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Gravimetric, electrochemical and quantum chemical studies of some pyridazine derivatives as corrosion inhibitors for mild steel in 1 M HCl solution

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ABSTRACT

The corrosion inhibition performances of three pyridazine derivatives, 6-methyl-4,5-dihydro-2H-pyridazine-3-one (MPYO), 6-phenyl-2H-pyridazine-3-one (PPYO) and 6-phenyl-2H-pyridazine-3-thione (PPYS) for mild steel in 1 M HCl solution were studied by gravimetric, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. Some thermodynamic parameters were calculated and discussed. The effect of molecular structure on the inhibition efficiency was theoretically studied by density functional theory (DFT). Experimental and theoretical studies agreed well and confirmed that PPYS is the best corrosion inhibitor among the studied organic compounds which was related to the presence of a more favorable adsorption center of S atom in its molecular structure.

1. Introduction

Acid solutions are commonly used for removal of undesirable scale and rust in metal working, cleaning of boilers and heat exchangers, oil-well acidizing in oil recovery [1–4]. HCl solution is one of the most widely used agents for these aims. However, steel and other ferrous alloys could readily corrode during these applications. The use of corrosion inhibitors is one of the most effective methods for protecting metals against corrosion and it is becoming increasingly popular. Organic compounds bearing heteroatoms with high electron density such as oxygen, nitrogen, sulfur, phosphorus, unsaturated bonds or plane conjugated systems are effective as corrosion inhibitor [5–9]. As a representative type of organic inhibitors, pyridazine derivatives have been reported to be effective corrosion inhibitors for protection of metals in various corrosive media [10–29]. The choice of pyridazine compounds is based on their well-known pharmaceutical applications in the inhibition of aldose reductive and exhibiting antioxidant properties [30,31] as well as the presence of heteroatoms, unsaturated bonds and plane conjugated systems which are considered to be active centers for adsorption. In another way, theoretical studies of organic corrosion inhibitors are increasingly being popular. Quantum chemical calculations have been widely used to study adsorption and reaction mechanisms, to interpret the experimental results as well as to resolve chemical ambiguities [32].

The aim of this work is to investigate the inhibition performances of three pyridazine derivatives, 6-methyl-4,5-dihydro-2H-pyridazine-3-one (MPYO), 6-phenyl-2H-pyridazine-3-one (PPYO) and 6-phenyl-2H-pyridazine-3-thione (PPYS) for mild steel corrosion in 1 M HCl solution. For this aim, gravimetric and electrochemical measurements as well as quantum chemical calculations were studied.

2. Experimental and theoretical details

Three organic compounds whose chemical structures are shown in Fig. 1 were tested as the corrosion inhibitors.

6-methyl-4,5-dihydro-2H-pyridazine-3-one and, 6-phenyl-2H-pyridazine-3-one were synthesized according to the method described in the literature [33,34]. 6-phenyl-2H-pyridazine-3-thione was prepared as described in [35]. The final yields were characterized

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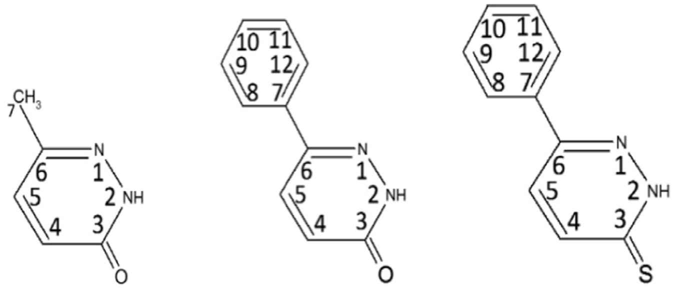

MPYO PPYO PPYS

Fig. 1. Chemical structures of the studied pyridazine derivatives.

by NMR. MNR ^{1}H ($CDCl_3$) (MPYO): δ 2.05 (m, 2H, CH_2); 2.12 (s, 3H, CH_3); 2.48 (m, 2H, CH_2); 8.71 (s, 1H, NH). MNR ^{13}C ($CDCl_3$) (MPYO): δ 22.9 (CH_3); 25.9 (CH_2); 26.1 (CH_2); 152.9 (C-6); 167.2 (CO). MNR ^{1}H ($CDCl_3$) (PPYO): d 2.61 (m, 2H, CH_2); 2.98 (m, 2H, CH_2); 7.68 (m, 3H); 7.73 (m, 2H); 9.3 (s, 1H, NH). MNR ^{13}C ($CDCl_3$) (PPYO): d 22.6 (CH_2); 26.3 (CH_2); 125.9 (2CH); 128.7 (2CH); 129.9 (CH). 150.7 (C-6); 167.65 (C=O). MNR ^{1}H ($CDCl_3$) (PPYS): 5.31 (m, 1H, CH); 5.48 (m, 1H, CH); 7.30 (s, 1H, NH); 7.31 (m, 3H, Hph); 7.61 (m, 2H, Hph); 7.68 (m, 3H); 7.73 (m, 2H). MNR ^{13}C ($CDCl_3$) (PPYS): 128.91 (2Cph); 129.21 (2Cph); 131.25 (Cph); 133.23 (Cph); 141.92 (C3); 146.83 (C4); 155.24 (C5); 195.25 (C2).

The corrosive solution (1 M HCl) was prepared by dilution of an analytical grade of 37% HCl with bi-distilled water. Mild steel specimens had the chemical composition of (wt. %) 0.21% C, 0.38% Si, 0.05% Mn, 0.05% S, 0.09% P, 0.01% Al and the remainder iron (Fe). The steel samples were mechanically abraded with different grades of sand papers (400, 600 and 1200), rinsed with bi-distilled water, dried and immersed into the test solutions. In the gravimetric measurements, the mild steel specimens were immersed into the test solutions (50 mL) without and with the inhibitors for 6 h. Corrosion rate was calculated using weights loss of the specimens during the exposure time.

Electrochemical measurements were performed in a conventional three-electrode cylindrical pyrex glass cell using a computer-controlled Tacussel Radiometer PGZ 100. The working electrode had the form of a disc which was cut from a mild steel specimen and embedded into a polytetrafluoroethylene block. The exposed surface area of the steel electrode was 1 cm^2. A saturated calomel electrode (SCE) and a platinum electrode were used as reference and auxiliary electrodes, respectively. Temperature of the test solutions was thermostatically controlled.

Before each experiment, the working electrode was exposed to the test solutions (no de-aeration and no stirring). After obtaining a steady state open circuit potential (E_{ocp}) (1 h), electrochemical measurements were performed. The EIS experiments were realized in the frequency range from 100 kHz to 10 mHz at E_{ocp} with perturbation amplitude of 0.005 V peak-to-peak and the data density of 10 points per decade. The impedance data were fitted and analyzed with a ZView 2.8 equivalent circuit software.

The polarization measurements were recorded after the EIS measurements using the same electrode without any further surface treatments. After EIS measurements and during each polarization experiments, the test solutions were stirred with a magnetic stirrer and de-aerated in the electrochemical cell with the help of pure nitrogen. The polarization curves were obtained potentiodynamically from –800 mV to –200 mV (SCE) with a scan rate of 1 mV/s.

Quantum chemical studies were performed using density function theory (DFT) method, B3LYP with electron basis set $6-31+G$ (d,p) for all atoms. All calculations were performed with Gaussian 03 [36].

Table 1
Corrosion rates and inhibition efficiencies in the absence and presence of the pyridazine compounds at 308 K after 6 h immersion.

Inhibitor	C (mM)	W_{corr} (mg/cm^2 h)	E_w (%)
Blank	–	2.03	–
MPYO	0.5	1.67	17.7
PPYO	0.5	1.51	25.6
PPYS	0.5	0.04	98.0

Table 2
Corrosion parameters of mild steel obtained from gravimetric measurements in 1 M HCl solution containing various concentrations of PPYS at 308 K after 6 h immersion.

C (mM)	W_{corr} (mg/cm^2 h)	E_w (%)
Blank	2.030	–
0.01	0.852	58.0
0.025	0.406	80.0
0.05	0.142	93.0
0.1	0.081	96.0
0.25	0.041	98.0
0.5	0.040	98.0

3. Results and discussion

3.1. Gravimetric measurements

The comparison of inhibition effects of pyridazine compounds for mild steel corrosion in 1 M HCl solution was tested by gravimetric measurements in the presence of 0.5 mM inhibitors at 308 K for 6 h exposure. The values of corrosion rate, W_{corr} (mg/cm^2 h) and inhibition efficiency, E_w (%) were calculated using Eqs. (1) and (2), respectively and the data obtained are summarized in Table 1.

$$W_{corr} = \frac{m_b - m_a}{S\,x\,t} \tag{1}$$

$$E_w(\%) = \left(1 - \frac{W_{corr}}{W^o_{corr}}\right) \tag{2}$$

where m_b and m_a are the mass of the specimens before and after immersion to the test solutions, S is the exposed surface area of the mild steel specimens (cm^2), t is the exposure time (h), w_{corr} and w^o_{corr} are the corrosion rates of mild steel in inhibited and uninhibited solutions, respectively. The data in Table 1 shows that the inhibition efficiency of the tested pyridazine compounds follow the order of PPYS > PPYO > MPYO. The better inhibition efficiency of PPYS could be assigned to the presence of an S atom in its molecular structure (Fig. 1).

In order to understand the inhibition mechanism of the best inhibitor (PPYS) among the studied compounds, a detailed study on this compound was performed. Table 2 gives the results obtained from gravimetric measurements at different concentrations of the inhibitor in 1 M HCl solution and the results show that the corrosion rate decreases while the inhibition efficiency E_w (%) increases with increasing PPYS concentration, which suggests that the inhibition efficiency takes place through the adsorption of PPYS molecules on the steel surface.

3.2. Adsorption isotherm

The adsorption isotherms are used to describe the interaction of inhibitor molecules with metal surfaces [37]. For the PPYS inhibitors in this study, several adsorption isotherms such as Frumkin, Temkin, Freundlich and Langmuir were attempted to fit the values of surface coverage θ, which was obtained by the ratio E_w (%)/100. Those