

Electrochemical and quantum chemical calculations on 4,4-dimethyloxazolidine-2-thione as inhibitor for mild steel corrosion in hydrochloric acid

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ABSTRACT

The inhibition ability of 4,4-dimethyloxazolidine-2-thione (DMT) for mild steel corrosion in a 1 M HCl solution at 30 °C was studied by means of potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) technique, and scanning electron microscopy (SEM). Quantum chemical calculation based on PM3 method was performed on DMT. The molecule structural parameters, such as the frontier molecular orbital energy HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital), the charge distribution and the fraction of electrons (ΔN) transfer from inhibitor to mild steel were calculated and discussed. Results showed that DMT performed as good inhibiting effect for the corrosion of mild steel in a 1 M HCl solution and inhibition efficiency is higher than 82% at 4×10^{-3} M DMT. Results indicate that the inhibition efficiencies increased with the concentration of DMT and the area containing S atom is most possible site for bonding the mild steel surface by donating electrons to the metal. Adsorption of the inhibitor on the mild steel surface followed Langmuir adsorption isotherm and the value of the free energy of adsorption $\Delta G_{\text{ads}}^{\circ}$ indicated that the adsorption of DMT molecule was a spontaneous process and was typical of chemisorptions.

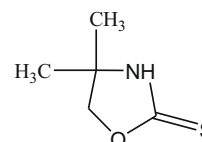
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1. Introduction

Mild steel is widely used as a constitutional material in many industries due to its good mechanical properties and low cost. The corrosion of mild steel is of fundamental academic and industrial concern that has received a considerable amount of attention [1,2]. Acid solutions are generally used for the removal of rust and scale in industrial processes. Hydrochloric acid is widely used in the pickling, cleaning and descaling of steel and ferrous alloys [1]. Inhibitors are often used in these processes to control the metal dissolution. It has been commonly recognized that an organic inhibitor usually promotes formation of a chelate on a metal surface, by transferring electrons from the organic compounds to the metal and forming a coordinate covalent bond during the chemical adsorption [3]. In this way, the metal acts as an electrophile; and the nucleophile centers of inhibitor molecule are normally heteroatoms with free electron pairs that are readily available for sharing, to form a bond and thus decrease the corro-

sion rate [4]. Most of the well known acid inhibitors are organic compounds containing nitrogen, sulfur and oxygen atoms [5]. Theoretical chemistry has been used recently to explain the mechanism of corrosion inhibition, such as quantum chemical calculations [6–8]. Quantum chemical calculations have been proved to be a very powerful tool for studying the mechanism [9,10].

In this work, the inhibitory effect of 4,4-dimethyloxazolidine-2-thione (DMT) on mild steel corrosion in 1 M HCl at 30 °C was studied. Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) were performed in this study. Theoretical studies on electronic and molecular structures of DMT were conducted using quantum chemical calculations. The choice of this compound was based on molecular structure considerations, i.e., this is an organic compound with an adsorption center. The molecular structure of DMT is as follows:



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2. Experimental work

Mild steel specimens obtained from the Metal Samples Company were used as the working electrodes throughout the study. The composition (wt.%) of the mild steel was: Fe, 99.21; C, 0.21; Si, 0.38; P, 0.09; S, 0.05; Mn, 0.05; Al, 0.01, and with an exposed area of 4.52 cm². The specimens were cleaned according to ASTM standard G1-03 [11]. Measurements were carried out in aerated non-stirred 1 M HCl acid solutions at 30 °C with a DMT concentration range of 1×10^{-4} – 4×10^{-3} M as corrosion inhibitor. Solutions were freshly prepared from analytical grade chemical reagents using distilled water.

Electrochemical measurements were conducted with a Gamry water jacketed glass cell. The cell contained three electrodes, the working, counter and reference electrodes, comprised of mild steel, a graphite bar and a saturated calomel electrode (SCE), respectively. Measurements were performed using a Gamry Instrument Potentiostat/Galvanostat/ZRA model. The potentiodynamic current–potential curves were recorded by changing the electrode potential automatically from –200 to 200 mV at a scan rate of 1 mV s⁻¹. EIS measurements were performed at corrosion potentials (E_{corr}) over a frequency range of 10 kHz–0.1 Hz, with a signal amplitude perturbation of 10 mV. Electrochemical measurements were initiated about 30 min after the working electrode was immersed in solution to stabilize the steady state potential.

The quantum chemical calculations were performed using VAMP 10.0 in Material Studio 4.3. PM3 semi-empirical method was employed to obtain the optimized geometry [12].

3. Results and discussion

3.1. Polarization measurements

The numerical values of the variation of corrosion current density (i_{corr}), corrosion potential (E_{corr}), anodic Tafel slope (β_a), cathodic Tafel slope (β_c), and the degree of surface coverage (θ) with the concentrations of DMT at 30 °C is given in Table 1. These values were calculated from the Tafel fit routine provided by Gamry Echem. Analyst software, this routine uses a non-linear chi squared minimization to fit the data to the Stern–Geary equation. The surface coverage (θ) was calculated using [13]:

$$\theta = \frac{i_{\text{corr(uninhib)}} - i_{\text{corr(inih)}}}{i_{\text{corr(uninhib)}}} \quad (1)$$

where $i_{\text{corr(uninhib)}}$ and $i_{\text{corr(inih)}}$ are the corrosion current densities in the absence and presence of inhibitor, respectively.

The inhibition efficiency ($IE\%$) is given by:

$$IE\% = \theta \times 100 \quad (2)$$

Table 1 shows that i_{corr} decreased with increasing concentration of DMT. Additionally, inhibition efficiencies increased with the concentration of inhibitor. E_{corr} values were shift towards more negative values with addition of DMT, indicating the inhibiting ef-

Table 1
Polarization parameters for mild steel in 1 M HCl with various concentrations of DMT at 30 °C.

Concentration ($\times 10^{-4}$ M)	β_a (V dec ⁻¹)	β_c (V dec ⁻¹)	i_{corr} ($\mu\text{A cm}^{-2}$)	E_{corr} (mV vs. SCE)	θ	$IE\%$
Blank	0.124	0.3136	454	-470	0.0	0.0
1	0.1168	0.092	294	-479	0.352	35.2
4	0.1062	0.074	125	-465	0.724	72.4
10	0.088	0.0697	118	-477	0.74	74
20	0.098	0.0771	90.1	-476	0.815	81.5
40	0.797	0.0745	79.5	-473	0.825	82.5

fect of DMT on mild steel corrosion [1]. In acid solutions, anodic corrosion involves the passage of metal ions from the metal surface into the solution, and the cathodic process involves the discharge of hydrogen ions to produce hydrogen gas or oxygen reduction. The inhibitor may affect either or both the anodic and cathodic processes [14].

The anodic Tafel slope (β_a) and the cathodic Tafel slope (β_c) of DMT changed with inhibitor concentration, indicating that the inhibitor controlled both of the reactions. The polarization profile of mild steel in 1 M HCl at 30 °C in the presence and absence of DMT is shown in Fig. 1.

3.2. Electrochemical impedance spectroscopy (EIS) measurements

The experimental results obtained from EIS measurements of the corrosion of mild steel in the presence and absence of inhibitor at 30 °C were plotted by Nyquist in Fig. 2. The plots show a depressed capacitive loop which arises from the time constant of the electrical double layer and charge-transfer resistance. The impedance of the inhibited mild steel increases with increase in the inhibitor concentration and consequently the inhibition efficiency increases. A depressed semicircle could be attributed to different physical phenomena such as roughness and inhomogeneities of the solid surfaces, impurities, grain boundaries and distri-

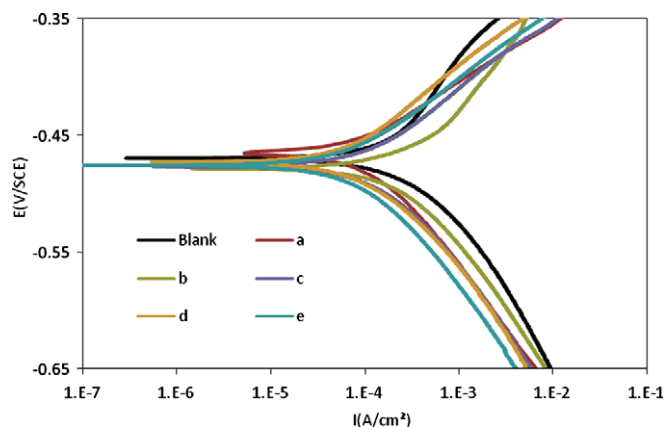


Fig. 1. Potentiodynamic polarization curves for mild steel in 1 M HCl at 30 °C in absence and presence of various concentrations of DMT: (a) 1, (b) 4, (c) 10, (d) 20, (e) 40×10^{-4} M.

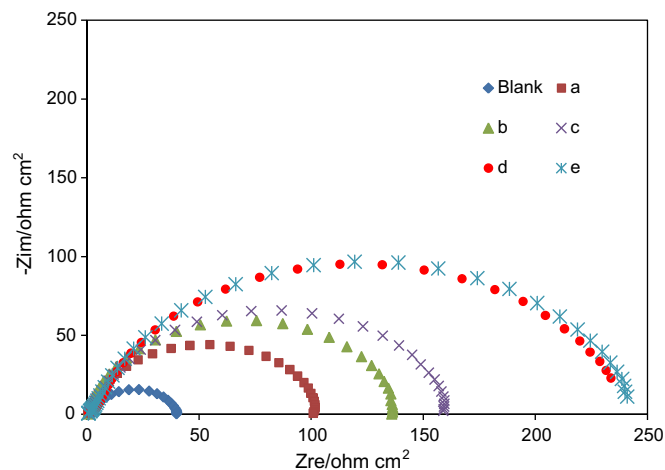


Fig. 2. Nyquist plots for mild steel in 1 M HCl at 30 °C in absence and presence of various concentrations of DMT: (a) 1, (b) 4, (c) 10, (d) 20, (e) 40×10^{-4} M.

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