODT acts as an efficient corrosion inhibitor for copper up to exposure times of 160 hours. Also shorter alkane chain lengths exhibit corrosion protection, and the protection efficiency increases with chain length. This has been attributed to the hydrophobic CH₃ tail group and the perfect ordering of the alkyl chains that hinder the corrosion stimulating molecules to reach the copper surface. The hindrance, however, is selective and the transport rate through the ODT-layer decreases as O₂ > HCOOH > H₂O. With increased exposure an oxide growth and also a simultaneous degree of disordering of the alkane chains could be monitored in situ with sum frequency vibrational spectroscopy. As a result, the corrosion protection efficiency of alkanethiols was observed to gradually decrease with exposure time.

For pure zinc the kinetics of corrosion product formation is fast up to the first 2 hours and then levels off to reach a constant growth rate. Due to the relative structural uniformity of pure zinc, the anodic and cathodic reactions are occurring more or less randomly on the zinc surface during the beginning of the exposure, and the fast anodic reaction (zinc dissolution) results in an increasing zinc ion concentration in the water adlayer. When the concentration of zinc and formate ions is sufficiently high, aqueous zinc formate complexes form and precipitate on the zinc surface as corrosion products, which block part of the zinc surface and reduce the anodic area. After this initial period, the anodic and cathodic reactions are slowed down by the thin layer of corrosion products on the surface, leading to a lower growth rate of corrosion product.

The corrosion product formation is significantly slower on ODT-covered zinc compared to bare zinc in the beginning of the exposure, Fig. 7A, due to the inhibiting effect of the ODT-layer. The scattering of data for ODT-covered zinc is considerable, however, and reflects differences in quality of the ODT-layers between different samples. Similar to ODT on copper, there is transport of the corrosive species O₂, HCOOH and H₂O through the ODT layer. This leads to slow corrosion product formation on the zinc surface, a gradual disordering of alkyl chains, local disbonding of Zn-S bonds and, finally, partial removal of ODT on local areas. The corrosion product formation rate gradually increases during the first 10 hours, Fig. 7B, which suggests that during this period there is an increasing amount of anodic sites, i.e. local areas where the corrosion protection of ODT is lost, see the distribution of local corrosion products in Fig. 3A. The kinetics of corrosion product growth is here governed by a high cathode/anode area ratio, since the anodic reaction occurs at local imperfections in the ODT-layer and the cathodic reactions can occur anywhere on the SAM. After about 10 hours the growth rate becomes constant for the next 20 hours. During this period, the amount of anodic sites on ODT-covered zinc appears to be the same and the growth of zinc formate is mainly due to the development of existing corroding sites. It is interesting to note that the growth rate of zinc formate between 10 and 30 hours is higher than that observed for bare zinc, Fig. 7A and 7B. Hence, the growth of zinc formate on ODT-covered zinc eventually exceeds that of bare zinc.

This higher corrosion rate for ODT-covered zinc than on bare zinc is similar to what has been observed for alkaneselenolates as a corrosion inhibitor for copper. In this case, the local removal of alkaneselenolates gave areas of unprotected copper surface. This resulted in an increased corrosion rate due to a micro-galvanic action whereby the SAM surface acted as cathode and the local unprotected metal area with partially removed SAM as anode.

To explore if this micro-galvanic action also occurs on zinc, the surface potential measurements along the border between pure zinc and ODT-covered zinc were performed by using the AFM, the averaged data are given in Fig. 8. The results in Fig. 8 show that there is a significant difference in the measured surface potential between zinc with and without adsorbed ODT. Unlike clean metallic surfaces, here the interpretation of the data must take into account the effect of adsorbed ODT layer. The physical concept of this surface potential is closely related to work function of the metal, i.e. the energy required to push an electron from the Fermi level of a metal to vacuum. A change in work function can be induced by the adsorption of a molecule onto the metal, as well explained in literature for the adsorption of alkanethiols onto a gold surface. Similarly as on gold, the adsorption of ODT on zinc presumably has two contributions: i) the dipole moment induced by the charge transfer between the metal and the sulfur atom upon adsorption, which results in a positive but small dipole moment from the metal to the sulfur atom; ii) the intrinsic dipole moment of the molecule itself. ODT has a negative and relatively strong dipole pointing from the CH₃-group to the sulfur atom. The overall result is a negative change in work function upon adsorption of ODT on zinc.

The changes in the measured surface potential due to the adsorption of ODT on different metals will be explored further in our future research, to gain an improved understanding of their effects on the corrosion and protection of the metals.

To summarize, ODT shows initially a corrosion inhibiting ability on zinc. This ability decreases with time due to local removal of ODT. With prolonged exposure the total corrosion product formation rate exceeds that of uncovered zinc, due to micro-galvanic action between bare zinc and ODT-covered zinc.

**Corrosion inhibiting ability of ODT on Zn-Cu patterned sample.—** It has previously been shown that the uncovered Zn-Cu patterned sample has a six-fold increase in the formation rate of zinc formate compared to pure zinc. This was attributed to strong galvanic effects, with the corrosion products preferentially formed adjacent to the copper patches. It was also concluded that the galvanic action resulted in structurally more complex corrosion products, i.e., crystalline zinc oxide and zinc formate dihydrate on the patterned sample, as compared to amorphous zinc oxide and zinc hydroxy formate on zinc. In all, the results on the bare samples followed the common finding that the corrosion rate of zinc under similar conditions is accelerated by
galvanic effects. The question is how well the Zn-Cu patterned sample may be protected by ODT through the straightforward one-step process without optimizing the ODT-deposition for both zinc and copper simultaneously.

As inferred from Fig. 7, there is a significant inhibition effect of the ODT-layer not only on pure zinc but also on the patterned sample. During the ~6 hours of initial exposure, the corrosion rate, measured as the zinc formate formation rate, is almost ten times lower than that for the bare Zn-Cu patterned sample. Thus, ODT has initially a pronounced inhibition effect despite the possible galvanic effects. The ODT-layer on the patterned samples provides an increased resistance for the ionic transport between the anodic and cathodic initially a pronounced inhibition effect despite the possible galvanic effects. The ODT-layer on the patterned sample provides an increased resistance for the ionic transport between the anodic and cathodic sites as compared to the bare patterned sample. This contributes to a decreased overall corrosion rate during this initial period, despite the galvanic driving force for zinc dissolution.

However, during prolonged exposure the corrosion rate for the ODT-coated patterned sample increases significantly, Fig. 7C, and the curve intercepts that of bare zinc after around 9 hours, marked with an arrow in Fig. 7A. This change of the corrosion rate demonstrates that the protection by the ODT-layer is mostly lost, and the galvanic effect by the copper patches dominates over the inhibiting effect of the ODT-layer.

The shape of the kinetic curve for ODT-covered Zn-Cu is similar to that observed for ODT-covered zinc, i.e., the corrosion rate is slow in the beginning but increases after a certain time of exposure. This suggests a similar progress in the degradation of the ODT-layer on both samples, i.e. a gradual disordering of alkyl chains, local desorption of metal-sulfur bonds and local removal of ODT, which creates conditions for micro-galvanic corrosion effects. The faster degradation of ODT on Zn-Cu than on zinc is likely due to the faster metal-sulfur disbonding at the zinc-copper junction with its higher density of defects in the ODT-layer and the strong galvanic coupling.

An important implication of the present results is the application of ODT as a temporary corrosion inhibitor not only on copper and silver, but also on a much lesser noble metal such as zinc. Even if the corrosion inhibition so far only lasts for a few hours, it should be emphasized that the conditions for adsorbing the ODT-layer on zinc or on the Zn-Cu patterned samples not yet have been optimized. It should also be added that the current exposure conditions represent accelerated corrosion conditions of between one and two orders of magnitude relative those of many representative indoor atmospheres.

In all, the results show clearly that the ODT-layer has a corrosion inhibiting effect also on the Zn-Cu patterned sample. However, the inhibition efficiency is limited to a shorter period of time than on ODT-covered zinc. After that, a local degradation of the ODT-layer takes place, which is enhanced by the presence of Zn-Cu junctions.

Chemical differences between ODT-covered and uncovered samples.— The in situ IRAS-data presented in Fig. 1 show two major differences between the samples investigated, both of which are demonstrated by the chemical information extracted from IRAS. The first concerns the broader $v_{\text{OH}}$(COO) peak on both Zn-Cu samples (ODT-covered and bare) compared to pure zinc, and the second concerns the detection of formic acid on both ODT-covered samples (Zn-Cu and pure zinc) as opposed to both uncovered samples where no formic acid was detected.

The broad $v_{\text{OH}}$(COO) peak on both Zn-Cu samples consists of a main peak centered around 1605 cm$^{-1}$ and a second gradually evolving peak which shifts to lower wavenumber, Fig. 1. As discussed in a previous section, the broader peak is in agreement with complementary CRM-data performed in this study, suggesting the formation of hydrated zinc formate, Zn(HCOO)$_2$·xH$_2$O, and of hydrated zinc hydroxy formate, Zn$_5$(OH)$_8$(HCOO)$_2$·xH$_2$O, on ODT-covered Zn-Cu. This differentiation in corrosion product composition was discussed in a previous study for uncovered zinc and Zn-Cu showing that the galvanic effect in the latter case not only resulted in an accelerated corrosion rate but also in structurally more complicated corrosion products. The same observation is seen also for ODT-covered samples according to Fig. 1, with structurally more advanced corrosion products on ODT-covered Zn-Cu compared to ODT-covered zinc.

Hence, we conclude that both bare and ODT-covered zinc produce primarily hydrated zinc hydroxy formate, Zn$_5$(OH)$_8$(HCOO)$_2$·xH$_2$O with minor variations, while bare and ODT-covered Zn-Cu produce hydrated zinc formate, Zn(HCOO)$_2$·xH$_2$O, and hydrated zinc hydroxy formate, presumably Zn$_5$(OH)$_8$(HCOO)$_2$·xH$_2$O. The fact that physisorbed or solvated formic acid is detected on both ODT-covered samples, but not on the uncovered ones, suggests significant differences in atmospheric corrosion chemistry between the two pairs of samples. Thermodynamic calculations of stable species with comparable concentrations in the aqueous adlayer show that formic acid is the dominant species in the pH range between 0 and 2. Such low pH conditions are likely to form in local areas where the ODT-layer has been removed due to Zn-S disbonding. In such areas, the pH may locally decrease due to easy transport of protons from the aqueous adlayer toward the anodic sites, and also due to hydrolysis of anodically dissolved zinc ions. The local lowering of pH may lead to further Zn-S disbonding and extended removal of the ODT-layer, which accelerates the atmospheric corrosion process further.

To conclude, the IRAS-measurements show the presence of formic acid in undissociated form, which suggests that solvated formic acid may exist in local areas where the ODT-layer has been partially removed to reach highly acidic conditions.

Conclusions

In this study, the inhibition effects of ODT (octadecanethiol)-covered zinc and Zn-Cu patterned samples were investigated during exposure to humid air containing formic acid. The corrosion kinetics were monitored in situ, and the corrosion products were post-analyzed with complementary microscopic and spectroscopic techniques. Based on the results the following conclusions could be drawn.

- ODT shows initially a corrosion inhibiting ability on zinc. This ability decreases with time due to local removal of ODT. With prolonged exposure the total corrosion product formation rate exceeds that of bare zinc, due to an observed micro-galvanic action between bare zinc and ODT-covered zinc.
- ODT exhibits a corrosion inhibiting effect also on the Zn-Cu patterned sample. The inhibition effect is limited to a shorter exposure period than on ODT-covered zinc. The local degradation of the ODT-layer is enhanced by the presence of Zn-Cu junctions of the substrate and results in corrosion rates that exceed that of bare zinc.
- The degradation mechanism of the ODT-layer on zinc is similar to that previously observed on pure copper, and includes a gradual disordering of alkyl chains, local desorption of metal-sulfur bonds and local removal of ODT.
- On ODT-covered samples formic acid is observed, suggesting that solvated formic acid may exist locally, where the ODT-layer has been partially removed and reached highly acidic conditions.
- The galvanic action results not only in accelerated corrosion rates, but also in structurally more advanced corrosion products; hydrated zinc formate, (Zn(HCOO)$_2$·xH$_2$O) and hydrated zinc hydroxy formate (presumably Zn$_5$(OH)$_8$(HCOO)$_2$·xH$_2$O) on bare and ODT-covered Zn-Cu, as opposed to primarily hydrated zinc hydroxy formate on bare and ODT-covered zinc.
- Overall, the results suggest that ODT can function as a temporary corrosion inhibitor in representative indoor environments, not only on pure copper and silver, but also on a much lesser noble metal such as zinc or zinc with zinc-copper junctions.

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