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On the Inhibition Efficiency of Different Imidazole-Based Green Corrosion Inhibitors: Insights from Raman Spectroscopy and Electrochemical Techniques

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Extended Abstract

Adsorption of imidazole, 4-methylimidazole and guanine on copper in chloride solutions was investigated by a combination of weight loss tests with electrochemical and Raman techniques to understand their inhibition efficiency and interaction with the metal. Results revealed that imidazole and 4-methyimidazole are inefficient while guanine was an efficient inhibitor (86 %) due to formation of a passive film. Guanine was not efficient towards API 5L X65 steel corrosion in HCl (~22 %) and the low efficiency was due to physisorption. The insights obtained with the combination of spectroscopic and electrochemical results should aid selecting new efficient nontoxic inhibitors.

Keywords: green corrosion inhibitors, copper, steel, imidazoles, Raman spectroscopy.

Introduction

Corrosion of metallic materials is a recurring problem, and the use of corrosion inhibitors is a common strategy to mitigate it. Benzotriazole- and chromate-based compounds are highly efficient inhibitors for copper and steel in chloride media of acidic and near neutral pH, with inhibition efficiencies (IE) between 85 % and 95 % in NaCl and 60 % and 90 % in HCl [1-4]. However, these compounds are toxic and should be replaced by alternatives that are both efficient and environmentally friendly. Combining these characteristics with a high efficiency at low concentration is quite challenging and is still an ongoing effort. Imidazole and its derivatives are good candidates to meet these requirements because they are ubiquitous in nature, mostly nontoxic, and adsorb on many metals. These molecules have been tested as corrosion inhibitors for copper and steel surfaces, and it is found that substituted imidazoles have higher IE than the plain molecule. However, there is still controversy in the literature about the nature of the imidazole-metal interactions and the inhibition efficiency [1-4]. Imidazoles have a quite complex solution chemistry and the metal/inhibitor interface should be probed by spectroscopic and electrochemical techniques to ensure a reliable interpretation of IE and adsorption mechanism. Raman spectroscopy is a sensitive probe of molecule/metal interactions and is not affected by metal signals like XRD and XPS techniques. It also allows the acquisition of *in situ* spectra without significant water interference and can be combined with electrochemistry. Our group has successfully employed a combination of weight loss tests with electrochemical and surface-enhanced Raman spectroscopy (SERS) in the study of imidazole, 4-methylimidazole and guanine as inhibitors of copper corrosion in chloride media at different pH values [5-7]. Raman spectroscopy and electrochemical measurements were also used to study guanine as an inhibitor of API 5L X65 carbon steel corrosion in HCl solutions. The results are discussed below.

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Methodology

Imidazole or 4-methylimidazole were dissolved in 0.1 mol/L chloride solutions to give different concentrations (0.001 or 0.1 mol/L), and the pH of these solutions was adjusted with concentrated HCl or NaOH. Guanine was dissolved in 0.1 mol/L HCl to give solutions of 0.0001 to 0.001 mol/L and the pH of these solutions was adjusted to 2.0 by addition of a small amount of NaOH. Electrochemical measurements were carried out in a three-electrode electrochemical cell with either a copper or API 5L X65 carbon steel as the working electrode (~0.2 cm^2 of area), a saturated calomel reference electrode (SCE) and a platinum grid as the counter electrode, using an IVIUM CompactSTAT potentiostat. Weight loss tests were performed by immersion of copper samples of 14 – 15 cm^2 of area in 0.1 mol/L chloride solutions with or without the inhibitors for at least 72 h. Samples of API 5L X65 steel were immersed in solutions of HCl 0.1 mol/L with or without guanine, at pH = 2.0, for 48 h. Raman and SERS measurements were performed with a SENTERRA confocal Raman microscope (Bruker Optics) using a 785 nm laser with 25 mW power focused on the sample with a long working objective at 20x magnification (Olympus). SERS measurements were also carried out in a three-electrode electrochemical cell with the copper working electrode surface facing the objective.

Results and Conclusions

Imidazole (Imid) and 4-methylimidazole (4-MeImid) were tested as copper inhibitors in 0.1 mol/L chloride solution of near-neutral (pH = 6.0 to 8.8) and acidic pH (pH = 2.0), whereas Guanine was used only in acidic medium due to its very poor solubility at pH > 3.0 [4].

Cyclic voltammetry measurements performed on a copper electrode immersed in either Imid or 4-MeImid were very similar to those obtained for the blank solutions both at near neutral and acidic pH, indicating that these molecules were not able to significantly modify the metal surface (Figure 1(a)). On the other hand, the voltammograms obtained with guanine showed smaller peak currents in both anodic and cathodic peaks and the onset of the hydrogen evolution reaction changed to more negative values, thus showing that guanine modifies the copper surface and interacts more strongly with the metal than Imid and 4-MeImid (Figure 1(b)). The stronger interaction of guanine with copper was further confirmed by potentiodynamic polarization, where a peak can be clearly seen in the anodic branch of the curve and after the measurement was carried out, the working electrode was covered with a thick white layer of a copper-guanine complex (Figure 2). Electrochemical impedance revealed that guanine can protect copper from corrosion in 0.1 mol/L HCl solution, and that the protection improves with more concentrated solutions and longer immersion times. Impedance experiments were also carried out for Imid and 4-MeImid in acidic solutions and the results confirmed that these molecules cannot be considered as effective inhibitors for copper in chloride solutions.

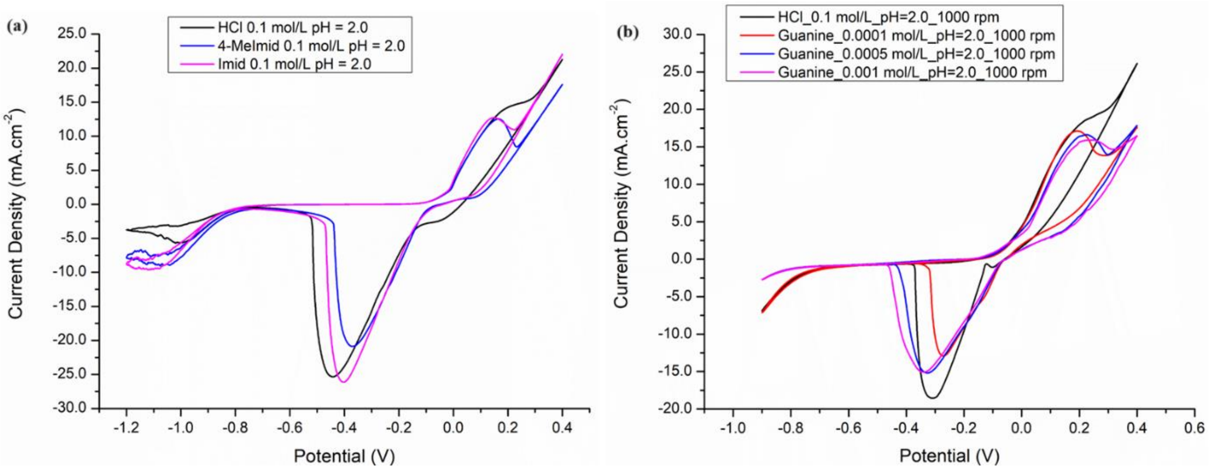

Figure 1 – Cyclic voltammograms of a copper electrode immersed in (a) 0.1 mol/L HCl solutions without and with 0.1 mol/L imidazole or 4-methylimidazole (optimal concentrations) or (b) 0.1 mol/L HCl solutions without or with different concentrations of guanine.

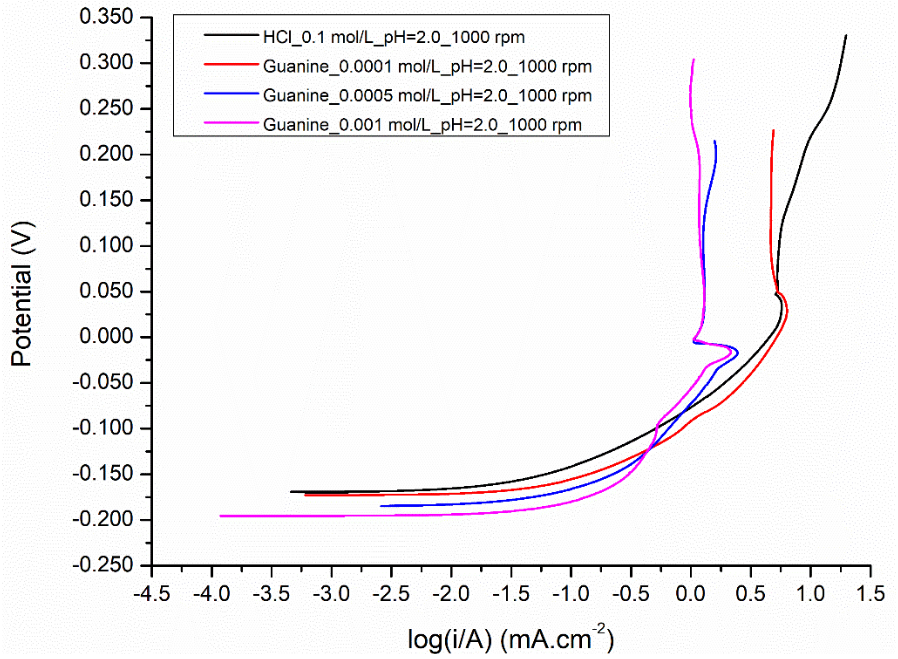

Figure 2 – Potentiodynamic polarization curves of a copper electrode immersed in 0.1 mol/L HCl solutions, pH = 2.0, without or with guanine at different concentrations.

Weight loss experiments were performed with copper coupons immersed in blank solutions of near neutral and acidic pH and in solutions of Imid, 4-MeImid and guanine of the same pH for either 72 h or 90 h of immersion. The results confirmed the electrochemical measurements showing that Imid and 4-MeImid cannot inhibit copper corrosion in acidic solution but they both accelerate it in near neutral media. In fact, the copper coupons immersed in Imid had a thinner Cu_2O layer on them and those immersed in 4-MeImid were covered with a thick green layer of clinoatacamite ($Cu_2(OH)_3Cl$). Weight loss results showed that guanine inhibited copper corrosion in 0.1 mol/L HCl solution at its optimal concentration (0.001 mol/L) with an inhibition efficiency of 86 %. The results of the gravimetric tests are summarized in Table 1.

Table 1 – Results of weight loss experiments carried out for copper in chloride solutions at different pH.

Condition	**Imid**	**Imid**	**4MeImid**	**4-MeImid**	**Guanine**
pH of solution	8.3	2.0	8.8	2.0	2.0
Optimal concentration	0.001 mol/L	0.1 mol/L (6807 ppm)	0.001 mol/L	0.01 mol/L (821 ppm)	0.001 mol/L (151 ppm)
Inhibition Eficiency by impedance, R_P	none	33 %	none	none	95 %
Inhibition Eficiency by weight loss	none	16 % (72 h)	none	10 % (72 h)	86 % (90 h)

SERS measurements were carried out on copper electrodes immersed in chloride solutions of either near neutral or acidic pH containing Imid, 4-MeImid or guanine at their optimal concentrations. Spectra acquired at cathodic polarization revealed that the neutral forms of Imid and 4-MeImid adsorb on the copper electrode at all pHs values tested and a band at ~315 cm^{-1}, due to Cu-N bonding, can be seen when CuCl and $CuCl_2^-$ or Cu_2O are reduced. This band and the high intensity of the in-plane bands suggest that these molecules adsorb in an upright or slightly tilted configuration. At the OCP, the band intensities of Imid and 4-MeImid are significantly smaller than at cathodic polarization, and the cuprous chloride or oxide becomes more prominent and at anodic polarization, the azole bands disappear, and the only feature seen in the spectra is due to $CuCl/CuCl_2^-$, indicating that the copper is in active dissolution. Physisorbed imidazolium ($ImidH^+$) ions can also be seen in the SERS spectra of Imid solutions and were identified at cathodic polarizations, whereas 4-$MeImidH^+$ was not observed, even in acidic solutions, where it is the major species. Analysis of the spectra thus revealed that Imid and 4-MeImid form a soluble complex with Cu_2O at near neutral pH and the complex migrates to the bulk solution leaving the metal unprotected. At acidic pH, the molecules seem to physisorb, interacting weakly with the metal surface and not withstanding anodic polarizations.

SERS spectra of guanine solutions at pH = 2.0 revealed that the neutral form of the molecule adsorbs on copper over a wide potential range and does not desorb at anodic polarizations, protecting the metal surface. The spectra acquired at the OCP at different immersion times showed the gradual formation of the Cu(guanine)Cl complex, which protects copper against the aggressive chloride anions. SERS spectra of Imid and Guanine solutions at acidic pH are shown in Figure 3.

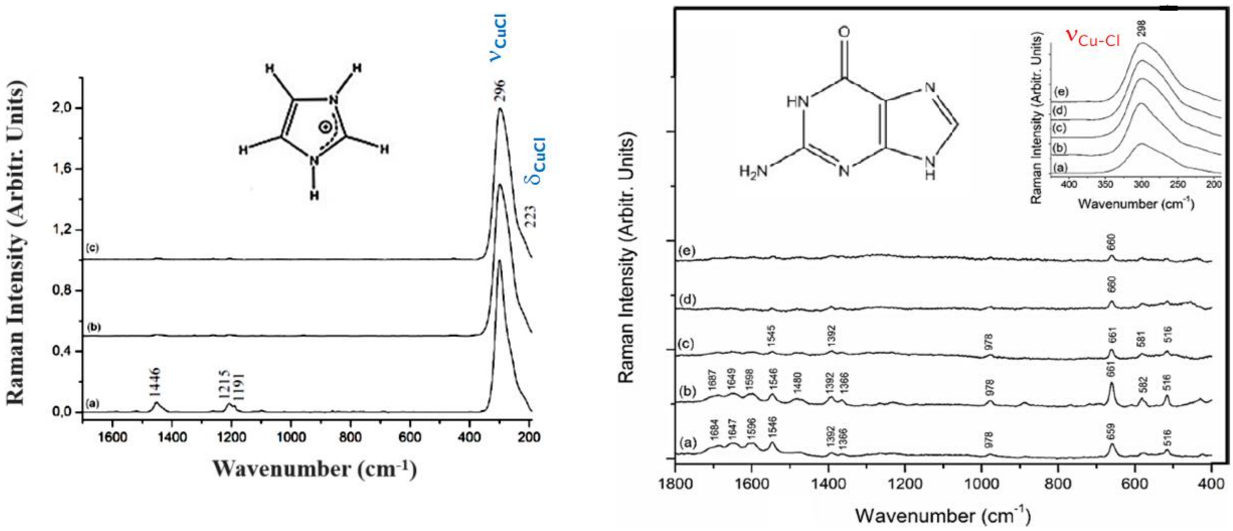

Figure 3 - SERS spectra of Imid (left panel) and guanine (right panel) solutions at pH = 2.0 on a copper electrode at different potentials. Left panel: (a) -0.07 V (OCP), (b) 0.2 V, (c) 0.4 V. Right panel: (a) 0.0 V to (e) 0.4 V.

Electrochemical and weight loss experiments were also carried out on API 5L X65 carbon steel electrodes in 0.1 mol/L HCl solutions at pH = 2.0, with or without 0.001 mol/L guanine. Surprisingly, the cyclic voltammetries and potentiodynamic polarization curves of blank and inhibited solutions are almost the same (Figure 4), showing that Guanine does not interact strongly with the steel surface, so it must not be an efficient corrosion inhibitor for this material. This trend was further confirmed by weight loss measurements where IE = 22 % was calculated. Raman spectra of the surface of the coupons exposed to a solution containing guanine for 48 h showed that this molecule physisorbs on the metal surface (Figure 5) and that such a weak interaction is not sufficient to effectively block the surface from aggressive species.

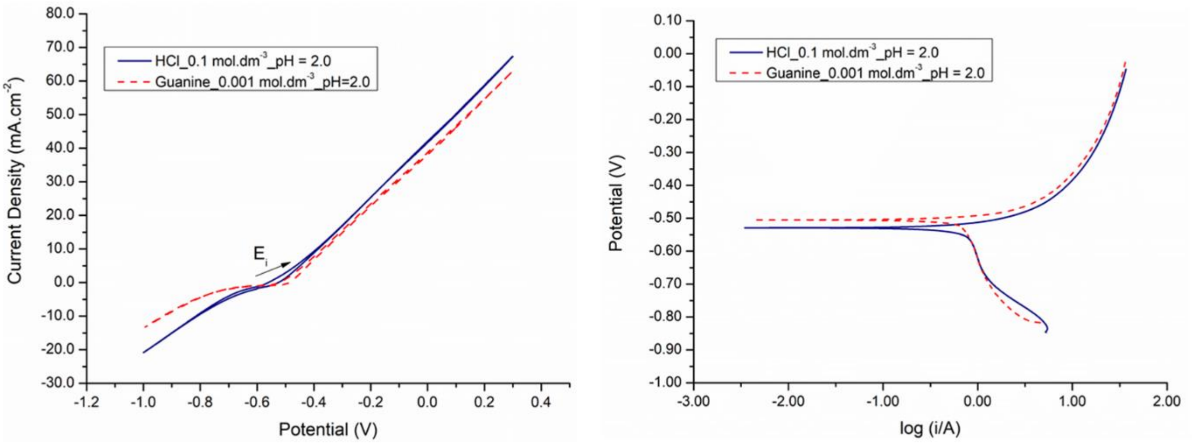

Figure 4 – Cyclic voltammetry and potentiodynamic polarization curves obtained for a API 5L X65 steel electrode immersed in 0.1 mol/L HCl solutions without or with 0.001 mol/L guanine, at pH = 2.0.

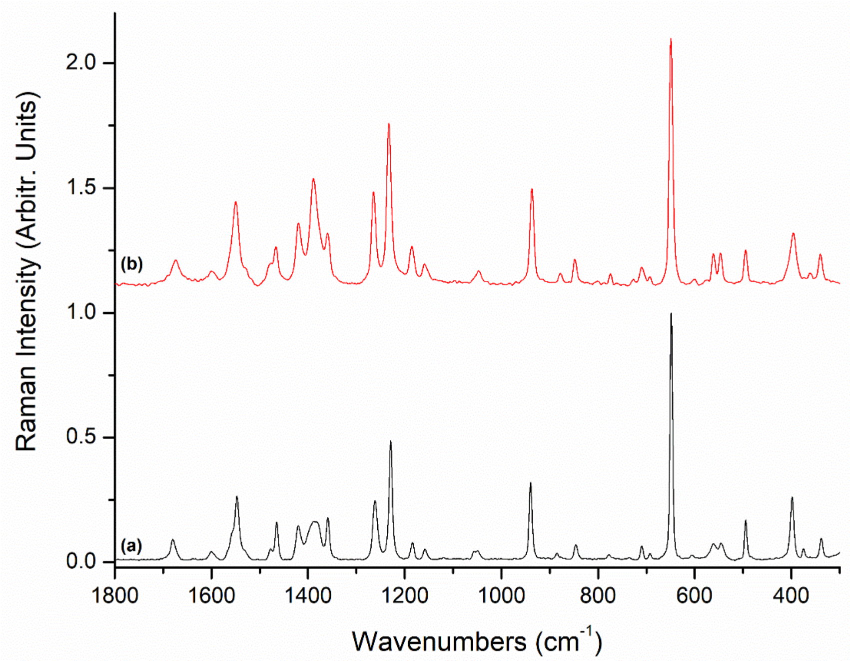

Figure 5 - Raman spectra of (a) solid Guanine and (b) the surface of a coupon obtained after the weight loss experiment.

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