



Effect of electron donating functional groups on corrosion inhibition of mild steel in hydrochloric acid: Experimental and quantum chemical study



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ABSTRACT

The corrosion inhibition performance of three triazine derivatives namely 4-((2-(5,6-diphenyl-1,2,4-triazin-3-yl)hydrazineylidene)methyl)-N,N-dimethylaniline (HT-1), 3-(2-(4-methoxybenzylidene)hydrazineyl)-5,6-diphenyl-1,2,4-triazine (HT-2) and 2-(2-(5,6-diphenyl-1,2,4-triazin-3-yl)hydrazineylidene)methylphenol (HT-3) on mild steel corrosion in 1M HCl has been studied using gravimetric method, electrochemical impedance spectroscopy (EIS), potentiodynamic polarization, scanning electron microscopy (SEM), Density functional theory (DFT) and molecular dynamics simulation. The corrosion inhibition efficiencies at optimum concentration (80 mg L⁻¹) are 98.6% (HT-1), 97.1% (HT-2) and 94.3% (HT-3) respectively at 308 K. The corrosion inhibition efficiency increases with increase in concentration and decreases with increase in temperature. The adsorption of HTs on the surface of mild steel obeyed Langmuir isotherm. Potentiodynamic polarization study confirmed that inhibitors are mixed type with cathodic predominance. SEM analysis confirmed that metal surface is smooth in presence of inhibitors. Quantum chemical calculation and Molecular dynamics simulation further support the experimental findings.

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1. Introduction

Mild steel is an important material used in petrochemical, oil, gas, nuclear, pulp and paper industries for the construction of reaction vessels, storage tanks and pipelines [1, 2]. A common way to remove rust and oxides from the surface of mild steel is to clean the metal in an acid bath which is known as pickling. However, the pickling solution is quite corrosive and the use of an organic inhibitor is one of the most practical methods for protection of the metal surface against corrosion. These organic inhibitors are added in small amounts to reduce and retard the corrosiveness of the environments [3–5]. The adsorption ability and efficiency of the inhibitors is based on their chemical composition, molecular

structure, type of functional groups and their attractions towards the steel surface [6].

Recently, various research papers have been published on the study of corrosion inhibition of mild steel using heterocyclic compounds having electron donating and withdrawing functional groups [7–12]. Today's scenario demands the replacement of toxic corrosion inhibitors with environment-friendly chemicals [13,14]. So, in view of this triazine based hydrazone derivatives have been synthesized and tested as corrosion inhibitors due to their pharmaceutical and biological activities [15,16].

In the present time it becomes necessary to find out an alternative route where we can predict which molecule behaves as a good corrosion inhibitor and which are not. In view of above, computer simulation (e.g.; Density Functional Theory (DFT) and Molecular dynamics (MD) simulation) are the most authentic technique which has enormous advantages of evaluating microcosmic inhibition performance and exploration of their mechanism [20,21].

Herein, the main stress is focused on the corrosion inhibition performance of electron donating functional groups

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present in the synthesized triazine based hydrazone derivatives namely 2, 4-((2-(5,6-diphenyl-1,2,4-triazin-3-yl) hydrazineylidene) methyl)-N,N-dimethylaniline (HT-1), 3-(2-(4 methoxybenzylidene) hydrazineyl)-5,6-diphenyl-1,2,4-triazine (HT-2) and, 2-(2-(5,6-diphenyl-1,2,4-triazin-3-yl) hydrazineylidene) methyl phenol (HT-3) on mild steel in 1M HCl. The investigation of corrosion inhibition efficiency and mechanism of inhibition were carried out by gravimetric and electrochemical techniques such as electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization. The morphology of the steel surface was studied using SEM measurements. Finally the experimental results were justified using quantum chemical calculation and molecular dynamics simulation.

2. Experimental details

2.1. Materials and methods

The mild steel used for gravimetric and electrochemical experiments has following composition (wt%): 0.076 C, 0.012 P, 0.026 Si, 0.192 Mn, 0.050 Cr, 0.135 Cu, 0.023 Al, 0.050 Ni and the remainder iron. Mild steel strips with dimension of 2.5 cm × 2 cm × 0.046 cm were used for gravimetric experiments and for electrochemical experiments; strips having dimensions 2.0 cm × 1.0 cm were used. The exposed area of steel strip in acid solution for electrochemical experiments was 1 cm².

The surface finishing and cleaning of mild steel coupons were done according to the NACE Recommended Practice like RP-0775 and ASTM G-1 & G-4 for weight-loss studies. Also the steel strips were polished to mirror-like finish using different grades of silicon carbide paper (600–1200). The steel specimens were washed with double distilled water, acetone and dried at room temperature and finally, enclosed in sealed water-proof bags and stored in desiccators. The test solution of 1 M HCl was prepared by diluting 37% HCl with double distilled water.

2.2. Inhibitor synthesis

The synthesis of inhibitors was carried out in three steps according to the literature [17] and is as follows:

(a) Synthesis of 5,6-Diphenyl-4H-[1,2,4]triazine-3-thione

In a round bottom flask, benzil (1 mmol) was dissolved in glacial acetic acid and was added to a solution of thiosemicarbazide (1 mmol) dissolved in hot water. The obtained mixture was refluxed for 4 h, and the precipitate was filtered while the solution was hot. The orange crystals obtained were recrystallized from ethanol to give reddish crystals.

(b) Synthesis of 3-Hydrazinyl-5,6-diphenyl-1,2,4-triazine

A mixture of 5,6-diphenyl-4H-[1,2,4]triazine-3-thione (1 mmol) and hydrazine hydrate (1 mmol) in ethanol was taken in a round bottom flask and refluxed for 4 h, until H₂S evolution stopped. The excess hydrazine hydrate was neutralized by adding drop wise acetic acid into reaction mixture. The mixture was cooled. The precipitate was filtered off and recrystallized from ethanol to give yellowish crystals.

(c) Synthesis of compounds (HT-1, HT-2 and HT-3)

In round bottom flask 3-hydrazinyl-5,6-diphenyl-1,2,4-triazine (1 mmol) was dissolved in ethanol and the respective aldehyde (1 mmol) were added into it and refluxed for 2 h with stirring. The precipitates obtained were filtered off and recrystallized from ethanol to yield the final products.

All the three synthesized triazine based hydrazone derivatives were characterized by melting point, IR, ¹H NMR and ¹³C NMR. The synthesis scheme is shown in Fig. 1 and the molecular structure, abbreviations and spectral data are tabulated in Table 1. The ¹H

NMR, ¹³C NMR and IR spectra are given in supplementary file (S1, S2, and S3).

2.3. Spectral data for inhibitors

(a) 4-((2-(5, 6-diphenyl-1, 2, 4-triazin-3-yl) hydrazineylidene) methyl)-N,N-dimethyl aniline (HT-1) m.p. 262–265 °C; IR (KBr cm⁻¹) 3347, 3181, 3002, 2866, 2861, 1489, 1602

¹H NMR (500 MHz, DMSO) δ (ppm) 11.60, (1H, NH), 9.71 (1H, = CH-), 7.55 (2H, Ar-H), 7.46 (3H, Ar-H), 7.33–7.37 (7H, Ar-H), 6.78 (2H, Ar-H), 2.98 (6H, CH₃);

¹³C NMR (DMSO, ppm): 189.91, 157.25, 154.23, 151.10, 150.14, 145.08, 137.08, 130.15, 129.42, 128.96, 128.29, 128.25, 128.23, 127.95, 124.48, 122.13, 111.87, 111

(b) 3-(2-(4 methoxybenzylidene) hydrazineyl)-5,6-diphenyl-1,2,4-triazine (HT-2) m.p. 268–270 °C; IR (KBr cm⁻¹) 3375, 3185, 3010, 2833, 1608, 1461

¹H NMR (500 MHz, DMSO) δ (ppm) 11.78, (1H, NH), 8.25 (1H, = CH-), 7.61 (2H, Ar-H), 7.45 (3H, Ar-H), 7.37 (7H, Ar-H), 7.00 (2H, Ar-H), 3.78 (3H, CH₃);

¹³C NMR (DMSO, ppm): 160.34, 158.6, 156.38, 150.61, 143.94, 136.18, 135.97, 130.19, 129.43, 128.95, 128.38, 128.24, 128.21, 128.20, 127.34, 114.32, 55.28

(c) 2-(2-(5,6-diphenyl-1,2,4-triazin-3-yl)hydrazineylidene) methylphenol (HT-3) m.p. 274–276 °C; IR (KBr cm⁻¹) 3418, 3334, 3075, 2867, 1417, 1607

¹H NMR (500 MHz, DMSO) δ (ppm) 1H-NMR (DMSO, ppm): 12.28, (1H, NH), 11.46, (1H, OH), 8.52 (1H, = CH-), 7.46 (3H, Ar-H), 7.44 (1H, Ar-H), 7.40–7.42 (2H, Ar-H), 7.37–7.48 (5H, Ar-H), 7.24 (1H, Ar-H), 6.91–6.95 (2H, Ar-H); ¹³C NMR (DMSO, ppm): 158.10, 157.15, 156.50, 151.12, 145.05, 136.10, 135.85, 130.63, 130.45, 129.47, 129.10, 128.58, 128.32, 119.35, 118.91, 116.42

2.4. Corrosion measurement methods

2.4.1. Gravimetric method

In gravimetric experiments, pre-weighted mild steel strips were immersed in 1 M HCl solution for 12 h. The below equations were used for the calculation of corrosion rate (C_R) and inhibition efficiency (η%):

$$C_R = \frac{87.6(w_a - w_p)}{\rho A t} \quad (1)$$

$$\eta\% = 100 \left(\frac{w_a - w_p}{w_a} \right) \quad (2)$$

where w_a and w_p are weight loss in absence and presence of inhibitors, respectively, ρ is the density of iron, A is the area (cm²) of the mild steel strip and t is the immersion time (h). The corrosion rate was further converted to the other unit i.e. mm y⁻¹ using the conversion factor [18].

The experiment was carried out at 308–338 K.

2.4.2. Electrochemical studies

Electrochemical impedance spectroscopy (EIS) and polarization measurements were performed under static conditions using Gamry Potentiostat/Galvanostat (Model G-300) instrument. The analysis of data was done using Gamry Echem Analyst 5.5 software. The tests were conducted at

308 K. EIS and polarization was implemented in a three-electrode cell including mild steel sample as working electrode, saturated calomel as reference electrode and graphite as counter electrode. Before each electrochemical experiment the working electrode was immersed in the test solution for 30 min, in order to attain a stable open circuit potential.

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