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The inhibitive effect of 6-amino-*m*-cresol and its Schiff base on the corrosion of mild steel in 0.5 M HCl medium

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ABSTRACT

6-Amino-*m*-cresol (ACr) and newly synthesized Schiff base 2-(3-hydroxybenzylideneamino)-5-methylphenol (ACr–S) using ACr and salicylaldehyde have been investigated as inhibitors for corrosion of mild steel (MS) in 0.5 M hydrochloric acid. For this purpose; polarization curves measurements, electrochemical impedance spectroscopy (EIS) and linear polarization resistance (LP) techniques were utilized. Polarization curves reveal that both compounds are mixed type inhibitors and inhibition efficiency (%IE) increases with increasing concentration of compounds. CPE and polarization resistance (R_p) are derived from Nyquist plots obtained from AC impedance studies. The results of the electrochemical studies have illustrated that the inhibition efficiency of ACr–S is higher than ACr. Both ACr and ACr–S obeyed the Langmuir isotherm, and thermodynamic calculations revealed that ACr–S had larger adsorption constant and more negative free energy of adsorption with respect to ACr. The effect of exposure time on the corrosion behaviour of mild steel in the absence and presence of inhibitor over 168 h was also studied. Possible inhibition mechanism also discussed by establishing potential of zero charge (PZC) of ACr and ACr–S on mild steel surface. The greater inhibitive power of ACr–S may be due to presence of more π-electrons of an extra substituted phenyl group in the ACr–S molecule.

1. Introduction

Corrosion inhibitors are of great practical importance, being extensively employed in minimising metallic waste in engineering materials. The wide spread use of mild steel in a variety of petroleum applications, such as down hole tubular, flow lines and transmission pipelines are well known. Hydrochloric acid solutions are widely used in petroleum fields, for cleaning and descaling of iron and steel alloys [1].The use of inhibitors is one of the best-known methods of corrrosion protection. Organic compounds used as inhibitors act through a process of surface adsorption, so the efficiency of an inhibitor depends not only on the characteristics of the environment in which it acts, the nature of the metal surface and electrochemical potential at the interface, but also on the structure of the inhibitor itself, which includes the number of adsorption active centres in the molecule, their charge density, the molecule size, the mode of adsorption, the formation of metallic complexes and the projected area of the inhibitor on the metal surface [2]. Compounds with functional groups containing hetero-atoms, which can donate lone pair electrons are found to be particularly useful as inhibitors for metal corrosion [3–6]. Recently more study shows that the inhibitive effect is found to enhance several nitrogen containing organic compounds for mild steel in acid solutions. Organic nitrogen compounds which usually employed for their rapid action in acidic solutions specify the corrosion behaviour of iron and steel [2]. Compounds with π-bonds also generally exhibit good inhibitive properties by providing electrons to interact with metal surface [7–11]. Both features obviously can be combined within the same molecule such as Schiff bases.

In literature many studies have been reported for various metals such as iron [12], copper [13,14], zinc [15] and mild steel [16–18]. Schiff bases can conveniently be synthesized from relatively cheap starting materials. Its also reported that, Schiff bases show more inhibition efficiency than corresponding amine [19].

In the present paper, in order to obtain as effective inhibitors, ACr and synthesized Schiff base ACr–S have been studied by electrochemical techniques to investigate electrochemical behaviour of mild steel in 0.5 M HCl solution. Adsorption mechanism of studied compounds were also described by finding their PZC values.

2. Experimental

2.1. Inhibitors

The Schiff base compound was synthesized by a condensation reaction of amine with salicylaldehyde in ethanolic media. Schiff base was characterized by using FTIR

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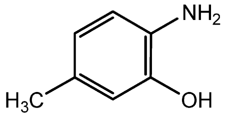
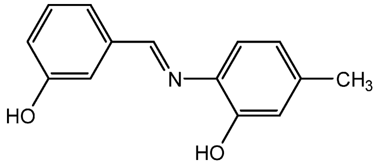
data; ν (cm^{-1}): 1633–1597 (C=N), 1290 (C—O) and melting point of the compound was found as 199.5 °C. The structure of amine, 6-amino-*m*-cresol (ACr), and synthesized Schiff base, 2-(3-hydroxybenzylideneamino)-5-methylphenol (ACr–S), were shown below:



6-amino-m-cresol (ACr)



2-(3-hydroxybenzylideneamino)-5-methylphenol (ACr-S)

2.2. Preparation of electrodes

The working electrode was prepared from a cylindrical mild steel (MS) rods having following chemical composition: C 0.7%, Mn 0.4%, Cu 0.12%, Si 0.05%, P 0.025%, S 0.025%, Sn 0.01%, Ni 0.009% and remainder iron. Samples were insulated with polyester resin such that the area exposed to solution was 0.24 cm^2. The surface preparation of the specimens was carried out using different grade emery papers up to 1200, degreased in acetone, washed with bi-distilled water.

2.3. Test solution

The test solution (0.5 M HCl) was prepared by dilution of analytical grade 37% HCl with double-distilled water. The concentration range of inhibitors employed was varied from 1.0×10^{-4} M to 5.0×10^{-3} M.

2.4. Polarization measurements

Electrochemical measurements were carried out in a conventional three-electrode system. An Ag/AgCl electrode was used as the reference electrode and a platinum sheet was used as the counter electrode. Before each experiment, the working electrode was immersed in the test cell for 2 h.

Potentiodynamic curves were obtained at open circuit potential (E_{ocp}) separately in anodic and cathodic direction at a scan rate of 2 mV s^{-1}. The working electrode was polarized from the E_{ocp} in anodic direction, then taken out from the cell and pretreated again followed the cathodic polarization. All the experiments were done at room temperature in solutions open to the atmosphere under unstirred conditions.

Corrosion current I_{cor} were calculated from Tafel extrapolation methods (I_{cor}^{Ex}) and the Stearn–Geary relationship (I_{cor}^{St}).

2.5. Linear polarization measurements (LP)

In order to determine the polarization resistance, R_p the potential of the working electrode was polarized ±10 mV from open circuit potential at a scan rate of 1 mV s^{-1}. The polarization resistance was calculated from the slope of the potential versus current plots.

2.6. Impedance measurements (EIS)

Electrochemical impedance measurements were carried out at open circuit potential in the frequency range of 10^5–10^{-2} Hz, after 2 h of immersion time, by amplitude of 5 mV. All electrochemical experiments were recorded using an CHI 660B electrochemical analyzer with 64721A serial number coupled to a computer and interpreted using ZView software from Scribner Associates, Inc.

3. Results and discussion

3.1. Potentiodynamic measurements

Polarization curves were obtained for mild steel in 0.5 M HCl solution with and without inhibitors. Tafel lines which obtained in various concentrations of ACr and ACr–S solutions were shown in Figs. 1 and 2, respectively. Both ACr and ACr–S decreased the anodic current which is related with dissolution of MS. Prepared Schiff base show more inhibitive effect more than corresponding amine.

In the presence of ACr after polarization about −0.28 V positive direction, a little inhibition was shown (Fig. 1), whereas ACr–S seem to be more effective (Fig. 2). This indicates that after −0.28 V a dissolution of metal leads to desorption of the adsorbed inhibitor from the electrode surface, having the desorption rate is higher than its adsorption rate. But in case of ACr–S inhibition still could be seen after desorption potential.

The introduction of both ACr and ACr–S into 0.5 M HCl solution with various concentrations also affects the cathodic parts of polarization curves. The curves give rise to parallel Tafel lines which indicate that hydrogen evolution reaction is activation controlled, and the inhibiting action is simply blocking of the metal surface.

Electrochemical corrosion kinetic parameters, such as corrosion potential (E_{cor}), cathodic and anodic Tafel slopes (b_a, b_c), corrosion current (I_{cor}) which obtained by two different ways (Tafel extrapolation method and Stearn–Geary equation), corrosion rate (CR) and weight loss (WL) are given in Table 1. Percentage of inhibition efficiency (IE%) are also given in the same table. IE% were calculated from polarization measurements according to the equation given below:

$$\text{IE}\ (\%) = \left(\frac{I_{cor} - I_{cor(inh)}}{I_{cor}}\right) \times 100 \qquad (1)$$

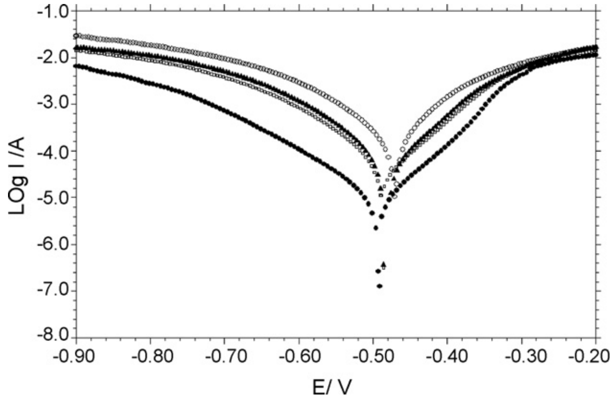


Fig. 1. Polarization curves of MS obtained in 0.5 M HCl (○), 5×10^{-3} M (●), 1×10^{-3} M (□) and 1×10^{-4} M (▲) ACr containing solutions.

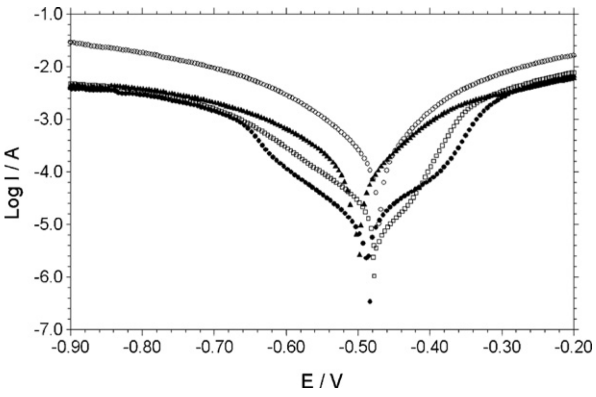


Fig. 2. Polarization curves of MS obtained in 0.5 M HCl (○), 5×10^{-3} M (●), 1×10^{-3} M (□) and 1×10^{-4} M (▲) ACr–S containing solutions.