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Investigation of adsorption and corrosion inhibition of mild steel in hydrochloric acid solution by 5-(4-Dimethylaminobenzylidene)rhodanine

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ABSTRACT

The adsorption and corrosion inhibition of mild steel in 0.5 M HCl solution by 5-(4-Dimethylaminobenzylidene)rhodanine (DABRh) were investigated by electrochemical and scanning electron microscopy (SEM) techniques. It was found that DABRh has high inhibitory efficiency against the corrosion of mild steel in HCl solution. This compound is classified as the mixed type corrosion inhibitor with predominant control of cathodic reaction. The high inhibitory efficiency of DABRh was related with the adsorption of DABRh molecules at the meal/solution interface and a protective film formation. The surface inhibitor film was found to be very stable at low anodic and cathodic overpotentials.

1. Introduction

Acid solutions are generally used for removal of undesirable scale and rust on the metals, cleaning of boilers and heat exchangers, oil-well acidizing in oil recovery, and so on. [1–4]. HCl solution is one of the most widely used agents for these goals. However, iron and its alloys could be corroded during these applications which result in a waste of resources. Corrosion prevention systems favor the use of chemicals with low or no environmental impacts. The reduction in the corrosion rate of metals has numerous advantages such as saving of resources, economic benefits during the industrial applications, increasing the lifetime of equipment and decreasing the dissolution of toxic metals from the components into the environment. Therefore, the prevention of metals against corrosion is vital and must be dealt with. Commercial inhibitors are generally inorganic and some kind of organic compounds. However, the usage of some of them has been restricted due to the toxicity of their insufficient inhibitory efficiencies at low dosages [5–7]. In recent years, considerable amount of efforts have been devoted to find novel, healthy and efficient corrosion inhibitors. The use of organic inhibitors is one of the most practical methods for protection of metals against corrosion, and is becoming increasingly popular according to recent studies.

The existing data show that organic inhibitors act by adsorption and a film formation on the surface of metals. The adsorption of organic inhibitors on the metal surface can change the corrosion resistance properties of metals. Earlier studies have shown that organic compounds bearing heteroatoms with high electron density such as phosphorus, sulfur, nitrogen, oxygen or those containing multiple bonds, which are considered as adsorption centers, are effective inhibitors for the corrosion of metals [8–15]. The organic inhibitors are generally adsorbed on the metal surface through physical adsorption or chemical adsorption, which reduce the reaction area susceptible to corrosive attack [16,17].

Recently, we have focused on the inhibitory efficiencies of rhodanine and its derivatives. Our previous studies have shown that rhodanine is a good corrosion inhibitor for mild steel [18,19] and copper [20]. Some rhodanine azosulpha drugs were studied as corrosion inhibitors for the corrosion of 304 stainless steel in HCl solution [21]. It was reported that the presence of an extra acetate group in the rhodanine molecule enhances its inhibitory efficiency [22,23]. We have electrochemically polymerized rhodanine on Pt [24] and copper [25]. The results showed that this polymer has good corrosion protection ability. In this study, the adsorption and the inhibitory efficiency of DABRh against the corrosion of mild steel in 0.5 M HCl solution was investigated. DABRh molecule contains an extra dimethylamine benzene group in the rhodanine molecule. The presence of additional electron density in the benzene ring with the attached dimethylamine group is expected to cause an easier electron transfer from the functional groups to the metal surface, which provides greater adsorption ability and inhibitory efficiency. The large size and high molecular weight of DABRh molecule, in comparison to the

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rhodanine molecule, can also contribute to a greater inhibitory efficiency.

In order to determine the inhibitory efficiency of DABRh on the mild steel corrosion, some common electrochemical techniques and SEM were used in this study. The effect of temperature and the stability of the adsorbed inhibitor film were also investigated. The surface charge of mild steel in the inhibited solution was determined by electrochemical impedance spectroscopy (EIS) as well as a possible inhibition mechanism was discussed.

2. Experimental

2.1. Preparation of mild steel electrodes

The working electrode was mild steel, which was cut from a cylindrical mild steel rod to a length of about 5 cm. The chemical composition of mild steel (wt%) was 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 steel specimen was coated with polyester except for its bottom surface. The surface area of the steel exposed to the test solution was 0.50 cm^2. Before the measurements, the surface of mild steel was mechanically abraded using different grades of sand papers, which ended up with the 1000 grade. Then, the electrode was cleaned by washing with distilled water, acetone, distilled water, respectively, and immersed into the test solution quickly. After washing with each cleaning agent, the surface was dried with a filter paper.

2.2. Test solutions

The corrosion tests were performed in 0.5 M HCl solution in the absence and presence of various concentrations of DABRh ranging from 0.1 mM to 0.001 mM. The HCl solution was prepared by dilution of an analytical grade HCl solution (37%) with distilled water. The organic inhibitor, whose chemical structure is given in Fig. 1, was used as received. The electrochemical tests were carried out under air atmosphere without stirring the solutions. The temperature of the solutions was controlled thermostatically.

2.3. Electrochemical measurements

The electrochemical measurements were carried out using a CHI 660D A.C. Electrochemical Analyzer under computer control. For these tests, an electrochemical cell with three-electrode configuration was used. A platinum sheet (with 2 cm^2 total surface area) and an Ag/AgCl (3 M KCl) were used as the auxiliary and the reference electrodes, respectively. All potential values were referred to Ag/AgCl electrode. Before electrochemical measurements, the mild steel electrode was immersed into the corrosive solutions for 1 h in order to establish a steady-state open circuit potential (E_{ocp}). Then, EIS, linear polarization resistance (LPR) and potentiodynamic polarization measurements were carried out subsequently. The EIS experiments were realized in the frequency range from 100 kHz to 0.01 Hz at E_{ocp} with perturbation amplitude of 0.005 V peak-to-peak. The EIS experiments were also carried out at various potentials, and the surface charge of mild steel in the inhibited solution was determined. LPR measurements were carried out by recording the electrode potential ±0.010 V around E_{ocp} starting from cathodic potentials. The scan rate was 0.001 V s^{-1}. The polarization resistances (R_p) of mild steel in the test solutions were calculated from the slope of the obtained current–potential curves. The potentiodynamic polarization curves were conducted starting from cathodic potentials to the anodic domain with 0.005 V s^{-1} scan rate.

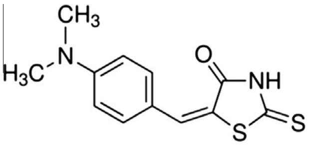

Fig. 1. Chemical structure of 5-(4-Dimethylaminobenzylidene)rhodanine.

In order to determine the effect of temperature on the inhibition efficiency, the potentiodynamic polarization measurements were carried out in 0.5 M HCl solution in the absence and presence of 0.1 mM inhibitor at different temperatures (298–328 K). The stability of the surface film was tested in 0.5 M HCl solution in the presence of 0.1 mM inhibitor by chronoamperomety (CA) under 100 mV anodic and cathodic overpotentials for 1 h. The similar tests were repeated in the absence of DABRh in order to make comparison with the presence of DABRh.

2.4. Scanning electron microscopy

The surface of mild steel after its exposure to 0.5 M HCl solution in the absence and presence of 0.1 mM DABRh for 24 h was examined by a Jeol model scanning electron microscopy (SEM) (JEOL 6510).

3. Results and discussion

3.1. Potentiodynamic polarization

The representative potentiodynamic polarization curves of the mild steel electrode, which were obtained in 0.5 M HCl solution in the absence and presence of various concentrations of DABRh, are given in Fig. 2. In order to obtain information about the kinetics of the corrosion, some electrochemical parameters, *i.e.*, corrosion potential (E_{corr}), corrosion current density (i_{corr}), weight loss (W) and inhibition efficiency ($\eta\%$) values were calculated from the corresponding polarization curves and the obtained data are given in Table 1. The $\eta\%$ was calculated using the following equation:

$$\eta\% = \left(\frac{i_{corr} - i'_{corr}}{i_{corr}}\right) \times 100 \tag{1}$$

In this equation, i_{corr} and i'_{corr} are corrosion current densities in the absence and presence of the inhibitor, respectively. The i_{corr} values were determined by the extrapolation of the linear portions of the anodic current–potential curves to the corresponding corrosion potentials. The W (g m^{-2} h^{-1}) was theoretically calculated using following equation.

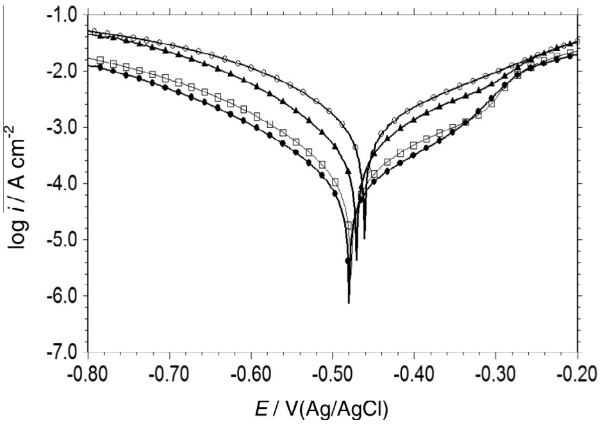

Fig. 2. Polarization curves of mild steel in 0.5 M HCl solution in the absence (○) and presence of 0.001 (▲), 0.01 (□) and 0.1 mM (●) DABRh.