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Copper phthalocyanine as corrosion inhibitor for ASTM A606-4 steel in 16% hydrochloric acid☆

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Abstract

A study based on the corrosion inhibition properties of copper phthalocyanine is described. Coverage degrees of copper phthalocyanine (Cu-phcy) on ASTM-A606-4 steel, obtained by weight loss measurements, were fitted to Langmuir, Frumkin, Temkin and Flory–Huggins adsorption isotherms. A better fit to the Langmuir isotherm was obtained. The polarization curves showed that polarization of both the anodic and cathodic reactions were verified for concentrations higher than 10^{-4} M, indicating a mixed type action. Only the anodic reactions were polarized for lower concentrations. At high frequencies the Nyquist diagrams showed one capacitive loop attributable to double layer charging and a small one at intermediary frequencies attributable to the faradaic process of hydrogen evolution. The formation of an adsorbed film was characterized by increasing charge transfer resistance values in the low frequency range for increasing inhibitor concentrations. According to the techniques used in this study, copper phthalocyanines showed a high corrosion inhibiting efficiency for all concentrations.

1. Introduction

HSLA steels have very similar chemical composition to carbon steel; nevertheless a few differences apply, especially with respect to some constituents; copper, chromium, phosphorus, silicon and nickel are added to improve their mechanical properties. These steels are commonly used in the structure of buildings, bridges and industrial plants. HSLA steels are known for their outstanding behaviour in polluted atmospheres as 'weathering steel'; they acquire a protective corrosion product layer. Otherwise, little is known about their corrosion behaviour in hydrochloric acid.

The ASTM-A606-4 steel, known as weathering steel and high strength low alloy steel (HSLA steel), are an important category of metallic materials in engineering. To improve their range of application a deeper knowledge of the corrosion inhibiting mechanism of these metals is necessary. Therefore, their behaviour in acid media is an important property to be studied and explored. In the last few years there has been increasing interest in macrocyclic compounds as corrosion inhibitors in acid environments. Among these compounds, metallic phthalocyanines, which exhibit several interesting properties and applications due to their highly delocalized conjugated π electron system, have been studied. The high inhibition action of the phthalocyanines is attributable to their strong chemical adsorption on the metal surface, which is determined by planarity and lone pairs of electrons in heteroatoms [1–4]. Figure 1 shows the planar copper phthalocyanine molecule structure, forming a complex with the copper ion in the central part of the molecule (coordination number 4).

Since the 1970s there have been studies on the performance of porphirins and phtalocyanines as corrosion inhibitors in acidic media [5, 6]. This study intends to verify the efficiency of copper phthalocyanine as a corrosion inhibitor for ASTM A606-4 in 16% hydrochloric acid, as well as the degree of protection, from weight loss measurements and from anodic and cathodic potentiodynamic polarization curves.

2. Experimental details

The efficiency of the inhibitor for ASTM-A606-4 steel in 16% w/w hydrochloric acid solution at 50 °C was investigated by weight loss measurements and by electrochemical techniques: monitoring of the open circuit potential with time (OCP), electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization curves.

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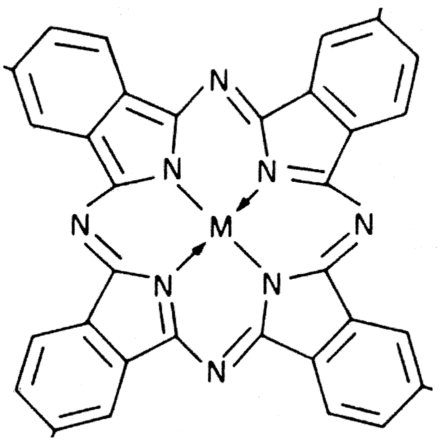

Fig. 1. Planar copper phthalocyanine molecule structure.

Table 1. Chemical composition of HSLA steel specimens (wt %)

C	Mn	Si	P	Cr	Cu	Ni	S	Fe
0.12	0.40	0.38	0.095	0.52	0.35	0.30	0.016	Bal.

2.1. *Weight loss experiments*

HSLA steel samples, with chemical composition shown in Table 1, were cut to 19 × 10 × 8.8 mm dimension. These samples were sequentially treated with SiC emery papers 320, 400 and 600 grit, washed in distilled-deionized water, rinsed with ethanol and acetone and dried in hot air. They were weighed in an analytical balance before and after immersion in 16% w/w HCl solution, at a controlled temperature of 50 °C. The steel samples were also immersed in naturally aerated media for 2 h in the presence and absence of inhibitor. Subsequently, the coverage degree, θ, was obtained by

$$\theta = \frac{v_{\mathrm{corr,o}} - v_{\mathrm{corr},i}}{v_{\mathrm{corr,o}}},$$

where $v_{\mathrm{corr,o}}$ is the corrosion rate in the absence and $v_{\mathrm{corr},i}$ is the corrosion rate in the presence of the inhibitor. All solutions were prepared from pure reagents and distilled-deionized water. The results are presented in Table 2.

Table 2. Corrosion rates and coverage degrees for ASTM 606-4 steel in 16% HCl in the presence of Cu-phcy

Concentration of Cu-phcy/M	Corrosion rate /mg cm^{-2} h^{-1}	Coverage degree, θ
0.00	21.01	0.00
1×10^{-5}	19.32	0.08
5×10^{-5}	18.32	0.13
1×10^{-4}	17.60	0.16
5×10^{-4}	14.33	0.32
1×10^{-3}	6.96	0.67
5×10^{-3}	1.36	0.94

2.2. *Electrochemical techniques*

ASTM A606-4 steel specimens were cut in disc form and treated with SiC emery papers 320, 400 and 600 grit, washed in distilled-deionized water, rinsed with ethanol and acetone and dried in hot air. They were placed in a special holder to expose a 1 cm^2 area. The tests were performed with a Voltalab 40 Radiometer potentiostat in a glass cell supporting 350 mL electrolyte (16% w/w HCl), at 50 °C temperature, with a Ag/AgCl electrode provided with a Luggin capillary as reference electrode and a Pt foil as counter electrode. Initially, the open circuit potential was recorded for 90 min. Subsequently, electrochemical impedance spectroscopy data was obtained with a Dynamic EIS system attached to a Voltalab 40 Radiometer potentiostat. The steady state open circuit potential (OCP) was disturbed with a 10 mV a.c. sine wave with amplitude within a frequency range of 50 kHz to 5 mHz. The EIS data is presented in the form of Nyquist diagrams. Following the EIS, the polarization curves were obtained from −800 mV vs Ag/AgCl to 0 mV vs Ag/AgCl using a static working electrode in a naturally aerated media, in the absence and in the presence of copper phtalocyanine. A 1 mV s^{-1} scan rate was used.

3. Results and discussion

3.1. *Weight loss experiments*

Based on results obtained through weight loss, coverage degrees of the copper phthalocyanine (Cu-phcy) on ASTM-A606-4 steel were calculated from Table 2. The results show how the Cu-phcy acts as a corrosion inhibitor for ASTM A606-4 steel in 16%w/w HCl. When Cu-phcy is present, the corrosion rate obtained is lower than that observed in the absence of Cu-phcy. All coverage degree results were positive, indicating that the Cu-phcy acts as an inhibitor for ASTM A606-4 steel in 16% w/w HCl.

The best trend line and related statistical parameters, such as determination coefficient R^2 and standard deviation for linear and angular coefficients, were obtained by fitting coverage degree results to Langmuir, Frumkin, Temkin and Flory–Huggins adsorption isotherms, as per equations given in Table 3. These are shown in Figure 2.

Table 3. Adsorption isotherms and the corresponding equations

Isotherm to be tested	Corresponding equation	Plotted graphic
Langmuir	$\theta/(1-\theta) = kC$	$\theta/(1-\theta)$ vs C
Frunkin	$\log[\theta/(1-\theta)/C] = \log k + g\theta$	$\log[\theta/(1-\theta)/C]$ vs θ
Temkin	$\log(\theta/C) = \log k + g\theta$	$\log(\theta/C)$ vs θ
Flory–Huggins	$\log(\theta/C) = \log xk + x\log(1-\theta)$	$\log(\theta/C)$ vs $\log(1-\theta)$

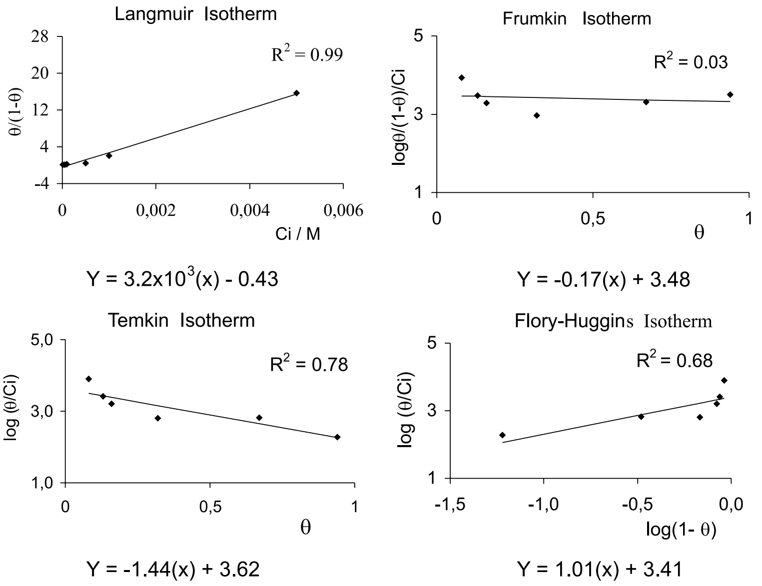

Fig. 2. Adsorption isotherm to ASTM A606-4 steel in 16%w/w HCl with and without Cu-phcy.

Here C represents the inhibitor concentration; θ is the coverage degree; k is the adsorption equilibrium constant; g is the side interaction parameter between the inhibitor adsorbed molecules and, finally, x denotes the number of previous adsorbed water molecules replaced by one inhibitor molecule.

Taking into account all R^2 values shown in Table 4, it is clear that a better fitting was obtained by the Langmuir isotherm. A larger value for R^2 means a narrow range of variation for the best trend-line linear and angular coefficients, as can be seen in Table 4. On the other hand, the negative slopes found for the Frunkin and Temkin isotherms mean that there are repulsive side interactions between adsorbed inhibitor molecules. Otherwise, the Flory–Huggins isotherm slope, 1.01, confirms that only the Langmuir isotherm is a valid representation of the adsorption of Cu-phcy, because when the slope or x value is 1.0, it means that the Flory–Huggins isotherm is not valid and is equal to the Langmuir isotherm. These results cannot explain how the inhibitor molecule is adsorbed onto the steel surface.

For the Langmuir isotherm, the angular coefficient represents the adsorption equilibrium constant, k. Its value, $k = 3.18 \times 10^3\ \text{M}^{-1}$, can be used to calculate the adsorption free energy which provides $\Delta G = -RT \ln k = 5.2\ \text{kcal mol}^{-1}$. Based on this value, physical adsorption takes place. Considering that when an inhibited solution contains adsorbable anions, such as chloride ions, they adsorb on the metal surface by creating oriented dipoles therefore increasing the adsorption of the organic cations on them [8], it can be concluded that this is how Cu-phcy is adsorbed. Taking into account previous results [9] for Cu-phcy in sulfuric acid, which showed lower inhibiting efficiencies, confirms that the intermediary adsorption of chloride ions onto steel surface is a mechanism which enhances the efficiency of this inhibitor.

Table 5. Open circuit potential (OCP) for ASTM A606-4 steel after 90 min of immersion in 16% w/w HCl with and without increasing Cu-phcy concentrations

Cu-phcy concentration/M	OCP vs Ag/AgCl/mV
0	−360
1×10^{-5}	−398
5×10^{-5}	−352
5×10^{-4}	−366
1×10^{-3}	−343

3.2. *Open circuit potential*

The steady state open circuit potential was monitored for 90 min and did not change significantly; only slightly more positive values of open circuit potential are observed for higher copper phthalocyanine (Cu-phcy) concentrations (see Table 5). This indicates that Cu-phcy acts mainly as a mixed type inhibitor for ASTM A606-4 steel in hydrochloric acid media.

Table 4. Statistical results for the linear regression analysis for all tested isotherms

Parameter	Langmuir	Frunkin	Temkin	Flory–Huggins
R^2	0.99	0.03	0.78	0.68
Linear coefficient ± σ	-0.43 ± 0.30	3.48 ± 0.22	3.62 ± 0.19	3.41 ± 0.19
Angular coefficient ± σ	$(3.18 \pm 0.14) \times 10^3$	-0.17 ± 0.45	-1.44 ± 0.38	1.01 ± 0.35

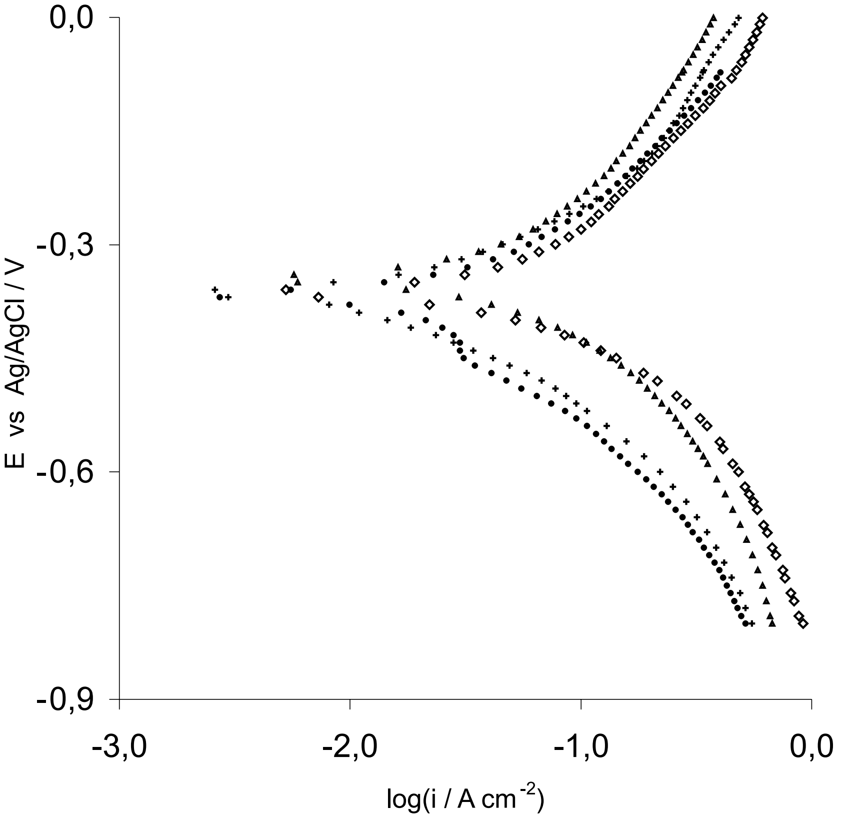

Fig. 3. Potentiodynamic polarization curves for ASTM-A606-4 carbon steel in 16% w/w HCl. Key: (□) without Cu-phcy. With: (▲) 5×10^{-5} M; (●) 1×10^{-4} M and (+) 5×10^{-4} M of Cu-phcy.

3.3. *Potentiodynamic polarization curves*

Figure 3 shows polarization curves for ASTM A606-4 steel with and without additions of Cu-phcy, in16% w/w HCl. All Cu-phcy concentrations polarize both cathodic and anodic reactions. However, higher polarization is obtained for higher concentrations showing a better efficiency and a well defined mixed inhibitor behaviour. These results agree with weight loss values. As was observed, the corrosion rate was lower for higher Cu-phcy concentrations.

3.4. *Electrochemical impedance spectroscopy*

The Nyquist diagrams are shown in Figure 4. The diagrams show two capacitive and one inductive arc. The first capacitive arc, at high frequencies, represents the phenomenon associated with the double electric layer

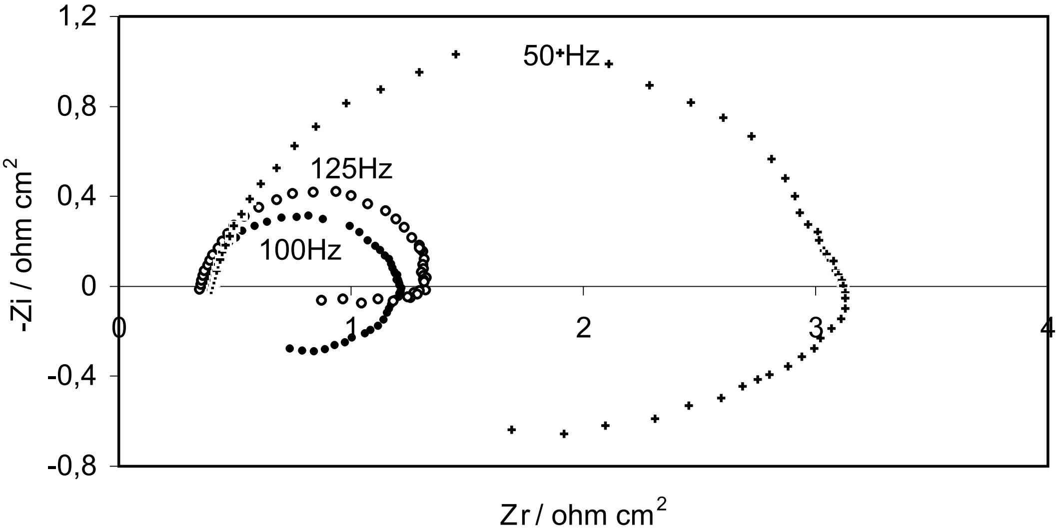

Fig. 4. EIS data represented by Nyquist diagrams for ASTM-A606-4 steel in 16% w/w HCl. Frequency range: from 50 kHz to 5.0 mHz. Ten points per decade. Key: (●) without Cu-phcy. With: (○) 1×10^{-4} M and (+) 1×10^{-3} M of Cu-phcy.

at the metal–electrolyte interface. The second capacitive arc, which is not well defined, at the intermediary frequencies, may represent a faradaic process at the interface, such as a hydrogen reduction. The inductive arc, at low frequency, is commonly associated with a relaxation process of adsorbed species on the metal–electrolyte interface. The observed deformation of the inductive arc may represent the presence of two arcs, as discussed by Barcia and Mattos [7]. The frequency of the maximum point of the first capacitive arc is changed for Cu-phcy concentrations higher than 10^{-4} M thus, showing that the inhibitor effectively adsorbs on the metal surface, decreasing its corrosion in the aggressive medium.

4. Conclusions

(i) The Langmuir isotherm presented the best fitting to the coverage results.
(ii) The free adsorption energy showed that Cu-phcy adsorbs physically on the negative sites created by the previous adsorption of chloride ions on ASTM A606-4 steel in 16% HCl.
(iii) The slight changes in open circuit potential and the polarization curves showed that Cu-phcy acts as a mixed inhibitor for ASTM A606-4 steel in 16% HCl.
(iv) As also shown by the impedance diagrams, the inhibitor efficiency is observed for increasing Cu-phcy concentrations.
(v) EIS results agree with the polarization curves, related to the corrosion protection provided by Cu-phcy for ASTM A606-4 steel in 16% HCl at 50 °C.

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