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Evaluation of the Inhibitive Effect of Novel Quinoline Schiff Base on Corrosion of Mild Steel in HCl Solution

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***Abstract*—**Schiff base (E)-2-methyl-N-(tetrazolo[1,5-a]quinolin-4-ylmethylene)aniline (QMA) was synthesized, and its inhibitive effect for mild steel in 1N HCl solution was investigated by weight loss measurement and electrochemical tests. From the weight loss measurements and electrochemical tests, it was observed that the inhibition efficiency increases with the increase in the Schiff base concentration and reaches a maximum at the optimum concentration. This is further confirmed by the decrease in corrosion rate. It is found that the system follows Langmuir adsorption isotherm.

***Keywords*—**Schiff base, acid corrosion, electrochemical impedance spectroscopy, polarization.

I. Introduction

ACID solutions are used for the removal of undesirable scale &rust in many industrial processes. The use of inhibitors is one of the most practical methods to protect against excessive corrosion, especially in the acidic media [1]. The use of organic compounds containing oxygen, sulfur, and nitrogen to reduce corrosion attack on steel has been studied in detail [2]. Organic inhibitors generally protect the metal from corrosion by forming a film on the metal surface. The effectiveness is related to chemical composition, their molecular structure, and their affinities for the metal surface. The addition of corrosion inhibitors effectively protects the metal against an acid attack. Inhibitors are used in these processes to control metal dissolution [3]. Schiff base compounds are the condensation product of an amine and a ketone/ aldehyde. Schiff base inhibitors have been reported as corrosion inhibitors for steel, copper and aluminum [4]-[8]. The adsorbed species protect the metal from corrosion. Adsorption depends on the nature, charge of the metal and the chemical structure of the inhibitor. The efficiency of Schiff's bases is much higher than that of corresponding aldehyde and amines, and this may be due to the presence of a >C=N- group in the molecules. The planarity (π) and lone pairs of electrons present on N atoms are important structural features that determine the adsorption of Schiff's base molecules on a metal surface. The aim of the present investigation was to synthesize and evaluate a novel Schiff base, (E)-2-methyl-N-(tetrazolo[1,5-a]quinolin-4-ylmethylene)aniline (QMA)and its performance as acid corrosion inhibitor for mild steel in 1M HCl by weight loss, polarization, and electrochemical impedance spectroscopy.

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II. Experimental

A. Materials

Mild steel (MS) specimens having a composition of 0.09% P, 0.37% Si, 0.01% Al, 0.05% Mn, 0.19% C, 0.06% S, and the remainder Fe, were used for electrochemical polarization and impedance measurements. Specimens of 1cm × 1cm area were polished with emery paper number 120-1000, degreased with acetone, washed with double distilled water, and dried at room temperature before immersing in acid solution. The acid solutions were made from analytical grade 37% HCl and double-distilled water.

A Schiff base compound QMA with a structural formula as shown in Fig. 1 was synthesized to a stirred mixture of 2-chloro-quinoline-3-carbaldehyde (0.005 mol) and sodium azide (0.005 mol) in ethanol with a catalytic amount of PTSA and refluxed for 5-6 hours. After the reaction was complete, the reaction mixture was poured onto crushed ice; the solid mass thus separated out, was filtered, washed with distilled water, and dried. Then, tetrazolocarbaldehyde was treated with 2-methylaniline in ethanol with catalytic amount of sulphuric acid and refluxed for 6-7 hours .After the reaction was complete, the reaction mixture was poured onto crushed ice; the solid mass thus separated out, was filtered, washed with distilled water, and dried.

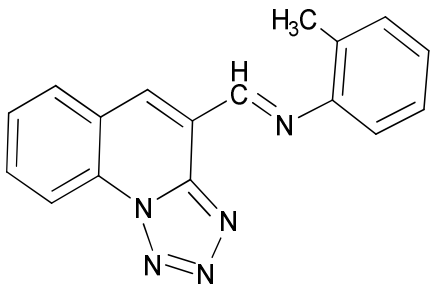


Fig. 1 (E)-2-methyl-N-(tetrazolo[1,5-a]quinolin-4-ylmethylene) aniline (QMA)

B. Weight Loss Method

Weight loss measurements were carried out by weighing the prepared specimens before and after immersion for 4h in 100mL stagnant test solutions of 1NHCl in the presence and absence of various concentrations of QMA. From the weight loss data, percent inhibition efficiency (IE %) was calculated at different concentrations at 30°C. At the end of testing the specimens were carefully washed with acetone, dried, and then weighed.

C. Electrochemical Measurements

Polarization and impedance measurements were carried out in a conventional three electrode Cylindrical borosilicate glass cell consisting of a carbon steel working electrode(WE), a platinum counter electrode (CE), and saturated calomel electrode (SCE) as the reference electrode using a CH electrochemical analyzer model 608 C USA Potentiostat/ galvanostat. Polarization curves were obtained at a scan rate of 0.01V/s in the range of -250mV to +250mV vsE_{corr}. 1cm^2 surface area of a polished carbon steel specimen was exposed to 200mL of 1M HCl solution at 30°C, without and with various concentrations of inhibitor.

The Electrochemical impedance measurement was made in the frequency range of 0.1Hz to 1000Hz. The AC signal was 5mV peak to peak with 12 data points per decade. The double layer capacitance (Cdl) and the charge transfer resistance (R_t) were calculated from Nyquist plots.

III. Results and Discussion

A. Weight Loss Measurements

Corrosion of MS in 1NHCl in the absence and presence of various concentrations (5-25 ppm) of QMA was determined by weight loss experiments. The corrosion rate (W_{corr}) and the values of inhibition efficiency (IE %) were calculated according to following equation:

$$IE\ \% = \frac{Wcorr - Wcorr\ (inh)}{Wcorr} \times 100 \qquad (1)$$

where $W_{corr(inh)}$ and W_{corr} are the corrosion rates of MS with and without inhibitor respectively.

TABLE I
Inhibition Efficiency of Mild Steel in 1N HCl solution in the Presence and Absence of Different Concentrations of the QMA (Weight Loss Method)

Concentration of QMA in ppm	Corrosion Rate (mpy)	IE %
1 N HCl	19.3	-
5	1.98	89.74
10	1.70	91.19
15	1.34	93.05
20	1.08	94.40
25	0.95	95.07

The values of IE %, $W_{corr\ (inh)}$ and W_{corr} were obtained from weight loss measurements with the addition of various concentrations of QMA after 4 h of immersion in 1N HCl solutions.

From Table I, it was found that the value of IE % increased with an increase in the concentration of QMA, confirming that the number of molecules adsorbed increased over the MS surface, blocking the active sites of acid attack and protecting the metal from corrosion. At 25 ppm of QMA added, the IE% was 95.07% and showed that QMA was a very effective inhibitor.

The nature of interaction between MS surface and inhibitor can be established by studying the type of isotherm for the system.

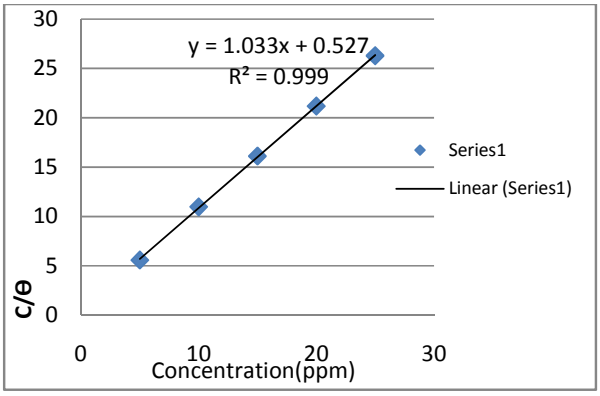


Fig. 2 Langmuir isotherm adsorption of QMA on mild steel in 1 N HCl at room temperature

The inhibition efficiency increases with increase in the concentration of QMA. Thus QMA is adsorbed strongly on the MS surface forming a protective layer and shielding the metal from corrosion [9]-[11]. The observed inhibitive action of the QMA is attributed to the adsorption of the molecule on the metal surface by the interaction of the π electrons of the C=N group and the π electrons of the aromatic ring [12], [13]. Adsorption of QMA on the steel surface forms a barrier between metal and the aggressive environment. More over the presence of the electron donating groups on the Schiff base such as CH_3 increases the electron density on the nitrogen of -C=N group resulted in the high inhibition efficiency. As concentration of QMA is increased, the fraction of steel covered by the adsorbed molecules, θ increases, leading to higher inhibition efficiency. Because of the direct relation between IE % and θ, the latter can be estimated using the relation θ=IE % /100. Fig. 2 shows the graphical relation between concentration C and ratio of concentration C and θ (C/θ) is a straight line with an approximate slope of unity. The system follows a Langmuir adsorption isotherm. The Langmuir isotherm is a linear relationship between C/θ and concentration C with a slope of ideally unity.

The adsorption behavior was described by using the Langmuir isotherm expressed as:

$$K\,C = \theta / (1 - \theta) \qquad (2)$$

where K is the equilibrium constant of the inhibitor adsorption process, C is the inhibitor concentration.

The free energy Δ G was calculated as follows:

$$\Delta G_{ads} = -2.303RT\log(55.5K_{ads}) \quad (3)$$

The negative value of ΔG indicates a spontaneous adsorption of inhibitor molecules on the metal surface [14], [15].

B. Polarization Measurement

To evaluate the effect of QMA on the electrochemical behavior of MS, cathodic as well as anodic polarization studies were carried out as shown in Tafel plots in Fig. 3. The corrosion kinetic parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), and anodic and cathodicTafel slopes (b_a and b_c) were derived from these curves and are given in Table II. The values of inhibition efficiency (IE%) were calculated using the following equation:

$$IE\ (\%) = \frac{Icorr - I''corr}{Icorr} \times 100 \quad (4)$$

where I_{corr} and I''_{corr} were the values of corrosion current densities without and with the different concentrations of QMA, respectively, which were determined by extrapolation of the cathodic and anodic Tafel lines to the corrosion potential E_{corr}. It was observed from Table II that the values of IE% increased from 94.18 to 98.29 with increase in the concentration of QMA, the highest IE% was observed at 25ppm concentration of QMA, and the I_{corr} values decreased from 0.2373mA/cm^2 to 0.0697 mA/cm^2 with the increase in QMA concentration from 5 to 25 ppm, which confirmed the strong adsorption of QMA on the MS surface.

TABLE II
THE VALUES OF TAFEL POLARIZATION PARAMETERS FOR THE CORROSION OF MS IN 1 N HCL SOLUTION CONTAINING DIFFERENT CONCENTRATIONS OF THE QMA

Concentration of inhibitor (ppm)	$-E_{corr}$ V	Tafel Constant (mV/decade) b_a	b_c	i_{corr} (mA/cm^2)	Rp (ohm cm^2)	IE_I%	IE_{Rp}%
1 N HCl	0.508	145	135	4.0800	7	-	-
5	0.462	85	105	0.2373	86	94.18	91.86
10	0.464	91	106	0.2044	104	94.99	93.26
15	0.460	92	108	0.1528	141	96.25	95.03
20	0.459	111	136	0.0977	272	97.60	97.42
25	0.446	116	151	0.0697	410	98.29	98.29

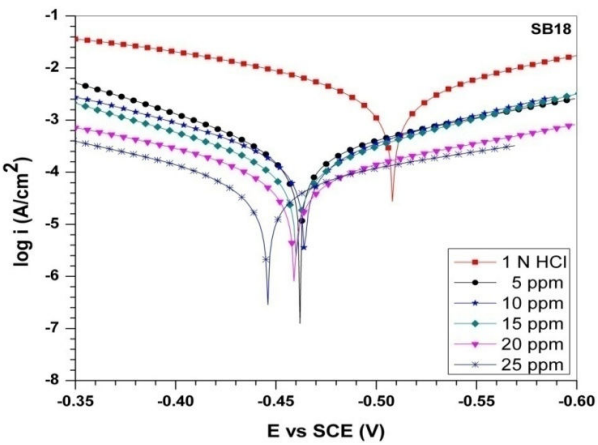


Fig. 3 Polarization curves for mild steel in 1NHCl in the absence and presence of different concentrations of QMA

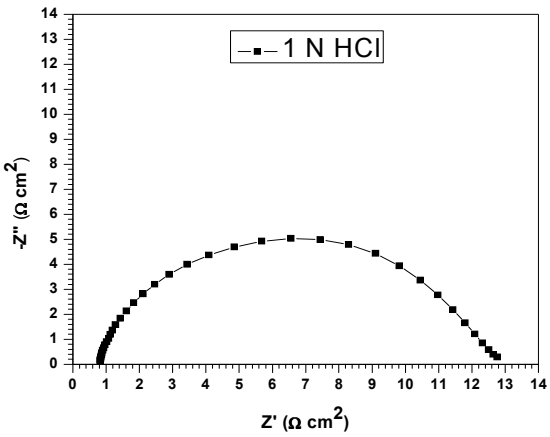
The inhibiting property of QMA has also been evaluated by determining the polarization resistance $R_p(\Omega cm^2)$. The corresponding polarization resistance (R_p) values for MS in 1 N HCl in the absence and presence of different concentrations of the QMA is given in Table II. The values of inhibition efficiency (IE%) were calculated as follows:

$$IE\ \% = \frac{R_{p(inh)} - Rp}{Rp\ (inh)} \times 100 \quad (5)$$

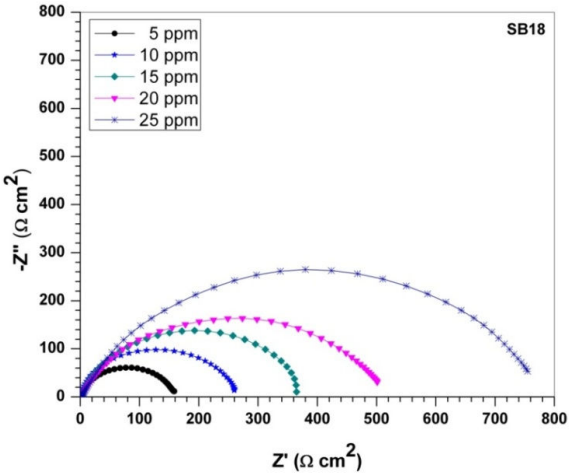
where R_p and $R_{p(inh)}$ were the polarization resistance in the absence and in the presence of the inhibitor respectively.

It was observed that the Tafel plot in 1 N HCl solutions for MS with different concentrations of QMA was similar (Fig. 2). Corrosion currents obtained with the additions of QMAwas lower than the corrosion current obtained for MS in 1NHCl solution without the inhibitor. The IE % increased with an increase in the concentration of QMA (Table II). QMA has acted as an effective corrosion inhibitor suppressing both anodic and cathodic reactions due to their adsorption on the MS surface blocking the active sites [16]. Moreover, there was an anodic shift in E_{corr} values to show that the inhibitor may have retarded anodic reaction.

It was observed that the R_p values gradually increased with increase in the concentration of the inhibitor (Table II).



(a)



(b)

Fig. 4 (a) Nyquistplot of MS in 1 N HCl solution without Schiff base, (b) Nyquist plot for mild steel in 1N HCl in the presence of different concentrations of QMA

Nyquist plots of electrochemical impedance spectroscopy for MS in 1 N HCl containing different concentrations of QMA is presented in Fig. 4 (b).

The values of inhibition efficiency (E_R %) were calculated by following equation:

$$E_R\% = 100 \times \frac{R_{t(inh)} - R_t}{R_{t(inh)}} \quad (6)$$

where R_t and $R_{t(inh)}$ were the charge-transfer resistance (Ω cm^2)values in the absence and the presence of the inhibitor respectively.

Nyquist plots in Fig. 4 (b) contained depressed semi-circles with the center on the real axis, whose sizes increased with the increase in concentration of the inhibitor QMA, confirming that the charge transfer processes were mainly controlling the corrosion of MS. The minimum value of real impedance (Z') was 12 Ω $cm^2$and there was a gradual increase in the diameter of each of the semicircles of the Nyquist plots when the concentrations were raised from 5 to 25 ppm (Fig. 4). The gradual increase of the diameters of Nyquist plots agreed with the increase of R_t values. At a concentration of 25 ppm of the inhibitor QMA, due to the formation of the barrier layer of the inhibitive molecules the value of R_t was found to be maximum.

TABLE III
ELECTROCHEMICAL IMPEDANCE PARAMETERS FOR MS IN 1 N HCL SOLUTION IN THE PRESENCE OF DIFFERENT CONCENTRATIONS OF THE QMA

Concentration (ppm)	R_t(Ω cm^2)	Cdl (μF/cm^2)	IE (%)
1 N HCl	12	163	-
5	160	123	92.50
10	260	76	95.38
15	365	45	96.71
20	520	31	97.69
25	780	17	98.46

It can be seen from Table III, there was a gradual decrease in the value of C_{dl} with an increase in the concentration of QMA. The double layer between the charged metal surface and the solution is considered an electrical capacitor. The decrease of the capacitance with increase in the concentration of QMA can be related to the formation of a protective layer on the MS electrode surface. Inhibition efficiency (IE%) was found to increase with the increase in concentration of QMA. The results obtained from electrochemical impedance spectroscopy study have shown a similar trend as those obtained from electrochemical polarization and weight loss measurements.

The results suggest that the corrosion rate of MS was significantly decreased due to adsorption mechanism affecting both the anodic and cathodic processes.

IV. CONCLUSION

A novel Schiff base, QMA has shown good corrosion inhibiting characteristics for controlling corrosion of mild steel in 1NHCl.The inhibition efficiency increases with the increase in the inhibitor concentration and attains a maximum value at 25ppm. The inhibitor acted as a mixed type inhibitor controlling both cathodic and anodic reactions. The weight loss results, results of electrochemical impedance spectroscopy and polarization study are in good agreement. The adsorption of QMA on the metal surface follows Langmuir adsorption isotherm.

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