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Inhibition of copper corrosion in saline solution by mono-hydroxamic acid

G. Ezznaydy[1], A. Shaban[2], J. Telegdi[2], B. Ouaki[3], S. El Hajjaji[1*]
[1] *Laboratory S3ME, Team Physical Chemistry of Materials and Environment, Faculty of Sciences Rabat,Med V University, Rabat, Morocco*
[2] *Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, Hungary H-1117 Budapest, Magyar tudósokkörútja 2.*
[3] *Engineering material Department, National School of Mineral Industry Rabat.*

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**Corresponding Author. E-mail: hajjajisouad@yahoo.fr, Tel (+212 661303102)*

Abstract

The main objective of the present work involved the study of the inhibitive properties of organic product as environmentally friendly as copper corrosion inhibitor, in 3% NaCl solution. The effectiveness of Mono-hydroxamic acid (C12N)used as a corrosion inhibitor for copper in 3% NaClwas investigated by weight loss and electrochemical techniques. Surfaces were characterized by scanning electron microscopy (SEM). The results showed that the chemical investigated provided efficient inhibition of copper corrosion. The inhibition efficiency improved with increasing the inhibitor concentration. C12N acts mainly as a cathodic-type inhibitor.

Keywords: Hydroxamic acid, corrosion, inhibitors, copper, saline solution.

1. Introduction

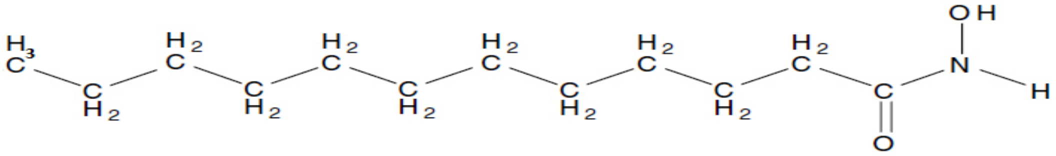
Copper and many of its alloys possess favorable combinations of thermal, electrical and mechanical properties [1-2] in addition to a moderate cost and are extensively used in various applications. These materials face various forms of corrosion, which limit their performance [3-6]. Organic inhibitors are largely used, with success, to protect copper and copper alloys from the corrosion. Many papers reported that nitrogen containing organic compounds reveal a marked inhibiting efficiency [7-18]. Previous investigations showed hydroxamic acid derivatives as potentially effective inhibitors for carbon steel [19-20] and copper corrosion [21-22]. Hydroxamic acids have generally good chelating properties toward different metal ions, and form stable complexes [23–25].

In the present work, HOHNOC $((CH_2)_{10})CH_3$ (C12N) was evaluated at various concentrations as inhibitor of copper corrosion in saline solution by using weight loss method (WL), potentiodynamic polarization measurements (DC) and electrochemical impedance spectroscopy (EIS).

2. Experimental methods

2.1. Chemicals and solutions

The aggressive solution (3% NaCl) was prepared by dilution of 30 g of NaCl (solid) with distilled water. This solution was used for electrochemical studies. Model water ($CaSO_4$, $MgSO_4$, $NaHCO_3$, and $CaCl_2$) adjusted to a pH: 8, by NaOH, was used for WL measurements. This medium was used to increase the corrosive action of the solution. The structure of the studied molecule, Mono-hydroxamic acid C12N, is shown in scheme 1, C12N was synthesized in laboratory.



Scheme1: structure of Mono-hydroxamic acid (C12N)

2.2. Self-assembled molecular layers preparation.

The used copper specimens have a rectangular form with an area of 1.5 cm². The electrode was mechanically polished with emery paper (320-2000 grit), and was sonicated for 10 min with acetone, THF and distilled water then dried in air. Polished metal coupons were immersed into a solution of C12N dissolved in chloroform and after several time intervals (2-24 hrs), followed by rinsing off the residual and finally drying in air. These samples are used for electrochemical and weight loss studies in 3% NaCl solution and model water respectively, as aggressive medium.

2.3. Weight loss analysis.

After weighting precisely, the specimens were immersed in beakers, which contained 200 mL of Model Water without and with different concentrations of C12N. After 24 h, the specimens were washed, dried, and reweighted.

The inhibition efficiency Ew (%) in the case of gravimetric analysis method was calculated using the following equation:

$$\boldsymbol{E_w}(\%) = \frac{\boldsymbol{W^{\circ}_{cor} - W_{cor}}}{\boldsymbol{w^{\circ}_{cor}}}\ \boldsymbol{x\,100} \qquad (\mathbf{1})$$

Where W°_{cor} and W_{cor} are the corrosion rates of copper without and with the addition of the inhibitor, respectively.

2.4. Electrochemical measurements

Electrochemical measurements were realized in three-electrode glass cell at room temperature, a platinum electrode was used as a counter electrode, and saturated calomel electrode (SCE) was used as a reference electrode. The working electrode was made from copper. The polarization curves were recorded using a potentiostat model (PGZ301) and using the Voltascan 4 software.

The inhibition efficiency is determined as:

$$\boldsymbol{E}(\%) = \frac{\boldsymbol{i^{\circ}_{corr} - i_{corr}\,(inh)}}{\boldsymbol{i^{\circ}_{corr}}}\boldsymbol{x\,100} \qquad (\mathbf{2})$$

Where i°_{corr} and $i_{corr(inh)}$ are the corrosion current density values without and with the addition of the inhibitor, respectively. The values of $i^{\circ}_{corr}$and $i_{corr(inh)}$were determined by Tafel extrapolation.

The EIS results are presented in the form of real vs. imaginary parts of the impedance amplitude. EIS measurements were performed using VoltaLab 40 (PGZ301). Impedance spectra were obtained in thefrequency range of 100 kHz to 0.01 Hz with perturbation amplitude of 10 mV. R_p values from the Nyquist plots are used to calculate the inhibition efficiency as:

$$\mathbf{E_{eis}} = \left(\mathbf{1} - \frac{\mathbf{R_{t0}}}{\mathbf{R_{ti}}}\right) \times \mathbf{100} \qquad \mathbf{(3)}$$

Where R_{ti} and R_{to} are the polarization resistances with and without the presence of the inhibitor, respectively.

3. Results and discussion

3.1. Weight loss tests

The inhibition efficiency EW (%) of C12N monolayers was evaluated by weight loss technique after 24hrs of immersion in model water at room temperature. Obtained results by weight loss data are represented in Table 1. We notice that when the inhibitor concentration increases, the corrosion rate decreases which lead to the increasing of inhibitor efficiency. This behavior is due to the fact that the adsorption of inhibitor on copper electrode surface increases with the inhibitor concentration. It is noted that 6 hours constitutes the optimum treatment time with an excellent corrosion inhibition for copper in Model water. It is assumed that after 6hrs we have a total adsorption our molecule and may be desorption a result in treatment solution, which explains the dissolution of copper.

3.2. Electrochemical measurements

The weight loss were given an idea about optimal treatment time and concentrations for obtained high efficiency inMW for studying electrochemical we will work in a saline environment which is more aggressive. The polarization curves of copper electrode in the absence and the presence of C12N in 3% NaCl are presented in Fig. 1. The treatment time for copper in presence of C12N has been fixed to 6hrs. Electrochemical parameters, corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were determined and listed in Table 2.

Table 1: Copper weight loss data and inhibition efficiency of C12N after 24h of immersion time in model water.

Solution	**Concentration of C12N**	**Time of Immersion (h)**	**Δm (mg)**	**Corrosion Rate (mmpy)**	**E_W (%)**
Blank	0	-	1.2	0.0271	-
C12N	$5x10^{-4}$	2	0.9	0.0203	25
		4	0.6	0.0135	50
		6	0.2	0.0045	83
		8	0.5	0.0113	58
		24	0.4	0.0090	66
	$5x10^{-3}$	2	0.8	0.0181	33
		4	0.5	0.0113	58
		6	0.1	0.0023	91
		8	0.4	0.0090	66
		24	0.3	0.0068	75

Table2: Electrochemical parameters for copper in 3% NaCl at different concentrations of C12N.

Solution	**Concentration [M]**	**E_{corr} (mV/SCE)**	**i_{corr} (A/cm²)**	**Corrosion Rate (mmpy)**	**E (%)**
Blank	-	-212	$3.11x10^{-4}$	0.0061	-
C12N	$5x10^{-4}$	-265	$1.58x10^{-4}$	0.0031	49.1
	$5x10^{-3}$	-285	$1.21x10^{-4}$	0.0023	62

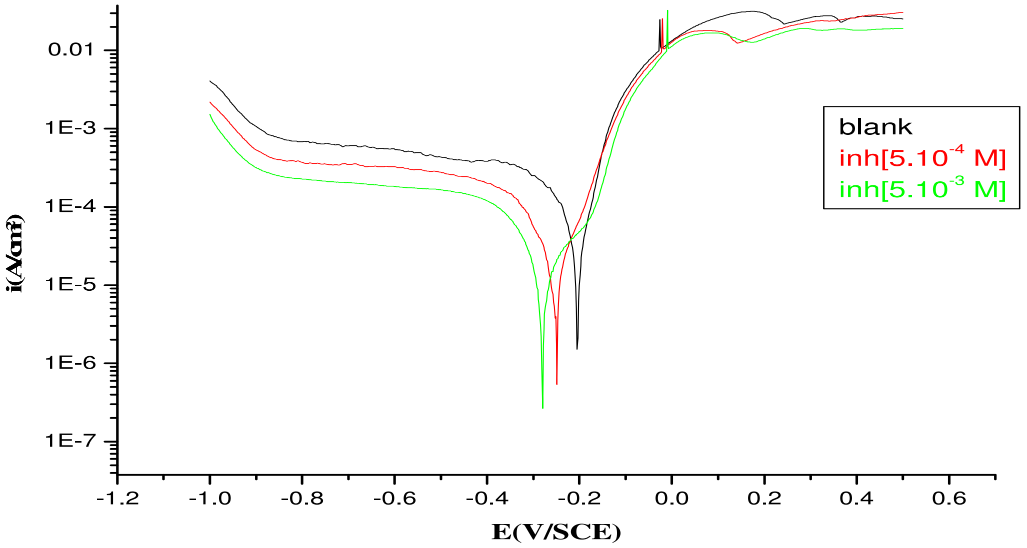


Figure 1: Polarization curves for copper treated or not by various concentrations of C12N in 3% NaCl.

The polarization curves show that C12N shifted the corrosion potential E_{corr} to more cathodic (negative) values, which classifies it as cathodic inhibitor. The efficiency of inhibition increases with increasing concentration of inhibitor.

Electrochemical data indicate that presence of C12N reduce the corrosion process by decreasing the corrosion current density. Figure 1 also shows the decrease of the corrosion current density in the cathodic side by increasing the C12N concentration. In anodic domain, the effectiveness is minimal.

3.3. Electrochemical impedance spectroscopy measurements

60 min after the electrode has been immersed in 3% NaCl solution, impedance measurements of copper are plotted in the form of Nyquist plots. The impedance diagram is characterized by semi-circles. The transfer resistances (R_t) were obtained graphically from the Z_{real} axis.

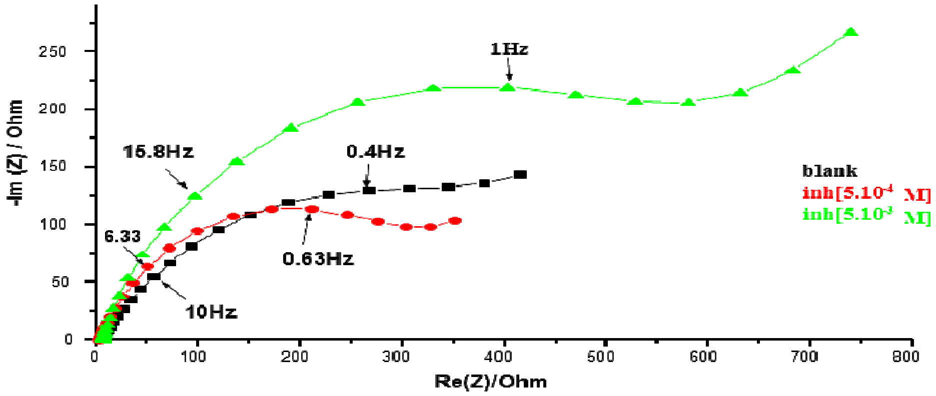


Figure 2: EIS spectra for copper in 3% NaCl before and after treatment by inhibitor C12N at different concentrations.

Electrochemical parameters derived from the Nyquist plots are represented in Table 3. In addition to inhibition efficiency, transfer resistances (R_t) also increases with inhibitor concentrations, this can be explained by the presence of a protective film on the electrode/solution interface.

The Nyquist curve for copper in 3% NaCl, obtained at the corrosion potential, shows two more-or-less poorly separated semi-circles as seen in Figure 2. One semicircle is at high frequency range and another is at low frequency range. The radius of the low frequency semi-circle varied from one concentration to another. All investigated concentrations of C12N produced higher R_t values than the solution without inhibitor.

Table 3: Electrochemical parameters calculated from R_t for copper corrosion in 3% NaCl obtained by EIS.

Solution	**Inh.Conc [M]**	**E_{corr} (mV/SCE)**	**R_t (Ω .cm²)**	**E (%)**
Blank	-	-192	289.7	-
C12N	$5x10^{-4}$	-224	354.8	18
	$5x10^{-3}$	-236	591.2	51

The used EC-LAB software (figure3), the equivalent circuit shows the satisfactory simulation of the impedance characteristic of the inhibitor-filmed electrode surface by EC model, as shown in Figure 4, indicate that the inhibitor film has a multi-layered structure.

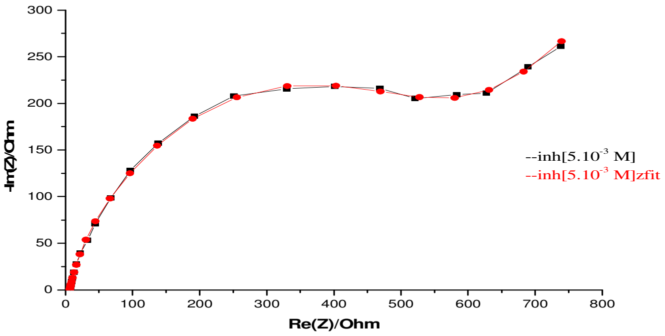


Figure 3: Nyquist curves for interfacecopper after treatment by 5.10^{-3} M C12N in a solution of 3% NaCl (--) experimental curve; (--) Curve fitted.

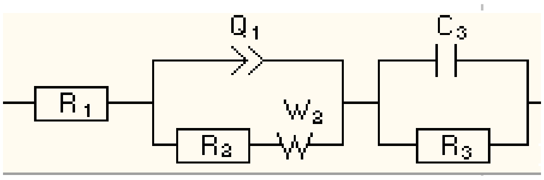


Figure 4: EC models used in fitting the experimental impedance data.

Conclusion

Mono-Hydroxamic acid (C12N), deposited on the copper surface, form protective self-assembled layers. Electrochemical and weight loss measurements showed that the adsorption of C12N molecules on copper surfaces reduce the corrosion process and the inhibition efficiency reached 91%. The effectiveness of the deposited films in aggressive environment was demonstrated by electrochemical measurements. The C12N layers showed the effectiveness of the coating technique.

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