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Dry and wet lab analysis on benzofused heterocyclic compounds as effective corrosion inhibitors for mild steel in acidic medium

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ABSTRACT

The influence of two benzofused heterocyclic compounds, namely 2-phenylquinazolin-4(3*H*)-one(PQO) and 2-phenyl-4*H*-benzo[*d*]oxazin-4-one(POO) in controlling mild steel corrosion in 1 M H_2SO_4 solution was investigated using gravimetric and electrochemical methods. The experimental results revealed that both the inhibitors inhibit corrosion and their inhibition efficiency follows the order PQO > POO. A mixed mode of inhibition from polarization and a charge transfer mechanism from impedance study in the absence and presence of inhibitors were found. The passive film formed on the mild steel surface was characterized using SEM-EDX. Quantum chemical parameters derived using DFT performed at B3LYP/6-31G(d, p) level were used to correlate the molecular structure.

Introduction

Corrosion is invariably present in industries where mechanical and structural facilities such as bridge work, building, boiler parts, steam engine parts, vessels, tanks, pipes, etc., are created by metallic structures. This generates huge material and economic losses due to partial or total replacement of equipment and structures and plant-repairing shutdowns. In addition, corrosion also has social implications such as health and safety of people working in industries or living nearby. The use of organic corrosion inhibitors constitutes one of the most economical and practical preventive maintenance methods to mitigate and control the corrosion rate, protect metal surfaces against corrosion and preserve industrial facilities [1,2]. A through literature survey reveals that most of the inhibitors act by adsorption onto the metal surface which takes place through heteroatoms such as N, O, P and S atoms, triple bonds or π electrons of aromatic rings which tend to form stronger coordination bonds. Several nitrogen, oxygen, and sulphur containing heterocyclic compounds such as benzoxazoles [3], benzothiazole derivatives [4], benzimidazoles derivatives [5], triazines [6], pyrazole derivatives [7], pyrimidines derivatives [8], thiosemicarbazones [9], thiophenederivatives [10], thiourea derivatives [11], and quinoxaline derivatives [12] have been reported as good corrosion inhibitors. Literature survey shows that anti corrosive performance of quinazolinones is scanty and benzooxazinones have not been studied, in our knowledge, as mild steel corrosion inhibitors in sulphuric acid medium.

Benzoxazinone and quinazolinone are fused heterocyclic compounds respectively consisting of an oxazine and pyrimidine have caused universal concerns owing to their distinct biological applications. Benzoxazinone derivatives are regarded as important chemical synthons of various physiological significances and pharmaceutical utilities. They possess numerous biological activities such as antiphlogistic [13], antiplatelet aggregation activity [14], antibacterial, antifungal [15,16], antimuscular contractor and hypnotic activities [17]. Also, benzoxazinones have attracted considerable attention as inhibitors of serine proteases and human leukocyte elastase [18,19]. In addition benzoxazinone showed some important industrial applications in the synthesis of optical bleaching agents [20].

Quinazolinone derivatives have received universal concern due to their divergent biopharmaceutical activities. The stability of quinazolinone derivatives inspired many researchers to synthesize new potential medicinal agents and to study their therapeutic activities, including anti-cancer [21], anti-tuberculosis [22], anti-inflammation [23], anti-bacterial [24], anti-cytotoxin [25], anti-spasm [26], anti-oxidation [27] etc. Nonionic surface active

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agents having quinazolinone nucleus with long chain fatty acids have also been reported [28]. They find application in the dye stuff industry as coupling components [29]. This prompted us to synthesize and study the corrosion inhibition potential of these compounds.

The present study was undertaken to investigate and compare the corrosion inhibitive performance of 2-phenylquinazolin-4(3*H*)-one (PQO) and 2-phenyl-4*H*-benzo[*d*]oxazin-4-one (POO) for mild steel in 1 M H_2SO_4. To achieve this objectives the following techniques; weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy and surface analysis by SEM-EDX and AFM technique were employed. In order to support the experimental data, quantum chemical calculations were performed using Density Functional Theory (DFT) to describe the interaction between the inhibitor molecule and the metal surface along with the properties of these inhibitors concerning their reactivity.

Experimental work

Materials

Mild steel coupons composed of 0.079% C, 0.025% P, 0.018% S, 0.021% Mn and the rest Fe and dimensions 3 cm × 1 cm × 0.05 cm were used for gravimetric measurements. A mild steel rod of same composition with exposed area 0.785 cm^2 was used for electrochemical measurements. The specimens were abraded with 1/0, 2/0, 3/0 and 4/0 grades of emery sheets, degreased with acetone and rinsed with doubly distilled water. Finally the coupons were dried and kept in desiccator to avoid moisture absorption. All chemicals used in this study were of analar grade and double distilled water was used for their preparation. The inhibitors were prepared by following the scheme.

$$\text{Corrosion rate (mmpy)} = 87,600\,W/ATD \quad (2)$$

W_0 and W_i are the weight loss in the absence and presence of inhibitor, respectively. W is the weight loss, A is the area of the specimen (cm^2) exposed to 1 M H_2SO_4, D is the density of mild steel in g/cm^3 and T is the exposure time in hour. To find out the effect of temperature on inhibition efficiency weight loss measurements were carried out in the temperature range 303–333 ± 1 K.

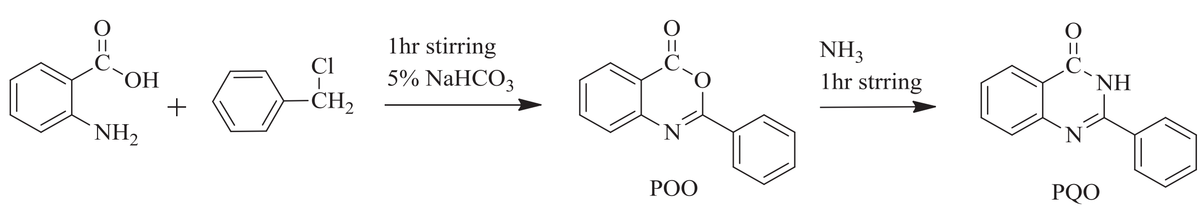
Electrochemical studies

Electrochemical measurements were performed on an Ivium compactstat instrument using a three electrode cell assemblage in a glass cell of 100 mL capacity. A cylindrical mild steel rod embedded in Teflon with exposed area of 0.785 cm^2 used as working electrode was immersed in the test solution for 10–15 min before the electrochemical measurements were carried out. A platinum foil and a saturated calomel electrode were used as counter and reference electrodes respectively. Anodic and cathodic polarization curves were recorded in the potential range of −200 mV to +200 mV, at a scan rate of 1 mV s^{-1}. IE% was determined from the corrosion current densities (i_{corr}) obtained by extrapolation of the cathodic and anodic linear Tafel segments to corrosion potential.

$$\mathrm{IE}(\%) = \frac{I_{corr(b)} - I_{corr(i)}}{I_{corr(b)}} \times 100 \quad (3)$$

$I_{corr(b)}$ and $I_{corr(i)}$ are the corrosion current densities in the absence and presence of inhibitor. The AC impedance measurements were performed in the frequency range from 0.01 Hz to 10 kHz with signal amplitude of 25 mV. From the Nyquist plots

Scheme: Synthetic route of inhibitors



2-phenyl -4 H- benzo[d][1,3]-oxazin-4-one (POO)

2-phenyl-quinazoline-4(3H)-one (PQO)

Weight loss method

The initially cleaned and weighed mild steel specimens were suspended in beakers containing 100 mL of 1 M H_2SO_4 with and without addition of different concentration of inhibitors at 303 ± 1 K using glass hooks. After 3 h exposure period the specimens retrieved, cleaned thoroughly with distilled water, dried and reweighed to determine the weight loss. Triplicate measurements were carried out for reproducibility. From the weight loss, percentage inhibition efficiency (IE%) and corrosion rate were calculated by the following equations

$$\mathrm{IE}(\%) = \frac{W_0 - W_i}{W_0} \times 100 \quad (1)$$

(Z_{real} vs $Z_{imaginary}$). The charge transfer resistance and double layer capacitance were calculated.

$$\mathrm{IE}(\%) = \frac{R_{t(i)} - R_{t(b)}}{R_{t(i)}} \times 100 \quad (4)$$

$R_{t(i)}$ and $R_{t(b)}$ signifies the charge transfer resistance in the presence and absence of inhibitor.

Surface analysis

Surface morphology studies

Surface morphology of mild steel specimens treated, with and without optimal concentration of inhibitor were examined using Scanning electron microscope (SEM) equipped with Energy