Chapter III
Results And Discussion

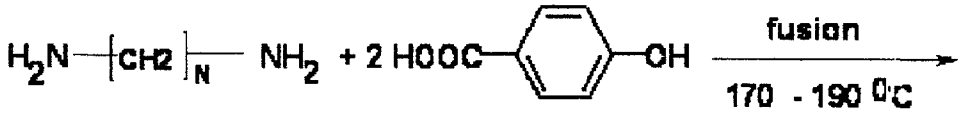
III- RESULTS AND DISCUSSITON

This chapter deals the preparation of organoamide and organoamide siloxane compounds with the results and measurements of them as corrosion inhibitors for carbon steel alloy in acid solution media (HCl), which were obtained by applying the different techniques, they are represented in deals. Moreover the interconnection matching, agreement and disagreement...etc., between the output of the different applied techniques will be discussed with the protection mechanism.

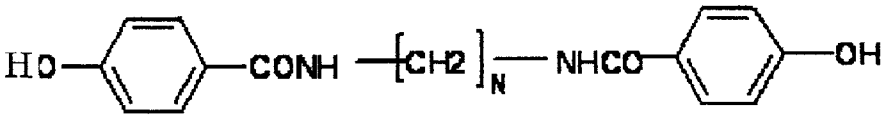
III-1. Preparation of Different organoamide (I – III) Compounds.

III.1.a.Preparation of organoamide I and II compounds.

The preparation of different compounds of organoamide (I – II) were carried out in free solvent by reaction of terminal aliphatic di-amine, 1,4-diamino butane and 1,8- diamino octane , respectively, with ρ- hydroxy-benzoic acid by fusion at 170-190°C as following equation: -



Diamine p-hydroxy benzoic acid

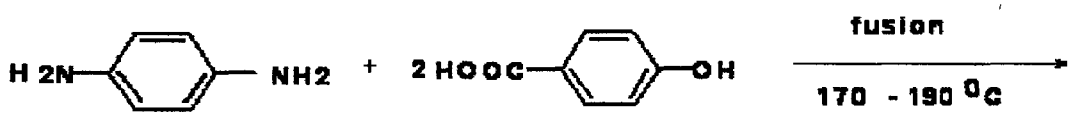


Organoamid I & II

where N = 4 & 8

III.1.b. Preparation of organoamide compound III.

The reaction was carried out without solvent by reaction of phenelene diamine with ρ- hydroxybenzoic acid by fusion at 170-190◦C as following equation: -



1,4 phenylenediamine p-hydroxy benzoic acid

Organoamid III

The prepared compounds of organoamides (I, II and III) were purified and confirmed by FT.IR and ^{1}HNMR spectroscopy analysis techniques, respectively

III.2.1. FT.IR spectroscopy analyses

The structures of the prepared compounds II and III were confirmed by using FT.IR spectroscopy. A representative infrared spectral of organoamide derivatives compound I and II were shown in Fig.(3) as example of aliphatic organoamide compound and FT.IR of compound III was shown in Fig .(4) respectively.

Fig.(3) Shows the FT.IR spectrum for aliphatic organoamide II The characteristic bands appeared at 504,532,550, 814,828,1021 and 1069 cm^{-1} represented the bending and stretching vibration for *p*-substituted of aromatic compound, the bands at 1258 and 1401 cm^{-1} for stretching vibration of –CONH- groups, the bands appear at 1475 and 2854 cm^{-1} for stretching vibration of $-CH_2-$ groups and C – H aromatic, the bands at 1163 , 1150,1591 and 2927 cm^{-1} for stretching

vibration of Ph –C=O- group. And the bands appear at 3068 and 3346 cm^{-1} for stretching vibration of –OH and –NH group respectively.

Fig. (4) Shows the spectrum of aromatic amid compound III. The characteristic bands appeared at 514, 822, 1015 and 1098 cm^{-1} bending and stretching vibration for *p*-substituted aromatic. The bands at 1261 and 1400cm^{-1} for stretching vibration of –CO-NH- The bands at 1517,2963 cm^{-1} for stretching vibration of carbonyl aromatic group HN-CO-Ph and C – H aromatic and the bands at 3144 and 3378.15 $cm^{-1}$for stretching vibration of –OH and –NH groups respectively.

III.2.2. ^{1}HNMR spectroscopy analyses.

The ^{1}HNMR spectra of compounds II and III are shown in Figs. (5, 6) respectively, as example. It shown that the signal was splitting octet at chemical shift δ=7.175- 7.114 for hydrogen proton of aliphatic hydrocarbons. Its deshelding due to the attachment by hetero, N, atoms at tow terminals as amide groups, a splitting quartet at chemical shift δ= 6.75-6.721 for hydrogen proton of phenyl ring, a splitting broad single signal for hydrogen proton of ρ substituted – OH group for aromatic ring at chemical shift δ= 3.523, and was shifted. A splitting strong sharp single signal for hydrogen proton of ρ- substituted –NH group for aromatic ring at chemical shift δ= 2.493, δ= 1.297 for hydrogen proton of (S, 16H, $8CH_2$).

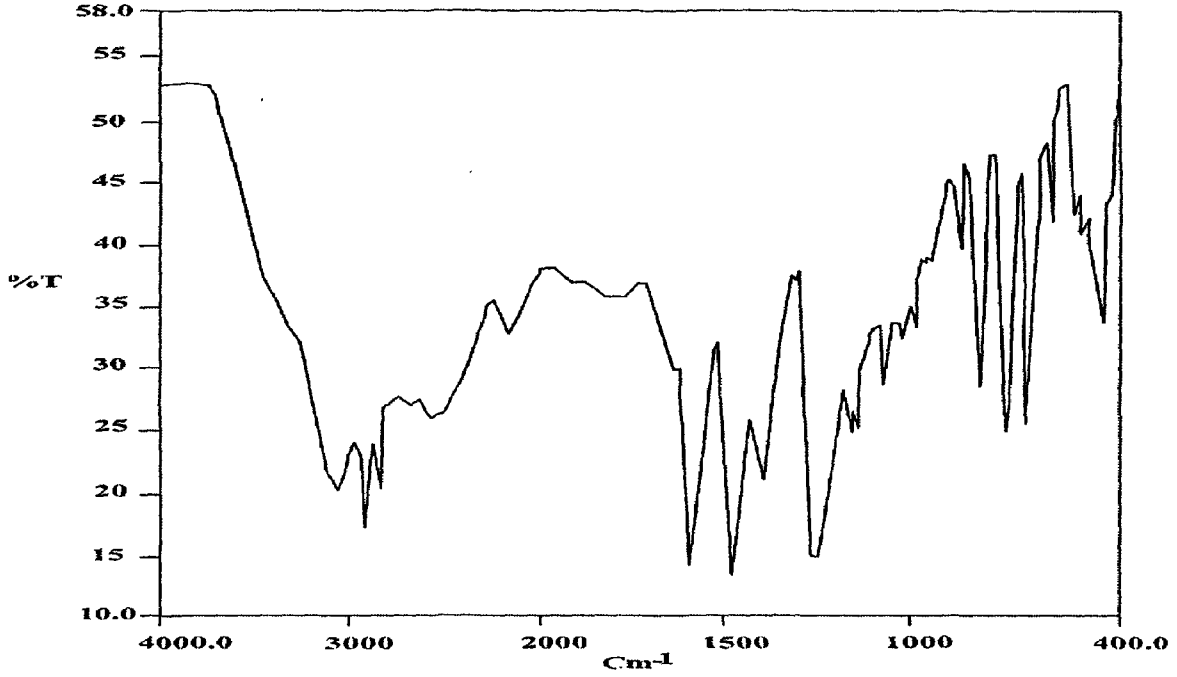


Fig. (3): I.R spectra of compound (II) as example of aliphatic organoamide

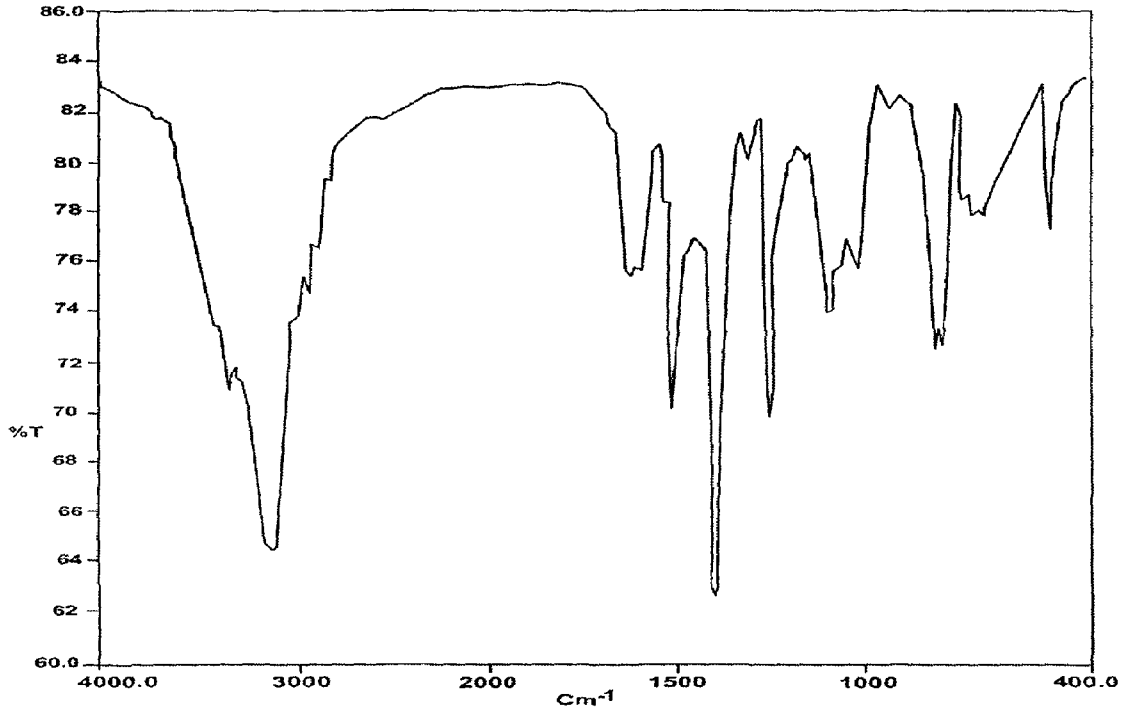


Fig. (4): I.R spectra of compound (III) as example of aromatic organoamide

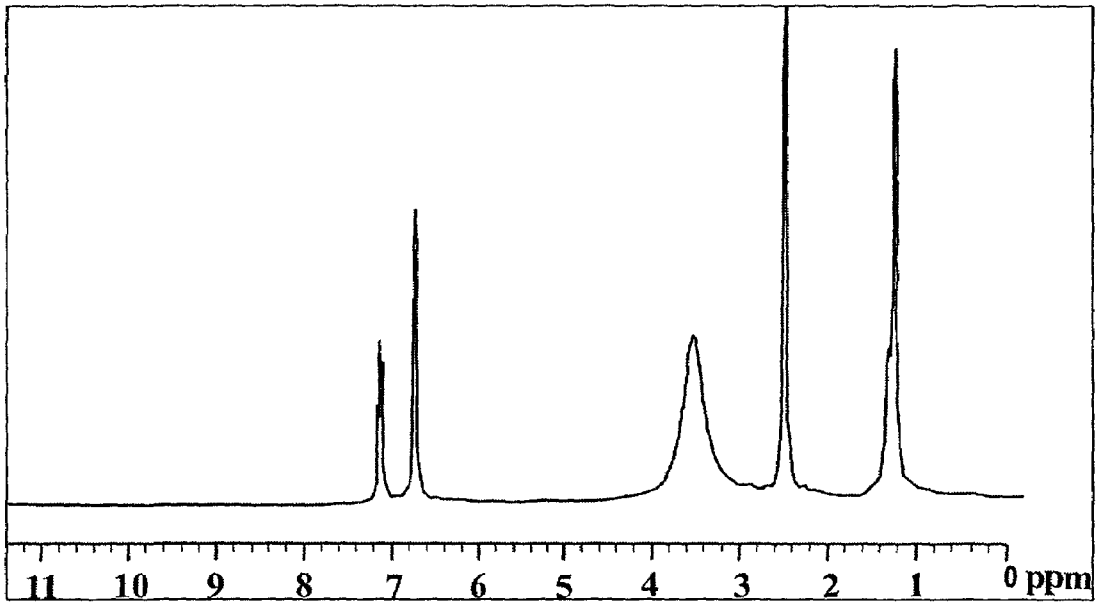


Fig. (5): ^{1}HNMR spectra of compound (II) as example of aliphatic organoamide

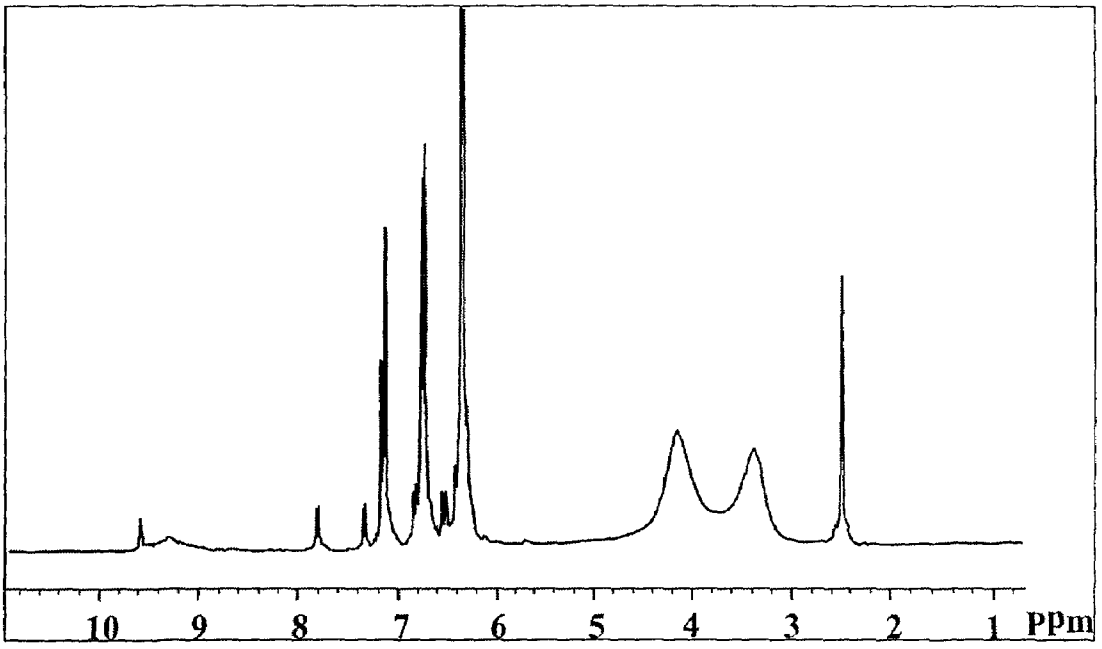


Fig. (6): ^{1}HNMR spectra of compound (III) as example of aromatic organoamide

III.3. – The evaluation of prepared organoamide compound (I-III) as corrosion inhibitor for carbon steel alloy in different concentration of aggressive hydrochloric acid solution.

The evaluation of the influence of prepared organoamide compounds (I – III) derivatives as corrosion inhibitor for carbon steel alloy in different concentration, 0.5, 1.0 and 2M hydrochloric acid solutions was carried out, respectively. The weight-loss technique was employed as the chemical testing technique. While the electrochemical polarization open circuit potential (OCP), potentiodynamic polarization (Tafel) and electrochemical impedance spectroscopy (EIS) were applied at definite concentration to evaluate the corrosion inhibitor parameter. And also the validity of the prepared organoamide compound (I – III) derivatives as corrosion inhibitor for protection of petroleum carbon steel alloy. Finally, the scanning electron microscope (SEM) was applied for studies the surface morphology for the test specimen and the formation of inhibition films at definite experiment condition.

III.3.1-Corrosion of carbon steel alloy in 0.5, 1.0 and 2.0M hydrochloric Acid solution

III.3.1.a-Weight loss method

The corrosion behavior of carbon steel in an aggressive aqueous environment should be characterized by the extent to which it dissolves in the solution. The degree of dissolution, of course, dependent on the surface area of the metal exposed and the time of exposure; hence the amount of corrosion was given with respect to area and time. The resulting quantity and corrosion rate were thus a fundamental measurement in corrosion science. Corrosion rates, surface coverage area and efficiency of inhibitors were evaluated by measuring the weight of a specimen before and after immersion in aggressive, 0.5, 1.0 and 2M HCl acid solutions, respectively. The 100, 200, 300, 400, 500 and 600ppm as concentration of the prepared

organoamide compounds (I – III) derivatives at room temperature were used. The period times for immersion of specimens were 12, 24, 36, 48, 60, 72, 84 and 96 hr respectively, and applying the equation (II.1and II.2). The weight-loss method was usually preferred because the loss quantities are directly related to the extent of corrosion and does not rely on any assumptions about reactions occurring during corrosion processes (immersion time).

Figs. (7 – 15) show that the weight loss versus time curves for carbon steel alloy in 0.5, 1.0 and 2.0 M hydrochloric acid solution in the absence and presence of different concentrations of prepared organoamides derivatives (I – III) . It is evident from these Figs. that, by increasing the concentration of these derivatives, the weight loss of carbon steel specimens are decreased respect to the blank specimen. This means that the presence of these compounds are retarded the corrosion of carbon steel (dissolution) in 0.5, 1.0 and 2.0M hydrochloric acid, respectively, or in other words, these compounds act as inhibitors through formation a barrier film between the metal surface of specimens and environment aggressive media. The linear variation of weight loss with time in uninhibited and inhibited 0.5, 1.0 and 2 M HCl solutions are indicated the absence of insoluble surface films during corrosion processes. In the first stage, the inhibitors are adsorbed on the metal surface and there after impede corrosion either by merely blocking the reaction sites anodic and cathodic or by altering the mechanism of the anodic and cathodic partial processes. The formation films on the surfaces of specimens are respect to the chemisorptions process. This phenomenal are carried out due to the presence of many active polar of amide and hydroxyl groups, while these polar groups are having hetero N and O atoms. These atoms are donating a lone pair of electrons to Fe^{+} atoms and working as a ligand. Therefore, these groups are chaired by their lone pair of electrons with pre-ionization of metal and could be adsorbed with the formation of protective

film on the surfaces of specimen. Moreover, the construction on this phenomenon also these films were protected the surfaces of carbon steel from any attack by any aggressive ions, due to the formation of films on the surfaces of specimen. The electrochemical studies and SEM were carried elsewhere to provide this phenomena and should be confirmed the formation of semi complex which having a good adhesion and stability on the surface of metal.

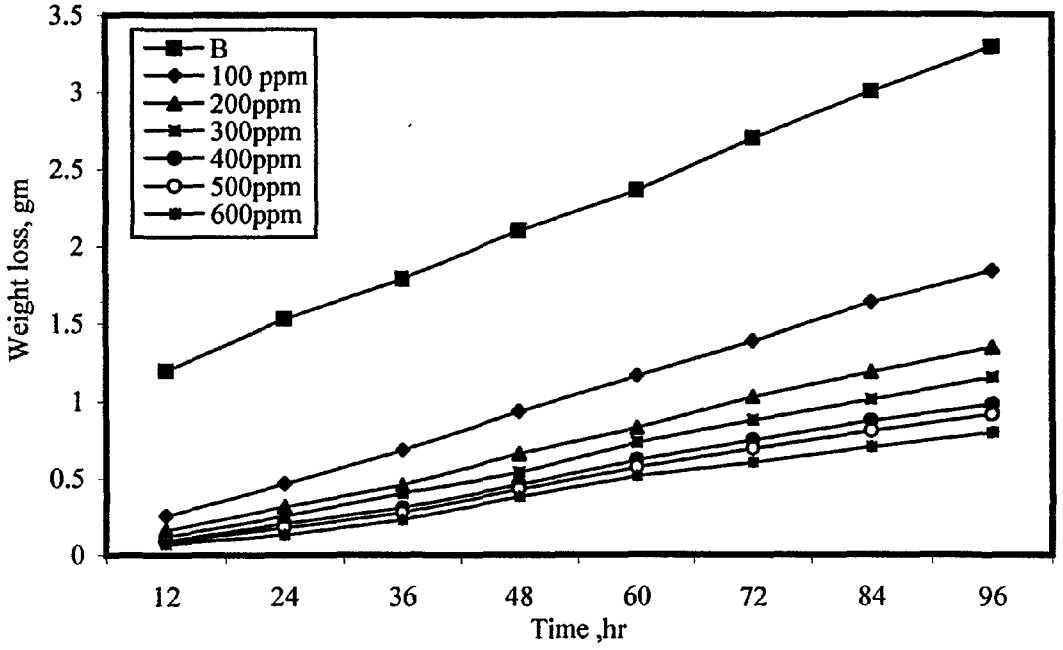


Fig.(7): Weight loss-time curves for carbon steel alloy in 0.5 M HCl in absence and presence of differnet concentrations of compound (I)

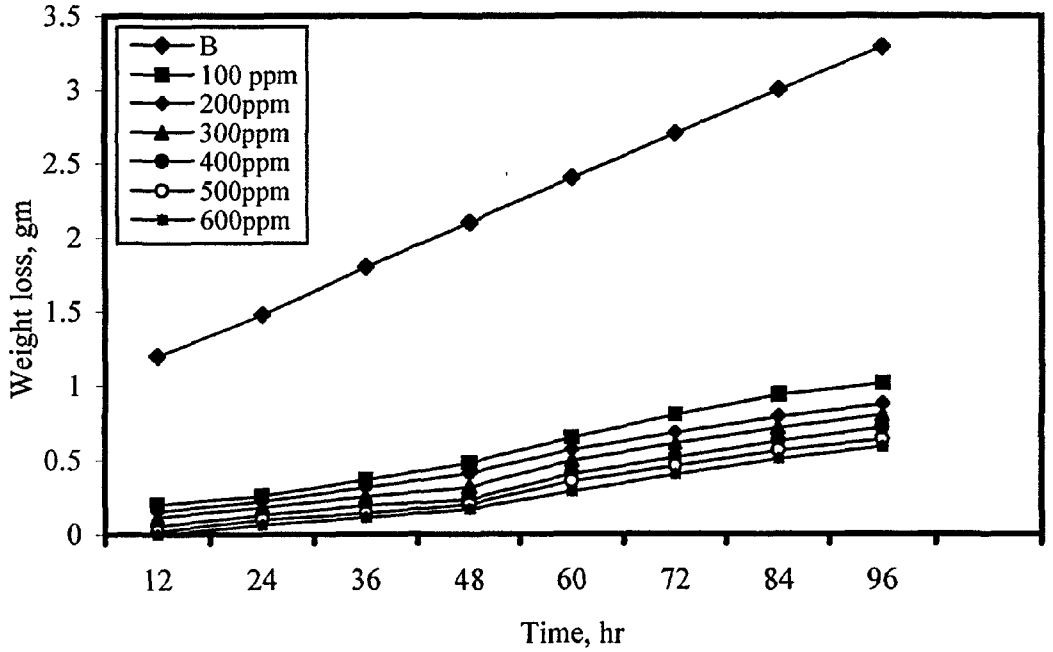


Fig.(8): Weight loss-time curves for carbon steel alloy in 0.5 M HCl in absence and presence of differnet concentrations of compound (II)

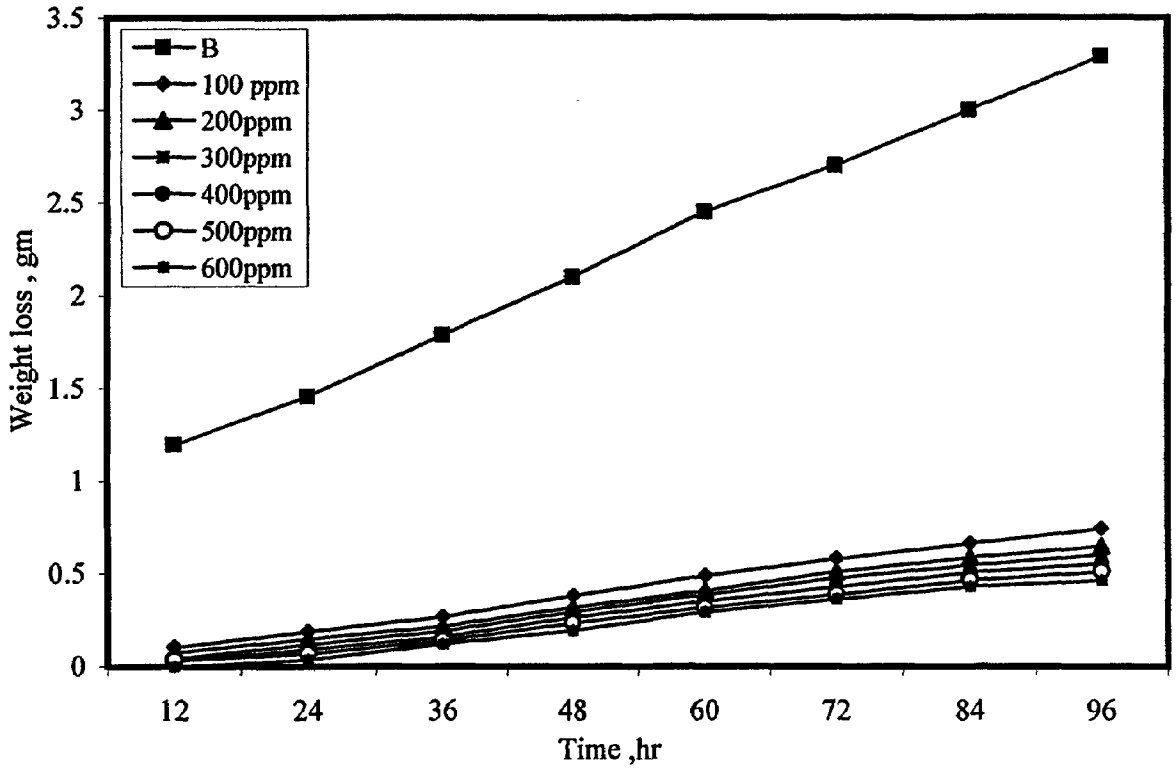
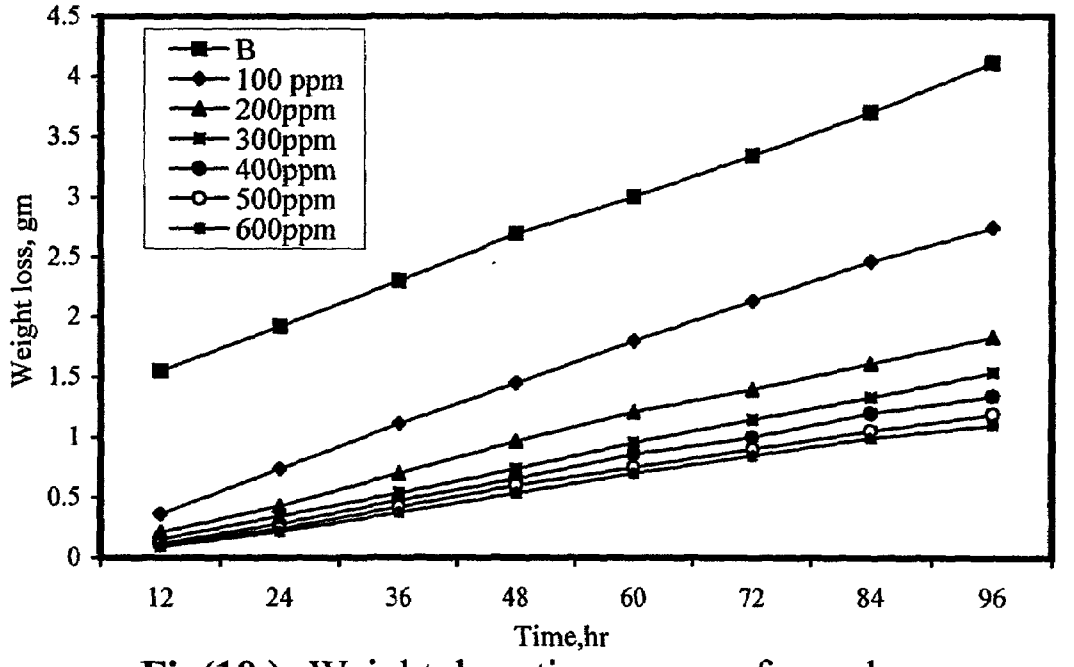
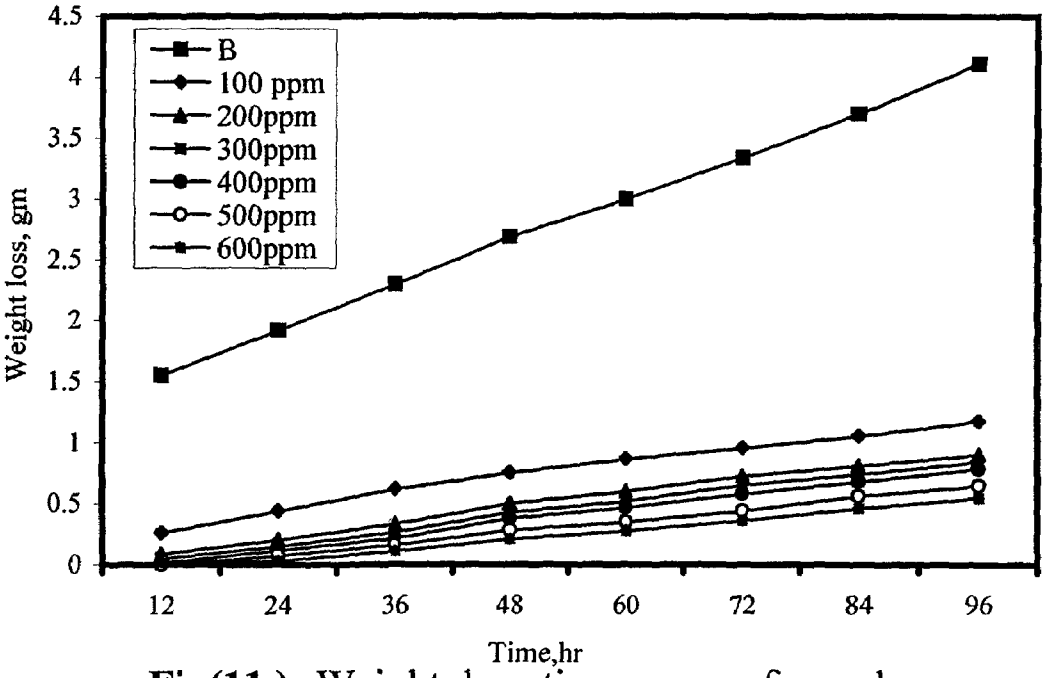


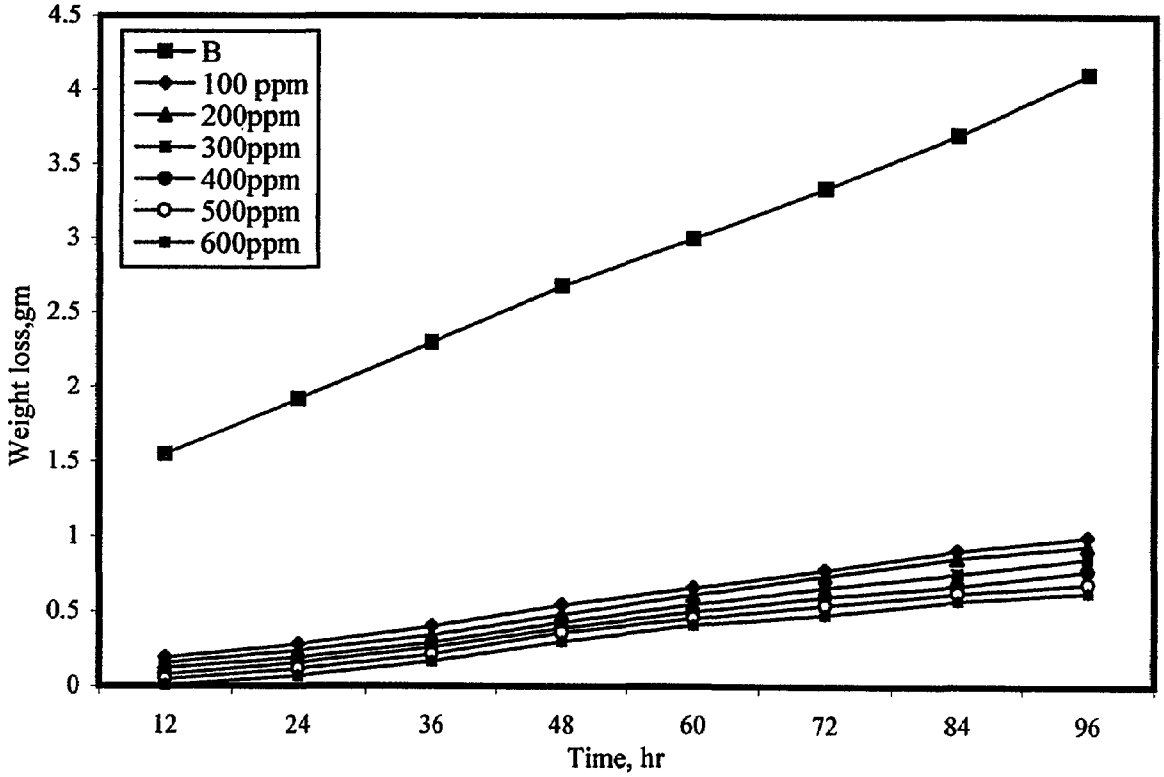
Fig.(9): weight loss-time curves for carbon steel alloy in 0.5 M HCl in absence and presence of differnet concentrations of compound (III)



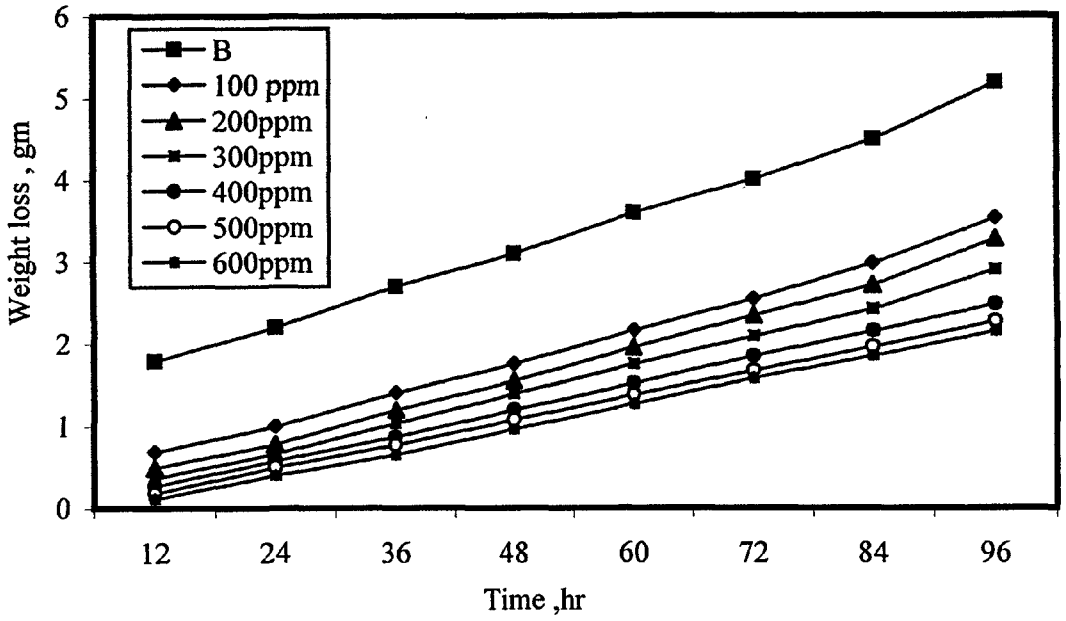
Fig(10): Weight loss-time curves for carbon steel alloy in 1 M HCl in absence and presence of differnet concentrations of compound (I)



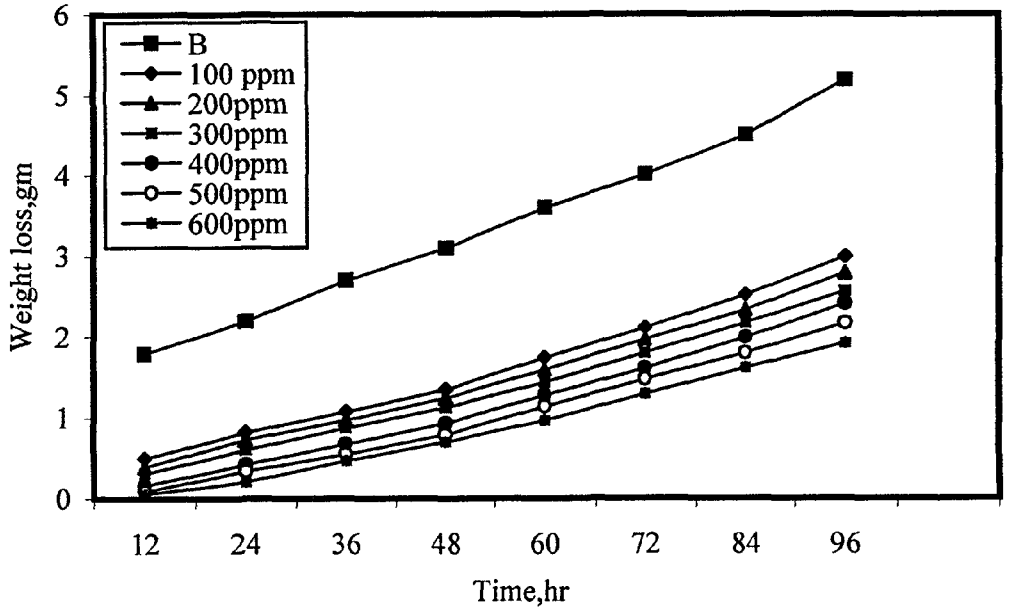
Fig(11): Weight loss-time curves for carbon steel alloy in 1M HCl in absence and presence of differnet concentrations of compound (II)



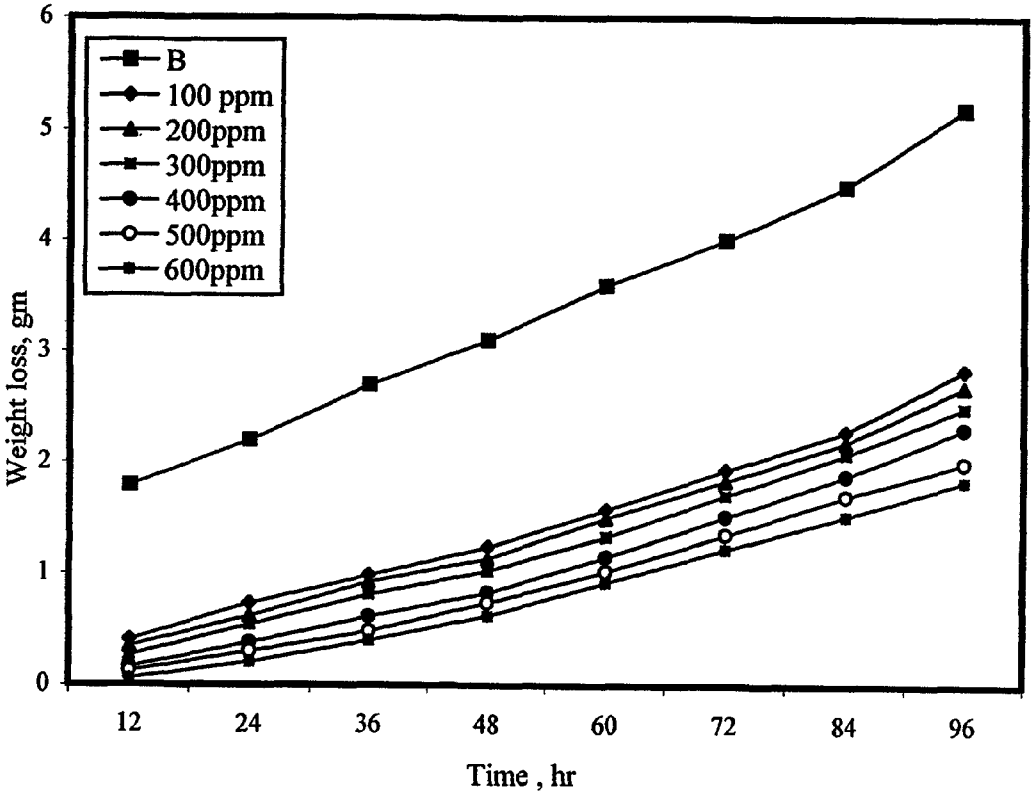
Fig(12): weight loss-time curves for carbon steel alloy in 1M HCl in absence and presece of differnet concentrations of compound (III)



Fig(13): Weight loss-time curves for carbon steel alloy in 2M HCl in absence and presence of differnet concentrations of compound (I)



Fig(14): Weight loss-time curves for carbon steel alloy in 2M HCl in absence and presence of differnet concentrations of compound (II)



Fig(15): Weight loss-time curves for carbon steel alloy in 2M HCl in absence and presence of differnet concentrations of compound (III)

From the weight loss / time curves one should be concluded that, while the concentration of the organoamide compounds I, II and III derivatives increased , the weight loss of carbon steel specimens decreased in 0.5,1.0 and 2M HCl, respectively. This means that the presence of these compounds retard the corrosion (dissolution) of carbon steel in HCl acid media, i, e., the organoamide compounds I, II and III derivatives are acting as corrosion inhibitor.

Moreover the rate of corrosion (K) decreased with increasing of inhibitor concentration and increased with immersion time; these data are given in Figs. (16 – 18) and Tables (4 -12). On the other hand the inhibition efficiency was increased with increasing inhibitor concentration. This fact suggests that the mechanism of inhibition by the inhibitor molecules may firstly chemically adsorbed on the carbon steel surface and cover the sites of the electrode surface. Then probably form monomolecular layers by forming a semi complex with iron ions on the steel surfaces. These layers protect steel surface from attack by chloride and any ions in the media. From these results one should be concluded that the interaction between the molecules adsorbed at the metal surface happened.

The linear variation of the weight loss with time in uninhibited and inhibited solutions respectively indicates that the formed of films are obtained during the experiment. In the absence of any spots of corrosion on the surface films, the inhibitors are first adsorbed on to the metal surface and there after impede corrosion either by merely blocking the reaction sites (anodic and cathodic) or by altering the mechanism of the anodic and cathodic partial processes.

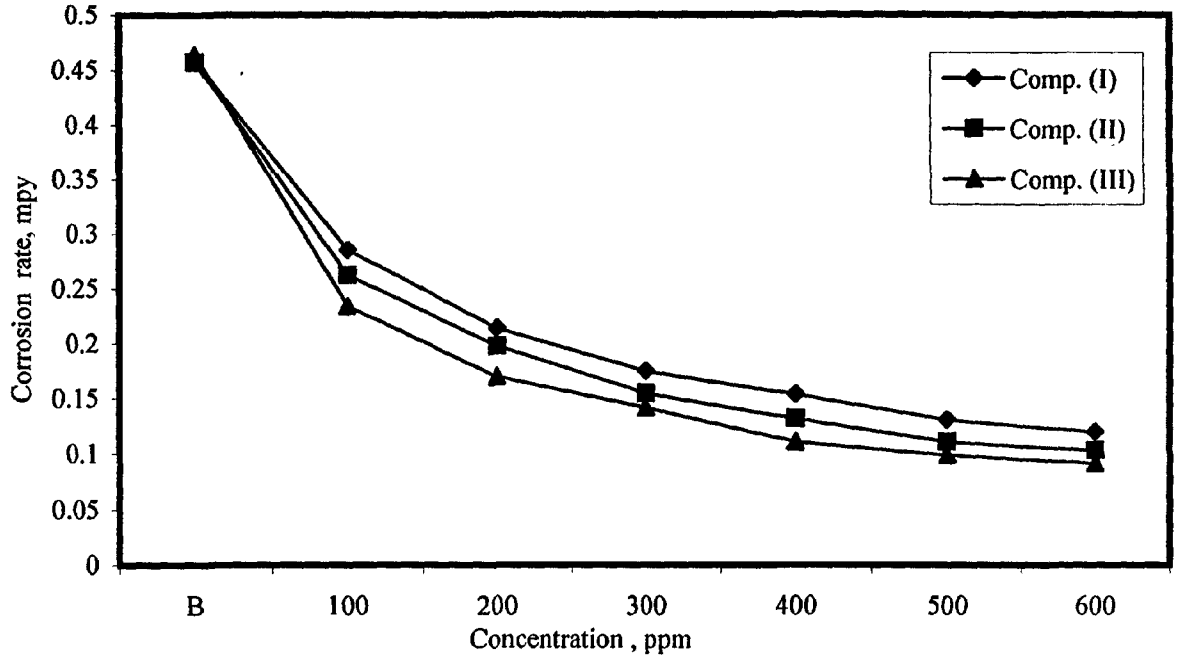


Fig.(16): Effect of concentration of different inhibitors on the corrosion rate of carbon steel in 0.5M HCl after 48 hr

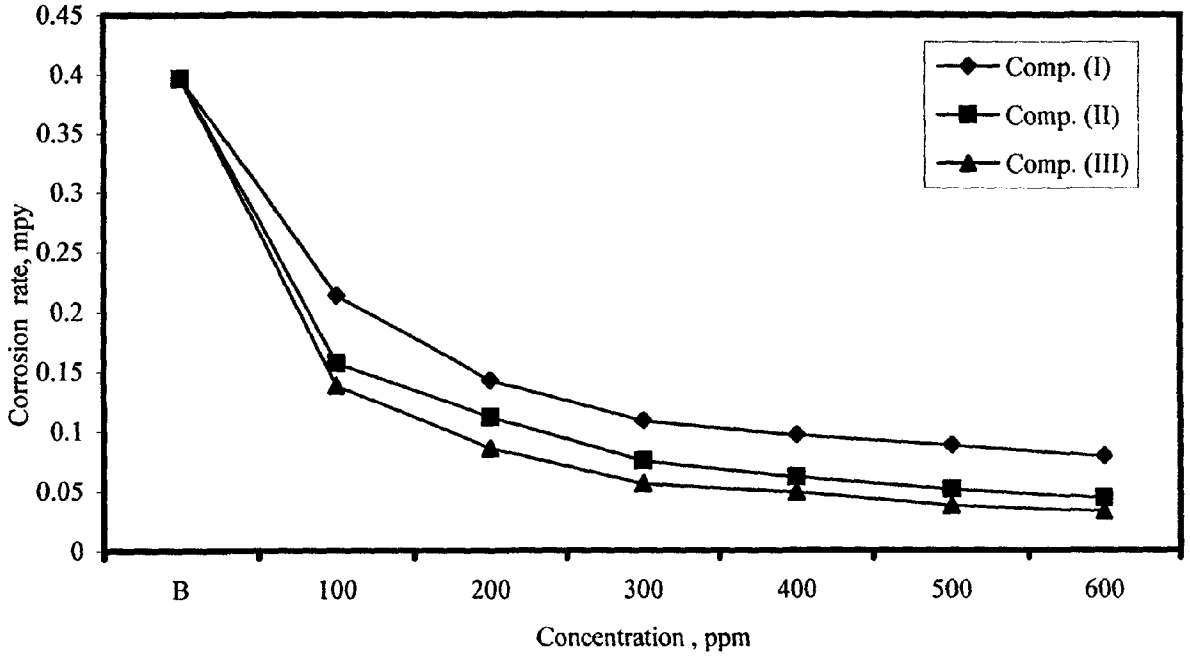


Fig.(17): Effect of concentration of different inhibitors on the corrosion rate of carbon steel in 1 M HCl after 48 hr

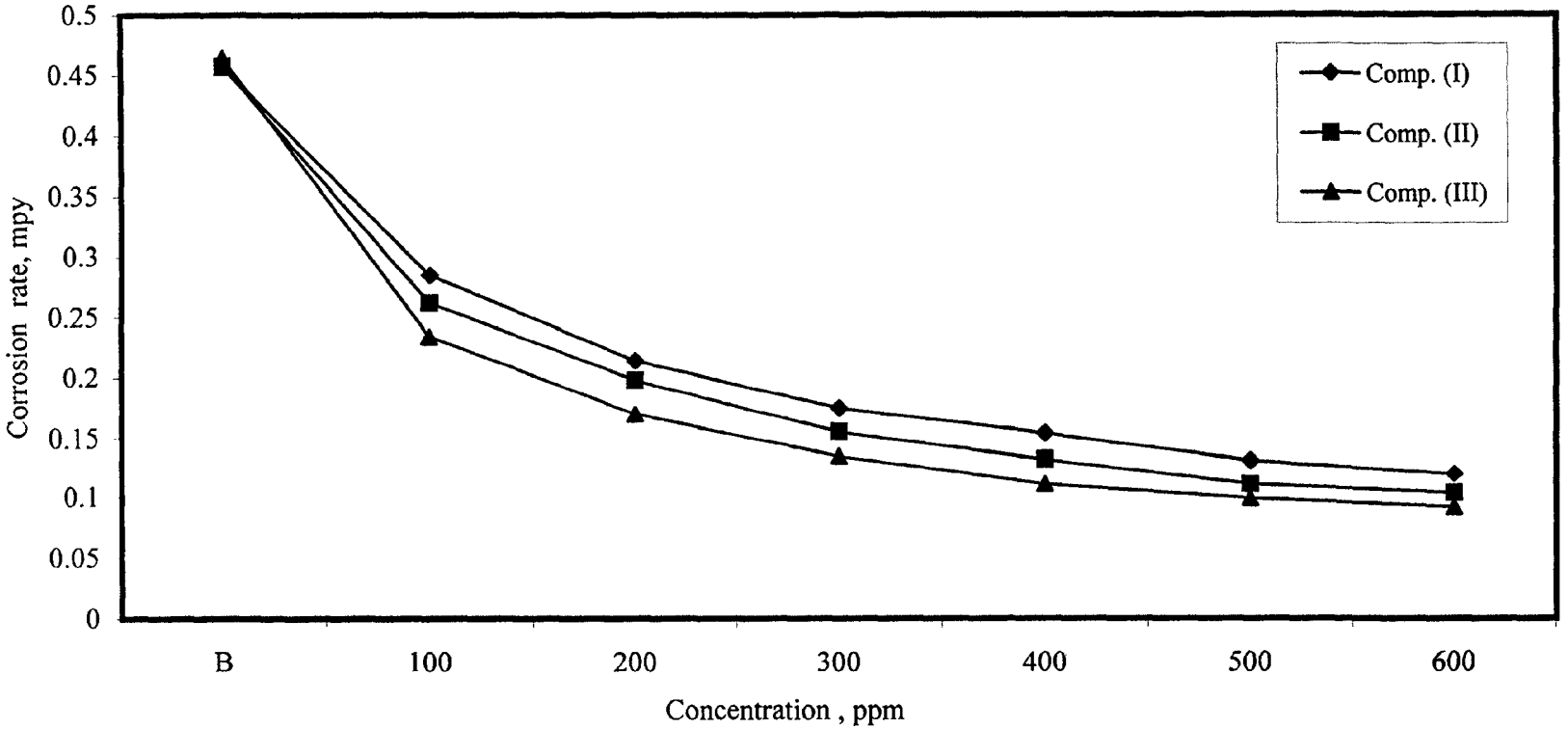


Fig.(18): Effect of concentration of different inhibitors on the corrosion rate of carbon steel in 2 M HCl after 48 hr

Table (4): Results data for corrosion inhibition of inhibitor compound (I) at different concentrations and 298° K in 0.5HCl

Concentration (ppm)	Rate of corrosion (mpy)	Coverage surface (θ)	Efficiency (I %)
Blank	30.95	-	-
100	13.80	0.5539	55..39
200	9.78	0.6840	68.40
300	7.93	0.7434	74..34
400	6.78	0.7855	78.06
500	6.32	0.7955	79.55
600	5.63	0.8178	81.78

Table (5): Results data for corrosion inhibition of inhibitor compound (II) at different concentrations and 298° K in 0.5 M HCl

Concentration (ppm)	Rate of corrosion (mpy)	Coverage surface (θ)	Efficiency (I %)
Blank	30.95	-	-
100	7.13	0.7695	76.95
200	6.09	0.8029	80.29
300	4.71	0.8475	84.75
400	3.45	0.8884	88.84
500	2.99	0.9033	90.33
600	2.53	0.9182	91.82

Table (6): Results data for corrosion inhibition of inhibitor compound (III) at different concentrations and 298° K in 0.5 M HCl

Concentration (ppm)	Rate of corrosion (mpy)	Coverage surface (θ)	Efficiency (I %)
Blank	30.95	-	-
100	5.63	0.8178	81.78
200	4.71	0.8475	84.75
300	4.37	0.8587	85.87
400	3.91	0.8736	87.36
500	3.45	0.8884	88.84
600	2.87	0.9070	90.70

Table (8): Results data for corrosion inhibition of inhibitor compound (I) at different concentrationsand 298° K in 1 M HCl

Concentration (ppm)	Rate of corrosion (mpy)	Coverage surface (θ)	Efficiency (I%)
Blank	39.65	-	-
100	21.34	0.4617	46.17
200	14.23	0.6408	64.08
300	10.87	0.7256	72.56
400	9.66	0.7561	75.61
500	8.84	0.7769	77.69
600	7.91	0.8003	80.03

Table (8): Results data for corrosion inhibition of inhibitor compound (II) at different concentrations and 298° K in 1 M HCl

Concentration (ppm)	Rate of corrosion (mpy)	Coverage surface (θ)	efficiency (I%)
Blank	39.65	-	-
100	11.45	0.7323	73.23
200	8.84	0.7695	76.95
300	7.53	0.8100	81.00
400	5.89	0.8513	85.13
500	5.15	0.8698	86.98
600	4.42	0.8959	89.59

Table (9): Results data for corrosion inhibition of inhibitor compound (III) at different concentrations and 298° K in 1 M HCl

Concentration (ppm)	Rate of corrosion (mpy)	Coverage surface (θ)	Efficiency (I%)
Blank	39.65	-	-
100	8.00	0.8104	81.04
200	7.07	0.8284	82.84
300	6.33	0.8401	84.01
400	5.74	0.8550	85.50
500	5.30	0.8661	86.61
600	4.42	0.9219	92.19

Table (10): Results data for corrosion inhibition of inhibitor compound (I) at different concentrations and 298° K in 2 M HCl

Concentration (ppm)	Rate of corrosion (mpy)	Coverage surface (θ)	Efficiency (I%)
Blank	45.69	-	-
100	25.90	0.4331	43.31
200	22.86	0.4997	49.97
300	20.55	0.5501	55.01
400	15.32	0.6133	61.33
500	15.28	0.6654	66.54
600	13.41	0.7063	70.63

Table (11): Results data for corrosion inhibition of inhibitor compound (II) at different concentrations and 298° K in 2 M HCl

Concentration (ppm)	Rate of corrosion (mpy)	Coverage surface (θ)	Efficiency (I%)
Blank	45.69	-	-
100	19.87	0.5650	56.50
200	18.34	0.5985	59.85
300	16.64	0.6356	63.56
400	13.75	0.6988	69.88
500	11.71	0.7434	74.34
600	10.36	0.7732	77.32

Table (12): Results data for corrosion inhibition of inhibitor compound (III) at different concentrations and 298° K in 2 M HCl

Concentration (ppm)	Rate of corrosion (mpy)	Coverage surface (θ)	Efficiency (I %)
Blank	45.69	-	-
100	17.32	0.6208	62.08
200	16.30	0.6431	64.31
300	15.11	0.6691	66.91
400	12.23	0.7323	73.23
500	11.79	0.7769	77.69
600	9.17	0.7992	79.92

The inhibition efficiencies (I %) results of organoamide derivatives I, II and III are determined by using the equation (II.2). Also, the efficiency of the organoamide compounds I - III are increased by increasing the duration immersion time and also the concentration of inhibitors. These results are shown in Tables (4 -12) and Figs. (19-21). From these observation data, one should be concluded that the formation of a multilayer from inhibitors compound I, II and III on the surfaces of specimen occurred. A completely formation barrier of protective films on the surfaces of specimen are obtained. On the other hand the coverage surface (θ) is calculated by the following equation (III.1), these data are shown in Tables (4-12)

$$\theta = \frac{\Delta W - \Delta W_i}{\Delta W} \qquad \textbf{(III.1)}$$

Where ΔW and ΔW_i are the weight losses per unit area in absence and presence of the inhibitors, respectively.

From the data, one should be observed that the coverage area was increased by increasing the concentration of inhibitors and immersion time in different aggressive acid solution media.

The calculated data of results for the %I and θ are given in Table (4 -12). Careful inspection of these results showed that, at the same organoamide derivatives concentration, and different HCl concentration the inhibition efficiency decrease according to the following order:

III > II > I

This order is depended on the chemical structure of inhibitor.

Plots of the inhibition efficiency %I versus the concentration of organoamide derivatives I - III in 0.5, 1.0 and 2.0 M HCl

solutions for carbon steel alloy at 23.0 ± 2 °C are shown in Figs. (19 - 21).

From the obvious Figs. the % inhibitions is increased by increasing the concentration of organoamide derivatives I- III, also the order of inhibition efficiency increased as following:

III > II > I

III.3.1.b. Adsorption isotherm

The obtained data for θ are summarized in Tables (4 -12). It was recognizable that, there is an inverse relation between the rate of corrosion and the surface coverage area. In other words, the inhibitor having higher surface coverage area are those having higher inhibition rate. Also, it was found that, the surface coverage area values approach unity. Their values are in the rang of ≈ 0.5 for the lowest inhibitor at low concentrations and ≈ 0.93 for the highest one at high concentrations. The θ value near unity indicates almost a full coverage of the metal surface with adsorbed organoamide compounds I- III. Conclusively, the inhibitor, having near unity θ, is considered as a good physical barrier shielding the corroding surface from corrosive medium and dumping the corrosion rate of carbon steel significantly.

The values of surface coverage area of the metal surface with the adsorbed species together with the inhibitor concentration in the solution can be utilized to get the adsorption isotherms.

Inspecting Langmuir plots for organoamide compounds I, II and III Fig. (22), it is found that, all the investigated inhibitors showed linear plots. This behavior suggests that these inhibitors obey Langmuir adsorption which is represented by the following equation:

$$\log C = \log \theta/1-\theta - \log A \qquad \text{(III.2)}$$

$$\log A = -1.74 - \Delta G/ 2.303RT \qquad \text{(III.3)}$$

Besides, these isotherms slopes deviate from unity as expected. This deviation may be explained on the basis of the assumption given by Langmuir. He assumed that, there is no interaction between the adsorbed molecules. But in practice, there is a mutual repulsion or attraction between the adsorbed species on the metal surface [319- 321]

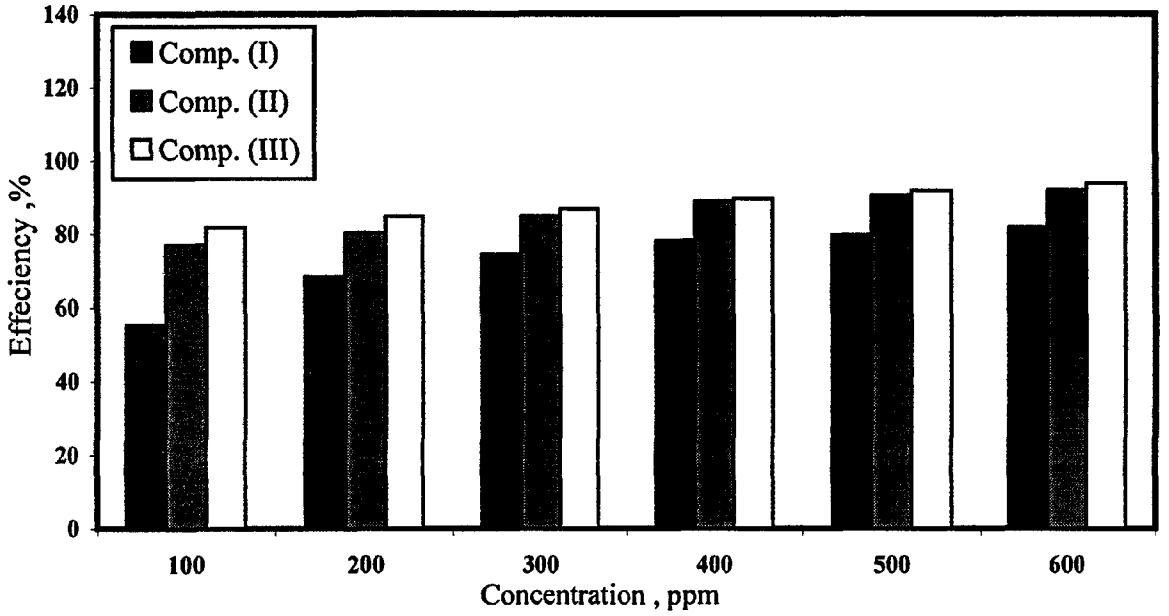


Fig.(19): Effect of concentration of different inhibitors on the effeciency of carbon steel in 0.5M HCl after 48 hr

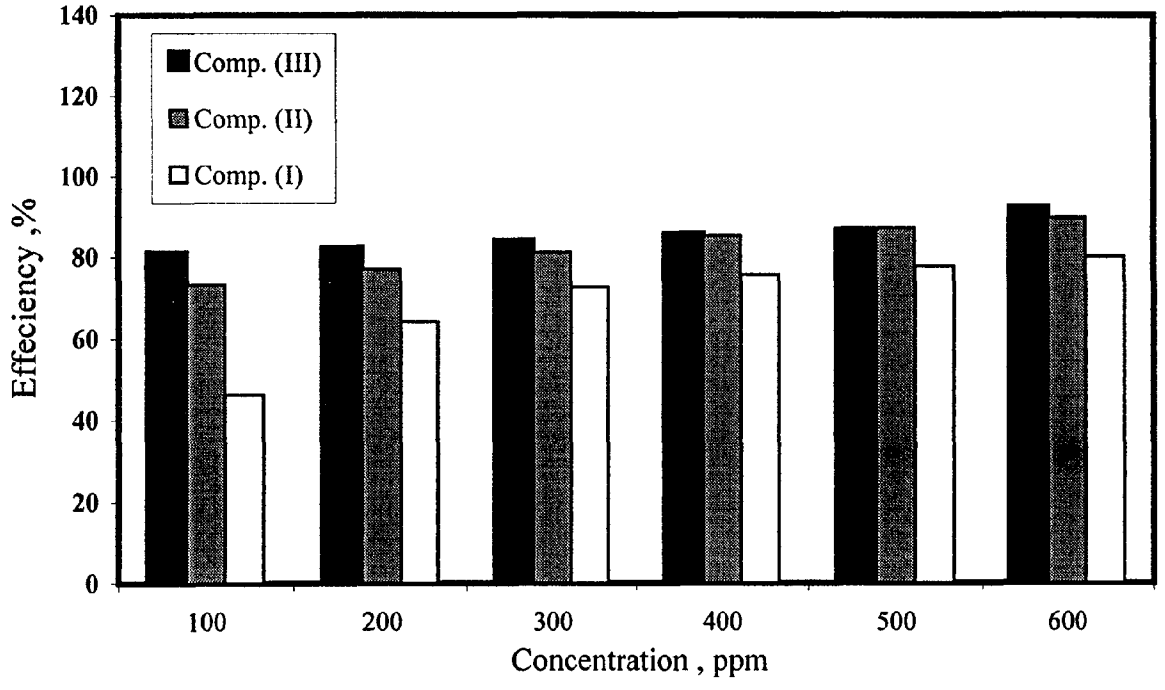


Fig.(20): Effect of concentration of different inhibitors on the effeciency of carbon steel in 1M HCl

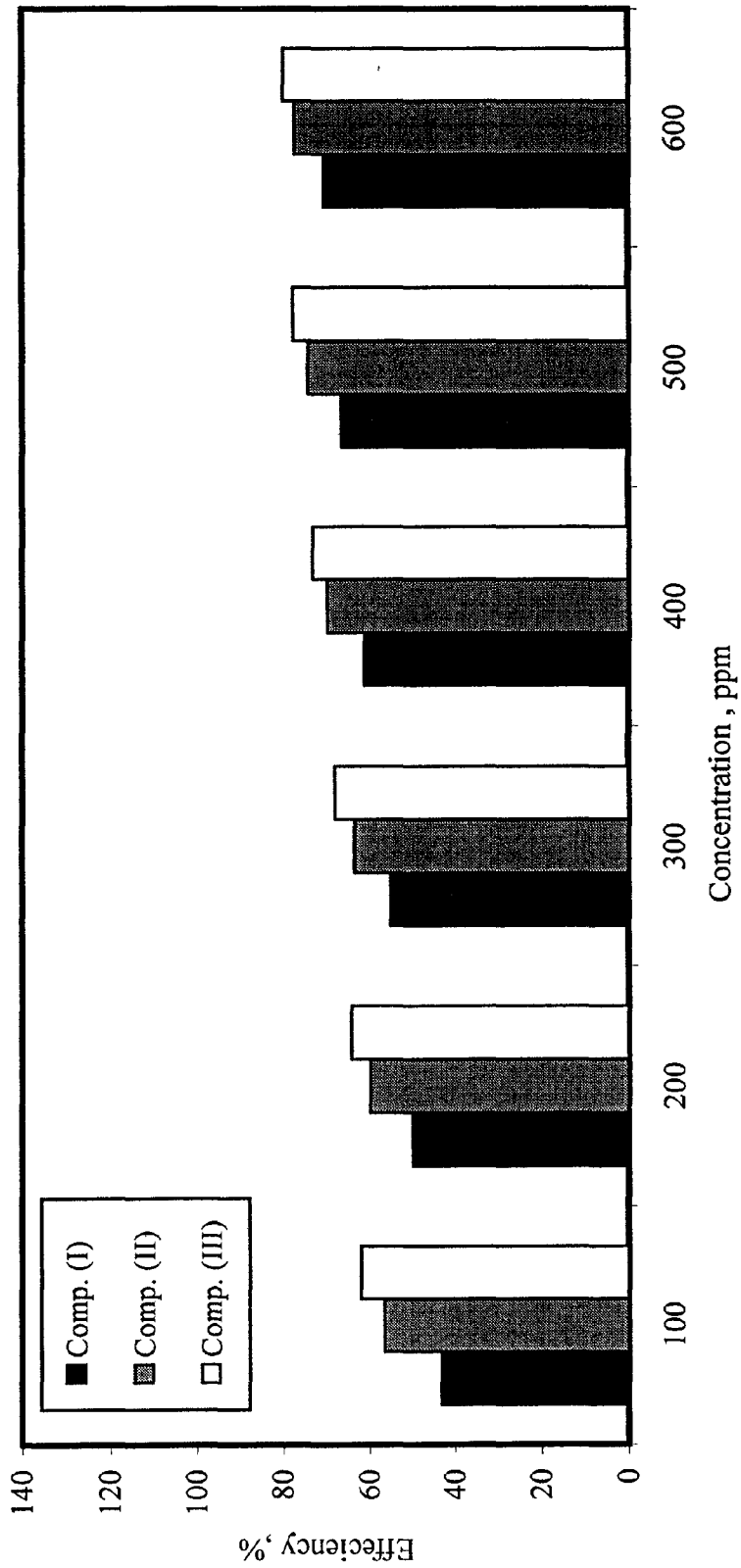


Fig.(21): Effect of concentration of different inhibitors on the effeciency of carbon steel in2M HCl after 48 hr

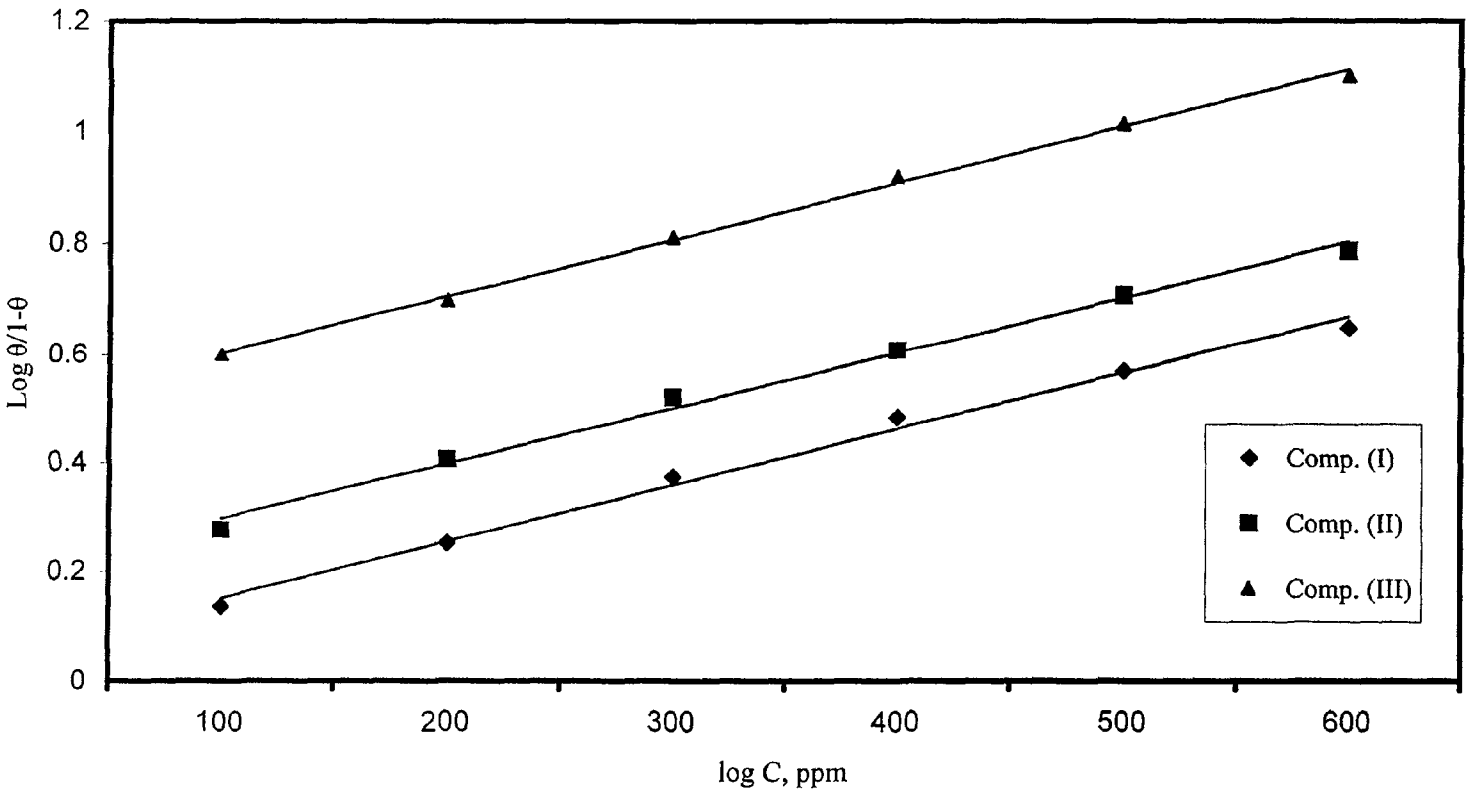


Fig. (22): dependence of Log θ/1-θ on logarithm of concentration for the inhibitors (I- III)

III.3.2-Studies the effect of chemical structure of compounds I, II and III on the efficiency.

The order of efficiency depend on the chemical structure of the organoamide derivatives inhibitor, where the organoamide inhibitor III having three aromatic (phenyl), two amid and two hydroxyl groups. These groups are having high mobility clouds of electrons. While the organoamide inhibitor I and II having the two aromatic (phenyl), two amid and hydroxyl groups. On the other hand also the inhibitor II has long hydrocarbon chain more than I. So that the mobility of clouds of electrons are fixed at the molecules terminal , for this reason the corrosion inhibitor III is more effective and stable than I and II respectively.

Tables (4 -12) illustrate the weight loss , corrosion rate , surface area coverage and efficiency of the compounds I,II and III in 0.5 M HCl at ambient condition. From these tables the obtained data are indicated that , the inhibition efficiency are increased by increasing the concentration of inhibitors. Also, the efficiency at concentration 400, 500 and 600 ppm are nearly the same, on the other hand the efficiency at period time of immersion 24 hr nearly the same i.e. the change in efficiency are not remarkable. The stability of efficiency indicated on the stability of the formed thin protective films from the inhibitors by the surface of specimens. From the results showed that, the efficiency are increased from I > II > III, respectively. These results indicated that , the compound II has – CH_2 – groups more than the compound I, where the center of hetero atoms N,O are the same in two compound. These phenomena were indicated that, the long chain of hydrocarbon in compound II is more effective than the short chain in compound I. On the other hand the phenyl group in compound III was more efficiency due to the cloud of electrons between the phenyl groups and amide groups respectively these phenomena are cleared that, the aromatic amides are high efficiency for corrosion protection than aliphatic amides.

III.4. Comprehensive studies for the effect of different concentrations of HCl on the corrosion inhibition of organoamide derivatives (I, II and III).

From ofermintiond results, one should be concluded that, the different HCl concentration solutions has been affected on the efficiency, corrosion rate, weight loss and coverage surface by organoamide inhibitor derivatives. While the 0.5 M was lower effective than 1.0 and 2M HCl concentration on the behaviors of inhibitors as shown in above Tables (4 -12) and Figs (19-21). On the other hand, the effective of 1.0 and 2.0 M HCl on the behaviors of inhibition of organoamide compounds were nearly the same, it is clearly shown in Tables (7-12) and Figs. (10 - 15). From these observations, one should be concluded that the organoamide derivatives are having good efficiency in high concentration of aggressive HCl media. Therefore, one is selected the 1.0 MHCl solution as optimum concentration of aggressive media for completed this study, because it is more common applied concentration in a wide range of industries. This study was completed by applying the open circuit potential, Potentiodynamic polarization, electrochemical impedance spectroscopy and scanning electron microscope.

III.5.Effect of Temperature and study of Activation and thermodynamic Parameters

The study of the effect of temperature on the inhibition efficiency for corrosion inhibitors is an important factor. This factor helps to elucidate the mechanism and the kinetics of inhibitors and ultimately the proper selection of inhibitors for the specific practical situation. Accordingly, the effect of temperature of the corrosion medium on the reaction proceeding in pure acids was reported by many methods. [322-323]

The effect of temperature on the corrosion rate and the efficiency of inhibitors had a great importance for study, the

corrosion of carbon steel alloy and medium composition in presence and absence of organoamide compound I, II and III derivatives, respectively, are studied in the present work. For that the effect of temperature has been studied by the weight loss method in temperature range 303-333°K, in absence and presence of 500ppm for each inhibitor, respectively, the results of which are shown in Figs. (23- 26).

The effect of temperature on the corrosion rate of carbon steel in 1M HCl solution in absence and presence of 500 ppm for each compound are recorded. From the observation results in Fig (23 - 26) one should be concluded that, in the absence of inhibitor the corrosion rate was high increased with increasing of temperature, while in the presence of inhibitors the corrosion rate is decreased with increasing of the temperature. Therefore one should be concluded that, these compounds act as corrosion inhibitors in acid 1M HCl for carbon steel at low and high degrees of temperature. The increasing in the temperature has a reverse relationship with the percentage efficiency this means that the adsorption of amide I, II and III compounds on the metal surface was physicochemical adsorption.

The values of corrosion rate obtained at different temperatures permit the calculation of the Arrhenius activation energy, Ea*, according to the following equation

$$\log K = -Ea^*/2.303RT + \log A \qquad \text{(III.4)}$$

Where A is the Arrhenius pre-exponential factor, it is a constant depends on a metal type and the electrolyte, where K is corrosion rate, R is the universal gas constant and T is the absolute temperature.

This form of Arrhenius equation is applicable in this case, where the plot of, log corrosion rate, mpy of 500ppm for each compounds against the reciprocal of absolute temperature, (1/T) are shown graphically in Fig. (27).The values of the activation

energies, E_a^*, were calculated from the slopes of these lines. These values were indicated that, the presence of organoamide inhibitor compounds increase the activation energy of the metal dissolution reaction and that the process is activation controlled, i.e., decreases the corrosion rate and increases the efficiency. Generally one could say that the nature of electrolyte and concentration of inhibitors are affected greatly on the activation energy for the corrosion process. So that, the addition of 500ppm of every one of the organoamide I, II and III compounds to the solution increased the activation energy (E_a^*), as shown in Table (13).The extent of the increases was proportional to the inhibition efficiency of the inhibitor. These results are indicated that the energy barrier for the corrosion reaction increases in the presence of these additives of inhibitors. This means that by addition of the inhibitor in the acid solution, the corrosion reaction could be further pushed far from to surface sites. These are characterized by higher values of activation energy E_a^* indicating that carbon steel corrosion occurs at the uncovered part of the surface. Thus, adsorption of the inhibitor is assumed to occurs on the higher energy sites[322], the presence of inhibitor, which results in the blocking of the active sites, must be associated with an increase in the activation energy, E_a^*.

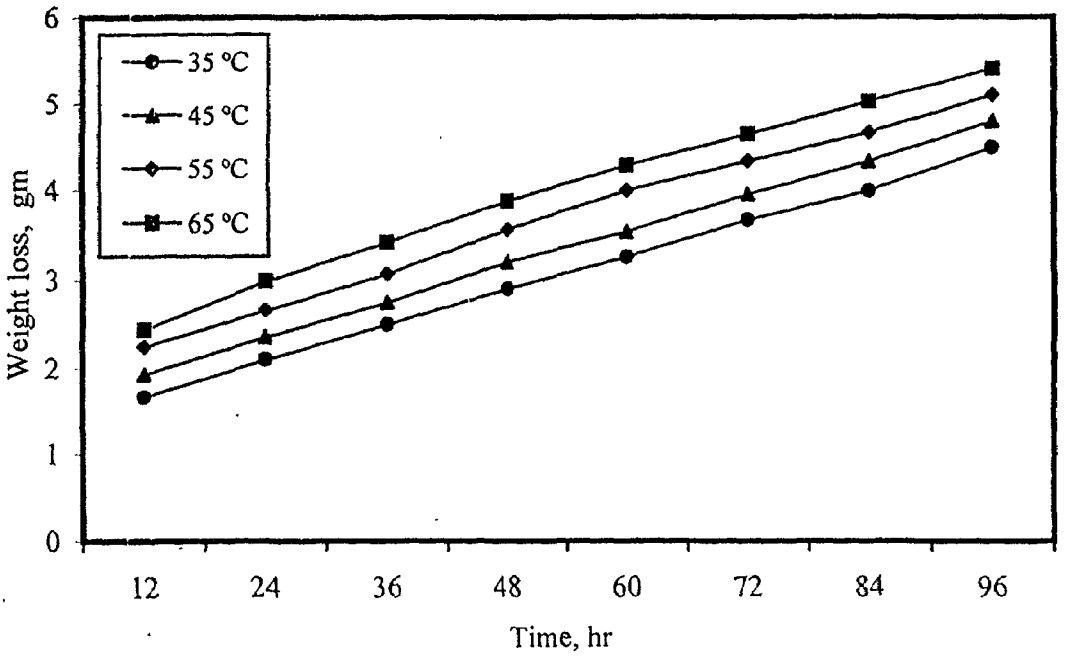


Fig. (23): Weight loss- time curves for carbon steel in 1M HCl at different temperatures

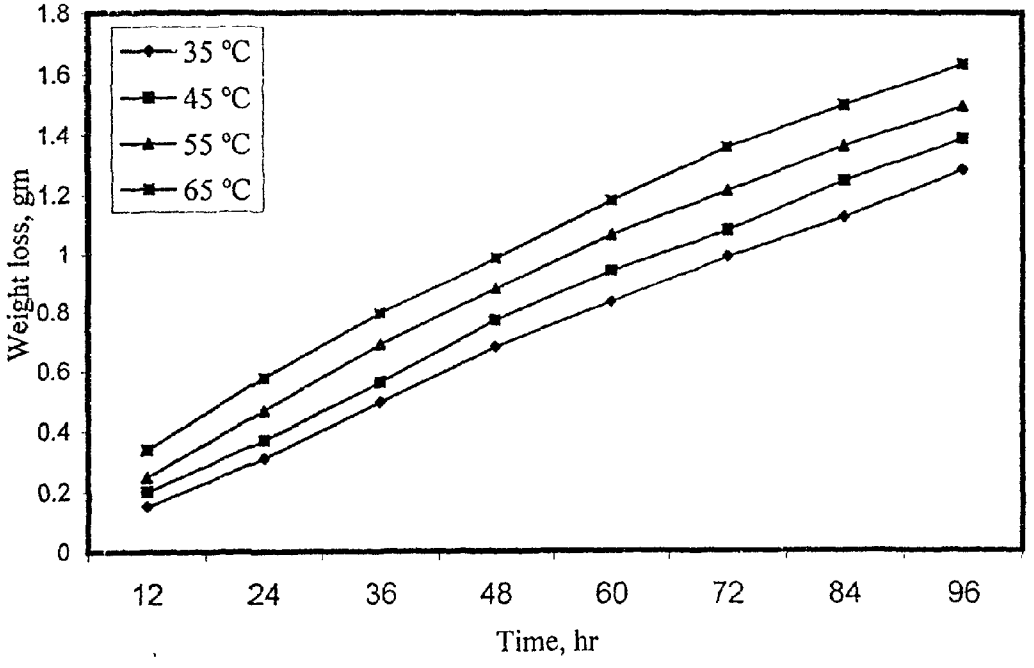


Fig. (24): Weight loss- time curves for carbon steel in 1M HCl in presence of 500 ppm of inhibitor (I) at different temperatures

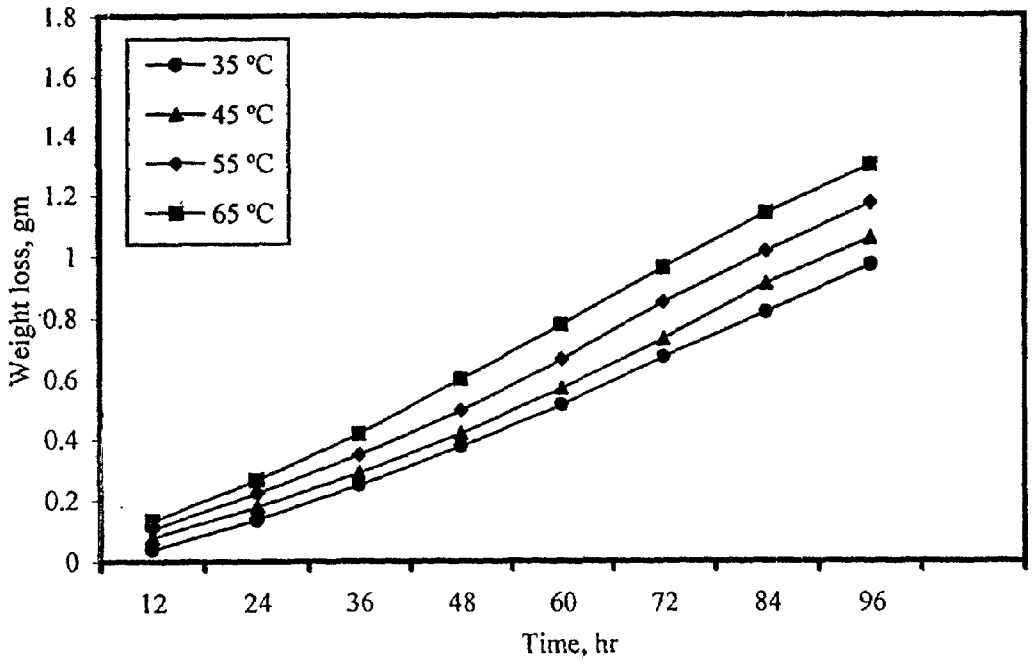


Fig. (25): Weight loss- time curves for carbon steel in 1M HCl in presence of 500 ppm of inhibitor (II) at different temperatures

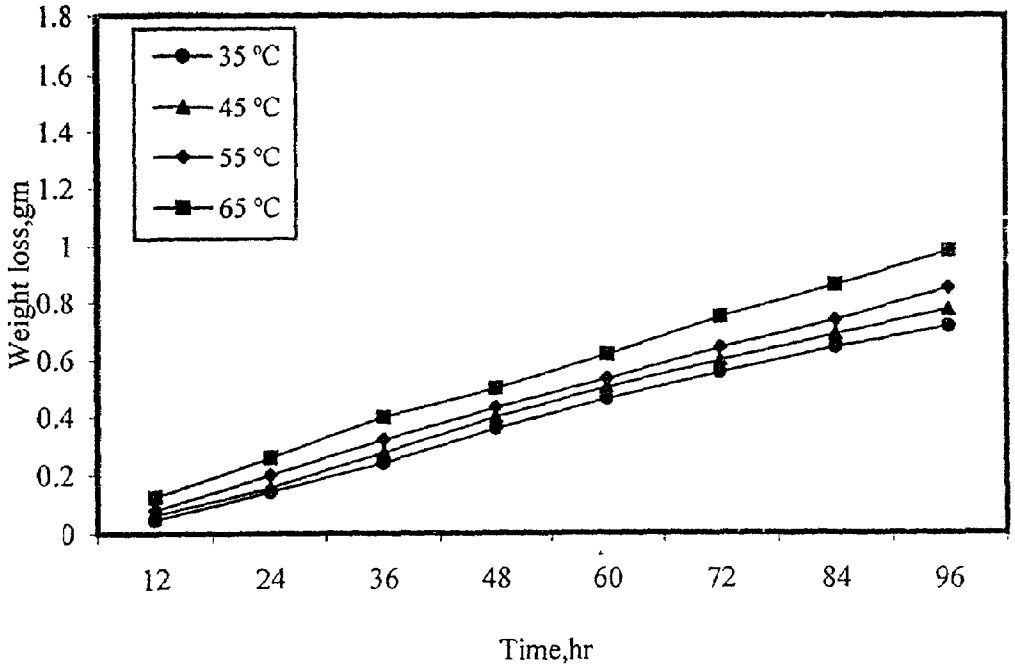
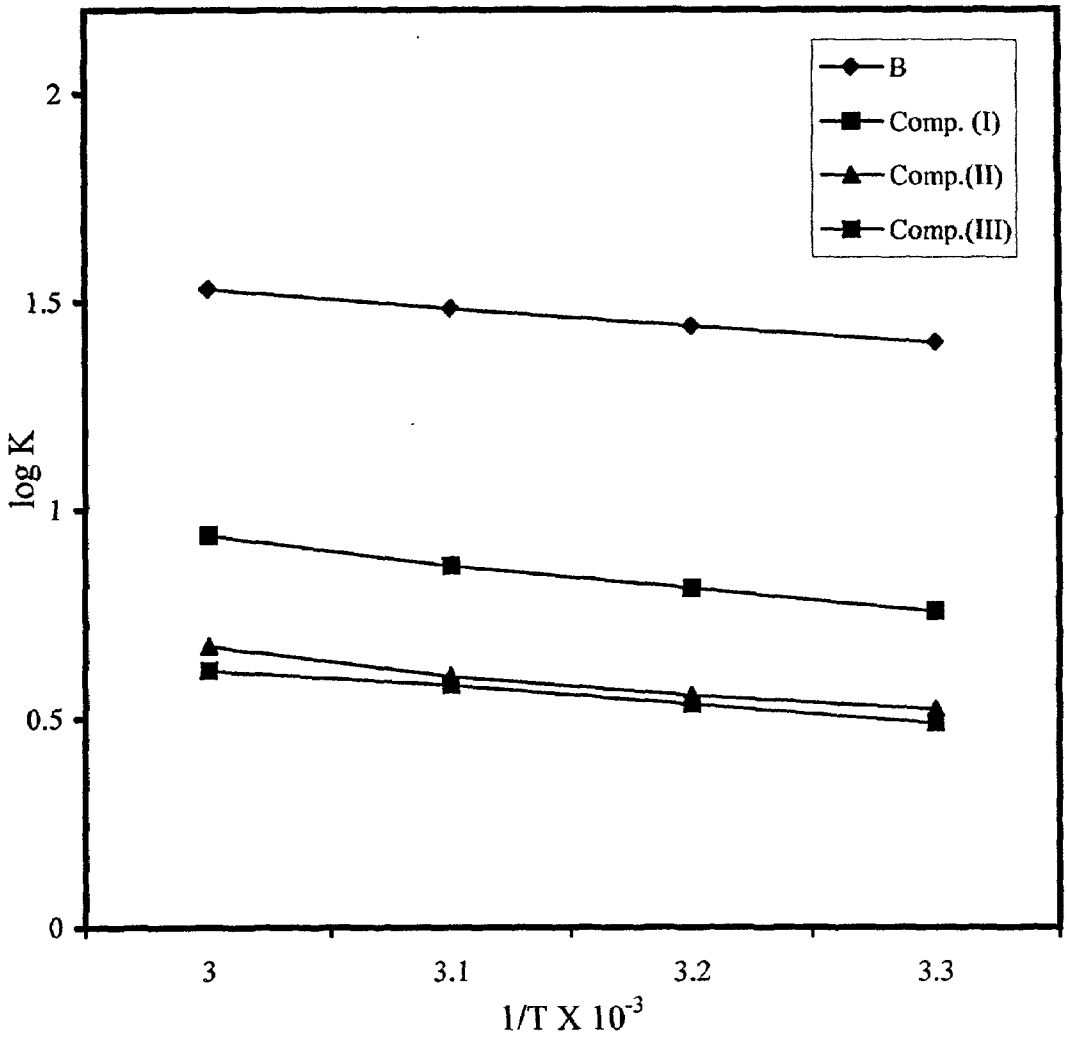


Fig. (26): Weight loss- time curves for carbon steel in 1M HCl in presence of 500 ppm of inhibitor (III) at different temperatures



Fig(27): Log K-1/T curves for carbon steel dissolution in 1M HCl in absence and presece of 500 ppm of inhibitors (I - III)at different temperatures .

Thermodynamic parameters for corrosion process play an important role in defining the spontaneity of the conversion of the metal to corrosion products that can form in the environmental to corrosion which the metal is exposed [315,324]. Based on Ea* for corrosion process values, the thermodynamic parameters of activation for the corrosion process were calculated. Thermodynamic parameters including enthalpy of activation (ΔH*), free energy of activation (ΔG*) and entropy of activation (ΔS*) were calculated using the following equations[324]:

$$\Delta H^* = Ea^* + RT \qquad \text{(III.5)}$$

$$\Delta G^* = RT\,(\ln k_t / h - \ln K) \qquad \text{(III.6)}$$

$$\Delta S^* = (\Delta H^* - \Delta G^*)/T \qquad \text{(III.7)}$$

Where: **R:** universal constant (= 8.314 J/mole.K)
h: Blanks constant,
k: Boltzmann constant, **K:** corrosion rate

The obtained values are listed in Table (13). The positive values of ΔH* reflect the endothermic behavior of the used inhibitors on the steel surface for the conversion of the metal to the corrosion products. With respect to the influence of the inhibitor efficiency, the data reveal that ΔH* increases generally with increasing the inhibitor efficiency. This increase may be due to the powerful of the inhibitor and the stronger the adsorption on the metal surface. The values of ΔG* are all positive reflecting the high energy barrier for the corrosion process. On the other hand, ΔG* values in presence of the inhibitors are higher than that obtained from 1M HCl (blank), and hence, the process is activation controlled. The larger negative values of ΔS* imply that the activated complex in the rate determining step represents association rather than dissociation.In other words, there is a decrease in the

disordering takes place on going from reactants to activated complex [323].

Table (13): Thermodynamic parameters for carbon steel alloy dissolution in 1M HCl in absence and presence of 500ppm inhibitor for amide derivatives (I-III) at different temperatures.
(ΔH^*, ΔG^*: KJ mol^{-1} ; ΔS^*: KJ $mol^{-1}K^{-1}$)

Temp (K)	E*a , KJ	303	313	323	333
B 1MHCL					
ΔH^*	36.18	38.74	38.82	38.90	38.99
ΔG^*		52.11	53.54	54.93	56.32
$-\Delta S^*$		0.0434	0.0462	0.0488	0.0512
Inhibitor (I)					
ΔH^*	44.03	46.59	46.67	46.75	46.84
ΔG^*		55.82	57.31	58.65	59.96
$-\Delta S^*$		0.0299	0.0334	0.0362	0.0328
Inhibitor (II)					
ΔH^*	51.69	54.25	54.33	54.41	54.50
ΔG^*		57.33	58.91	60.31	61.61
$-\Delta S^*$		0.01	0.014	0.017	0.0210
Inhibitor (III)					
ΔH^*	53.42	55.98	56.06	56.14	56.23
ΔG^*		57.45	59.04	60.68	62.12
$-\Delta S^*$		0.0047	0.0093	0.0136	0.0174

III.6. Electrochemical studies

The electrochemical studies are important for determination the validity of the inhibitors. In this study one could be used three types of electrochemical techniques open circuit potential, potentiodynamic polarization and electrochemical impedance spectroscopy. These studies were carried out for organoamide compounds I, II and III as corrosion inhibitors at concentrations 100, 200, 300, 400, 500 and 600 ppm respectively, and ambient temperature in 1.0 M HCl electrolyte solution as aggressive media. These studies were happened in cell contained on unused carbon steel alloy as working electrode, saturated calomel electrode as reference electrode and platinum wire ascounter electrode

III.6.1-Open circuit potential measurements (OCP).

The variation of the open circuit potential (OCP) data for the working carbon steel electrode and time as a function of the period of exposure was measured against saturated calomel electrode (SCE). The evaluation are carried at starting potential of steel 510 V and period time 60 min. in absence and presence of various concentrations of the organoamide compounds I, II and III inhibitors. The obtained results are investigated and shown in Table (14) and Figs. (28-30).It is clear that in absence of the inhibitor molecules (blank), the open circuit potential curve tends from the moment of immersion towards more negative value and increased after 5 min. This behavior represents the break down of the permission of the ions in bulk electrolyte were formed weak ferrous oxide and hydroxides film on the surface of carbon steel alloy (working electrode), then the potential was shifted to more positive direction and stable after 10 min. to 37 min. and slowly decreased until the end of time immersion (60 min), the potential reached to -575mv. i.e the dissolution of formed iron oxide/ hydroxide films of the metal surface was continuous. On the other hand the addition of the inhibitor molecules produces

a positive shift in ($E_{corr.}$) .These results were shown in Table (14) and Figs (28-30).The OCP for all inhibition concentration solutions to inhibitors organoamide remained slowly increasing until stable at steady state to 41 min. and after that slowly increased and stable secondary to the end of test. This behavior suggests possibility, the inhibitor molecules have been adsorbed on the metal surface to form a stable protective film of organoamide inhibitor with alloy, which might control and reduce the alloy dissolution. The OCP is reached to steady state during 60 min immersion for each inhibitor. The results of final steady-state potential ($E_{corr.}$) are listed in Table (14). The results are clearly indicated that, as the concentration of each inhibitor from I, II and III are increased the corrosion potential ($E_{corr.}$) increased and shifted to more positive direction. From these results clearly that the inhibitor were act as anodic protection (i.e) decreasing the anodic dissolution of carbon steel alloy. Therefore one could be noted that OCP values are very different for each inhibitor due to variation in of the molecular structure of each inhibitor. So that, the shifted to-more positive direction in the following orders

(III) > (II) > (I)

Generally one should be concluded that, the OCP is monitored continuously in absence and presence of corrosion inhibitors. Figs. (28-30) show that the inhibitor application affects on the OCP values in inhibited and uninhibited solutions and shifted to positive values with increasing of concentration of inhibitor and period time. It also causes oscillations on OCP. This behavior is probably due to the more stability of the formation of thin films and the many of layers are formed also. The OCP data for the corrosion inhibitor I, II and III at concentration ratios from 100 to 600 ppm at period time 60 min. are given in Table (14) and Figs (28 -30). From these data one should be deduced that the potential at first 5 min. shifted toward negative values and return again to positive direction.

The potential increased from low concentration to high concentration of inhibitor, layers are formed and stable on the surface of specimens the adhesion force between the surface of metal and formed films from inhibitors were strong and also the layers with each others, this phenomena due to the adsorption of inhibitors. These phenomena were carried out by chemisorptions process. In solicited blank solution, there are two phenomena ,first removing adsorbed species by cavitations and final hydrogen evolution (because of acidic corrosive medium). However, in inhibited solution, the inhibitor chains are adsorbed on metal surface and are chemisorbed. Thus, the OCP oscillation is higher in these solutions. From the OCP results one should be recommended that the application of organoamide derivatives I, II and III as corrosion inhibitor in aggressive media. So that, one should be say these results are matched with the obtained results from weight loss calculations.

Table (14): Data from open circuit potential measurements of carbon steel electrode in1M HCl containing different concentrations of various inhibitors at 298° ±2K

Conc. (ppm)	potential mV (vs. SCE)		
	I	II	III
b	-575	-575	-575
100	-558	-555	-547
200	-555.6	-550	-543
300	-553	-548	-541
400	-549.2	-544	-593
500	-546.5	-542	-537
600	-544	-540.	-533.8

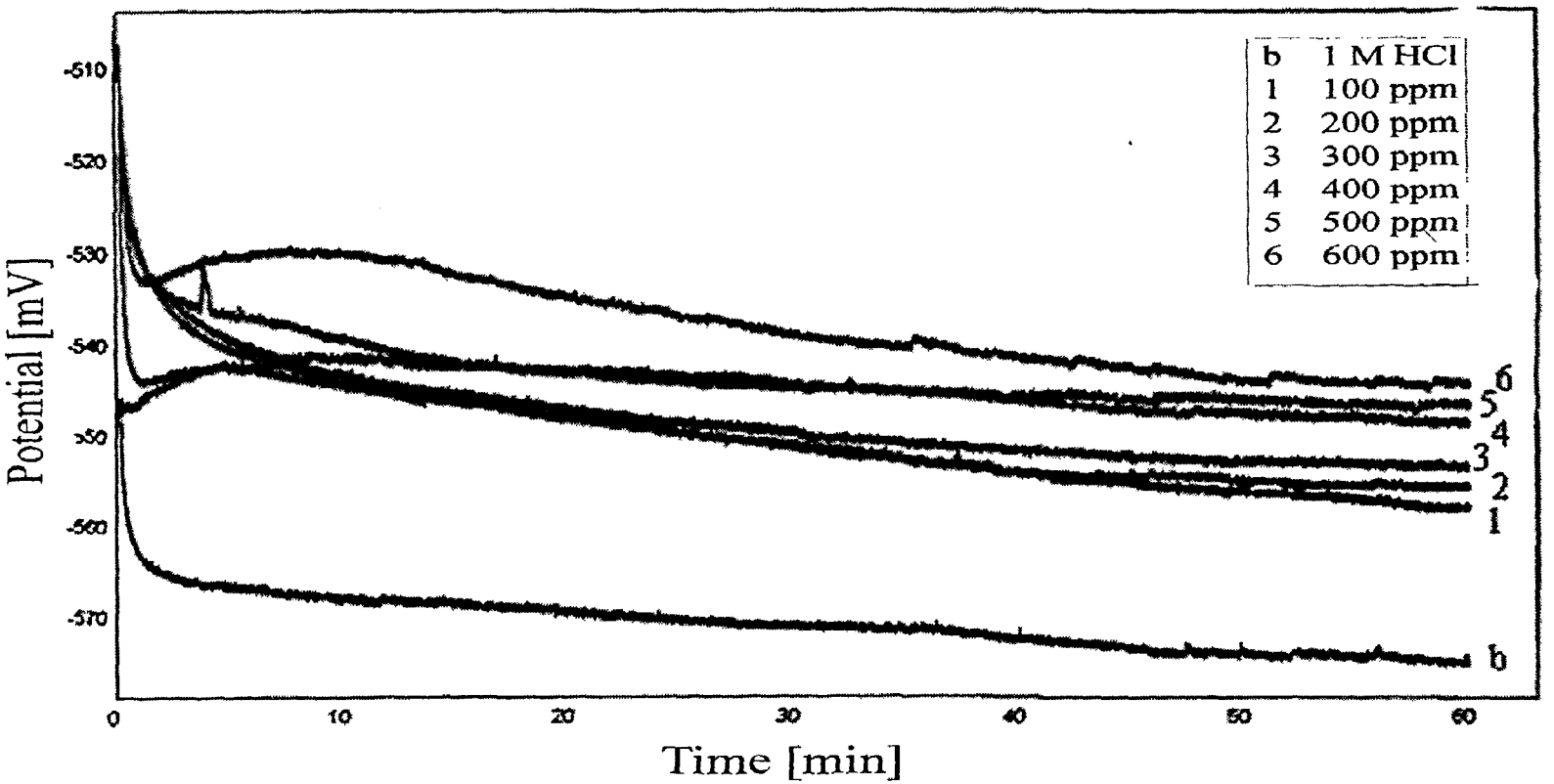


Fig. (28): Open circuit potential–time plot for carbon steel in the 1M HCL in absence and presence of different concentrations of inhibitor (I)

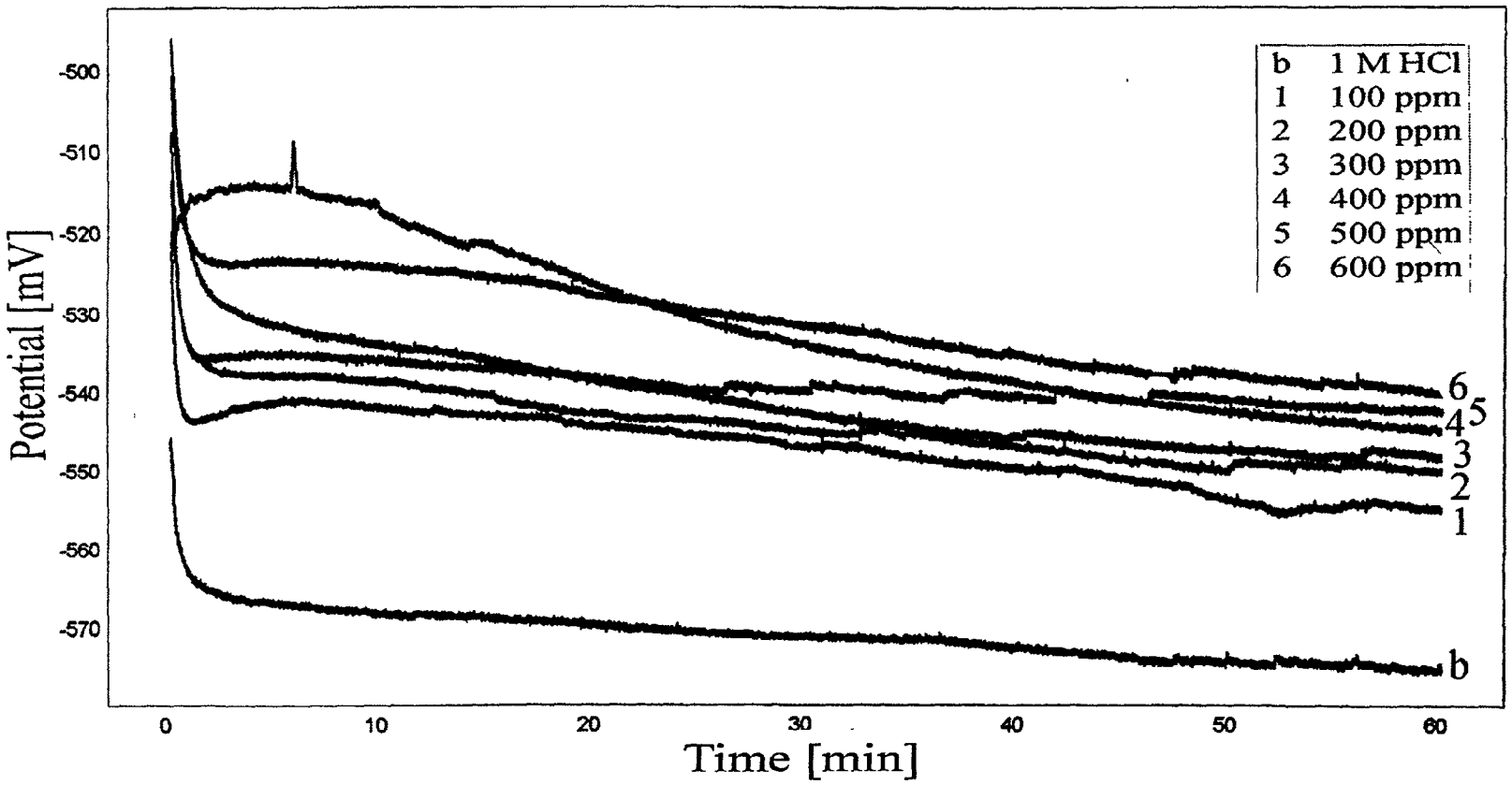


Fig. (29) : Open circuit potential–time plot for carbon steel in the 1M HCL in absence and presence of different concentrations of inhibitor (II*)*

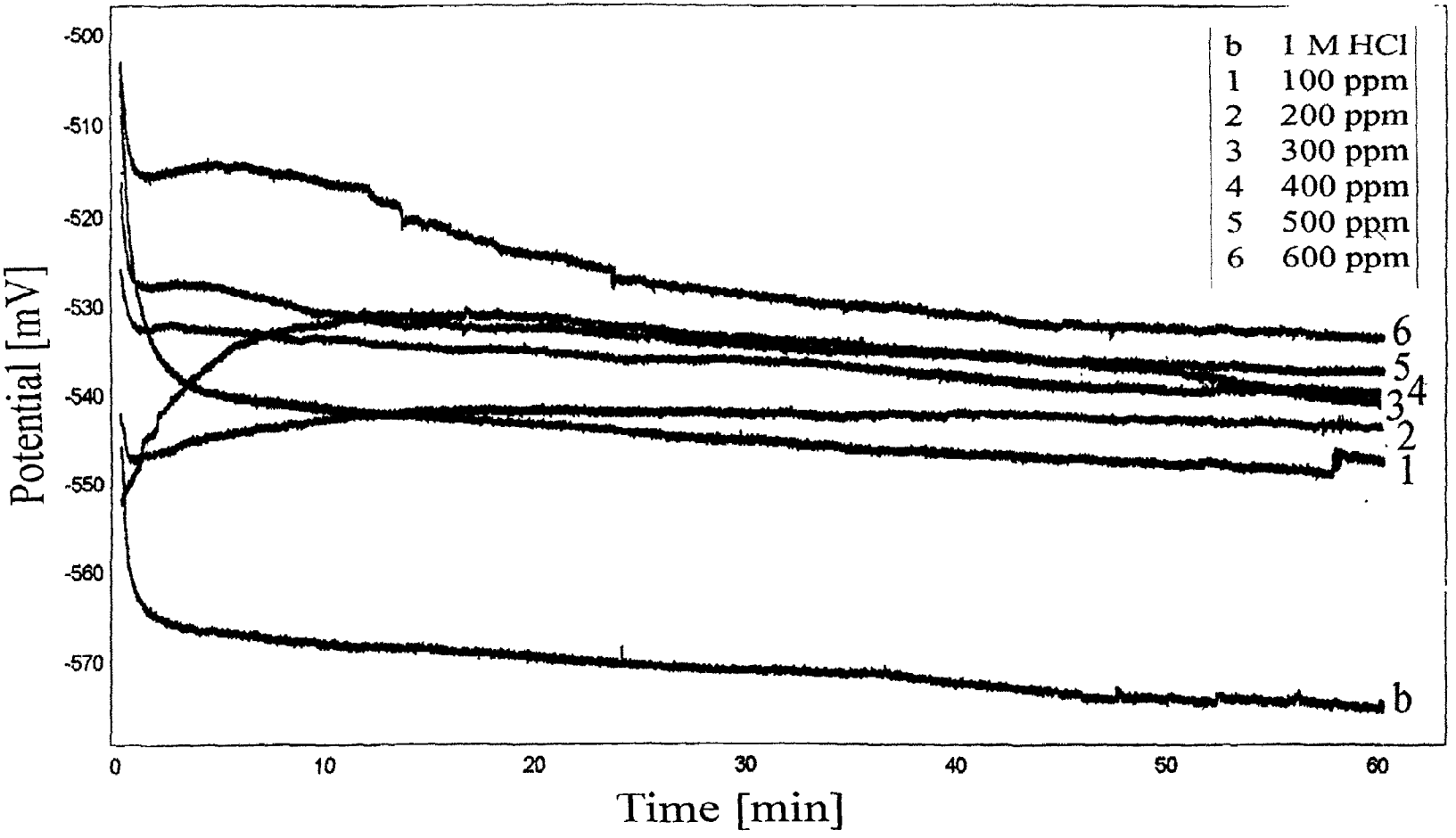


Fig. (30): Open circuit potential–time plot for carbon steel in the 1M HCL in absence and presence of different concentrations of inhibitor (III)

III.6.2. Electrochemical polarization curves

Both anodic and cathodic polarization curves for carbon steel alloy, in 1.0 M HCl at various concentrations from 100 to 600 ppm of organoamides I, II and III inhibitor compounds are shown as potentiodynamic polarization curves

Figs. (31 – 33) show the polarization curves of carbon steel in a 1.0 M HCl solution in the absence and presence of inhibitors, respectively. Electrochemical corrosion kinetic parameters, such as corrosion potential (E_{corr}), cathodic (bc) and anodic (ba) Tafel slopes, corrosion current density (I_{corr}), coverage surfaces (θ) and I% are determined in presence of organoamides derivative I, II and III inhibitors. These parameters are summarized in Tables (15-17). It is clear that the presence of inhibitor molecules causes a decrease in I_{corr} and The I_{corr} decreased with increasing concentration demonstrates the efficiency of the additive compound as corrosion inhibitor of carbon steel. The values of inhibition efficiency increased markedly with increasing of inhibitor concentration that indicating a higher coverage of inhibitor on the surface is obtained in a solution with higher concentration of inhibitor. The addition of inhibitor shifted the E_{corr} value towards the positive direction. The shifted to-more positive direction in the following order

(III) > (II) > (I)

These results showed that the inhibition process of this inhibitor depends on electrode potential. For very negative values, the inhibition effect disappears. One should be concluding that organoamides derivatives I, II and III inhibitors act as a mixed inhibitors. The results obtained from the polarization technique are in good agreement with those obtained from weight loss method and OCP data.

Figs. (31 -33) show the polarization curves of carbon steel in a 1.0 M HCl solution in the absence and presence of inhibitors, respectively. Electrochemical corrosion kinetic parameters, such as corrosion potential (E_{corr}), cathodic (bc) and anodic (ba) Tafel slopes and corrosion current density (I_{corr}), are determined without and with inhibitors (I, II and III). These parameters are summarized in Tables (15-17). Similar polarization curves are obtained for the other inhibitors. These values are obtained by extrapolation of the Tafel slopes for all the compounds at the evaluated concentrations. These data show that the I_{corr} values decreased considerably with the increasing in the inhibitor concentration. E_{corr} shifted to more positive values with the inhibitors (I, II and III), which suggests that these inhibitors are primarily affected the anodic processes [325-327]. Consequently adsorption mechanism is much more likely at the cathodic sites. The effect of inhibitor type and concentration is observed on the values of ba and bc, so that these inhibitors obstruct the available surface area; it seems that film formed on the metallic surface became more uniform with concentration, while molecular structure may affect film resistance due to chemical bonding nature with metallic surface. The inhibition efficiency, I (%), was calculated according to procedures developed by other authors [328,329]; it was obvious that the I (%) increases with increasing the concentration of each inhibitor. The inhibiting effect of these compounds is attributed to the formation of a chemical bonding between inhibitor and metallic surface [329,330]. Adsorption of compounds is more likely through nitrogen element of primary amino group in molecules due to its capability of shearing lone pair electrons; the difference in inhibitor efficiencies are probably associated with a dissimilar structural distribution of molecules on the substrate. For instance, inhibitors I, II have a linear structural arrangement that allows having a considerable surface chemisorption. In the case of compound III, it's high inhibitive force may be ascribed to the presence of a phenyolic ring, which provides some of its electronic density along with a steric effect to the inhibitor

structure. In this way, molecules are permitted to have a more uniform structural arrangement and thus more adsorption on the metallic surface. Comparing the values of I (%) of these inhibitors, the inhibition efficiency tend to increasing in the following order:

(III) > (II) > (I)

We may conclude that organoamides derivative I, II and III inhibitors act as an anodic inhibitors. The results obtained from the polarization technique are in good agreement with those obtained from weight loss method and OCP data.

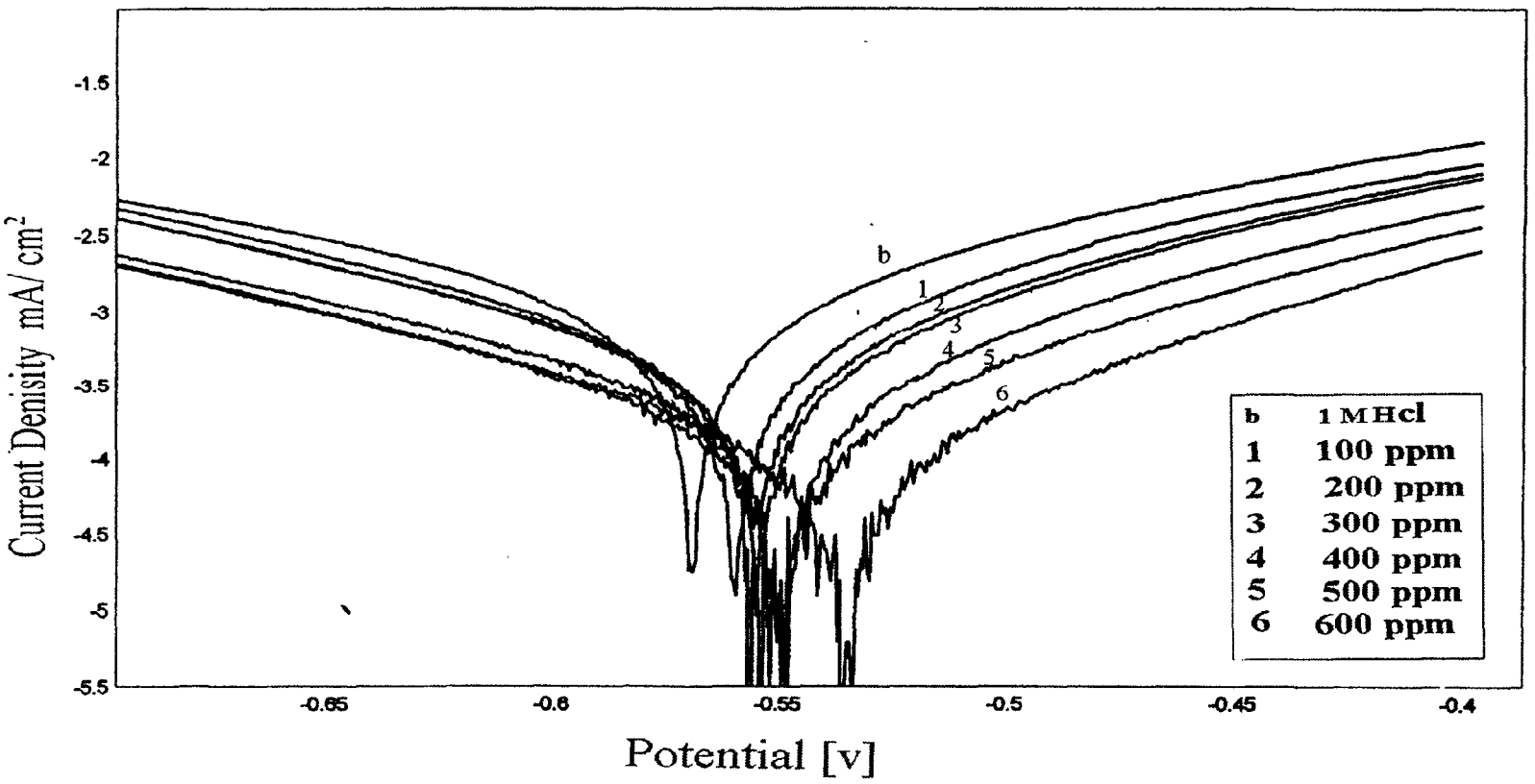


Fig.(31) : Polarization curves for carbon steel in the 1M HCL in absence and presence of different concentrations of inhibitor (I)

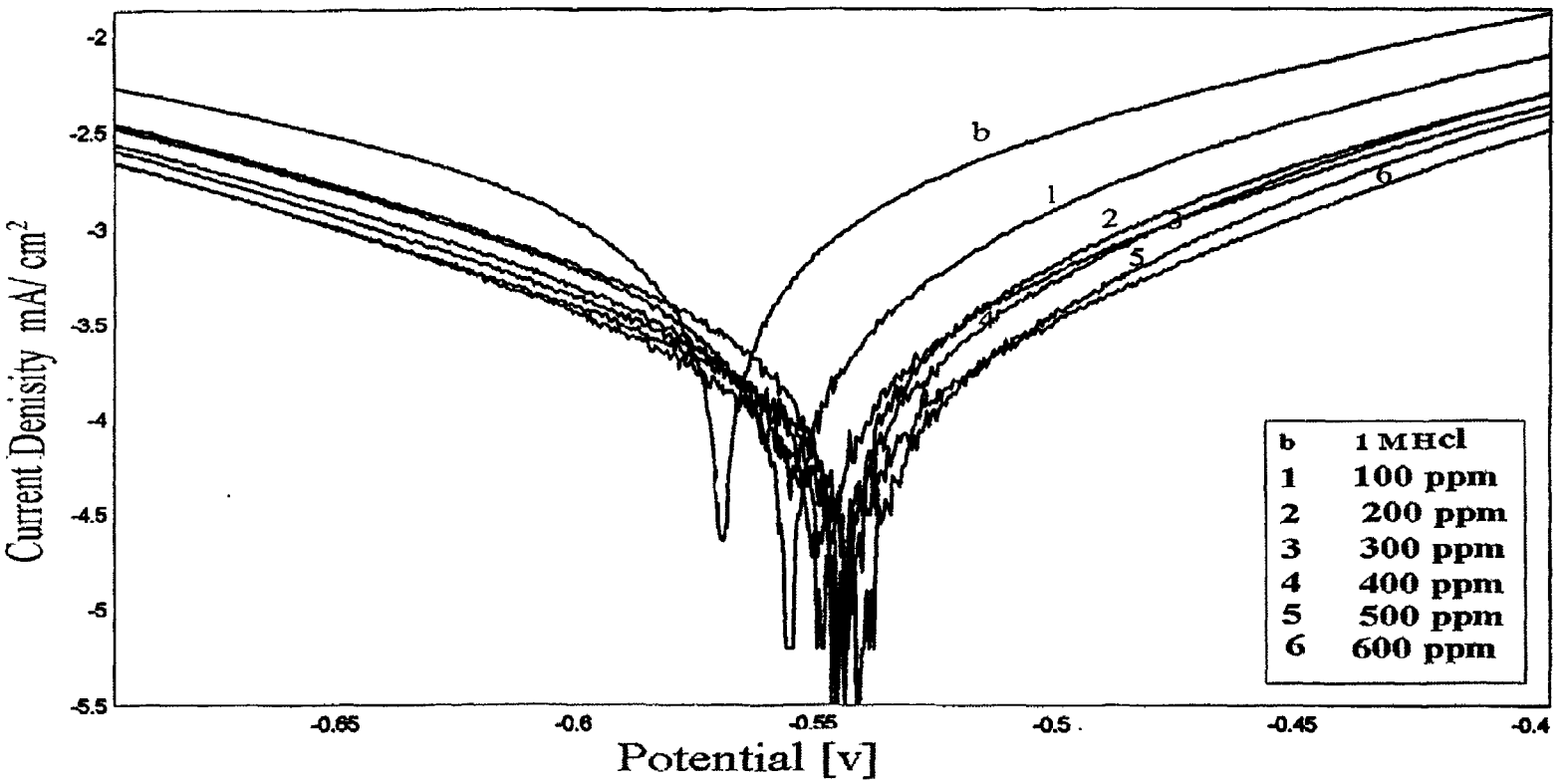


Fig.(32) : Polarization curves for carbon steel in the 1M HCL in absence and presence of different concentrations of inhibitor (II)

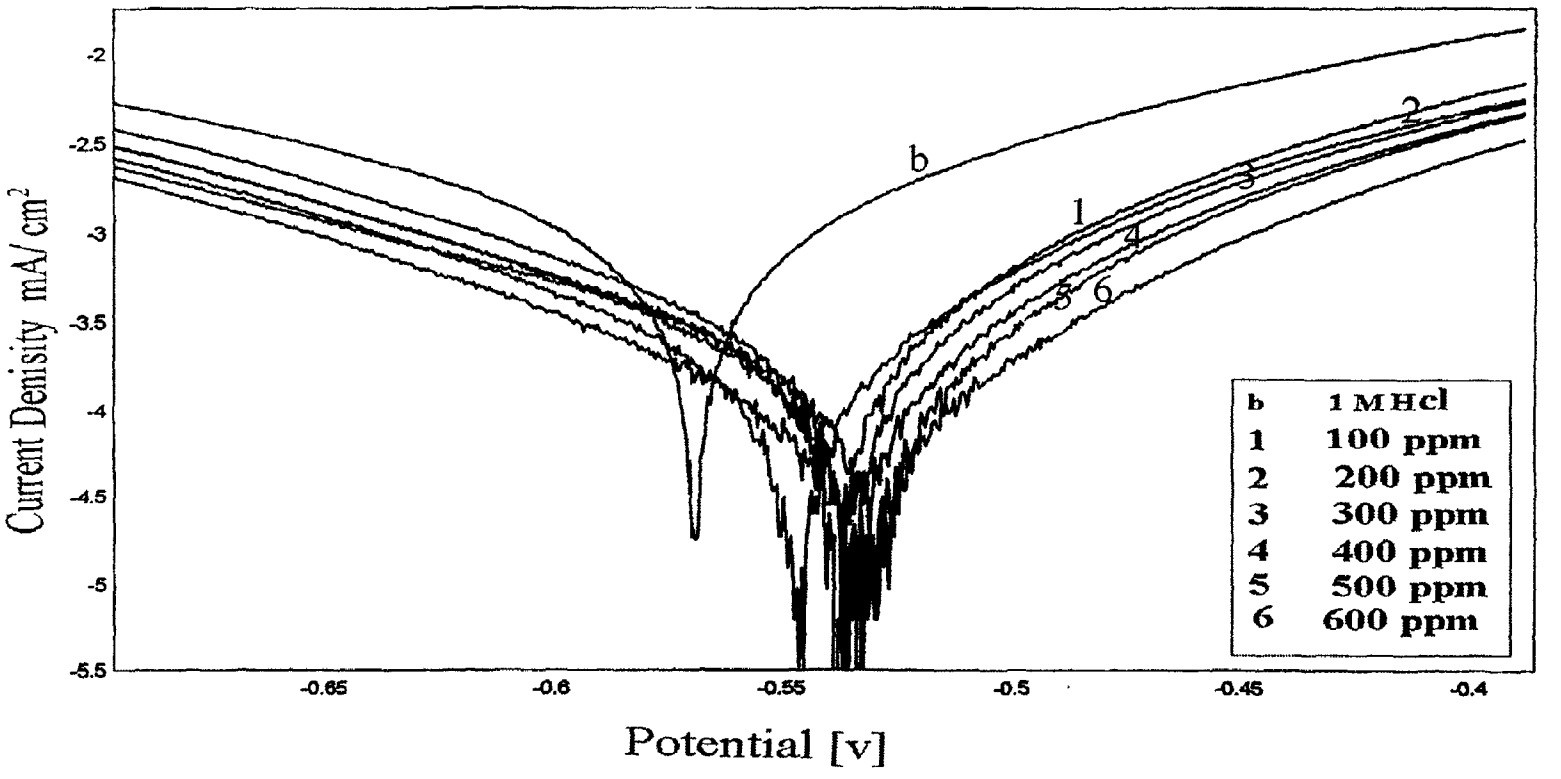


Fig.(33) : Polarization curves for carbon steel in the 1M HCL in absence and presence of different concentrations of inhibitor (III)

Table (15): parameters of potentiodynamic polarization of carbon steel electrode in 1M HCl containing various concentrations of inhibitor (I) at 298° ±2K.

Conc. (ppm)	$-E_{corr}$, mV	I_{corr}, mA/Cm^2	R_P, ΩCm^2	b_a, mV/dec	b_c, mV/dec	θ	I%
b	574.51	1.28	27.39	175.90	-206.31	-	-
100	564.82	0.66	54.89	153.81	-162.20	0.4821	48.21
200	559.73	0.49	44.69	133.12	-149.02	0.6155	61.55
300	554.82	0.35	55.94	104.53	-124.53	0.7245	72.45
400	554.61	0.28	75.16	121.64	-158.54	0.7819	78.19
500	549.24	0.26	112.03	136.52	-159.32	0.7921	79.21
600	539.53	0.26	83.10	124.51	-134.05	0.7947	79.47

Table (16): parameters of potentiodynamic polarization of carbon steel electrode in 1M HCl containing various concentrations of inhibitor (II) at 298° ±2K.

Conc. (ppm)	$-E_{corr}$, mV	I_{corr}, mA/Cm^2	R_P, ΩCm^2	b_a, mV/dec	b_c, mV/dec0	θ	I%
b	574.51	1.28	27.39	175.90	206.31	-	-
100	566.51	0.34	74.45	121.92	-146.62	0.7319	73.19
200	553.82	0.30	100.17	143.41	-151.10	0.7594	75.94
300	552.34	0.23	105.09	127.64	-138.91	0.8135	81.35
400	549.81	0.19	119.16	119.13	140.13	0.8490	84.90
500	549.72	0.18	115.39	110.12	-132.04	0.8584	85.84
600	545.13	0.16	161.86	107.20	139.22	0.87.25	87.25

Table (17): parameters of potentiodynamic polarization of carbon steel electrode in 1M HCl containing various concentrations of inhibitor (III) at 298° ±2K.

Conc. (ppm)	$-E_{corr}$, mV	I_{corr}, mA/Cm^2	R_P, ΩCm^2	b_a, mV/dec	b_c, mV/dec0	θ	I%
b	574.51	1.28	27.39	175.90	206.31	-	-
100	548.91	0.25	82.59	125.51	-149.90	0.8028	80.28
200	543.50	0.23	90.37	118.43	-126.93	0.8198	81.98
300	541.04	0.21	120.12	108.52	-148.61	0.8391	83.91
400	539.62	0.20	125.69	113.00	-141.82	0.8420	84.20
500	537.00	0.19	134.76	112.71	-134.51	0.8459	84.59
600	534.20	0.11	210.51	100.42	-129.60	0.9101	91.01

III.6.3. EIS Measurements

Figs (34, 36 and 38) show a typical Nyquist impedance plots obtained for carbon steel alloy electrode at an open circuit potential, the experimental procedure were carried out after 24hrs immersion of the working electrode in 1M HCl in absence and presence of the different concentrations 100, 200, 300, 400, 500 and 600ppm of inhibitors I, II and III respectively at temperature, 23°±2C. The dots line represents the actual data and solid lines represent the best fit using the equivalent circuit shown in Figs. (35, 37 and 39) .The parameters obtained by fitting the equivalent circuit are listed in Tables (18 - 20). Figs (34, 36 and 38) and Tables (18 - 20) indicated that the increase in organoamide derivatives I, II and III inhibitor concentrations raises the polarization resistance (Rp). The constant phase elements(Q) with their n values close to 1.0 represent double-layer capacitors with some pores; the Q decrease upon of organoamides derivative I, II and III inhibitor and upon increase in their concentrations, which are expected to cover the charged surfaces reducing the capacitive effects. It has been reported that, the semicircles at high frequencies are generally associated with the relaxation of electrical double –layer capacitors, and the diameters of the high – frequency capacitive loops can be considered as the charge – transfer resistance. This suggests that the electron- transfer reaction corresponding to the second semicircle takes place through the surface layer, which limits mass transport (Warburg) or acts just like another resistor. The presence of the Warburg (W) impedance indicates that the mass transport is limited by the surface covered with organoamide derivatives I, II and III inhibitor layers.

The inhibition efficiency, I%, of organoamide derivatives I, II and III inhibitors for the carbon steel alloy electrode can then be calculated from the following equation :

$$\mathbf{I\% = Rp- Rs / Rp \times 100} \qquad \textbf{(III. 8)}$$

Where Rs and Rp are the charge transfer resistance in blank and in presence of organoamide derivatives I, II and III inhibitors, respectively. The attained results are shown in Tables (18 - 20). The increasing of Rs value verified for 1MHCl in presence of organoamide derivatives I, II and III inhibitors pointed out a reduction in the alloy corrosion tendency, resulting in an I% of 80 ,88 and 90.5 respectively. A slightly decrease of CdI values has also been detected, which corroborates the above proposal that organoamide derivative I, II and III inhibitors act as corrosion inhibitors by adsorption onto the metallic surface [318, 332-336].

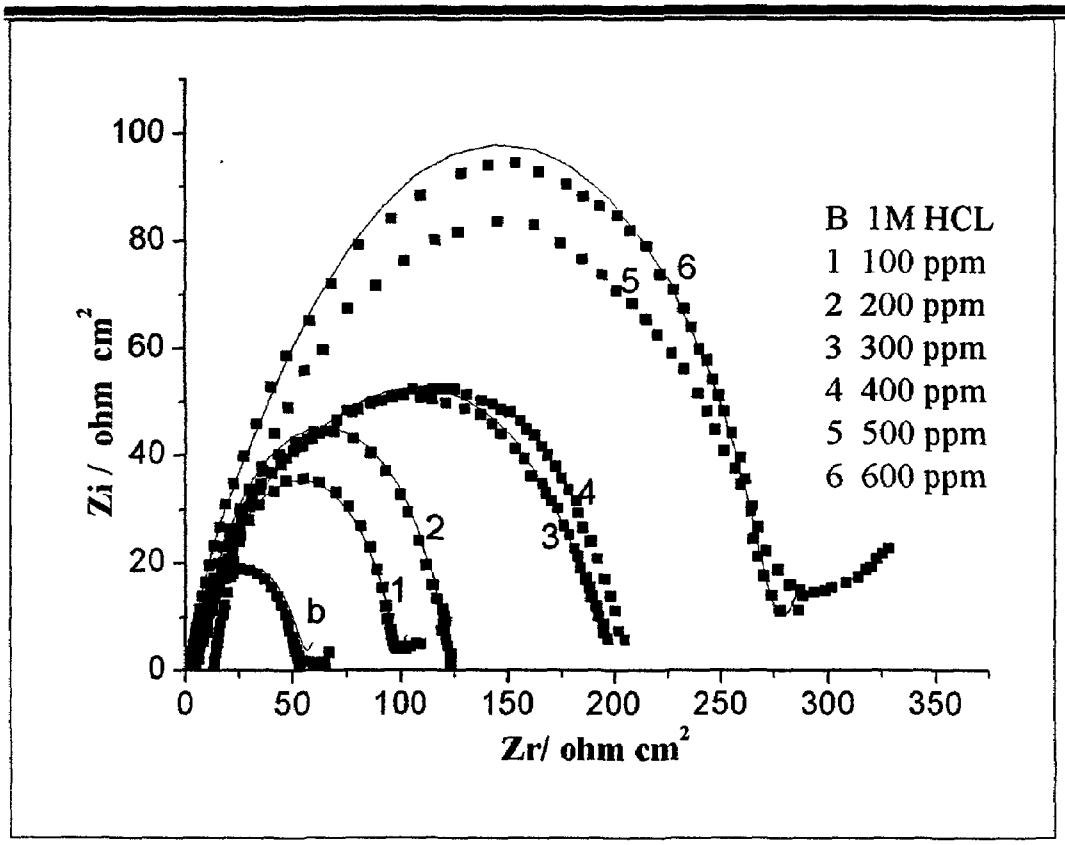


Fig.(34): Niquist diagram for the carbon steel electrode after immersion in 1M HCl solution in absence and presence of different concentrations of compound (I)

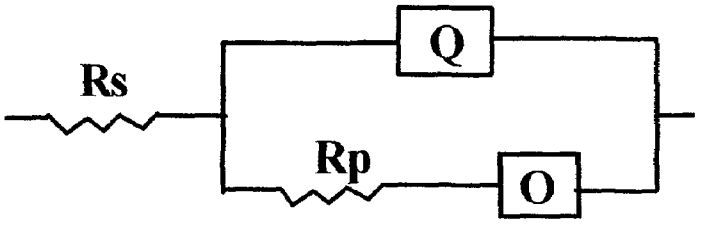


Fig. (35): Equivalent circuit R(Q(RO)) used to fit experimental data represented in fig. (34).

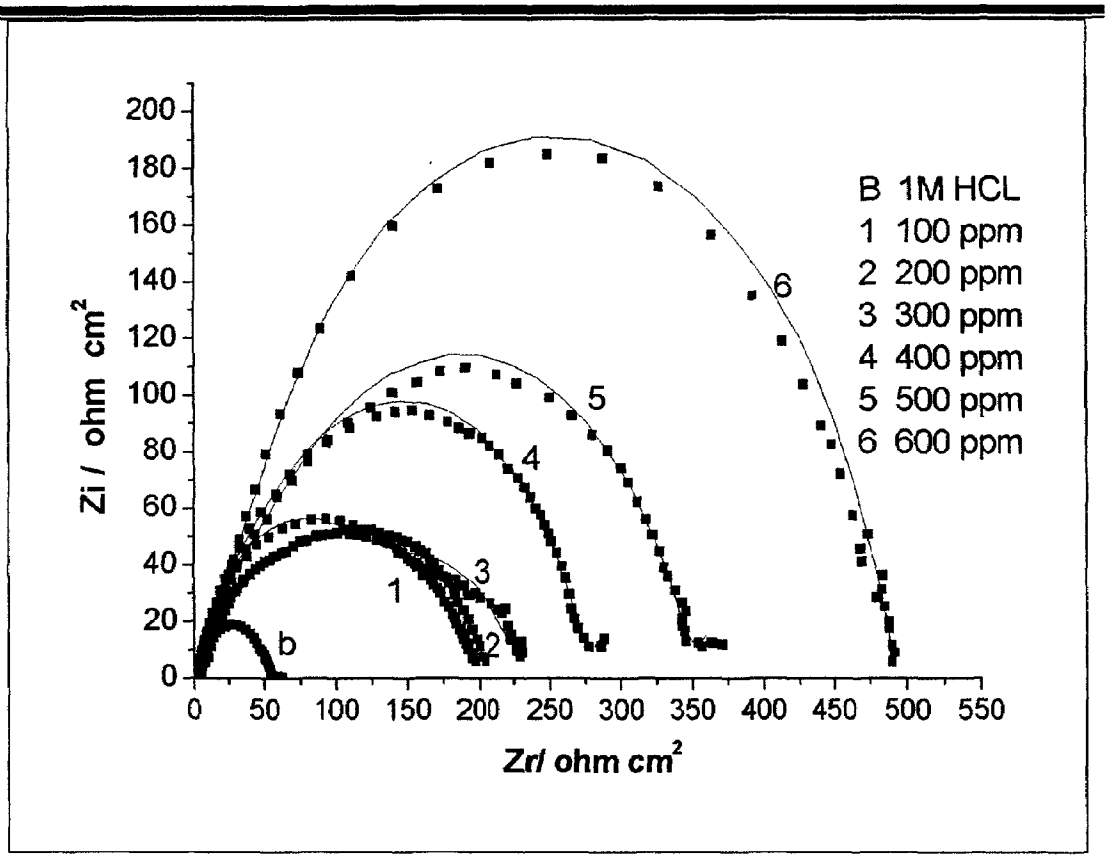


Fig.(36): Niquist diagram for the carbon steel electrode after immersion in 1M HCl solution in absence and presence of different concentrations of compound (II)

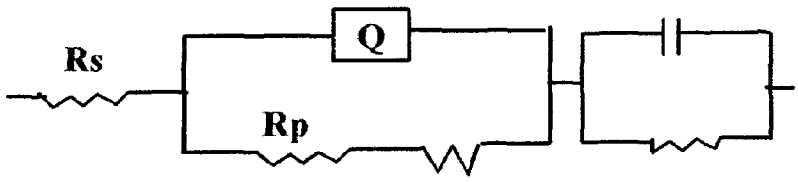


Fig.(37): Equivalent circuit R(Q(RW))QR used to fit experimental data represented in fig (36) .

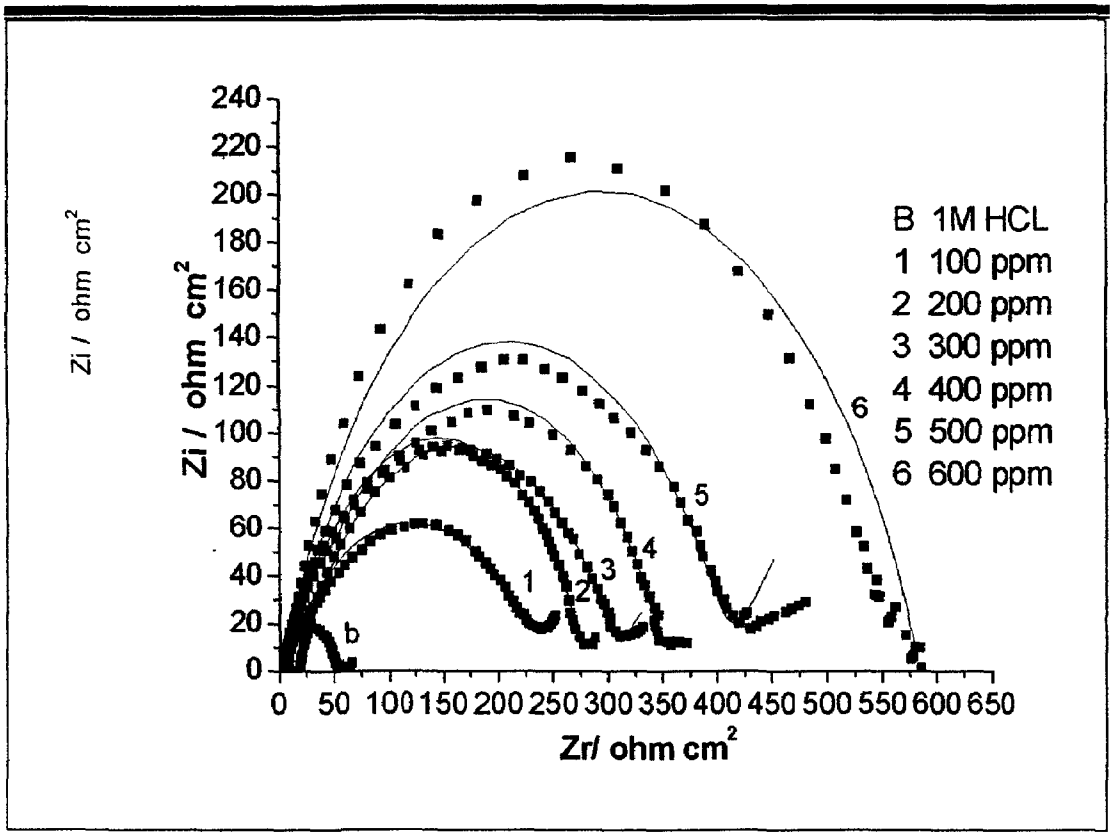


Fig.(38): Niquist diagram for the carbon steel electrode after immersion in 1M HCl solution in absence and presence of different concentrations of compound (III)

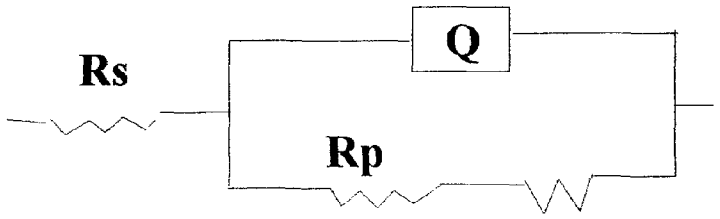


Fig.(39): Equivalent circuit R(Q(RW)) used to fit experimental data represented in fig.(38) .

Table(18): Impedance measurements and inhibition efficiencies for carbon steel in 1M HCL containing different concentrations of compound (I)

Conc. ppm	R_t ΩCm^2	n	C_{dl} $\mu F\ cm^{-2}$	I%
B	55	0.82	16.5	-
100	98	0.72	0.00075	43.88
200	122	0.86	0.00037	54.92
300	200	0.75	0.00026	72.50
400	210	0.78	0.00018	73.81
400	275	0.83	0.00015	80.00
600	281	0.85	0.000129	80.43

Table(19):Impedance measurements and inhibition efficiencies for carbon steel in 1M HCL containing different concentrations of compound (II)

Conc. ppm	R_t ΩCm^2	n	C_{dl} $\mu F\ cm^{-2}$	I%
B	55	0.82	16.5	-
100	200	0.81	0.00062	72.50
200	206	0.75	0.00026	73.30
300	223	0.76	0.00017	75.34
400	275	0.83	0.00015	80.00
500	350	0.81	0.000125	84.29
600	480	0.83	0.000127	88.45

Table (20): Impedance measurements and inhibition efficiencies for carbon steel in 1M HCL containing different concentrations of compound (III)

Conc. ppm	R_t Ohmcm^2	n	C_{dI} µF cm^{-2}	Efficiency (I%)
B	55	0.82	16.5	-
100	236	0.8	0.00058	76.60
200	275	0.8	0.00036	80.00
300	312	0.76	0.000174	82.37
400	350	0.8	0.00017	84.28
400	420	0.84	0.00015	86.9 0
600	585	0.8	0.000123	90. 59

III.7. Scanning Electron Microscopy (SEM)

Scanning electron microscopy was used to examine the surface morphology of the mechanically polished carbon steel specimens and those which were immersed in 1M hydrochloric acid solution in absence and presence of 500 ppm of organoamide derivatives I, II and III respectively. Fig (40) shows a characteristic inclusion observed on the polished carbon steel, which is probably an oxide inclusion. Fig. (41) shows SEM image of the surface of carbon steel specimen after immersion in 1M hydrochloric acid for 24 hr, while Figs (42-44) show SEM image of the surface of another carbon steel specimen after immersion for the same time interval in 1M hydrochloric acid containing 500 ppm of inhibitors I, II and III respectively . The resulting of scanning electron micrographs reveal that The surface was strongly damaged owing to corrosion in absence of inhibitor , but when 500 ppm of inhibitors were added to the solution test , there are much less damage of the surface , presumably as a result of a protective film on the inhibitor on the metal surface. From the micrographs it is clear that compounds provided good protection. The protective film formed on the surface of carbon steel in presence of 500 ppm of inhibitor I appears as multilayer of inhibitor I mag. 750 and 2000 Figs. (42 a and b), respectively, while in case of inhibitor II the formed film appears to be smooth and to cover surface at X =750, 2000 Figs. (43 a and b), respectively and in case of inhibitor III the formed film appears to be very smooth and to cover the whole surface at X =750, 2000 Figs. (44 a and b) respectively. This confirms the observed high inhibition efficiency of each inhibitor at this concentration, the inhibition efficiency tend to decrease in the following order:

(III) > (II) > (I)

The results obtained from the (SEM) technique are in good agreement with those obtained from weight loss method and all elector chemical technique data.

Fig. (40): scanning electron micrographs of carbon steel sample after polishing $X = 750$

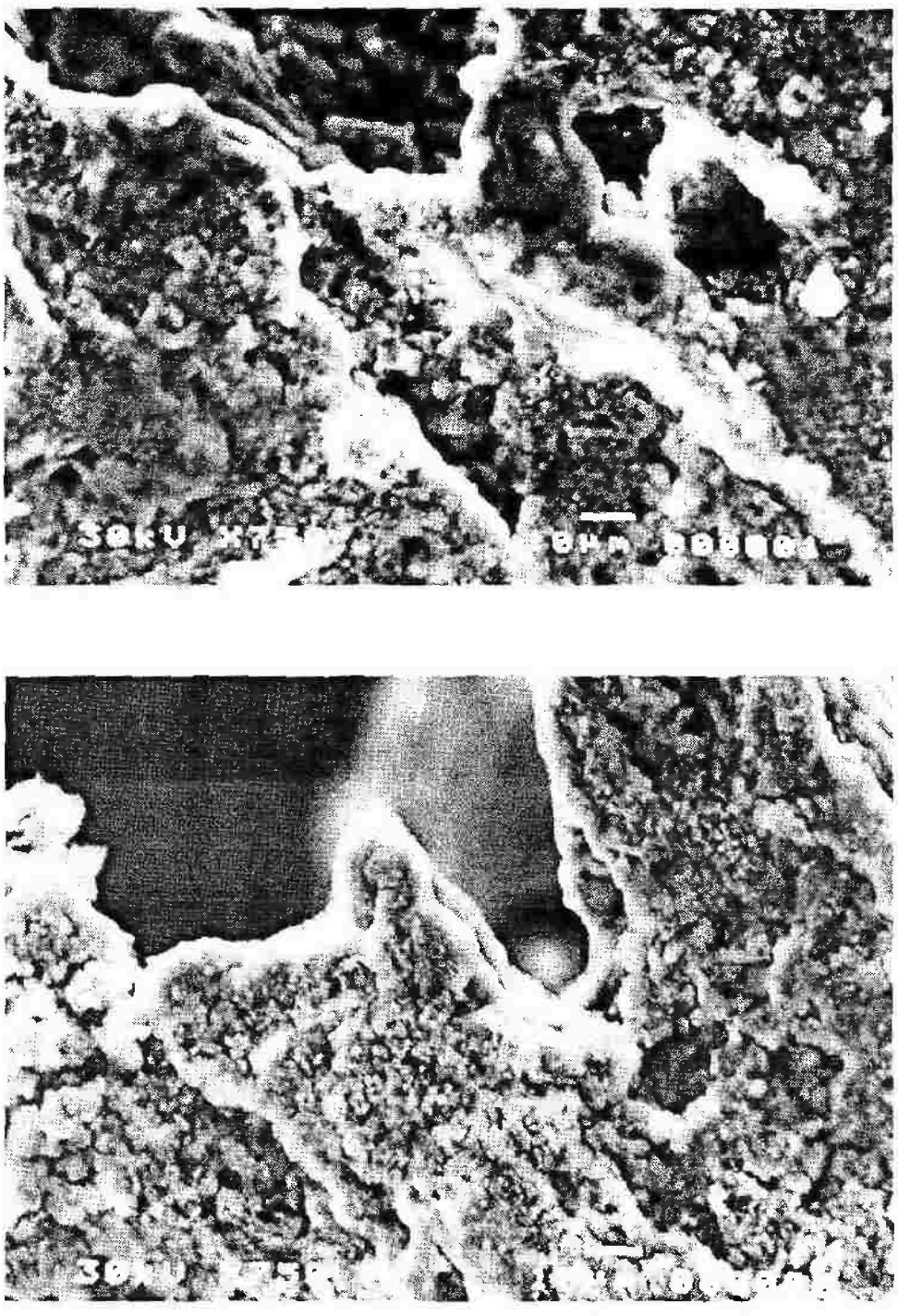
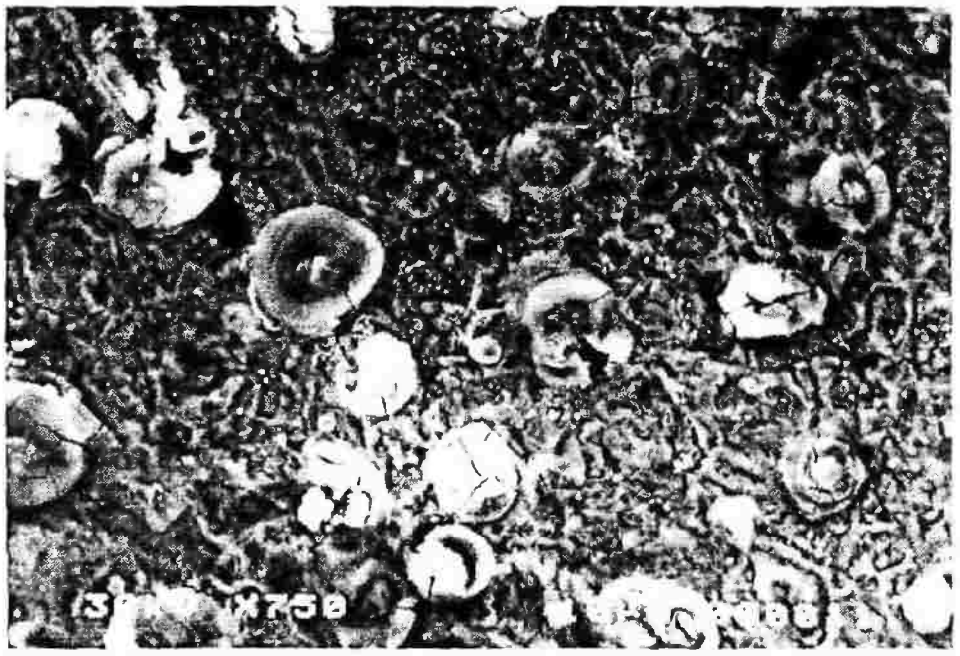


Fig. (41): scanning electron micrographs of carbon steel sample after immersion in 1M HCL solution without inhibitor X = 750

a



b

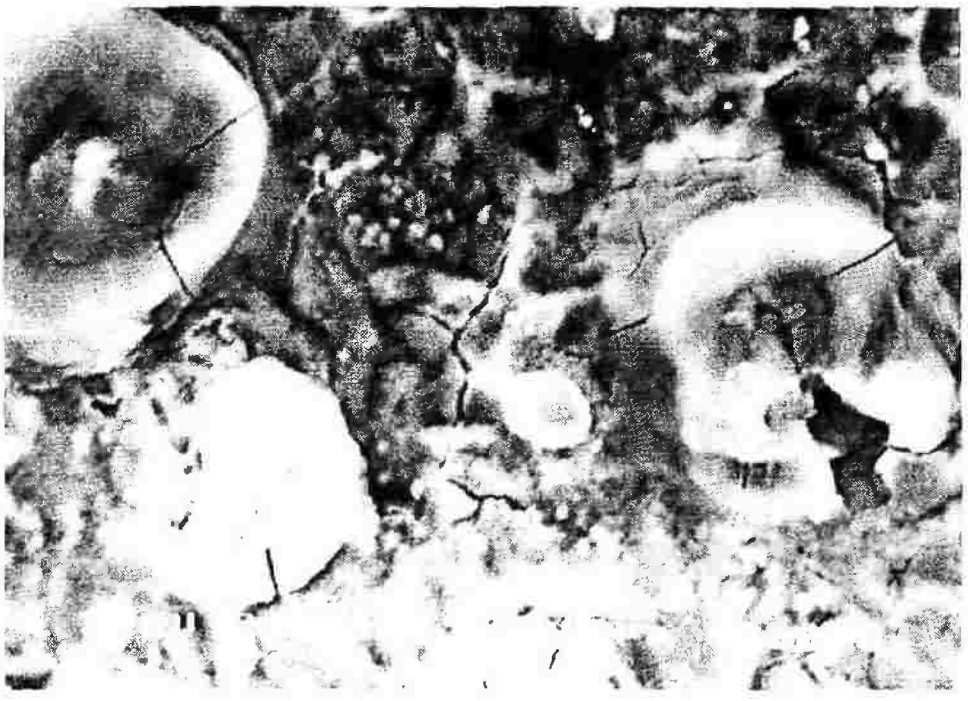
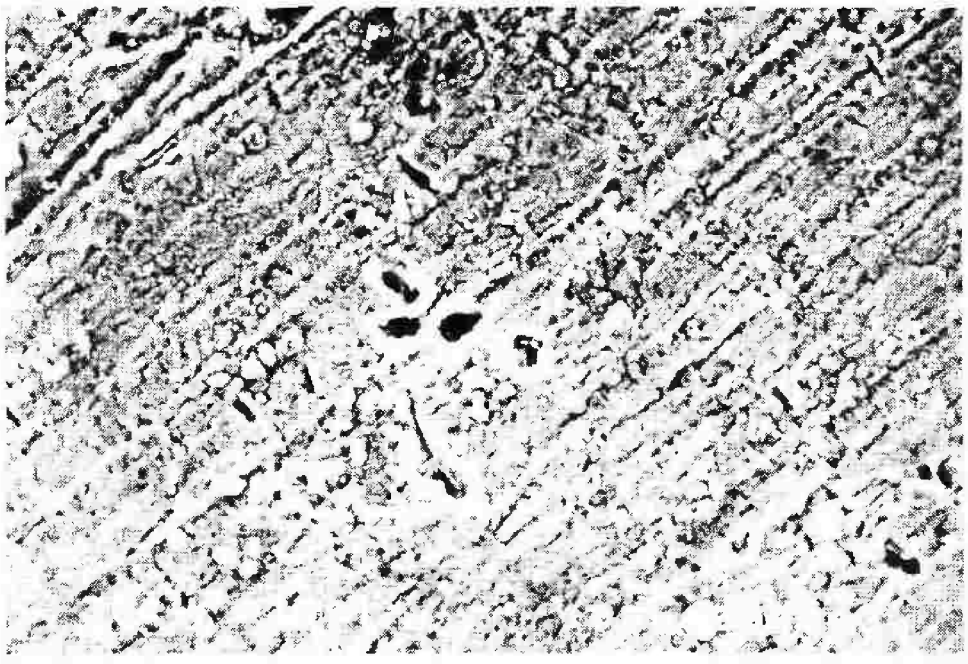


Fig.(42) : scanning electron micrographs of carbon steel sample after immersion in 1M HCL solution containing 500 ppm of inhibitor (I) a: X = 750 b: X = 2000

a



b

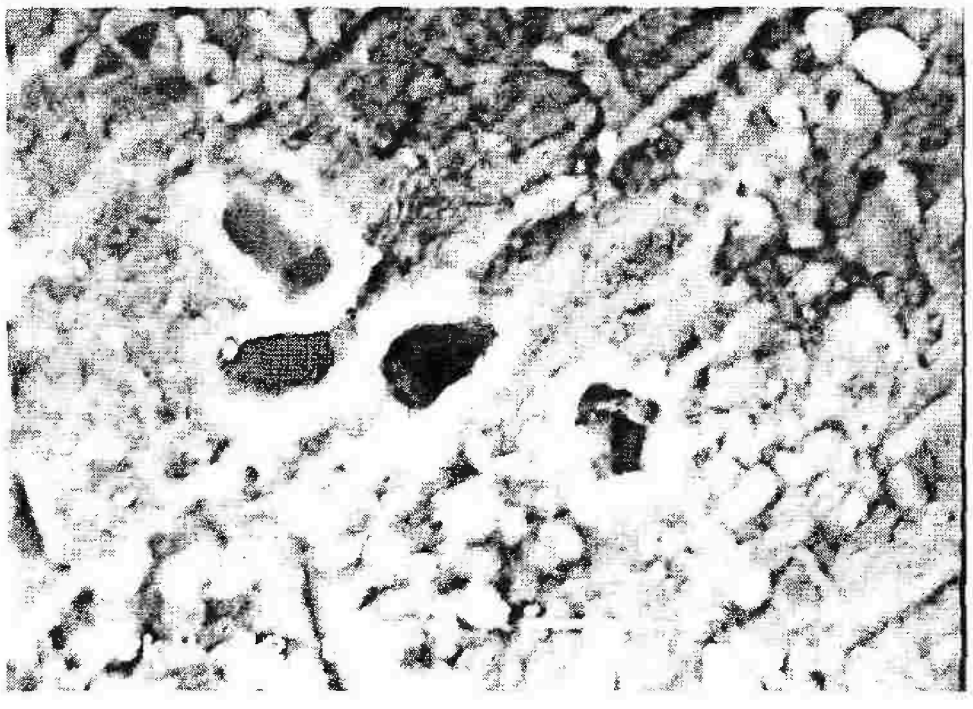


Fig.(43) : scanning electron micrographs of carbon steel sample after immersion in 1M HCL solution containing 500 ppm of inhibitor (II) a: X = 750 b: X = 2000

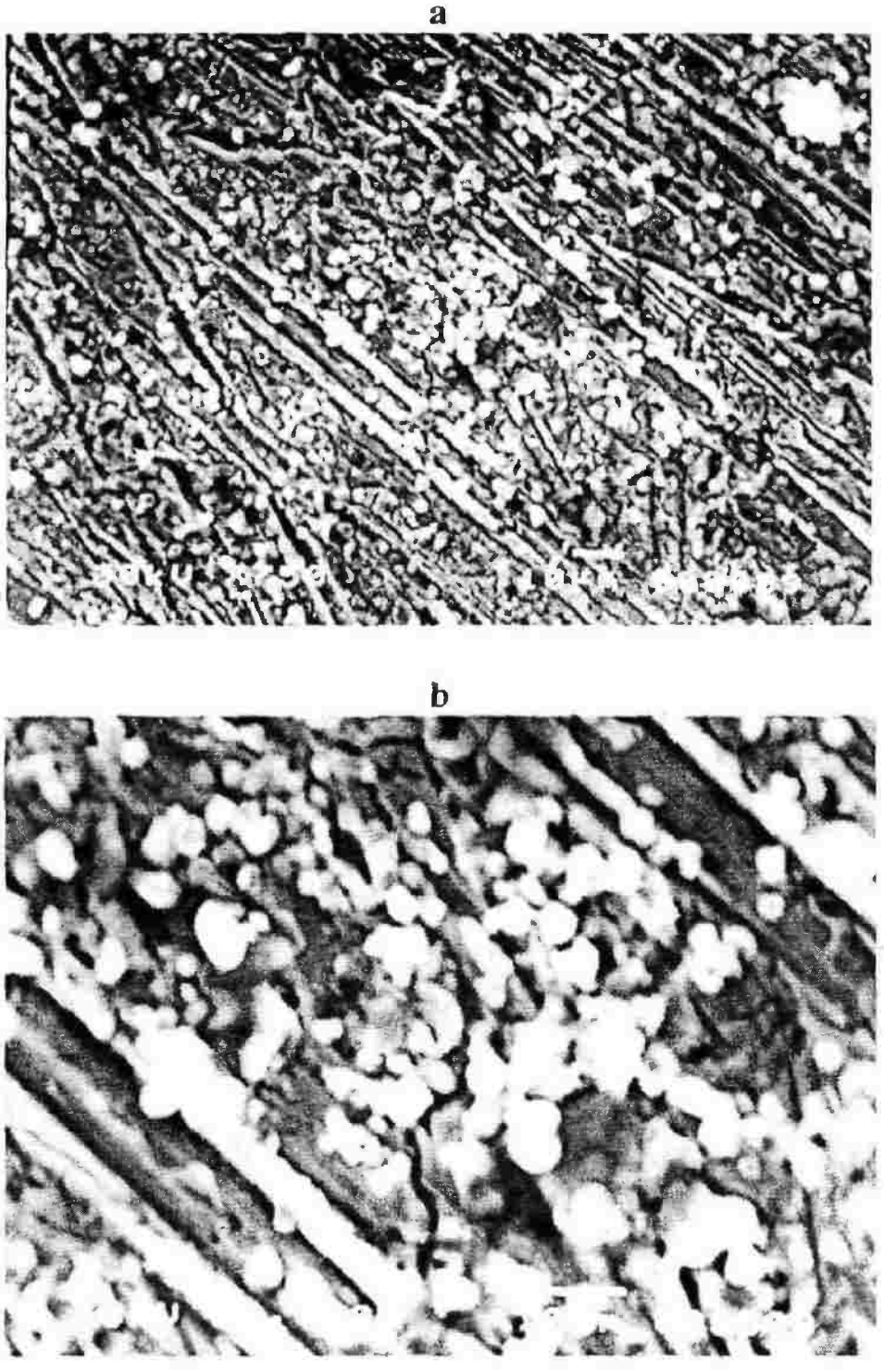


Fig. (44) : scanning electron micrographs of carbon steel sample after immersion in 1M HCL solution containing 500 ppm of inhibitor (III) a: X = 750 b: X = 2000

Table (21): inhibition efficiency of organoamides derivatives I, II and III inhibitors at different concentrations as determined by weight loss measurements at 298° K

Conc. (ppm)	Percentage inhibition efficiency (I %)		
	I	II	III
100	46.17	73.23	81.04
200	64.08	76.95	82.84
300	72.56	81	84.01
400	75.61	85.13	85.50
500	77.69	86.98	86.61
600	80.03	89.59	92.19

Table (22): inhibition efficiency of organoamides derivatives I, II and III inhibitors at different concentrations as determined by polarization measurements at 298° K

Conc. (ppm)	Percentage inhibition efficiency (I %)		
	I	II	III
100	48.21	73.19	80.28
200	61.55	75.94	81.98
300	72.45	81.35	83.91
400	78.19	84.90	84.20
500	79.21	85.84	84.59
600	79.47	87.25	91.01

Table (23): inhibition efficiency of organoamides derivatives I, II and III inhibitors at different concentrations as determined by (EIS) measurements at 298° K

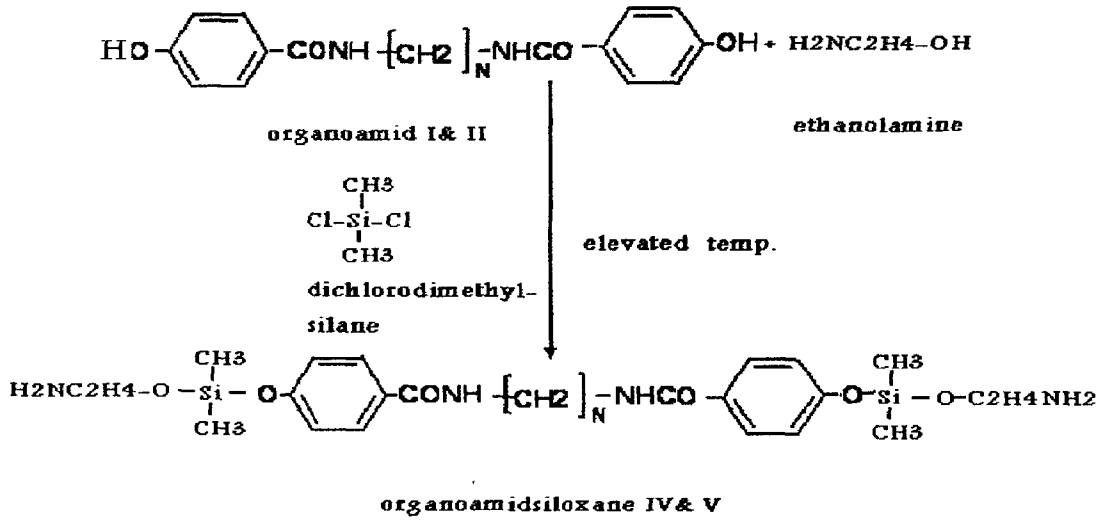
Conc. (ppm)	Percentage inhibition efficiency (I %)		
	I	II	III
100	43	72.6	76.60
200	54.9	73.3	80.00
300	72.6	75.3	82.30
400	73.8	80	84.00
500	80	84	86.90
600	80.4	88	90.50

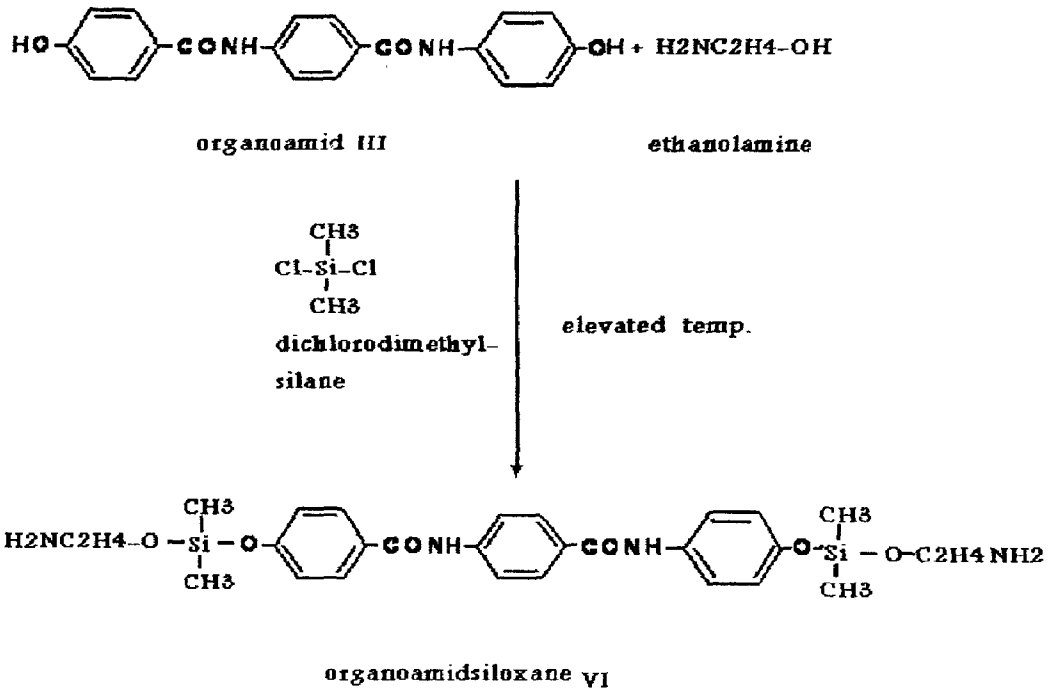
III. 8- Novel Organoamide Siloxane Derivatives IV, V and VI Compound as Corrosion Inhibitor for Petroleum C. Steel in HCl

In this chapter prepartion of novel organoamide siloxane derivatives IV, V and VI compounds are prepared and confirmed by FT.IR and ^{1}HNMR. The measurement results of them as corrosion inhibitors for carbon steel alloy in electrolyte of 1.0 M HCl solution were obtained by applying the different techniques, which represented in deals. Moreover the interconnection matching, agreement and disagreement...etc., between the output of the different applied techniques should be discussed with the protection mechanism.

III-8.1.Synthesis of Different organoamide siloxane IV, V and VI derivatives Compound.

The different compounds of organoamide siloxane IV, V and VI derivatives were prepared in free solvent. The reactions were carried out by the reaction of organoamide derivatives I, II and III compounds, respectively, with dichlorodimethylsiloxane and ethanolamine at elevated temperature as following equations: -





The products of the organoamidesiloxane derivatives IV, V and VI were purified and confirmed by FT.IR and ^{1}HNMR techniques.

III.9. FT.IR spectroscopy analyses

The structures of the product compounds IV, V and VI were confirmed by using FT.IR spectroscopy. A representative infrared spectral of organoamide siloxane derivatives compound V is shown in Fig. (45) aliphatic amide siloxane compound as example and compound VI as aromatic is shown in Fig. (46), respectively.

Fig. (45) showed the FT.IR spectrum for aliphatic amide siloxane V. The characteristic bands appeared at 504,532,550, 814,828,1021 and 1069 cm^{-1} represented the bending and stretching vibration for Para substituted of aromatic compound, the band at 745 cm^{-1} stretching vibration for aliphatic -CH_2- groups, the bands at 1258 and 1401 cm^{-1} for stretching vibration of – CONH- groups, the bands appear at 1475 and 2854 cm^{-1} for stretching vibration of -CH_2- groups,

the bands at 1163 , 1150,1591 and 2927 cm^{-1} for stretching vibration of Ph –C=O- group. And the bands appear at 3068 and 3346 cm^{-1} for stretching vibration of –OH and –NH group respectively.

Fig. (46) Showed the spectrum of aromatic amide siloxane compound VI. The characteristic bands appeared at 514, 822, 1015 and 1098 cm^{-1} bending and stretching vibration for *p*-substituted aromatic. The bands at 1261 and 1400cm^{-1} for stretching vibration of –CO-NH- The bands at 1517,2963 cm^{-1} for stretching vibration of carbonyl aromatic group HN-CO-Ph and the bands at 3144 and 3378.15 $cm^{-1}$for stretching vibration of –OH and –NH groups respectively.

III. 10. ^{1}HNMR spectroscopy analyses.

The ^{1}HNMR spectra of compounds V and VI are shown in Figs (47, 48), as example. It is shown that the signal was splitting octet at chemical shift δ=7.175- 7.114 for hydrogen proton of aliphatic hydrocarbons. Its deshelding due to the attachment by hetero, N, atoms at tow terminals as amide groups, a splitting quartet at chemical shift δ= 6.75-6.721 for hydrogen proton of phenyl ring, a splitting broad single signal for hydrogen proton of ρ substituted –OH group for aromatic ring at chemical shift δ= 3.523, and was shifted a splitting strong sharp single signal for hydrogen proton of ρ substituted –NH group for aromatic ring at chemical shift δ= 2.493, δ= 1.297 for hydrogen proton of (S, 16H, 8CH2) signal for hydrogen proton of Si – CH_3 at chemical shift 0.189 for compound (V)and at chemical shift 0.09 for compound (VI)

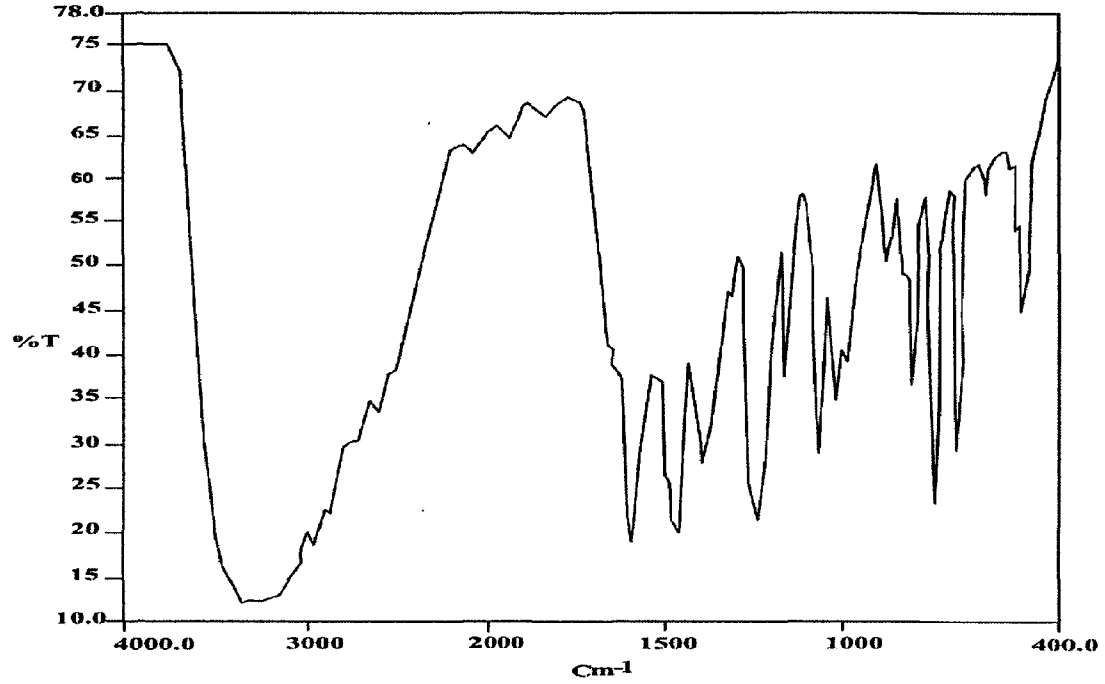


Fig.(45): I.R spectra of compound (V) as example of aliphatic organoamide siloxane

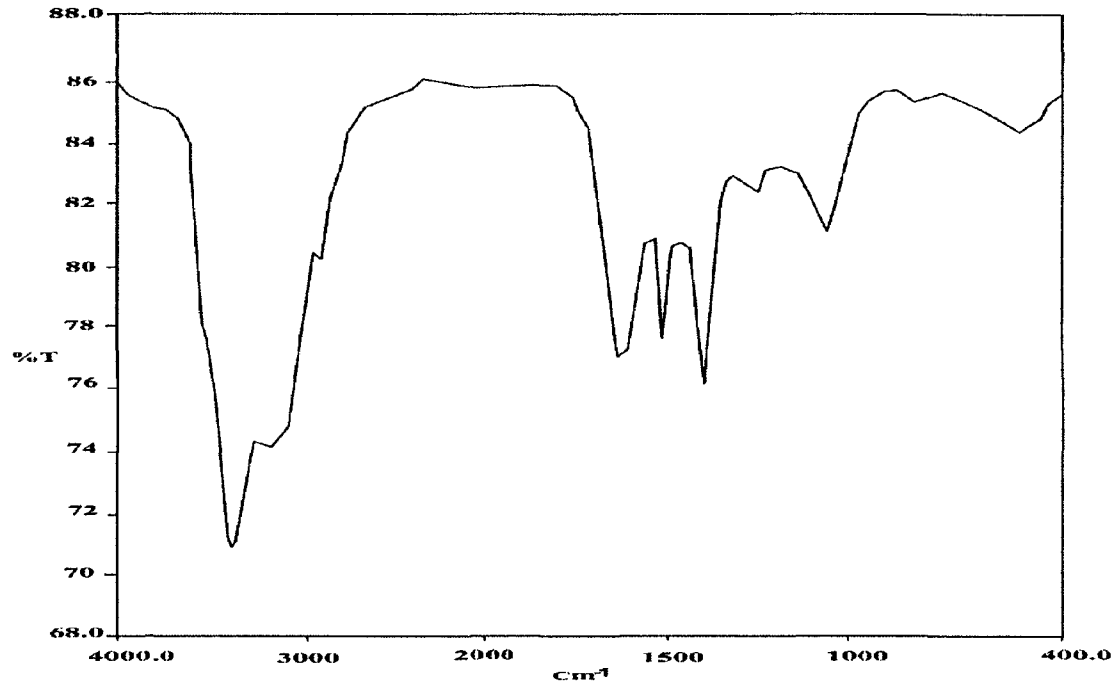


Fig. (46): I.R spectra of compound (VI) as example of aromatic organoamide siloxane

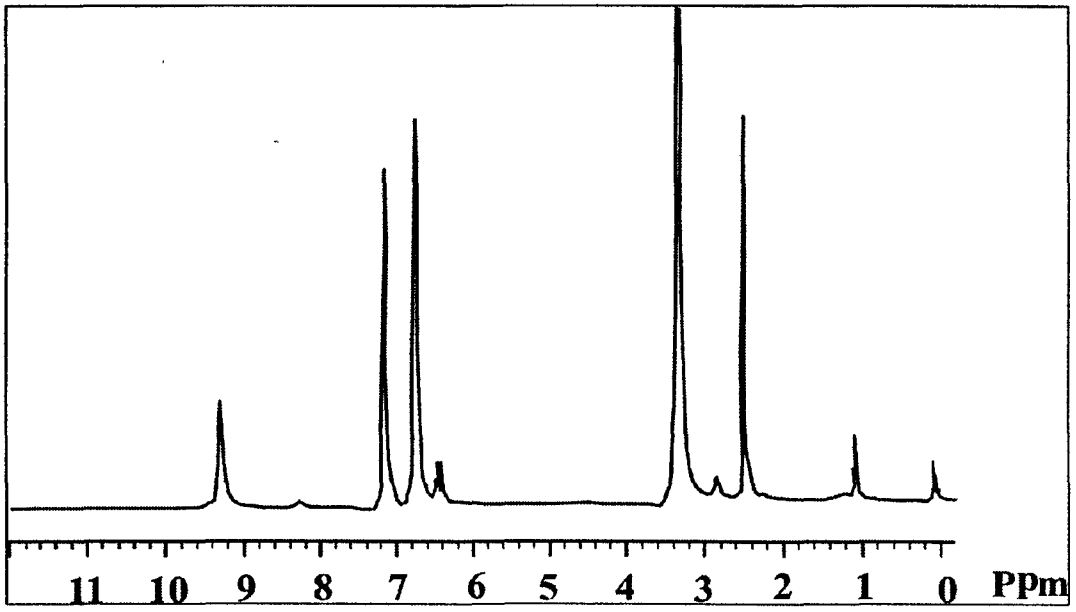


Fig.(47): ^{1}HNMR spectra of compound (V) as example of aliphatic organoamide siloxane

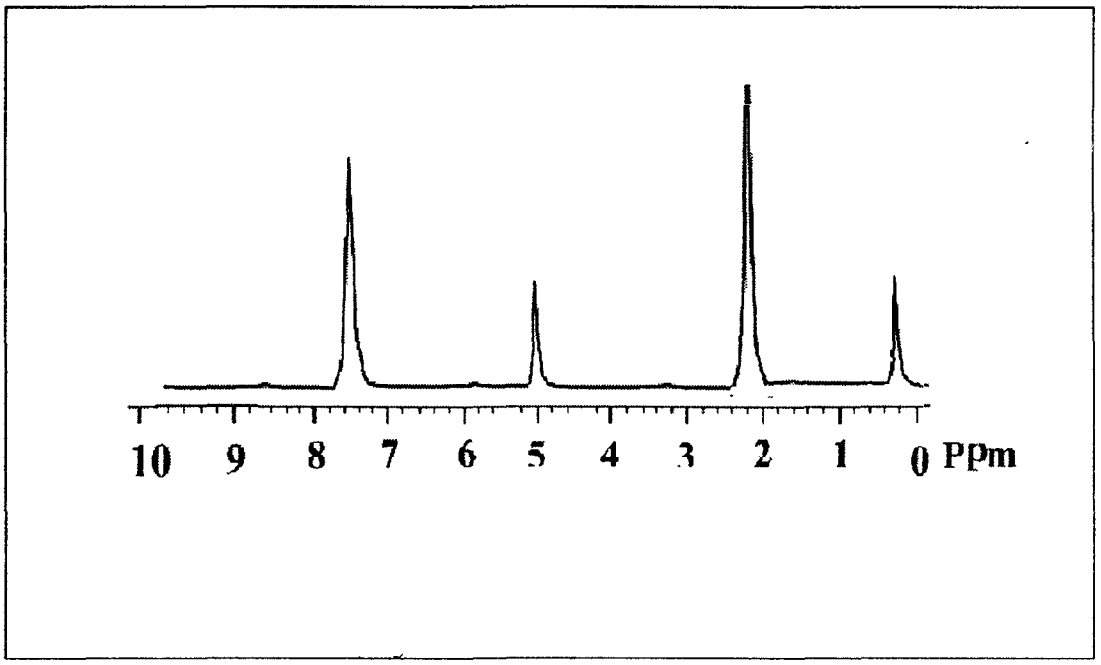


Fig.(48): ^{1}HNMR spectra of compound (VI) as example of aromatic organoamide siloxane

III.11. The evaluation of prepared organoamide-dimethylsiloxane derivatives (IV, V and VI) as corrosion inhibitor for carbon steel alloy in different concentrations of aggressive hydrochloric acid solutions.

The evaluation of the influence of prepared organo amide dimethylsiloxane derivatives IV, V and VI as corrosion inhibitor for carbon steel alloy in different concentration, 0.5, 1.0 and 2M hydrochloric acid solutions was carried out, respectively. The weight-loss technique was employed as the chemical testing technique. While the electrochemical polarization open circuit potential (OCP), potentiodynamic polarization (Tafel) and electrochemical impedance spectroscopy (EIS) were applied at definite concentration to evaluate the corrosion inhibitor parameters. The validity of the prepared organoamide dimethylsiloxane compound (IV, V and VI) derivatives was deduced as corrosion inhibitor for protection of petroleum carbon steel alloy. Finally, the scanning electron microscope (SEM) was applied for studies the surface morphology for the test specimen and the formation of inhibition films at definite experiment condition.

III.11.1 -Weight loss method

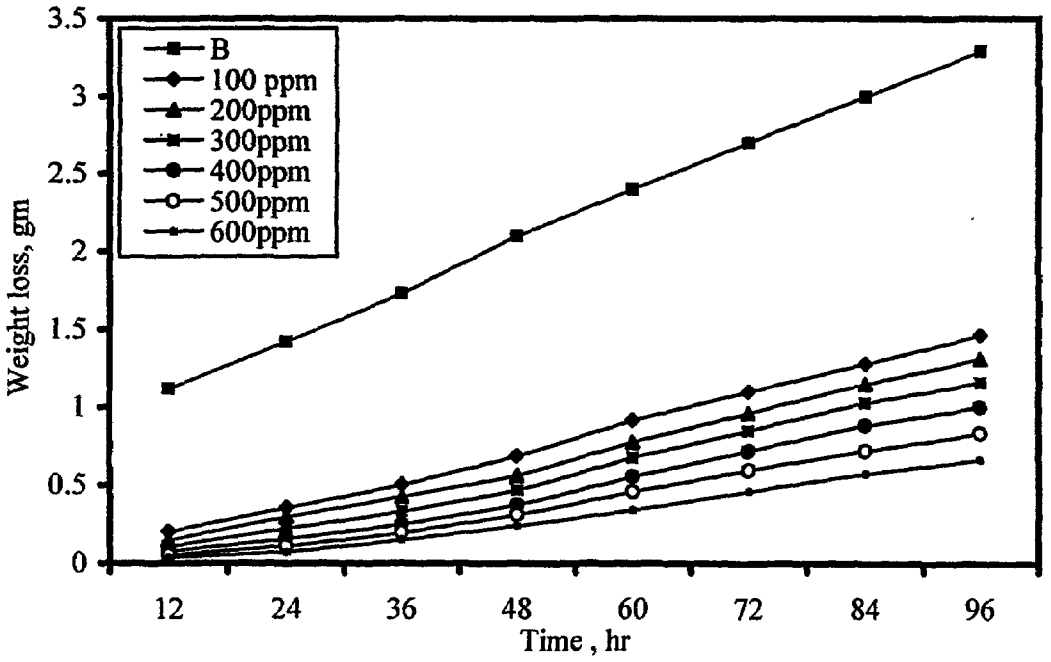
The corrosion behavior of a metal in an aqueous environment is characterized by the extent to which it dissolves in the solution. The degree of dissolution, of course, dependent on the surface area of the metal exposed, concentration of aggressive media and the time of exposure; hence the amount of corrosion is given with respect to area and time. The resulting quantity, corrosion rate, is thus a fundamental measurement in corrosion science. Corrosion rates, surface coverage area and inhibitors efficiency were evaluated by measuring the weight of a specimen before and after immersion (exposure) in aggressive, 0.5, 1.0 and 2M HCl acid solutions, respectively, the 100, 200, 300, 400, 500 and 600ppm as concentration of the prepared organoamide dimethylsiloxane compounds (IV, V and

VI) derivatives at room temperature, the period time for immersion of specimens were studied at 12, 24, 36, 48, 60, 72, 84 and 96 hr., respectively, and applying the equations (II.1and II.2). The weight-loss method was usually preferred because the loss quantities are directly related to the extent of corrosion and does not rely on any assumptions about reactions occurring during corrosion processes.

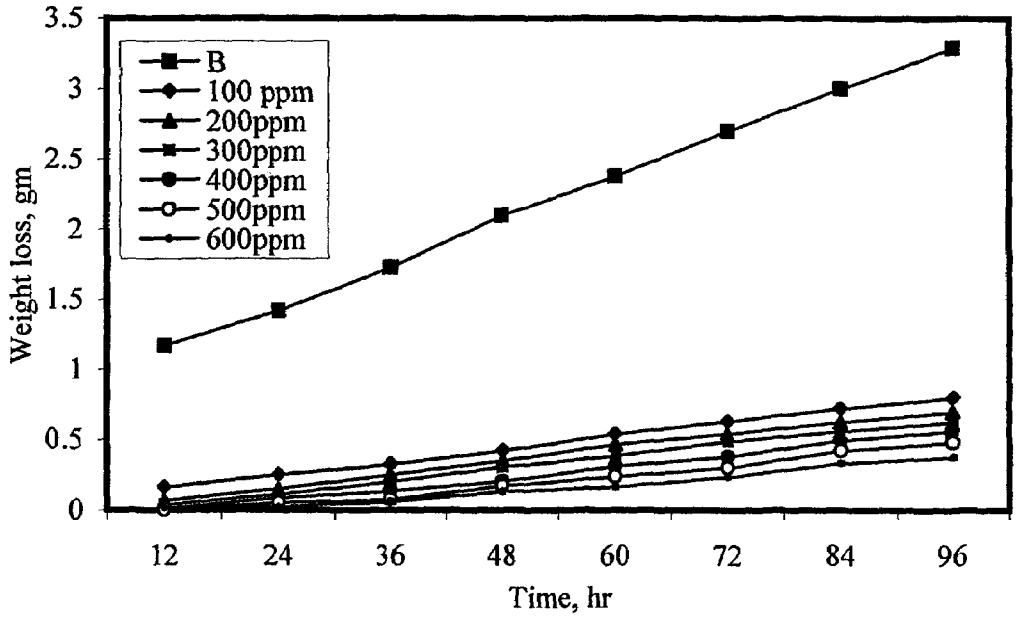
Figs. (49-57) show the weight loss versus time curves for carbon steel alloy in 0.5, 1.0 and 2.0 M hydrochloric acid solution in the absence and presence of different concentrations of prepared organoamide dimethylsiloxane (IV, V and VI) derivatives. As shown from these Figures, by increasing the concentration of these derivatives, the weight loss of carbon steel specimens are decreased respect to blank specimen. This means that the presence of these derivatives are retarded the corrosion of carbon steel (dissolution) in 0.5, 1.0 and 2.0M hydrochloric acid, respectively, or in other words, these compounds act as inhibitors. Also, one can be deduced that, from data the effective of the organoamide dimethylsiloxane derivatives higher than the organoamide derivatives. These observations due to the dimethylsiloxane groups and terminal aminoethyl groups. Moreover, one is deduced that the organoamide dimethylsiloxane derivatives V and VI nearly have the same efficiency.

The linear variation of weight loss with time in uninhibited and inhibited 0.5, 1.0 and 2M HCl indicates the absence of insoluble surface films during corrosion processes. In the first stage, the inhibitors are adsorbed on the metal surface and there after impede corrosion either by merely blocking the reaction sites anodic and catholic or by altering the mechanism of the anodic and cathodic partial processes. And also the formation films on the surfaces of specimens are respect to the chemisorptions process. This phenomenal are carried out due to the presence of many active polar of amide , silicon and hydroxyl groups. While these polar groups are having hetero N and O atoms. While the silicon atom has a vacant d orbital and

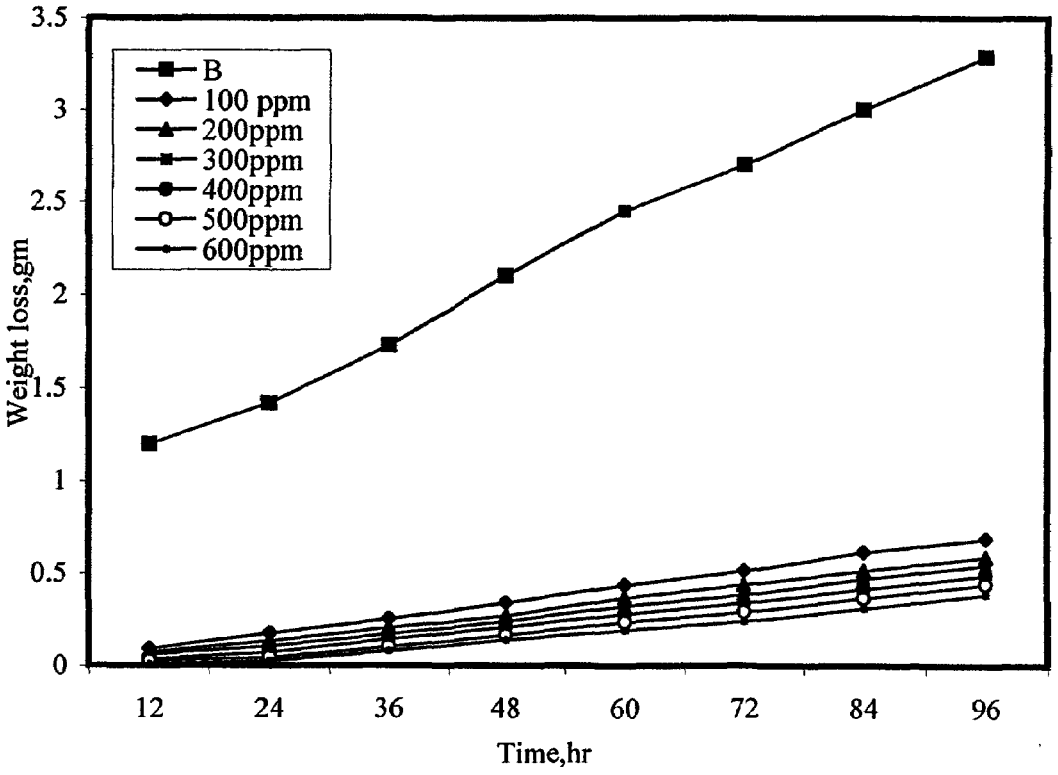
has tetra, penta and hexavalent also, and has high surface active agent. The O and N atoms are donating groups by lone pair of electrons and working as a ligand with iron. Therefore, these their groups are chaired by lone pair of electrons with pre-ionization of metal and could be adsorbed with the formation of a protective film on the surfaces of specimen. On the other hand the silicon atom can be chaired by vacant orbital. Moreover, the construction on this phenomenon also these films are protected the surfaces of carbon steel from any electro attack, due to the formation of films on the surfaces of specimen which they are semi complex and having a good adhesion and stability on the surface of metal, i.e. complete covering and protection of the metal surfaces.



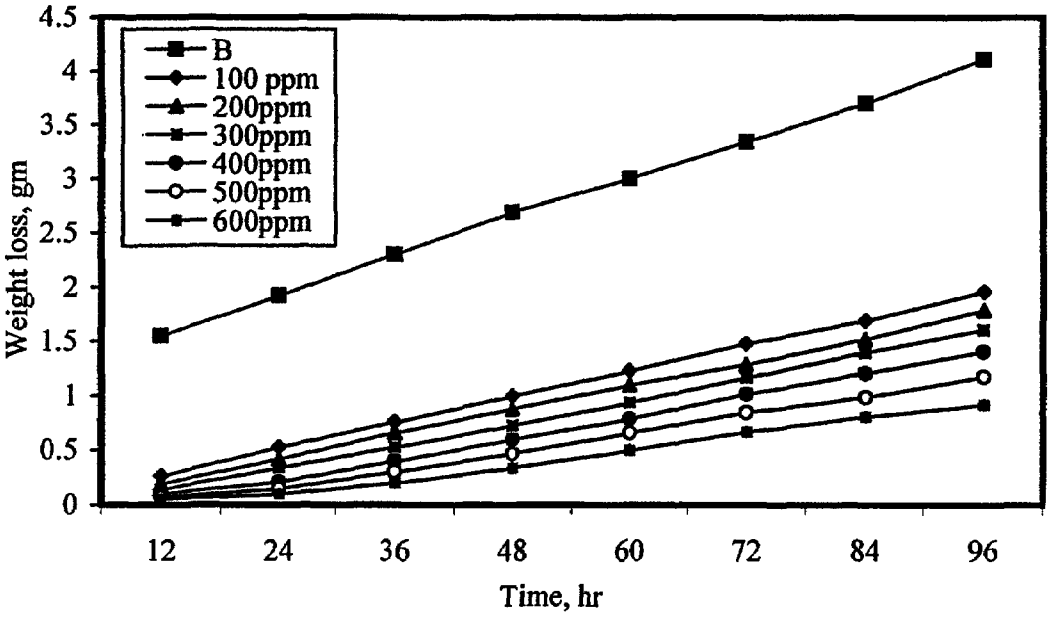
Fig(49): Weight loss-time curves for carbon steel alloy in 0.5 M HCl in absence and presence of differnet concentrations of compound (IV)



Fig(50): Weight loss-time curves for carbon steel alloy in 0.5 M HCl in absence and presence of differnet concentrations of compound (V)



Fig(51): Weight loss-time curves for carbon steel alloy in 0.5 M HCl in absence and presence of differnet concentrations of compound (VI)



Fig(52): Weight loss-time curves for carbon steel alloy in 1 M HCl in absence and presence of differnet concentrations of compound (IV)

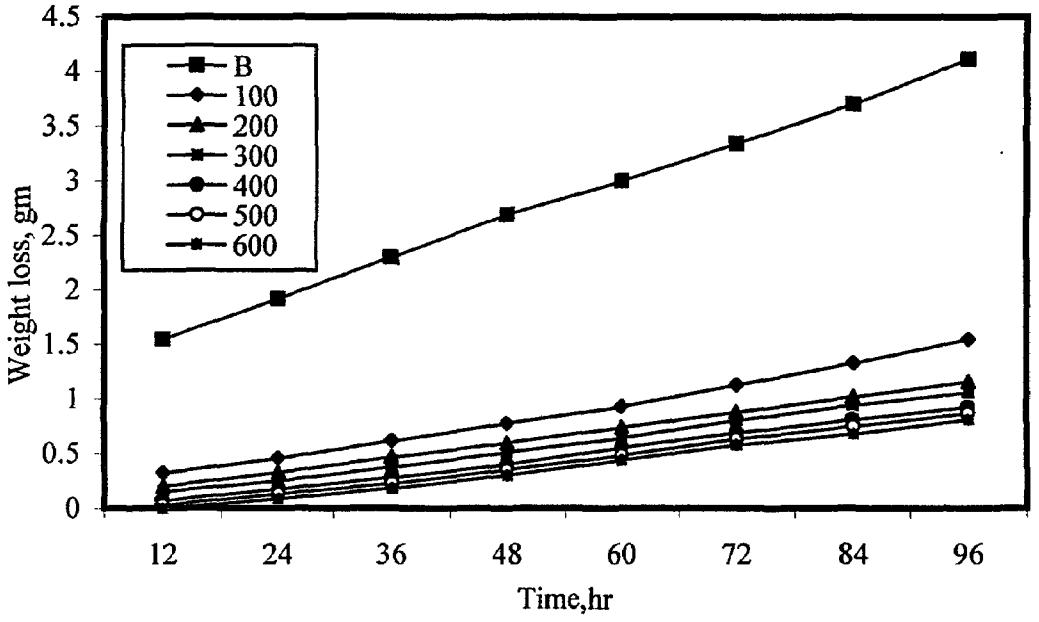
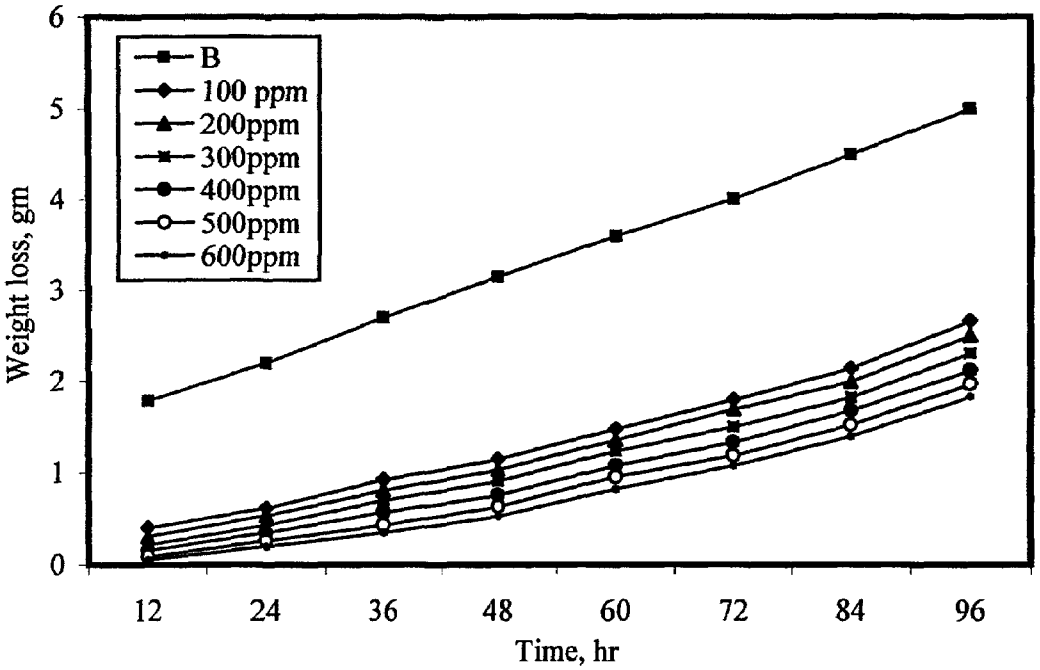


Fig.(53): Weight loss-time curves for carbon steel alloy in 1M HCl in absence and presence of differnet concentrations of compound (V)



Fig(57): Weight loss-time curves for carbon steel alloy in 2 M HCl in absence and presence of differnet concentrations of compound (VI)

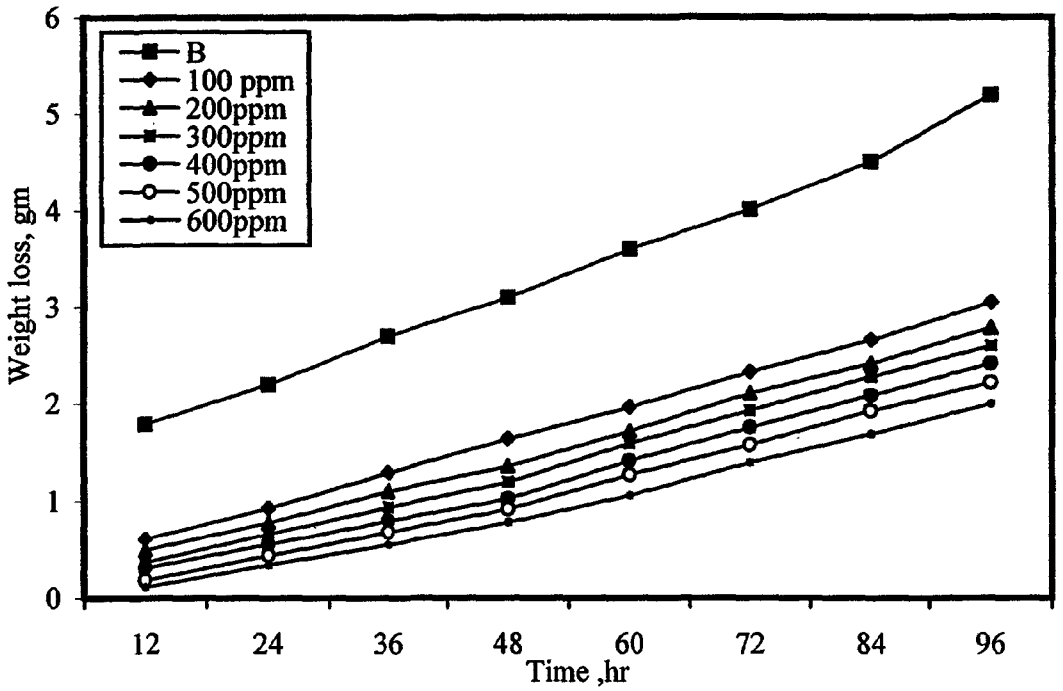


Fig.(55): Weight loss-time curves for carbon steel alloy in 2 M HCl in absence and presence of differnet concentrations of compound (IV)

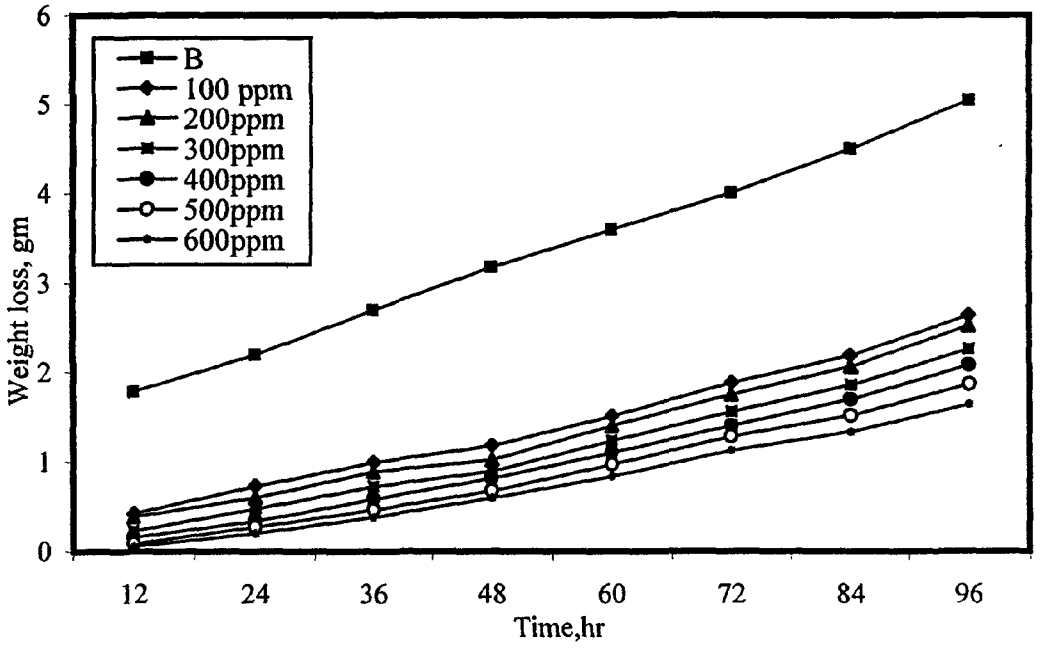
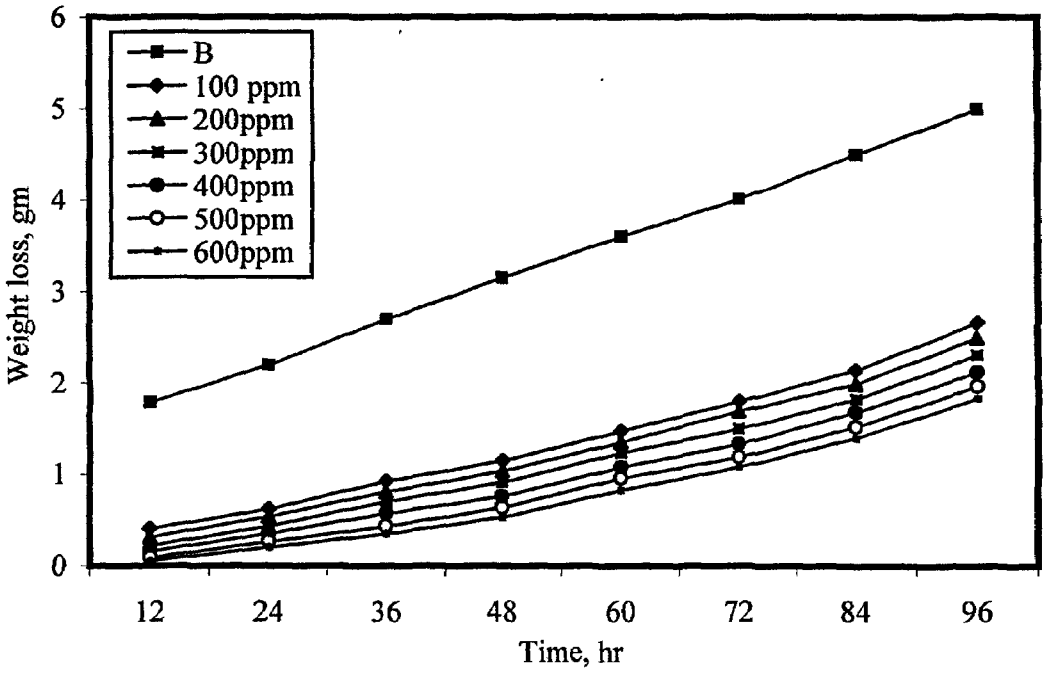


Fig.(56): Weight loss-time curves for caron steel alloy in 2 M HCl in absence and presence of differnet concentrations of compound (V)

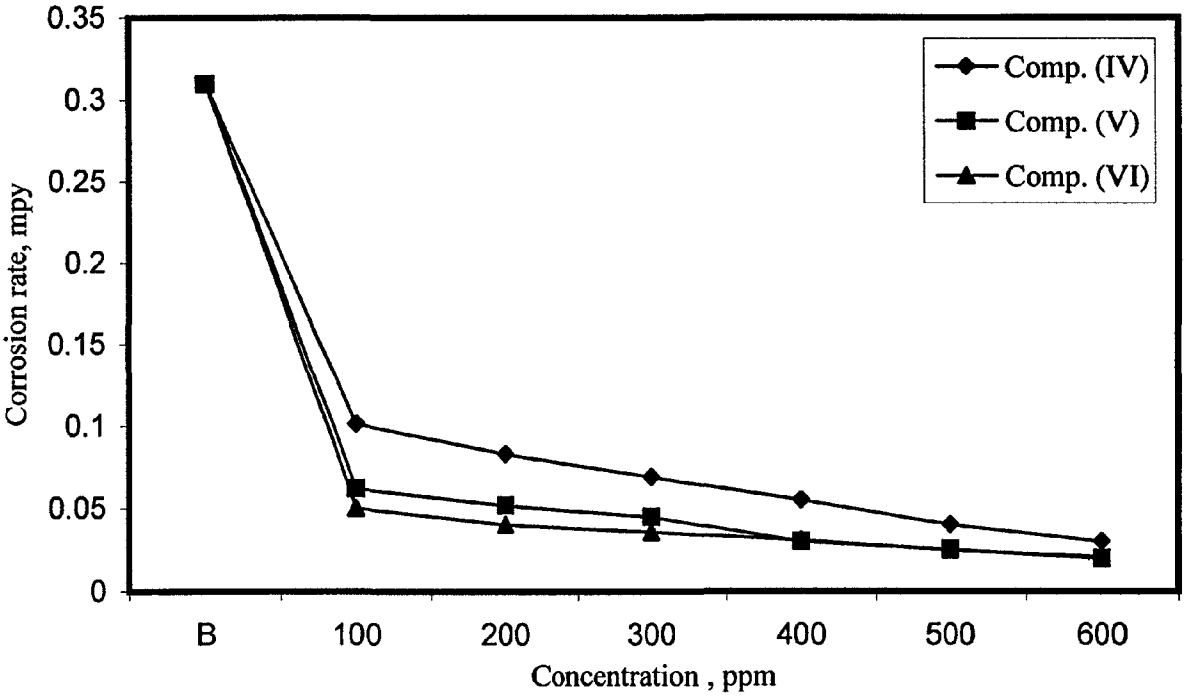


Fig(57): Weight loss-time curves for carbon steel alloy in 2 M HCl in absence and presence of differnet concentrations of compound (VI)

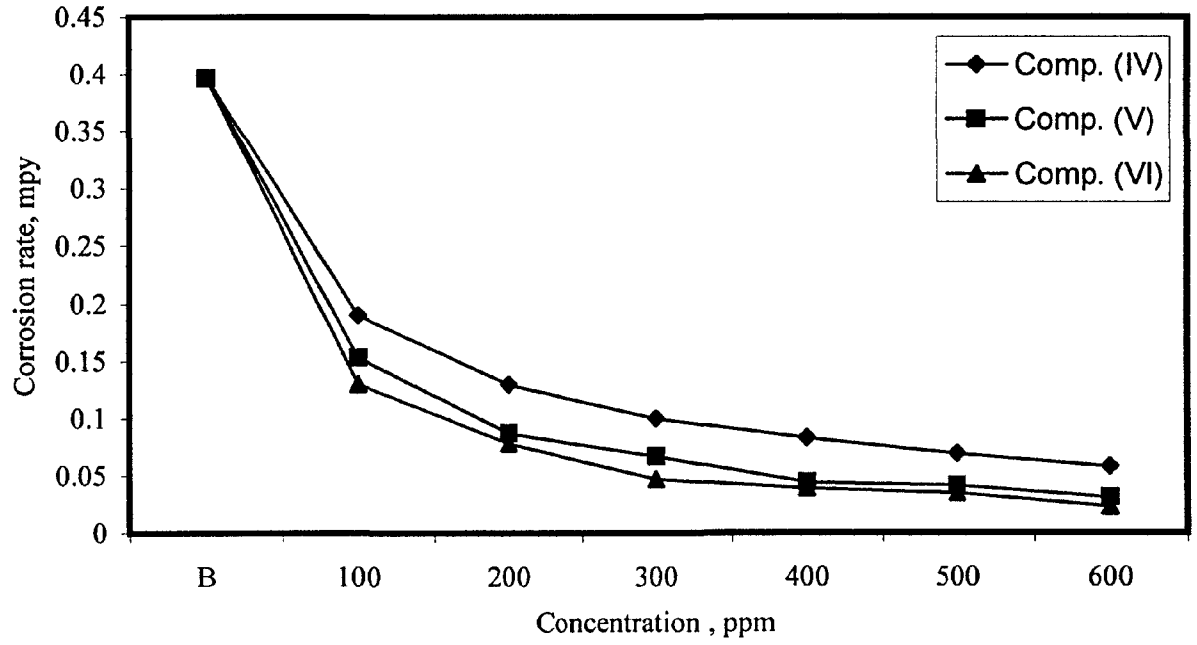
From the weight loss / time curves one should be conclude that, while the concentration of the organoamide dimethylsiloxane compounds IV, V and VI derivatives increased the weight loss of carbon steel specimens decreased in 0.5,1.0 and 2M HCl, respectively. This means that the presence of these compounds retard the corrosion (dissolution)of carbon steel in HCl acid media, i, e., the organoamide dimethylsiloxane compounds IV, V and VI derivatives acting as corrosion inhibitor.

Moreover the rate of corrosion (K) decreased with increasing of inhibitor concentration and increase with immersion time and stable at 36 hr.; these data are given in Figs. (58 – 60) and Tables (24 – 32), on the other hand the inhibition efficiency was increased with increasing inhibitor concentration. This fact suggests that the mechanism of inhibition by the inhibitor molecules may firstly chemically adsorbed on the carbon steel surface and cover the sites of the electrode surface. Then probably form monomolecular layers by forming a semi complex with iron and any ions on the steel surfaces. These layers protect steel surface from attack by chloride and any ions. From these results one should be concluded that the interaction between the molecules adsorbed at the metal surface happened.

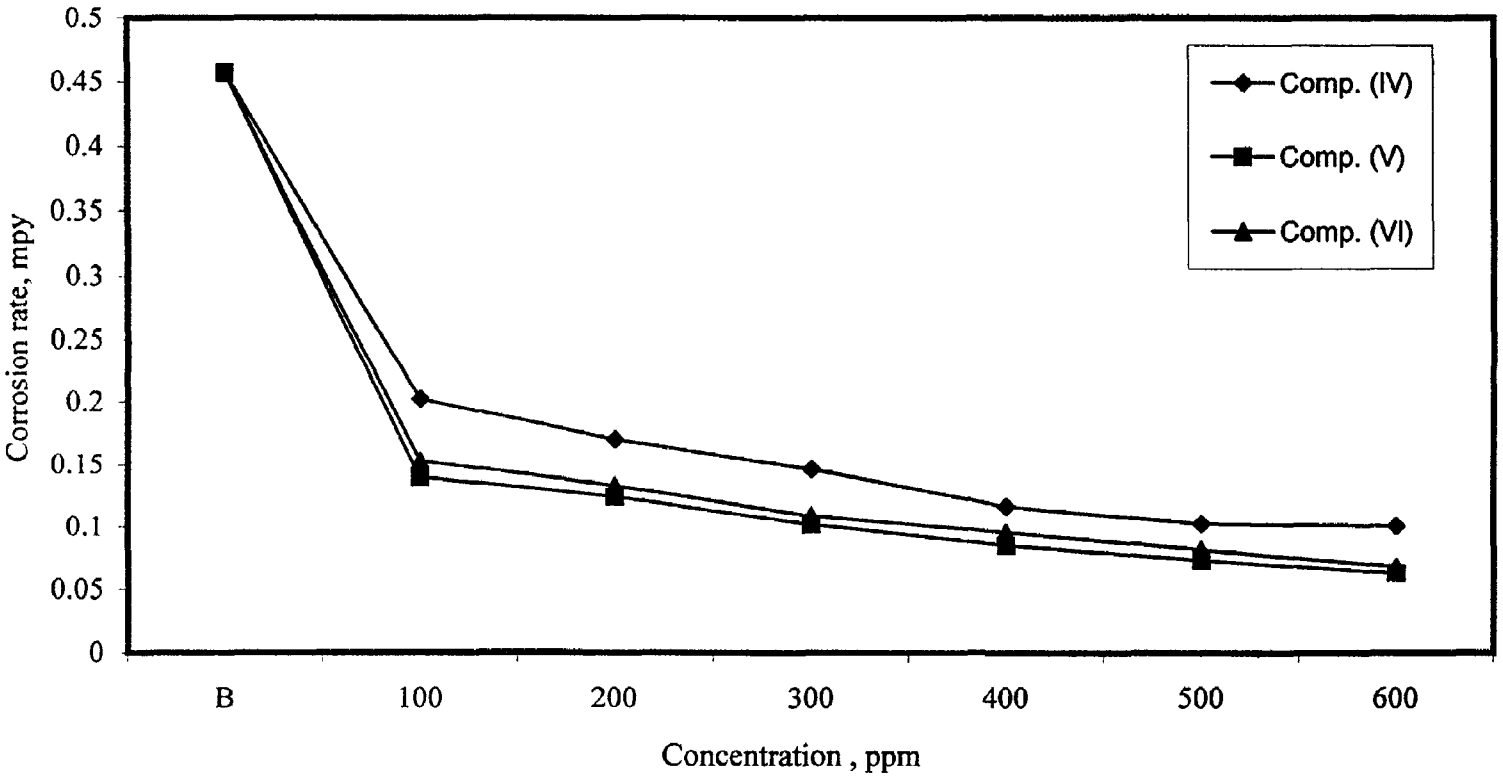
The linear variation of the weight loss with time in uninhibited and inhibited 0.5, 1.0, and 2.0 M HCl solutions indicates that the absence of insoluble surface of films are obtained during corrosion processes. In the absence of any surface films, the inhibitors are first adsorbed on to the metal surface and there after impede corrosion either by merely blocking the reaction sites (anodic and cathodic) or by altering the mechanism of the anodic and cathodic partial processes.



Fig(58): Effect of concentration of different inhibitors on the corrosion rate of carbon steel in 0.5 M HCl after 48 hr



Fig(59): Effect of concentration of different inhibitors on the corrosion rate of carbon steel in 1M HCl after 48 hr



Fig(60): Effect of concentration of different inhibitors on the corrosion rate of carbon steel in 2 M HCl after 48 hr

Table (24): Results data for corrosion inhibition of inhibitor compound (IV) at different concentrations and 298° K in 0.5 M HCl

Concentration (ppm)	Rate of corrosion (mpy)	Coverage surface (θ)	Efficiency (I%)
Blank	30.954	-	-
100	10.12	0.6728	67.28
200	8.28	0.7323	73.23
300	6.90	0.7769	77.69
400	5.52	0.8215	82.15
500	4.02	0.8698	86.98
600	2.99	0.9033	90.33

Table (25): Results data for corrosion inhibition of inhibitor compound (V) at different concentrations and 298° K in 0.5 M HCl

Concentration (ppm)	Rate of corrosion (mpy)	Coverage surface (θ)	Efficiency (I%)
Blank	30.95	-	-
100	6.21	0.7992	79.92
200	5.17	0.8327	83.27
300	4.48	0.8550	85.50
400	2.99	0.9133	90.33
500	2.53	0.9182	91.82
600	1.95	0.9368	93.68

Table (26): Results data for corrosion inhibition of inhibitor compound (VI) at different concentrations and 298°K in 0.5 M HCl

Concentration (ppm)	Rate of corrosion (mpy)	Coverage surface (θ)	Efficiency (I%)
Blank	30.95	-	-
100	5.03	0.8371	83.71
200	4.02	0.8698	86.98
300	3.56	0.8847	88.47
400	3.09	0.9000	90.00
500	2.47	0.9200	92.00
600	2.07	0.9330	93..30

Table (27): Results data for corrosion inhibition of inhibitor compound (IV) at different concentrations and 298° K in 1 M HCl

Concentration (ppm)	Rate of corrosion (mpy)	Coverage surface (θ)	Efficiency (I%)
Blank	39.65	-	-
100	14.74	0.6282	62.82
200	12.97	0.7434	74.34
300	10.76	0.7769	77.69
400	8.84	0.7881	78.81
500	6.92	0.8066	80.66
600	5.01	0.8178	81.78

Table (28): Results data for corrosion inhibition of inhibitor compound (V) at different concentrations and 298°K in 1 M HCl

Concentration (ppm)	Rate of corrosion (mpy)	Coverage surface (θ)	Efficiency (I%)
Blank	39.65	-	-
100	11.06	0.7063	70.63
200	7.37	0.8104	81.04
300	5.60	0.8401	84.01
400	4.42	0.8513	85.13
500	4.17	0.9048	90.48
600	3.11	0.9338	93.38

Table (29): Results data for corrosion inhibition of inhibitor compound (VI) at different concentrations and 298°K in 1 M HCl

Concentration (ppm)	Rate of corrosion (mpy)	Coverage surface (θ)	Efficiency (I%)
Blank	39.65	-	-
100	7.95	0.7992	79.92
200	6.80	0.8141	81.41
300	5.45	0.8624	86.24
400	4.74	0.8802	88.02
500	4.00	0.9182	91.82
600	2.94	0.9256	92.56

Table (30): Results data for corrosion inhibition of inhibitor compound (IV) at different concentrations and 298°K in 2 M HCl

Concentration (ppm)	Rate of corrosion (mpy)	Coverage surface (θ)	Efficiency (I%)
Blank	45.69	-	-
100	22.84	0.5	50
200	20.72	0.5464	54.64
300	17.66	0.6133	61.33
400	15.11	0.6691	66.91
500	13.58	0.7026	70.26
600	11.55	0.7472	74.72

Table (31): Results data for corrosion inhibition of inhibitor compound (V) at different concentrations and 298° K in 2 M HCl

Concentration (ppm)	Rate of corrosion (mpy)	Coverage surface (θ)	Efficiency (I%)
Blank	45.69	-	-
100	16.98	0.6282	62.82
200	15.11	0.6691	66.91
300	13.24	0.7100	71.00
400	12.06	0.7360	73.60
500	10.02	0.7806	78.06
600	8.83	0.8066	80.66

Table (32): Results data for corrosion inhibition of inhibitor compound (VI) at different concentrations and 298° K in 2 M HCl

Concentration (ppm)	Rate of corrosion (mpy)	Coverage surface (θ)	Efficiency (I%)
Blank	45.69	-	-
100	16.47	0.6397	63.97
200	15.28	0.6654	66.54
300	13.41	0.7063	70.63
400	11.20	0.7546	75.46
500	9.34	0.7955	79.55
600	7.81	0.8289	82.89

The inhibition efficiencies (%I) results of organoamide dimethylsiloxane derivatives IV, V and VI are determined by using the equation (II.2). Also, the efficiency of the organoamide dimethylsiloxane derivatives IV, V and VI are increased by increasing the duration immersion time and also the concentration. These fact results are shown in Tables (24 – 32)and Figs. (58-60) took place .From these observation data, one should be concluded that the formation of a multilayer and formation a completely barrier of protective films on the surfaces of specimen. On the other hand the coverage surface (θ) is calculated by equation (III.1), and the coverage area increased by increasing the concentration of inhibitors and immersion time in different aggressive acid solution media. These results are shown in Tables (24 – 32).

The data for the inhibition efficiency of organoamide dimethylsiloxane derivatives IV, V and VI are ordering as following:

$$\mathbf{VI \approx V > IV}$$

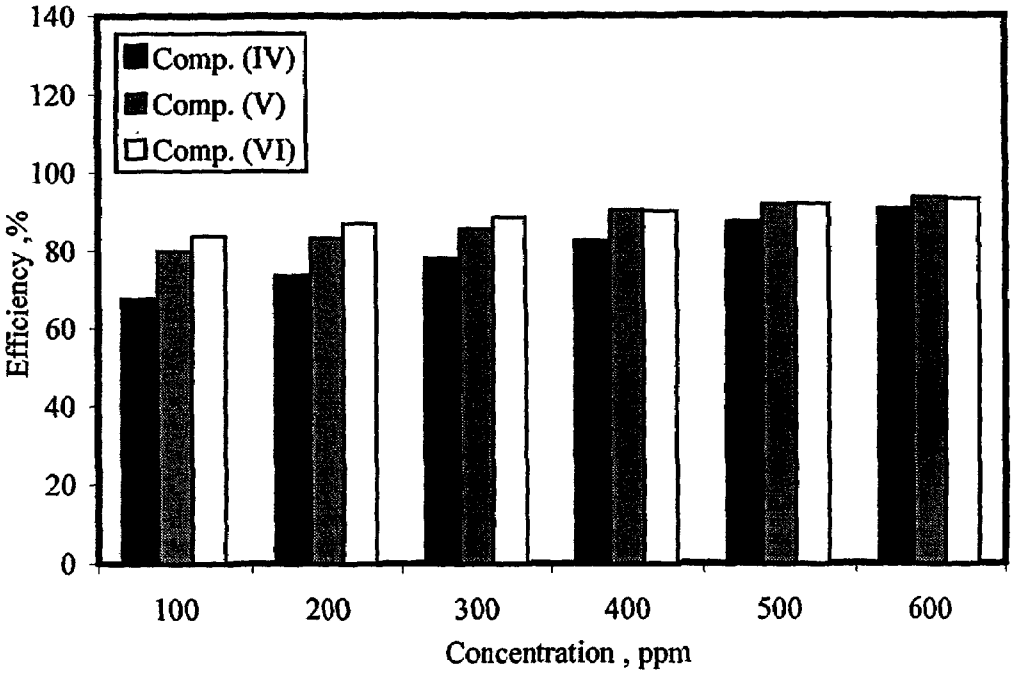
This order depend on the chemical structure of inhibitor, where the organoamide dimethylsiloxane derivatives VI inhibitor having the three aromatic ring (phenyl), two amide, siloxane and amino groups. These groups are having high mobility clouds of electrons. While the organoamide dimethylsiloxane derivatives IV and V inhibitors having the two aromatic rings (phenyl), two amide and siloxane with terminal amino groups, while the inhibitor V has long hydrocarbon chain more than IV.

Plots of the inhibition efficiency %I versus the concentration of organoamide dimethylsiloxane derivatives IV, V and VI in 0.5, 1.0 and 2.0 M HCl solutions for carbon steel alloy at 23.0 ± 2 °C are shown in Figs (61-63).

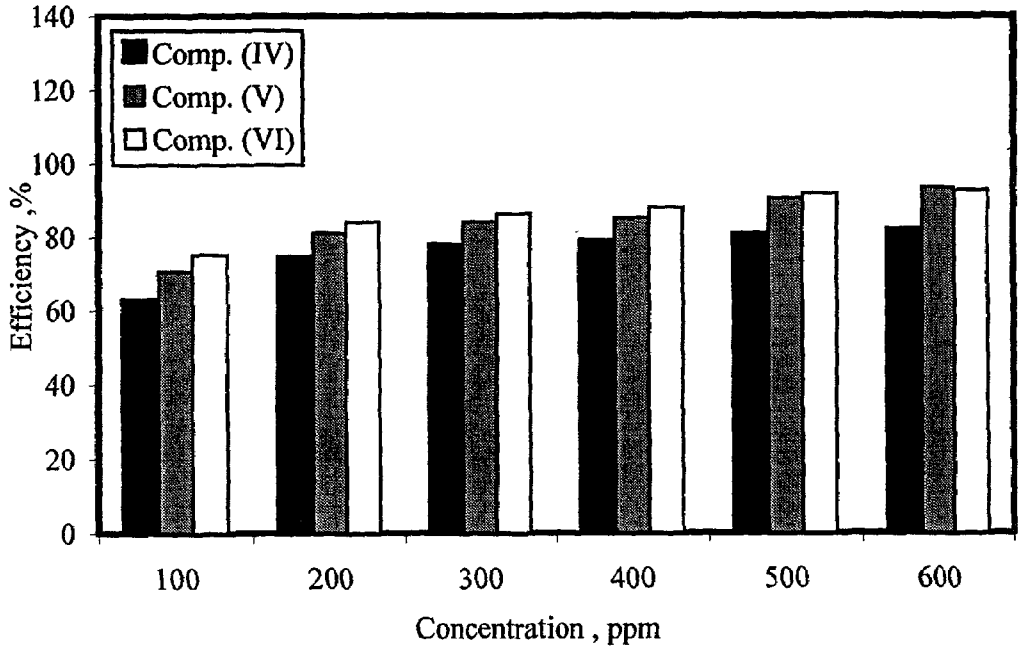
From the obvious Figs. , the % inhibitions increased as increasing the concentration of organoamide dimethylsiloxane derivatives IV, V and VI, also the order of inhibition efficiency increased as following:

$$\mathbf{VI \approx V > IV}$$

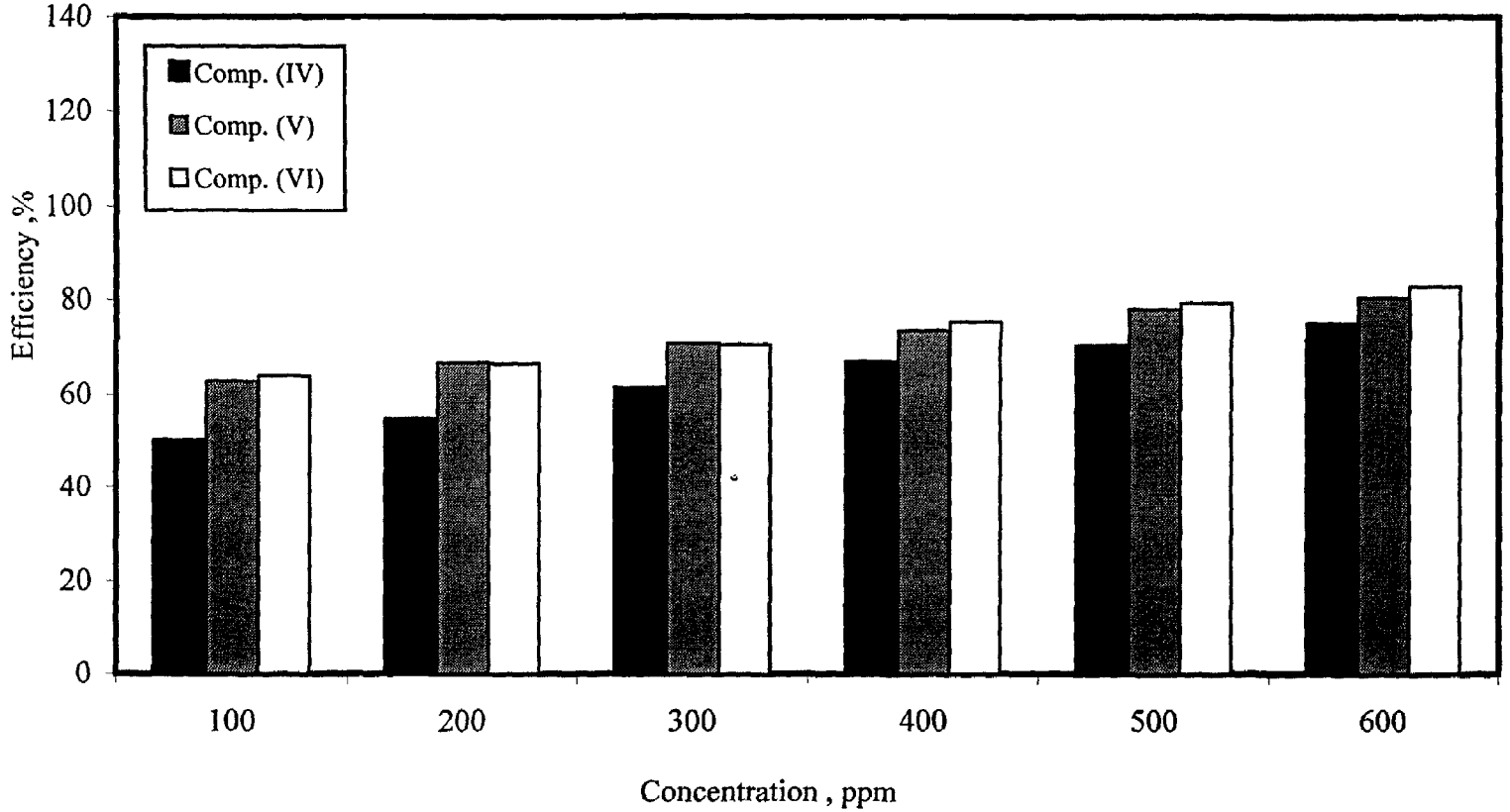
Plots of log θ / 1- θ vs. logarithm of concentration of organoamide dimethylsiloxane derivatives IV, V and VI inhibitors are illustrated in Fig. (64). All isotherm reasonably linear, in accordance with Langmiur adsorption isotherm, with slopes less unity. This deviation from unity may be attributed to the interaction of adsorbed species by mutual repulsion or attraction.



Fig(61): Effect of concentration of different inhibitors on the efficiency of carbon steel in 0.5M HCl after 48 hr



Fig(62): Effect of concentration of different inhibitors on the efficiency of carbon steel in 1M HCl after 48 hr



Fig(63): Effect of concentration of different inhibitors on the efficiency of carbon steel in 2M HCl after 48 hr

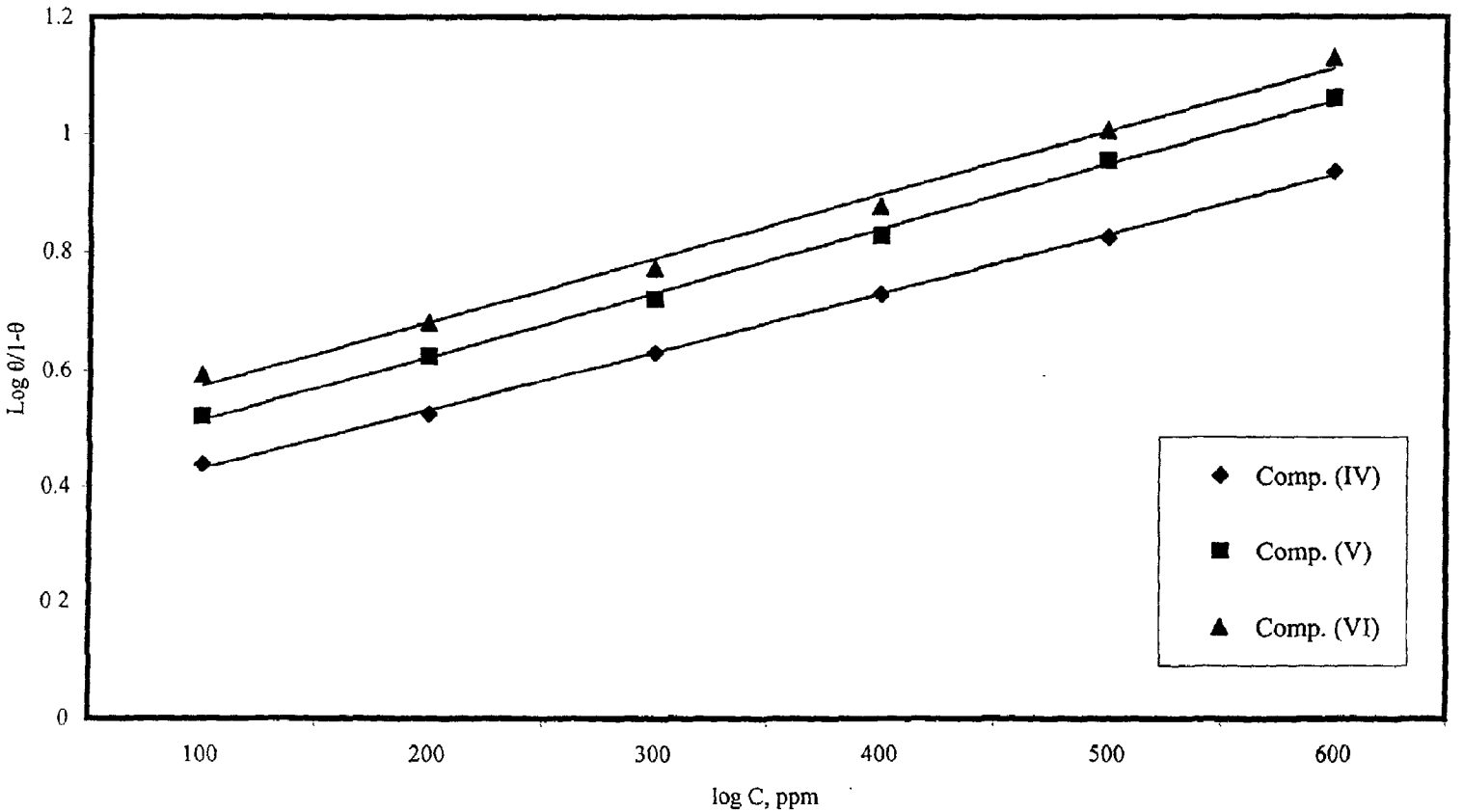


Fig. (64): dependence of Log θ/1-θ on logarithm of concentration for the inhibitors (IV- VI)

III.11-2-Studies of the effect of chemical structure of organoamide dimethylsiloxane derivatives IV, V and VI compounds on the efficiency.

The order of efficiency is depend on the chemical structure of the organoamide dimethylsiloxane derivatives IV, V and VI, inhibitors, where the organoamide dimethylsiloxane derivatives inhibitor VI having three aromatic (phenyl), two amide, two siloxane and two amino groups. These groups are having high mobility clouds of electrons, while the organoamide dimethylsiloxane derivatives, inhibitor IV and V having the two aromatic (phenyl), two amid, siloxane and amino groups. On the other hand also the inhibitor V has long hydrocarbon chain more than IV.

Tables (21-29) illustrate the weight loss , corrosion rate , surface area coverage and efficiency of the compounds IV, V and VI in 0.5 M HCl at ambient condition. From these tables the obtained data are indicated that , the inhibition efficiency increased by increasing the concentration of inhibitors. Also, the efficiency at concentrations 300, 400, 500 and 600 ppm are nearly the same, on the other hand the efficiency at period of time of immersion 24 hr nearly the same i.e. the change in efficiency are not remarkable. The stability of efficiency indicated by the stability of the formed thin protective films from the inhibitors on the surface of specimens. From the results we were showed that, the efficiency is increased from IV to VI, respectively. These results indicated that , the compound V has – CH_2 – groups more than the compound IV, where the center of hetero atoms N,O and siloxane groups are the same in two compounds. These phenomena indicated that, the long chain of hydrocarbon in compound V is more effective than the short chain in compound IV. On the other hand the phenyl group in compound VI is increased the efficiency due to the cloud of electrons between the phenyl groups and amide groups respective to this phenomena are cleared that, the aromatic

amides are high efficiency for corrosion protection than aliphatic amides.

Moreover, the effect of different temperature degrees on the efficiency of organoamide dimeyhylsiloxane compound IV, V and VI derivatives studied and also the thermodynamic properties of them. On the other hand the electrochemical polarization techniques (open circuit potential (OCP), potentiodynamic polarization, Tafel, and electrochemical impedance spectroscopy) are studied. Finally, the morphology of the formation inhibitor films on the surface of specimens was investigated by scanning electron microscope (SEM).

III.12.Effect of Temperature and Activation Parameters

The effect of temperature studied by the weight loss method in temperature range 308-338°K, in absence and presence of 500ppm for organoamide dimeyhylsiloxane compound IV, V and VI, respectively, the results of which are shown in Figs. (65-68). From the observation results in Figs. (65 - 68) , one should be concluded that, in the absence of inhibitor the corrosion rate is high increased with increasing of temperature, while in the presence of inhibitors the corrosion rate are decreased with increasing of the temperature. Therefore one should be concluded that, these compounds act as corrosion inhibitors in 1M HCl for carbon steel at low and high degree of temperatures. The increasing in the temperature has a reverse relationship with the percentage efficiency this means that the adsorption of different compounds on the metal surface was physicochemical adsorption.

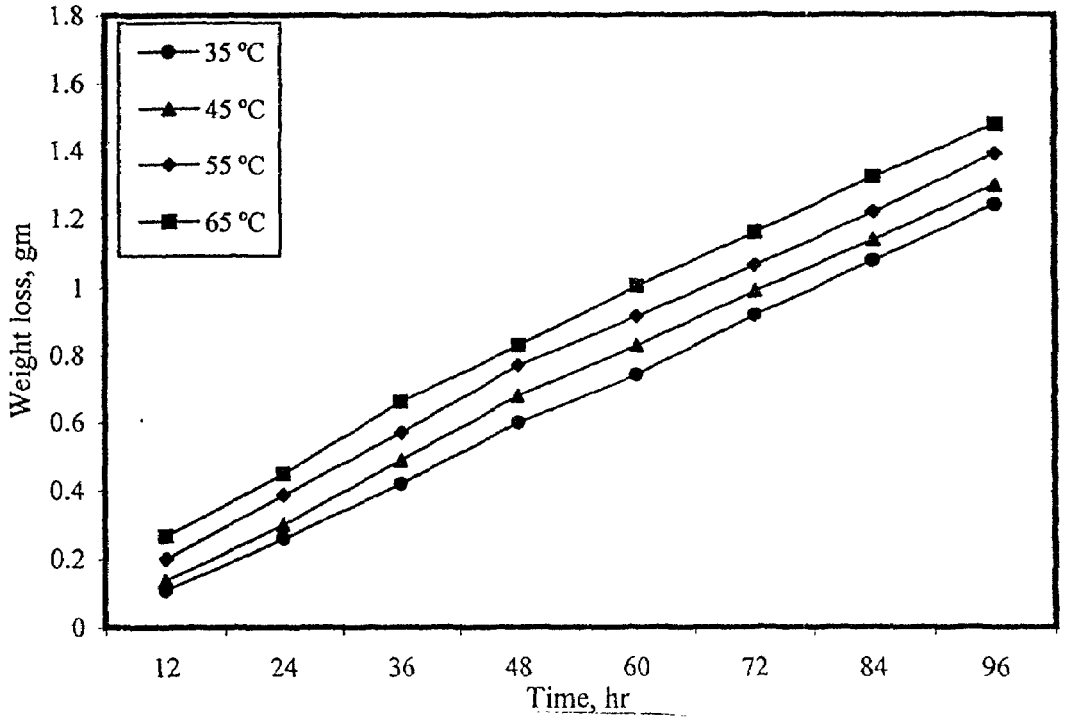


Fig. (65): Weight loss- time curves for carbon steel in 1M HCl in presence of 500 ppm of inhibitor (IV) at different temperatures

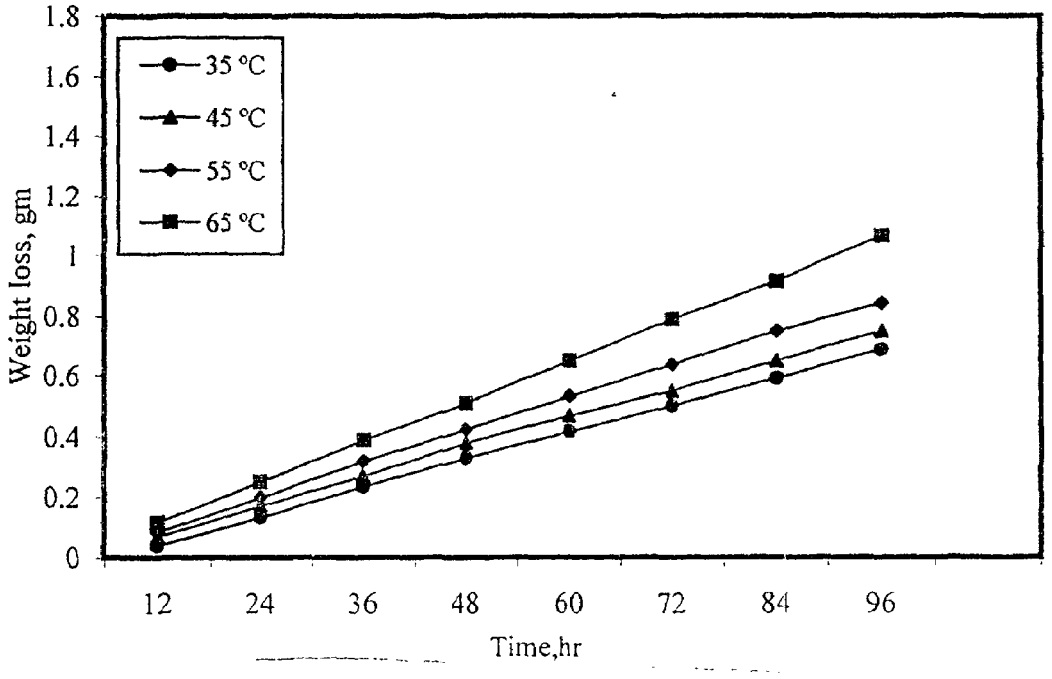


Fig. (66): Weight loss- time curves for carbon steel in 1M HCl in presence of 500 ppm of inhibitor (V) at different temperatures

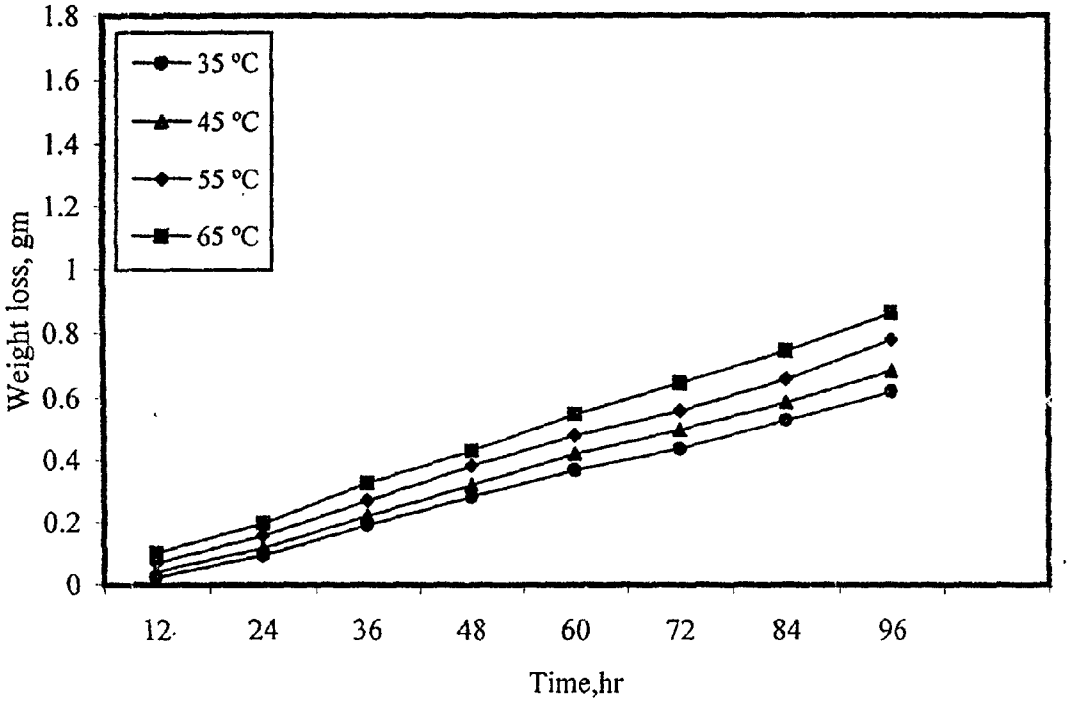
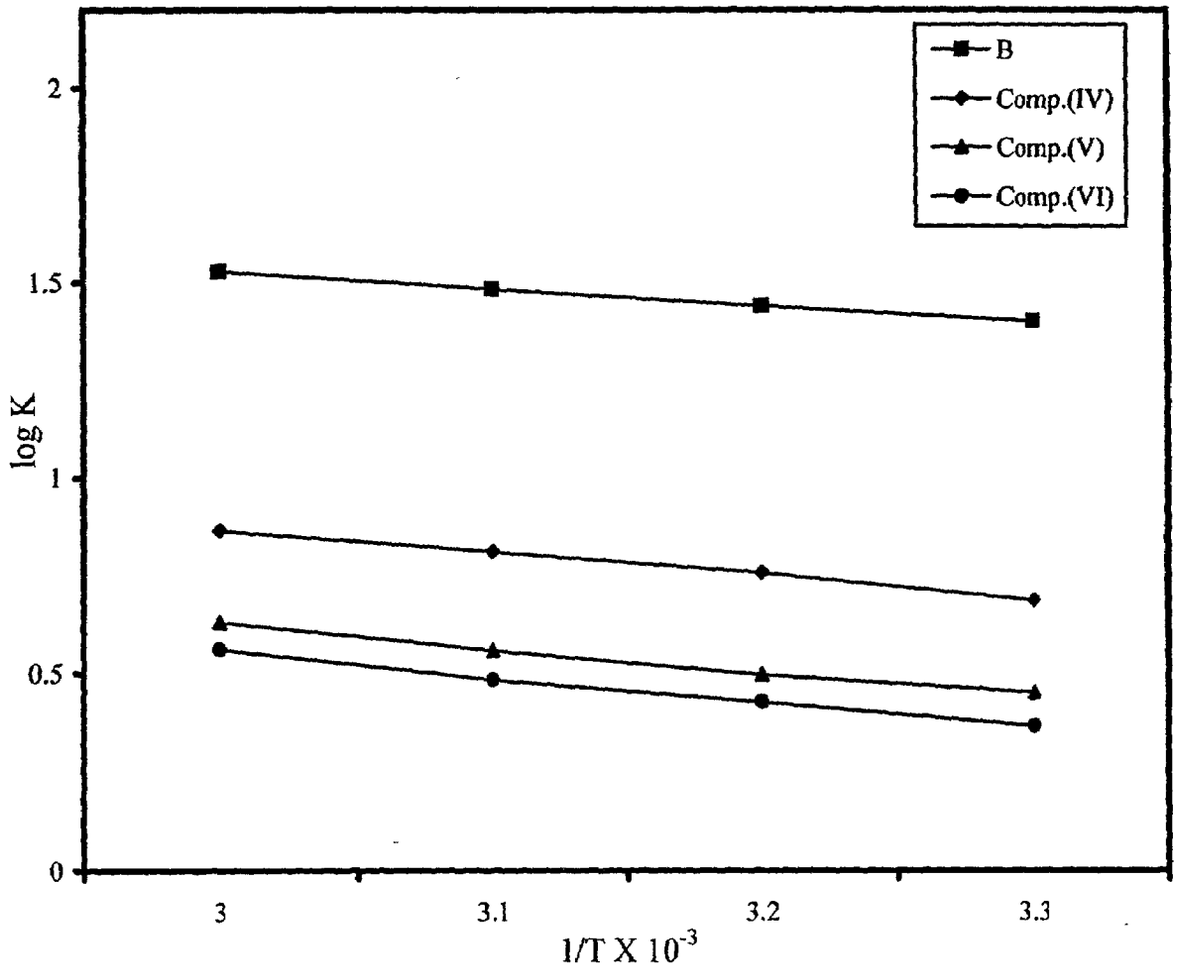


Fig. (67): Weight loss- time curves for carbon steel in 1M HCl in presence of 500 ppm of inhibitor (VI) at different temperatures

The values of corrosion rate obtained at different temperatures permit the calculation of the Arrhenius activation energy, Ea, This form of Arrhenius equation is applicable in this case, where the plot of, log corrosion rate of 500ppm for each compounds against the reciprocal of absolute temperature, (1/T) are shown graphically in Fig. (69).The values of the activation energies, E_a*, were calculated from the slopes of these lines. These values indicated that, the presence of organoamide inhibitor compounds increase the activation energy of the metal dissolution reaction and that the process is activation controlled, i.e., decreases the corrosion rate and increases the efficiency. Generally one could say that the nature of electrolyte and concentration of inhibitors are affected greatly on the activation energy for the corrosion process. So that, the addition of 500ppm of every one of the organoamide dimeyhylsiloxane compounds IV, V and VI, to the solution increased the activation energy (E_a*), as shown in Table (33).The extent of the increase was proportional to the inhibition efficiency of the inhibitor. These results are indicated that the energy barrier for the corrosion reaction increases in presence of these additives of inhibitors. This means that by addition of the inhibitor in the acid solution, the corrosion reaction could be further pushed far from to surface sites. These are characterized by higher values of activation energy E_a* indicating that carbon steel corrosion occurs at the uncovered part of the surface. Thus, adsorption of the inhibitor is assumed to occurs on the higher energy sites, the presence of inhibitor, which results in the blocking of the active sites, must be associated with an increase in the activation energy, E_a*.

The thermodynamic functions, entropy of activation, ΔS^*, enthalpy of activation, ΔH^* and free energy of activation, ΔG^* are calculated and tabulated in Table (33).Inspection of these data reveal that the values of ΔH^* and ΔS^* in the presence of the additives, increase over that of the uninhibited solution. This implies that energy barrier of the corrosion reaction in the



Fig(69): log K-1/T curves for carbon steel in 1M HCl in absence and presece of 500 ppm of inhibitor (IV- VI).

presence of inhibitors increases, which is expected. ΔS^* in the absence and presence of additives is larger and has negative values meaning that a decrease in disordering takes place in going from reactants to the activated complex[327] . It is evident that the ΔH^* has positive values and increase with increasing adsorption power of the used compounds, the magnitude of the values of ΔS^*, ΔH^* are characteristics of the occurrence a replacement process during adsorption of inhibitor molecules on the metal surface.

Table (33): Thermodynamic parameters for carbon steel alloy in 1M HCl in absence and presence of 500 ppm of inhibitor (IV-VI) at different temperature.
(ΔH^*, ΔG^*: KJ mol^{-1}; ΔS^*: KJ $mol^{-1}K^{-1}$)

Temp (K)	E*a , KJ	308	318	328	338
B 1MHCL					
ΔH^*	36.18	38.74	38.82	38.90	38.99
ΔG^*		52.11	53.54	54.93	56.32
$-\Delta S^*$		0.0434	0.0462	0.0488	0.0512
Inhibitor (IV)					
ΔH^*	52.10	54.66	54.74	54.82	54.91
ΔG^*		56.14	57.64	59.11	60.57
$-\Delta S^*$		0.0048	0.0091	0.0130	0.0167
Inhibitor (V)					
ΔH^*	54.10	56.66	56.74	56.82	56.91
ΔG^*		57.67	59.17	60.74	62.07
$-\Delta S^*$		0.0033	0.0076	0.0119	0.0152
Inhibitor (VI)					
ΔH^*	54.50	57.06	57.14	57.22	57.31
ΔG^*		58.08	59.63	61.02	62.36
$-\Delta S^*$		0.0033	0.0078	0.0115	0.0149

III.13. Electrochemical studies

III.13.1-Open circuit potential measurements (OCP).

Table (34) and Figs. (70-72),clear that in absence of the inhibitor molecules (blank), the open circuit potential curve tends from the moment of immersion towards more negative value and increased after 5min. This behavior represents the break down of the permission of the ions in bulk electrolyte, were formed weak ferrous oxide and hydroxides film on the surface of carbon steel alloy (working electrode), then the potential was shifted to more positive direction and stable after 10 min. to 37 min. and slowly decreased until the end of time immersion (60 min), the potential reached to -575mV. i.e the dissolution of formed films of metal was continuous. On the other hand the addition of the inhibitor molecules produces a positive shift in ($E_{corr.}$),these results are shown in Table (34). The OCP for all inhibition solutions remained slowly increased until stable at steady state to 41 min. and after that slowly increased and stable secondary to the end of test. This behavior suggests possibility which the inhibitor molecules adsorbed on the metal surface to forma a stable protective film of organoamide dimeyhylsiloxane compound IV, V and VI with alloy, which were might control and reduce the alloy dissolution. The OCP is reached during 60 min immersion for each inhibitor to steady state. The results of final steady-state potential ($E_{corr.}$) are listed in Table (34). The results were clearly indicated that, while the concentration of each inhibitor from IV, V and VI increasing the corrosion potential ($E_{corr.}$) shifted to more positive direction. From these results clearly that the inhibitors act as anodic protection (i.e) decreasing the anodic dissolution of carbon steel alloy. Therefore one could be noted that OCP values are very different for each inhibitor due to variation in the molecular structure of inhibitors. So that, the shift to-more positive direction in the following orders

VI > V > IV

Generally should be concluded that, the OCP is monitored continuously in absence and presence of corrosion inhibitors. The results, Figs. (70-72) show that the inhibitor is affected on the OCP value in inhibited and uninhibited solutions and shifted to positive values with increasing of concentration and period of time. It is also causes oscillations on OCP. This behavior is probably due to the more stability of the formation of thin films formed with the multi layers surfaces also.

The OCP data for the corrosion inhibitor IV, V and VI at concentrations ratios from 100 to 600 ppm at period time 60 min. and potential mV are given in Table (34) and Figs (70 - 72). From these data one should be deduced that the potential at first 5 min. is shifted toward negative values and return again to positive direction. The potential increased from low concentration, while the layers of, are formed and stable on the surface of specimens (the adhesion force between the surface of metal and formation films are strong and stable, also the layers with each others, this phenomena due to the adsorption of inhibitors are carried by chemisorptions process. In solicited blank solution, there are two phenomena, first removing adsorbed species by cavitations and final hydrogen evolution (because of acidic corrosive medium). However, in inhibited solution, the inhibitor chains are adsorbed on metal surface and are chemisorbed. Thus, the OCP oscillation is higher in these solutions. From the OCP results, one should be recommended that the application of organoamide dimeyhylsiloxane compounds IV, V and VI as corrosion inhibitors in aggressive media. So that, one should be say these results are matched with the obtained results from weight loss calculations.

Table (34): Data from open circuit potential measurements of carbon steel electrode in1M HCl Containing different concentrations of various inhibitors at 298° ±2K

Concentration (ppm)	potential mV (vs. SCE)		
	IV	V	VI
b	-575	-575	-575
100	-563	-550	-543
200	-555	-549	-526
300	-546	-542	-526
400	-542	-540	-524
500	-539	-534	-518
600	-537	-530	-511

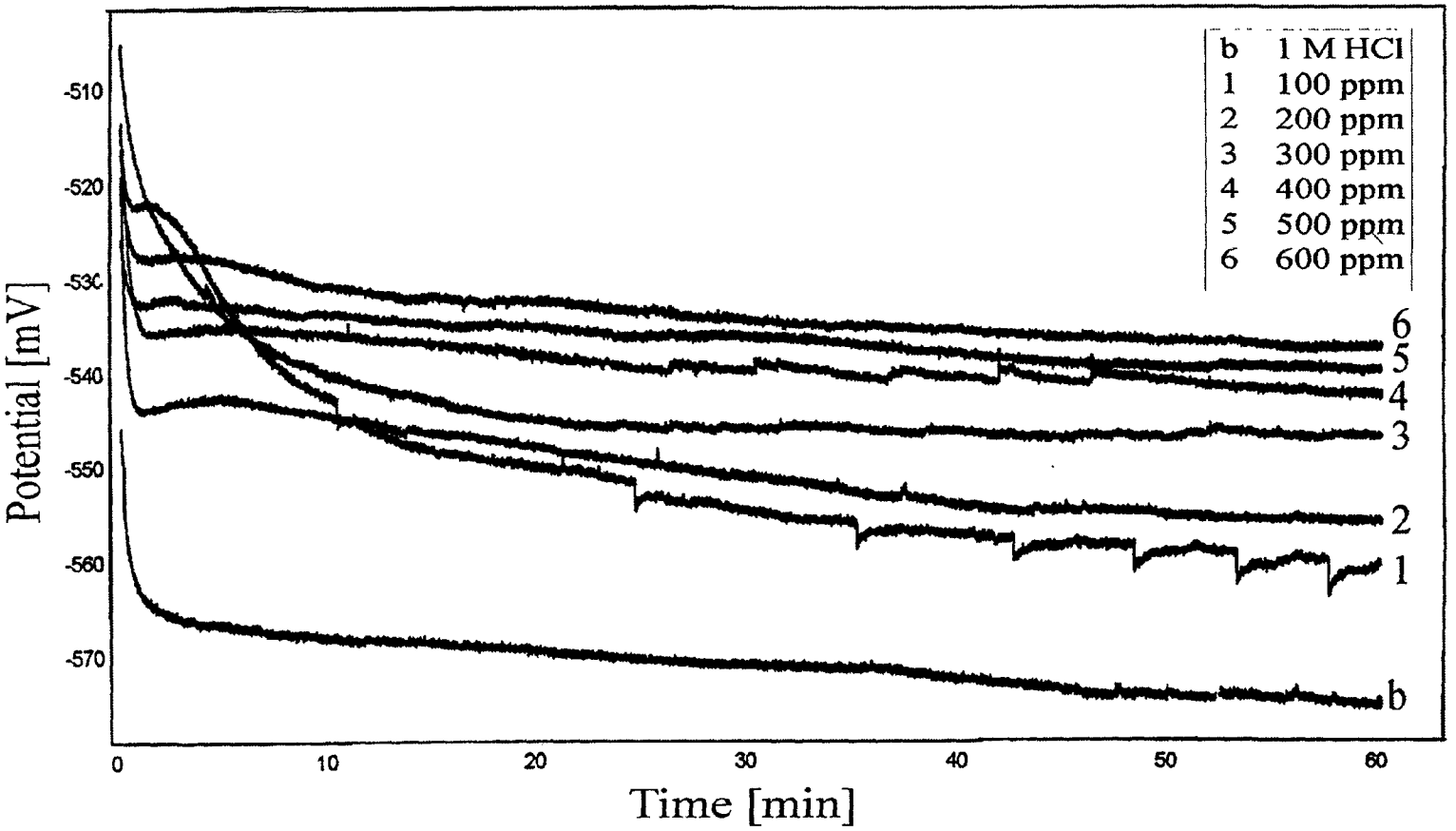


Fig. (70): Open circuit potential–time plot for carbon steel in the 1M HCl in absence and presence of different concentrations of inhibitor (IV)

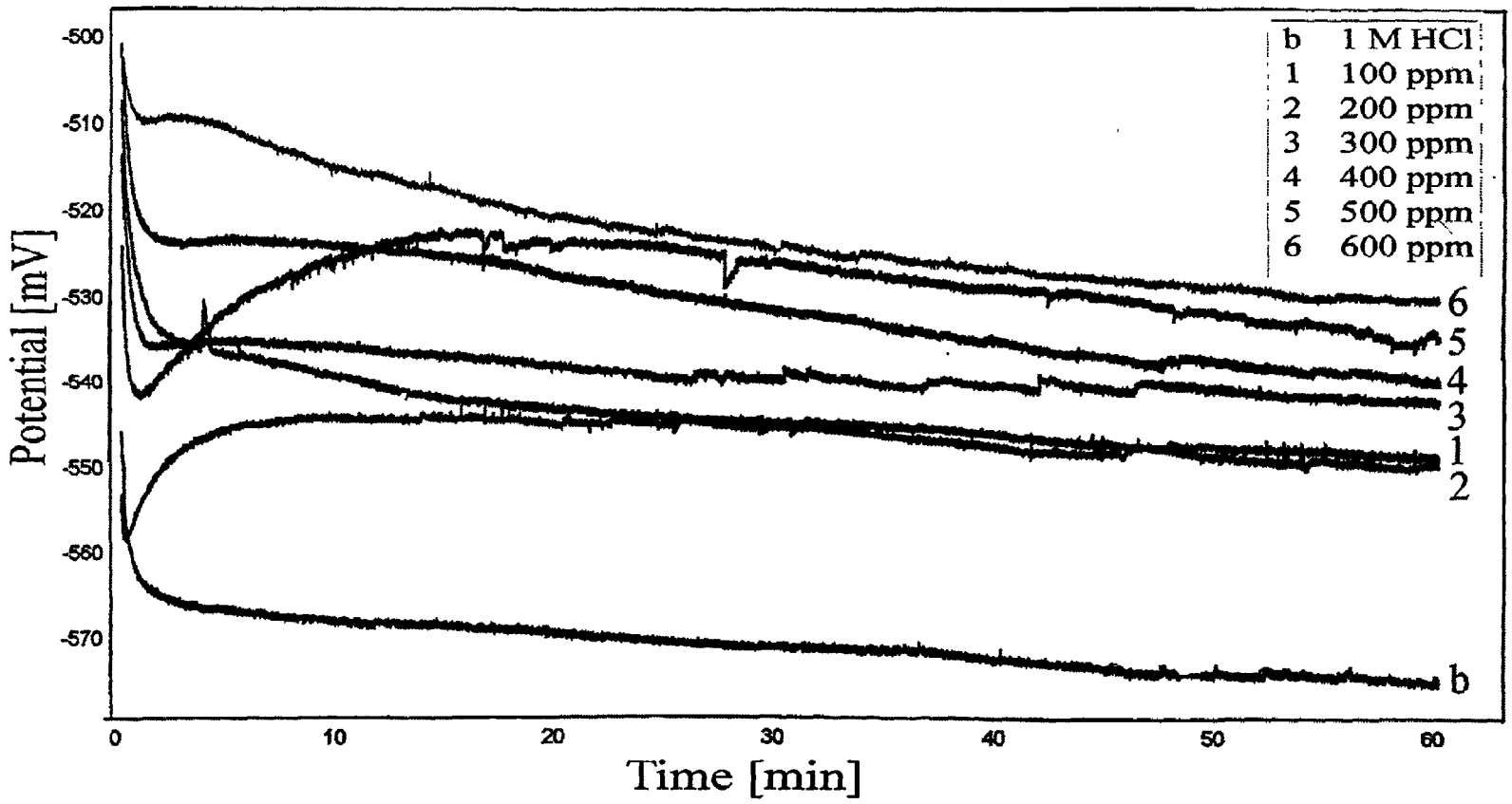


Fig. (71): Open circuit potential–time plot for carbon steel in the 1M HCl in absence and presence of different concentrations of inhibitor (V)

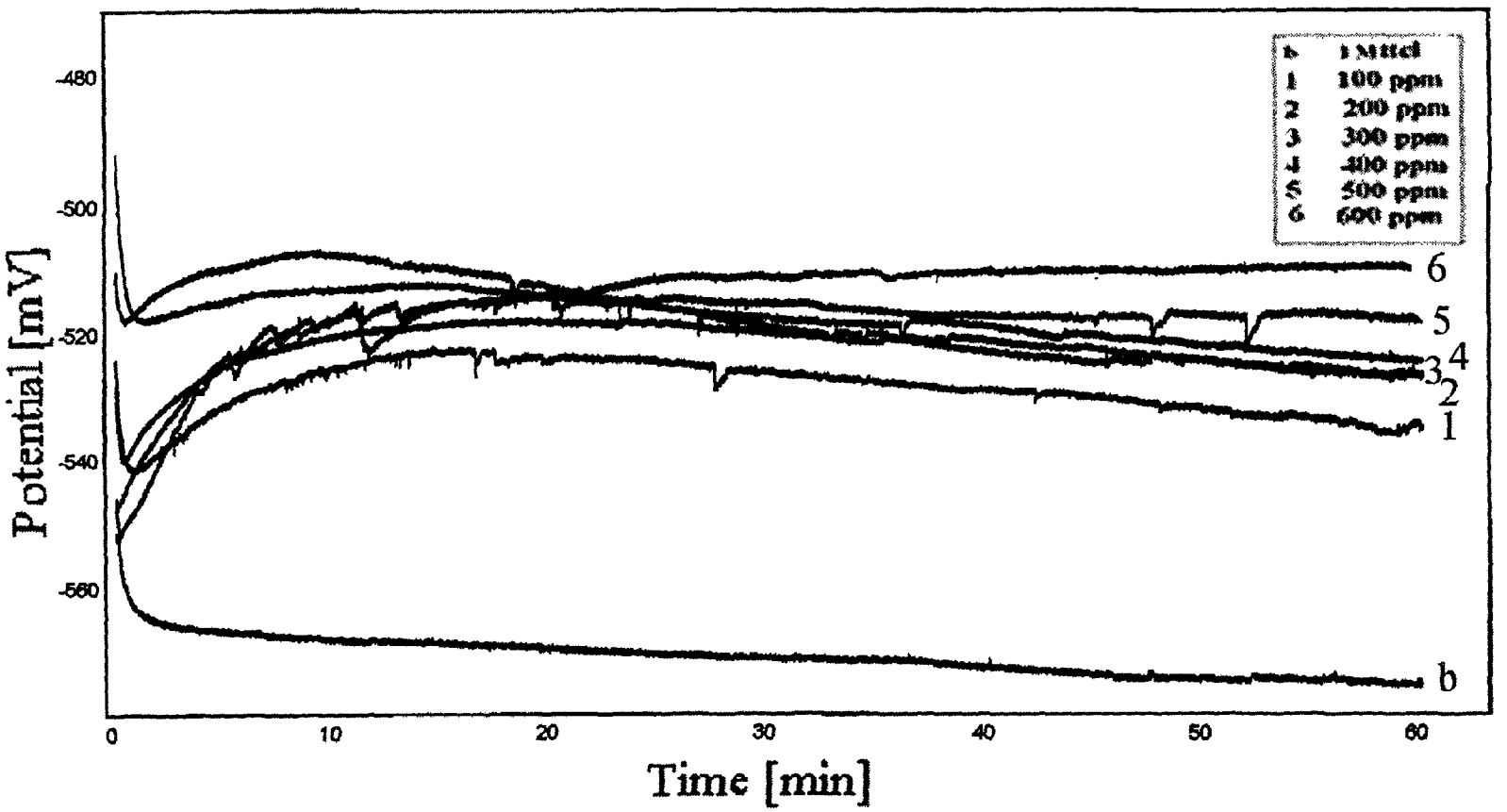


Fig. (72): Open circuit potential–time plot for carbon steel in the 1M HCL in absence and presence of different concentrations of inhibitor (VI)

III.13.2. Potentiodynamic polarization curves

Figs. (73 – 75) show the polarization curves of carbon steel. in 1M HCl solution in the absence and presence of inhibitors, respectively. Electrochemical corrosion kinetic parameters, such as corrosion potential (E_{corr}), cathodic (bc) and anodic (ba) Tafel slopes, corrosion current density (I_{corr}), coverage surfaces (θ) and I% are determined in presence of organoamide dimeyhylsiloxane IV, V and VI inhibitors. These parameters are summarized in Tables (35-37). It is clear that the presence of inhibitor molecules causes a decrease in I_{corr} .The decrease in I_{corr} with increasing concentration demonstrates the efficiency of the additive compound as corrosion inhibitor of carbon steel. The values of inhibition efficiency increased markedly with increasing of inhibitor concentration, there is way indicated that a higher coverage of inhibitor on the surface is obtained in a solution with high concentration of inhibitor. The addition of inhibitor was shifted the E_{corr} value towards the positive direction. This may be shifted to more positive direction in the following order

VI > V > IV

This result shows that the inhibition process of this inhibitor depends on electrode potential. For very negative values, the inhibition effect disappears. It can may conclude that organoamide dimeyhylsiloxane IV, V and VI inhibitors act as an anodic inhibitors. The results obtained from the polarization technique are in good agreement with those obtained from weight loss method and OCP data.

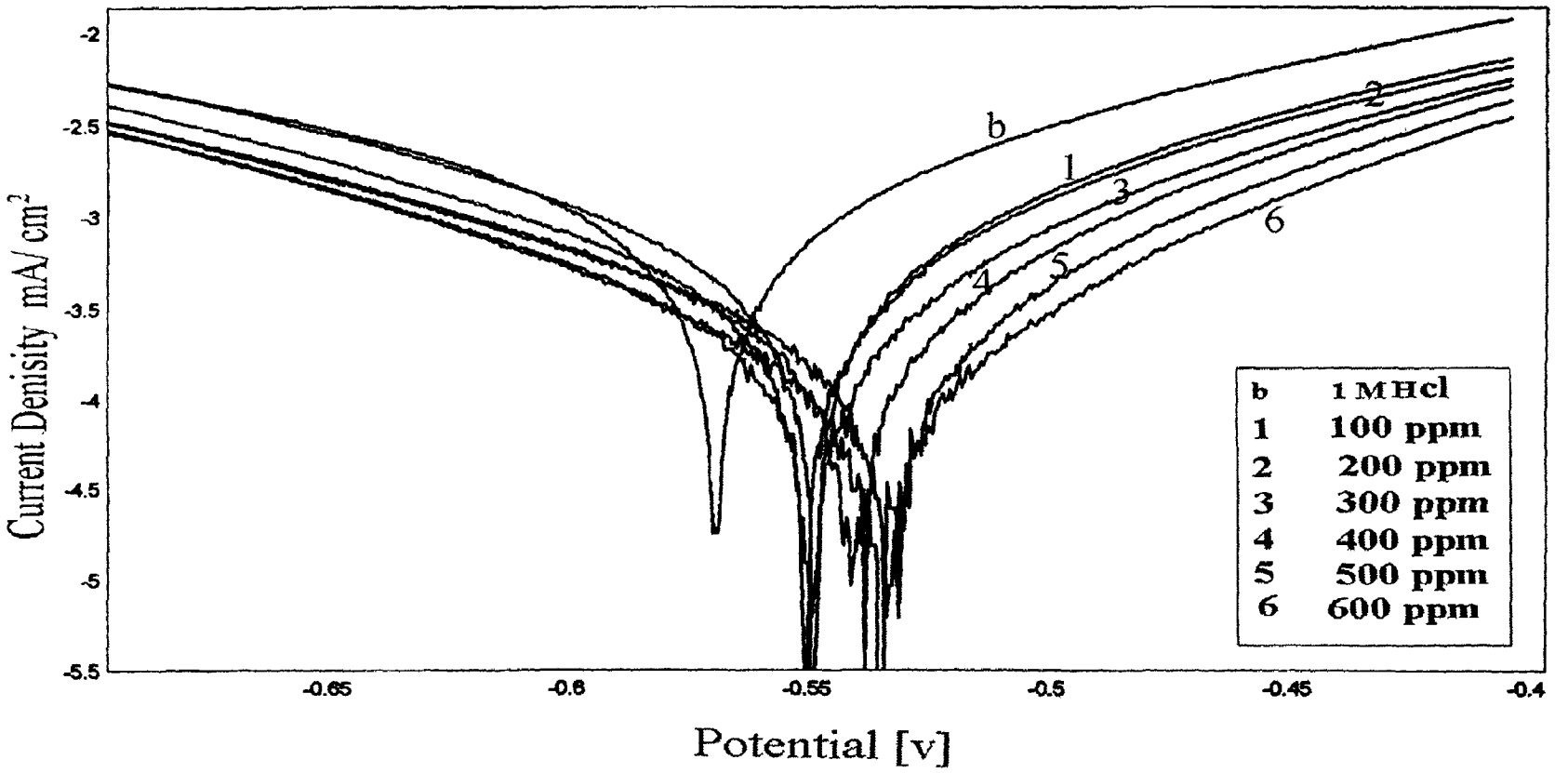


Fig.(73): Polarization curves for carbon steel in the 1M HCL in absence and presence of different concentrations of inhibitor (IV)

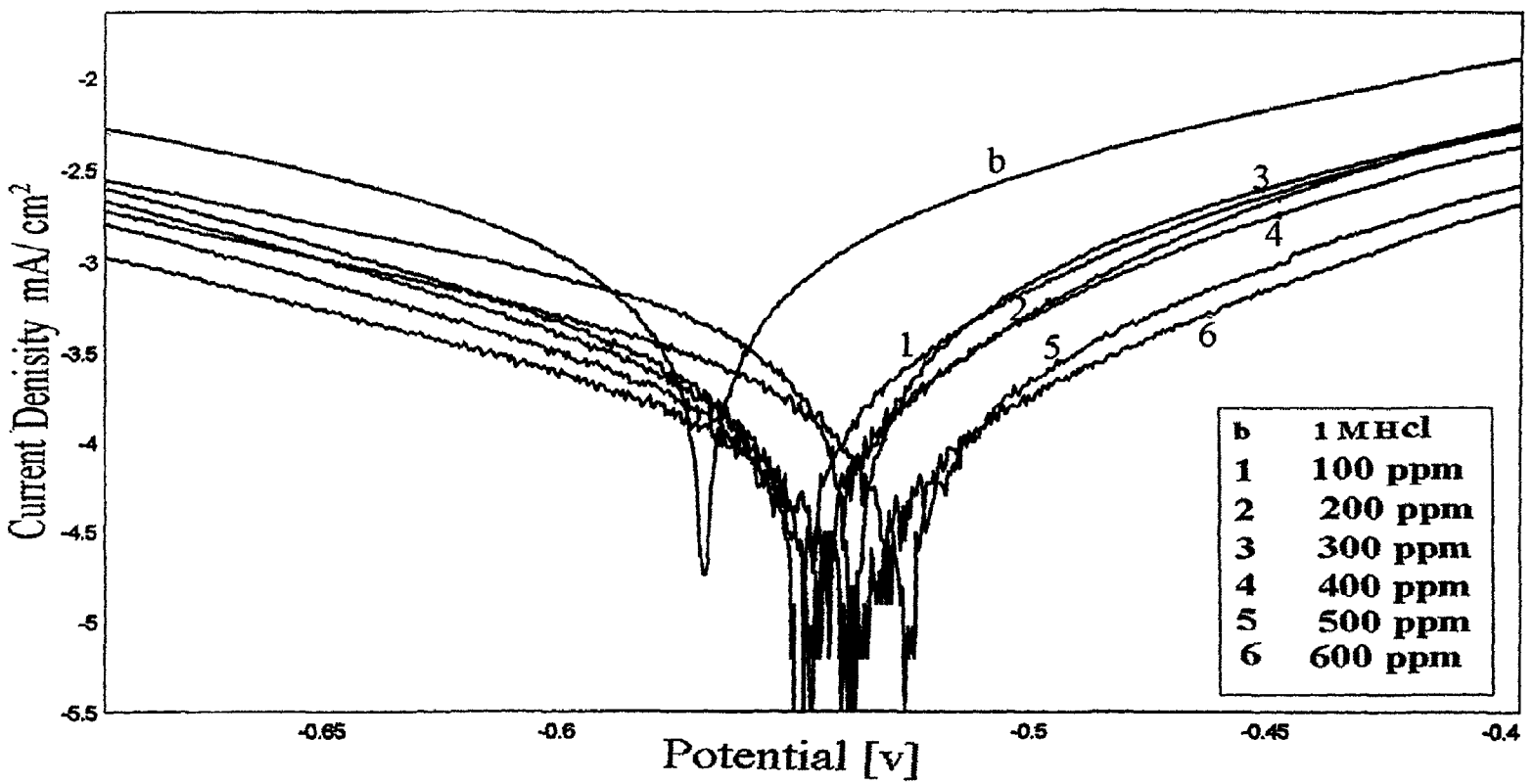


Fig.(74) : Polarization curves for carbon steel in the 1M HCL in absence and presence of different concentrations of inhibitor (V)

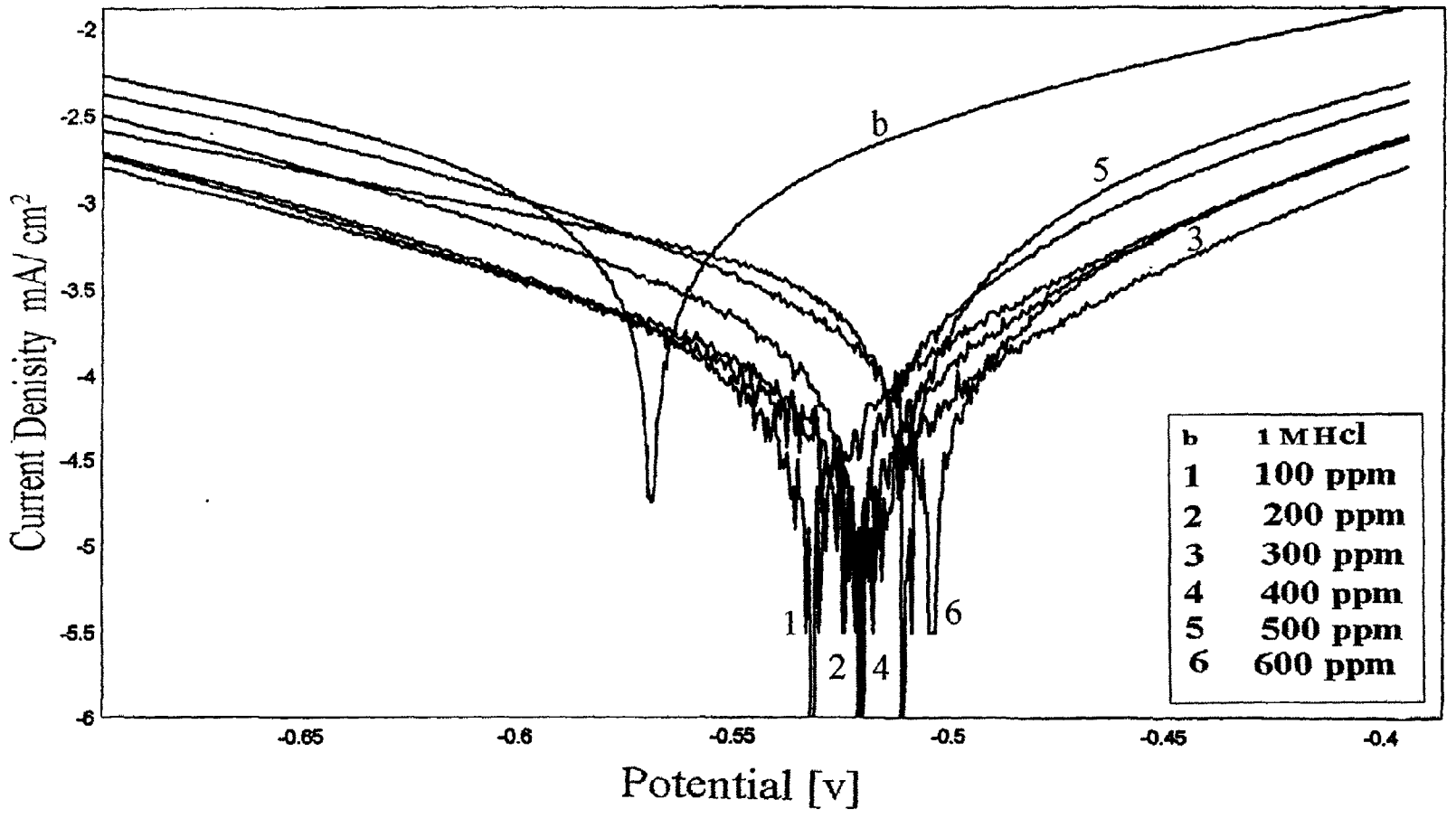


Fig.(75): Polarization curves for carbon steel in the 1M HCL in absence and presence of different concentrations of inhibitor (VI)

Table (35): parameters of potentiodynamic polarization of carbon steel electrode in 1M HCl containingvarious concentrations of the inhibitor (IV) at 298° K ±2K.

Conc. (ppm)	$-E_{corr}$, mV	I_{corr}, mA/Cm^2	R_P, Ohm.Cm^2	b_a, mV/dec	b_c, mV/dec	(θ)	(I%)
0.0	574.51	1.28	27.39	175.90	-206.31	-	-
100	564.52	0.45	58.56	144.94	-156.04	0.6437	64.37
200	554.51	0.32	79.00	126.23	-151.82	0.7499	74.99
300	545.80	0.28	85.14	117.41	-144.71	0.7788	77.88
400	541.03	0.27	92.34	123.32	-139.84	0.7892	78.92
500	540.11	0.23	104.75	112.65	-143.22	0.8136	81.36
600	538.32	0.23	168.38	116.91	-148.53	0.8159	81.59

Table(36): parameters of potentiodynamic polarization of carbon steel electrode in 1M HCl containing various concentrations of the inhibitor (V) at 298° K ±2K.

Conc. (ppm)	$-E_{corr}$, mV	I_{corr}, mA/Cm^2	R_P, Ohm.Cm^2	b_a, mV/dec0	b_c, mV/dec	(θ)	(I%)
0.0	574.51	1.28	27.39	175.90	-206.31	-	-
100	551.00	0.38	59.80	136.30	-184.60	0.6976	69.76
200	548.31	0.24	103.49	114.91	-145.21	0.8086	80.86
300	542.52	0.20	136.21	115.23	-147.41	0.8380	83.80
400	541.73	0.19	149.19	136.61	-173.52	0.8446	84.46
500	540.11	0.14	158.98	96.10	-143.04	0.8872	88.72
600	540.10	0.10	259.31	117.03	-156.31	0.9203	92.03

Table (37): parameters of potentiodynamic polarization of carbon steel electrode in 1M HCl containing various concentrations of the inhibitor (VI) at 298° K ±2K

Conc. (ppm)	$-E_{corr}$, mV	I_{corr}, mA/Cm^2	R_P, $_{Ohm}.Cm^2$	b_a, mV/dec	b_c, mV/dec0	(θ)	(I%)
0.0	574.51	1.28	27.39	175.90	206.31	-	
100	537.02	0.30	60.13	121.21	-200.11	0.7623	76.23
200	526.50	0.27	114.36	128.80	-158.61	0.7878	78.78
300	526.61	0.17	118.30	10.6.51	-134.52	0.8649	86.49
400	524.82	0.14	228.87	115.52	-146.73	0.8861	88.61
500	515.31	0.11	246.53	99.31	-151.74	0.9112	91.12
600	509.04	0.10	368.33	114.03	-142.80	0.9162	91.62

III.13.3. EIS Measurements

Figs (76, 78 and 80) show a typical Nyquist impedance plots obtained for carbon steel alloy electrode at an open circuit potential the experimental procedure were carried out after 24hrs immersion of the working electrode in 1M HCl in absence and presence of the different concentrations 100, 200, 300, 400, 500 and 600ppm of inhibitors IV, V and VI respectively at temperature, 23 ±2°C. The dots line represents the actual data and solid lines represent the best fit using the equivalent circuit shown in Figs. (77, 79 and 81) .The parameters obtained by fitting the equivalent circuit are listed in Tables (38 - 40). Figs (76, 78 and 80) and Tables (38 - 40) indicated that the increase in organoamide siloxane derivatives IV, V and VI inhibitors concentrations raises the polarization resistance (Rp). The constant phase elements(Q) with their n values close to 1.0 represent double-layer capacitors with some pores; the Q decrease upon of organoamide siloxane derivative IV, V and VI inhibitors and upon increase in their concentrations, which are expected to cover the charged surfaces reducing the capacitive effects. It has been reported that, the semicircles at high frequencies are generally associated with the relaxation of electrical double –layer capacitors, and the diameters of the high – frequency capacitive loops can be considered as the charge – transfer resistance. This suggests that the electron- transfer reaction corresponding to the second semicircle takes place through the surface layer, which limits mass transport (Warburg) or acts just like another resistor. The presence of the Warburg (W) impedance indicates that the mass transport was limited by the surface covered with organoamide siloxane derivatives IV, V and VI inhibitor layers.

The inhibition efficiency, I%, of organoamides siloxane derivatives IV, V and VI inhibitors for the carbon steel alloy electrode can then be calculated from the following equation :

$$I\% = (Rp - Rs) / Rp \times 100 \qquad \text{(III. 8)}$$

Where Rs and Rp are the charge transfer resistance in blank and in presence of organoamide derivatives IV, V and VI inhibitors, respectively. The attained results are shown in Tables (38 - 40). The increasing of Rs value verified for 1MHCl in presence of organoamides siloxane derivatives IV, V and VI inhibitors pointed out a reduction in the alloy corrosion tendency, resulting in an I% of 82 ,91 and 91respectively. A slightly decrease of CdI values has also been detected, which corroborates the above proposal that organoamide siloxane derivatives IV, V and VI act as corrosion inhibitors by adsorption onto the metallic surface .

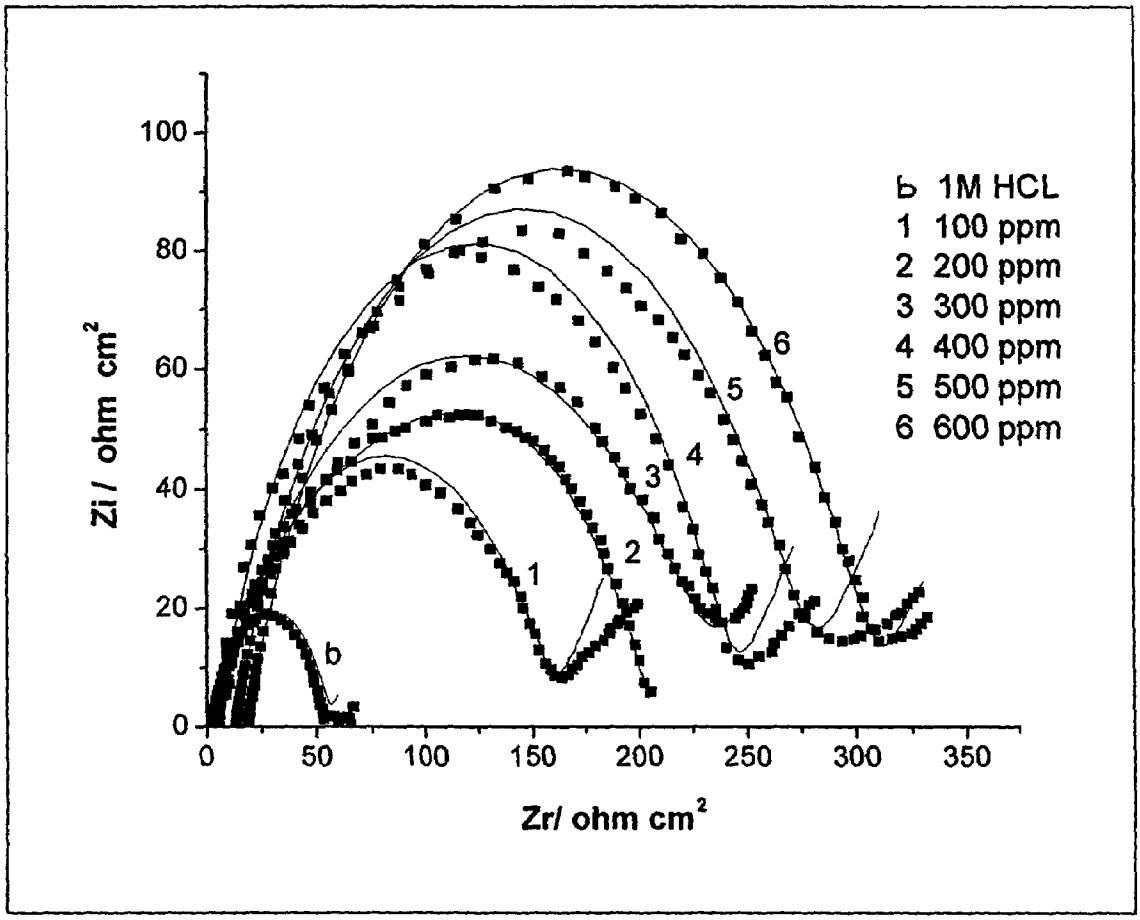


Fig.(76): Niquist diagram for the carbon steel electrode after immersion in 1M HCl solution in absence and presence different concentrations of compound (IV)

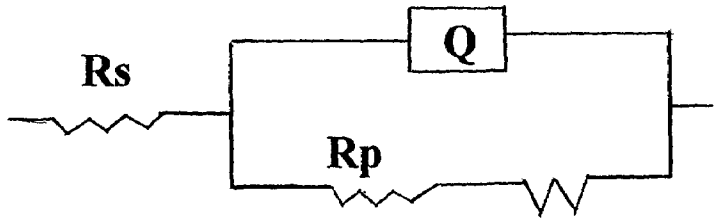


Fig.(77): Equivalent circuit R(Q(RW)) used to fit experimental data represented in fig.(76) .

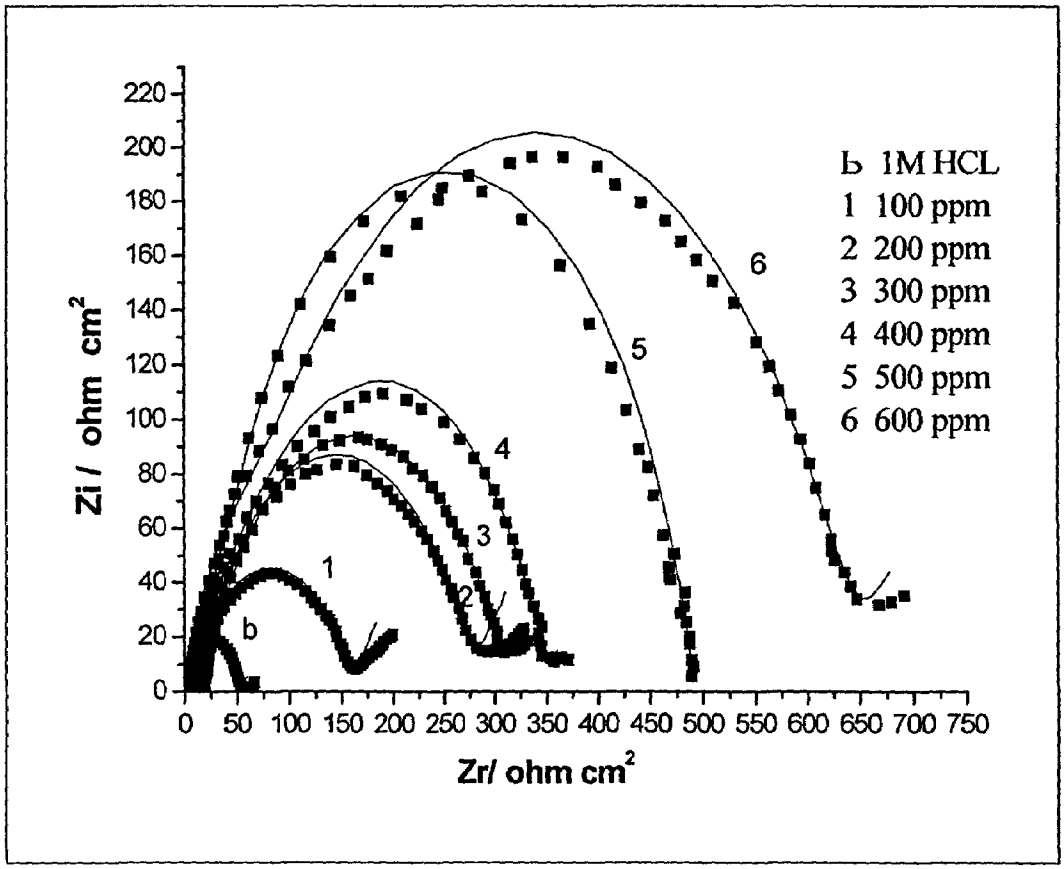


Fig.(78): Niquist diagram for the carbon steel electrode after immersion in 1M HCl solution in absence and presence different concentrations of compound (V)

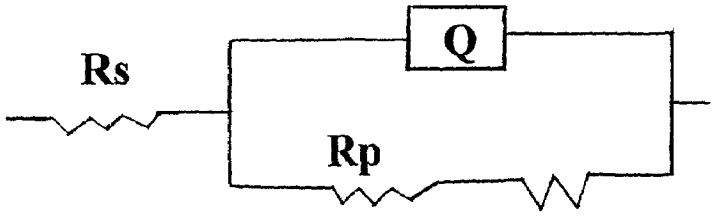


Fig.(79): Equivalent circuit R(Q(RW))used to fit experimental data represented in fig.(78) .

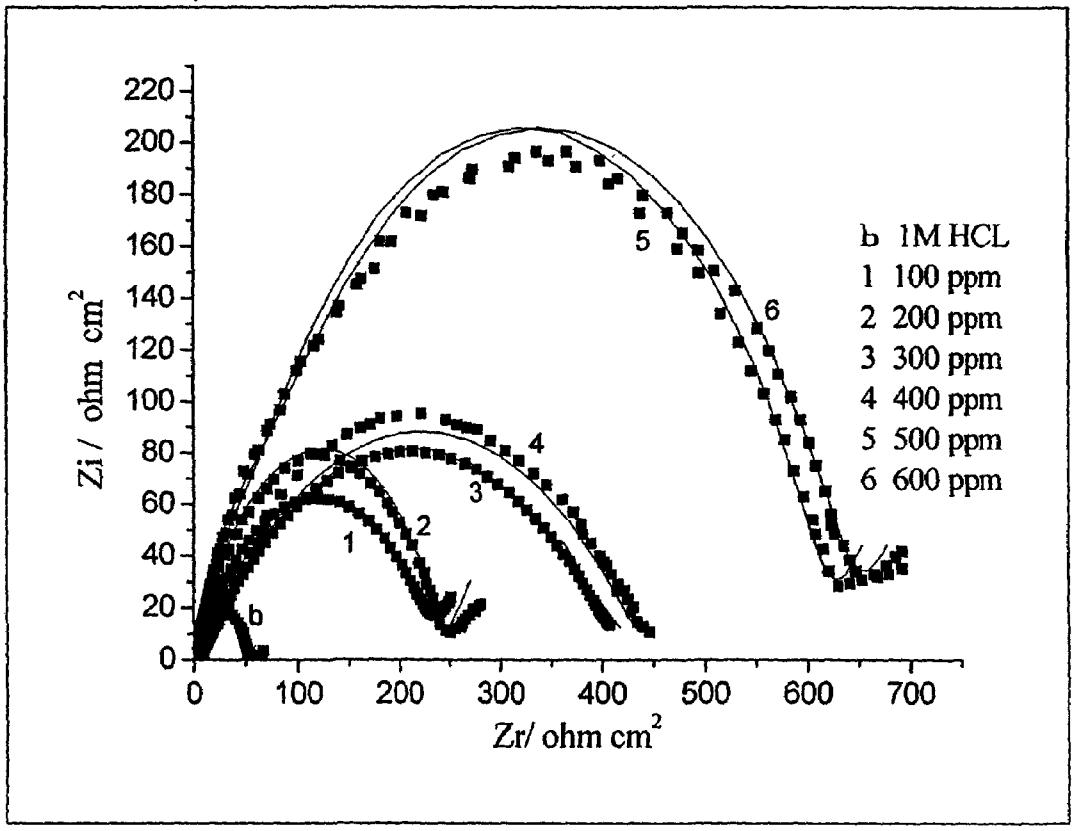


Fig.(80): Niquist diagram for the carbon steel electrode after immersion in 1M HCl solution in absence and presence different concentrations of compound (VI)

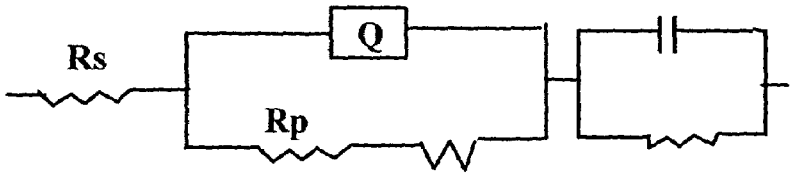


Fig.(81): Equivalent circuit Q(RW)) QR used to fit experimental data represented in fig (80) .

Table(38): Impedance measurements and inhibition efficiencies for carbon steel in 1M HCL containing different concentrations of compound (IV)

Conc. ppm	R_t Ωm^2	n	C_{dl} $\mu F\ cm^{-2}$	Efficiency (I%)
B	55	0.82	16.5	-
100	163	0.8	0.001	66.25
200	206	0.79	0.0008	73.30
300	236	0.8	0.0004	76.69
400	250	0.8	0.0002	78.00
500	281	0.8	0.0001	80.42
600	312	0.8	0.0001	82.37

Table(39): Impedance measurements and inhibition efficiencies for carbon steel in 1M HCL containing different concentrations of compound (V)

Conc. ppm	R_t $Ohmcm^2$	n	C_{dl} $\mu F\ cm^{-2}$	Efficiency (I%)
B	55	0.82	16.5	-
100	161	0.8	0.0002	65.83
200	282	0.81	0.00013	80.49
300	312	0.78	0.00014	82.37
400	350	0.83	0.000175	84.28
500	480	0.82	0.000127	88.54
600	650	0.8	0.00012	91.53

Table (40): Impedance measurements and inhibition efficiencies for carbon steel in 1M HCL containing different concentrations of compound (VI)

Conc. ppm	R_t Ohmcm^2	n	C_{dl} µF cm^{-2}	Efficiency (I%)
B	55	0.82	16.5	-
100	236	0.8	0.00019	76.69
200	250	0.84	0.00017	78.00
300	417	0.8	0.00017	86.81
400	445	0.81	0.00014	87.64
500	600	0.79	0.00013	90.83
600	652	0.8	0.00012	91.56

III.14. Scanning Electron Microscopy (SEM)

Scanning electron microscopy was used to examine the surface morphology of the mechanically polished carbon steel specimens and those which were immersed in 1M hydrochloric acid solution in absence and presence of 500 ppm of organoamidesiloxane derivatives IV, V and VI respectively. Fig (82) shows a characteristic inclusion observed on the polished carbon steel, which is probably an oxide inclusion. Fig. (83) shows SEM image of the surface of carbon steel specimen after immersion in 1M hydrochloric acid for 24 hr, while Figs(84-86) shows SEM image of the surface of another carbon steel specimen after immersion for the same time interval in 1M hydrochloric acid containing 500 ppm of inhibitors organoamidesiloxane derivatives IV, V and VI respectively . The resulting of scanning electron micrographs reveal that the surface was strongly damaged owing to corrosion in absence of inhibitor , but when 500 ppm of inhibitors were added to the solution test , there are much less damage of the surface , presumably as a result of a protective film on the inhibitor on the metal surface. From the micrographs it is clear that compounds provided good protection. The protective film formed on the surface of carbon steel in presence of 500 ppm of inhibitor IV appears as multilayer of inhibitor IV mag. 750 and 2000 Figs. (84 a and b), respectively, while in case of inhibitor V the formed film appears to be smooth and to cover surface at X =750, 2000 Figs. (85 a and b), respectively and in case of inhibitor VI the formed film appears to be very smooth and to cover the whole surface at X =750, 2000 Figs. (86 a and b) respectively. This confirms the observed high inhibition efficiency of each inhibitor at this concentration, the inhibition efficiency tend to decrease in the following order:

(VI) > (V) > (IV)

The results obtained from the (SEM) technique are in good agreement with those obtained from weight loss method and all electrochemical techniques data.

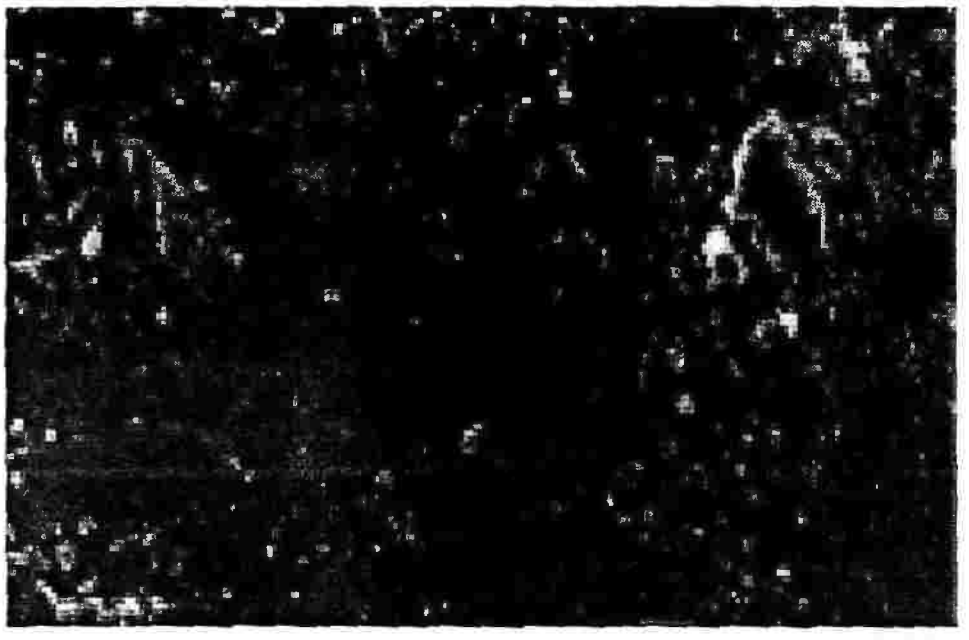


Fig (82): scanning electron micrographs of carbon steel sample after polishing X = 750

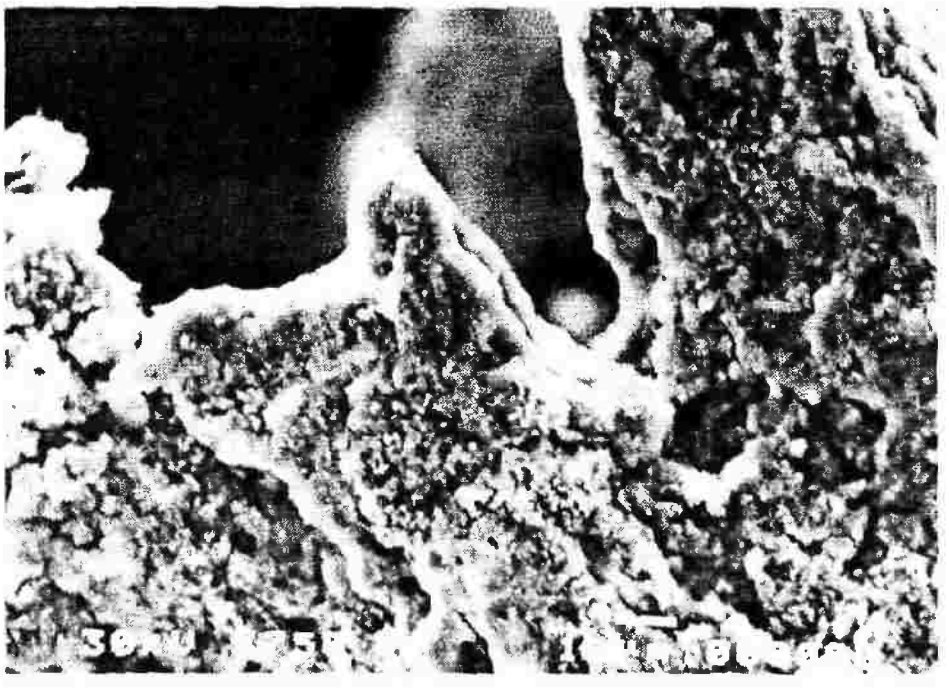
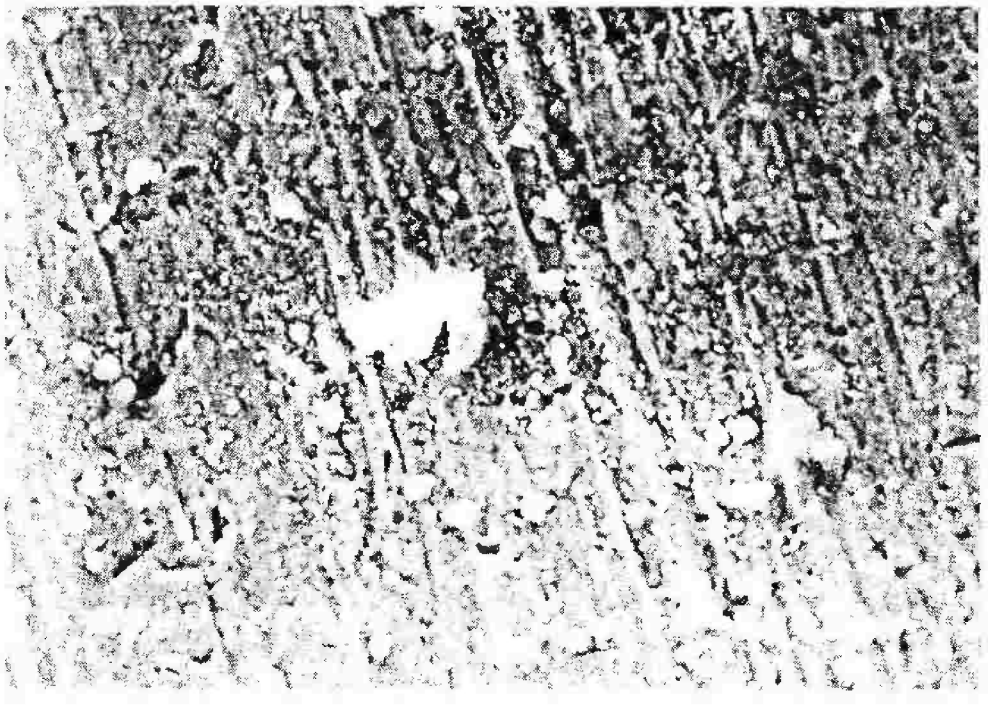


Fig (83): scanning electron micrographs of carbon steel sample after immersion in 1M HCL solution without inhibitor X = 750

a



b

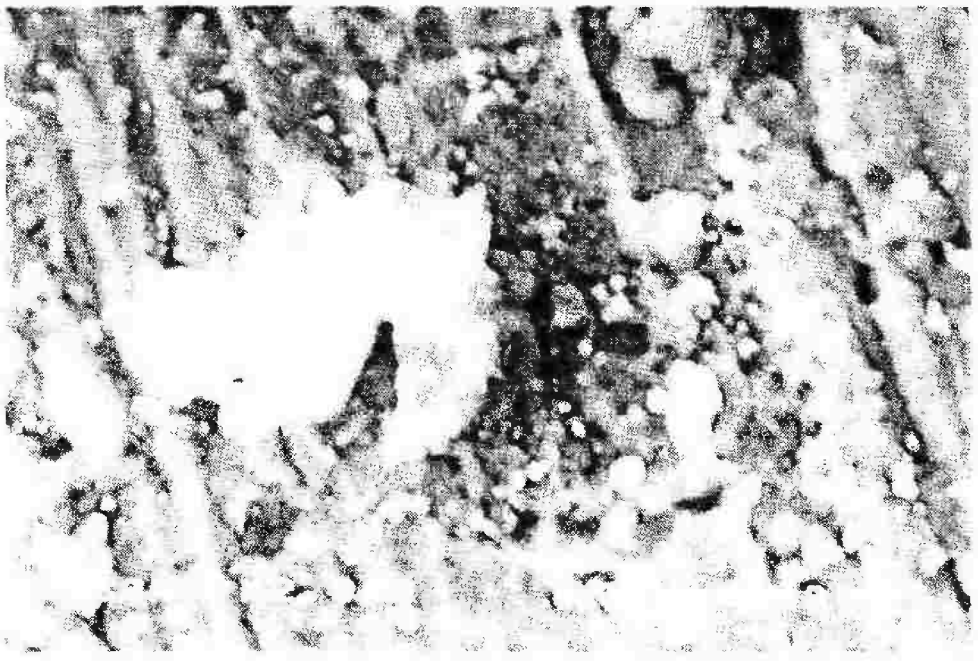
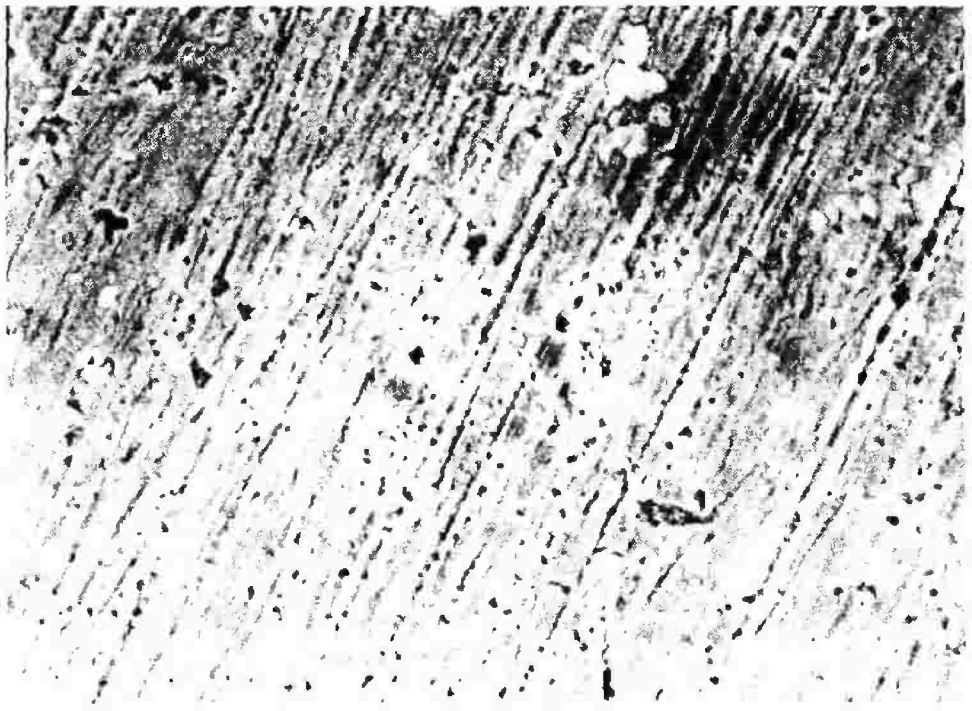


Fig (84) : scanning electron micrographs of carbon steel sample after immersion in 1M HCL solution containing 500 ppm of inhibitor (IV) a: X = 750 b: X = 2000

a



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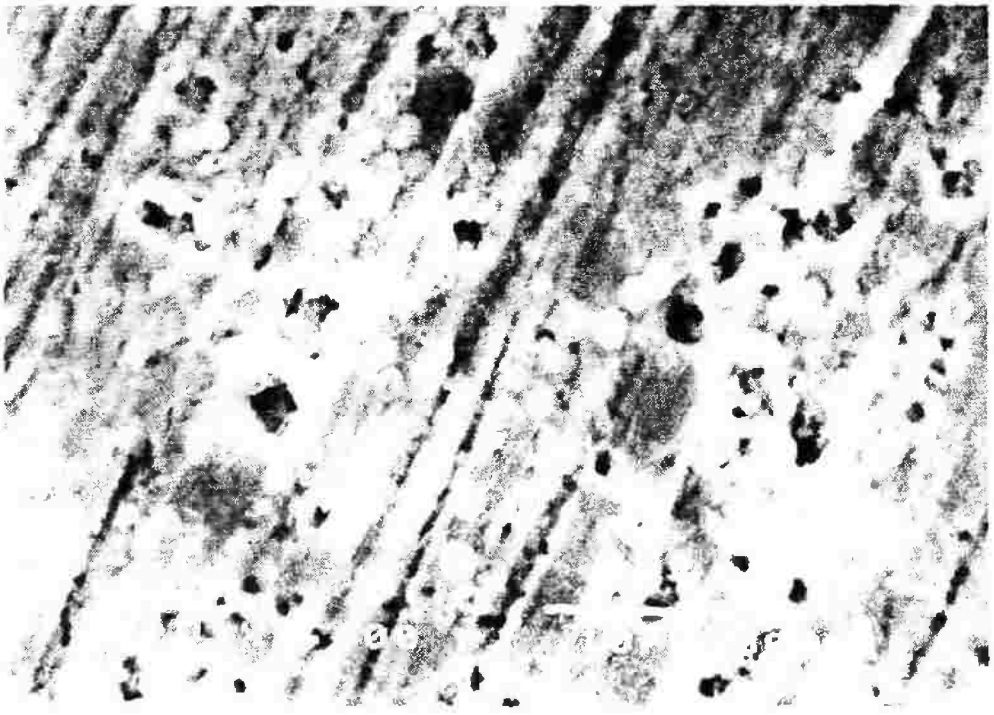
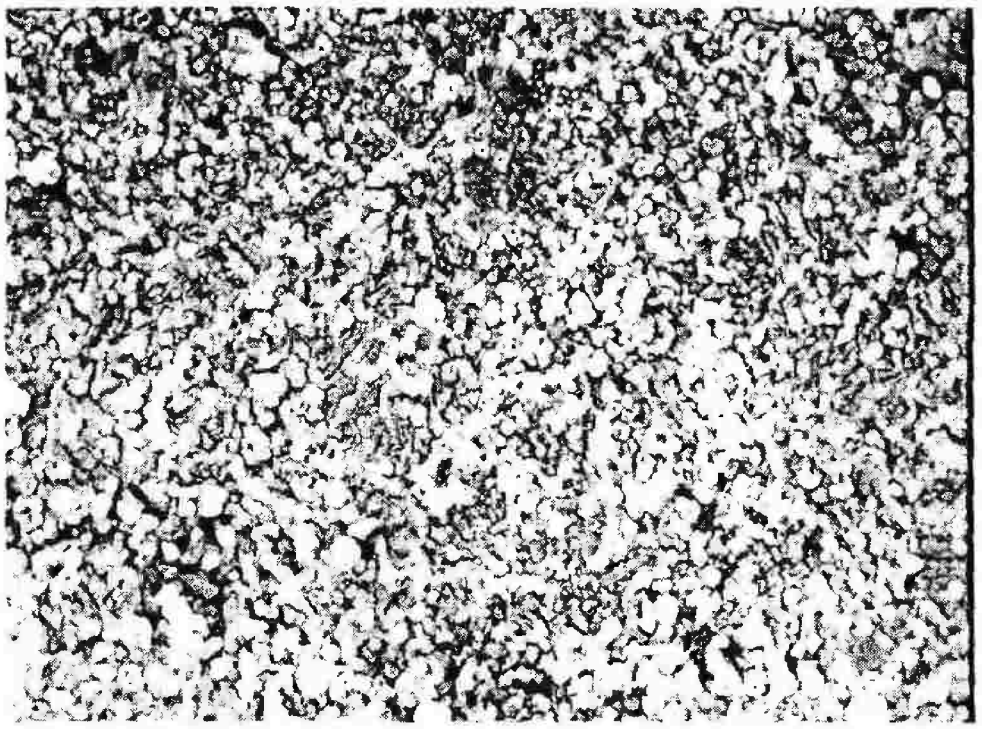


Fig (85) : scanning electron micrographs of carbon steel sample after immersion in 1M HCL solution containing 500 ppm of inhibitor (V) a: X = 750 b: X = 2000

a



b

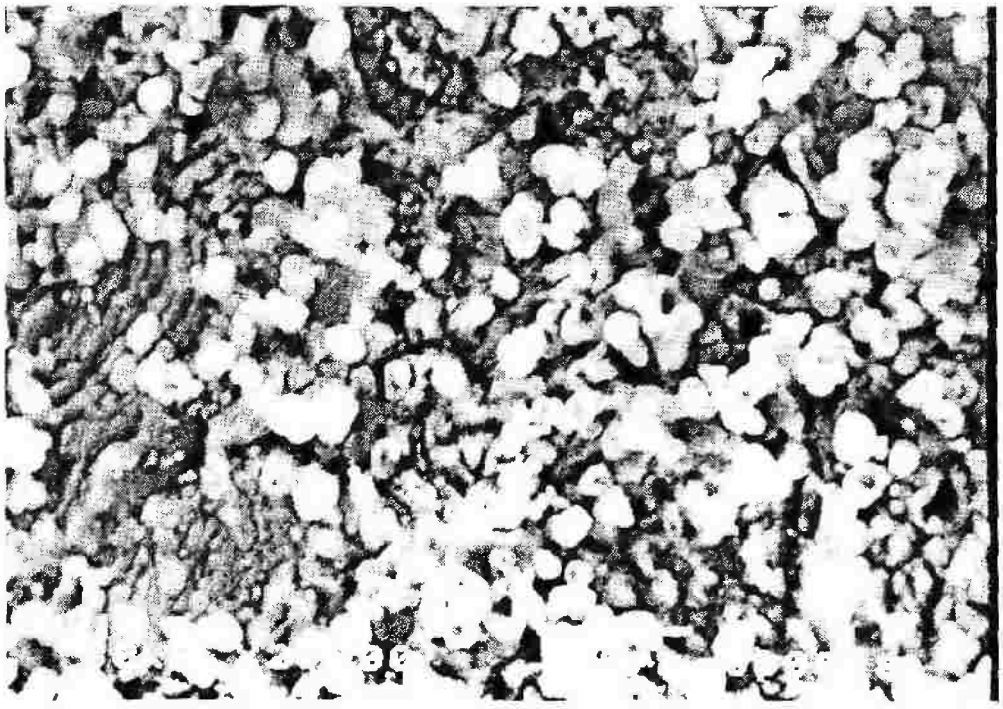


Fig (86) : scanning electron micrographs of carbon steel sample after immersion in 1M HCL solution containing 500 ppm of inhibitor (VI) a: X = 750 b: X = 2000

Table (41): inhibition efficiency of organoamidesiloxane derivatives IV, V and VI inhibitors at different concentrations as determined by weight loss measurement at 298°K

Conc. (ppm)	Percentage inhibition efficiency (I %)		
	IV	V	VI
100	62.82	70.63	79.92
200	74.34	81.04	81.41
300	77.69	84.01	86.24
400	78.81	85.13	88.02
500	80.66	90.48	91.82
600	81.78	93.38	92.56

Table (42): inhibition efficiency of organoamidesiloxane derivatives IV, V and VI inhibitors at different concentrations as determined by polarization measurement at 298° K

Conc. (ppm)	Percentage inhibition efficiency (I %)		
	VI	V	VI
100	76.23	69.76	76.23
200	78.78	80.86	78.78
300	86.49	83.80	86.49
400	88.61	84.46	88.61
500	91.12	88.72	91.12
600	91.62	92.03	91.62

Table (43): inhibition efficiency of organoamidesiloxane derivatives IV, V and VI inhibitors at different concentration as determined by (EIS) measurement at 298° K

Conc. (ppm)	Percentage inhibition efficiency (I %)		
	VI	V	VI
100	66.2	66.00	76.69
200	73.3	80.5	78.00
300	76.69	82.37	86.80
400	78.00	84.00	87.60
500	80.40	88.00	90.80
600	82.37	91.50	91.60