Electrochimica Acta 53 (2008) 5941–5952

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Investigation of adsorption and inhibitive effect of 2-mercaptothiazoline on corrosion of mild steel in hydrochloric acid media

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ARTICLE INFO

Article history:
Received 18 February 2008
Received in revised form 20 March 2008
Accepted 25 March 2008
Available online 29 March 2008

Keywords:
Corrosion inhibitors
Adsorption mechanism
Atomic force microscopy (AFM)
Thermogravimetric analysis (TGA)
Potential of zero charge (PZC)

ABSTRACT

The inhibition effect of 2-mercaptothiazoline (2MT) on the corrosion behavior of mild steel (MS) in 0.5 M HCl solution was studied in both short and long immersion times (120 h) using potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and linear polarization resistance (LPR) techniques. For long-term tests, hydrogen gas evolution ($V_{H_2} - t$) and the change of the open circuit potential with immersion time ($E_{ocp} - t$) were also measured in addition to the former three techniques. The surface morphology of the MS after its exposure to 0.5 M HCl solution with and without 1.0×10^{-2} M 2MT with the different immersion times was examined by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The thermal stability of the inhibitor film was investigated by thermogravimetric analysis (TGA). The value of activation energy (E_a) for the MS corrosion and the thermodynamic parameters such as adsorption equilibrium constant (K_{ads}), free energy of adsorption (ΔG_{ads}), adsorption heat (ΔH_{ads}) and adsorption entropy (ΔS_{ads}) values were calculated and discussed. The potential of zero charge (PZC) of the MS in inhibited solution was studied by the EIS method, and a mechanism for the adsorption process was proposed. The results showed that 2MT performed excellent inhibiting effect for the corrosion of the MS. Finally, the high inhibition efficiency was discussed in terms of adsorption of inhibitor molecules and protective film formation on the metal surface. TGA results also indicated that the inhibitor film on the surface had a relatively good thermal stability.

1. Introduction

The adsorption of organic molecules at the metal/solution interface is of a great interest in surface science and can markedly change the corrosion resisting properties of metals. The protection of corroding surfaces prevents the waste of both resources and money during the industrial applications and it is vital for the extension of the lifetime of the equipment and limiting the dissolution of the toxic metals from the components into the environment. Therefore, the prevention from the corrosion of metals used in industrial applications is an important issue that must be dealt with. The use of inhibitors is one of the most practical methods for protecting against the corrosion and it is becoming increasingly popular. The organic molecules are recently used as corrosion inhibitors. The efficiency of these molecules is mainly dependent on their ability to be adsorbed on the metal surface, which results with the replacement of water molecules at a corroding interface [1]. In recent years, there is a considerable amount of effort devoted to find novel and efficient corrosion inhibitors and sulphur and/or nitrogen containing molecules have been found to be effective corrosion inhibitors [2–6].

The 2MT is a molecule that has practical applications in the plating solution of printed wiring board industry such as brightening and stabilization agents [7]. The chemically modified 2MT was used for the purpose of the selective adsorption of the heavy metal ions and reported to be very selective to Hg(II) ions in aqueous solutions [8]. A 2MT molecule has two sulphur atoms and one nitrogen atom as well as π electrons which are assumed to be active centre of adsorption. The corrosion inhibition effect of 2MT has not been studied as corrosion inhibitor in details. Wang et al. [9] was studied 2MT as inhibitor for the corrosion of low carbon steel in phosphoric acid solution by weight loss method. However, a detail study on the adsorption mechanism and inhibition effect of 2MT on the corrosion of MS has not been reported yet.

The aim of this study is to report on the inhibition effect of 2MT on the corrosion behavior of MS in 0.5 M HCl solution in both short and long immersion times and clarify its inhibition mechanism.

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doi:10.1016/j.electacta.2008.03.055

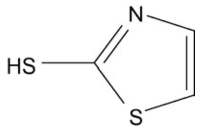

Fig. 1. The chemical structure of 2-mercaptothiazoline (2MT).

Table 1
Electrochemical parameters for the MS determined from polarization measurements in 0.5 M HCl and containing 1.0×10^{-2} M 2MT solutions

C_{inh} (M)	E_{corr} (V)	I_{corr} ($A\,cm^{-2}$) ($\times 10^{-5}$)	W_L ($g\,m^{-2}\,h^{-1}$)	IE%
Blank	−0.460	71.50	7.4482	
1.0×10^{-4}	−0.461	20.28	2.1126	71.6
5.0×10^{-4}	−0.459	19.90	2.0730	72.2
1.0×10^{-3}	−0.460	14.54	1.5146	79.7
5.0×10^{-3}	−0.446	10.02	1.0438	86.0
1.0×10^{-2}	−0.457	4.96	0.5167	93.1

2. Experimental

2.1. Preparation of electrodes

The working electrode was a cylindrical disc cut from an MS rod with following chemical composition (wt); C (0.21%), Si (0.36%), Mn (1.25%), P (0.025%), S (0.046%), Cr (0.16%), Ni (0.16%), Cu (0.41%), Mo (0.017%), Sn (0.017%), Al (0.003%), V (0.081%) and Fe (remainder). The preparation of working electrode before measurements is the same as described before [10]. The exposed surface area of the MS was 0.50 cm^2.

2.2. Test solutions

The tests were performed in 0.5 M HCl solution and containing various concentrations of 2MT, whose chemical structure is given in Fig. 1. An aggressive solution (0.5 M HCl) was prepared by dilution of 37% HCl. The concentration range of the inhibitor employed was varied from 1.0×10^{-2} M to 1.0×10^{-4} M. All the test solutions were prepared from analytical-grade chemical reagents in distilled water without further purification. For each experiment, a freshly prepared solution was used.

During the experiments, the test solutions were opened to air. For potentiodynamic polarization measurements, the test solutions were continuously stirred using a magnetic stirrer while all the others were performed under un-stirring conditions. The solution temperature was thermostatically controlled at a desired value.

2.3. Electrochemical measurements

A CHI 604 model computer controlled electrochemical analyzer (serial number: 6A721A) was used for the electrochemical measurements. A double-wall one-compartment cell with a three-electrode configuration was used. A platinum sheet (with 2 cm^2 surface area) and Ag/AgCl electrode were used as the auxiliary and the reference electrodes, respectively. All potential values were referred to this reference electrode. The working electrode was first immersed in the test solution and after establishing a steady state open circuit potential, the electrochemical measurements were performed. The polarization curves were potentiodynamically obtained in the potential ranges from −0.90 V to −0.10 V with a scan rate of 0.005 $V\,s^{-1}$. The EIS experiments were conducted in the frequency range of 100 kHz to 0.003 Hz at an open circuit potential by applying alternating current signal of 0.005 V peak-to-peak. The linear polarization measurements were carried out by recording the potential ±0.010 V around open circuit potential at a scan rate of 0.001 $V\,s^{-1}$. The polarization resistance (R_p) was determined from the slope of the obtained current–potential lines.

In order to investigate the mechanism of the inhibition and calculate the activation energy of the corrosion process, the polarization curves were obtained at various temperatures (25–55 °C) in the absence and the presence of 1.0×10^{-2} M 2MT. To determine the potential of zero charge of the MS, the impedance of the MS was determined at different potentials in 1.0×10^{-2} M 2MT containing 0.5 M HCl solutions.

The corrosion behavior of the MS in inhibited and uninhibited solutions with immersion time was also performed with immersion time up to 120 h. For this purpose, the potentiodynamic polarization, EIS, LPR, PZC, the hydrogen gas evolution ($V_{H_2} - t$) and the change of open circuit potential with immersion time ($E_{ocp} - t$) were utilized. During the long-term tests, the working electrode was immersed in a beaker which contains 200 mL test solution. After different immersion times, electrochemical measurements were performed under the un-stirring conditions. In the hydrogen gas evolution measurements, a burette was filled with 0.5 M HCl solution and turned over the working electrode. The initial volume of air in the burette was recorded and the volume of H_2 gas evolved from the corrosion reaction was monitored by the volume change in the level of the solution as a function of time. The same experiment was repeated in the presence of 1.0×10^{-2} M 2MT. The long-term tests were carried out at room temperature (∼25 °C) under un-stirring conditions.

2.4. SEM and AFM studies

In order to examine the changes in surface morphology of the electrodes covered with a thin film of 2MT, the electrodes were immersed in 200 mL 0.5 M HCl and 1.0×10^{-2} M 2MT containing 0.5 M HCl solutions. After 24 h and 120 h waiting time, the electrodes were removed from the cells, washed with distilled water and dried. The SEM images were taken using a Carl Zeiss Evo 40 SEM instrument at high vacuum and 10 kV EHT, AFM images were taken with Park SYSTEMS using non-contact mode.

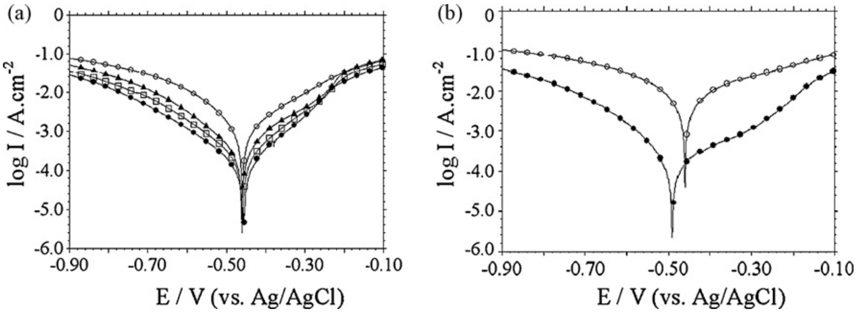

Fig. 2. Polarization curves for MS recorded after 1 h (a) and 120 h (b) of exposure time in 0.5 M HCl solution free (○) and containing 1.0×10^{-4} (▲), 1.0×10^{-3} (□) and 1.0×10^{-2} M (●) 2MT.