



## Corrosion inhibition of new thiocarbohydrazides on the carbon steel in hydrochloric acid solution



N. Esmaili<sup>a</sup>, J. Neshati<sup>b</sup>, I. Yavari<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, Tarbiat Modares University, P.O. Box 14115-175, Tehran, Iran

<sup>b</sup> Industrial Protection Division, Research Institute of Petroleum Industry, P.O. Box 14665-137, Tehran, Iran

### ARTICLE INFO

#### Article history:

Received 17 March 2014

Received in revised form 2 July 2014

Accepted 3 July 2014

Available online 11 July 2014

#### Keywords:

Thiocarbohydrazides

Scanning electrochemical microscopy

Corrosion inhibition

Adsorption

### ABSTRACT

The effect of *N,N'*-[2,2'-thiocarbonylbis(hydrazine-2,1-diyl)bis(thioxomethylene)]dibenzamide (T1) and *N,N'*-[2,2'-thiocarbonylbis(hydrazine-2,1-diyl)bis(thioxomethylene)]bis(4-methoxybenzamide) (T2) on the corrosion behavior of carbon steel in 1 M HCl solution, using potentiodynamic, electrochemical impedance spectroscopy, and scanning electrochemical microscopy (SECM), is reported. The efficiency of  $2.0 \times 10^{-4}$  M solutions of T1 and T2 reached 96.9 and 98.2%, respectively. Adsorption of these thiocarbohydrazides on the carbon steel surface obeyed Langmuir's adsorption isotherm. The SECM results confirmed the existence of adsorption film on carbon steel.

© 2014 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved.

### Introduction

Chemical inhibitors play an important role in protection strategies for retarding corrosion, especially in acidic media [1,2]. Acid solutions are extensively used in acid pickling, acid descaling, and oil well acidizing industries [3,4]. The most effective inhibitors are organic compounds having  $\pi$  bonds and heteroatoms, such as S, N, or O [5–7]. Many studies were done on the corrosion inhibition of steels in acidic media [8–15]. Some thiocarbohydrazides were reported earlier as corrosion inhibitors for steels [16–18].

In this work, the corrosion behaviors of carbon steel in 1 M HCl solutions of two new thiocarbohydrazides [19], namely *N,N'*-[2,2'-thiocarbonylbis(hydrazine-2,1-diyl)bis(thioxomethylene)]dibenzamide (T1) and *N,N'*-[2,2'-thiocarbonylbis(hydrazine-2,1-diyl)bis(thioxomethylene)]bis(4-methoxybenzamide) (T2), were investigated (see Scheme 1). Electrochemical techniques including polarization curves, EIS, and SCHEM measurements were employed in this study. The adsorption mechanism was studied by calculating isotherm equations.

### Experimental

#### Materials and instruments

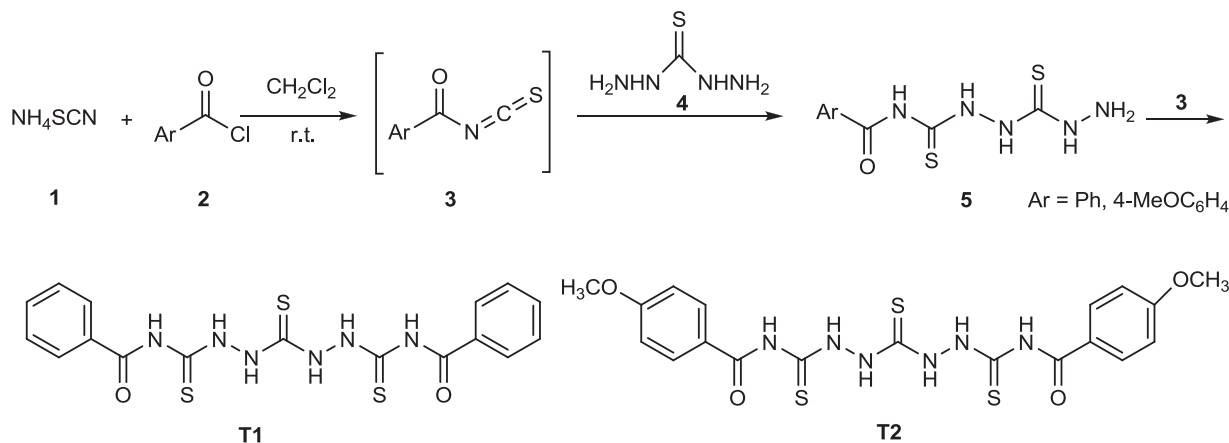
The reagents and solvents used in this study were obtained from Merck and used without further purification. Thiocarbohydrazides, T1 and T2, were prepared by the method described in Ref. [19]. Buchi 535 melting point apparatus; IR spectra, Shimadzu IR-460 spectrometer; <sup>1</sup>H and <sup>13</sup>C NMR spectra, Bruker DRX-300 Avance instrument; Elemental analyses (C, H, N), Vario Max CHN. Potentiostat/Galvanostat (Zahner model MeX6, Germany) and SCHEM (Uniscan model 370, UK) instruments were used for electrochemical measurements.

#### Electrochemical measurements

The carbon steel (wt.%: 0.19 C, 0.4 Mn, 0.04 P, 0.005 S, and Fe for the balance) was cut into cylindrical rods with surface area of 5 cm<sup>2</sup> as working electrode (WE). The surface preparation of the specimens was carried out using emery paper grade 800 and 1200. The reference electrode was a saturated calomel electrode (SCE) externally connected to the cell through a Luggin capillary tube positioned close to the WE to minimize the ohmic potential drop. The counter electrode was two graphite rods.

Electrochemical tests were carried out using a conventional three electrode electrochemical cell. EIS measurements were conducted at open circuit potential after 1 h immersion in the

\* Corresponding author. Tel.: +98 21 82883465; fax: +98 21 82883455.  
E-mail address: [yavarisa@modares.ac.ir](mailto:yavarisa@modares.ac.ir) (I. Yavari).



Scheme 1. Synthesis of T1 and T2.

frequency range of  $10^5$  to  $10^{-2}$  Hz with potential perturbation AC amplitude of 10 mV. Potentiodynamic polarization curves were obtained with a sweep rate of 1 mV/s in the potential range of  $\pm 0.25$  V vs. SCE.

SEM photographs obtained from carbon steel surface by using a scanning electrochemical microscope. The electrodes were a 25  $\mu\text{m}$  platinum ultramicroelectrode (UME) tip, an Ag/AgCl/KCl (saturated) reference electrode, sample electrode (carbon steel) and a platinum counter electrode, all set up in a cell made of poly(tetrafluoroethylene). Scans were conducted parallel to the sample surface in area of 500  $\mu\text{m} \times 500 \mu\text{m}$  in X and Y directions. The measurements were performed with the UME tip at a height of 25  $\mu\text{m}$  over the specimen surface.  $\text{Fe}^{2+}/\text{Fe}^{3+}$  redox couple was used as electrochemical mediator at the tip. The potential of the tip was held at +0.6 V vs. the reference electrode.

## Results and discussion

### Polarization measurements

Fig. 1 shows the polarization curves in the absence and presence of T2 for carbon steel in 1 M HCl solution. The corrosion current density ( $i_{\text{corr}}$ ), corrosion potential ( $E_{\text{corr}}$ ), anodic Tafel slope ( $\beta_a$ ) and cathodic Tafel slope ( $\beta_c$ ), corresponding inhibition efficiency (IE%) and surface coverage ( $\theta$ ) of T1 and T2 are given in Table 1. Polarization curves showed that the inhibition mechanism of T1 and T2 were mixed. The inhibition efficiency and  $\theta$  were determined from polarization measurements according to Eqs. (1) and (2):

$$\text{IE}\% = \left( \frac{i_{\text{uninh}} - i_{\text{inh}}}{i_{\text{uninh}}} \right) \times 100 \quad (1)$$

$$\theta = \frac{\text{IE}\%}{100} \quad (2)$$

where  $i_{\text{uninh}}$  and  $i_{\text{inh}}$  are uninhibited and inhibited corrosion current densities, respectively. The addition of  $2.0 \times 10^{-5}$  M to  $4.0 \times 10^{-4}$  M of T1 or T2 to the solution reduced the anodic dissolution of the carbon steel and retarded the cathodic reaction. Thus, the inhibition efficiency of T1 and T2 rose to the maximum of 96.9 and 98.2%, respectively. These results reveal that after adding inhibitor the corrosion current density decreases with increasing inhibitor. The inhibiting effect of these compounds can be attributed to the presence of the donor atoms N, O, S and aromatic  $\pi$  system for adsorption [5–7].

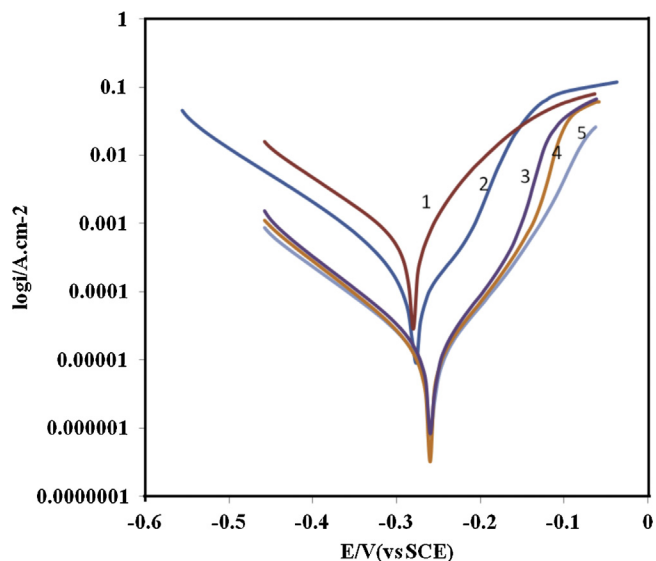


Fig. 1. The polarization curves for carbon steel in 1 M HCl solution containing different concentrations of T2: (1) blank, (2)  $2.5 \times 10^{-5}$ , (3)  $1.0 \times 10^{-4}$ , (4)  $2.0 \times 10^{-4}$ , and (5)  $4.0 \times 10^{-4}$  M.

### EIS measurements

EIS studies of carbon steel in HCl medium were carried out for various concentrations of T1 and T2. The EIS plots for T2 are shown in Fig. 2. The impedance curves analysis showed the time constant of T2 at  $2.0 \times 10^{-4}$  M. As shown in Fig. 3, the EIS plots can be modeled using a simple equivalent circuit, where  $R_s$  is the solution resistance and  $R_t$  represents the charge transfer resistance whose value is inversely proportional to corrosion rate (CR). The constant phase element, CPE, is introduced into the circuit instead of a pure double-layer capacitor to give a more accurate fit. The impedance of the CPE is defined as follows [20]:

$$Z_{\text{CPE}} = Y_0^{-1} (j\omega)^{-n} \quad (3)$$

where  $Y_0$  and  $n$  are the CPE constant and exponent, respectively,  $\omega = 2\pi f$  is the angular frequency (rad/s), and  $j$  is an imaginary number.

Table 2 shows the values of circuit elements obtained by applying the equivalent circuit in Fig. 3. The decrease of capacitance and increase of resistance could be attributed to the decrease in local dielectric constant and/or an increase in the

Download English Version:

<https://daneshyari.com/en/article/228700>

Download Persian Version:

<https://daneshyari.com/article/228700>

[Daneshyari.com](https://daneshyari.com)