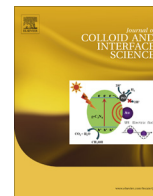




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Electrochemical investigation on the corrosion inhibition of mild steel by Quinazoline Schiff base compounds in hydrochloric acid solution



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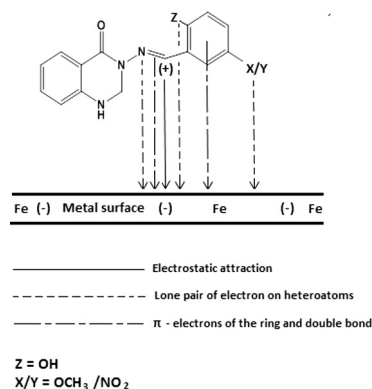
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GRAPHICAL ABSTRACT



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ABSTRACT

The inhibitory effect of two Schiff bases 3-(5-methoxy-2-hydroxybenzylideneamino)-2-(5-methoxy-2-hydroxyphenyl)-2,3-dihydroquinazoline-4(1H)-one (MMDQ), and 3-(5-nitro-2-hydroxybenzylideneamino)-2-(5-nitro-2-hydroxyphenyl)-2,3-dihydroquinazoline-4(1H)-one (NNDQ) on the corrosion of mild steel in 1 M hydrochloric acid were studied using mass loss, potentiodynamic polarization technique and electrochemical impedance spectroscopy measurements at ambient temperature. The investigation results indicate that the Schiff Bases compounds with an average efficiency of 92% at 1.0 mM of additive concentration have fairly effective inhibiting properties for mild steel in hydrochloric acid, and acts as mixed type inhibitor character. The inhibition efficiencies measured by all measurements show that the inhibition efficiencies increase with increase in inhibitor concentration. This reveals that the inhibitive mechanism of inhibitors were primarily due to adsorption on mild steel surface, and follow Langmuir adsorption isotherm. The temperature effect on the inhibition process in 1 M HCl with the addition of investigated Schiff bases was studied at a temperature range of 30–60 °C, and the activation parameters

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(E_a , ΔH and ΔS) were calculated to elaborate the corrosion mechanism. The differences in efficiency for two investigated inhibitors are associated with their chemical structures.

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1. Introduction

Nowadays the study of corrosion of mild steel in acidic solution has found extensive application in various chemical process industries including: acid pickling, acid descaling, petrochemical, and oil well acidizing, etc. [1,2]. Several studies on the application of organic compounds as effective corrosion inhibitor for mild steel in various acidic solutions have been reported [3–7]. The well-known organic compounds, containing heteroatoms like nitrogen, sulfur, and oxygen as well as aromatic ring or those containing π -electron in multiple bonds in their structure having high electron density are usually effective inhibitors [8–17]. These organic inhibitors act on the metal surface by the virtue of adsorption and influenced by the several factors including: the type of electrolyte, the nature and surface morphology of metal as well as their chemical structure [18,19]. Usually, a higher inhibition efficiency caused by a strong co-ordination bond, the presence of heteroatoms increases the inhibition efficiency in the order $O < N < S < P$ [20].

Many studies have been reported that some Schiff bases are effective for the inhibition of mild steel, copper, zinc, and aluminum in aggressive solutions [20–23]. Schiff bases, in general become effective and having the tendency to adsorb on the metal surface, by blocking the active corrosion centers, therefore protecting the metal from aggressive solution, causes the metal decomposition. Literature revealed that due to the presence of $>C=N-$ group, electron clouds on the aromatic rings and electronegative heteroatoms like oxygen, nitrogen and sulfur atoms in the molecular structure of Schiff bases, they are considered to be effective corrosion inhibitor than that of corresponding aldehydes and amines [24,25].

The aim of the present study is to investigate the inhibition action of two newly synthesized Schiff bases (Fig. 1) on the mild steel in 1 M HCl solution and comparing their inhibition efficiencies at different temperature. Moreover, the influence of the functional groups like: $-OCH_3$, $-OH$, and $-NO_2$ present in their structure, on the inhibitory efficiencies were studied and analyzed. To investigate the inhibition efficiencies of these compounds, the gravimetric and electrochemical measurements were employed in the present work. The Surface morphology of the samples was examined using scanning electron microscopy (SEM) and inhibitor adsorption mechanism was also described.

2. Experimental

2.1. Materials

The employed working electrode was mild steel having the chemical composition (wt.%) of: 0.039 C, 0.038 S, 0.021 P, 0.36 Mn and the remainder is Fe. The working electrode of dimensions $2\text{ cm} \times 2\text{ cm} \times 0.1\text{ cm}$ were used for weight loss method and of $1.6\text{ cm} \times 1.6\text{ cm}$ with an exposed flat surface area of 2.56 cm^2 mounted in polyster base exposed to the corrosive environment were used for electrochemical measurements. Before each experimental run the electrodes were mechanically abraded to mirror finish by a sequence of emery papers of grade Nos. 400, 600, 800, 1200 and 1500 followed by thoroughly washing with double distilled water and degreased with trichloroethylene. The acid solution of

1 M HCl were prepared from analytical grade HCl (37% Merck, density 1.185).

2.2. Preparation of Schiff base inhibitors (MMDQ and NNDQ)

The quinazoline Schiff base compounds were synthesized generally through the well known procedure according to the earlier published report [26] as follows: Aminobenzhydrazone (2.5 mmol) was properly mixed with 50 ml of ethanol in a 500 ml conical flask and stirred by employing a magnetic stirrer. Aromatic salicylaldehyde (5.0 mmol); 2-hydroxy-5-methoxy benzaldehyde (2.01 g, 10 mmol) dissolved in 25 ml of ethanol and added drop wise to the solution, the reaction mixture was refluxed for 2 h and allowed to cool down at ambient temperature. The brown (MMDQ) and yellow (NNDQ) precipitate was filtered and re-crystallized from ethanol. Anal. Calc. for MMDQ: $C_{21}H_{15}N_3O_3OCH_3$: C, 48.63%; H, 2.86%; N, 8.153%; mp 236–238 °C; IR (KBr); $\nu_{(C=N)}$ 1589 cm^{-1} . Anal. Calc. for NNDQ: $C_{23}H_{19}NO_2N_3O_5$: C, 47.86%; H, 3.32%; N, 7.28%; mp 216–218 °C; IR (KBr) $\nu_{(C=N)}$ 1610 cm^{-1} .

2.3. Weight loss measurements

The gravimetric measurements for corrosion were conducted according to ASTM standard G1-3 procedure [27]. The weight loss of mild steel specimen in 1 M HCl were determined using electrical balance (accuracy 0.01 mg) with and without the addition of investigated inhibitors at 25 °C for each inhibitor concentration (1 mM) for 6 h exposure in 50 ml test solution. For each case a duplicate experiment was conducted and was repeated for other two inhibitors as well. In the case of the present study, the relative mass differences between the duplicate experiments were observed less than 4%, at definite experimental conditions, demonstrating good data reproducibility. The average mass loss was calculated by the difference between the original and duplicate sets of data and corrosion rate was expressed in (mpy). The inhibition efficiency $IE_{WL}\%$ was calculated using Eq. (1) [28]:

$$IE_{WL} (\%) = \frac{W_1 - W_2}{W_1} \times 100 \quad (1)$$

$$\text{Corrosion rate (mpy)} = \frac{534 \times \text{Weightloss in mgm}}{\text{Density (g/CC)} \times \text{Area (Sq. cm)} \times \text{Time (hrs)}} \quad (2)$$

$$\text{Surface coverage } (\Theta) = \frac{W_1 - W_2}{W_1} \quad (3)$$

where W_1 and W_2 denoting the mass losses in uninhibited and inhibited test solution respectively.

2.4. Electrochemical studies

A conventional three electrode cell was utilized in these experiments, with mild steel (2.56 cm^2) as the working electrode, a platinum wire and saturated calomel electrode (SCE) as the counter electrode and reference electrode respectively. General purpose electrochemical software (GPES) and Frequency response analysis (FRA) software were used for anodic and cathodic Tafel curves and EIS experimental measurements and open circuit potential (OCP) techniques. These softwares were installed in a computer

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