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Pyridine derivatives as corrosion inhibitors for N80 steel in 15% HCl: Electrochemical, surface and quantum chemical studies

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ABSTRACT

The present paper deals with the adsorption and inhibitory effects of the pyridine derivatives, namely 2-amino-6-(2,4-dihydroxyphenyl)-4-(4-methoxyphenyl)nicotinonitrile (ADP) and 2-amino-4-(4-methoxyphenyl)-6-phenylnicotinonitrile (AMP) on N80 steel corrosion in 15% HCl. Among the studied compounds, ADP showed the inhibition efficiency of 90.24% at 200 mg/L. The corrosion study was performed by gravimetric, electrochemical impedance spectroscopy (EIS), Tafel polarization, scanning electron microscopy (SEM), scanning electrochemical microscopy (SECM) and energy-dispersive X-ray spectroscopy (EDX) techniques. The Langmuir isotherm model showed the best fit. The quantum chemical study was used to support the experimental results.

1. Introduction

In the petroleum industry, N80 steel is used in manufacturing tubing, casing, and transmission pipelines. 15% HCl is used for acidizing oil well for enhancing oil flow. Due to the corrosive nature of HCl, inhibitors are usually added to the acid solution in order to minimize the corrosive attack of acid on tubing and casing of pipeline [1,2]. Previously reported acidic corrosion inhibitors are having atoms such as nitrogen, sulphur, phosphorous, oxygen along with aromatic rings and multiple bonds [3,4].

Pyridine derivatives are one of the important classes of compound which have various pharmacological properties such as antioxidant, anti-atherosclerosis, anti-tumor, anti-mutagenic, anti-diabetic, neuromodulator, anti-vasodilator, hepatoprotector, neuroprotector and memory enhancer [5]. The literature survey reveals that several pyridine derivatives were used as corrosion inhibitors, but they were effective at higher inhibitor and lower acid concentrations respectively [6–12]. In the present investigation, we have synthesized two pyridine derivatives using microwave technique and studied their corrosion inhibition behavior on N80 steel in 15% HCl.

Quantum chemical studies are one of the important tools, which act as a bridge between experimental and theoretical studies. Density functional theory (DFT) was used for predicting the geometric and electronic properties of corrosion inhibitors [13–19].

The aim of the present study is to assess the inhibition effect of two pyridine derivatives namely 2-amino-6-(2,4-dihydroxyphenyl)-4-(4-methoxyphenyl) nicotinonitrile (ADP) and 2-amino-4-(4-methoxyphenyl)-6-phenylnicotinonitrile (AMP) on N80 steel in 15% HCl using gravimetric measurements, polarization measurements, electrochemical impedance spectroscopy, quantum chemical calculations, scanning electron microscopy (SEM) and scanning electrochemical microscopy (SECM). To the best of our knowledge, these pyridine derivatives have not used as a corrosion inhibitor for N80 steel in 15% HCl.

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2. Experimental

2.1. Materials and sample

The composition of N80 steel sample (wt%) used for corrosion testing is as follows: C 0.31; Si 0.19; Mn 0.92; P 0.010; S0.008; Cr 0.2, balance Fe. The dimensions of N80 steel strips used for gravimetric and electrochemical experiments are 5.0 cm × 2.5 cm × 0.2 cm and 2.0 cm × 1.0 cm × 0.025 cm respectively. The strips were polished using SiC abrasive papers having grades ranging from 600 to 1200, degreased with acetone and lastly dried at room temperature. The test solution (15% HCl) was prepared by diluting 35% analytical grade HCl with double distilled water.

The inhibitors were synthesized according to the reported literature [20]. The molecular structure, abbreviations, and synthetic scheme are given in Table 1 and Fig. 1 respectively.

2.2. Gravimetric experiments

Gravimetric experiments were done according to ASTM methods described previously [21].

The corrosion rate C_R (mg cm^{-2} h^{-1}) was calculated from the following equation [22].

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

where W is the weight loss of a N80 steel strip, A is the total area of a N80 steel strip and t is immersion time (6 h).

The surface coverage (θ) and inhibition efficiency (η%) were calculated by using following equations [22]:

$$\theta = \frac{C_R - C_{R(i)}}{C_R} \quad (2)$$

$$\eta\% = \frac{C_R - C_{R(i)}}{C_R} \times 100 \quad (3)$$

where C_R and $C_{R(i)}$ are corrosion rates (mg cm^{-2} h^{-1}) of N80 steel in the absence and presence of inhibitors, respectively.

2.3. Electrochemical measurements

The electrochemical experiments were carried out using a three-electrode cell assembly where a N80 steel strip with an exposed area of 1 cm^2 was used as working electrode, graphite rod as counter electrode and a saturated calomel electrode (SCE) as reference electrode. The working electrode was immersed in the test solution at open circuit potential (OCP) for 30 min before measurement in order to attain a steady state condition. For all electrochemical measurements, GamryPotentiostat/Galvano stat (Model G-300) connected with a personal computer with EIS software Gamry Instruments Inc., USA. The analysis of experiments was carried out using Echem Analyst 5.0 software package.

The potentiodynamic polarization measurements were performed by changing the electrode potential automatically from −250 to +250 mV versus SCE at OCP at a scan rate of 1 mV s^{-1}.

Impedance measurements was carryout by an AC signal with the amplitude of 10 mV peak to peak at the open circuit potential in the range of 100 kHz to 0.01 Hz frequency. All electrochemical measurements i.e. potentiodynamic polarization and impedance were carried out at 308 K.

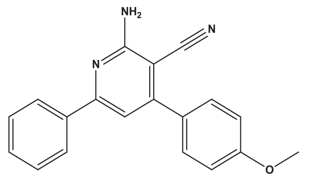
2.4. Surface morphology: SEM

In order to get insight into the changes on N80 steel surface corrosion before and after the addition of inhibitors, the N80 steel specimens were first immersed in 15% HCl solution in the absence and presence of higher concentration (200 mg/L) of ADP and AMP for 6 h at 308 K respectively. A Ziess Evo 50 XVP instrument model, at an accelerating voltage of 5 kV and magnification 5kx, conducted the SEM.

2.5. Scanning electrochemical microscopy (SECM)

Scanning electrochemical microscopy (SECM) is a versatile technique having a wide range of prospects in corrosion research [23]. This instrument has 10 μm platinum tip as the probe, Ag/AgCl/KCl (saturated) and platinum as

Table 1
Molecular structure of inhibitors.

Inhibitor	Structure
2-Amino-4-(4-methoxyphenyl)-6-phenylnicotinonitrile (AMP)	
2-Amino-6-(2,4-dihydroxyphenyl)-4-(4-methoxyphenyl)nicotinonitrile (ADP)