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

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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, polarization 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 sulfuric 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 was studied, and the activation parameters (Ea, ΔH and ΔS) were

calculated to elaborate the corrosion mechanism. The differences in efficiency for two investigated inhibitors are associated with their chemical structures.

Key words

Mild Steel; Corrosion inhibition; EIS; Schiff Bases; SEM; Kinetic parameters

1. INTRODUCTION

Nowadays the study of corrosion of mild steel in acidic solution has find extensive application in various chemical process industries including: acid pickling, acid descaling, petrochemical, and oil wet cleaning 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 acts 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].

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 - 25]. Schiff bases, in general become effective and having the tendency to adsorb on metal surface, by blocking the active corrosion centers by protecting the metal from aggressive solution, causes the metal decomposition. Literature revealed that due to the presence of >C=N- group in the molecular structure of Schiff bases, they are considered to be effective corrosion inhibitor than that of corresponding aldehydes and amines [26, 27].

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 reminder is Fe. The working electrode of dimensions 2cm x 2cmx 0.1 cm were used for weight loss method and of 1.6 cm x 1.6 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 polished mechanically by a sequence of emery papers of grade Nos. 400, 600, 800, 1200 and 1500 folloews by throughly washing with double distilled water and degreased with acetone. 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 acording to the earlier published report [28] as follows: aminobenzyhydrazide (2.5mmol) was properly mixed with 50 ml of ethanol in a 500 ml conical flak and stirred by employing a mangnetic stirrer. Aromatic salicyaldehyde (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 misture was refluxed for 2 hr and allowed to cool down at ambient temperature. The brown (MMDQ) and yellow (NNDQ) preciptate was filtered and re-cystallized from ethanol. Anal. Calc. for MMDQ: $C_{21}H_{15}N_3O_3OCH_3$: C, 48.636; H, 2.864; N, 8.153 %; mp 236–238°C;IR (KBr); $\upsilon_{(C=N)}$ 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) $\upsilon_{(C=N)}$ 1610 cm^{-1}.
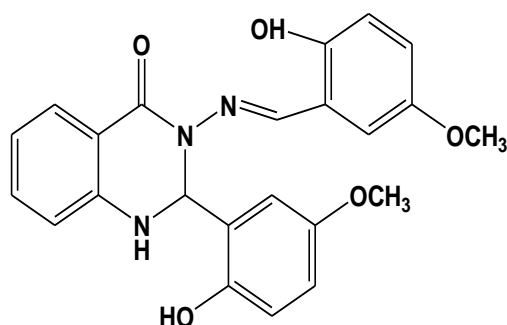
3-(5-methoxy-2-hydroxybenzylideneamino)-2(5-methoxy-2-hydroxyphenyl)-2,3-

dihydroquinazoline-4(1H)-one (MMDQ)
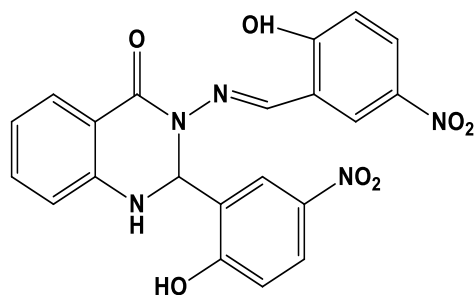
3-(5-nitro-2-hydroxybenzylideneamino)-2(5-nitro-2-hydroxyphenyl)-2,3-dihydroquinazoline-

4(1H)-one (NNDQ)

Fig.1: **S**tructure of the investigated Schiff bases

2.3 Weight loss measurements

The gravimetric measurements for corrosion were conducted according to ASTM standard G1-3

procedure [29]. 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 $^{\circ}$C for each inhibitor concentration (1 mM) for 6 h exposure in 50 ml test solution. For each

case a duplicate experiment were 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 expressed in mg cm $^{-2}$ h^{-1}. The inhibition efficiency IE_{WL} % was

calculated using equation (1) [30]:

$$IE_{WL} (\%) = \frac{W_1 - W_2}{W_1} X100 \qquad\qquad (1)$$

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 utilizes 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 software were installed in a computer interfaced with an (AUTOLAB PGSTAT 30, Netherlands) instrument. The current-potential range were between +0.3 to -0.3 V_{SCE} at a scan rate of 10 mV s^{-1}. The impedance measurements were carried out at OCP values in a frequency range of 100 kHz – 10 mHz with peak to peak amplitude of 5 mV. Prior to all electrochemical measurements (Tafel curves and EIS) the mild steel specimens were immersed into the test solution containing inhibitors at various concentration for a time period of 30 minutes in order to establish a steady state open circuit potential (E_{ocp}).

The linear Tafel segments of the anodic and cathodic curves were extrapolated to obtain the corrosion potential (E_{corr}) and corrosion current density (I_{corr}). The inhibition efficiency, IE$_P$ (%) was calculated by the following relation (2) [30]:

$$IE_P \% = \frac{I^0_{corr} - I_{corr}}{I^0_{corr}} \text{ X } 100 \qquad (2)$$

Where, i^0_{corr} and i_{corr} are the corrosion current densities ($\mu A\ cm^{-2}$) in the absence and presence of the inhibitors, respectively and can be calculated by extrapolation of Tafel lines to the corresponding corrosion potential.

The inhibition efficiency IE_{EIS} (%) was determined from the values of charge transfer resistance (R_{ct}) from the relation (3) [30]:

$$IE_{EIS} \% = \frac{R_{t(inh)} - R_t}{R_{t(inh)}} \text{ X } 100 \qquad (3)$$

Where, $R_{ct(inh)}$ and R_{ct} are charge transfer resistance values of the inhibited and uninhibited solutions respectively.

2.5 Scanning Electron Microscope (SEM) studies

The surface morphological images of each investigated mild steel specimen after immersion in 1 M HCl in the absence and the presence of 1.0 mM of Schiff base inhibitors was studied by employing a JEOL JSM-840A scanning electron microscope at an accelerating voltage of 10 KeV. The electrodes immersion time for SEM analysis was 6 h.

3. RESULTS AND DISCUSSION

3.1 Weight loss measurements

The weight loss experiments were carried out in a glass cell in 1M HCl with the absence and presence of different concentrations of the Schiff Base inhibitors (0.05, 0.1, 0.5 and 1 mM) at ambient temperature for 6 h imersion. The initial and the final weight of the specimen were recorded using a digital balance (precision ± 0.1 mg). Table 1 summerizs the data for corrosion

rate (C_R), and inhibition efficiency IE_{WL} (%) and suggests that, the investigated Schiff bases inhibit the milds teel corrosion in HCl medium at all concnetration to different degree. Further the decrease in weight loss (C_R) with the increase of Schiff base inhibitor concnetration indicates that the corrosion inhibition process is attributed to the adsorption of the inhibitor molecules on the metal surface [31].

Table 1: Corrosion parameters obtained from gravimetric measurements on mild steel in 1 M HCl solution with various concentrations of Schiff Bases at ambient temperature

Inhibitor concnetration (mM)	Corrosion rate (mg cm^{-2} h^{-1})	IE$_{WL}$ (%)
MMDQ		
Blank	9.8	-
0.05	6.6	48
0.1	6	63
0.5	5.4	81
1	5.1	92
NNDQ		
Blank	9.8	-
0.05	6.8	44
0.1	6.2	58
0.5	5.6	75
1	5.2	88

3.2 OCP with time measurement

The OCP of mild steel was monitored carefully at different inhibitors concentration with and without the addition of Schiff Base corrosion inhibitors. Fig. 2 represents the variation of OCP of mild steel in 1 M HCl solutions with and without the addition of Schiff base inhibitors. Furthermore, the additions of Schiff bases to acidic solution, a more positive shift of OCP values were observed at all concentrations. This result suggests that MMDQ and NNDQ inhibitors have the ability to inhibit the corrosion of mild steel in 1 M HCl solution. Maximum shifts in OCP

were 76 mV and 63 mV for both inhibitors occurred at 1.0 mM. This preliminary outcome under OCP conditions recommends that the investigated Schiff Bases can suppress or retard both the oxidation of oxide-free ion and liberation of hydrogen ions on the surface of mild steel [32]. The shift of OCP values in a more positive direction with increasing concentration of Schiff base inhibitors, suggests the solidity of the surface layer for inhibitors [33].
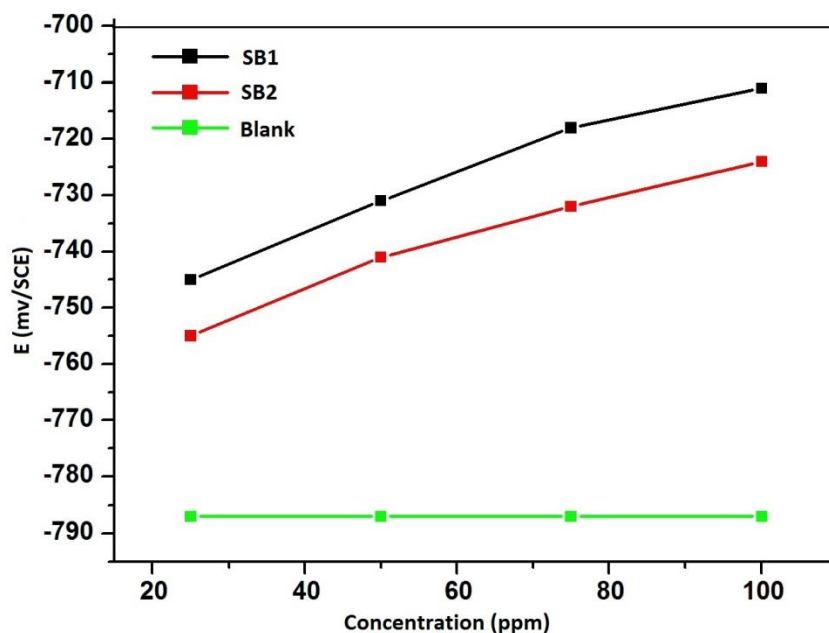

Fig. 2: The change in OCP as a function of different concentration of Schiff bases for mild steel

in 1 M HCl solution

3.3 Potentiodynamic polarization measurements

In fig. 3, the anodic and cathodic plots were recorded on mild steel electrode in 1M HCl with the absence and presence of different concentration of Schiff Bases at ambient temperature. The associated electrochemical parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), anodic and cathodic Tafel slopes (b_a and b_c) were obtained from the intersection

of anodic and cathodic Tafel lines, and corrosion inhibition efficiencies IE_P (%) were claculated and presented in table 2.

From fig. 3, it can be seen that by the addition of Schiff Base corrosion inhibitors to the aggressive solution, the magnitude of corrosion current densities for both the anodic and cathodic curves are decreased and shifted to a lower direction for both inbibitors then thoses obtained in 1 M solution alone. This phenomenon indicated that the inhibitor may suppress both anodic metal dissolution and cathodic reaction to produce hydrogen gas or to reduce oxygen with the increase in the inhibitor concentration. Furthermore, both anodic *(ba)* as well as cathodic Tafel *(bc)* slopes for MMDQ and NNDQ were observed to be change with increasing inhibitor concnetration, resulting that the investigated inhibitors affect both reactions [41]. Also from table 2, corrosion current densities decreases with the increase in inhibitor concentration, while the inhibition efficienies increases as expected.

Table 2: Potentiodynamic polarization parameters and the corresponding corrosion inhibition efficiencies on mil steel in 1 M HCl solution in absence and presence of various concentrations of Schiff Bases at ambient temperature

Inhibitors	Concentration (mM)	- E_{corr} (mV vs. SCE)	ba (mV/dec)	bc (mV/dec)	Icorr (μAcm^{-2})	IE_P (%)
Blank	-	787.5	126.3	121.2	950.5	-
MMDQ	0.05	745.3	92.1	113.1	480.2	49
	0.1	731.1	76.5	98.2	360.1	62
	0.5	718.4	63.3	86.6	190.6	80
	1.0	711.5	54.7	71.4	700.3	92
NNDQ	0.05	755.1	109.4	114.7	730.4	45
	0.1	741.1	92.2	91.6	520.1	57
	0.5	733	84.2	79.1	210.2	77
	1.0	724.5	71.6	65.4	100.2	89

Data in table 2, reveals that the addition of both inhibitors, shifts the E_{corr} values in a more positive direction folowing *OCP* trend. If the displaced values of corrosion potential is higher than 85 mV to the crossesponding values in the blank solution, then the inhibitor can be classifed as anodic or cathodic type [42]. In the present work, the largest displacement observed was 76 mV and 63 mV for MMDQ and NNDQ respectively at a concnetration of 1.0 mM, which strongly suggests that the Schiff bases may be classifed as mixed type inhibitor in HCl solution with a predominantly anodic character, suggesting that the addition of both MMDQ and NNDQ to a 1 M HCl solution reduces both anodic metal dissolution of milds steel and suppress the cathodic hydrogen evolution reaction.
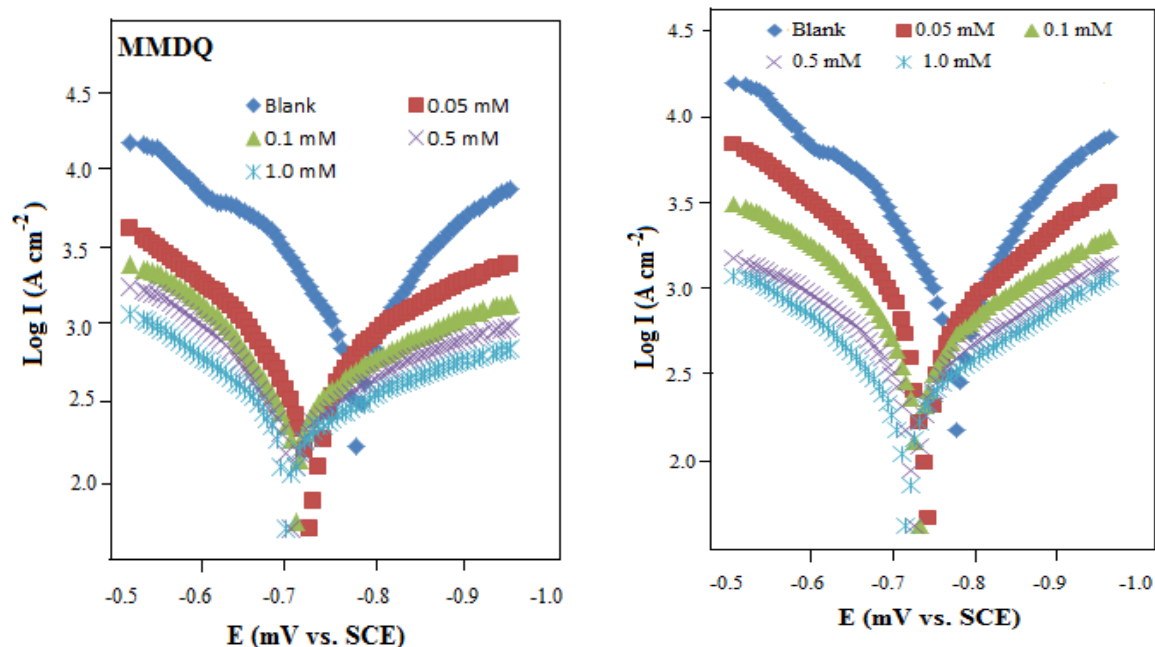
Fig. 3: Tafel polarization curves for mild steel in 1 M HCl solution at ambient temperature, with and without the optimum concentrations of Schiff Bases: (a) 0.05 mM (b) 0.1mM (c) 0.5 mM (d) 1.0 mM

The electrochemical reaction is closely associated to the adsorption of inhibitor molecules on metal surface and the chemical constituents of the inhibitor [43]. Table 4 illustrates that these employed Schiff base compounds perform as effective corrosion inhibitor for carbon steel in 1 M HCl solution at a very small concentration and designated their effectiveness to steel surface.

The occurrence of –N=C, phenolic group (-OH), and aromatic rings are responsible for their greater activity and inhibition efficiency. The analysis of inhibition efficiency data revealed that the presence of weak electron donor i.e. methoxy (-OCH_3) and strong deactivating group as nitro group (-NO_2) in MMD and NNDQ, responsible for strong interaction of former inhibitor to the later one.

3.4 Electrochemical Impedance spectroscopy measurements

The corrosive behaviour of mild steel with and without the Schiff base compounds in 1 M HCl have been reported by employing EIS measurements at ambient temeprature. Nyquist plots on mild steel in the absence and presence of various concentration of Schiff base inhibitors in 1 M HCl are given in Fig 4. It was manifest that in the presence of Schiff bases to the aggressvie solution the impedance of the crbon steel in HCl solution has significantly imporved. The impedance polts for both Schiff bases were found to be similar.

Charge transfer resistance (R_{ct}) is unambiguously interrelated to the corrosion current density in comparatively simple corrosion methods described by a charge transfer controlled process [44]. However the obtained semicircles cut the real axis at higher and lower range of frequencies.

The obtained EIS spectra for MMDQ and NNDQ were interpreted in the terms of the equivalent circuit in Fig. 5, which express a single charge transfer reaction and fits well with the present experimental outcomesThe inner portion of capacitive loop along real axis expresses the ohmic resistances of the deposited film of corrosion products and the solution trapped in between reference and working electrode, R_s [45]. The charge transfer resistance, R_{ct} is a measure of electron transfer across the surface and inversely proportional to rate of corrosion [46]. In order to get a more accurate fit, constant phase element *CPE* is established in the equivalent circuit instead of double layer capacitance C_{dl} [47]. The impedance for *CPE* is followed by Eq. (6) [48]:

$$Z_{CPE} = \frac{1}{Y_o(j\omega)^n} \tag{6}$$

Where n denotes CPE exponent commonly termed as phase shift, ω angular frequency ($\omega =$ $2\pi f$, where f is AC frequency), and j is imaginary unit. Depending on the values of the component n, a CPE may be resistance R, Capacitance C, Warburg impedance W or may be an inductance L for n = 0, 1, 0.5, and -1 respectively [49].
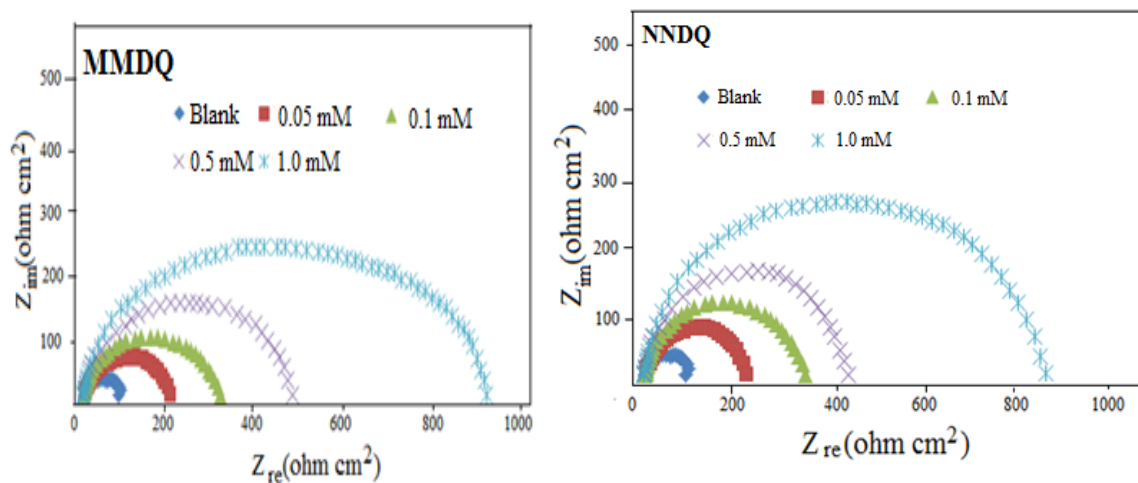

Fig. 5. The Nyquist plots for CS in 1 M H_2SO_4 at ambient temperature with the addition of various concentrations of Schiff bases.

It can be seen clearly from fig. 5, that the Nyquist plots show a single capacitive semicircle shape at higher frequencies in the presence and absence of inhibitors for only one time constant. This indicates that corrosioon of CS in 1 M H_2SO_4 soultion is mainly controlled by charge transfer process [4,6,24]. The deviation of the depressed Nyquist plots from ideal semicircle appreance, $0.5 \leq n \leq 1$ genereally atttributed to the frequency dispersion of interfacial impedance which results as inhomogenities of the surface, impurities, adsorption of inhibitors as well as surface roughness and the formation of porous layers [50,51].

The corroection of double layer capitance C_{dl}, for a circuit including CPE is given by the relation [52]:

$$C_{dl} = Y_o(\omega_{max})^{n-1} \qquad (4)$$

Where ω_{max} is the frequency at which the imaginary compenet od impedance $(-Z_{im})$ is maximal [53]. Various parameters like constant phase element (CPE), charge trnasfer resistance (R_{ct}), double layer capacitance (C_{dl}), solution resistacne (R_s), and inhibitor efficiency ($(IE_{EIS}$ %) for various concnetration of Schiff base inhibitors were claulated and tabulated in table 5. In fig. 4, it can be observed that the diameter of the semi circle increases more by the addition of Schiff base to the aggressive solution. It can be inferred that the Schiff base inhibits corrosion of mild steel in 1 M HCl at all the concentration as well as inhibition efficiency increases as a result of adsorption of the inhibitor molecules on the metal surface.

Figure 6, shows the electrical equivalent circuit diagram to model MS/HCl interface which consists of a constant phase element (*CPE*), charge trnasfer resistance (R_{ct}), and solution resistacne (R_s), and n represents the phase shift which may be attributed to the degree of surface inhomogenities [43, 44, 50, 51, 54]. *CPE* was used instead of double layer capacitance for getting a more accurate fit to the experimental results [10]. The fitted parameters obtained were tabulated in table 4.
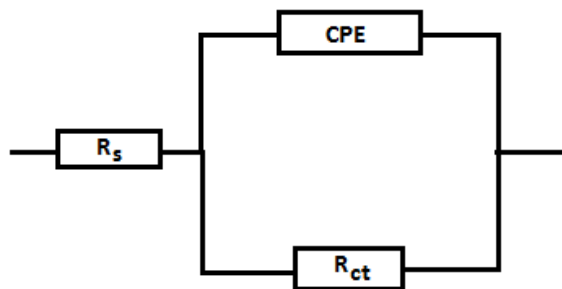
Fig. 5. Equivalent circuit diagram to fit the EIS data for mild steel in 1 M HCl

Table 4: EIS parameters and inhibition efficiencies on mild steel in 1 M HCl solution, with the

presence and absence of various concentrations of Schiff bases

Inhibitors	Concentration	R_S	R_{ct}	Q		C_{dl}	IE_{EIS}
	(ppm)	$(\Omega.cm^2)$	$(\Omega.cm^2)$	Yo $(\mu F\ cm^{-2})$	n	$(\mu F\ cm^{-2})$	(%)
	Blank	1.03	107.282	264.1	0.89	200.7	-
SB1	25	1.09	205.129	92.1	0.87	195.7	47
	50	1.11	310.769	76.2	0.88	134.4	65
	75	0.95	492.261	48.6	0.87	110.9	78
	100	0.88	955.057	21.1	0.89	89.5	93
SB2	25	1.03	198.429	85.7	0.9	155.6	46
	50	1.02	249.971	70.4	0.87	85.1	57
	75	0.97	424.887	59.1	0.84	81.3	75
	100	0.89	893.221	33.3	0.85	73.5	90

In table 4, the values of R_s are very small in comparision to that of R_{ct}. It is evident that the

values of R_{ct} increase and the capacitance values C_{dl} decrease by increasing the inhibitors

concnetration. Decrease in C_{dl}, which can result from a decrease in local dieletric constant and/or

an increase in thickness of double layer, suggesting that the inhibitors molecules inhibit the

corrosion of iron by the virtue of adsorption process at metal solution interface [55, 56]. It is well

known that capacitance is the reciprocal of the thickness of the double layer [57]. A low values

of cpacitance may also result a larger replacement of water molecules by the Schiff base through the adsorption at electride surface [57]. Also larger molecules of the inhibitor may also reduce the capcitance through an increse in double layer capicatance. Moreover, the thickness of protective layer increased by increasing the inhibitor concnetration reslut a sifnificant decrease in C_{dl}. This behaviour is in accordance in Helmholtz model by the following realtion [56]:

$$C_{dl} = \frac{\varepsilon \varepsilon_o A}{d} \qquad\qquad (5)$$

Where ε is dielectric constant of the medium, ε_o denotes vacuum permitivity, d presnets the thickness of protective layer and A is surface area od elecrode. As a consequence of effective adsorption of the Schiff base inhibitor, C_{dl} always found smaller in values in the presence of inhibitors than in its absence [57]. Therefore it is obvious that a causal relationship exists between asborption and inhibition.

3.5 Adsorption isotherms

It is generally accepted that the efficiency of a successful corrosion inhibitor mainly depends on its adsorption tendency on the metal surface. Therefore, adsorption isotherms can provide important information on the interaction of inhibitors and corresponding active sites on the metal surface. For this purpose the surface coverage values (θ) for different inhibitor concentration were calculated to present the best adsorption isotherm. Several attempts were made to fit the (θ) values to the standard isotherms including Langmuir, Temkin, Freundlich Fumkin and Floy-Huggins [58, 59]. A plot of (*C*) versus (*C/ θ)* in Fig. 6, gives a straight line which suggests Langmuir adsorption isotherm. According to this model it is assumed that the solid surface

consists of a fixed number of adsorption sites and each site hold one adsorbed species. This isotherm can be expressed as equation (6) [60]:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \qquad (6)$$

Where C is inhibitor concentration, K_{ads} is the adsorption equilibrium constant relative to the interaction of the inhibitor with the metal surface. Large adsorption equilibrium constant represents a higher adsorption tendency of the Schiff base inhibitors on the mild steel surface. The standard free energy of adsorption of the Schiff Base inhibitor on the mild steel surface can be calculated from the equation (7) [61].

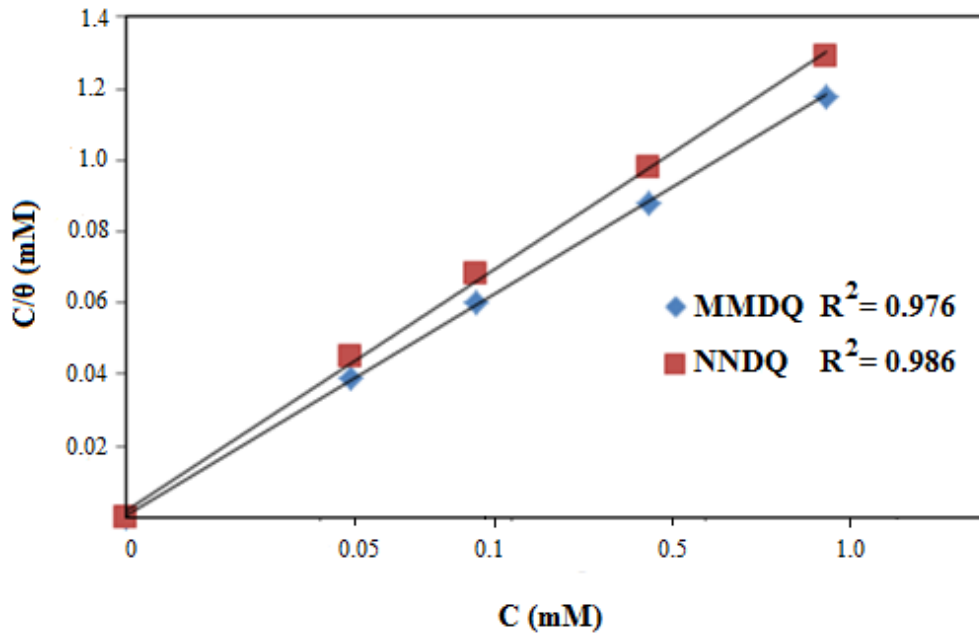$$\Delta G^o{}_{ads} = - RT \ln(55.5 \, K_{ads}) \qquad (7)$$

Fig. 6: Langmuir adsorption isotherm of synthesized Schiff bases on mild steel in 1M HCl at ambient temperature

The calculated $\Delta G^o{}_{ads}$ values for the investigated inhibitors are - 45.6 (MMDQ) and - 44.6 kJmol^{-1} (NNDQ) respectively, as reported in table 5. These results reveal that the adsorption process of the inhibitors on the CS surface is chemisorption, indicating a strong adsorption due to the charges sharing between Schiff bases molecules and the surrounding CS surface. The negative value of the free energy of adsorption indicates a spontaneous adsorption process and strong interaction between the Schiff base molecules and mild steel surface [65, 66]. It is generally accepted that the values of the Free Energy around -20 kJmol^{-1} or less are consistent with a physical adsorption process (an electrostatic interaction between the charged inhibitor and the charged metal surface), while those around -40 kJmol^{-1} or higher is associated with a chemical adsorption process (involves the transfer or sharing of electrons between the inhibitor molecules and the metal surface, resulting in a coordinated covalent bond) [67]. The calculated values of the free energy of adsorption indicates that the adsorption process of the Schiff Base compounds on mild steel surface in acid media at ambient temperature is chemical adsorption processes by the virtue of a coordinate bond formed between the investigated inhibitor molecules and the surrounding d-orbital of the surface of mild steel through lone pair of electron of N, and O atoms.

Table 5: Thermodynamic parameters for the adsorption of Schiff Bases at optimum concentrations on the mild steel surface immersed in 1 M HCl at ambient temperature

Inhibitors	Slop	K_{ads} (M^{-1})	R^2	$\Delta G^O{}_{ads}$ (kJmol^{-1})
MMDQ	-2.67	17.54x10^3	0.976	- 45.6
NNDQ	-2.1	13.08x10^3	0.986	- 44.6

3.6 Effect of temperature

Temperature effect on the corrosion of carbon steel in the presence and absence of investigated Schiff base inhibitor in 1 M H_2SO_4 solution was studied employing polarization experiments in a temperature range of 30 - 60 $^\circ$C in the presence and the absence of 1.0 mM of inhibitor. The associated corrosion parameters and inhibition efficiency for all the Schiff bases listed in table 7. Table 6 revealed that the values of corrosion current density were found to be increased by increasing the temperature in the presence and absence of inhibited solution, and the inhibition efficiency of MMDQ and NNDQ decreases in the studied temperature range. Thus, the efficiencies of the investigated inhibitors are strongly temperature dependent.

Table 6: Polarization parameters and their inhibition efficiencies for the corrosion of the mild steel in 1 M HCl solution in the presence and absence of 1.0 mM of Schiff bases at various temperatures

Inhibitor	Temperature (ᵒC)	Ecorr (mV vs SCE)	Icorr (µA.cm⁻²)	ba (mV/dec)	bc (mV/dec)	ηP (%)
Blank	30	769.2	1045.8	129.1	123.3	-
	40	755.4	1096.2	94.3	116.2	-
	50	746.5	1135.5	78.2	99.7	-
	60	738.7	1190.2	65.3	88.6	-
MMDQ	30	766.7	90.4	102.2	111.3	91.3
	40	763.3	96.5	97.5	106.4	90.1
	50	760.1	115.5	91.2	99.6	89.8
	60	766.9	123.5	86.6	95.4	89.6
NNDQ	30	764.5	98.8	81.2	90.1	90.6
	40	759.1	108.4	98.8	91.2	90.1
	50	756.4	115.5	93.2	97.4	89.8
	60	754.6	127.3	88.6	936	89.3

In order to calculate the activation energy parameter of corrosion process in the presence and absence of inhibitors, using Arrhenius equation [68]:

$$K = Ar\ Exp\ \left(\frac{-E_a}{RT}\right) \qquad (8)$$

Where, Ea representing activation corrosion energy, T is absolute temperature, R the gas constant, Ar the Arrhenius pre-exponential factor, and K corrosion rate reaction, and proportional to corrosion current density. The pre-exponential factor (A) and activation energy (E_a) at 1.0 mM ppm of inhibitors are calculated on the basis of linear regression by plotting the values of ln (I_{corr}) versus 1/T (Fig. 7), and summarized in table 7. The calculated values for linear regression coefficients are close to unity, signifying that the corrosion of carbon steel in sulfuric acid can be explained using kinetic model. Examination of Table 7 result that Ea values for solution containing MMDQ and NNDQ are higher than those in the inhibitor-free acid solution may be interrupted the occurrence of physical adsorption in preliminary stage [69]. This phenomenon can be explained that increase in activation energy can be endorsed to a substantial decrease in the adsorption values of inhibitor on steel surface with the rise in temperature [70]. A resultant increase in the corrosion rate observed due to the availability of larger area of metal surface is exposed accordingly to the aggressive solution [71].

Table 7: Activation parameters of the dissolution of mild steel in 1 M HCl solution

in the absence and the presence of 1.0 mM of studied Schiff bases

Inhibitor	Ea (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (kJ mol^{-1})
Blank	18.37	72.1	495.08
MMDQ	24.19	86.8	485.45
NNDQ	22.19	80.7	486.95

In Arrhenius equation for heterogeneous reaction (electrochemical corrosion process), the pre-exponential factor is interrelated to the number of active sites [72]. On the basis of energy surface heterogeneity assumption, these active sites or centers possess different energy. If the activation energy for inhibitor is greater than the inhibitor-free solution (i.e. $E_{a,inh} > E_{a,HCl}$) than the adsorption of the inhibitor molecules takes place on the most active adsorption sites (lowest energy) and corrosion occur predominantly on the active sites having a higher energy.

On the otherhand, where $E_{a,inh} < E_{a,HCl}$, the assumption favors the values of pre-exponential factor values (*A*) are lower that in pure HCl solution, corrosponds to the particpation of lesser number of more active sites still remain uncovered in corrosion process [73].
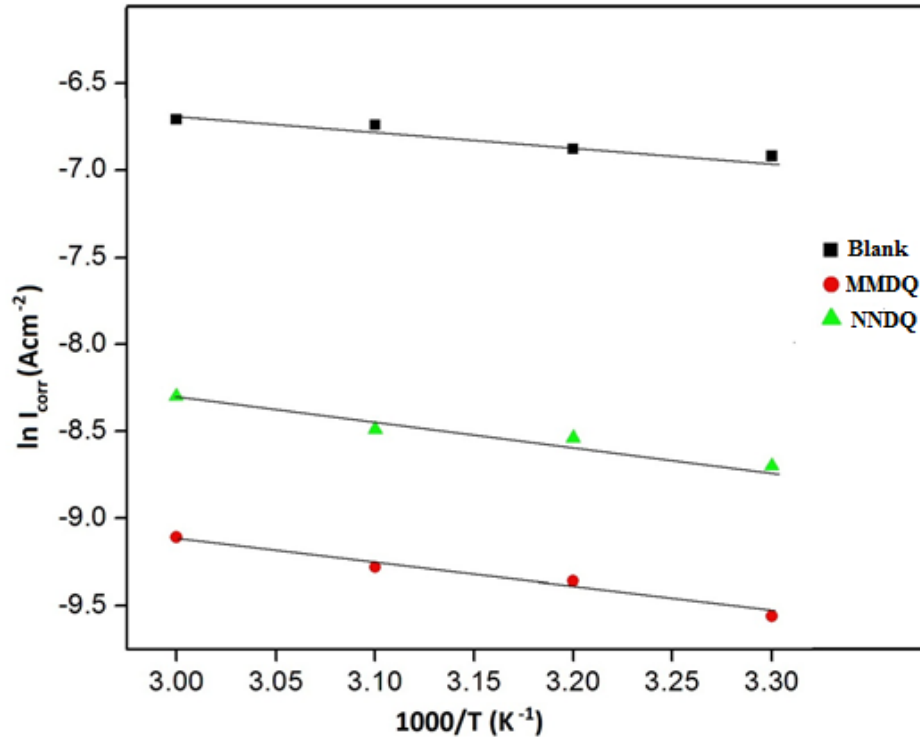
Figure 7: A plot of ln (Icorr) vs. 1/T for activation energy of corrosion reaction in the presence of 1 mM of MMDQ and NNDQ

The values for enthalpy and entropy of activation (ΔH, ΔS) were derived from transition state theory by the following relation [74]:

$$K = \left(\frac{RT}{Nh}\right) \exp\left(\frac{\Delta S}{R}\right) \exp\left(\frac{-\Delta H}{RT}\right) \qquad (9)$$

Where h represents Planck's constant, N stands for Avogadro's number and ΔS and ΔH the entropy and enthalpy of activation. A plot between ln (I_{corr}/T) against 1/T, provided a straight line (Fig. 9) for the dissolution of carbon steel in 1 M sulfuric acid solution, in the presence and absence of 100 ppm of inhibitors (MMDQ and NNDQ). The derived values of ΔH and ΔS obtained from straight line with a slop of $-\Delta H/R$ and ln (R/Nh) + ($\Delta S/R$) as intercept are

calculated and tabulated in table 8. The positive sign of enthalpies (ΔH) reveals the endothermic reaction of the steel dissolution process and signify that the dissolution of steel in acidic solution is difficult. The negative sign for the entropy of activation in both inhibited and uninhibited solutions indicate that the activation complex in rate determining step denotes association instead of dissociation step, indicating a decrease in disorder ness occur from reactant to the activated complex [40].
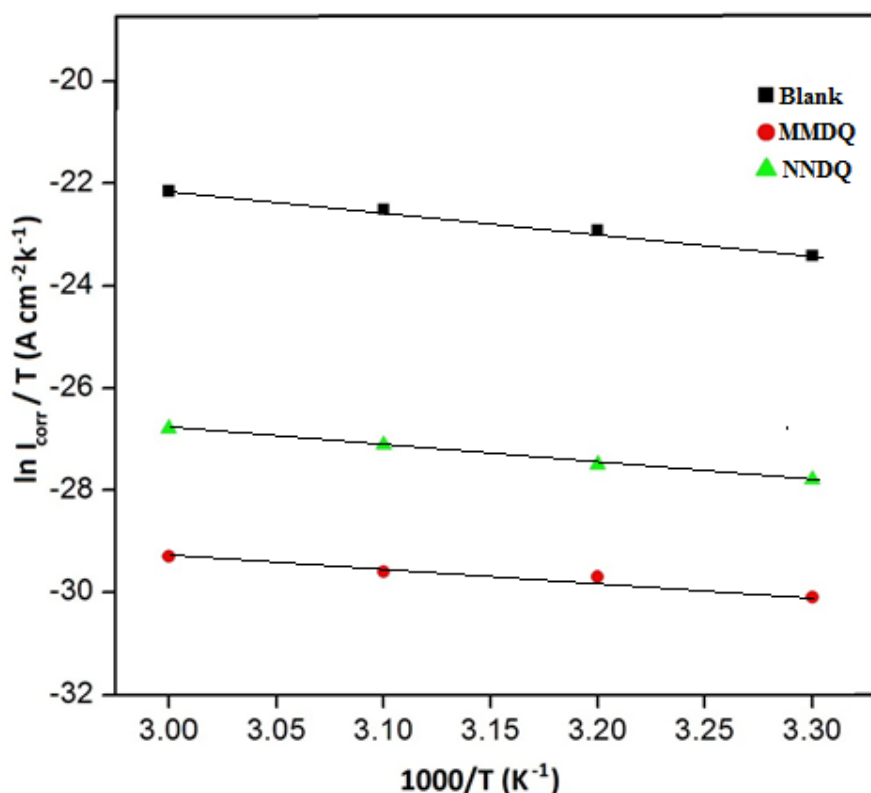

Figure 8: Arrhenius plots of ln (Icorr) versus 1/T for mild steel in 1 M HCl in the absence and presence of 1 mM of Schiff bases MMDQ and NNDQ

3.7 Inhibition mechanism

The inhibition process of the metal is mainly due to the adsorption (chemical or physical) of the inhibitor molecules on the solid surface, which results in the formation of a protective layer. The

adsorption process is controlled by various parameters such as electron density of the donor atoms, functional group, and requires a full knowledge of the interaction between the p and d orbitals of the inhibitor and the metal surface. The inhibition efficiency increases up to a certain critical inhibitor concentration resulting in the formation of a clear and uniform layer of inhibitor at the liquid /solid interface, whereas, at higher concentration beyond the critical concentration limit leads to the formation of micelles instead of successive layers. Analysis of the thermodynamic parameters reveals that the adsorption of the Schiff bases on mild steel surface in 1 M HCl is more chemical than physical adsorption. Generally, the adsorption process may be established by the displacement reaction between the inhibitors and water molecules, according to the equation (10) [75]:

$$SB.Inh_{(sol)} + nH_2O_{(ads)} \longrightarrow SB.Inh_{(ads)} + H_2O_{(sol)} \qquad (10)$$

Where, $SB.Inh_{(ads)}$ are the Schiff Base inhibitors in the acid solution adsorbed on the metal surface, and n is the number of water molecules displaced by the Schiff base inhibitor. Furthermore, the inhibitor molecules combine with the newly generated Fe^{2+} ions, resulting the formation of the metal-inhibitor complex by the following equation (11) and (12) respectively [76]:

$$Fe^{2+} \longrightarrow Fe^{2+} + 2e^- \qquad (11)$$

$$Fe^{2+} + SB.Inh_{(ads)} \longrightarrow [Fe\text{-}SB.Inh]^{2+}_{(ads)} \qquad (12)$$

Where, $[Fe\text{-}SB.Inh]^{2+}_{(ads)}$ presents the formation of metal ions inhibitor complex at interface. Depending on the relative solubility of initially formed complex, it may catalyze or inhibit additionally the metal dissolution; as a consequence of the coherence of the complex which

strongly relies on the surrounding environment to dilute it. Low concentrations of Schiff Bases inhibitor in the acidic solution was insufficient to form a compact protective layer formed by the mutual interaction of complex and metal ions, due to the readily solubility of the intermediate solution in the acidic medium. Therefore, it is strongly suggested that concentration of Schiff bases must be increased, as more Schiff bases molecules are available for the formation of intermediate complex, which subsequently suppress the solubility of surface layer, leading the promotion of corrosion inhibition as well.

Since Schiff base compounds are expected having a protonation behavior in equilibrium with the surrounding strong aggressive acidic solutions. Furthermore, the steel surface in 1 M HCl is negatively charge due to a negative potential difference ($E_{corr} - E_{q=0}$) < 0, promoting the approach of positively charged inhibitors molecules towards negatively charged steel surface as a result of electrostatic attraction [77, 78]. Finally, the larger size and high molecular weight of Schiff base inhibitor can also cause higher inhibition efficiency [79].

In the present work it was observed ad concluded that the inhibition efficiency of MMDQ> NNDQ in1 M HCl solution. The difference of inhibition efficiency strongly attributed to the molecular structure of the investigated Schiff bases. Moreover, the rigidity of π-delocalized electrons of Schiff base inhibitor may later the adsorption of electron density at the active sites, leading to an easier approach of electron transfer to the metal surface from the functional group (>C=N-) of the Schiff base. Therefore, producing a higher extend of covalent bond and hence promote to different adsorption sites and inhibition efficiency.

Inhibitor adsorption on surface can be explained on the basis of donor-accepter mutual interaction of π −electrons on inhibitor molecules and the vacant d-orbit of the iron atoms.

From table 2, it is clear that, the inhibition efficiency increases with the increase in inhibitor concentration, and is attributed to the substitution reaction of the electron-donating group present in the benzene ring of the inhibitor molecules. These results verify the adsorption phenomenon of these organic compounds on the mild steel surface.

Generally, phenolic group (-OH) is a strong electro donating group, due to the presence of lone pair of electron on oxygen (o) atom, increasing the electron density on the imine ($>C=N$). The existence of (-OCH$_3$) group in SB1 inhibitor, which is a weak electron donor or moderately activating than hydroxyl group (-OH). On the other hand, SB2 show a lower inhibition efficiency ($\eta\%$), due to the presence of (-NO2) group, responsible for electron with drawing or strongly deactivating group, leads to a lower corrosion inhibition efficiency as a result of weak binding of azomethine ($>C=N$) with the metal [80, 81].

3.7 SEM analysis

SEM imaging was performed to establish a link between the experimental parameters and the morphology of the mild steel surface. Figure 8(a, b) represents the surface image of the abraded sample before and after immersion in 1M acid solution for 6 h, whereas Fig. 8(c, d) are the images of carbon steel surface in the presence of 1 mM of Schiff Bases. It can be observed from Fig. 8(b) that, the visible cracking and pitting marks on the surface are due to the formation of corrosion products and attack of the aggressive solution in absence of inhibitors. The photomicrograph of the mild steel surface in the presence of inhibitors shown in Fig. 8(c, d) represents comparatively a smooth surface with minimized pits or cracks. These results indicates that the presence of Schiff Base inhibitors (MMDQ and NNDQ) hinders the dissolution of the

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mild steel due to the formation of a protective film by the adsorption of inhibitor molecules onto the surface, which decreases the corrosion rate of mild steel in 1 M HCl solution.
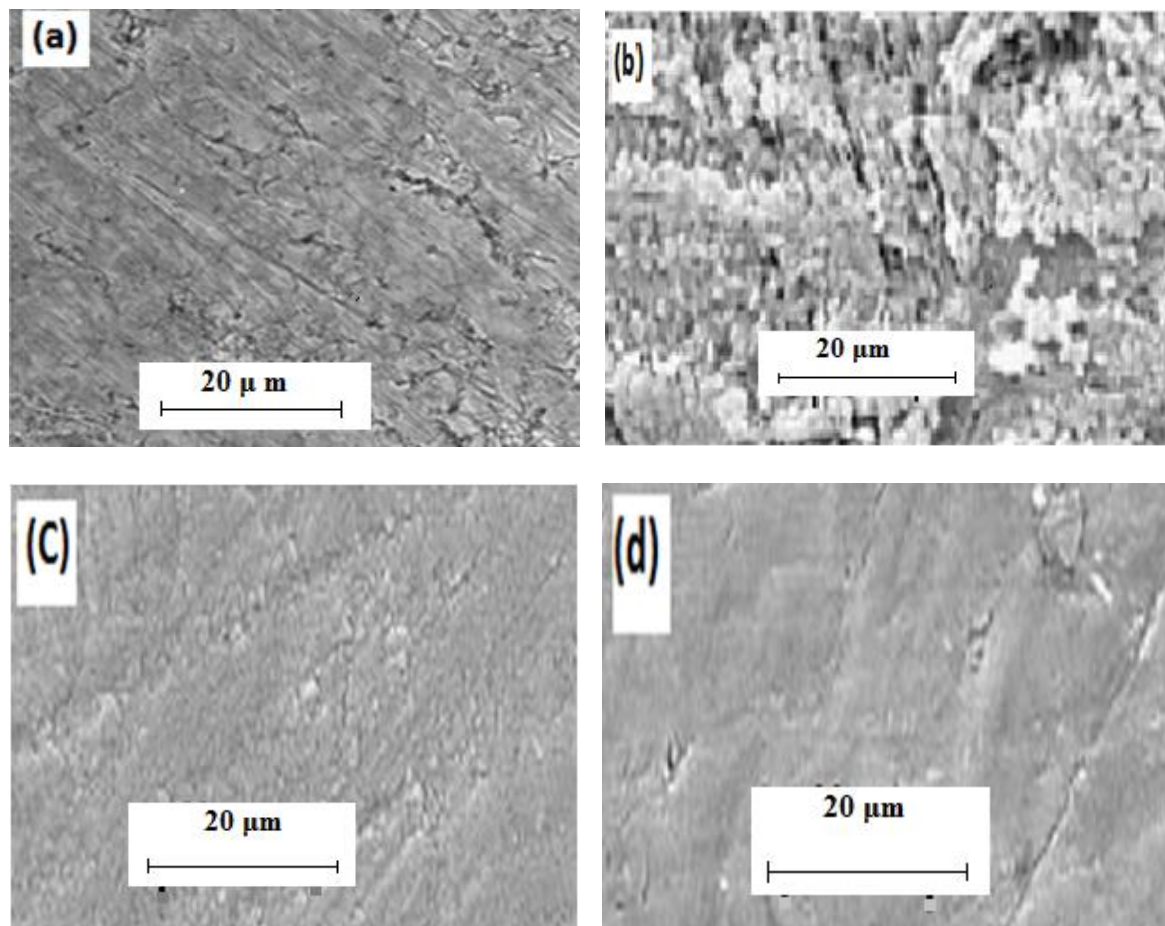

Fig. 8: SEM micrographs of mild steel surface after immersion in 1 M HCl for 6 h at ambient temperature: abraded MS without immersion in test solutions (a); immersion in 1 M HCl without inhibitor (b); immersion in 1 M HCl containing 1 mM of inhibitor MMDQ (c); immersion in 1 M HCl containing 1 mM of inhibitor NNDQ (d)

4. CONCLUSIONS

1. The Schiff bases MMDQ and NNDQ acts as efficient corrosion inhibitor for mild steel in HCl medium, providing inhibition efficiencies in the extent of 92% at a concentration of 1mM.

2. The inhibition efficiency of Schiff base MMDQ is greater than NNDQ. Polarization studies revealed that the investigated inhibitors are mixed type inhibitor with a predominantly anodic character.

3. Corrosion efficiencies increased with increasing inhibitor concentration and decreased with decreasing temperature for all investigated compounds. In addition, inhibition efficiencies are associated to the temperature, concentration and the chemical structure of the Schiff bases.

4. The obtained results signify that the inhibitions by Schiff bases were attributed to the adsorption of inhibitor molecules on mild steel electrode. On the other hand, double layer capacitance values (C_{dl}) have exhibit a tendency to decrease, which can result from a decrease in local dielectric constant and/or an increase in thickness of the electrical double layer. Therefore, it can be inferred that the ihibiton role of the synthesized Schiff bases are through the adsorption at the emtal/solution interface disclosed by the SEM microgrphs.

5. Adsorption process of the Schiff abses on mild steel surface from HCl solution obyed by Langmuir adsorption isotherm and regarded as chemical adsorption.

6. The thermodynamics adsorption parameters like K_{ads} and ΔG^o_{ads} for the investigated inhibitors are calculated from their respective adsorption isotherm. Moreover, the negative values of ΔG^o_{ads} revealed the spontaneity of the adsorption process.

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