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Experimental and theoretical investigations of a newly synthesized azomethine compound as inhibitor for mild steel corrosion in aggressive media: A comprehensive study

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ABSTRACT

A new azomethine compound viz. 3-(2-amino-4,5-dimethylphenyl)imino)methyl) benzaldehyde (ADMB) was synthesized following a greener approach at room temperature and its anti-corrosion characteristics for mild steel (MS) corrosion were examined at various temperatures (298 K to 328 K) and concentrations (1 mM to 0.001 mM) in 0.5 M H_2SO_4 via electrochemical methods allied with surface characterization techniques. The adsorption of the ADMB molecules on the metal surface follows Langmuir's adsorption isotherm. To ascertain the mode of adsorption process, various adsorption and activation parameters were evaluated. Surface characterization studies viz. ATR-FTIR, SEM, AFM and EDS depict the formation of protective layer of ADMB on MS specimen. Density functional theory (DFT) treatment of ADMB established that the lower energy gap (ΔE) between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) resulted in significantly high inhibition efficiency. These results have shown that ADMB act as an effective inhibitor for MS corrosion in H_2SO_4. The inhibition efficiencies predicted from experimental measurements are in agreement with the theoretically evaluated parameters and results of spectroscopic techniques.

1. Introduction

The diverse physical properties of mild steel alloy account for its extensive commercial use in several industries [1,2] but due to its restricted corrosion resistance, this alloy gets severely corroded because of its non-homogeneous surface and inability for forming stable passive films on its surface [3]. This alloy gets heavily oxidized and subsequently corroded in the sulphuric acid medium, during some important industrial processes viz. acid pickling, cleaning, acid descaling and oil well acidizing [4–7]. In the chemical industry, sulphuric acid is used in numerous processes and one of the most important and extensively used commodity due to its ability to take part in various chemical reactions. The major applications of sulphuric acid, amid others, is in iron and steel making industries where it is utilized for eradicating the scale and rust from the billets and rolled sheets. It is also used on large scale for washing out impurities from gasoline and several other refinery products in petroleum refineries. During these many processes, the interaction of this acid with the metals, drastically influence the durability and stability of the metal concerned in a negative manner via initializing and accelerating the corrosion reactions. Appropriate additive/inhibitor is generally employed to weaken the corrosion reactions in an acidic medium based on its effectiveness [8]. Chromate and dichromate based inhibitors were tested to have significant corrosion inhibition efficiencies but due to their toxic nature, the use of these compounds is generally restricted, taking environmental concerns into account. Therefore, researchers have focused to develop environmentally benign inhibitors which can be used sustainably without leaving the environment vulnerable [9].

Organic compounds having structural properties like electron cloud density on the aromatic ring and the presence of hetero atoms are found to work as better corrosion inhibitors. The mitigation efficiency of these compounds depends on electron density present around the hetero atoms, the number and charge density of adsorption active reaction centers, the size of the molecule and affinity for forming metallic complexes [10–13]. Azomethine compounds comprise of all these desirable properties and its environmental friendly nature make these compounds most suited for protection of several metals and their alloys from corrosion in aggressive medium [14–21]. These compounds can easily be synthesized from cost-effective starting materials and have the capacity to spontaneously form a thin protective layer on the surface of the metal under investigation, protecting it from aggressive media.

The present research work led by the search for a new and better eco-friendly organic corrosion inhibitor. As a part of this work, a new azomethine compound (ADMB) was synthesized and characterized. The corrosion inhibition studies of this compound on mild steel in

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H_2SO_4 have not been yet reported elsewhere. The anticorrosion performance of ADMB towards MS in 0.5 M H_2SO_4 was assessed via electrochemical methods allied to surface characterization techniques and DFT treatment of ADMB molecule. The mode of corrosion inhibition mechanism was also ascertained by temperature kinetics study.

2. Materials and methods

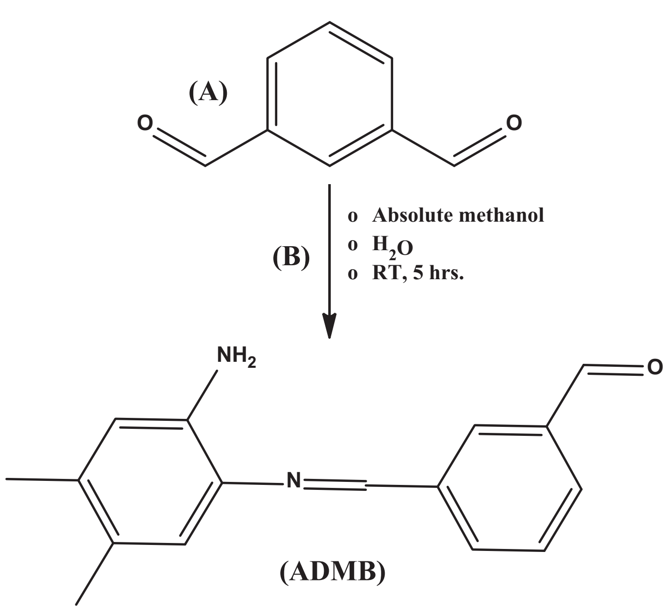
2.1. Materials

The reactants (Isophthalaldehyde and 4,5-dimethyl benzene-1,2-diamine) and solvents were purchased from Sigma-Aldrich, Alfa-Aesar and Merck. All solvents used were of analytical grades. For reactions to be performed under dry conditions, solvents were dried by the usually reported laboratory procedures.

2.2. Synthesis and characterization of inhibitor

The inhibitor 3-(2-amino-4,5-dimethylphenyl)imino)methyl) benzaldehyde (ADMB) was synthesized by allowing a nucleophilic addition reaction [22,23] (Scheme 1) of 4,5-dimethylbenzene-1,2-diamine (B) with Isophthalaldehyde (A). 4,5-Dimethylbenzene-1,2-diamine (0.73 mmol, 100.0 mg) was added in a three neck round bottom flask and dissolved in distilled water. Finally, a solution of Isophthalaldehyde (0.73 mmol, 98.3 mg) dissolved in dry methanol added dropwise to the reaction mixture and the reaction was stirred at room temperature on a magnetic stirrer for 5 h.

The reaction conditions were optimized and TLC was monitored at regular intervals. The precipitates obtained by filtration of the reaction mixture at the vacuum filtration pump were washed thoroughly with a mixture of double distilled water and methanol (1:1). The resultant compound was isolated in good yields (78.96%) as a bright yellow colored solid compound. The synthesis of the final compound was confirmed using ^1H NMR (Fig. S1), ESI-MS (Fig. S2), FT-IR (Fig. S3) and UV–Visible Spectroscopy (Fig. S4). M.P.: 142 °C–144 °C. ^1H NMR (DMSO d_6, 400 MHz): δ values (ppm) = 2.273 (s, 6H, $-2CH_3$), 6.539 (s, 1H, ArH), 7.014 (s, 1H, ArH), 7.966–8.033 (m, 4H, ArH), 8.758 (s, 1H, CH=N), 10.090 (s, 1H, —CHO). Elemental Analysis Data for $C_{16}H_{16}N_{2O}$ (252.31): Calculated: C 76.16, H 6.39, N 11.10, O 6.35; Found: C 76.13, H 6.43, N 11.10, O 6.31. ESI-MS: m/z = 253.1 amu $[M + H]^+$. Characteristic IR peaks (KBr disk, cm^{-1}): ν(C—H Stretch, Aromatic) 3061, ν(C=O) 1693, ν(C=N) 1608, ν(C—C Stretch, Aromatic) 1441–1468, ν(C—C) 1252. UV–Vis. [EtOH, λ_{max}/nm (ε/M^{-1} cm^{-1})]: π-π* = 314, n-σ* = 245.



Scheme 1. Synthetic route of ADMB.

2.3. Electrochemical, surface characterization and theoretical studies

The experimental specifications, fabrication of working electrode, method for electrolyte preparation, details of instrumental techniques and scientific software used have been discussed elsewhere [24–27,54,55].

3. Results and discussion

3.1. Electrochemical investigations of ADMB on mild steel corrosion

3.1.1. Galvanostatic polarization and linear polarization resistance measurements

The corrosion mitigation characteristic of ADMB was studied in 0.5 M H_2SO_4 at four different temperatures (298 K, 308 K, 318 K and 328 K) and concentrations (1 mM, 0.1 mM, 0.01 mM and 0.001 mM), the Tafel polarization plots obtained are shown in Fig. 1a to d and the corresponding corrosion parameters i.e., corrosion potential (E_{corr}), cathodic and anodic Tafel slopes, corrosion current (I_{corr}) obtained by Tafel extrapolation method and inhibition efficiency (η_{Tafel}) calculated using Eq. (1) are given in Table 1.

$$\text{Inhibition Efficiency } (\eta_{Tafel})\% = \frac{I_{Acid} - I_{Inh}}{I_{Acid}} \times 100 \qquad (1)$$

where I_{Acid} and I_{Inh} are the corrosion current densities of uninhibited and inhibited systems respectively.

The Tafel polarization curves in presence of ADMB at all the temperatures depict the drastic inhibition of both cathodic and anodic reactions which relates to the evolution of H_2 gas and dissolution of metal process respectively. The difference in observed E_{corr} values of the inhibited system in comparison with the uninhibited system was <85 mV, which further suggests that this inhibitor is of mixed type. The irregular variation of the observed cathodic and anodic Tafel slopes indicate that the corrosion inhibition of MS in aggressive media was due to the adsorption of ADMB molecules along with the blocking of active sites and formation of $[Fe\text{-}ADMB]_{ads}$ and $[Fe\text{-}ADMB\text{-}OH]_{ads}$ type of complexes on the MS surface [28].

With increase in the concentration of ADMB and decrease in the temperature, the inhibition efficiency increases. At higher concentration of ADMB i.e., 1 mM the evaluated inhibition efficiency is 98.82% which is attributed to the multilayer type of adsorption [29,30]. The surface coverage decreases with the decrease in the concentration of ADMB resulting in lesser corrosion inhibition.

The Linear polarization resistance (R_P) values given in Table 1 indicate that ADMB molecules were adsorbed on the metal surface, leading to the formation of a non-conducting physical barrier [31]. The inhibition efficiency (η_{LPR}) was calculated using the value of resistance polarization (R_P) by Eq. (2):

$$\text{Inhibition Efficiency } (\eta_{LPR}) = \frac{R_P - R_P^{\circ}}{R_P} \times 100 \qquad (2)$$

where R_P and R_P° are the resistance polarization values of inhibited and uninhibited systems respectively.

3.1.2. Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance studies were conceded in 0.5 M sulphuric acid containing different concentrations of ADMB at 298 K. The corresponding Nyquist and Bode's plot obtained are shown in Fig. 2a and b respectively. The impedance parameters obtained are given in Table 2. The inhibition efficiencies were calculated using