



## Corrosion Inhibition of Two Schiff Base Complexes on The Mild Steel in 1M HCl Solution



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**C**ORROSION inhibition of two Schiff base complexes were examined for mild steel in 1M HCl solution. These two Schiff base complexes, Cd(II) and UO<sub>2</sub>(II) were synthesized through the reaction of CdCl<sub>2</sub>.H<sub>2</sub>O and UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O with the Schiff base ligand N-carbamimidoyl-4-((4-chlorobenzylidene) - amino) benzenesulfonamide in ethanol. The corrosion behavior was studied for the mild steel by weight loss method, Open circuit potential measurements (OCP), Potentiodynamic polarization, and Electrochemical impedance spectroscopy (EIS). The compounds have a promising corrosion inhibition materials for the mild steel in the investigated acid medium.

**Keywords:** Schiff base complexes, Corrosion inhibition, HCl solution, Mild steel.

### Introduction

Corrosion inhibition of two Schiff base complexes were examined for mild steel in 1M HCl solution. These two Schiff base complexes, Cd(II) and UO<sub>2</sub>(II) were synthesized through the reaction of CdCl<sub>2</sub>.H<sub>2</sub>O and UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O with the Schiff base substance N-carbamimidoyl-4-((4-chlorobenzylidene) - amino) benzenesulfonamide in plant product. Schiff bases have a many applications for example anti-oxidant, antimicrobial, anti-inflammatory, dyes and corrosion inhibitors [1- 6]. Mild steel has a wild applications as chemical processing industries, petroleum production, and refining, pipeline industries, mining, marine applications, nuclear power and fossil fuel power plant, constructions, and metal processing equipment etc.; due to its

good mechanical strength, high conductivity, ease of manufacturing and low cost [7-9-10, 11]. In several industrial processes, the corrosive acid solutions such as hydrochloric acid, sulphuric acid and nitric acid are generally used for acid cleaning, acid de-scaling, steel pickling, cleaning of boilers, oil well acidizing, recovery of ion exchangers and various other techniques [8,10]. During the pickling process, the metal dissolution from an already cleaned metal surface could be occur after get rid of the oxides, scale or other coatings which led to metals loss as more acid consumption [9]. The most difficult common acid to handle is hydrochloric acid from the standpoints of corrosion and materials of constructions thus needed extreme care in the container that transport it because of the highly corrosive of

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it to most common metals and alloys [9]. The biomedical corrosion is the effect on the metals by various micro-organisms [12]. The electrochemical corrosion affects a large economical loss of metal. The corrosion inhibition is a surface which involves the adsorption of the organic compounds on metal surface. Corrosion inhibitors for metal have been studied by using many organic compounds containing gas, nitrogen and sulphur. Corrosion inhibitors are very important practically and used for minimizing the metallic waste in engineering material [13]. Schiff base with  $-\text{CH}=\text{N}-$  linkage (azomethine) have each the higher than options combined with their structures that create them effective potential corrosion inhibitors [14-16]. The main aim of this study is investigating the effect of two Schiff base complexes (Cd(II) and  $\text{UO}_2(\text{II})$ ) on the mild steel in a corrosive media of 1M HCl solution.

### **Experimental**

Schiff base complexes have been synthesized from the condensation of 4-amino-N(quinoxalin-2-yl) benzenesulfonamide 1 with 4-chloro-benzaldehyde according to the reported in the literature [17, 18]. The compound was prepared with high yield and purity via stirring of 1 with 4-chloro-benzaldehyde at 70-100 °C. The structure of compound was established by the spectral data. In a typical procedure to prepare the complexes, 1 mol of appropriate metal salts solution,  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CdCl}_2 \cdot \text{H}_2\text{O}$  (in turn, each time one) dissolved in 30 mL of absolute ethanol was added drop-wise to the mixture of EtOH solution (20 mL) of HL. The solution was heated at reflux while stirring for 3 h. The working electrode was made from mild steel rod with a chemical composition as shown in Table 1. The rod was mounted into a glass tube and fixed by araldite leaving a circle surface geometry of 1 cm<sup>2</sup> diameter to contact the test solution. Prior to every experiment, the working electrode was polished with a different grades of emery paper up to 1200 grit, rinsed with acetone and finally with doubly distilled water. The auxiliary conductor was noble metal wire, while a saturated calomel electrode (SCE) connected to conventional electrolytic cell of capacity 100 ml. The experiments were conducted in 1 M HCl solution and with different concentration (100 ppm, 200 ppm and 500 ppm) of metal complexes compounds, Cd(II) and  $\text{UO}_2(\text{II})$  complexes. All solutions

were freshly prepared using analytical grade reagents and doubly distilled water. All experiments were performed at a required temperature ( $25 \pm 1$  °C). Chemical and different electrochemical methods were used to evaluate the corrosion behavior of mild steel. The Weight loss measurements, Open circuit potential measurements (OCP), Potentiodynamic polarization, and Electrochemical Impedance spectroscopy (EIS) were performed using the Voltalab 40 Potentiostat PGZ301 made in Germany. The Volta Master 4 software was designed to measure and analyze corrosion rate.

Weight loss measurements were administrated during a glass vessel with one hundred cubic centimeter of 1 M HCl solution with and without 100 ppm, 200 ppm and 500 ppm concentration of metal complexes inhibitors. The immersion time for weight loss was 72 h at  $25 \pm 1$  °C. After immersion the coupons were withdrawn, rinsed with double distilled water, washed with acetone, dried and weighed. The experiment was administrated in duplicate and therefore the average price of weight loss was noted.

The percentage of Inhibition efficiencies (IE %) were calculated using Eq. (1) [19].  
$$(\text{IE} \%) = (\text{W}_o - \text{W}_{\text{corr}}) \times 100/\text{W}_o \quad (1)$$

Where  $\text{W}_{\text{corr}}$  and  $\text{W}_o$  square measure the burden loss of low-carbon steel within the presence and absence of substance, respectively.

The electrochemical behavior of mild steel in 1 M HCl solution was studied by monitoring change in corrosion potential ( $E_{\text{corr}}$ ) with time. Electrochemical measurements were administrated on the steady state electric circuit potential (OCP). The variation of corrosion potential of mild steel in 1 M HCl solution was measured against saturated calomel electrode in absence and presence of various concentrations of inhibitors. The time dependence of open circuit potential for different experiments was recorded for 15 min. exposure period. Before potentiodynamic polarization, and EIS experiments the open circuit potential (OCP) of the working electrode, which was measured as a function of time during 15 minute, the time needed to achieve a steady state. The same sample was used for potentiodynamic polarization (PD) experiments. Different electrochemical results were obtained from

potentiodynamic polarization. Potentiodynamic polarization curves of mild steel was swept potential between  $-1.0$  to  $+1.0$  V at the scan rate of  $5$  mV/s. the inhibitive efficiency (IE %) was calculated using combining weight Eq.(2):

$$IE \% = \theta \times 100 = [1 - (CR_{inh} / CR)] \times 100 \quad (2)$$

Where CR and CR<sub>inh</sub> are the corrosion rates in the absence and presence of inhibitor respectively. Electrochemical impedance spectroscopy measurements of mild steel was carried out in frequency range from (50 kHz to 100 mHz) with amplitude of 10 mV peak-to-peak using ac signals at open circuit potential. The inhibition efficiencies (IE %) and the surface coverage ( $\theta$ ) obtained from the impedance measurements are defined by the following Eq. (3) [20].

$$IE \% = \theta \times 100 = [1 - (R_{ct} / R_{ct}(inh))] \times 100 \quad (3)$$

Where R<sub>ct</sub> and R<sub>ct</sub>(inh) are the charge transfer resistance in the absence and presence of inhibitor, respectively.

The scanning electron microscope (SEM) images were obtained by using SEM Model Quanta 250 FEG (Field Emission Gun) attached with Energy Dispersive X-ray Analyses unit

(EDAX), with accelerating voltage 30. SEM and EDAX analyses were used to define the morphology of surface attack and the chemical composition of corrosion products on mild steel from testes terminated just after the film breakdown occurred. The surface morphology of corrosion product on mild steel samples after 72 h immersion in 1 M HCl solution with 500 ppm of representative Cd(II) and UO<sub>2</sub>(II) complexes and without inhibitors was studied by SEM.

## Results and Discussion

### Weight loss measurement

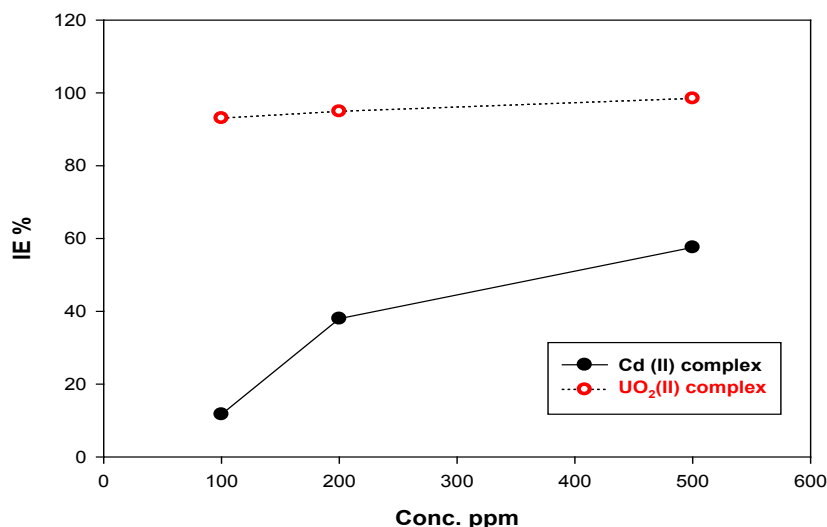
The weight loss measurement is very reliable technique to study the anti-corrosive behavior of the two Schiff base molecules and also very useful to corroborate the obtained results from the electrochemical analysis [8]. In order to study the effect of the metal complexes on corrosion of mild steel in 1M HCl solution, weight loss measurements of mild steel was investigated at room temperature. The inhibition efficiency percentage and corrosion rate calculated from the weight loss results for 72 h are illustrated in Table 2 and plotted in Fig. 1.

TABLE 1. Chemical composition (wt. %) of mild steel

Elements	C	Si	Mn	P	S	Cr	Cu	Ni	Fe
Composition (wt. %)	0.316	0.218	0.825	0.0225	0.0572	0.0869	0.122	0.0592	98.24

TABLE 2. Weight loss data for inhibition of corrosion on mild steel exposed to 1 M HCl solution with different concentration of [1 and 2] complexes

Inhibitor	Concentration (ppm)	Weight loss (g)	Weight loss (mg)	Surface coverage ( $\theta$ )	Inhibition Efficiency (IE %)
Blank (1 M HCl solution)	-	0.9674	967.40	-	-
	100	0.8542	854.15	0.1171	11.71
	200	0.5999	599.98	0.3797	37.97
1 Cd(II) complex	500	0.4106	410.55	0.5756	57.56
	100	0.0672	67.20	0.9305	93.05
	200	0.0490	48.99	0.9493	94.93
2 UO <sub>2</sub> (II) complex	500	0.0147	14.70	0.9848	98.48



**Fig. 1.** Inhibition efficiency obtained from Weight loss data for mild steel in 1 M HCl solution as a function of different concentration of complexes.

From Table 2 and Fig. 1, the two metal complexes appeared a good corrosion inhibition behavior via corrosion of mild steel in 1M HCl solution which is used as oxidizing agent for metal corrosion and study inhibition efficiency. The results of the inhibition efficiency percentage determined that both the complexes are good inhibitors this may be due to coordination by the donor-acceptor interactions between the unshared electron pairs of donor atoms of the ligand and metal [21]. The metal complexes **appeared of higher** inhibition efficiency than the free ligand that might be due to their larger size and molecular planarity [22]. Thus, the higher efficiency of UO<sub>2</sub>(II) complex **is more than** Cd(II) complex.

#### *Open circuit potential measurements (OCP)*

The electrochemical behavior of mild steel in 1 M HCl solution was studied by monitoring change in corrosion potential ( $E_{\text{corr}}$ ) with time. The changes in OCP of mild steel of 100 ppm, 200 ppm and 500 ppm concentrations of inhibitor Cd(II) and UO<sub>2</sub>(II) complexes, and without complexes in 1 M HCl solution are plotted in Fig. 2. The potential attains steady state after exposure of 1 min. The steady state potential is in equilibrium state at that  $I_{\text{ox}}$  is equal to the  $I_{\text{red}}$ . It has been observed that OCP of mild steel from moment of immersion in 1 M HCl solution tends towards more negative value in absence of inhibitor. This shows corrosiveness of medium that is due to breakdown of pre-immersion, air fashioned compound film on the surface of metal.

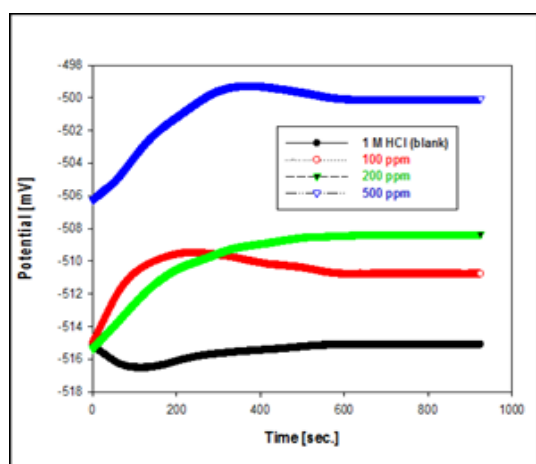
For different concentrations of inhibitors, the steady state potential of mild steel shifts more toward positive value because of the inhibitor adsorption on metal surface resulting in passivation of metal. The influence of different concentration 100 ppm, 200 ppm and 500 ppm for the Cd(II) and UO<sub>2</sub>(II) complexes on OCP of mild steel in 1 M HCl solution compared to the blank one is given in Fig. 2. This figure indicate that the two complexes with concentration 500 ppm exhibit good inhibition performance. This might be due to the formation of protective film on the metallic surface.

#### *Potentiodynamic polarization measurement*

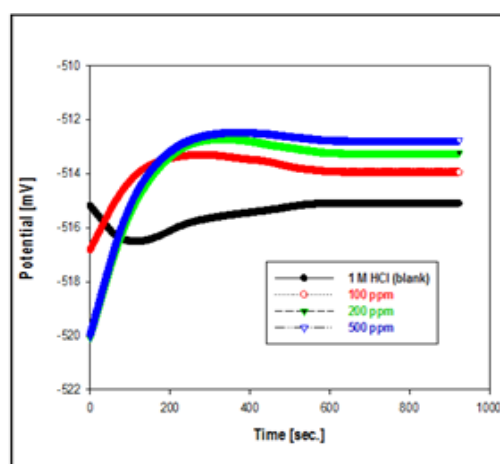
Potentiodynamic polarization curves for mild steel in 1 M HCl solution for a blank sample and various concentrations 100 ppm, 200 ppm, and 500 ppm for Cd(II) and UO<sub>2</sub>(II) complexes at 25 °C are listed in Table 3 and Fig. 3. Various corrosion parameters like corrosion potential ( $E_{\text{corr}}$ ), anodic and cathodic Tafel slopes ( $\beta_a$ ,  $\beta_c$ ), the corrosion current density and the inhibition efficiency (IE %) are given in Table 3. It is noticed from Table 3 that the corrosion current density decreases with increases the concentration of the investigated complexes and the negative shift of corrosion potential indicates that the investigated compounds square measure mixed-type matters however chiefly electrode inhibitor than anodic one. The corrosion current density decreased and inhibition efficiency increased that might be due to the adsorption of the investigated compounds on the metal surface. The results of experiments derived from polarization curves

**TABLE 3. Corrosion parameters and inhibition efficiency for mild steel at 25 °C in 1 M HCl solution for blank and different concentration of investigated complexes.**

Inhibitor concentration (ppm)	$E_{\text{corr}}$ (mV)	$I_{\text{corr}}$ (mA/cm <sup>2</sup> )	$\beta_a$ (mV)	$\beta_c$ (mV)	C.R. (mm/y)	$\theta$	IE (%)
1 M HCl solution (blank)	-520.5	0.9814	77.1	-85.5	11.37	-	-
Cd(II) complex	100	0.2525	87.8	-106.6	2.93	0.7426	74.26
	200	0.1589	71.9	-133.3	1.84	0.8379	83.79
	500	0.1185	39.4	-57.3	1.37	0.8792	87.92
UO <sub>2</sub> (II) complex	100	0.1663	65.6	-55.3	1.93	0.8306	83.06
	200	0.1219	57.2	-80.5	1.41	0.8757	87.57
	500	0.1080	58.1	-86.7	1.25	0.8899	88.99

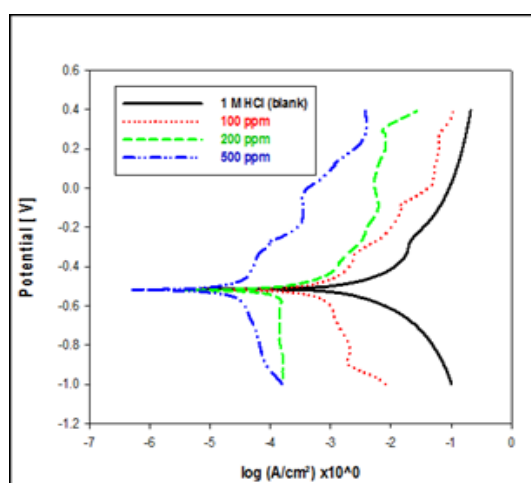


(a) Cd(II) complex

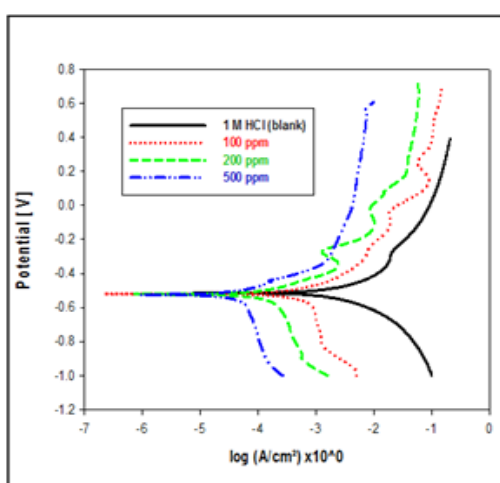


(b) UO<sub>2</sub>(II) complex

**Fig. 2. Variation of open circuit potential as function of time record at 25 °C for mild steel in 1 M HCl solution for blank sample and different concentrations of complex Cd(II) (a) and complex UO<sub>2</sub> (b)**



(a) Cd(II) complex



(b) UO<sub>2</sub>(II) complex

**Fig. 3. Potentiodynamic polarization curve of mild steel exposed to 1 M HCl solution of blank sample and different concentrations of complex Cd(II) (a) and complex UO<sub>2</sub>(II) in ppm.**

shown that within the presence of those compounds  $I_{\text{corr}}$  decreases considerably in the least of the studied concentrations. The presence of [Cd(II) and  $\text{UO}_2(\text{II})$ ] complexes resulted in a slight shift of the corrosion potential towards the active direction in comparison to the result obtained in the absence of the inhibitor. This phenomenon might be attributed to the existence of a phenylring having high electron density [9]. Among the  $\text{UO}_2(\text{II})$  complex shows maximum inhibition efficiency of about 89% at 500 ppm this might be attributed to the presence of nitrogen in  $\text{UO}_2(\text{II})$  structure.

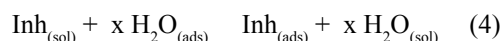
#### *Electrochemical Impedance spectroscopy (EIS)*

The inhibitor concentration effect on the impedance behavior representative Nyquist and Bode modulus plots of mild steel in 1 M HCl solution at 25 °C for blank sample and different concentration of investigated complexes are illustrated in Table 4 and Fig. 4. The obtained Nyquist plot appears a single capacitive loop and there is only one time constant in the Bode plot. The presence of a single capacitive loop implies that the control of electrochemical process is by charge transfer phenomenon. The two curves show a similar type of Nyquist plots for mild steel of various concentrations of inhibitor Cd(II) and  $\text{UO}_2(\text{II})$  complexes. The founding of single semi-circle showed the single charge transfer process during dissolution which is unaffected by the existence of inhibitor molecules. Deviations from excellent circular form area unit typically noted the frequency dispersion of surface ohmic resistance that arises because of surface roughness, impurities, dislocations, grain boundaries, sorption of inhibitors, and porous layers formation and in homogenates of the electrode surface [20, 23]. The  $R_{\text{ct}}$  values for the systems containing inhibitors are larger than that of the blank. It is also noticed that the diameter of the Nyquist plot increases concomitantly with inhibitor concentration increase into 1M HCl solution. It suggests that the mild steel surface is getting coated by the inhibitor molecules that separates the mild steel from the direct contact with the acidic solution and thereby suppresses the metallic dissolution process. Electrochemical kinetic parameters obtained by EIS technique for mild steel in the presence of different concentrations of inhibitor Cd(II) and  $\text{UO}_2(\text{II})$  complexes are reported in Table 4. From Table 4, the polarization resistance increases with increases the studied compounds concentrations while Cd(II) values tend to decrease because of the adsorption of

the studied compounds on the alloy surface. It might be discussed on the basis that the double layer between charged alloy surface and the solution is considered as an electrical capacitor. The decrease in the capacitance might be attributed to the protective layer formation on the alloy surface [20, 23].

#### *Adsorption Isotherm*

The electrochemical studies revealed that the formation of thin layer of inhibitor molecule on the mild steel surfaces act as a promising protective layer which efficiently prevent the metallic dissolution of mild steel in the corrosive acidic solution. The inhibitor molecules adsorbed on the metallic surfaces by displacing the surface adsorbed water molecules. The adsorption of inhibitor molecules on the electrode surface is aquasi-substitution process between the inhibitor molecule in the aqueous phase and water molecules at the electrode surface. The inhibitor molecule displacing the surface adsorbed water molecule is shown by Eq. (4):

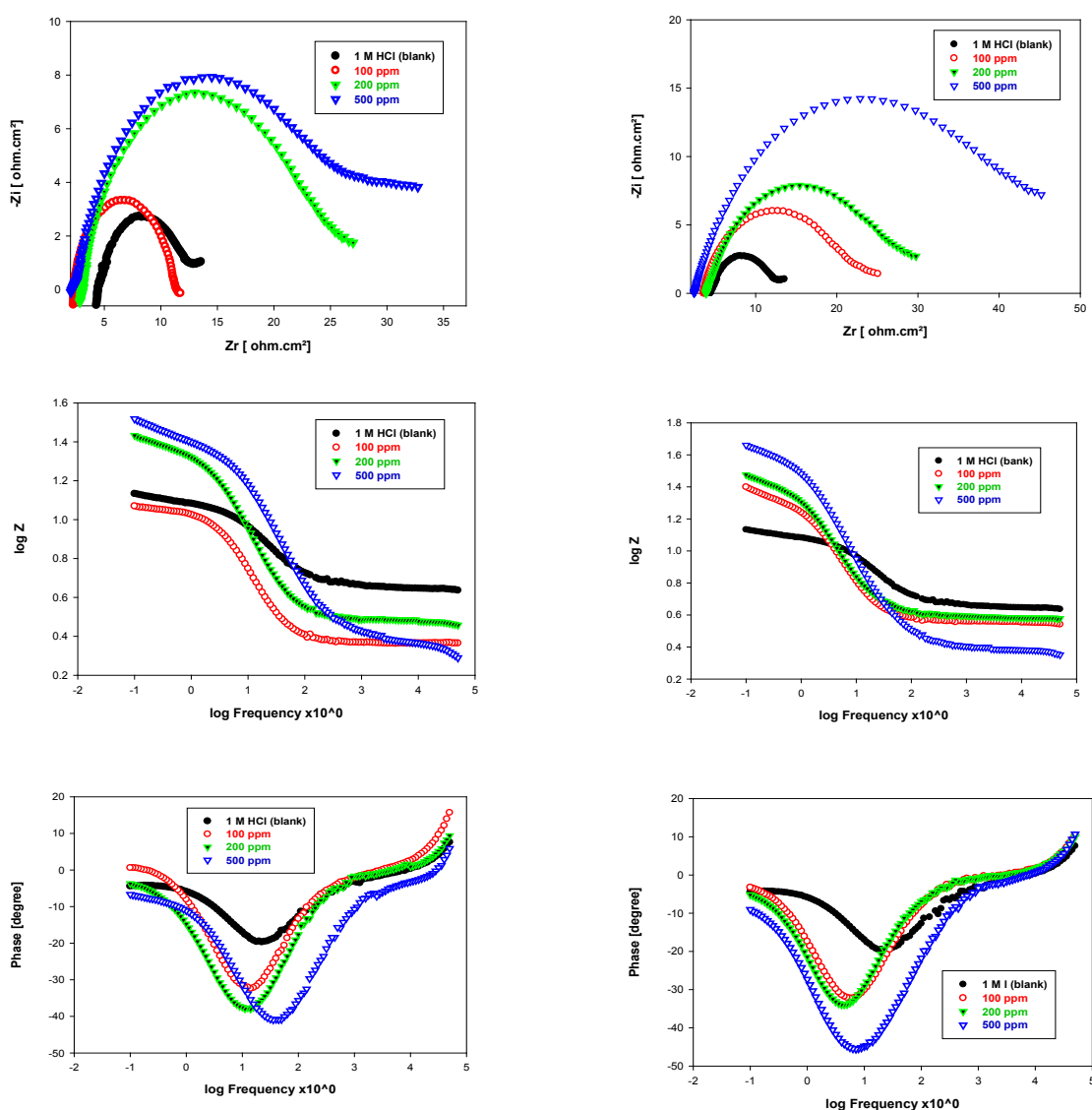


Where  $\text{Inh}_{(\text{sol})}$  refers to the inhibitor dissolved in the solution,  $\text{H}_2\text{O}_{(\text{ads})}$  refers to the surface adsorbed water molecules,  $x$  is the number of water molecule displaced by the organic inhibitor,  $\text{Inh}_{(\text{ads})}$  symbolizes the surface adsorbed inhibitor molecules on the surface of metal electrode and  $\text{H}_2\text{O}_{(\text{sol})}$  represents the water molecules in the bulk solution. This kind of phenomenon occurring between the inhibitor molecule and the metal surface gives rise to the adsorption of the inhibitor molecules. Surface adsorption is directly related to the surface coverage by the inhibitor molecules. Therefore, a small variation in the degree of surface coverage by the inhibitor molecule affects its corrosion inhibition efficiency. The efficiency of corrosion inhibition is said to be the function of the electrode surface covered by the inhibitor molecules. The relationship between the surface coverage ( $\theta$ ) and the concentration of the inhibitor molecules ( $C_{\text{inh}}$ ) are used to get the adsorption isotherm. Several adsorption isotherms like Frumkin isotherm, Temkin isotherm, Freundlich isotherm and Langmuir isotherm have been tried to obtain the best fit. It has been found that the best fitting of EIS data follows the simplest Langmuir adsorption isotherm [24].

Using Langmuir adsorption isothermal equation to calculate the absorption isotherms as in Eq. (5) [11, 25, 26, 27]:

TABLE 4. Electrochemical kinetic parameters obtained from EIS technique for mild steel at 25 °C in 1 M HCl solution for blank and different concentration of investigated complexes

Inhibitor	$R_s$	$R_{ct}$	$C_{dl}$	Phase angle Degree	$\theta$	IE
concentration (ppm)	ohm.cm <sup>2</sup>	ohm.cm <sup>2</sup>	mF/cm <sup>2</sup>			%
1 M HCl solution (blank)	4.446	8.89	1.790	-13.3	-	
Cd(II) complex	100	2.303	3.517	-8.31	0.0175	1.75
	200	2.920	23.25	-12.4	0.6176	61.76
	500	2.073	29.96	-16.0	0.7033	70.33
UO <sub>2</sub> (II) complex	100	3.529	4.379	-13.7	0.5631	56.31
	200	3.868	25.79	-13.2	0.6553	65.53
	500	2.357	45.36	-12.4	0.8040	80.40



(a) Cd(II) complex

(b) UO<sub>2</sub>(II) complex

Fig. 4. Potentiodynamic polarization curve of mild steel exposed to 1 M HCl solution of blank sample and different concentrations of complex Cd(II) (a) and complex UO<sub>2</sub>(II) in ppm.

$$C/\theta = 1/K_{\text{ads}} + C \quad (5)$$

Where  $K_{\text{ads}}$  is the equilibrium constant for the adsorption/ desorption process,  $C$  is the inhibitor concentration in the bulk of the solution. From the intercepts of the straight lines on the  $C/\theta$  axis, one can calculate  $K_{\text{ads}}$  values that relate the standard free energy of adsorption, ( $\Delta G_{\text{ads}}^0$ ), as given by Eq. (6) [11, 26, 27, 28]

$$K_{\text{ads}} = 1/55.5 \exp^{-(\Delta G_{\text{ads}}^0/RT)}$$

or (6)

$$\Delta G_{\text{ads}}^0 = -RT \ln(55.5 K_{\text{ads}})$$

Where,  $R$  is gas constant,  $T$  is absolute temperature (room temperature 25 °C). The value of 55.5 is the concentration of water in the bulk solution. Free energy,  $\Delta G_{\text{ads}}^0$ , values were calculated. Calculated values of  $\Delta G_{\text{ads}}^0$  are exist in Table 5 for mild steel in 1 M HCl solution for blank sample and different concentration of investigated complexes from potentiodynamic and EIS method. The negative values of  $\Delta G_{\text{ads}}^0$  indicate spontaneous adsorption of inhibitors on mild steel surface [29]. Generally, values of  $\Delta G_{\text{ads}}^0$  up to  $-20 \text{ kJmol}^{-1}$  are consistent with electrostatic interaction between charged molecules and a charged metal which indicates physical adsorption, while those around  $-40 \text{ kJmol}^{-1}$  or higher are associated with chemisorptions as a result of the sharing or transfer of electrons from inhibitor molecules to the metal surface to form coordinate bond [30]. The mode of adsorption (physisorption and chemisorption) noticed could be due to the fact that investigated inhibitor contains many different chemical compounds which some can adsorbed chemically and other adsorbed physically [31]. Fig. 5. illustrates that the plot of  $C/\theta$  vs.  $C$  for mild steel in 1 M HCl solution for blank sample and different concentration of investigated complexes from potentiodynamic and EIS methods are linear plots, determining that the adsorption of these compounds followed Langmuir adsorption isotherms.

#### *Effect of temperature on inhibition process of mild steel*

The inhibition efficiency percentage values on mild steel are 87.92 for Cd(II) complex and 88.99 for  $\text{UO}_2(\text{II})$  complex at 500 ppm. The effect of temperature ( $T$ ) on the rate of corrosion of this inhibitor was studied in 1 M HCl solution for blank sample and concentration of 500 ppm of investigated complexes as plotted in Fig. 6. The electrochemical parameters as obtained from potentiodynamic polarization measurements of the examined samples at 25, 50 and 70 °C are summarized and illustrated in Table 6. Fig. 6. and Table 6 show that the values of corrosion current density,  $I_{\text{corr}}$ , and hence the corrosion rate of mild steel in 1 M HCl solution for the blank sample and concentration of 500 ppm of investigated complexes increase with increase in the temperatures from 25 °C to 70 °C. The temperature effect on the inhibited mild steel surface is complex due to many changes happened on the metal surface such as rapid etching and desorption of the inhibition and the inhibitor itself, in some cases, many undergo decomposition and /or rearrangement.

The apparent activation energy value,  $E_a$ , was calculated using the Arrhenius equation as given by Eq. (7) [30]:

$$C.R = A \exp^{-E_a/RT} \quad (7)$$

Where C.R is the corrosion rate of mild steel surface,  $A$  is Arrhenius constant or pre-exponential factor,  $R$  is the universal gas constant and  $T$  is absolute temperature. Linearization of Equation 6 is given in Eq. (8):

$$\ln C.R = \ln A - E_a/RT \quad (8)$$

The linear regression plots between  $\ln C.R$  and  $1/T$  gives a slope of  $-E_a/RT$  are plotted in Fig. 7. The calculated activation energy,  $E_a$ , pre-exponential factor,  $A$ , and regulation factor,  $R$ , for mild steel in 1 M HCl solution for blank sample and concentration of 500 ppm of investigated

**TABLE 5. Values of parameters of Langmuir adsorption isotherm for mild steel 25 °C in 1 M HCl solution for blank sample and different concentration of investigated complexes from potentiodynamic and EIS method**

Investigated inhibitors		slope	$K_{\text{ads}}$	$R^2$	$\Delta G_{\text{ads}}^0$
Cd(II) complex	potentiodynamic method	1.0885	$2.374 \times 10^{-5}$	0.99998	16.431
	EIS method	-9.3239	$4.736 \times 10^{-3}$	0.41674	3.310
$\text{UO}_2(\text{II})$ complex	potentiodynamic method	1.1055	$8.742 \times 10^{-6}$	0.99997	18.906
	EIS method	1.0980	$7.542 \times 10^{-5}$	0.99839	13.567



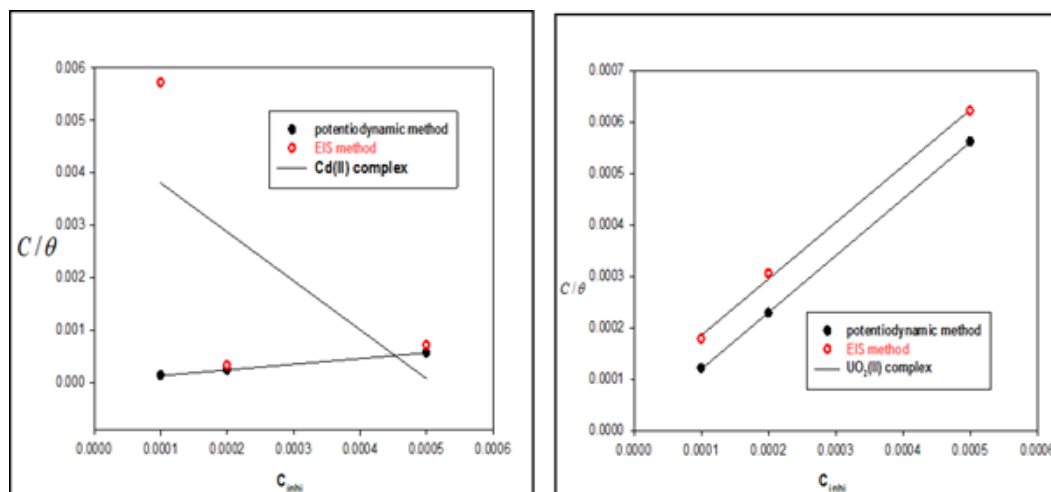


Fig. 5. Langmuir adsorption isotherm model for mild steel in 1 M HCl solution at 25 °C for blank sample and different concentration of investigated complexes from potentiodynamic and EIS method.

TABLE 6. Corrosion parameters for mild steel in 1 M HCl solution for blank sample and concentration of 500 ppm of investigated complexes at different temperature.

Inhibitor	Temperature,	$E_{\text{corr}}$	$I_{\text{corr}}$	$\beta_a$	$\beta_c$	C.R. mm/y	IE
	°C	mV	mA/cm <sup>2</sup>	mV	mV		
1 M HCl solution (blank)	25	-520.5	0.9814	77.1	-85.5	11.37	-
	50	-532.1	1.2699	184.4	-800.1	14.71	-
	70	-760.1	1.9770	388.2	-92.9	22.91	-
500 ppm Cd(II) complex	25	-524.9	0.1185	39.4	-57.3	1.37	87.92
	50	-525.3	0.2451	189.0	-152.5	2.84	80.68
	70	-520.5	0.2661	300.9	-170.3	3.09	86.53
500 ppm UO <sub>2</sub> (II) complex	25	-531.0	0.1080	58.1	-86.7	1.25	88.99
	50	-527.6	0.2121	220.8	-162.3	2.46	83.29
	70	-527.9	0.2249	152.4	-150.8	2.61	88.62

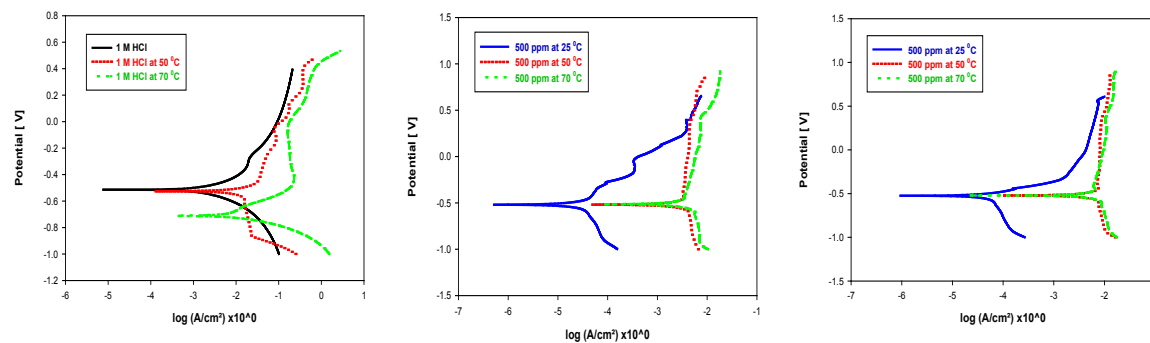


Fig. 6. Potentiodynamic polarization curve for mild steel in 1 M HCl solution at different temperature for blank sample (a), concentration of 500 ppm of Cd(II) complex (b), and UO<sub>2</sub>(II) complex (c)

complexes at different temperature are mentioned in Table 7.

The change of the apparent activation energy values,  $E_a$ , may be discussed by the modification of the corrosion process mechanism in the presence of adsorption inhibitor molecules [31]. The apparent activation energy value,  $E_a$ , of the blank is larger than the inhibited, however it did not change significantly in the presence of inhibitor, supportive of the proposed chemical adsorption mechanism. Due to reports, activation energy  $E_a$  due to chemical adsorption ( $> 80$  KJ/mol) is considerably larger than because of physical adsorption ( $< 80$  KJ/mol) [20]. The heat of adsorption values  $Q_{ads}$  of Cd(II) and  $UO_2(II)$  complexes adsorption on mild steel surface were obtained using Eq. (9) [32]:

$$\log(\theta/1-\theta) = \log A + \log k - Q_{ads}/2.303 R (1/T) \quad (9)$$

where  $\theta$  is the degree of surface coverage,  $T$  is the temperature and  $A$  is temperature independent constant. Values of heat of adsorption were obtained from the slope ( $-Q_{ads}/2.303 R$ ) of a plot of  $\log(\theta/1-\theta)$  against  $(1/T)$  for mild steel in concentration of 500 ppm of investigated complexes are shown in Table 8. Obtained values of  $Q_{ads}$  are all negative, indicative of exothermic nature of the dissolution

process of mild steel surface in the acidic solution [20]. The apparent enthalpy of activation  $\Delta H_{ads}$  and entropy of activation  $\Delta S_{ads}$  values were obtained through the linearized transition – state theory equation given by Eq. (10):

$$\ln(C.R/T) = \ln(R/Nh) + \Delta S_{ads}/R - \Delta H_{ads}/RT \quad (10)$$

where  $h$  is plank's constant and  $N$  is Avogadro's number.

The figure of  $\ln C.R/T$  versus  $1/T$  will give a straight line and the slope is equal to  $-\Delta H_{ads}/R$  and the intercept is  $\ln R/Nh + \Delta S_{ads}/R$ , are collected in Fig. 9, from where values of  $\Delta H_{ads}$  and  $\Delta S_{ads}$  were calculated and are existence in Table 8. From Table 8, it is found that the positive values of  $\Delta H$  reflect that the process of adsorption of the inhibitors on the mild steel surface is an endothermic process; it is shared unequivocally to chemisorption [20]. The negative values of  $\Delta S_{ads}$  in presence of the inhibitor imply that the activated complex in the rate – determining step was association rather than a dissociation step, a decrease in disorderliness took place on going from reactants to the activated complex. Values of free energy adsorption of Cd(II) and  $UO_2(II)$  complexes onto the mild steel surface were calculated using the Eq. (11):

TABLE 7. Activation Energy  $E_a$  for mild steel in 1 M HCl solution for blank sample and concentration of 500 ppm of investigated complexes at different temperature.

Inhibitor	A	R	$E_a$
Blank (1 M HCl solution )	1.9778	0.96198	11.97
500 ppm Cd(II) complex	1.8158	0.85802	14.22
500 ppm $UO_2(II)$ complex	1.7085	0.84348	12.91

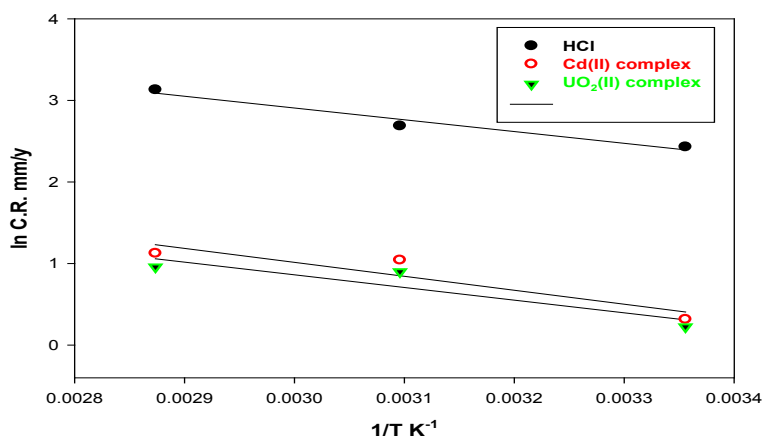
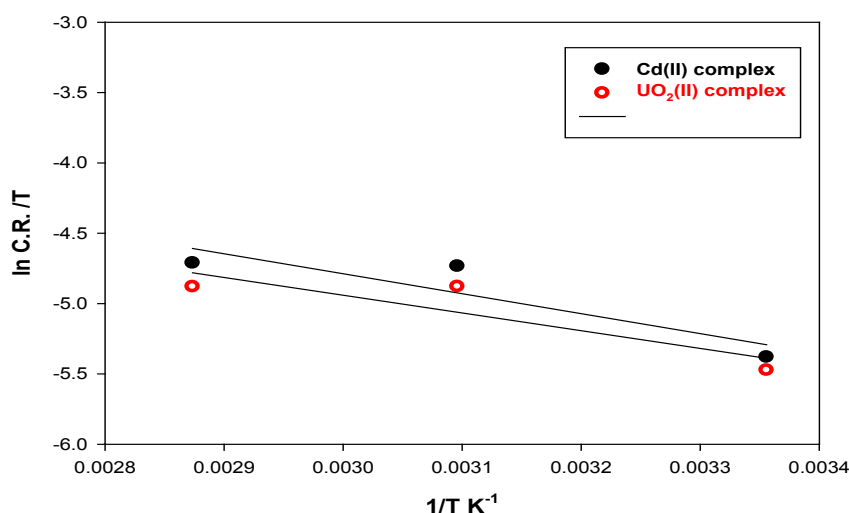


Fig. 7.  $\ln C.R.$  against  $1/T$  of mild steel for concentration of 500 ppm of investigated complexes at different temperature.

TABLE 8. Thermodynamic parameters of the adsorption of investigated complexes onto the mild steel.

Inhibitor	$Q_{\text{ads}}$	$\Delta H_{\text{ads}}$	$S_{\text{ads}} \Delta$
Cd(II) complex	-2.5869	11.7875	-201.98
UO <sub>2</sub> (II) complex	-1.05347	10.48113	-207.17

Fig. 8.  $\ln C.R./T$  versus  $1/T$  of mild steel for concentration of 500 ppm of investigated complexes

$$\Delta G_{\text{ads}} = -2.303 RT \log (55.5K) \quad (11)$$

where  $K = \theta / (1-\theta) C$ ,  $C$  is the concentration of the inhibitor.

Calculated values of  $\Delta G_{\text{ads}}$  and  $K$  are mentioned in Table 9. The values are all negative, a good indication that adsorption of the inhibitor onto the mild steel surface is spontaneous and the increase in values with rise in temperature is show that the spontaneity of the adsorption increased as temperature was raised. However, the values which are below  $-20$  KJ/mol are the threshold value for physical adsorption mechanism. Generally, values of  $\Delta G_{\text{ads}}$  up to  $-20$  KJ/mol are consistent with electrostatic interaction between charged molecules and a charged metal which indicates physical adsorption, while those above  $-40$  KJ/mol involves charge sharing or transfer from the matter molecules to the metal surface to make a co-ordinate kind of bond that indicates chemisorption. The mode of adsorption (physisorption and chemisorption) observed could be attributed to the fact that inhibitor contains many different chemical compounds which some can adsorbed

chemically and other adsorbed physically [20]. For the two inhibitors, IE% values decreased with temperature increased and they have a significant decrease in its protective properties with increasing the temperature. This might be due to connected with two effects, a certain drawing of the adsorption-desorption equilibrium towards desorption (meaning that the strength of adsorption process decreases at higher temperatures) and roughening of the metal surface which ends from increased corrosion.

#### Surface characterization and morphological studies

The macrostructure of the polished sample before corrosion and *the corroded samples* of blank sample and for concentration of 500 ppm in investigated inhibitors are collected in Fig. 9. The scanning electron micrographs shows the protective film formed on the mild steel surface. SEM images obtained from unexposed and exposed specimen coupons in 1 M HCl solution for 24 h for blank sample and concentration of 500 ppm for Cd(II) and UO<sub>2</sub>(II) complexes are mention in Fig. 10. From Fig. 10 (b), the specimen surface of the mild steel are extensively oxidized, rougher

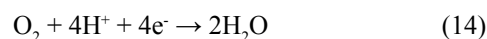
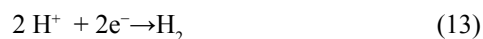
and was strongly damaged of the blank sample. On the other hand, Fig. 10 (c and d) show for the investigated inhibitors complexes relatively cleaner and smoother surface is observed and this is mainly due to the formation of protective film on the mild steel surfaces. This protective film acts as a barrier and isolates the surface of the vulnerable mild steel from the corrosive environments. Lower extent of damage to mild steel surface and corrosion rate considerably in the existence of inhibitors. This revealed that there was a good protective film adsorbed on metal surface, which acted as a barrier and was responsible for the inhibition of corrosion. The SEM micrographs show an adherence of inhibitors on the metallic surfaces which are in good agreement with the electrochemical measurements results. Also, EDAX analyses confirmed the inhibitors existence on the iron surface which indicated the presence of oxygen, Cd and  $\text{UO}_2$  with greater intensity of carbon peak. It hereby confirms the deposition or adsorption of the inhibitor molecule on the mild steel surface.

#### Mechanism of corrosion inhibition

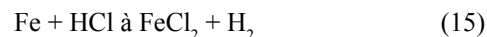
Mechanism of mild steel corrosion in 1 M HCl by Eq. (12):



There are several different cathodic reactions that are the most common reactions in acidic media [10]:



When iron corrodes, the rate is usually controlled by the cathodic reaction.

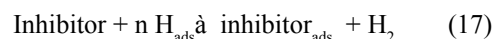


Fe is oxidised to  $\text{Fe}^{2+}$  by  $\text{H}^+$ ; the  $\text{Cl}^-$  ions was not strong enough to act as an oxidizing agent so, it plays no role in the reaction according to Le Chatelier's principle. Reduction reaction is hydrogen gas evolution as follows:



Where  $\text{H}_{\text{ads}}$  is hydrogen ions adsorbed on mild steel surface which catalyze to react with another hydrogen ions to contain covert hydrogen gas in bubble form on cathode surface. The amount of hydrogen gas evolved in presence of inhibitor depends on its ability to prevent this reaction and protected the mild steel from corrosion [10].

The action of inhibitor molecules is due to the adsorption of the inhibitor molecules on an exposed mild steel surface. Inhibitors may be adsorbed over the mild steel surface in the form of neutral molecules involving replacement of hydrogen ions adsorbed from the mild steel surface as [10]:



or by displacement water molecules of the surface as equation (14) Organic molecules maybe adsorbed on the mild steel surface in

TABLE 9. Free energy adsorption on investigated complexes for mild steel at different temperature.

Inhibitor		298 K	323 K	343 K
Cd(II) complex	$K_{\text{ads}}$	1.4556	0.8352	1.28478
	$\Delta G_{\text{ads}}$	-10.883	-10.3039	-12.1703
$\text{UO}_2(\text{II})$ complex	$K_{\text{ads}}$	1.6165	0.9969	1.5575
	$\Delta G_{\text{ads}}$	-11.1428	-10.7792	-12.7190



Fig. 9. Macrostructure of the mild steel for the blank sample and for investigated complexes [Cd(II) and  $\text{UO}_2(\text{II})$ ]

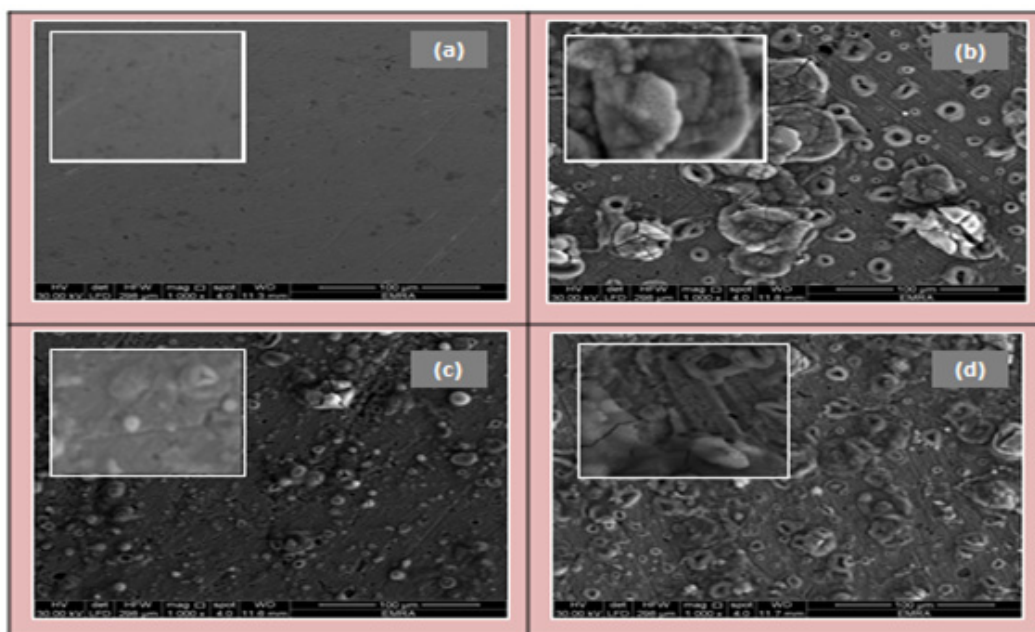


Fig. 10. SEM micrographs of mild steel samples for unexposed polished mild steel surface (a), after immersion in 1 M HCl solution in absence of inhibitor (b), after immersion in 1 M HCl solution in presence of 500 ppm Cd(II) complex (c) and after immersion in 1 M HCl solution in presence of 500 ppm UO<sub>2</sub>(II) complex(d)

four ways namely; (i) electrostatic interaction between the charged molecules and the charged metal, (ii) interaction of unshared electron pairs in the molecule with the metal, (iii) interaction of  $\pi$ -electrons with the metal and (iv) a combination of types (i-iii) [10]. Due to adsorption, inhibitor molecules block the reaction sites and reduce the rate of corrosion reaction. The adsorbed bond strength is determined by the electron density of these atoms [10]. Adsorption of inhibitors usually involves at least two types of adsorption simultaneously, first establishing a physisorbed on crystalline surface film, which may further stabilized through chemisorption to form a donor type bond. Chemisorption involves charge charring or charge transfer from the inhibitor molecules to the surface in order to form a coordinate bond [10]. So, we can considered these inhibitors affect corrosion inhibition by their physical and chemical interaction with the alloy surface, forming a protective film, acting as a barrier and increases the activation energy for metal dissolution.

Electrochemical and weight loss methods have been employed to study the behavior of mild steel in acid media, in the presence of Cd(II) and UO<sub>2</sub>(II) complexes. The increasing of inhibition efficiency with increasing inhibitor concentra-

tion means that a higher coverage of inhibitor on the surface with higher concentration of inhibitor. The first stage in mechanism of corrosion inhibition in acid media is adsorption of inhibitor molecule on the metal surface. In most inhibition studies, the donor-accepter surface formation complexes between p-electrons of inhibitor and the vacant d-orbital of metal were postulated [9]. The process of adsorption is influenced by the nature and charge of the metal, chemical structure of inhibitor and the type of aggressive electrolyte. The zero charge potential (PZC) is that the metal potential measured against the reference conductor at that the ionic double layer is absent at the conductor and also the conductor is best able to adsorb substance dissolved in the electrolyte. The ability of an electrode to adsorb the molecule is reduced in the existence of potential difference at the ionic double layer. This is as a result of the sector pulls in water molecules having high electrical constant, dislodging complex from the surface. Thus, the surface simulation capability of associate conductor maybe assimilation capability of associate conductor maybe a most about to the zero charge potential.

Accordingly, chloride ions from HCl solution are firstly adsorbed on the metal surface and the mild steel surface becomes negatively charged which led to adsorb the molecules of the

complexes that give the sample high inhibition [9]. The Cd(II) and UO<sub>2</sub>(II) complexes get adsorbed on the mild steel surface through unshared pair of electrons presence on metal chelates and shows higher efficiency in HCl solution. Besides, static interaction, chemisorptions of those compounds is most probable through the vacant d-orbitals of iron that acts as associate acceptor of electrons. Hence, d-p bonds are also formed by the overlap of vacant d-orbitals of Fe-atom with p-orbital electrons of donor atoms of the ligands in the complexes. Thus, UO<sub>2</sub>(II) complex is strongly adsorbed on the mild steel surface.

### Conclusions

Two Schiff bases complexes were studied as potential corrosion inhibitors for mild steel, and the factors govern their use. The corrosion behavior is a promising restrictive action against corrosion of mild steel in these compounds. They reported a good corrosion inhibitors for mild steel in 1M HCl solution in a 500ppm concentration. Corrosion inhibition efficiency of Schiff base complexes, Cd(II) and UO<sub>2</sub>(II), in 1M HCl solution have been studied using chemical and electrochemical method. They inhibit the oxidation of metal in acid medium might be due to adsorption of two metal complexes Cd(II) and UO<sub>2</sub>(II) addition. The inhibition efficiency of synthesized inhibitors increased by additions of complexes where the maximum achieved for UO<sub>2</sub>(II) complex. The results proved that presence of UO<sub>2</sub>(II) complex displayed good corrosion inhibition for mild steel in 1 M HCl solution. The complexes work as mixed type of inhibitor because both cathodic and anodic curves are shifted in positive direction. Morphology of mild steel surface showed the presence of protective surface film formed on mild steel surface which inhibits metal dissolution in HCl solution and retards hydrogen evolution and supports to the mixed-type inhibitor activity.

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