

Synthesis and characterization of benzoin α -oxime and 2,6-pyridine dimethanol and its application of anti-corrosion behaviour

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Synthesis of benzoin α -oxime and 2,6-pyridine dimethanol through eco-friendly method. These synthesized compounds are characterized by UV-Visible, FTIR and NMR spectral techniques. Anti-corrosion behaviour of benzoin α -oxime and 2,6-pyridine dimethanol both the compounds studied with 2 N sulphuric acid on mild steel. The anti-corrosion behaviour of the synthesized compounds was studied by subjecting to weight loss measurements, polarisation studies and electrochemical impedance spectra (EIS) for the assessment of its performance. The studies were made with 2 N sulphuric acid as the corroding medium, but with the inhibitors concentration in the range of 50–350 ppm. The results revealed that the inhibitor studied perform better in the medium and function by the mechanism of adsorption on the metal surface.

Keywords: Mild steel, sulphuric acid, benzoin α -oxime, 2,6-pyridine dimethanol.

Introduction

Inhibitors are often added in industrial processes to secure metal dissolution from acid solutions. Standard anti-corrosion coatings developed till date passively prevent the interaction of corrosion species and the metal. The known hazardous effects of most synthetic organic inhibitors and the need to develop cheap, nontoxic and ecofriendly processes have now urged researchers to focus on the use of natural products. Increasingly, there is a need to develop sophisticated new generation coatings for improved performance¹. The electro active compounds form a thin film or molecular layers on the metal surface. Traditionally, hetero aromatic compounds have been used for mild steel (MS) protection².

The performance of an organic inhibitor is related to the chemical structure and physicochemical properties of the compound like functional groups, electron density at the donor atom, p-orbital character, and the electronic structure of the molecule. The results of these studies confirm that the inhibition effect principally depends to adsorptions centers of inhibitory molecules which heteroatoms and aromatic rings in their structure³. The adsorption of these inhibitors on the metal surface for protect the metal surface from the corrosive medium depends on nature and charge of the metal,

the type of electrolyte, and the inhibitor structure⁴. In the present study, were used for evaluate the effect of synthesized organic compounds on the inhibition behaviour of high carbon steel in 2 M sulphuric acid.

Experimental

The compounds of benzoin α -oxime and 2,6-pyridine dimethanol were synthesised using the method reported in the literature. The course of the reaction was monitored by thin layer chromatography (TLC). After the completion of the reaction, the catalyst was separated by filtration. The excess solvent was removed by distillation at high vacuum and the product was separated by column chromatography using silica gel column packed with 15% methanol in chloroform. The compounds were analyzed by FTIR spectroscopy using the instrument, NICOLET iS5 model, Thermo Scientific Instrument, USA. JASCO 630V UV-Vis spectrophotometer and NMR. Polarization and electrochemical impedance studies for the mild steel specimens were carried out with a CHI electrochemical workstation, Model 650C, USA. Scanning Electron Microscope model Hitachi, Japan Model No: SN 3000. The inhibition efficiency and the corrosion rate were calculated from the observed weight losses.

Results and discussion

The UV-Visible spectrum of the synthesized benzoin α -oxime is recorded. The spectrum shows one sharp peak at about 250 nm is attributed to the π - π^* transition. Another peak appearing at 330 nm is attributed to chromophores of benzoin α -oxime. 2,6-Pyridine dimethanol also shows cleavage two broad peak at 250 nm and 350 nm. Here also observed the same transition like other nitrogen compounds.

FT-IR spectrum of the 2,6-pyridine dimethanol and benzoin α -oxime which are highly characteristic of the aromatic ring. The ring carbon-carbon stretching vibrations occur in the region 1430 – 1225 cm^{-1} . The bands at 3068 cm^{-1} are due to C-H stretching vibration resulting from the pyridine ring. The C=N stretching vibrations are predicted at 1660 cm^{-1} . The broad band obtained at 3206 due to OH group of benzoin α -oxime molecule. There are four main common peaks observed to 2,6-pyridine dimethanol which are due to, O-H stretching at 3351 cm^{-1} , the stretching vibration peaks of the CH_2 group at 2358 cm^{-1} , the stretching vibration peak of the C-O group at 1726 cm^{-1} , and the CH stretching vibration peak at 1219 cm^{-1} . The presence of 1532 cm^{-1} peak due to the CHN vibration.

Benzoin α -oxime shows ^1H NMR signals at 3.7, 6.8, 7.1, 7.3, 7.8, 8.5 and 9.5 ppm for aromatic and hydroxyl protons respectively. This compound exhibits ^{13}C NMR signals at 53, 113, 115, 122, 129, 143, 156, 157 and 162 ppm. ^1H NMR spectroscopy showed of 2,6-pyridinedimethanol shows three different signals at 4.7, 7.4 and 7.8 ppm for Hydroxyl and aromatic proton respectively. ^{13}C NMR behavior of 2,6-pyridinedimethanol exhibits four different carbon position at 65, 124, 140 and 160 ppm.

The calculated inhibition efficiencies (IE) and corrosion

rates (CR) of organic compounds in controlling corrosion of carbon steel immersed in $2\text{ N H}_2\text{SO}_4$ solution in the absence and presence of inhibitors are given in Fig. 1. It is found that the inhibition efficiency of nitrogen presented organic compounds increases by the addition inhibitors. The calculated value indicates the ability of compounds to be a good corrosion inhibitor.

The effect of addition of the inhibitor tested at different concentrations on the corrosion of mild steel in $2\text{ N H}_2\text{SO}_4$ solution is studied by weight loss at room temperature after different time interval of immersion period. For every concentration of inhibitor, the mean value of the corrosion rate W_{corr} ($\text{mg cm}^{-2} \text{ h}^{-1}$) was determined and the inhibitor efficiency, ΔW , was calculated. It is very clear that the corrosion rate (W_{corr}) decreases with increasing inhibitor concentration and the inhibition efficiency increases with inhibitor concentration and attains 95.56%.

Organic inhibitors generally act by means of physical adsorption or chemical adsorption on the metal surface. Adsorption isotherms are frequently used to describe the adsorption. In order to gain more information about the mode of adsorption of the inhibitor on the surface of mild steel, the experimental data have been tested with several adsorption isotherms. The values of surface coverage (θ) for different concentrations at different temperatures have been used to explain the best isotherm that determines the adsorption process. The values of surface coverage (θ) were evaluated from weight loss measurements: The correlation of θ with concentration of inhibitor was evaluated by different adsorption isotherms such as Langmuir, Frumkin and Temkin. However, the best fit was obtained from the Langmuir isotherm (Fig. 2).

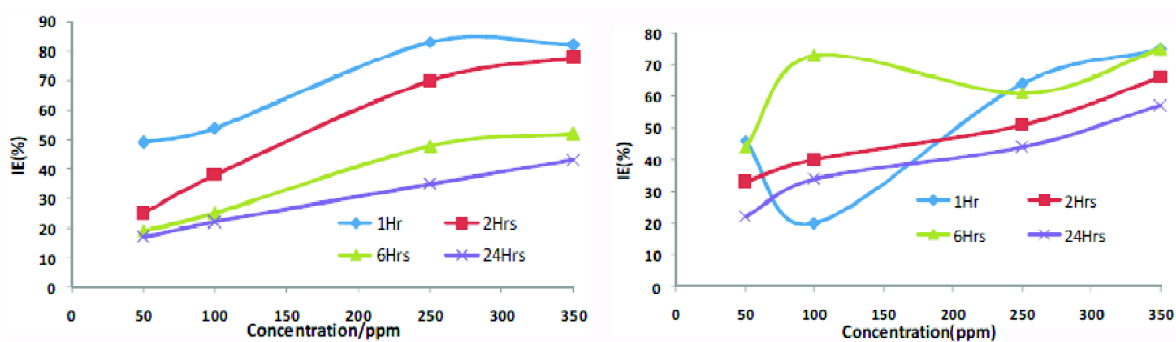


Fig. 1. Efficiency of inhibitor curve of (a) benzoin α -oxime and (b) 2,6-pyridine dimethanol.

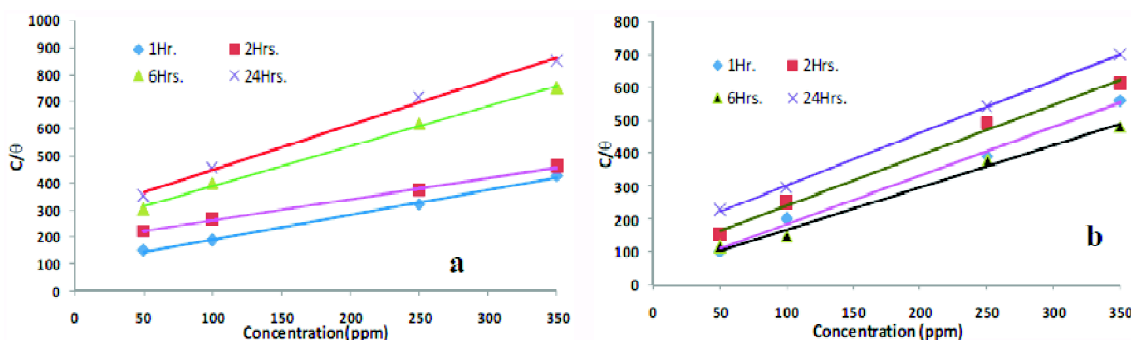


Fig. 2. Langmuir adsorption isotherm of (a) benzoin α -oxime and (b) 2,6-pyridine dimethanol.

The potentiodynamic polarization curves for benzoin α -oxime on steel recorded in $2\text{ N H}_2\text{SO}_4$ solution are shown in Fig. 3. The Tafel plot show that the protective action of the benzoin α -oxime a change of the corrosion potential to positive values. The observations of the present results pointed out the remarkable capability of benzoin α -oxime to protect steel against corrosion in $2\text{ N H}_2\text{SO}_4$ solutions. Also, the Tafel measurements clearly show that a substantial reduction in the corrosion current density (i_{corr}) occurs.

Open Circuit Potential (OCP) values are in the presence of inhibitor shifted towards more positive potential with time compared to those of acid solution. For example, the steady state value of OCP for mild steel in blank solution was -880 mV whereas, in the presence of 2,6-pyridine dimethanol it was shifted towards the positive direction to -755 mV . Thus, there is a shift in the steady state value of OCP in the presence of 2,6-pyridine dimethanol. Typical Tafel plots for the corrosion of mild steel in $2\text{ N H}_2\text{SO}_4$ and in the presence of

2,6-pyridine dimethanol are shown in Fig. 3.

The presence of a single semi circle (Fig. 3) the benzoin α -oxime acts as a barrier. The charge transfer resistance (R_{ct}) value of mild steel is low, whereas for the inhibitor it is high. Also the decrease in C_{dl} is attributed to increase in thickness of double layer. The increase in R_{ct} value is attributed to the formation of protective film on the metal/solution interface. These observations suggest that benzoin α -oxime adsorption on metal surface thereby causing the decrease in C_{dl} values and increase in R_{ct} values.

SEM photographs of the specimens immersed in the benzoin α -oxime (Fig. 4) solutions are in better conditions having retained smooth surface/polish. There appears the presence of less roughness on mild steel surface. This observation indicates that the inhibitor molecules hinder the dissolution of steel by forming organic film on the MS surface and thereby reduce the rate of corrosion. SEM image of mild steel sample in $2\text{ N H}_2\text{SO}_4$ inhibited with 2,6-pyridine

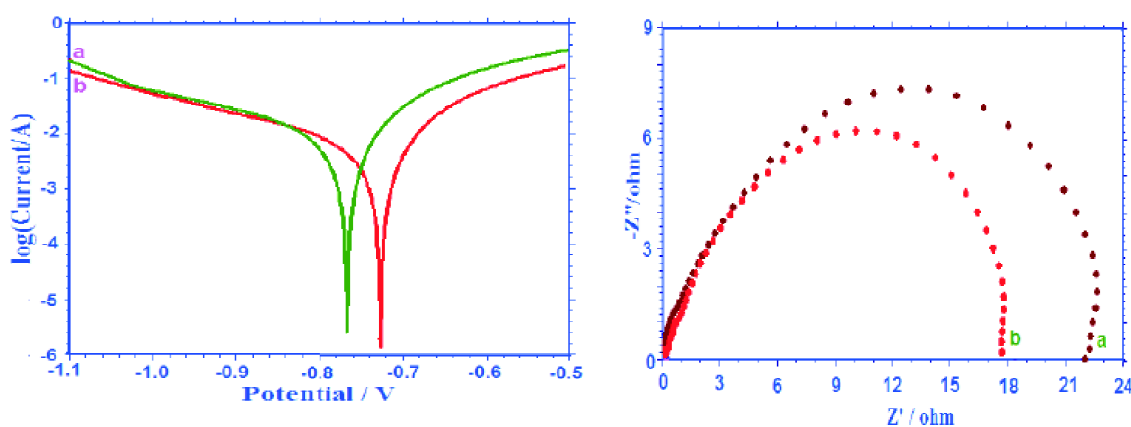


Fig. 3. Tafel and electrochemical impedance behaviour of (a) benzoin α -oxime and (b) 2,6-pyridine dimethanol.

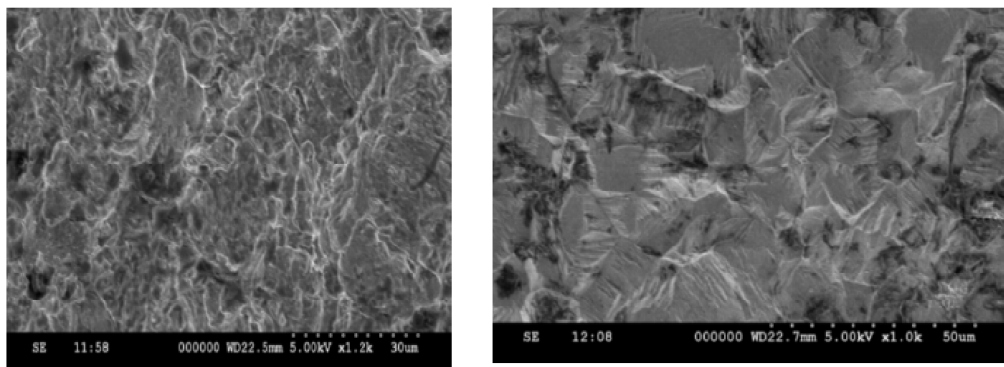


Fig. 4. SEM photographs of (a) benzoin α -oxime and (b) 2,6-pyridine dimethanol film on MS.

dimethanol shown in Fig. 4. The mild steel is reasonably inhibited by 2,6-pyridine dimethanol and surface also exhibit less reduced roughness in structure.

Conclusion

UV-Vis spectra was exhibits the π - π^* transition of both compounds confirmed ring structure. From FT-IR spectrum of the 2,6-pyridine dimethanol and benzoin α -oxime shows bands at 3068 cm^{-1} are due to C-H stretching vibration from the pyridine ring. Both compounds examined by ^1H NMR and ^{13}C NMR results exhibits hydroxyl and aromatic proton. Inhibition efficiencies (IE) and corrosion rates (CR) were found that the nitrogen presented organic compounds. The calculated value indicates good corrosion inhibitor. The values of surface coverage (θ) were evaluated from weight loss measurements: The correlation of θ with concentration of inhibitor was evaluated by Langmuir isotherm. The Tafel plots show that the protective action of the benzoin α -oxime. The decrease in C_{dl} is attributed to increase in thickness of double layer. The increase in R_{ct} value is attributed to the formation of protective film on the metal/solution interface. The mild steel is reasonably inhibited by 2,6-pyridine dimethanol and surface also exhibit less reduced roughness in structure.

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