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L-Cysteine methyl ester hydrochloride: A new corrosion inhibitor for copper in nitric acid

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ABSTRACT

Potentiodynamic polarisation, electrochemical impedance spectroscopy (EIS) and weight loss measurements were used to investigate the inhibitory effect of L-Cysteine Methyl Ester Hydrochloride (L-CMEH) on corrosion of copper in 2M HNO_3 solution. The inhibitor showed > 97% inhibition efficiency at 10^{-3}M. EIS results show that the change in the impedance parameters (R_t and C_{dl}) with concentration of L-Cysteine Methyl Ester Hydrochloride (L-CMEH) is indicative of the adsorption of molecules leading to the formation of a protective layer on the surface of copper. Potentiodynamic polarization studies suggested that it is a mixed type inhibitor. The inhibitor studied reduces the corrosion rates. The results obtained from weight loss, polarisation, and impedance measurements are in good agreement.

Keywords: Copper; Nitric Acid; Inhibition; EIS; Potentiodynamic polarisation; Weight Loss.

INTRODUCTION

Copper and its alloys have many industrial applications such as electronics because of their excellent corrosion resistance properties as well as their superior electrical and thermal performance [1]. The most widely used corrosive solution contains nitric acid, so this medium has induced a great deal of research on copper corrosion [2-6]. One of the most important methods in the corrosion protection of copper is the use of organic inhibitors [7-9]. Most of the excellent acid inhibitors are organic compounds containing nitrogen, sulfur and oxygen [10-24]. Amino acids form a class of non-toxic organic compounds that are completely soluble in aqueous media and produced with high purity at low cost. These properties would justify their use as corrosion inhibitors. The encouraging results obtained by aminoacids [25] towards copper in nitric acid solution and the selection of cysteine as the good inhibitor of the tested compounds, have incited to develop a detailed study on cysteine.

In this work, the weight loss measurements, potentiodynamic polarisation and electrochemical impedance spectroscopy (EIS), were made using copper immersed in nitric acid 2M without and

with addition of L-Cysteine Methyl Ester Hydrochloride (L-CMEH). The molecular structure of L-CMEH is shown in Figure 1.

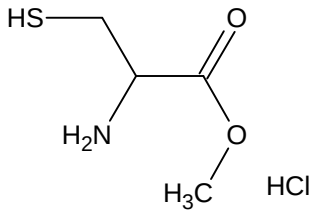

Figure 1. The molecular structure of L-CMEH.

MATERIALS AND METHODS

2. Experimental details

2.1. Materials and reagents

Copper strips containing 99.5 wt.% Cu, 0.001wt.% Ni, 0.019 wt.% Al, 0.004 wt.% Mn, 0.116 wt.% Si and balance impurities were used for electrochemical and gravimetric studies. The Copper samples were mechanically polished using different grades of emery paper, washed with double distilled water, and dried at room temperature. Appropriate concentration of aggressive solutions used (2M HNO_3) was prepared using double distilled water. L-Cysteine Methyl Ester Hydrochloride (L-CMEH) is analytical grade.

2.2. Electrochemical measurements

❖ **Electrochemical cell**

The electrolysis cell was a pyrex of cylinder closed by cap containing five openings. Three of them were used for the electrodes. The working electrode was copper with the surface area of 0.28 cm^2. Before each experiment, the electrode was polished using emery paper until 2000 grade. After this, the electrode was cleaned ultrasonically with distillate water. A saturated calomel electrode (SCE) was used as a reference. All potentials were given with reference to this electrode. The counter electrode was a platinum plate of surface area of 1 cm^2.

The aggressive medium used here is 2M HNO_3 solution was prepared with concentrated HNO_3 and distilled water. The molecule structures of quinoxalines tested are shown in Fig. 1. The concentration range of this compounds was 10^{-6} to 10^{-3} M.

❖ **Polarisation measurements**

The working electrode was immersed in test solution during 30 minutes until a steady state open circuit potential (E_{ocp}) was obtained. The polarization curve was recorded by polarization from -150 mV to 150 mV under potentiodynamic conditions corresponding to 1 mV/s (sweep rate) and under air atmosphere. The potentiodynamic measurements were carried out using Tacussel Radiometer PGZ 301, which was controlled by a personal computer.

❖ **EIS measurements**

The electrochemical impedance spectroscopy measurements were carried out using a transfer function analyser (Tacussel Radiometer PGZ 301), with a small amplitude ac. Signal (10 mV rms), over a frequency domain from 100 KHz to 10 mHz at 303 K and an air atmosphere. The polarization resistance R_p, is obtained from the diameter of the semicircle in Nyquist representation.

2.3. Weight loss measurements

Gravimetric experiments were carried out in a double walled glass cell. The solution volume was 50 cm^3; the temperature of 303 K was controlled thermostatically. The weight loss of copper in 2M HNO_3 with and without the addition of inhibitor was determined after immersion in acid for 1 h. The copper specimens were rectangular in the form (2 cm ×2 cm × 0.20 cm).

RESULTS AND DISCUSSION

3.1. Weight loss tests

The effect of addition of L-CMEH tested at different concentrations on the corrosion of copper in 2M HNO_3 solution is studied by weight loss at 303K after 1 h of immersion period. Inhibition efficiency (E_w%) is calculated by the equation 1:

$$E_w\% = \left(1 - \frac{W_{corr}}{W^{o}_{corr}}\right) \times 100 \qquad (1)$$

Where W^{o}corr and W_{corr} are the corrosion rates of pure iron samples in the absence and presence of the organic compound, respectively. The results obtained are given in Table 1.

From gravimetric measurements, these results show that copper corrosion rate values decrease in the presence of the L-Cysteine Methyl Ester Hydrochloride tested. The relatively large decrease in weight loss in the presence of different concentration of L-CMEH indicates that this compound has inhibition effect on the corrosion of copper in acidic solution. The inhibition efficiency increases with the inhibitor concentration and attains 96.5% at 10^{-3}M L-CMEH.

Table 1 : Copper weight loss data and inhibition efficiency of L-CMEH.

Inhibitor	Conc (M)	W(mg/cm^2.h)	E_w (%)
Blank	2	1.78	-
	10^{-3}	0.0618	96.5
	5×10^{-4}	0.1004	94.4
L-CMEH	10^{-4}	0.1762	90.1
	5×10^{-5}	0.2629	85.2
	10^{-5}	0.3674	79.4
	10^{-6}	0.5527	69.0

3.2. Polarisation measurements

Current-potential characteristics resulting from polarisation curves of copper in 2M HNO_3 at various concentrations of the tested L-CMEH are shown in Figure 2. Table 2 collects the corrosion kinetic parameters such as E_{corr}, I_{corr}, E_I and β_c obtained from potentiodynamic polarisation curves for copper in acid containing different concentrations of L-CMEH. E_I% was calculated using the equation 2:

$$E_I\% = \frac{I_{corr} - I_{corr(inh)}}{I_{corr}} \times 100 \qquad (2)$$

Where I_{corr} and $I_{corr(inh)}$ are the corrosion current density values without and with the inhibitor, respectively, determined by extrapolation of cathodic Tafel lines to the corrosion potential.

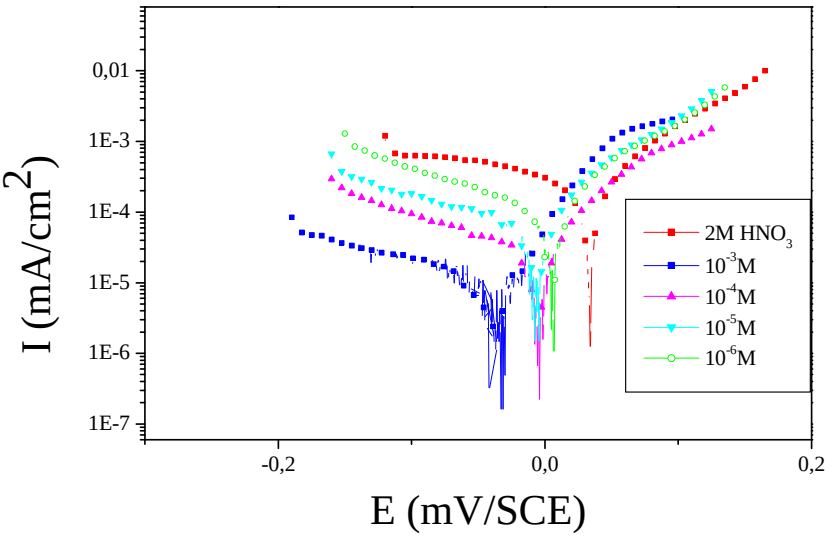

Figure 2. Polarization curves of copper at various concentrations of L-CMEH in 2M HNO_3.

Table 2. Corrosion parameters of copper in 2M HNO_3 at various concentrations of L-CMEH at 303K and corresponding inhibition efficiencies

Inhibitor	Conc (M)	E_{corr} (mv/SCE)	$-\beta_c$ (mV/dec)	I_{corr} (µA/cm^2)	E_I (%)
Blank	2	34.00	304.71	365.10	-
	10^{-3}	-34.37	233.66	09.74	97.33
L-CMEH	10^{-4}	-05.80	202.14	30.27	91.71
	10^{-5}	-08.60	192.64	62.70	82.82
	10^{-6}	05.08	166.15	102.09	72.04

From electrochemical polarisation measurements, it is clear that the addition of the L-CMEH at various concentrations leads to a decrease in the cathodic current densities (Fig. 2). The cathodic current versus potential curves gave rise to Tafel lines indicating that the hydrogen evolution reaction is activation-controlled. The change in cathodic Tafel slope (β_c) values (Tab 2), suggest that the reaction mechanism of the hydrogen reduction is not the same in the absence and presence of inhibitor. The anodic branches are also affected in the presence of this compound. The anodic effect is well shown when curves are compared at E-E_{corr}. The inhibiting action is increased with the concentration to reach the maximum value of 97.33% at the 10^{-3} M. The addition of L-CMEH shifted the E_{corr} value towards the negative direction. This indicates that the L-CMEH compound acts as a mixed type inhibitor.

3.3. EIS measurements

Corrosion behaviour of copper, in acidic solution with and without L-Cysteine Methyl Ester Hydrochloride (L-CMEH) compound at different concentrations after immersion for 30 min is investigated by electrochemical impedance spectroscopy (EIS) measurements at 303 K. The corresponding Nyquist diagrams are shown in Figure 3. The charge transfer resistance (R_t) values are calculated from the difference in impedance at lower and higher frequencies, as suggested by Tsuru et al. [26]. The double layer capacitance (C_{dl}) and the frequency at which the imaginary component of the impedance is maximal ($-Z_{max}$) are found as represented in equation 3:

$$C_{dl} = \left(\frac{1}{\omega R_t} \right) \qquad \text{where } \omega = 2\pi f_{\max} \tag{3}$$

The impedance parameters derived from these investigations are mentioned in Table 3. The inhibition efficiency is calculated using charge transfer resistance from equation 4[27]:

$$E_Z\% = \frac{R_{t(inh)} - R_t}{R_{t(inh)}} \times 100 \tag{4}$$

Where $R_{t(inh)}$ and R_t are the charge transfer resistance in the presence and absence of L-CMEH, respectively.

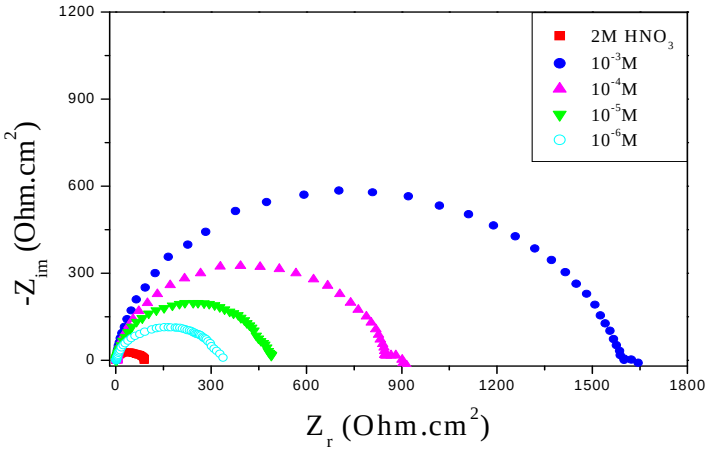

Figure 3. Nyquist diagrams of copper in acid at various concentrations of L-CMEH.

As we notice in Fig. 3, the Nyquist plots of copper show a depressed semi circular shape and only one time constant was observed in Bode diagrams (Fig. 4). This observation indicates that the corrosion of Cu in 2M HNO_3 solution is mainly controlled by a charge transfer process [28].

The presence of one phase maximum at intermediate frequencies indicates the presence of one time constant corresponding to the impedance of the formed protective film. In Bode plots for pure capacitive behaviour the slope of Log (-Zi) vs. Log f relation should be -1. In present work, the resulting value is approximately -0.9988, which indicate a capacitive behaviour of copper electrode under the experimental conditions [29].

The examination of the results of Table 3 enables us to deduce the following points: Resistance from load transfer, R_t, increases with the concentration of the inhibitor, the values of R_t informs us about the kinetics of the reactions. R_t increases with the introduction of the inhibitor; this can be due to the blocking of the active sites by the film formed by the inhibitor at the surface of the metal while the capacity of the double layer decreases as the quantity of the inhibitor increases. The reduction in the capacity of the double layers is due to the adsorption of the inhibitor at the copper surface which causes the reduction of the active surface of the electrode. Furthermore, C_{dl} decreases with increase of the concentration of inhibitor (Fig. 5).

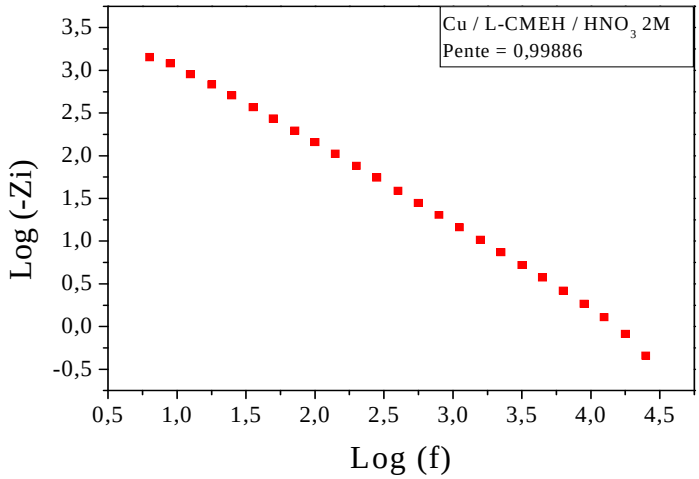

Figure 4. Variation of Log (-Zi) as function of logarithm of frequency of Cu / 10^{-3}M L-CMEH / 2M HNO_3.

This phenomenon is generally related to the adsorption of organic molecules on the metal surface and then leads to a decrease in the local dielectric constant and/or an increase in the thickness of the electrical double layer [30].

$$C_{dl} = \frac{\varepsilon_o \varepsilon}{\delta} S \qquad (5)$$

Where δ is the thickness of the protective layer, S is the electrode area, ε_o the vacuum permittivity of vide and ε is dielectric constant of the medium.

A low capacitance may result if water molecules at the electrode interface are largely replaced by organic inhibitor molecules through adsorption [31]. The larger inhibitor molecules also reduce the capacitance through the increase in the double layer thickness [32]. The inhibiting effectiveness increases with the concentration of the inhibitor to reach a maximum value from 94.29% to 10^{-3} M.

Table 3. Impedance parameters and inhibition efficiency for the corrosion of copper in 2M HNO_3 without and with addition of various concentrations of L-CMEH at 303 K

Inhibitor	Conc (M)	R_t ($\Omega.cm^2$)	f_{max} (Hz)	C_{dl} ($\mu F/cm^2$)	E_z (%)
Blank	2	91.41	15.82	110.11	-
	10^{-3}	1600.00	1.58	62.82	94.29
L-CMEH	10^{-4}	868.20	2.81	65.25	89.47
	10^{-5}	486.90	4.00	81.70	81.22
	10^{-6}	333.90	5.62	84.84	72.75

A comparison may be made between inhibition efficiency *E*(%) values obtained by different methods (weight loss, polarisation curves and EIS methods). Figure 6 shows a curves that compares the *E*(%) values obtained. One can see that whatever the method used, no significant changes are observed in *E*(%) values. We can then conclude that there is a good correlation with

the three methods used in this investigation at all tested concentrations and that L-CMEH is an efficient corrosion inhibitor.

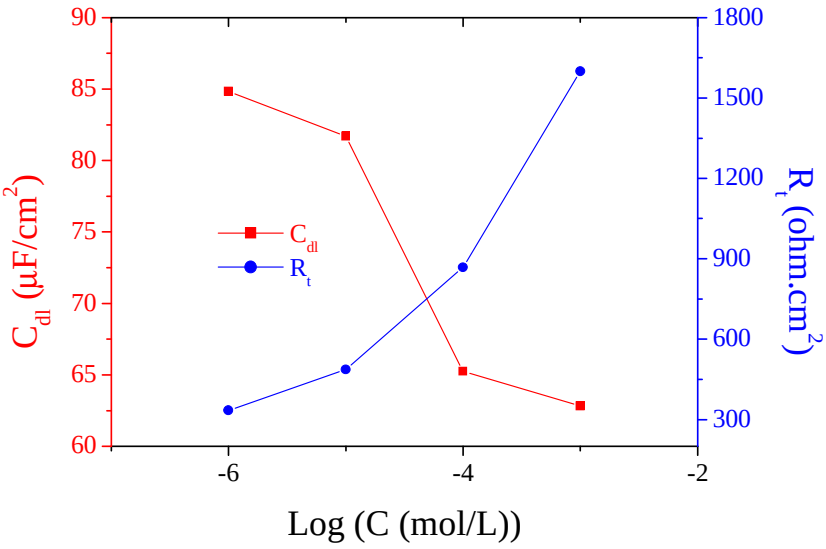

Figure 5. Evolution of transfer resistance and capacitance as function of logarithm of L-CMEH concentration

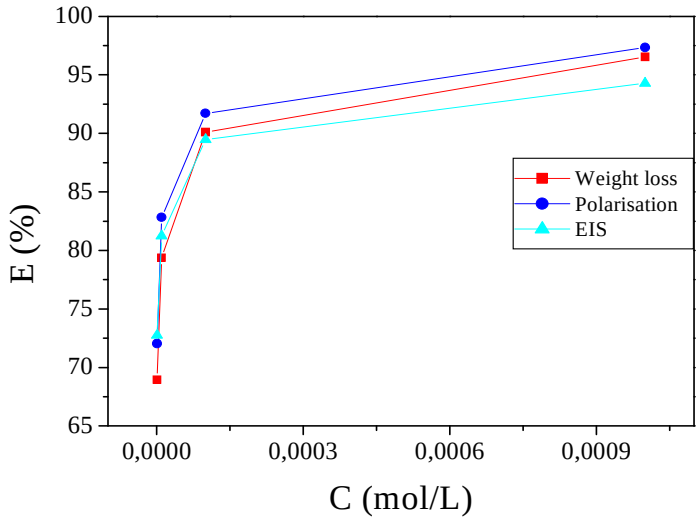

Figure 6. Comparison of inhibition efficiency (E%) values obtained by weight loss, polarisation and EIS methods

CONCLUSION

In this work, we have studied the behaviour of corrosion of copper in nitric acid taking account the effect of the addition of L-Cysteine Methyl Ester Hydrochloride at different concentrations by potentiodynamic polarisation, electrochemical impedance spectroscopy (EIS) and weight loss measurements. From the obtained results, we can have the following conclusions:

- The results obtained showed the effectiveness of the investigated L-Cysteine Methyl Ester Hydrochloride as a good inhibitor of copper in 2M HNO_3.

- The inhibition of L-CMEH was more pronounced with its concentration to attain 97 % at 10^{-3} M.
- Polarisation measurements show that the L-CMEH acts a mixed type inhibitor and the cathodic curves presented in the Tafel lines indicating that the hydrogen evolution reaction at the metal surface occurs through a pure mechanism of activation.

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