

ELECTROCHEMICAL INVESTIGATION OF 2-THIOHYDANTOIN DERIVATIVES AS CORROSION INHIBITORS FOR MILD STEEL IN ACIDIC MEDIUM

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Abstract:

Four 2-thiohydantoin derivatives were synthesized and their corrosion inhibition properties on mild steel (MS) in 0.5M HCl solution was evaluated using usual gravimetric and electrochemical methods (weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS). Morphology of the metal surface was characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The study has shown that these compounds provide good protection for mild steel against corrosion in the acidic medium.

Keywords: thiohydantoin, corrosion inhibition, mild steel, electrochemical measurements, surface analysis

1. Introduction

Corrosion is an issue that plagues many industries production-wise and cost-wise. Corrosion inhibitors have been shown to be the most convenient and cost-effective way of dealing with metal corrosion in aqueous environments [1]. Organic compounds with conjugated double bonds and heteroatoms such as nitrogen, sulfur and oxygen exhibit good inhibiting properties since they are easily adsorbed on metal surfaces, but a negative environmental impact has restricted their use. 2-Thiohydantoin is sulfur analogue of hydantoin, a family of drug-based compounds known for their non-toxicity, biological activities and pharmaceutical applications [2]. Some hydantoin derivatives and 2-thiohydantoin itself exhibited corrosion inhibition activities [3] as well as the molecules containing the Schiff base azomethine group [4]. In this study, four Schiff base 2-thiohydantoin derivatives were synthesized from cheap and commercially available substrates as candidates for environmentally benign corrosion inhibitors.

2. Materials and methods

0.5 M HCl solution, prepared from 37% HCl solution (Fisher Chemical, USA) diluted with Milli-Q water, was used as the corrosive electrolyte. Four thiohydantoin derivatives were synthesized by previously reported procedure [5]. The test solutions (0.05 mM; 0.1 mM; 0.5 mM; 1.0 mM and 10 mM) were prepared by dissolving inhibitors in 0.5 M HCl. The experiments were performed in a three-electrode Pyrex glass cell, with a saturated calomel electrode as the reference electrode, a platinum plate as the counter electrode and the cylinders of mild steel (Fe with C (max 0.17 wt.%), P (0.045 wt.%), S (0.045 wt.%), N (0.009 wt.%) as the working electrodes. For potentiodynamic polarization studies

EG&G PAR 2631A potentiostat/galvanostat controlled by Power Suite software (Princeton Applied Research, USA) was used. Potentiostat/galvanostat station (BioLogic SAS, SP-240, Grenoble, France) provided with corrosion and physical electrochemistry software was used for potentiostatic electrochemical impedance spectroscopy (PEIS) measurements. The PEIS data were fitted and analyzed using ZView® software. The morphology of the samples was studied using a scanning electron microscope (SEM) model JOEL JSM-IT300LV. The EDS spectra were recorded using the X-ray spectrometer (Oxford Instruments) attached to the SEM using Aztec software.

3. Results and discussion

Four 3-arylidene-2-thiohydantoin derivatives **a-d** (Table 1), containing the 2-thiohydantoin moiety as well as the Schiff base azomethine group, both of which exhibiting anticorrosion properties, were synthesized utilizing aromatic aldehydes and thiosemicarbazide. Their corrosion inhibition efficiency was investigated on mild steel (MS) in 0.5 M HCl solutions using different electrochemical techniques, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). Potentiodynamic polarization curves (Fig.1) were moved towards lower current densities, indicating reduced corrosion rate in the presence of inhibitors **a-d**, which may be attributed to the adsorption of inhibitors onto the MS surface. The adsorption of an inhibitor blocks active sites on the metal surface providing protection of the MS surface against acid dissolution [6] indicating that the inhibition effect can be cathodic as well as anodic (mixed type inhibitors). Thus, the presence of thiohydantoin **a-d** inhibited the anodic metal dissolution reaction, but also controlled the mechanism of cathodic hydrogen evolution. On the basis of Tafel curves, the inhibition efficiency ($\eta\%$) was calculated from the equation (1)

$$\eta\% = \left(\frac{i_{\text{corr}}^0 - i_{\text{corr}}^i}{i_{\text{corr}}^0} \right) \times 100 \quad (1)$$

where i_{corr}^0 and i_{corr}^i are corrosion current densities recorded without and with inhibitors **a-d**.

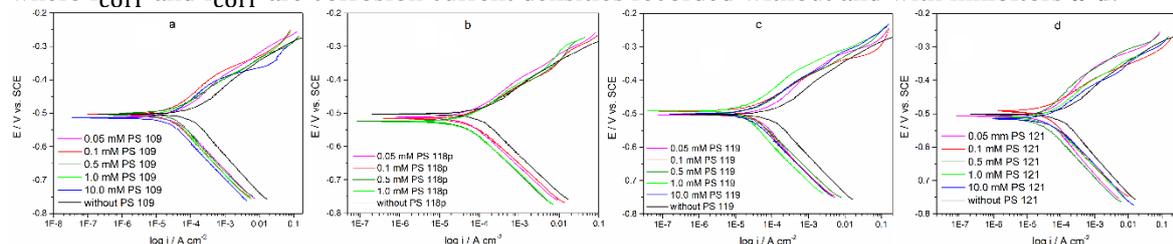


Fig. 1. Polarization curves of MS working electrode recorded in 0.5 M HCl solution without and with different concentrations of inhibitors **a-d** ; $v=1 \text{ mV s}^{-1}$.

The inhibition efficiency of all inhibitors increases with increasing concentration (Table 1). Anticorrosion ability may be associated with the structure of the inhibitors. Nonbonding electrons on the O atoms probably helped the adsorption of the inhibitor on the MS surface and protect the surface by occupying active sites. Inhibitor **c**, which has an additional O atom in its molecular structure, had the highest inhibition rate of 82%. The best performing concentrations of all inhibitors were chosen for further PEIS evaluation in order to characterize the various processes of corrosion and study the reaction mechanisms in the electrochemical interface (Fig. 2). The addition of inhibitors **a-d** causes an increase in the capacitive loops comparing to the reference solution. The Nyquist representations spectra consist of one single capacitive loop which is slightly depressed indicating that the charge transfer controls corrosion reactions on the inhomogeneous electrode surface. The electrochemical data was evaluated using a Randle's equivalent circuit (Fig. 3) and inhibition efficiency (η_{EIS}) (Table 1) was determined by equation (2) where R_s stands for solution resistance and R_{ct}^0 and R_{ct} are charge transfer resistances of inhibited and uninhibited solutions.

$$\eta_{EIS} = \left(1 - \frac{R_{ct}^0}{R_{ct}} \right) \times 100 \quad (2)$$

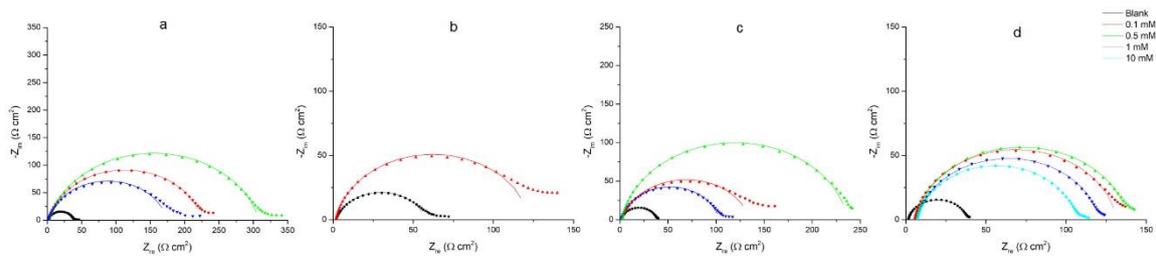


Fig. 2. Nyquist plot for MS electrode for different concentrations of the inhibitors **a-d**.

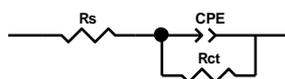


Figure 3. Randle's equivalent circuit employed for fitting all of the PEIS curves.

Table 1. Inhibition efficiency for MS in 0.5 M HCl solution obtained from the potentiodynamic polarization curves and EIS without and with inhibitors **a-d** present in different concentrations.

	Inhibitor	C _{inh} (mM)	η%	η _{EIS} %
a		0.05	59	-
		0.1	75	83
		0.5	72	-
		1.0	71	78
		10.0	77	88
b		0.05	51	-
		0.1	50	-
		0.5	58	-
		1.0	58	53
		10.0	-	-
c		0.05	51	-
		0.1	75	72
		0.5	74	-
		1.0	82	84
		10.0	74	63
d		0.05	51	-
		0.1	62	70
		0.5	75	72
		1.0	55	67
		10.0	49	63

Impact of various concentrations of the most potent inhibitor **c** on corrosion of MS in 0.5 M HCl was investigated using the weight loss method (Table 2). Inhibition efficiencies increase with increasing concentration, which may be attributed to larger coverage of the metal surface with inhibitor molecules. Corrosion rate (C_R) and inhibition efficiency ($\eta\%$) were estimated by using equations (3,4) where, w_I and w_F are initial and final weights (mg), S (cm^2) is the surface, t (h) is immersion time, and C_R and C_{R0} are the corrosion rates with and without inhibitor **c**, respectively.

$$C_R = \frac{w_I - w_F}{S t} \quad (4)$$

$$\eta\% = \left(\frac{C_{R0} - C_R}{C_{R0}} \right) \times 100 \quad (5)$$

Table 2. The weight loss parameters obtained for MS in 0.5 M HCl solution with and without inhibitor **c** present in different concentrations.

Medium	c_{inh} (mM)	Corrosion rate ($\text{mg cm}^{-2} \text{h}^{-1}$)	$\eta\%$ (%)
Blank	0.5 M	0.659	-
c	0.1	0.268	59.3
	1.0	0.075	88.6
	10.0	0.066	89.9

Energy dispersive X-ray spectroscopy (EDS) associated with scanning electron microscopy (SEM) was used to obtain chemical identification of corrosion products (Fig. 3). SEM images of uninhibited and inhibited MS surfaces in 0.5 M HCl solution (Fig. 3) showed that the surface of the sample immersed in the solution with the inhibitor **c** was uniform and significantly less corroded and cracked.

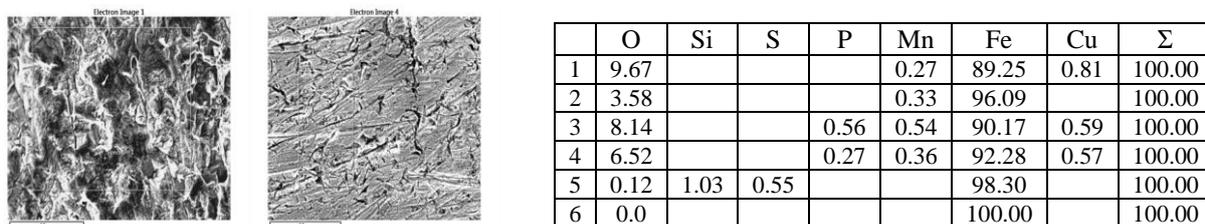


Fig. 3. SEM images without (left) and with the addition of inhibitor **c** (right). Table: Elemental composition of MS surfaces obtained by EDS analysis without (entries 1-4) and with inhibitor **c** (entries 5 and 6)

4. Conclusions

The results showed that the thiohydantoin based inhibitor **c** has good inhibition and protects the surface from the effects of acid by the formation of the protective film on the metallic surface.

Acknowledgments

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