



## Application of 1-Octadecanethiol Self-Assembled Monolayers for Corrosion Protection of Leaded Brass Surface

Cheikh Mokrani\* and Rokia Fakani

Department of Chemistry, Faculty of Science, University of M'sila, M'sila, Algeria

### ABSTRACT

The self-assembled monolayer (SAM) of 1-octadecanethiol (ODT) on leaded brass surface and their ability to inhibit the alloy corrosion process in non-complexing  $0.1\text{mol.L}^{-1}\text{HClO}_4$  solution at  $25^\circ\text{C}$  were investigated by different electrochemical methods. Results showed that the open circuit potential ( $E_{\text{OCP}}$ ) of uncoated brass presented an anodic potential jump of about 400 mV, which is attributed to the spontaneous dissolution of Zn, whereas, in the presence of ODT SAM this process is significantly hampered. Tafel polarization curves showed that the ODT is a mixed inhibitor type with predominantly cathodic action. It showed that the ODT SAMs suppresses tremendously the selective dissolution of brass alloy. EIS measurements revealed that the enhanced corrosion resistance performance could be ascribed to the compact film structure and the blocking characteristics against the permeation of the corrosive species to the underlying metal. The results collectively are in good agreement and show clearly that ODT SAM is a good corrosion inhibitor for leaded brass surface in  $0.1\text{M HClO}_4$ .

**Keywords:** Leaded brass; Perchloric acid; Self-assembled monolayers; Octadecanethiol; Corrosion

### INTRODUCTION

The selective corrosion of alloys involves preferential dissolution of the active component of the alloy, leaving behind a fragile surface that is enriched in the nobler component. It leads to serious deterioration of the surface and mechanical properties of the remaining alloy and hence increases the risk of corrosion failures, which may be costly or fatal. Brasses (copper-zinc alloys) provide a favorable combination of cost, thermal, mechanical, and electrical properties [1]. Hence, it finds extensive use in water distribution systems, water treatment units, condensers, heat exchangers in oil and in processing plants used for electricity generation and desalination [1]. Lead is often added to brass to increase machinability and reduce the corrosion of other metals in the alloy [2]. But, leaded brass fixtures are found to be an important source of lead in potable water [3], which causes serious health problems [4].

To mitigate problems with leaded brass corrosion, great efforts have been put into the investigation and lots of technologies have been used [5-7]. Self-Assembled Monolayers (SAMs) on solid surfaces are nowadays very popular because of the versatile functions they can implement, together with their easy preparation, the stability and reproducibility of the obtained systems. It has been showed that the protective properties of the monolayers are closely related to their thickness [8,9]. Since SAMs of n-alkanethiols were shown to be effective in protecting copper surface from air oxidation [10], they became one of the most investigated corrosion inhibitors for this metal [11-14]. More recently, the ability of alkanethiols SAMs to protect Cu-Zn alloys in accelerated indoor atmospheric corrosion condition has been examined [15,16]. To the best of our knowledge, no report has been published on the protection of leaded brass by alkanethiols SAMs. Hence, this study is a first effort to explore the application of 1-octadecanethiol (ODT) monolayers as corrosion inhibitor of leaded brass substrate in non complexing perchloric acid solution. This precludes the formation of oxide or hydroxide films on the alloy surface and the formation of zinc or copper complexes. Open circuit potentials ( $E_{\text{OCP}}$ ), Tafel polarization curves and electrochemical impedance spectroscopy (EIS) are the experimental tools used to address the question above.

## EXPERIMENTAL PROCEDURE

### Chemicals

1-Octadecanethiol (Aldrich, 98%), perchloric acid (Biochem, 70%), Acetone (Biochem, 99.9%), absolute ethanol (Aldrich, 99.8%) were used as received. The electrolyte solution of 0.1M HClO<sub>4</sub> was prepared with analytical grade chemicals and bi-distilled water. The temperature was fixed to 25 ± 0,2°C with a Daihon Labtech Circulator.

### Electrodes Treatment and Surface Modification Process

The chemical composition (wt.%) of the leaded brass used in this work was 57.73% Cu, 38.50% Zn, 3.30% Pb, 0.15% Sn, 0.15% Fe, 0.11% Ni and trace amounts of Ti, Mn, Sb, and Ag. The working electrode was prepared from a rod of leaded brass that is sealed with epoxy resin so that only the circular section of 0,196 cm<sup>2</sup> of the rod was exposed. Prior to each experiment, the brass electrode was polished with SiC abrasive papers (grade 800, 1200 and 2000). The polished brass electrode was rinsed with bi-distilled water and degreased in acetone and dried [17]. Then, the etched brass surface was immersed immediately into the deoxygenated 10mM ODT ethanol solution for 3 h. Then, the modified electrode were removed from the solution and rinsed with large amounts of ethanol and water to remove any physisorbed material.

### Electrochemical Measurements

All the electrochemical tests were carried out using a Potentiostat model Voltalab PGZ402 and piloted by Voltmaster 4. The tests were performed in a three-electrode one-compartment cell containing a working electrode of brass, a platinum foil auxiliary electrode and a saturated calomel electrode as a reference (SCE). Each experiment was carried out with a freshly prepared electrode and each experiment was repeated at least three times to check the reproducibility. In all cases, E<sub>OCP</sub> was established first and then the Tafel polarization curves or EIS experiment was carried out. The Tafel polarization curves were recorded in the range of -1.2 to 0.3V vs. SCE at a scan rate of 1 mV s<sup>-1</sup>. Impedance spectra were obtained in the frequency range from 100 kHz to 10 mHz with a 10 mV amplitude of the excitation signal and the experiments were conducted at the respective open circuit potential. The modeling of the obtained EIS data was made by EC-Lab Software using the Randomize + Simplex method.

## RESULTS AND DISCUSSION

### Open Circuit Potential (E<sub>OCP</sub>)

Figure 1 shows the variation of the E<sub>OCP</sub> of uncoated and ODT coated leaded brass (brass-ODT) electrodes in 0.1M HClO<sub>4</sub> solution during the first 2 hours of immersion. For comparison the E<sub>OCP</sub> vs. time plots for Cu and Zn are also presented. For pure copper, the E<sub>OCP</sub> shift, in the few first minutes, in the negative direction to reaches a value of ca. -80 mV after one hour of immersion. For pure zinc, immediately after immersion, the E<sub>OCP</sub> undergoes a slight positive shift. Afterward, it reaches a steady-state value around -965 mV. Conversely, leaded brass shows a strong different behavior indicating that the electrode is highly polarized when it is immersed in corrosive solution (Figure 1, curve 3). Upon immersion, the E<sub>OCP</sub> of -445 mV is located between those of pure Cu and Zn. Then, it begins to move slowly to the nobler values where a significant jump of potential from -400 to -60 mV is observed. This trend may be attributed to the dezincification of the alloy. Beyond 30 min, the E<sub>OCP</sub> remains almost constant in time nearby to that of pure copper, indicating that the leaded brass behaves as Cu<sup>2+</sup>/Cu couple [18]. The superimposition of the Cu and Zn diagrams E-pH, showing the existence of a zone wherein the Zn may be dissolved when the Cu is in its immunity state [19]. A quite different behavior is observed for brass-ODT electrode where the E<sub>OCP</sub> slightly shift from -415 mV in the negative direction to tend to stabilize around -470 mV after 40 min of immersion (Figure 1, curve 4). This trend demonstrates the formation of ODT SAM on leaded brass surface. It also indicates that the ODT film have a limited permeability to the corrosive species, leading to an effective protection to the spontaneous dissolution of brass. Likewise, the negative shift of E<sub>OCP</sub> suggests that the improvement in the protective properties is related to the inhibition of the cathodic reaction, i.e. the reduction of the dissolved oxygen [13].

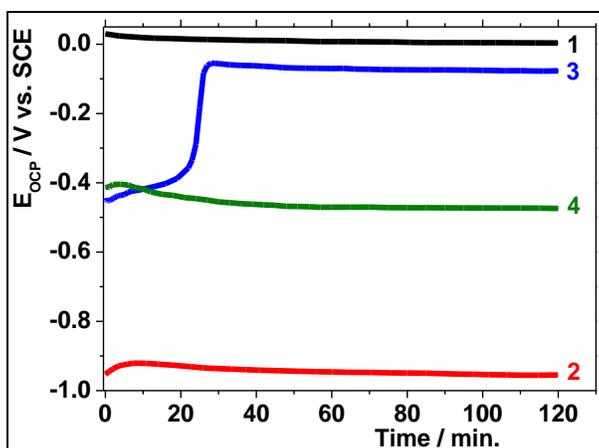


Figure 1: Open-circuit potential vs. immersion time curves obtained in 0.1M HClO<sub>4</sub> solution for: (1) pure Cu, (2) pure Zn, (3) uncoated leaded brass and (4) ODT SAM coated leaded brass

### Tafel Polarization Curves

Figure 2 shows the Tafel polarization curves of the uncoated and brass-ODT electrodes recorded in 0.1 M HClO<sub>4</sub> solution at 1 mV/s. The corresponding electrochemical kinetic parameters are listed in Table 1. Evidently, coating the leaded brass surface by an ODT SAM shifted the corrosion potential ( $E_{\text{corr}}$ ) in negative direction and dramatically reduced the corrosion current density ( $i_{\text{corr}}$ ) compared to that of uncoated brass. The  $i_{\text{corr}}$  value for bare brass electrode is  $76.6 \mu\text{A cm}^{-2}$ , which decreased to  $2.5 \mu\text{A cm}^{-2}$  for ODT monolayer. This evidences the formation of a compact ODT film on the leaded brass surface. Anodic and cathodic current densities are lowered in the whole potential range for brass-ODT electrode indicating that the SAMs acted as an effective barrier to the diffusion of oxygen from the solution to metal surface, thereby protecting the metal surface from corrosion. The simultaneous decrease of both anodic and cathodic current densities and the shift of  $E_{\text{corr}}$  in cathodic direction showed that the ODT SAM behaves as a mixed inhibitor type with predominantly cathodic action. In addition, the shift of the anodic branch towards the anodic region suggesting that the ODT film tremendously stabilize the surface of brass (Figure 2, Inset). From this, we conclude that the ODT monolayer is able to protect sufficiently the leaded brass surface against corrosion.

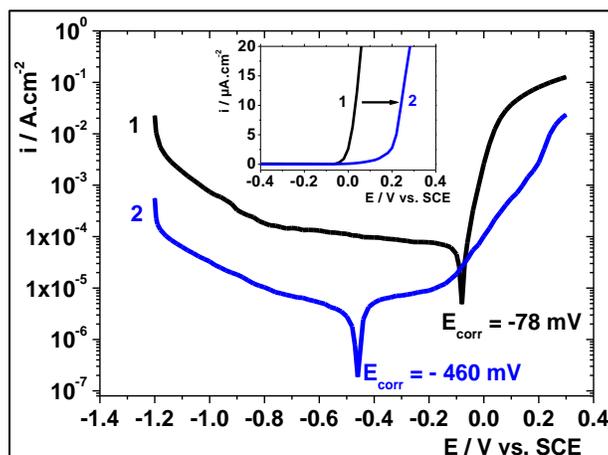


Figure 2: Tafel polarization curves obtained after 2h immersion in 0.1M HClO<sub>4</sub> solution for: (1) uncoated and (2) ODT SAM coated leaded brass substrate

Table 1: Corrosion parameters obtained from Tafel polarization curves of uncoated and ODT coated leaded brass substrate after 2h immersion in 0.1molL<sup>-1</sup> HClO<sub>4</sub> solution

Sample	$E_{\text{corr}}$ (mV. Vs SCE)	$i_{\text{corr}}$ ( $\mu\text{A.cm}^{-2}$ )	$b_c$ (mV.dec <sup>-1</sup> )	$b_a$ (mV.dec <sup>-1</sup> )	I.E. <sup>(a)</sup> (%)
Brass	-78	76.6	-1406	67	-
Brass-ODT	-460	2.5	-696	912	96.73

<sup>(a)</sup> I.E. (inhibition efficiency) =  $[(i_{\text{corr}}^0 - i_{\text{corr}})/i_{\text{corr}}^0] \times 100$ ,  $i_{\text{corr}}^0$  and  $i_{\text{corr}}$  are the corrosion current densities of uncoated and ODT coated leaded brass, respectively

### EIS Measurements

EIS is employed to estimate the integrity of the ODT SAMs and their ability to protect the underlying leaded brass surface. Figure 3 shows Nyquist and Bode plots of the uncoated and brass-ODT electrodes recorded at the respective open circuit potential after 2h of immersion in 0.1 M HClO<sub>4</sub> solution. The uncoated brass, display a capacitive loop at high frequencies and a straight line (Warburg impedance) at low frequencies. The capacitive loop is attributed to the relaxation time constant of the charge-transfer resistance and the double-layer capacitance at the electrode/electrolyte interface [8]. The Warburg impedance reflects the transport of oxygen from the bulk solution to the substrate surface or the corrosion products to the bulk solution [12].

On the other hand, the Nyquist plot of brass-ODT electrode differs from that of the uncoated one in shape and size. The larger semicircle diameter of the coated electrode suggested the excellent corrosion resistance of the ODT film, while, the disappearance of the Warburg impedance, showed that the SAMs is sufficiently densely packed to prevent the diffusion of oxygen to the copper substrate and thus inhibit corrosion of brass [14]. The result can be verified from the Bode plots. The impedance value  $|Z|$  of the ODT film is two times larger than that of the uncoated brass, implying the homogeneity and less permeability of the hydrophobic ODT SAMs, which is consistent with the results of Tafel polarization measurements.

EIS results of the uncoated and coated brass are fitted with the equivalent circuits in Figure 4 and the obtained results are listed in Table 2. The physical meaning of the components in the proposed circuits are as follows:  $R_{el}$  represents the testing solution resistance;  $R_{ct}$  and  $Q_{dl}$ , the resistance and the constant phase element (CPE) associated with the double layer capacitor;  $R_{sam}$  and  $Q_{sam}$  are identified with the resistance and CPE of the forming ODT films and  $W$  is the Warburg impedance. The impedance of the CPE is described as  $Z_{CPE} = (Q(j\omega)^n)^{-1}$ , where  $Q$  is the frequency-independent real constant,  $j$  is the imaginary number ( $j^2 = -1$ ),  $\omega$  is the angular frequency ( $\omega = 2\pi f$ ), and  $n$  is the CPE power. The factor  $n$  is defined as the degree of closeness to the pure capacitor ( $0 \leq n \leq 1$ ). Clearly, when the leaded brass substrate is coated with ODT film, the  $R_{ct}$  is significantly increased and the  $Q_{dl}$  is decreased compared to the uncoated state. This suggests that the film greatly increased the protection from corrosion conferred to the alloy substrate (Table 2). Furthermore, the increase of the value of  $n$  indicates that the brass surface become smoother due to formation of a non-porous and dense monolayer of ODT. In fact, the hydrophobicity of the ODT SAMs, the inter-chain interactions of adsorbed thiol molecules and the strong head group-substrate thiolate bonding (Cu-S, Zn-S and Pb-S) played a critical role in the formation of a densely packed quasi crystalline barrier film. Further investigations will be required to fully understand the reasons of this behavior.

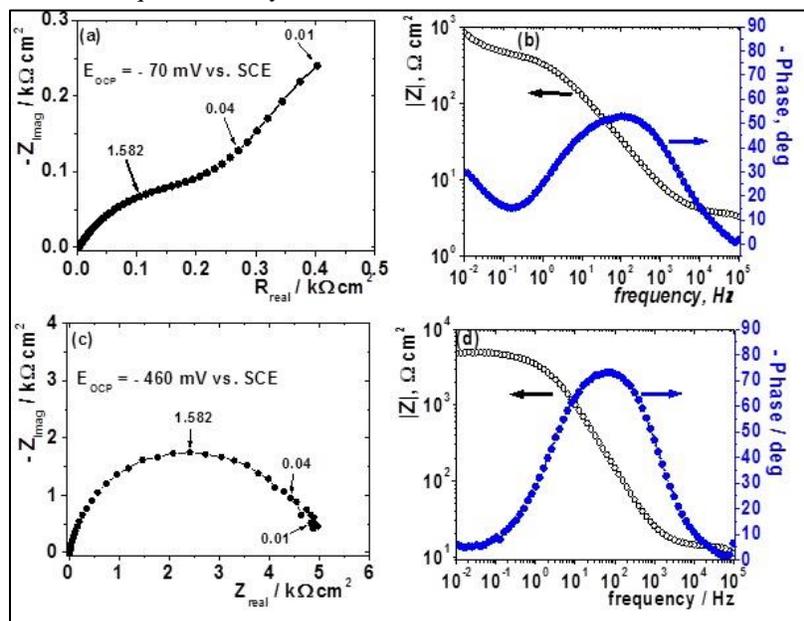


Figure 3: Impedance spectra of leaded brass recorded in 0.1M HClO<sub>4</sub> solution at open circuit potential: Nyquist (a) and Bode (b) plots for an uncoated electrode; Nyquist (c) and Bode (d) plots for an electrode with ODT SAMs

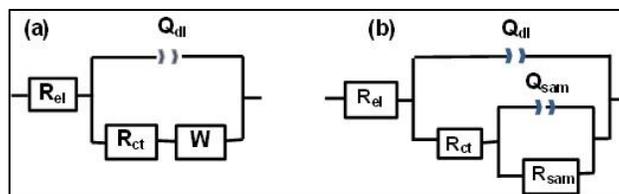


Figure 4: Equivalent electrical circuits used in the impedance measurements for: (a) uncoated leaded brass, (b) leaded brass coated with ODT SAM

Table 2: Impedance parameters extracted from the fit to the equivalent circuits for the uncoated and ODT SAM coated leaded brass substrate after 2h immersion in 0.1M HClO<sub>4</sub>

Sample	R <sub>el</sub>	Q <sub>dl</sub> (μF)	n <sub>1</sub>	R <sub>sam</sub>	Q <sub>sam</sub>	n <sub>2</sub>	W	I.E. (%) <sup>(a)</sup>
Brass	217.5	67.5	0.582	-	-	-	59.92	-
Brass-ODT	3405	2.17	0.875	1540.7	3.6	0.79	-	95.58

The dimensions are: Y<sub>0</sub>: (Ω<sup>-1</sup> cm<sup>-2</sup> s<sup>b</sup>); R: (Ω cm<sup>2</sup>); Q<sub>i</sub>: μF.cm<sup>-2</sup>; W: Ω<sup>-1</sup> cm<sup>-2</sup> s<sup>0.5</sup>

<sup>(a)</sup> I.E. (inhibition efficiency) = [(R<sub>p</sub> - R<sub>p</sub><sup>0</sup>)/R<sub>p</sub>] × 100, R<sub>p</sub><sup>0</sup> is the polarization resistance of the bare brass (R<sub>p</sub><sup>0</sup> = R<sub>ct</sub><sup>0</sup>) and R<sub>p</sub> is the total polarization resistance of the ODT coated electrode (R<sub>p</sub> = R<sub>ct</sub> + R<sub>sam</sub>)

## CONCLUSIONS

The performance of the ODT SAMs as corrosion leaded brass inhibitor in a non-complexing media of 0.1 M HClO<sub>4</sub> solution has been studied by different electrochemical methods and the results can be summarized as follows: (1) The open circuit potential (E<sub>OCP</sub>) vs time of uncoated brass shows an anodic potential jump of about 400 mV due to the dezincification of the substrate, while, the coating of leaded brass by the ODT-SAM affect strongly the spontaneously dissolution of the alloy. (2) Results indicate that ODT is a mixed inhibitor type which acts primarily as a cathodic inhibitor. (3) Potentiodynamic polarization measurements showed that the ODT SAM suppresses tremendously the selective dissolution of brass alloy. (4) The negative shift of E<sub>OCP</sub> accompanied with the noticeable increase of polarization resistance and a significant decrease of corrosion current density, demonstrating that the ODT SAM is densely packed act as effective barriers to the penetration of corrosive species like water, oxygen and aggressive ions to the metal surface, extending the protection against corrosion markedly. These encouraging results illustrate the high performance of the new class of inhibitor to protect effectively the leaded brass surface.

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