INHIBITIVE EFFECT OF SOME DIAZINE DERIVATIVES ON THE CORROSION OF STAINLESS STEEL (SS) TYPE 316 L IN ACIDIC MEDIA

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ABSTRACT

The inhibiting effect of some diazine derivatives on the corrosion of stainless steel (SS) type 316 L specimens in 3 M HCl in the presence of diazine derivatives at 30°C was studied using weight loss and galvanostatic polarization techniques. Polarization studies revealed that these derivatives behave as a mixed type inhibitors. The adsorption of these compounds on SS surface was found to obey Temkin adsorption isotherm. The inhibition efficiency increases with increasing the concentration of the inhibitor and decreases with increasing the temperature. Addition of I^-, Br^- and SCN^- ions to the solution containing diazine derivatives increases the inhibition efficiency of the system by synergistic effect.

1. INTRODUCTION

Stainless steel (type 316 L) is frequently used as a construction material in various aggressive environments such as chemical plants, destination plants, waste water treatment plants and petroleum industry [Bentiss et al., (2000)]. Organic compounds containing nitrogen atom are commonly used to reduce the corrosion attack on steel in acidic media [Popova et al., (2003); Abdallah & El-Naggar (2001); De Damborenea et al., (1996); Al-Neani et al., (1995); Bastidas et al., (1997); Abde Aal & Morad (2001); Mohamed et al., (2000); Abd El-Rehim et al., (1999); Bentiss et al., (2002) and Wiley Van (1994)].

The inhibition mechanism of these organic compounds is mainly based on adsorption [El-Kanonni et al., (1996)]. These compounds can

adsorb on the steel surface by blocking the active sites and hence decreasing the corrosion rate. They control corrosion acting over the anodic or the cathodic surface or both.

The aim of this work is to study of the effect of some diazine derivatives as corrosion inhibitors for dissolution of SS type 316 L in 3 M HCl solution using weight loss and galvanostatic polarization measurements. The effect of temperature on the dissolution of SS type 316 L in free and inhibited acid solution was also, investigated.
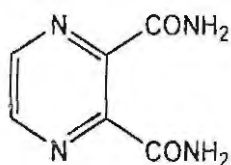
2. EXPERIMENTAL DETAIL

2.1. Materials and solutions

The chemical composition and mechanical properties of material specimen are given in Table (1).

Table (1): Chemical composition (wt %) of the SS type 316 L.

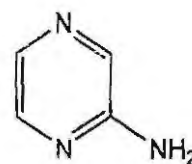| Material type	% composition									
	C	Mn	P	S	Si	Cr	Ni	Mo	Cu	Fe
SS type 316 L	0.02	1.0	0.054	0.02	1.0	16	11	3	0.2	is the remaining

HCl, KSCN, KI, KBr and diazine derivatives all of BDH made were used for preparing solutions. The names and molecular structures of diazine derivatives are given below:

pyrazine-2,3-dicarboxamide
inhibitor I
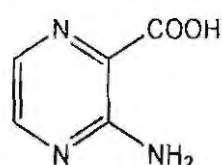
3-aminopyrazine-2-carboxylic acid
inhibitor II

pyrazin-2-amine
inhibitor III

2.2. Experimental
2.2.1. Chemical Technique (Weight loss method)

The reaction basin was a graduated glass vessel 6 cm inner diameter and having a total volume of 250 ml. 100 ml of the test solution were employed in each experiment. The test pieces were cut into

2×2×0.2 cm. They were mechanically polished with emery paper (a coarse paper was used initially and then progressively finer grades were employed), rinsed with double distilled water and finally dried between two filter papers and weighed. The test pieces were suspended by suitable glass hooks at the edge of the basin, and under the surface of the test solution by about 1 cm. After specified periods of time, 3 test pieces were taken out of the test solution, rinsed with double distilled water, dried as before and weighed again. The average weight loss at a certain time for each set of three samples was taken. The weight loss was recorded to the nearest 0.0001 g.

2.2.2-Electrochemical technique (Galvanostatic polarization method) Electrodes

Two different types of electrodes were used; disks with 12 mm diameter and 2 mm thickness and cylindrical specimens. The discs were welded from one side to a copper wire for electric connection and embedded in glass tube of larger diameter than the sample. Epoxy resin was used to stick the sample to the glass tube except the exposed tested surface area which was left to be exposed to the corrosive media.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1-Weight loss measurements
3.1.1-Effect of inhibitor concentrations

Weight-loss of SS type 316 L was determined, using equation (1), at various time intervals in absence and presence of different concentrations of diazine derivatives (I-III). The obtained weight loss-time curves are represented in Figure (1) for inhibitor (I), the most effective one. Similar curves were obtained for other two inhibitors (not shown)

$$\Delta w = (w_1 - w_2)/A \qquad (1)$$

where Δw is the weight loss in mg per unit area, w_1 and w_2 are the weights of the specimen before and after reaction, respectively, and A is the surface area in cm^2.

The curves obtained in the presence of inhibitors fall significantly below that of free acid. In all cases, the increase in the inhibitor concentration was accompanied by a decrease in weight-loss and an increase in the percentage inhibition. These results lead to the conclusion that, these derivatives are fairly efficient as inhibitors for SS type 316 L dissolution in hydrochloric acid solution. Also, the degree of surface

coverage, (θ) by the inhibitor, calculated from equation (2), would increase by increasing the inhibitor concentration.

$$\theta = 1 - (\Delta W_{inh.}/\Delta W_{free}) \tag{2}$$

Where ΔW_{inh} and ΔW_{free} are the weight losses per unit area in presence and absence of the inhibitor, respectively.

In order to get a comparative view, the variation of the inhibition efficiencies (IE%) of the inhibitors with their molar concentrations were calculated according to equation (3); values obtained are summarized in Table (3).

$$\%IE = \theta \times 100 \tag{3}$$

Careful inspection of these results showed that, at the same inhibitor concentration, the order of inhibition efficiencies decreases in the following order **I > II > III**.
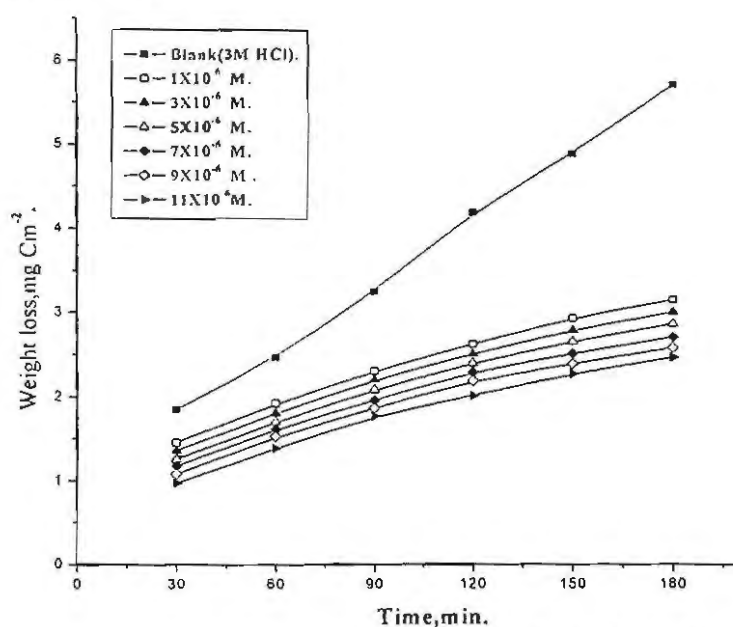

Fig. (1): Weight loss-time curves for the dissolution of SS type 316 L in absence and presence of different concentrations of compound (I) at 30°C.

3.2. Synergistic effect:

As seen from Table (2), the % inhibition efficiency of the tested derivatives is low, so in order to increase these values we use KI, KSCN, and KBr in addition to the different concentrations of the investigated derivatives. Table (3) shows the % inhibition of the investigated derivatives in presence of 1×10^{-2}M of KI.

Table (2): % Inhibition of SS type 316 L dissolution at 120 min. immersion in 3 M HCl in presence of different concentrations of inhibitors at 30°C.

Concentration, M	%Inhibition		
	(I)	(II)	(III)
1×10^{-6}	68.4	61.3	56.7
3×10^{-6}	71.5	65.7	59.3
5×10^{-6}	74.1	68.1	63.6
7×10^{-6}	77.0	71.2	65.4
9×10^{-6}	78.3	74.1	67.2
11×10^{-6}	81.2	77.3	70.8

Table(3) : %Inhibition efficiency of SS type 316 L dissolution at 120 min. immersion in 3M HCl in presence of 1×10^{-2}M KI at different concentrations of inhibitors at 30°C.

Concentration, M	% Inhibition		
	(I)	(II)	(III)
1×10^{-6}	78.2	70.2	65.0
3×10^{-6}	81.3	73.3	68.0
5×10^{-6}	83.7	76.2	71.2
7×10^{-6}	86.1	79.2	74.3
9×10^{-6}	89.0	82.1	78.5
11×10^{-6}	91.0	85.3	80.4

It can be seen from Table (3) that the addition 10^{-2} M of KI inhibits the corrosion of SS type 316 L to a large extent and by increasing the concentration of diazine derivatives (1×10^{-6} - 11×10^{-6} M). This can be interpreted according to Schmitt and Bedbur **[Schmilt & Bedbur (1985)]**, which proposed two types of joint adsorption namely competitive and cooperative. In competitive adsorption, the anions and cations are adsorbed at different sites on the electrode surface, and in case of cooperative adsorption, the anions are chemisorbed on the electrode surface and the cations are adsorbed on a layer of the anion, apart from the adsorption on the surface directly.

From the data of Table (3) it is seen that KI would be considered as one of the effective anions for synergistic action with respect to the investigated salts. The net increment of inhibition efficiency shows a synergistic effect of KI, KSCN and KBr with diazine derivatives. The synergistic effect depends on the type and concentration of anions. The

inhibition efficiency in presence of these anions decreases in the order: KI > KSCN > KBr [Khamis et al., (2000)] and this parallel to the increase of the covalent radii of these anions. The experimental results suggested that the presence of these anions in the solution stabilizes the adsorption of derivatives on the metal surface and improved the inhibition efficiency of these derivatives.

Fig. (2) demonstrates the weight loss time curves for the dissolution of SS type 316 L in 3 M HCl in absence and presence of different concentrations of compound (b) without and with addition of 10^{-2} M KI at 30°C.

$$S_\theta = (1 - \theta_{1+2}) / (1 - \theta'_{1+2}) \tag{4}$$

Where $\theta_{1+2} = \theta_1 + \theta_2 - \theta_1 \theta_2$

θ'_{1+2}: measured surface coverage by the anion in combination with cation. θ_1 and θ_2 are the surface coverage for anions and cations, respectively.
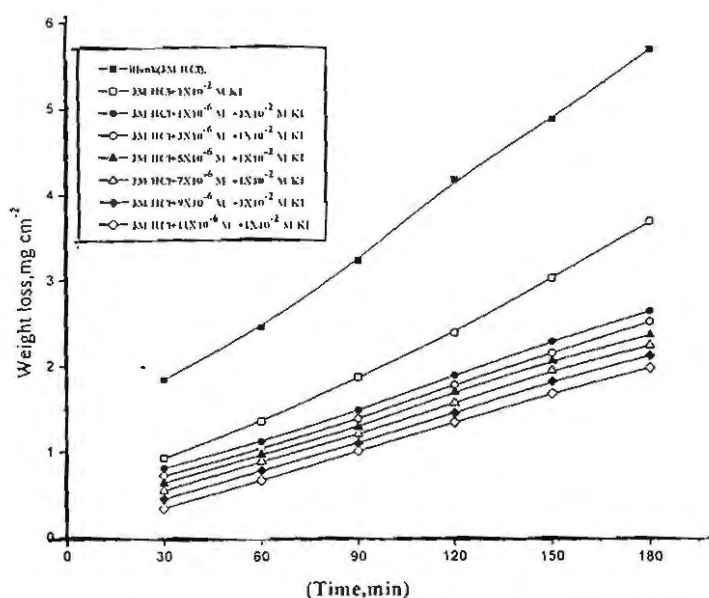

Fig.(2): Weight loss -time curves for SS type 316 L dissolution in 3 M HCl in absence and presence of 1×10^{-2}M KI and at different concentrations of inhibitor (I) at 30°C.

Table (4) lists the variation of the synergistic parameter (S_θ) in the presence of different concentrations of diazine derivatives. It is seen that all values of (S_θ) are more than unity and, therefore, the increase in % inhibition is due to synergistic effect. Thus, these diazine derivatives

significantly improved the coverage and hence, the inhibition efficiency of these derivatives increased.

These derivatives are nitrogen containing compounds, which contain unshared electron pairs on the N atom. In strong acidic solutions these derivatives may be protonated, leading a positive charge on the molecule. It is also known that SS type 316 L surface has positive charge, thus it is difficult for the positively charged derivatives to approach the positively charged SS type 316 L surface ,due to the electrostatic repulsion ,this is why these derivatives can not act as excellent inhibitors for SS type 316 L corrosion in 3M HCl solution without containing anions .In case of presence I^-, SCN^- and Br^- ions, these anions adsorbed on SS type 316 L surface and makes the surface negatively charged by means of electrostatic attraction, after that ,protonated diazine derivatives are easily reached the surface of SS type 316 L .

Table (4): Synergism parameter (S_θ) at different concentrations of inhibitors for 316L S dissolution in 3M HCl with addition of 1×10^{-2}M KI at 30°C.

Concentration, M	Synergism parameter (S_θ)		
	(I)	(II)	(III)
1×10^{-6}	1.0	1.1	1.1
3×10^{-6}	1.0	1.1	1.0
5×10^{-6}	1.0	1.1	1.1
7×10^{-6}	1.0	1.1	1.1
9×10^{-6}	1.2	1.2	1.0
11×10^{-6}	1.4	1.2	1.1

3.3. Adsorption isotherm:

Assuming the corrosion inhibition was caused by the adsorption of diazine derivatives, and the values of surface coverage at different concentrations of inhibitors in 3M HCl were evaluated from weight loss measurement using equation (2).

From the values of (θ), it can be seen that the values of (θ) increased with increasing the concentration of derivatives. Using these values of surface coverage, one can utilize different adsorption isotherms to deal with experimental data. The Temkin adsorption isotherm was applied to investigate the adsorption mechanism, by plotting (θ) vs. log C, a straight lines were obtained (Fig.3). On the other hand, it is found

that kinetic- thermodynamic model of El-Awady et al [**El-Awady & Ahmed (1985)**] which has the formula:

$$\log (\theta /1 - \theta) = \log K' - y \log C \qquad (5)$$

Is valid and verify the present adsorption data (Fig.4). The equilibrium constant of adsorption $K = K'^{(1/y)}$, where $1/y$ is the number of the surface active sites occupied by one diazine molecule and C is the bulk concentration of the inhibitor. From Table (5) it is noted that ΔG_{ads} values have a negative sign indicating that the adsorption process proceeds spontaneously and increase as the percentage inhibition increases. Table (5) shows the calculated thermodynamic parameters.

Table (5): Inhibitor binding constant (K), free energy of binding (ΔG_{ads}.), number of active sites (1/y) and later interaction parameter (a) for diazine derivatives at 30°C.

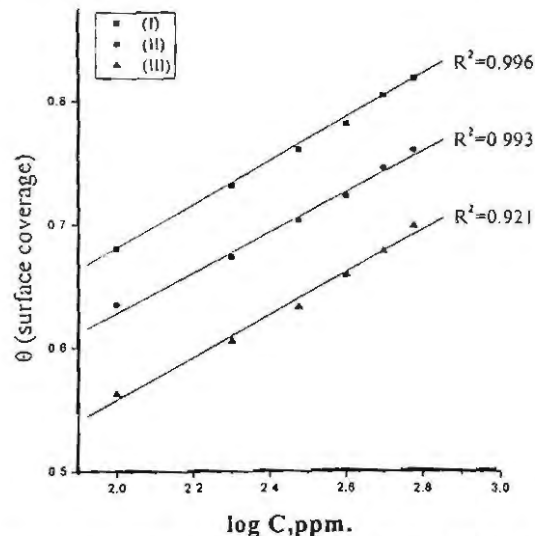| Inhibitors	Kinetic model			Temkin		
	1/y	K	$-\Delta G_{ads.}$, kJmol^{-1}	a	K	$-\Delta G_{ads.}$, kJmol^{-1}
(I)	3.200	0.985	60.7	14.03	72.3	63.0
(II)	3.121	0.874	58.9	13.33	67.1	62.2
(III)	3.023	0.655	54.5	13.24	17.1	52.1

Fig.(3): Curve fitting of corrosion data for SS type 316 L 3M HCl in presence of different concentrations of inhibitors to the Temkin isotherm at 30°C.
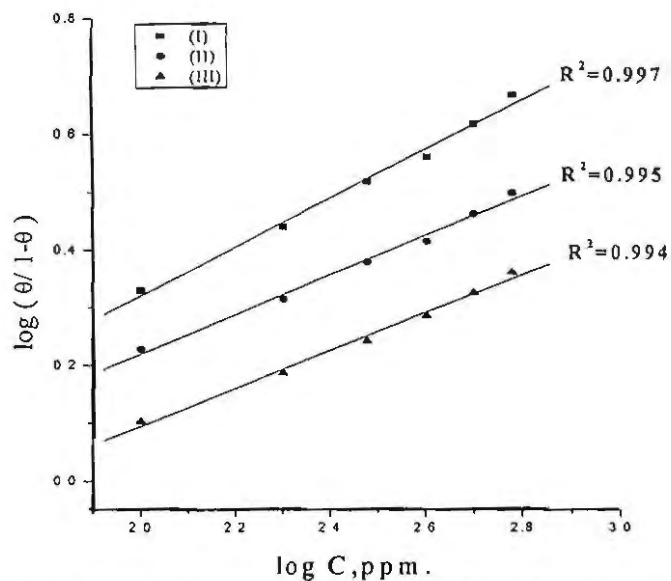
Fig.(4): Curve fitting of corrosion data for SS type 316 L
in 3M HCl in presence of different concentrations
of inhibitors to the kinetic model at 30°C.

3.4. Effect of Temperature:

The effect of temperature (30 – 55°C) on the performance of the inhibitors at a concentration of (1×10^{-6} - 11×10^{-6} M) for SS type 316 L in 3M HCl was studied using weight-loss measurements. Plots of log k (corrosion rate) against 1/ T (absolute temperature) Fig. (5) for SS type 316 L in 3M M HCl, gave straight lines. The values of the slopes obtained at different temperatures permit the calculation of Arrhenius activation energy (E_a^*). The activation energy values obtained from these lines were found to be 58 kJ mol^{-1} for SS type 316 L 3M HCl and (69 – 96) kJ mol^{-1} for acid containing inhibitors Table (6).

Activation parameters for corrosion of SS type 316 L were calculated from Arrhenius – type plot.

$$k = A \exp (-E_a^* / RT) \qquad (6)$$

and transition state- type equation:

$$k = RT / Nh \exp (\Delta S^*/R) \exp (-\Delta H^* / RT) \qquad (7)$$

The relation between log k / T vs. 1 / T gives straight line Fig (6), from their slopes, ΔH^* can be computed and from their intercepts ΔS^* can be also computed.

Table (6) exhibits the values of apparent activation energy E_a^*, enthalpies ΔH^* and entropies ΔS^* for SS type 316 L dissolution in 3M HCl solution. The presence of derivatives increases the activation energies of SS type 316 L indicating strong adsorption of the inhibitor molecules on the metal surface and the presence of these additives induces energy barrier for the corrosion reaction and this barrier increases with increasing the additive concentrations.
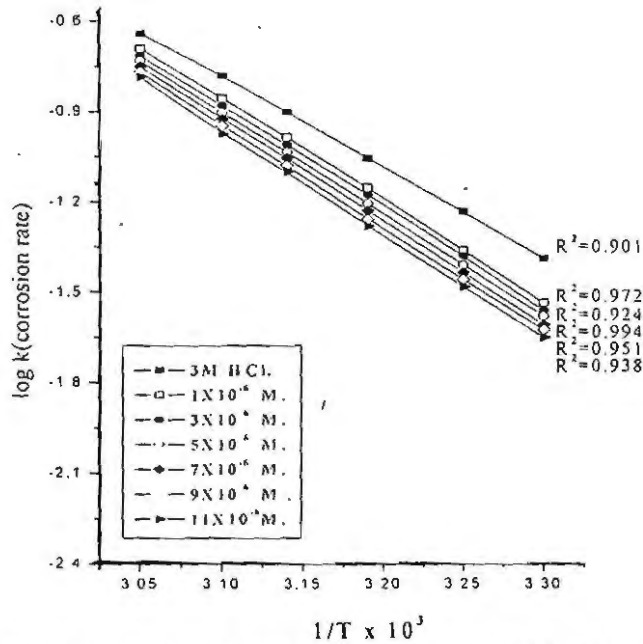

Fig.(5) :log k- 1/T curves for SS type 316 L dissolusion in 3M HCl in absence and presence of different concentrations of inhibitor(I).
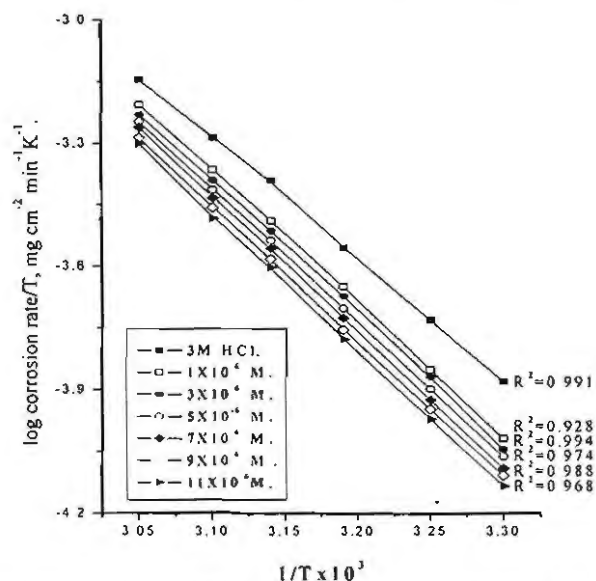
Fig.(6) :log (corrosion rate/T) -(1/T) curves for SS type 316 L dissolusion in 3M HCl in absence and presence of different concentrations of inhibitor (I).

Table (6): Effect of concentrations of inhibitors on the activation energy, activation enthalpy and activation entropy of SS type 316 L dissolution in 3M HCl.

Inhibitor	Concentration. M	E_a^*, kJ mol^{-1}	ΔH^*, kJ mol^{-1}	$-\Delta S^*$, K^{-1}J mol^{-1}
Blank	0.0	58.0	52.6	82.8
I	1×10^{-6}	94.4	87.4	7.3
	3×10^{-6}	96.4	89.5	13.4
	5×10^{-6}	96.6	92.2	20.9
	7×10^{-6}	97.3	92.6	21.7
	9×10^{-6}	97.6	94.3	26.0
	11×10^{-6}	90.0	94.3	26.7
II	1×10^{-6}	80.7	76.8	25.0
	3×10^{-6}	81.0	78.7	19.7
	5×10^{-6}	83.2	80.6	14.4
	7×10^{-6}	84.0	81.3	12.7
	9×10^{-6}	85.0	82.7	8.8
	11×10^{-6}	86.1	83.4	7.4
III	1×10^{-6}	67.8	71.4	41.0
	3×10^{-6}	74.1	71.9	36.9
	5×10^{-6}	75.2	74.1	33.5
	7×10^{-6}	76.8	75.5	29.5
	9×10^{-6}	78.2	79.4	17.4
	11×10^{-6}	80.2	80.2	13.4

3.5 Electrochemical measurement

Galvanostatic polarization studies were carried out on SS type 316 L in 3 M HCl solution without and with different concentrations of the inhibitors. All experiments were carried out at 30°C. The inhibition efficiency (%IE) is defined as [George (1988)]:

$$\%IE = ((i_{corr.} - i_{inh.})/ i_{corr}) \times 100 \tag{8}$$

Where $i_{corr.}$ and $i_{inh.}$ are the corrosion current density in the absence and presence of inhibitors, respectively. The degree of surface area coverage (θ) can be calculated from the relation:

$$\theta = (i_{corr.} - i_{inh.})/ i_{corr.} \tag{9}$$

3.5.1. Galvanostatic polarization curves

Corrosion behavior of SS type 316 L is studied in 3M HCl solution in absence and presence of $(1 \times 10^{-6} - 11 \times 10^{-6})$ M inhibitors (I – III) at 30°C. Fig. (7) shows the galvanostatic polarization curve of SS type 316L in 3M HCl in absence and presence of inhibitor (I) at different inhibitor concentrations similar curves were obtained for other two inhibitors (not shown). Table (7) gives the various corrosion parameters.

Tafel slopes (βa & βc) values, corrosion potential (E_{corr}), corrosion current (i_{corr}), degree of surface coverage (θ) and inhibition efficiency (% IE) indicate that:

1- The corrosion current density decreases with increasing the concentration of diazine derivatives. This indicates that the presence of these derivatives retards the dissolution of SS type 316 L in 3M HCl solution and the degree of inhibition depends on the concentration and type of the inhibitor present.

2- The degree of surface coverage was found to increase with increasing the concentration of inhibitor.

3- The presence of the tested inhibitors retards both anodic and cathodic reactions β_a and β_c are changed. This indicates that these inhibitors act as mixed-type inhibitors.

4- The order of decrease in inhibition efficiency for the diazine additives is: **(I) > (II) > (III)**
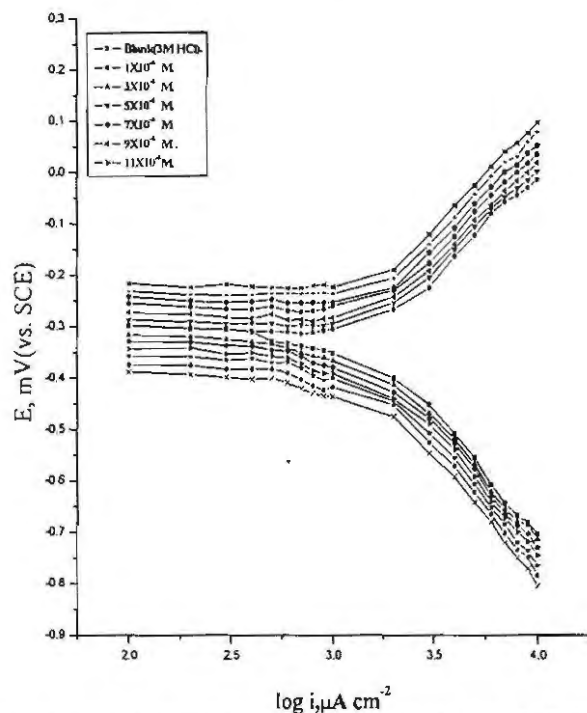
Fig.(7).:Galvanostatic polarization curve of SS type 316 L in 3M HCl in absence and presence of different concentrations of inhibitor (I) at 30°C.

The inhibition mechanism of the tested inhibitor is a combination of surface blockage and electrostatic repulsion between adsorbed diazine layer and chloride ions. The adsorption of inhibitor depends on the inhibitor concentration. At adsorption density less than that needed for monolayer coverage (Fig. 8a), most of the nucleation sites are still possibly exposed to HCl, as the inhibitor has less adsorption affinity on them. When the adsorption density reaches monolayer adsorption (Fig.8b), some of the nucleation sites begin to be completely covered by inhibitor molecules. At maximum adsorption density in Fig. (8c), the whole surface, including the nucleation sites, is covered by the inhibitor molecules and hence complete inhibition occurs.

Table (7): Corrosion parameters for SS type 316 L in 3M HCl in absence and presence of different concentrations of inhibitors (I-III) at 30°C.

Inhibitor	Conc., M	$-E_{corr}$, mV(SCE)	i_{corr}, μAcm^{-2}	β_a, mVdec^{-1}	β_c, mVdec^{-1}	θ	%IE
Blank	3M HCl	0.351	74.64	0.287	0.179	--	--
I	1×10^{-6}	0.317	54.81	0.109	0.462	0.3862	38.62
	3×10^{-6}	0.313	21.88	0.103	0.403	0.6143	61.43
	5×10^{-6}	0.303	20.79	0.162	0.351	0.7443	74.43
	7×10^{-6}	0.301	11.48	0.153	0.362	0.8462	84.62
	9×10^{-6}	0.297	11.21	0.148	0.298	0.8498	84.98
	11×10^{-6}	0.287	10.93	0.158	0.197	0.8535	85.35
II	1×10^{-6}	0.330	50.70	0.052	0.192	0.3208	32.08
	3×10^{-6}	0.319	32.81	0.056	0.243	0.5605	56.06
	5×10^{-6}	0.315	17.10	0.088	0.218	0.7709	77.09
	7×10^{-6}	0.306	13.68	0.113	0.207	0.8169	81.69
	9×10^{-6}	0.301	12.91	0.111	0.312	0.8270	82.70
	11×10^{-6}	0.297	11.56	0.103	0.301	0.8451	84.51
III	1×10^{-6}	0.333	51.40	0.051	0.190	0.2940	29.40
	3×10^{-6}	0.331	36.30	0.061	0.208	0.5355	53.55
	5×10^{-6}	0.327	28.18	0.083	0.206	0.6656	66.56
	7×10^{-6}	0.316L	14.36	0.069	0.347	0.7672	76.72
	9×10^{-6}	0.312	15.83	0.110	0.351	0.7879	78.79
	11×10^{-6}	0.297	14.96	0.097	0.309	0.7995	79.95

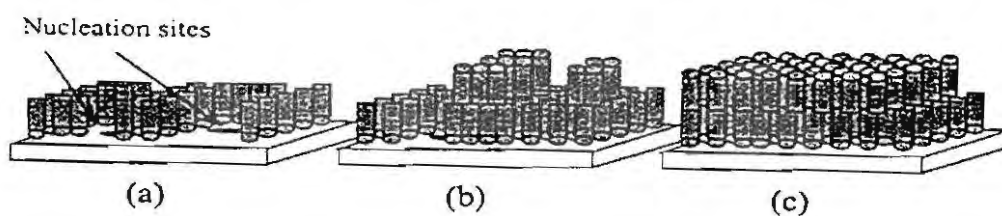Nucleation sites

(a)   (b)   (c)

Fig.8: Adsorption schemes for organic compound as an inhibitor on SS type 316 L stainless steel, (8a) at low concentration, (8b) intermediate concentration and (8c) high concentration.

4. CONCLUSIONS

The following conclusions can be deduced from the present study:

1- Diazine derivatives appear to be efficient inhibitors for corrosion of 316 L in 3M HCl solution, which act as mixed-type inhibitors, the %IE was found to increase with increase the inhibitor concentration and was found that the inhibition efficiency decrease in order:

$$(I) > (II) > (III).$$

2- The inhibition of corrosion of SS type 316 L in 3M HCl solution was found to obey the Temkin adsorption isotherm and the inhibitors appear to absorb on SS type 316 L surface.

3- The inhibition efficiency (%IE) increases with the increase in the inhibitor concentration, while decreases with the increase in the temperature according to the order: $(I) > (II) > (III)$.

This means that these inhibitors adsorbed physically on SS surface.

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التأثير المثبط لبعض مشتقات الديازين على تاكل الصلب المقاوم
نوع 316L فى الأوساط الحامضية

عبد العزيز السيد فودة ، عبد المنعم الحسينى العسقلانى ، على أحمد محمد كشك

قسم الكيمياء – كلية العلوم ــ جامعة المنصورة – جمهورية مصر العربية

تم دراسة التأثير المثبط لمشتقات الديازين على تاكل الصلب المقاوم نوع 316L فى 3 مولر حمض الهيدروكلوريك عند 30م بطريقتى الفقد فى الوزن والاستقطاب الجلفانوستاتيكى. وقد دلت طريقة الاستقطاب الجلفانوستاتيكى على ان هذه المشتقات تعمل كمثبطات مختلطة وأن ادمصاص هذه المركبات على سطح الصلب المقاوم 316 تتبع ايزوثرم تمكن. وتقل كفاءة التثبيط بارتفاع درجة الحرارة مما يدل أن ادمصاص هذه المركبات على سطح الصلب المقاوم 316L ادمصاص فيزيائى. وقد تم اضافة ايونات اليوديد والبروميد والثيوثيانات على التركيزات المختلفة من هذه المشتقات ووجد أنها تزيد من كفاءة تثبيط هذه المشتقات.