Inhibitive Effect of Some Pyrimidine Derivatives on the Cyclic Stressed Specimens of Stainless Steel Type 304 in Acidic Media

A.S. Fouda[1],[*] and H. El-Dafrawy[2]

[1] Chemistry Department, Faculty of Science, El-Mansoura University, El- Mansoura-35516, EGYPT
[2] Faculty of Engineering, Tanta University, Tanta, EGYPT
[*]E-mail: asfouda@yahoo.com

The inhibiting effect of different concentrations some pyrimidine derivatives on the cyclic stressed specimens in 0.1 M HCl at 30°C was studied using galvanostatic polarization technique. Some quantum – chemical quantities were calculated. The inhibition efficiencies of these compounds on the uniform corrosion was evaluated by recording anodic and cathodic polarization curves of the electrode in the aggressive media. The examined compounds exerted an inhibiting action towards the general corrosion, ranging between 22% to 85%, but the % inhibition efficiency (%IE) for cyclic stressed specimens ranging between 3% to 34%. Polarization studies revealed that these compounds behave as mixed type inhibitors and inhibit corrosion by parallel adsorption on the surface of stainless steel due to the presence of more than one adsorption active centre in the inhibitor molecule. The adsorption is obeyed Langmuir adsorption isotherm. The inhibitor efficiency increases with increasing the concentration of inhibitor and decreasing with increasing the cyclic stress and temperature.

1. INTRODUCTION

Stress corrosion cracking (SCC) is one of the most serious corrosion problems for metallic materials encountered in service. Much attention has been paid to mitigating or eliminating the damage of metallic materials due to SCC especially in the case of effecting cyclic stress on the metallic material. Since SCC is sensitive to corrosion environments, the addition of a small amount of proper inhibitor can mitigate SCC of austenitic steels in acidic solution [1].

A number of investigators have been studied the effect of the inhibitors on the SCC of austenitic stainless steel in acidic chlorides solutions [1-4].

Authors studied the synergistic inhibition effect of I^- ions with some amines in NaCl solution on SCC of AISI 321 stainless steel , they found that the inhibition efficiency was attributed to the effect of retarding both anodic and cathodic reactions of the corrosion processes [5]. Also SCC of AISI 321 stainless steel in acidic solution was inhibited by thiourea and its derivatives, primary amines and tetra-amine salts, by estimating the anodic and cathodic polarization of the corrosion process, it was found that these inhibitors reduce the rate of anodic dissolution of the steel [6,7].

In situ electrochemical measurements of stressed specimens under dynamic straining condition were performed and this may offers some interesting information on the role of the inhibitors.

In this paper, the effect of some pyrimidine derivatives on the corrosion fatigue of stainless steel type 304 stressed by cyclic frequency 10.5 Hz in hydrochloric acid solution using in situ electrochemical measurements was carried out and some quantum –chemical calculations were carried and were done.

2. EXPERIMENTAL PART

Chemical composition of AISI 304 austenitic stainless steel specimens were shown in Table (1). Two different types of electrodes were used during polarization measurements. Disk with 12 mm diameter and 2 mm thickness which machining to give surface area 1 cm^2 was cut from AISI 304 stainless steel rod and was weld from one side to a copper wire used for electric connection and was embedded in glass tube of just larger diameter than the sample. Epoxy resin was used to stick the sample to glass tube. This electrode was used in general corrosion after treatment with emery paper up to # 1000.

Table 1. Chemical composition of AISI 304 stainless steel (wt %)

C	Mn	P	S	Si	Ni	Cr	others	Fe
0.07	2.00	0.045	0.030	0.75	9.0	18.0	....	Reminder

Cylindrical tensile specimens were used in the fatigue test and in electrochemical measurements after fatigue test in air. The cylinder specimen with diameter 10 mm, the gage length of the middle part 20 mm with diameter 4 mm was used as test section and the overall length 140 mm as shown in Fig. (1). The gage length of all specimens were prepared by treatment with emery papers up to n. 1000, then degreased in acetone in ultrasonic bath, washed with bi-distilled water and then dried at 30°C.
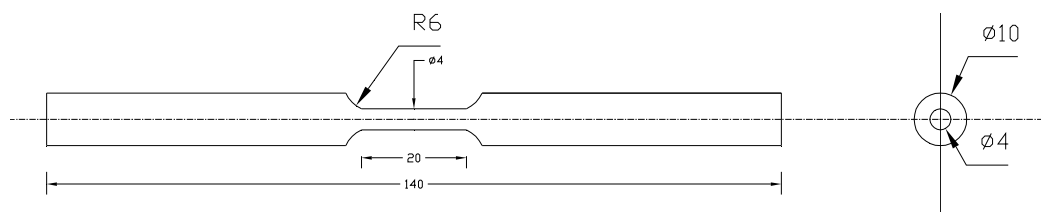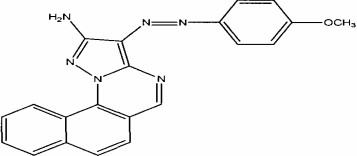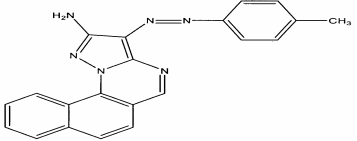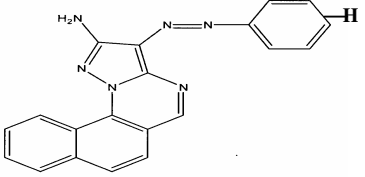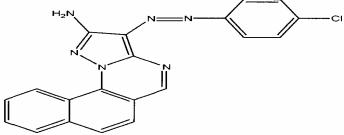

Figure 1. Specimen of fatigue test.

Fatigue tests were performed at 10.5 Hz on a cantilever rotary-bending fatigue test machine, with different cyclic stress (82MPa – 247MPa) and number of cycles (1000000). The specimens were coated with epoxy resin except for the gage section which was immersed in the solution during the entire galvanostatic polarization process. The corrosive solution was 0.1 M HCl which was prepared from analytical grade reagents and distilled water and was used as the blank solution. The structure of the pyrimidine derivatives which used as inhibitors are shown in Table (2).

Table 2. The structure of inhibitors used [8]

Inh. №	Inhibitor name	Inhibitor formula
I	3-(4-Methoxy-phenylazo)-1,4,11C-triaza-Cyclopenta [c] Phenanthren-2-ylamine	
II	3-(4-Methyl-phenylazo)-1,4,11C-triaza-Cyclopenta [c] Phenanthren-2-ylamine	
III	3-(4-Hydrogen-phenylazo)-1,4,11C-triaza-Cyclopenta [c] Phenanthren-2-ylamine	
IV	3-(4-Chlore-phenylazo)-1,4,11C-triaza-Cyclopenta [c] Phenanthren-2-ylamine	

3. RESULTS AND DISCUSSION

3.1. Electrochemical measurements

Galvanostatic polarization studies were carried out on AISI 304-SS in 0.1 M HCl solution without and with different concentrations of the investigated compounds. The sample was used as working electrode, saturated calomel electrode (SCE) was used as reference electrode while platinum wire as counter electrode. All experiments were carried out at $30^{o}C = 1^{o}C$. The inhibition efficiency (%IE) is defined as [10]:

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

θ is the degree of surface area coverage and can be calculated from the relation:

$$\theta = (I_{corr.} - I_{inh.})/ I_{corr.}$$

Where $I_{corr.}$ and $I_{inh.}$ are the corrosion current densities in absence and presence of inhibitors , respectively.

3.2. Polarization curves

The corrosion behavior of stainless steel type 304 is studied in 0.1M HCl solutions in absence and presence of ($3x10^{-6}$ – $1.2x10^{-5}$ M) inhibitors (I – IV) at 30°C. Figure. (2) shows the galvanostatic polarization curves of austenitic stainless steel type 304 in 0.1M HCl in absence and presence of inhibitor I at different concentrations and Table (3) shows the corrosion parameters.
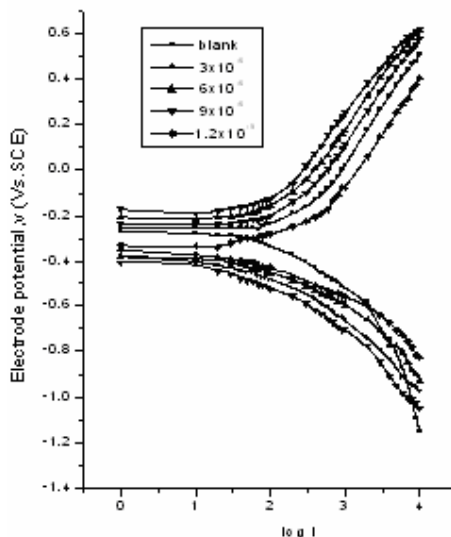

Figure 2. Polarization curves of stainless steel type 304 electrode in 0.1 M HCl in absence and presence of various concentarions at of inhibitor I at 30°C.

Table 3. Corrosion parameters of residual stressed SS type 304 in 0.1M HCl at 30°C in absence and presence of different concentrations of inhibitors (I– IV).

Inhibitor	Conc., M	$-E_{corr.}$, v	$i_{corr.}$ $\mu A\ cm^{-2}$	β_a v dec^{-1}	β_c v dec^{-1}	θ	%IE
Blank	0.1 M HCl	0.351	74.64	0.287	0.179	--------	--------
I	$3x10^{-6}$	0.317	45.81	0.108	0.464	0.3862	38.62
	$6x10^{-6}$	0.314	21.88	0.063	0.401	0.6143	61.43
	$9x10^{-6}$	0.305	20.79	0.157	0.345	0.7443	74.43
	$12x10^{-6}$	0.297	11.48	0.163	0.353	0.8462	84.62
II	$3x10^{-6}$	0.328	50.70	0.050	0.190	0.3208	32.08
	$6x10^{-6}$	0.316	32.81	0.061	0.204	0.5605	56.05
	$9x10^{-6}$	0.311	17.10	0.087	0.213	0.7709	71.09
	$12x10^{-6}$	0.302	13.68	0.067	0.203	0.8169	81.69
III	$3x10^{-6}$	0.333	51.40	0.051	0.346	0.2940	29.40
	$6x10^{-6}$	0.329	36.30	0.055	0.300	**0.**5355	53.55
	$9x10^{-6}$	0.326	28.18	0.081	0.348	0.6656	66.56
	$12x10^{-6}$	0.315	14.36	0.109	0.373	0.7672	76.72
IV	$3x10^{-6}$	0.338	57.81	0.063	0.427	0.2255	22.55
	$6x10^{-6}$	0.331	36.31	0.076	0.396	0.4962	49.62
	$9x10^{-6}$	0.327	29.38	0.082	0.397	0.6295	62.95
	$12x10^{-6}$	0.322	18.71	0.113	0.389	0.7407	74.07

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

1 - The corrosion current density decreases with increasing the concentration of pyrimidine derivatives, which indicates that the presence of these compounds retards the dissolution of austenitic stainless steel type 304 in 0.1M HCl solution and the degree of inhibition depends on the concentration and type of the inhibitor present as shown in Fig. (3).

2 - The degree of surface coverage was found to increase with increasing the concentration of inhibitors, and for certain range of inhibitor concentrations, where a monolayer adsorption occurs on the SS type 304 surface [10].

3 - Presence of these inhibitors retards both anodic and cathodic reactions of the metal. For this reason, these inhibitors act as mixed type inhibitors.

4 - The order of decreased inhibition efficiency for these additives is: I > II > III > IV.
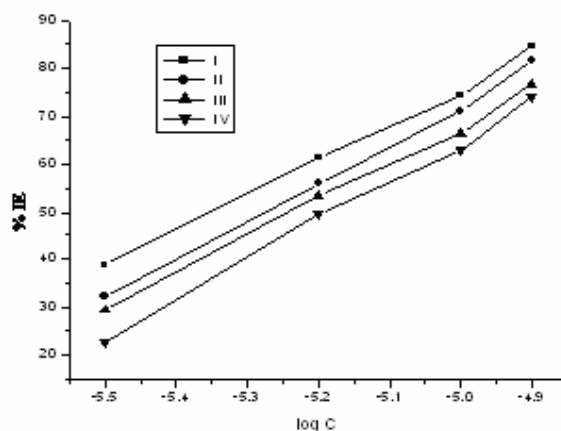

Figure 3. The relationship between % IE and logarithm of concentration of different inhibitors in 0.1M HCl.
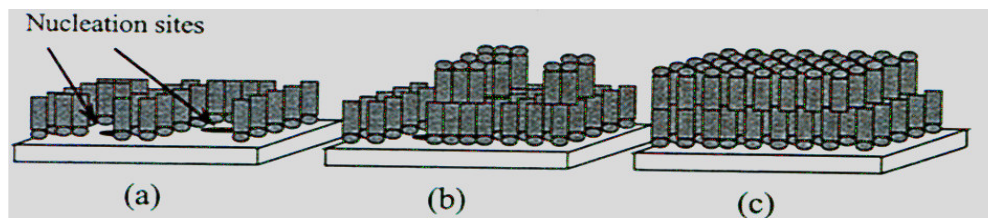

Figure 4. Adsorption schemes for pyrimidine derivatives: (a) at low concentrations, (b) at intermediate concentrations, and (c) at high concentrations on stainless steel type304.

The inhibition mechanism of these pyrimidine derivatives is a combination of surface blockage and electrostatic repulsion between adsorbed speices and chloride ions. The adsorption of pyimidine derivatives depends on the inhibitors concentrations.As shown from Fig.(4), at adsorption density less than a monolayer in (Fig. 4a) most of the nucleation sites are still possibly exposed to HCl, since

inhibitor adsorbs less likely on them. When the adsorption density reaches monolayer adsorption in Fig.(4b), some of the nucleation sites begin to be covered by inhibitor molecules. At maximum adsorption density in Fig.(4c), the whole surface, including the nucleation sites, are covered by the inhibitor molecules then complete inhibition occurs.

3.3. Adsorption isotherm

The Langmuir adsorption isotherm may expressed by [10]:

$$C/\theta = 1/K + C$$

Where C is the inhibitor concentration, and K is the equilibrium constant for adsorption process. The equilibrium constant (K) for adsorption process for each compound can be calculated from the reciprocal of the antilogarithm of the intercept.

The plot of log (C/ θ) Vs log C found to be linear for all additives as shown in Figure (5). This means that these compounds are adsorbed on the surface of stainless steel type 304 according to Langmuir adsorption isotherm, but the gradient is not equal to unity as expected for the ideal behavior. The deviation from unity can be explained on the basis of the interaction between the adsorbed species on the metallic surfaces. It has been postulated in the derivation of Langmuir isotherm that the adsorbed molecules do not interact with each other. This is not true in the case of organic molecules having polar atoms or groups, which are adsorbed on the anodic and cathodic sites of the metal surface such adsorbed species may interact by mutual repulsion or attraction.
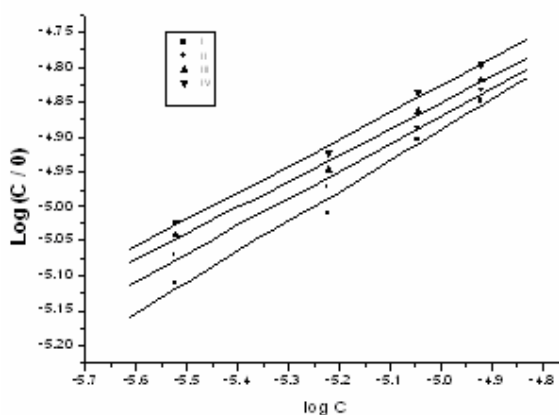

Figure 5. Langmuir adsorption isotherm for pyrimidine derivatives

3.4. A quantum-chemical study of the corrosion inhibition of stainless steel type 304 by means of pyrimidine derivatives in HCl solution.

The results obtained from the relation between inhibition characteristics and quantum chemical data show that log i_{corr} mostly depend upon the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). From Fig. (6) it is evident that the inhibition efficiency increases with increasing the energy of the HOMO, that is, the increase of the

ionization potential. It is further evident that the inhibition efficiency increases with the decrease of ionization of the molecule, which means that the molecule acts as an electron donor when blocking the corrosion reaction. The results in Table (4) were calculated at 1.2×10^{-5} M and show that the energies of HOMO orbital of the pyrimidine derivatives decrease in the following order: I > II > III > IV.

Table 4. Quantum - chemical parameters of the investigated pyrimidine derivatives.

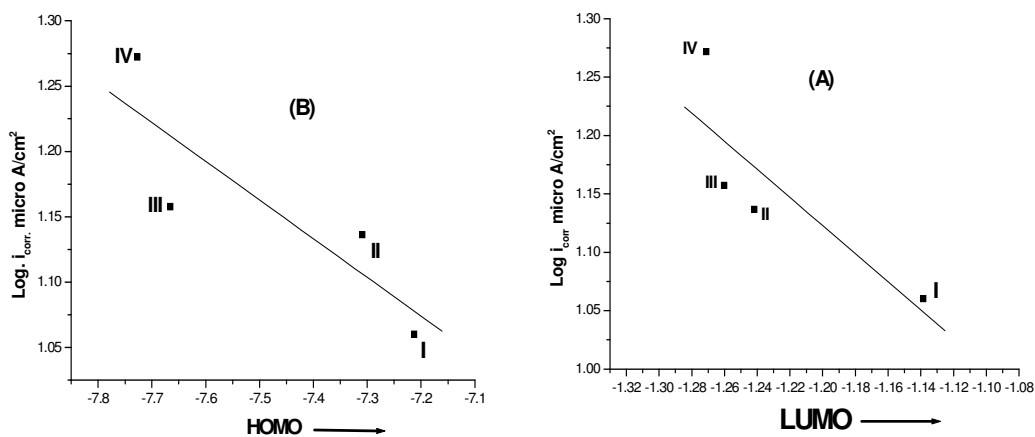| Inhibitor	Log i_{corr}	Atom	Charge density	HOMO energy Kcal/mole	LUMO energy Kcal/mole	%Inhibition
I	1.0599	N(1) O(9) N(8) S(10)	+0.249 +0.0853 +0.242 +0.109	-7.2126	1.13847	84.62
II	1.1361	N(1) O(9) N(8) S(10)	+0.249 +0.0853 +0.242 +0.109	-7.6654	1.2417	81.69
III	1.1571	N(1) O(9) N(8) S(10)	+0.249 +0.0853 +0.242 +0.109	-7.7270	1.2606	76.72
IV	1.2721	N(1) O(9) N(8) S(10)	+0.249 +0.0853 +0.242 +0.109	-7.8830	1.2713	74.07

Figure 6. Correlation of LUMO (A) and HOMO (B) energies with log i_{corr} for the investigated pyrimidine derivatives

3.5. Effect of applied cyclic stresses on the corrosion behavior of stainless steel type 304.

3.5.1. Effect of applied cyclic stresses

In these experiments the measurements were carried out in 0.1 M HCl solution at 30°C in absence and presence of different inhibitors at different concentrations (3×10^{-6} – 1.2×10^{-5} M), at

applied cyclic stresses (82Mpa - 247Mpa) and number of cycles (10^6) at 10.5 Hz. The galvanostatic polarization curves were plotted for each inhibitor. In the rotating cantilever bending fatigue test, the tension and compression cyclic stresses occur at the outer surfaces of the specimen, for this reason plastic deformation commonly occurs by the slip of one plane over another. This dislocation occur , results in effect of shear stresses onto the slip planes. This slip is very non-uniform within a polycrystalline solid and can occur on only some of the crystal planes within a metal grain. [9]. Stressed stainless steel type 304 surfaces by the rotating cantilever bending fatigue test, contain iron atoms that are more reactive since they have a less stable crystalline environment and more susceptible to attack. Whenever a metal is stressed, the metallic crystal lattice becomes severely strained, the atoms in the most severely distorted crystal lattice tend to become more anodic, and go into solution more readily than the atoms in less strained sites. Consequently, corrosion of the most strained regions of a metal is most rapid.

The corrosion behavior of stainless steel type 304 in 0.1 M HCl solution in the absence and presence of ($3x10^{-6}$ – $12x10^{-6}$) inhibitors (I – IV) 30^oC and applied cyclic stresses (82 – 247MPa). The galvanostatic polarization curves were plotted for each inhibitor as shown in Fig.(7) for stress 82MPa, Fig. (9) for 141MPa, Fig. (11) for stress 188 MPa,and Fig.(13) for stress 247MPa. The results indicate that, the inhibition efficiency of inhibitors (I – IV) for corrosion of SS type 304 in the acidic solution at 30^oC is decreased in order (I > II > II >IV) with increasing the concentration of inhibitors as shown in Figs. (8, 10, 12 & 14) and decreased with increasing applied cyclic stresses as shown in Fig.(15). The corrosion of the most strained regions of a metal is most rapid, also the adsorption layer of inhibitor on stainless steel surface becomes less stable and the corrosive media becomes more aggressive. Inspection of Tafel slopes values and E_{corr} values in these conditions indicate that these inhibitors act as mixed – type inhibitors. Also, the corrosion current density i_{corr} increased with increasing the applied cyclic stresses, as shown in Fig. (16). The increasing applied cyclic stress due to increasing the strained atoms i.e. more atoms go to the solution, i.e. increasing the corrosion current density.
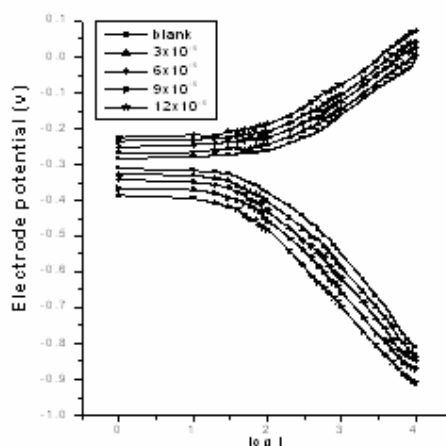

Figure 7. Galvanostatic polarization curves for dissolution stressed stainless steel type 304 at 82MPa and 1000000 cycles in 0.1 M HCl in absence and presence of different concentrations of inhibitor I at 30°C
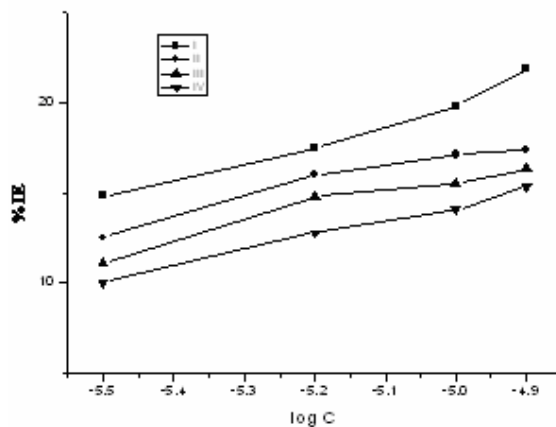
Figure 8. The relationship between % IE and logarithm of concentration of different inhibitors (I-IV) in 0.1M HCl at 82MPa and 1000000 cycles at 30°C.
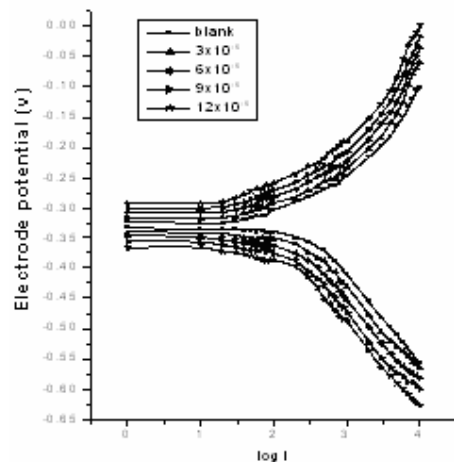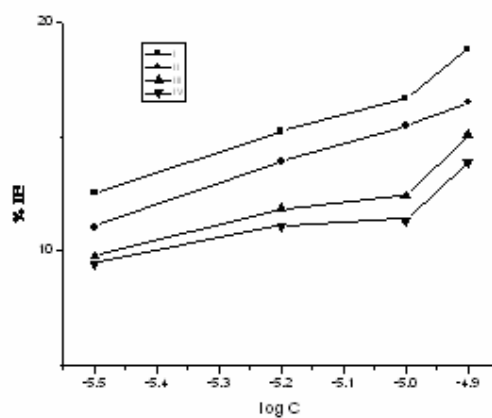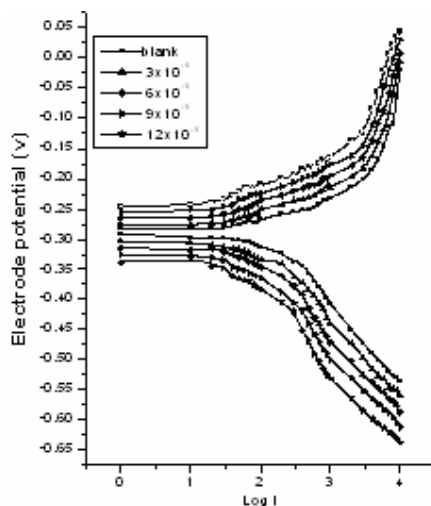

Figure 9. Galvanostatic polarization curves for dissolution stressed stainless steel type 304 at 141MPa and 1000000 cycles in 0.1 M HCl in absence and presence of different concentrations of inhibitor I at 30°C

Figure 10. The relationship between % IE and logarithm of concentration of different inhibitors (I-IV) in 0.1M HCl at 141MPa and 1000000 cycles at 30°C.

Figure 11. Galvanostatic polarization curves for dissolution stressed stainless steel type 304 at 188MPa and 1000000 cycles in 0.1 M HCl in absence and presence of different concentrations of inhibitor I at 30°C
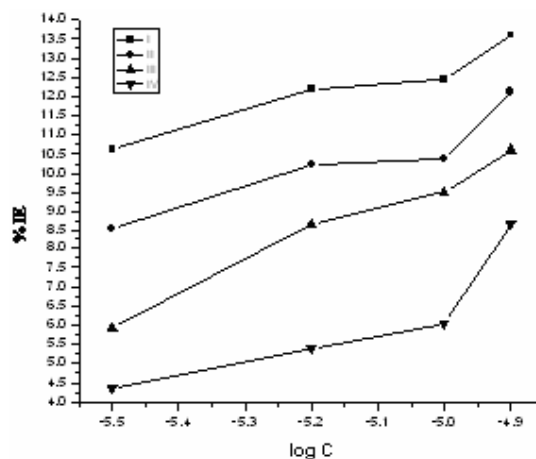

Figure 12. The relationship between % IE and logarithm of concentration of different inhibitors (I-IV) in 0.1M HCl at 188MPa and 1000000 cycles at 30°C.
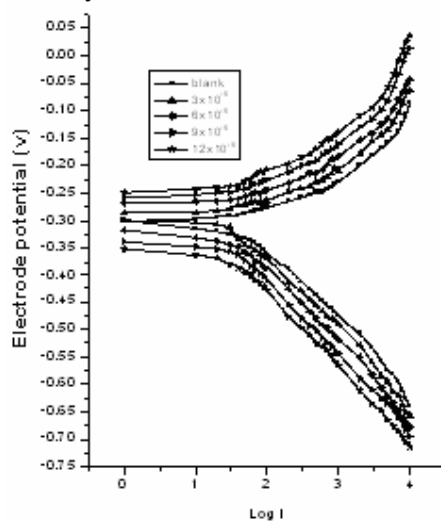

Figure 13. Galvanostatic polarization curves for dissolution stressed stainless steel type 304 at 247MPa and 1000000 cycles in 0.1 M HCl in absence and presence of different concentrations of inhibitor I at 30°C
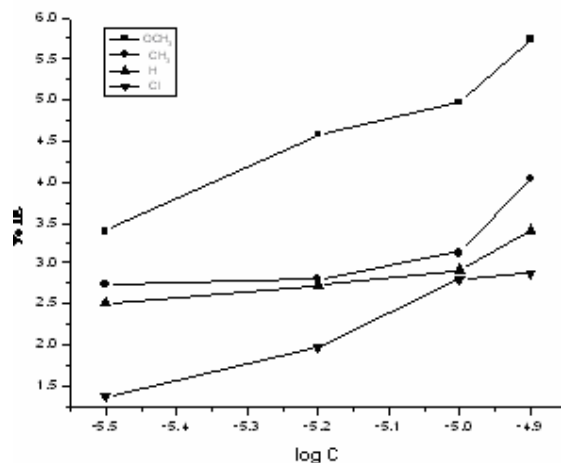
Figure 14. The relationship between % IE and logarithm of concentration of different inhibitors (I-IV) in 0.1M HCl at 247MPa and 1000000 cycles at 30°C.
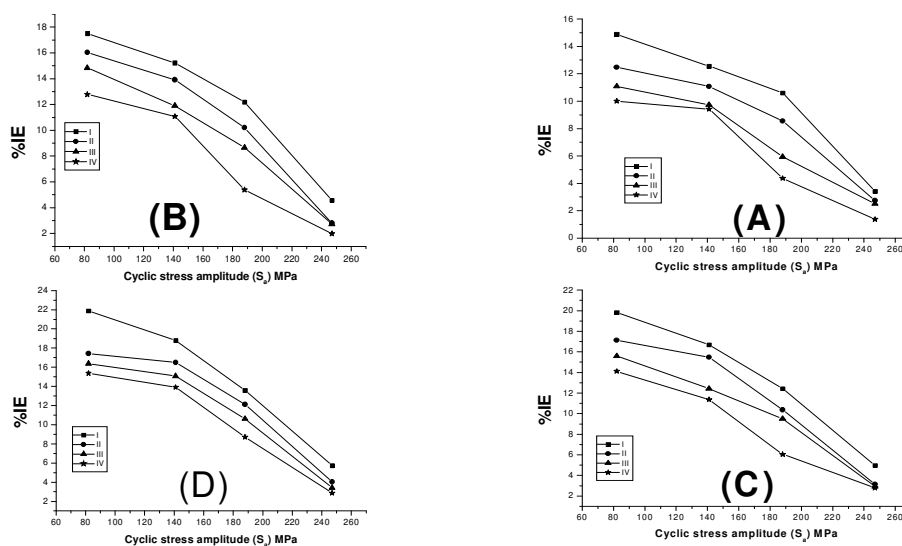

Figure 15. The relation between %IE and cyclic stress amplitude Sa for SS type 304 in 0.1 M HCl at 30°C in presence of different inhibitors (I– IV) at concentration (A) 3×10^{-6} M , (B) 6×10^{-6} M, (C) 9×10^{-6} M, (D) 12×10^{-6} M and 1000000 cycles.

4. CONCLUSIONS

Consideration of the results of the general corrosion revealed the following conclusions:

1 - Pyrimidine derivatives have proved to be efficient inhibitors for corrosion of stainless steel type 304 in 0.1MHCl solution.

2 - These derivatives act as mixed type inhibitors and the %IE was found to increase with increasing the inhibitor concentration.

3 - Compound I which contains one methoxy group gives the higher inhibition efficiency compared to the other compounds II , III , and IV.

4 - The inhibition of SS type 304 in 0.1M HCl solution was found to obey the Langmuir adsorption isotherm.

5 - These derivatives increase the efficiency of passive layer of SS type 304.

6 - Pyrimidine derivatives can be used as inhibitors for SS type 304 fatigue corrosion, can decrease the susceptibility to fatigue corrosion in HCl solution and act as mixed type inhibitors.

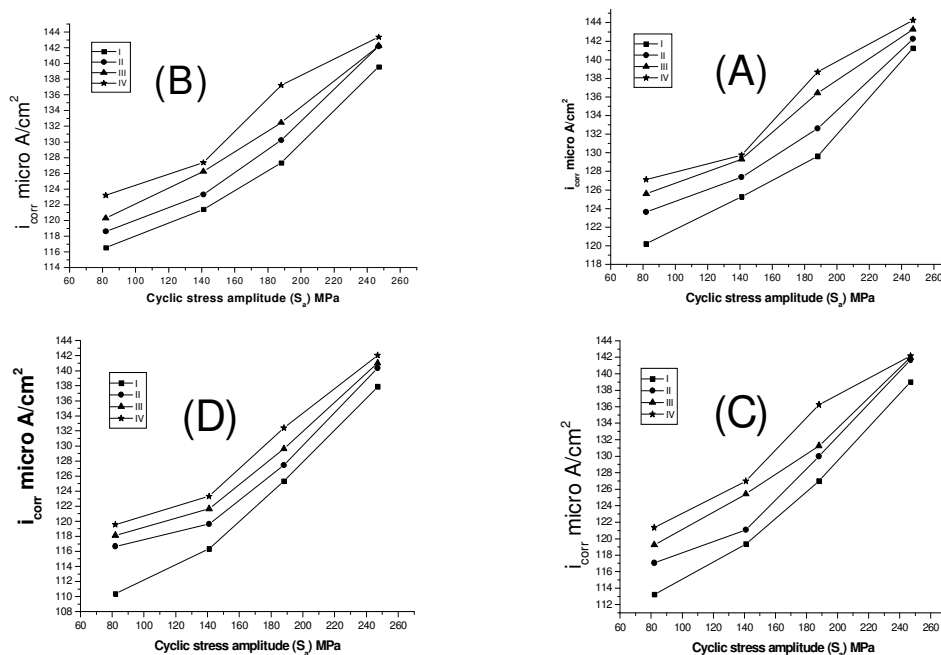7 - Inhibition efficiency (%IE) decreases with increasing the cyclic stresses.

Figure 16. The relation between %IE and cyclic stress amplitude Sa for SS type 304 in 0.1 M HCl at 30°C in the presence of different inhibitors (I – IV) at concentration (A) 3x10^{-6} M, (B) 6x10^{-6} M, (C) 9x10^{-6} M, (D) 12x10^{-6} M and 1000000 cycles.

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