



# Adsorption and corrosion inhibition characteristics of some organic molecules containing methoxy phenyl moiety on mild steel in hydrochloric acid solution



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## ABSTRACT

The influence of three newly synthesized molecules on the corrosion inhibition of mild steel in acid media is studied. From Tafel slopes, it is evident that the anodic reaction is more polarized. Impedance study reveals that the increase in  $R_{ct}$  values can be attributed to the formation of a protective film and the decrease in  $C_{dl}$  values is due to an increase in the thickness of the electrical double layer. Total energy,  $E_{HOMO}$  and softness are in the order of 3-MPTT > 4-AMTT > 3-MAH and dipole moment,  $E_{LUMO}$ , energy gap, ionization potential and hardness are in the order of 3-MPTT < 4-AMTT < 3-MAH.

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## 1. Introduction

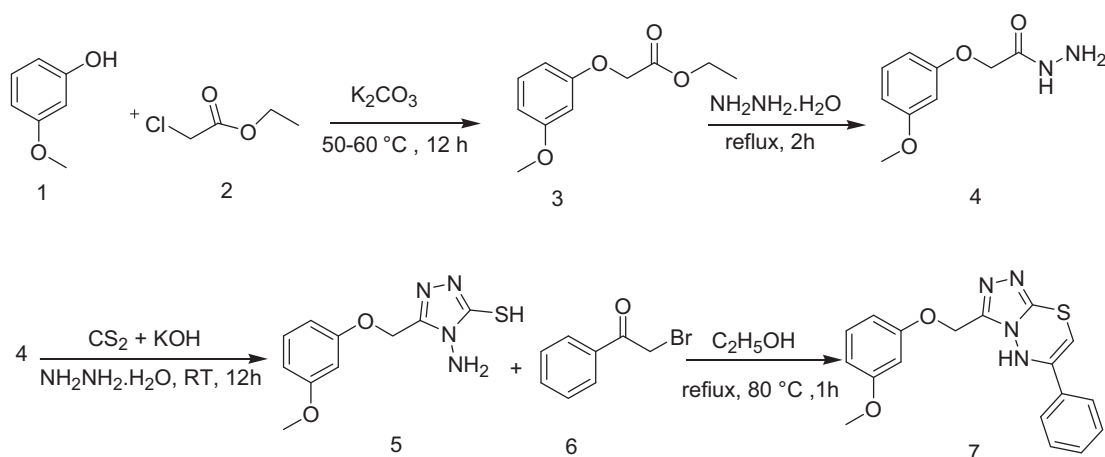
Mild steel is widely applied as constructional material in many chemical and petrochemical industries due to its excellent mechanical properties and low cost. In petrochemical industries, corrosion of MS is a major problem due to severe attack by hydrochloric acid when used as a cleaning agent, through chemical reactions [1]. The major disadvantage is that, it is prone to undergo corrosion on exposure to corrosive environment [2,3]. Aqueous solution of acids is among the most corrosive media. Hydrochloric acid solutions are widely used in several industrial processes such as acid pickling, acid cleaning, acid de-scaling and oil well acidizing [4]. Corrosion inhibitors are of great practical importance, and being extensively employed in minimising metallic waste in engineering materials [5]. Inhibitors are generally organic molecules containing phosphorous, sulphur, nitrogen, and oxygen atoms with high molecular size [6–10]. The inhibiting action of these inhibitors attributed to their interactions with the mild steel surface via adsorption. They change the structure of the electrical double layer by adsorption on the metal surface. The functional groups present in the organic compounds are acting as a reaction centers for adsorption process [11].

It has been known that efficient inhibitors should possess plentiful pi-electrons and unshared electron pairs on either nitrogen atoms or sulfur atoms of the inhibitors to the d-orbital of iron. The adsorption characteristics of organic molecules are also affected by sizes, electron density at the donor atoms and orbital character of donating electrons [12–16]. Organic compounds containing functional electronegative groups, pi-electron in triple or conjugated double bonds and presence of aromatic rings in their structure are the major adsorption centres and are usually good inhibitors [17]. These inhibitors are usually adsorbed on the metal surface by the formation of a coordinate covalent bond (chemical adsorption) or the electrostatic interaction between the metal and inhibitor (physical adsorption). The corrosion inhibition efficiency of organic compounds is mainly dependent on its ability to get adsorbed on metal surface. The adsorption of these compounds is influenced by the electronic structure of inhibiting molecules, steric factor, aromaticity, electron density at donor site etc. Recently large effort has been devoted to develop novel and efficient corrosion inhibitors. Benzimidazole derivatives [18,19], triazole derivatives [20,21], thiosemicarbazide derivatives [22] and bisthiadiazoles [23] have been tested as efficient inhibitors for steel in HCl media. Among various heterocyclic compounds, molecules containing both N and S provide excellent inhibition activity compared to those containing only N or S [24].

The present study was intended to ascertain and compare the ability of the synthesised inhibitor compounds to protect steel from

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**Scheme 1.** Scheme for the synthesis of inhibitors.

corrosive action of HCl at elevated temperatures, different concentration and longer period of immersion time using mass loss, Tafel and electrochemical impedance spectroscopy (EIS) methods. The effect of different functional groups, cyclization and aromaticity of the molecule on the inhibition efficiency was considered. These compounds contain many donor nitrogen groups in addition to the presence of mercapto, methoxy and amino groups in their heterocyclic structures. The presence of such donor groups has been reported to facilitate and increase the adsorption probability of these compounds, which in turn protects the metal's surfaces through reducing the severity of the surrounding environments.

## 2. Experimental

### 2.1. Materials

Mild steel (MS) specimens used in the present study having the following chemical composition (in wt %): C – 0.051; Mn – 0.179; Si – 0.006; P – 0.005; S – 0.023; Cr – 0.051; Ni – 0.05; Mo – 0.013; Ti – 0.004; Al – 0.103; Cu – 0.050; Sn – 0.004; B – 0.00105; Co – 0.017; Nb – 0.012; Pb – 0.001 and the remainder is iron. Prior to gravimetric and electrochemical measurements, the surface of the specimens was polished under running tap water using SiC emery paper up to 1200 grade, rinsed with distilled water, dried on a clean tissue paper, immersed in benzene for 5 s, dried and then immersed in acetone for 5 s and dried with clean tissue paper. Finally, the specimens were kept in desiccators until use. At the end of the test, the specimens were carefully washed with benzene and acetone, dried and then weighed. Appropriate concentrations of acid were prepared by using double-distilled water. The concentration range of inhibitors employed was 0.262–1.309 mM.

### 2.2. Synthesis of inhibitors

The general strategy for the synthesis of inhibitors is shown in [Scheme 1](#). The abbreviations, molecular structures and names of all the three synthesized inhibitors are given in [Table 1](#). All solvents and chemicals used were of analytical reagent grade and used as such. FTIR spectra were recorded using a Jasco FTIR 4100 double beam spectrophotometer. <sup>1</sup>H-NMR spectra were recorded on Bruker DRX-500 spectrometer at 400 MHz using DMSO-d<sub>6</sub> as solvent and TMS as an internal standard. LC Mass spectra were recorded using Agilent – SC/AD/10-017 instrument. (3-methoxy-phenoxy)-acetic acid ethyl ester (**3**), (3-methoxy-phenoxy)-acetic acid hydrazide (**4**), 4-amino-5-(3-methoxy-phenoxy-methyl)-4H-[1,2,4]triazole-3-thiol (**5**),

**Table 1**

The abbreviations, molecular structures and names of all the synthesized inhibitors.

Abbreviation	Molecular structure	Name
3-MAH		(3-Methoxy-phenoxy)-acetic acid hydrazide
4-AMTT		4-Amino-5-(3-methoxy-phenoxy-methyl)-4H-[1,2,4]triazole-3-thiol
3-MPTT		3-(3-Methoxy-phenoxy-methyl)-6-phenyl-7H-[1,2,4]thiadiazine

3-(3-Methoxy-phenoxy-methyl)-6-phenyl-7H-[1,2,4]thiadiazine have been synthesized according to the literature method [\[25–28\]](#).

#### 2.2.1. Synthesis of (3-methoxy-phenoxy)-acetic acid ethyl ester

Yield 13.54 g, 80%, m/e: (M+1), 211.2; IR (KBr) 1735 (C=O ester), 1039 cm<sup>-1</sup> (O–CH<sub>3</sub>), 1247, 1040 cm<sup>-1</sup> (C–O–C); <sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>): δ 1.13 (t, J = 7.20 Hz, 3H), 3.72 (s, 3H), 4.33 (q, J = 8.00 Hz, 2H), 4.90 (s, 2H), 6.57 (dd, J = 2.54, 8.22 Hz, 1H), 6.71 (d, J = 6.80 Hz, 2H), 7.18–7.22 (m, 1H).

#### 2.2.2. Synthesis of (3-methoxy-phenoxy)-acetic acid hydrazide (3-MAH)

Yield, 9.58 g 79%, m/e: (M+1), 197.2; IR (KBr) 3344 (NH, NH<sub>2</sub>), 3203 (NH<sub>2</sub>), 2963 (C–H), 1622 (CO–NH); <sup>1</sup>H-NMR (400 MHz,

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