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Pyranpyrazole derivatives as novel corrosion inhibitors for mild steel useful for industrial pickling process: Experimental and Quantum Chemical study

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ABSTRACT

In the present work three new corrosion inhibitors namely ethyl 6-amino-3-methyl-4-(*p*-tolyl)-2,4-dihydropyrano[2,3,C]pyrazole-5-carboxylate (EPP-1), ethyl 6-amino-3-methyl-4(phenyl)-2,4-dihydropyrano[2,3,C]pyrazole-5-carboxylate (EPP-2), ethyl 6-amino-3-methyl-4-(3-nitrophenyl)-2,4-dihydropyrano[2,3,C]pyrazole-5-carboxylate (EPP-3) were prepared, characterized and their corrosion inhibition properties on mild steel were investigated using gravimetric, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The surface morphology of the mild steel was examined using scanning electron microscopy (SEM) and atomic force microscopy (AFM). EPP-1 exhibited highest efficiency of 98.8% at 100 mg/L. AFM and SEM studies confirmed the formation of adsorbed film on the metal surface. The inhibitors followed the Langmuir adsorption isotherm. Density functional theory (DFT) was used to understand donor–acceptor relationship between inhibitors and metal. The orientation and binding energy of inhibitor molecules were investigated using molecular dynamic simulation (MD). A good relationship was obtained between theoretical and experimental results.

1 Introduction

Industrial processes such as pickling, descaling, cleaning often involve mineral acids. Hydrochloric acid is commonly used as an efficient pickling agent in chemical industry in general and steel industry in particular for the removal of rust, scale, cleaning etc. [1–3]. In order to minimize the metal dissolution organic compounds containing heteroatoms are often used as corrosion inhibitors [4–7]. Nitrogen containing heterocyclic compounds such as imidazole derivatives [8,9], pyrimidine derivatives [10,11], pyrazole derivatives [12,13] have been reported as effective corrosion inhibitors for hydrochloric acid medium. These heterocyclic compounds are adsorbed on the metal surface through pi electron and non bonding electrons present in the inhibitors molecules and inhibit corrosion [14–16].

Pyranopyrazols are important class of compounds that includes pharmaceuticals and exhibit various biological activities like anticancer, anti bacterial and anti inflammatory activities. Because of their wide range of pharmaceuticals applications they are produced in large quantity [17–19]. Survey of literature showed there are a few reports on use of pyranopyrazole derivatives as corrosion inhibitors for mild steel in hydrochloric acid. Yadav et al. [20,21] reported 5-carbonitrile substituted dihydropyranopyrazole derivatives as corrosion inhibitor. These compounds exhibited 88–98% inhibition efficiency at 300 mg/L. DFT and MD studies have been used to study the chemical reactivity and adsorption behavior of the inhibiting molecules on metal surface [22].

In the present work we have studied the corrosion inhibition performance and adsorption behavior of three 5-carboxylate functionalized pyranpyrazole derivatives namely ethyl 6-amino-3-methyl-4-(*P*-tolyl)-2,4-dihydropyrano[2,3]pyrazole-5-carboxylate (EPP-1), ethyl 6-amino-3-methyl-4-(phenyl)-2,4-dihydropyrano[2,3]pyrazole-5-carboxylate (EPP-2), ethyl 6-amino-3-methyl-4-(3-nitrophenyl)-2,4-dihydropyrano[2,3]pyrazole-5-carboxylate (EPP-3) for mild steel in 1 M hydrochloric acid solution using gravimetric method, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization methods. Surface morphology was examined by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The experimental results were

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further supported by using density functional theory (DFT) and molecular dynamic simulation (MD) methods. These compounds have been reported as corrosion inhibitors first time. The selection of these compounds as corrosion inhibitors is based on the basis of following structural features, oxygen containing pyran is fused with pyrazole ring which contains two N atoms. In addition to this two functional groups such as NH_2 and caroxylate group are attached with pyrano-pyrazole ring. All these structural features favors adsorption of inhibiting molecule on the metal surface there by giving high inhibition effect. The investigated inhibitors exhibited more than 98% efficiency at 100 mg/L. The corrosion inhibition efficiency of synthesized pyranpyrazole derivatives was also compared with hexamine inhibitor which is used in steel industry for pickling. It gave 90% inhibition efficiency at 100 mg/L. Also the use of hexamine is not safe due to its toxicity which limits its applications.

Experimental

Material and test solution

The tested inhibitors were synthesized as reported in the literature [23]. To a stirred aqueous mixture of hydrazine hydrate 96% (2 mmol) and ethyl acetoacetate (2 mmol), aromatic aldehyde (2 mmol), ethyl cyanoacetate (2 mmol) and triethylamine (1 ml) were added successively at room temperature with vigorous stirring for 20–30 min. The precipitated solid was filtered, washed with water and the product obtained was purified by recrystallization from ethanol. The synthetic scheme is shown in Fig. 1. The molecular structure, abbreviation and spectral data are tabulated in Table 1.

Mild steel sample containing composition (in 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 are used for gravimetric and the electrochemical measurements. The mild steel coupons were abraded with (600, 800, 1000 grade) silicon carbide papers, cleaned with acetone and dried at room temperature. The test solution 1 M HCl was prepared by diluting 37% HCl with double distilled water.

Gravimetric measurement

The dimensions of the mild steel coupons used in gravimetric tests are 2.5 cm × 2.0 cm × 0.046 cm. Gravimetric experiment was conducted by placing the coupons into the test solutions for 3 h, thereafter the samples were taken out, cleaned with distilled water, dried and weighed. The corrosion rates C_R (mg cm^2 h^{-1}) were calculated using equations.

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

Here, W is the weight loss of mild steel coupon, A is the total area of mild steel coupon and t is immersion time (3 h). With the calculated corrosion rate, the inhibition efficiency *ENTITY NOT DEFINED !!!*% was calculated as follows:

$$\eta\% = \frac{C_R - C_{R(i)}}{C_R} \times 100 \quad (2)$$

Surface coverage (θ) values were calculated by the following equation:

$$\theta = \frac{C_R - C_{R(i)}}{C_R} \quad (3)$$

Electrochemical measurement

The electrochemical study was conducted in the three-electrode cell assembly, using mild steel strip as working electrode (with an exposed area of 1 cm^2), graphite rod as counter electrode and saturated calomel electrode (SCE) as reference electrode respectively. The electrochemical measurements were carried out using a Gamry Potentiostat/Galvanostat (Model G-300) connected to a personal computer with EIS software Gamry Instruments Inc., USA. The electrochemical experiments were analyzed by electrochemical software Echem Analyst 5.5 Software package. The EIS measurement was carried in the frequency range of 10^6 Hz–10^{-2} Hz at open circuit potential (OCP). All the experiments were performed after immersion of mild steel for 30 min in 1 M HCl in the absence and presence of inhibitors. Potentiodynamic polarization curves were obtained by shifting the electrode potential automatically from −250 mV to +250 mV vs. OCP at a scan rate of 1 mV/s. All electrochemical experiments were performed at 308 K temperature.

Surface analysis

The surface of mild steel coupons was analyzed using scanning electron microscope (SEM) and atomic force microscope (AFM) by immersing the metal in 1 M HCl solution in the absence and presence of inhibitors for 24 h at 308 K. SEM images were performed at the magnification of 5K× and accelerating voltage of 5K V using a Ziess Evo 50 XVP instrument. AFM analysis was done using NT-MDT multimode, Russia, controlled by solver scanning probe microscope controller.

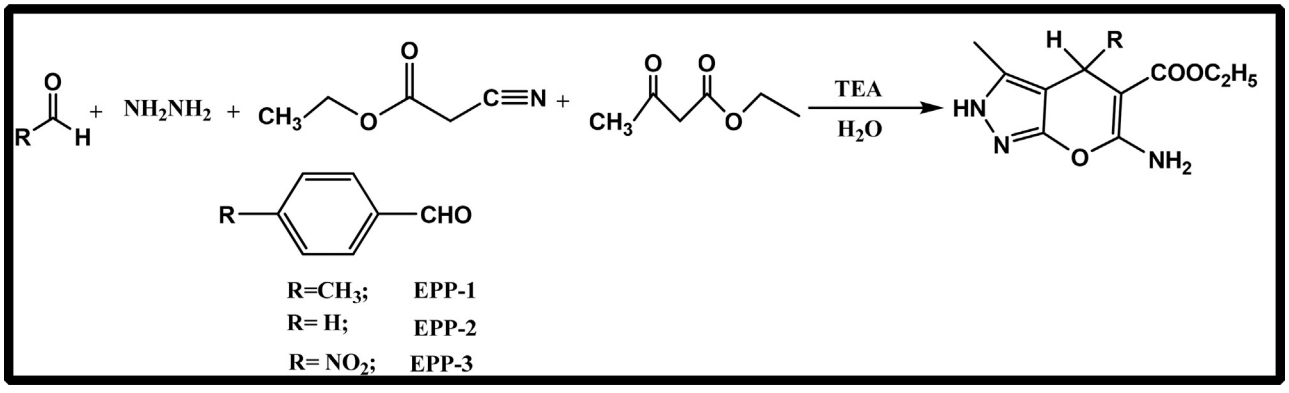

Fig. 1. Synthetic route of studied inhibitors.