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Corrosion inhibition of mild steel in hydrochloric acid by some pyridine derivatives: An experimental and quantum chemical study

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ABSTRACT

The adsorption and corrosion inhibition effect of three pyridine derivatives namely 2-amino-6-methoxy-4-(4-methoxylphenyl) pyridine-3,5-dicarbonitrile (PC-1), 2-amino-6-methoxy-4-(4-methylphenyl) pyridine-3,5-dicarbonitrile (PC-2) and 2-amino-6-methoxy-4-phenylpyridine-3,5-dicarbonitrile (PC-3) on mild steel in 1 M HCl was investigated using gravimetric, electrochemical impedance spectroscopy, potentiodynamic polarization techniques and quantum chemical study. PCs are mixed-type inhibitor mainly cathodic. Activation energy (E_a), equilibrium constant (K_{ads}), free energy of adsorption (ΔG°_{ads}) were calculated and discussed. The studied inhibitors (PCs) obeyed Langmuir's adsorption isotherm. Protective film of PCs on mild steel surface was investigated by using SEM and EDX. Quantum chemical parameters were carried out in the framework of the density functional theory (DFT).
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Introduction

Mild steel is widely used in fabrication of reaction vessels, storage tanks and petroleum refineries. Corrosion of mild steel is a fundamental academic and industrial concern that has received a considerable amount of attention [1]. Among numerous corrosion prevention measurements, the use of inhibitors is one of the most efficient alternatives to protect metals against corrosion, especially in acidic media due to its advantages of economy, high efficiency, and wide applicability [2–4].

The pyridine nucleus is one of the most important *N*-heterocycles found in natural products, pharmaceuticals and functional materials [5]. These *N*-heterocyclic compounds not only play an important role in biological activity but also act as a potential corrosion inhibitor [6–8]. Survey of literature reveals that pyridine compounds are effective corrosion inhibitors [9–12], which incited us to use them as a corrosion inhibitor for mild steel. The inhibition efficiency of previously reported pyridine derivatives at different acid concentration and temperature ranges (59–96%) at (1176–5400 mg L^{-1}) inhibitor concentration [9,10,13–15]. But in our case best inhibition efficiency of 97.6% at only 400 mg L^{-1} observed in 1 M HCl.

In the present study three pyridine derivatives namely 2-amino-6-methoxy-4-(4-methoxylphenyl) pyridine-3,5-dicarbonitrile (PC-1), 2-amino-6-methoxy-4-(4-methylphenyl) pyridine-3,5-dicarbonitrile (PC-2) and 2-amino-6-methoxy-4-phenylpyridine-3,5-dicarbonitrile (PC-3) were investigated as corrosion inhibitor for mild steel in 1 M HCl by using gravimetric measurements, electrochemical impedance spectroscopy and polarization measurements. The surfaces of the mild steel specimens were examined by Scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and Quantum chemical study. To date, no literature is available reporting the use of these heterocyclic compounds as corrosion inhibitors.

Experimental

Materials and chemicals

The inhibitors were synthesized according to the reported literature [16]. The molecular structure, IUPAC name and abbreviation of the inhibitors are given in Table 1. These inhibitors were purified by recrystallization from methanol.

Corrosion tests were performed on the mild steel strips with the following composition (wt%): C = 0.076, Mn = 0.192, P = 0.012,

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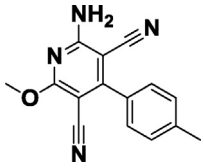
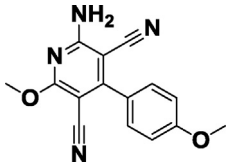
Table 1
Molecular structure and analytical data of PCs.

Inhibitor	Structure
2-Amino-6-methoxy-4-phenylpyridine-3,5-dicarbonitrile (PC-1)	
2-Amino-6-methoxy-4-(4-methylphenyl) pyridine-3,5-dicarbonitrile (PC-2)	
2-Amino-6-methoxy-4-(4-methoxylphenyl) pyridine-3,5-dicarbonitrile (PC-3)	

Si = 0.026, Cr = 0.050, Al = 0.023 and balance Fe. Mild steel strips used in gravimetric and electrochemical experiments were mechanically cut into $2.5 \times 2 \times 0.025$ and $8 \times 1 \times 0.025$ cm dimensions, abraded with SiC abrasive papers of grade 600, 800, 1000 and 1200, respectively, degreased with acetone and finally dried at ambient temperature. The test solution, 1 M HCl was prepared by dilution of analytical grade 37% HCl with double distilled water.

Methods

Gravimetric measurements

Gravimetric measurements were done according to the method described previously [17].

The corrosion rates C_R (mg cm^{-2} h^{-1}) were calculated from the following equation:

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

where W is the average weight loss of a mild steel strip, A is the total area of a mild steel strip and t is the immersion time (3 h). The inhibition efficiency η% was calculated as follows:

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

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

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

where C_R and $C_{R(i)}$ are the values of the corrosion rates (mg cm^{-2} h^{-1}) of mild steel in absence and presence of inhibitors, respectively.

Electrochemical measurements

The electrochemical experiments were carried out by using a three-electrode cell assembly, consisting of mild steel as a working electrode, platinum as a counter electrode and saturated calomel electrode (SCE) as a reference electrode. All experiments were performed without stirring by using a Gamry Potentiostat/Galvanostat with a Gamry framework system based on ESA 400. Gamry applications include EIS 300 for EIS measurements, DC 105 software for corrosion and Echem Analyst (version 5.50) software package for data fitting. The electrochemical experiments were allowed to stabilize for a period of 30 min prior to the experiment.

The EIS measurements were carried out in a frequency range from 100 kHz to 0.01 Hz under potentiostatic conditions, with amplitude of 10 mV peak-to peak, using the AC signal at $E_{corr.}$

The potentiodynamic polarization curves were recorded in the potential range of −250 to +250 mV (SCE) with a scan rate of 1 mV s^{-1}. All potentials were measured against SCE.

Surface analysis

The mild steel strips of size $2.5 \times 2 \times 0.025$ cm were immersed in 1 M HCl in absence and presence of optimum concentration (400 mg L^{-1}) of PCs for 3 h. Thereafter, the mild steel specimens were taken out, washed with distilled water, degreased with acetone, dried at ambient temperature, and mechanically cut into 1 cm^2 size for SEM and EDX investigations. SEM study was carried out at an accelerating voltage of 5 kV and 5K× magnification on a Ziess Evo 50 XVP instrument. Chemical composition of the same mild steel surface was recorded by an EDX detector.

Quantum chemical calculations

Quantum chemical calculations were performed using density function theory (DFT) method, B3LYP with electron basis set 6–31G (d, p) for all atoms. All the calculations were performed on the neutral molecules with Gaussian 03, *E* .01 [18]. The quantum chemical parameters obtained were electronegativity (χ), Hardness (η), global softness (σ), ionization potential (I), electron affinity (A), E_{HOMO} and E_{LUMO}, ΔE ($E_{LUMO} - E_{HOMO}$). These parameters can be given by equations which were reported elsewhere [19,20].

Results and discussion

Gravimetric measurements

Effect of inhibitor concentration

The inhibitive effect of the PCs with the variation of concentration ranging from 100 to 400 mg L^{-1} at 308 K is shown in Fig. 1(a). It is clear that as the PCs concentration increases the inhibition efficiency (η%) increases.

Effect of temperature

The effect of temperature (308–338 K) on the inhibition efficiency (η%) in the presence of optimum concentration (400 mg L^{-1}) of PCs in 1 M HCl is shown in Fig. 1(b). The observation of Fig. 1(b) reveals that as the temperature increases from 308 to 338 K the inhibition efficiency (η%) decreases. This may occurs due to the fact that as the temperature increases there will be an appreciable decrease in adsorption of inhibitor molecules on mild steel surface.

Adsorption isotherms

The performance of the PCs as a successful corrosion inhibitor, which mainly depends on their adsorption ability on the mild steel surface. So, it is essential to know the mode of adsorption which gives valuable information on the interaction of PCs with mild steel surface.

A plot between log (θ/1 – θ) verses log C (M) gives a straight line (Fig. 1(c), which suggests that PCs obeys the Langmuir adsorption isotherm and can be given by following equation [21]:

$$K_{ads}C = \frac{\theta}{1-\theta} \quad (4)$$

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