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Pyrimidine derivatives as novel acidizing corrosion inhibitors for N80 steel useful for petroleum industry: A combined experimental and theoretical approach

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ABSTRACT

The corrosion inhibition performance of two pyrimidine derivatives namely 5-styryl-2,7-dithioxo-2,3,5,6,7,8-hexahydropyrimido[4,5-d] pyrimidin-4(1H) one (PP-1) and 5-(2-hydroxyphenyl)-2,7-dithioxo-2,3,5,6,7,8-hexahydropyrimido[4,5-d]-pyrimidin-4(1H) one (PP-2) on N80 steel corrosion in 15% HCl has been studied using gravimetric method, electrochemical impedance spectroscopy (EIS), potentiodynamic polarization, atomic force microscopy (AFM), scanning electron microscopy (SEM), DFT, molecular electrostatic potential and Monte Carlo simulation. The corrosion inhibition efficiencies at optimum concentration (250 mg/L) are 89.1% (PP-1) and 73.1% (PP-2) respectively at 308 K. The corrosion inhibition efficiency increases with increase in concentration and decreases with temperature. PPs obeyed Langmuir adsorption isotherm. AFM and SEM analyses supported formation of protective film on N80 steel in presence of inhibitors. DFT and Monte Carlo simulation calculations supported experimental results.

Introduction

Corrosion of metals is considered as a challenging research area due to its impact on economic and safety issues [1]. Acidization of oil wells is one of the effective techniques for enhancing oil production. It is conducted by forcing a solution of 15% HCl into oil well through N80 steel tubes [2,3]. HCl causes severe corrosion of N80 steel and to reduce the corrosive effect of acid inhibitors are incorporated [1]. Organic compounds containing heteroatoms are considered as effective corrosion inhibitors for acid medium [4–6]. They are adsorbed on the metal surface and reduce corrosion [7,8].

Commercially available acidizing inhibitors are acetylenic alcohol, aromatic aldehyde, alkenylphenones, quaternary salts and some carbonyls and amines condensation products [9]. Most of these compounds are toxic, non-degradable and cause the adverse effect on living beings and environment [10–12]. Therefore, the current research is focused on the development of non-toxic eco friendly inhibitors. The literature survey shows that few pyrimidine derivatives have been previously reported as corrosion inhibitors at lower acid concentration [13–16]. The pyrimidine derivatives in the present study were synthesized from relatively inexpensive chemicals. The calculated cost of 100 L of acid solution containing 25 g of inhibitors is approximately Rs 40–45.

In the present study, two pyrimidine derivatives namely, 5-styryl-2,7-dithioxo-2,3,5,6,7,8-hexahydropyrimido[4,5-d] pyrimidin-4(1H)one (PP-1) and 5-(2-hydroxyphenyl)-2,7-dithioxo-2,3,5,6,7,8-hexahydropyrimido[4,5-d] pyrimidin-4(1H)one (PP-2) have been selected for corrosion inhibition study of N80 steel in 15% HCl. The selection is based on the facts that they are non-toxic and also show diverse biological activities such as antibacterial and fungicidal activities [17]. The corrosion inhibition study of investigated compounds has been performed using gravimetry, electrochemical impedance spectroscopy (EIS), Tafel polarization, quantum chemical methods and molecular dynamic simulation. The surface morphology was studied by AFM and SEM, which supported the adsorption of inhibitor molecules on the metal surface.

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Experimental

Synthesis of inhibitors

Pyrimidine derivatives were synthesized by the previously reported method [17]. A mixture of 2-thiobarbituric acid (0.01 mol), aromatic aldehyde (0.01 mol), thiourea (0.01 mol), absolute ethanol (10 ml) and 36% HCl (3 ml) are taken in a round bottom flash and heated under reflux for 4 h and the reaction mixture was allowed to cool. The formed precipitate was filtered off and washed with ethanol. The molecular structures of inhibitors were confirmed by IR and ^{1}H NMR and are shown in supplementary file (Supplementary Fig. S1). The synthetic scheme of inhibitors (PPs) is shown in Fig. 1. The molecular structure, abbreviation and spectral data are tabulated in Table 1. The detail characterization is as follows:

(a) 5-Styryl-2,7-dithioxo 2,3,5,6,7,8-hexahydropyrimido[4,5-d] pyrimidin-4(1H)-one (PP-1) ^{1}H NMR (500 MHz, DMSO-d6) δ (ppm) 3.91(1H, CH), 6.23, 6.52 (2H, CH=CH), 7.22–7.31 (5H, Ar-H),7.45 (1H, NH) 8.90 (1H, NH), 9.19 (1H, NH), 11.43 (1H, NH).
(b) 5-(2-Hydroxyphenyl)-2,7-dithioxo-2,3,5,6,7,8-hexahydropyrimido[4,5-d]-pyrimidin-4-one (PP-2) ^{1}H NMR (500 MHz, DMSO-d6) δ (ppm) 4.14 (1H, CH), 6.97–7.20 (4H, Ar-H), 7.49 (1H, NH), 9.14 (1H, NH), 9.69 (1H, NH), 9.70 (1H, OH), 11.52 (1H, NH).

Materials and test solution

The corrosion study was performed on N80 steel sample having composition (wt%): C 0.31%, Si 0.19% Mn 0.92%, P 0.01%, S 0.008% and Cr 0.2% and Fe in balance. N80 steel strips with area 5.0 cm × 2.5 cm and 2.0 cm × 1.0 cm were used for gravimetric and electrochemical experiments respectively. Only 1 cm^2 area of N80 steel is exposed for electrochemical test and rest are covered by epoxy resin. The surface of N80 samples for all the experiments were polished using different grades of emery paper (600–1200), cleaned with double distilled water and acetone, finally dried at room temperature [18]. All the solvents and chemicals used for synthesis are of analytical grade. Thiobarbituric acid was purched from avra chemicals from Hyderabad India, 2-hydroxybenzaldehyde, 5-chloro-2-hydroxybenzaldehyde, 2-hydroxy-5-nitrobenzaldehyde are purchased from Spectrochem and used without doing further purification. 35% HCl (GR grade) is purchased from Merck India. Analytical grade methanol and ether are purchased from Fluka and used without any further purification.

Methods

Gravimetric method

Gravimetric experiments were performed by immersing N80 steel in 15% HCl for 6 h. The corrosion rate (C_R), inhibition efficiency (η%) and surface coverage (θ) was calculated by the following equations:

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

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

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

where, W is the weight loss of specimen (mg), A is the area of specimen (cm^2), t represents the immersion time (h), C_R and $C_{R(i)}$ are the corrosion rates in the absence and presence of the inhibitor molecules respectively.

Electrochemical studies

Polarization and electrochemical impedance spectroscopy (EIS) studies were conducted using a three electrode cell consisting of working electrode as an N80 steel strips with an exposed area of 1 cm^2, counter electrode (graphite rod) and reference electrode (saturated calomel electrode: SCE) respectively. All electrochemical experiments were performed by a Gamry Potentiostat/Galvanostat (Model G-300) instrument, and data analysis was done by Gamry Echem Analyst 5.5 software. Prior to each electrochemical experiment, the working electrode was immersed in the test solution for 30 min in order to attain steady state condition of open circuit potential (OCP).

The impedance measurements were carried out at the open circuit potential (OCP) in the frequency range from 10^5 to 10^{-2} Hz using AC signal of amplitude 10 mV peak to peak.

Potentiodynamic polarization was carried out by changing the potential from −250 mV to +250 mV vs OCP at a constant sweep rate 1 mV/s.

Surface analysis (SEM and AFM)

The N80 steel specimens were immersed in 15% HCl in the absence and presence of optimum concentration of PPs for 6 h at 308 K. SEM studies were performed by using a ZiessEvo 50 XVP instrument model, at an accelerating voltage of 5 kV and magnification 5k×. AFM analysis was performed by using a NT-MDT multimode AFM, Russia, controlled by Solver scanning probe microscope controller having NOVA programme.

Quantum chemical study

Quantum chemical calculations of the studied inhibitor compounds (PPs) were carried out using the density functional theory (DFT) method [19]. The geometry of PPs was optimized using B3LYP having basis set 6-31G (d, p) [20,21]. All the calculations were performed by Gaussian 03 revision

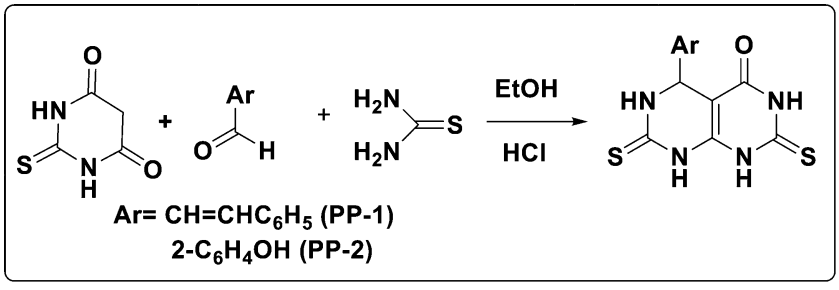

Fig. 1. Synthetic scheme of inhibitors (PPs).