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Inhibition activity of new thiazole hydrazones towards mild steel corrosion in acid media by thermodynamic, electrochemical and quantum chemical methods

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ABSTRACT

The mild steel anti-corrosion potential by newly synthesized thiazole hydrazones, 4-(4-methoxy-phenyl)-thiazole-2-carboxylic acid benzylidene-hydrazide (TH-1), 4-(4-methoxy-phenyl)-thiazole-2-carboxylic acid (3-hydroxy-benzylidene)-hydrazide (TH-2) and 4-(4-methoxy-phenyl)-thiazole-2-carboxylic acid (4-hydroxy-benzylidene)-hydrazide (TH-3) in 0.5 M hydrochloric acid was studied by gravimetric and electrochemical techniques. Thermodynamic parameters were evaluated for activation and adsorption processes. Adsorption of the inhibitors followed Langmuir isotherm. Electrochemical measurements showed that addition of inhibitors simultaneously decreased corrosion current density and double layer capacitance but increased charge transfer resistance. Potentiodynamic polarization studies revealed that thiazole hydrazones effectively suppressed both the anodic and cathodic processes of mild steel corrosion in acid solution and hence acted as mixed-type inhibitors. Quantum chemical parameters like E_{HOMO}, ΔE, softness and hardness were very well correlated with experimental data. SEM characterized the film formed on the mild steel.

1. Introduction

Mild steel (MS), owing to its high mechanical strength and low cost, has established itself as one of the leading materials in construction, pipelines and vessels in oil production and refinery plants. The use of acid media in the study of corrosion of MS has become important because sulfuric acid and hydrochloric acid are generally used for pickling in industrial cleaning and acid descaling [1]. Exposure of MS to mineral acids results in corrosion leading to the deterioration of surface affecting its durability. Attempts have been made to improve surface properties of MS by chemical treatments [2], plating [3], metal coatings [4], organic coatings [5], corrosion inhibitors [6], etc.

The contribution of organic compounds in inhibiting MS corrosion is remarkable particularly those containing more number of hetero atoms and conjugated systems [7,8]. Hydrazones are effective in inhibiting corrosion because their structure contains two nitrogen atoms and an imine bond which act as active adsorption centers. Hydrazones have been largely tested for corrosion inhibition properties and biological activities due to their reactivity towards both electrophiles and nucleophiles. The selection of thiazole hydrazones as corrosion inhibitors in the present study is based on the fact that they exhibit wide range of biological activities like antiglycation [9], antioxidant [10], antimicrobial [11] and anti-inflammatory [12]. Hydrazones have been established as corrosion inhibitors in acid and salt media. Sherif and co-workers studied anti-corrosion potential of some new hydrazone derivatives on Cu corrosion in NaCl medium and obtained maximum percentage inhibition efficiency {IE (%)} of 78 [13]. The efficiency of some 2-heterocarboxaldehyde-2′-pyridyl-hydrazones as inhibitors against acid dissolution of Al was studied by El-Tagouri and co-workers to get maximum IE (%) of 85 [14]. Some water-soluble hydrazones were tested as inhibitors against C-steel corrosion in acid medium by Moussa and co-workers to get maximum efficiency of 95% [15]. Fouda and co-workers studied pyrazole hydrazones [16], hydroxyphenyl hydrazones [17] and N-3-hydroxyl-2-naphtholyl hydrazone derivatives [18] as corrosion inhibitors and obtained promising results. From the literature survey it was clear that hydrazones successfully inhibited corrosion, therefore thiazole hydrazones were chosen as inhibitors in the present study.

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In continuation of our previous work [19–21], we report the synthesis of three thiazole hydrazones, namely, 4-(4-methoxy-phenyl)-thiazole-2-carboxylic acid benzylidene-hydrazide (TH-1), 4-(4-methoxy-phenyl)-thiazole-2-carboxylic acid (3-hydroxy-benzylidene)-hydrazide (TH-2) and 4-(4-methoxy-phenyl)-thiazole-2-carboxylic acid (4-hydroxy-benzylidene)-hydrazide (TH-3), along with their characterization using FTIR, ^{1}H NMR and LCMS and also testing their efficiency as corrosion inhibitors using weight loss, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization techniques. Protective film formed on the MS surface was characterized by scanning electron microscope (SEM). Results of the experiments were confirmed by quantum chemical parameters like energy of highest occupied molecular orbital (E_{HOMO}), energy of lowest unoccupied molecular orbital (E_{LUMO}), energy gap (ΔE), hardness (η), and softness (σ).

2. Experimental

2.1. Materials and sample preparation

Corrosion tests were performed on MS specimens of following composition (wt%): C - 0.051; Mn - 0.179; Si - 0.006; P - 0.005; S - 0.023; Cr - 0.051; Ni - 0.05; Mo - 0.013; Ti - 0.004; Al - 0.103; Cu - 0.050; Sn - 0.004; B - 0.00105; Co - 0.017; Nb - 0.012; Pb - 0.001 and the remaining being Fe. MS specimens used in gravimetric and electrochemical experiments were mechanically cut into 2 cm × 2 cm × 0.1 cm and 5 cm × 2 cm × 0.1 cm respectively in dimensions, abraded with SiC emery papers of different grades, degreased with acetone and dried with a clean tissue paper. For EIS and polarization studies, the MS specimens were implanted in epoxy resin and a geometrical surface area of 1 cm^2 was exposed to the electrolyte. Concentration range of 0.6–2.4 mM was prepared from stock solution made by dissolving appropriate amount of inhibitor in 0.5 M HCl. Melting range of the inhibitors was determined using Veego Melting Point VMP III apparatus.

2.2. Synthesis of inhibitors

Scheme for the synthesis of TH-1, TH-2 and TH-3 is outlined in Fig. 1. Detailed procedure for the synthesis of inhibitors and spectral data are provided briefly in Section 1 of the supplementary data.

Synthesis of 4-(4-methoxy-phenyl)-thiazole-2-carboxylic acid ethyl ester (Compound 3): Compound 3 was synthesized from 2-bromo-1-(4-methoxy-phenyl)-ethanone (compound 1) and amino-thioxo-acetic acid ethyl ester (compound 2) according to the reported procedure [22].

Synthesis of 4-(4-methoxy-phenyl)-thiazole-2-carboxylic acid hydrazide (Compound 4): Reported procedure [23] from literature was used to synthesize compound 4 from compound 3.

Syntheses of 4-(4-methoxy-phenyl)-thiazole-2-carboxylic acid benzylidene-hydrazide (Compound 5), 4-(4-methoxy-phenyl)-thiazole-2-carboxylic acid (3-hydroxy-benzylidene)-hydrazide (Compound 6) and 4-(4-methoxy-phenyl)-thiazole-2-carboxylic acid (4-hydroxy-benzylidene)-hydrazide (Compound 7).

Compounds 5, 6 and 7 were synthesized by reacting compound 4 with benzaldehyde, 3-hydroxy benzaldehyde and 4-hydroxy benzaldehyde, respectively according to the reported procedure [24]. Yields of products 5, 6 and 7 are 81%, 79% and 83%, respectively. Melting range of compounds 5, 6 and 7 are 169-171 °C, 175–177 °C and 170–173 °C, respectively.

2.3. Weight loss measurements

MS specimens were immersed in 0.5 M HCl without and with varying amounts of the inhibitors for 6 h in a thermostatically controlled water bath (Weber limited, Chennai, India) (accuracy ± 0.2 °C) at constant temperature under aerated condition. The specimens were removed after 6 h of immersion, thoroughly cleaned in distilled water, immersed in acetone for 5 s, cleaned with a tissue paper and weighed. Weight loss of the specimens was determined by analytical balance (Sartorius, precision ± 0.1 mg). Mean weight loss from three specimens was considered.

2.4. Electrochemical measurements

Potentiodynamic polarization was carried using CHI660D and EIS experiments were carried out using CHI608E electrochemical workstation. The three-electrode cell consisting of silver/silver chloride reference electrode, a platinum auxiliary electrode and the working MS electrode with 1 cm^2 exposed areas was used. Specimens were treated similar to gravimetric measurements. For polarization and impedance measurements, the MS specimens were inserted in epoxy resin to expose a geometrical surface area of 1 cm^2 to the electrolyte. The electrochemical tests were performed at 303 K with synthesized thiazole hydrazones at optimum concentration. Potentiodynamic polarization measurements were recorded by changing the electrode potential from -200 mV to +200 mV, related to the open circuit potential, with the scanning rate of 10 mV s^{-1}. Prior to EIS measurements open circuit potential was stabilized till half an hour. EIS data was recorded using AC sinusoidal signal at the frequency range 0.01 to 1,00,000 Hz with amplitude 0.005 V. Simulation of EIS data was done using Zsimpwin software.

2.5. Quantum chemical calculations

The geometrical optimization of thiazole hydrazones was done by Ab initio method at 6-31G** basis set for all atoms. For energy minimization, 1.0 convergence limit and 1.0 k cal/A mol rms gradient was maintained. The Polak–Ribiere conjugate gradient algorithm which is very fast and precise was used for geometrical optimization. The HYPERCHEM 7.52 (Hypercube Inc., Florida, USA, 2003) professional software was employed for all calculations.

2.6. Scanning electron microscopy (SEM)

The SEM images were taken using Zeiss electron microscope with the working voltage of 15 kV and with the working distance of 10 mm. In SEM micrographs, the specimens were exposed to 0.5 M HCl in the absence and presence of three inhibitors at optimum condition after 6 h of immersion. SEM images were taken for polished MS specimen and specimen immersed in acid solution with inhibitors and also without inhibitors.

3. Results and discussion

3.1. Weight loss measurements

3.1.1. Effect of inhibitor concentration

The effect of concentration of thiazole hydrazones on MS corrosion was studied in the concentration range 0.6–2.4 mM by weight loss method at 303 K. Corrosion rate (C_R) and inhibition efficiency {*IE (%)*} were calculated using the following formulae.

$$C_R = \frac{\Delta W}{St} \quad (1)$$

$$IE\ (\%) = \frac{(C_R)_a - (C_R)_p}{(C_R)_a} \times 100 \quad (2)$$

where, ΔW is the weight loss, S is the surface area of the specimen (cm^2), t is the immersion time (h), $(C_R)_a$ and $(C_R)_p$ are corrosion rates in the absence and presence of the inhibitor, respectively. Variation of *IE (%)* with various concentrations is depicted in

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