

# Effect of some organic inhibitors on the corrosion behaviour of Cu- Fe and Cu – Al – Fe alloys in sulphuric acid solution

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## Abstract

The effect of some organic compounds on the corrosion behaviour of copper - iron alloy (I) ( 95.53 % Cu, 4.47% Fe ) and copper - aluminium - iron alloys ( II) ( 84.31 % Cu , 10.67% Al, 5.02 % Fe ) in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution was investigated . The techniques of measurements were : weight loss , linear polarization and impedance. These organic compounds were : glycine (I), alanine (II), valine (III), Histidine (IV), 2- aminothiazole (V) and 3- methyl -1- phenyl -2- pyrazolin -5- one (VI).These compounds have high inhibiting effect on the corrosion of alloys ( I,II) in H<sub>2</sub>SO<sub>4</sub>.Their inhibition efficiency increases according to the order : I < II < III < IV < VI < V . The inhibitory effect of these compounds is achieved by their adsorption on the metallic surface via adsorption centers ( N - atom and / or S- atom ) . Their adsorption the metallic surface follows Temkin's isotherm of adsorption The values of standard free energy of adsorption ,  $\Delta G_{ads}^{\circ}$ , were calculated from the adsorption isotherms. The negative values of  $\Delta G_{ads}^{\circ}$  indicate the adsorption process occurs spontaneously. There is agreement between the results obtained from the different techniques of measurements.

**Keywords :** corrosion, inhibitors, copper alloys .

## Introduction

Copper and its alloys have a long history of use in marine applications and continue to be widely used for many purposes despite the emergence in recent years of other materials that have technical or economic attraction [1]. These related to their corrosion resistance, mechanical workability, excellent electrical and thermal conductivities and resistance to macrofouling [2].

The corrosion resistance of copper alloys has been attributed to the formation of a protective film of cuprous oxide ( $\text{Cu}_2\text{O}$ ) and to the doping of  $\text{Cu}_2\text{O}$  layer with ions such as iron [3, 4]. This doping reduces the ionic or electronic conductivity of the film, improving the corrosion resistance. In practice alloying additions of Al, Zn, Sn, Fe, Ni are used to dope the corrosion product films.

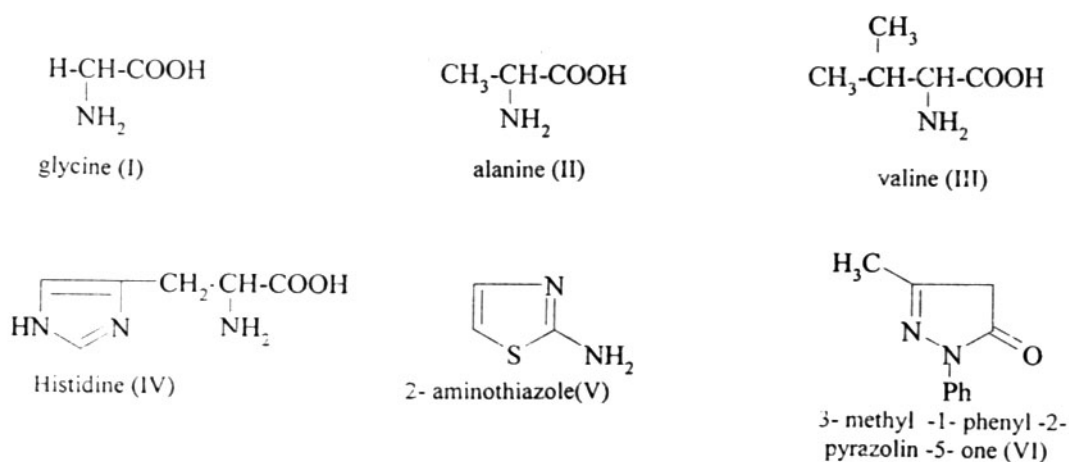
Inhibition by benzotriazole (BTA) [5-17], throurea [18-20] and different organic compounds containing NH or  $\text{NH}_2$  has been extensively studied [21-27] because of their high efficiency as inhibitors for the corrosion of copper and copper alloys in various media. The inhibition of aluminium bronze by 4-phenyl semicarbazide hydrochloride (PSC), both in the absence and in presence of KI was studied in pure HCl [28] and in acidified 4% NaCl solution [29].

In the present work the effect of some organic inhibitors on the corrosion behaviour of copper- iron and copper – aluminium iron alloys in 0.5 M  $\text{H}_2\text{SO}_4$  aqueous solution was studied.

## Experimental

Two types of copper alloys were used in this study. The first alloy (I) contains ( 95.53 % Cu, 4.47% Fe ) ,while the second alloy (II) contains (84.31 % Cu , 10.67% Al, 5.02 % Fe ) .

0.5 M  $\text{H}_2\text{SO}_4$  aqueous solution was prepared by appropriate dilution of the concentrated acid. The organic inhibitors were : glycine , alanine, valine, Histidine , 2- aminothiazole and 3- methyl -1- phenyl -2- pyrazolin -5- one. All chemical are chemically pure grades ( Analar). The organic additives have the following structural formulae:



The electrodes were jammed in a small copper mould with Araldite. The cross – sectional area (  $\simeq 1.54 \text{ cm}^2$  ) of the electrodes was only left to contact the test solution . Just before each experiment the electrodes were mechanically polished with successive grades emery paper. The electrode was rinsed several times with distilled water and degreased by acetone.

In the present investigation the techniques of measurements were : weight loss, linear polarization and impedance .

In the electrochemical measurements a Ag / AgCl /  $\text{Cl}^-$  ( 3 M KCl) and platinum foil (  $1 \times 1 \text{ cm}^2$  ) were used as a reference and auxiliary electrode , respectively. The potential and current were recorded by means of multimeter ( Keithley, Model 130 A, USA ). The impedance measurements were carried out using impedance measurements system

were conducted with an excitation amplitude of 10 mV peak to peak, and the frequency domain from 0.1 Hz to 100 K Hz.

In the weight loss measurements a test specimen of copper alloys has a total surface area of about 16 cm<sup>2</sup>.

## Results and Discussion

### 1. Weight-loss measurements :

The results of these measurements are listed in table (1) for alloy (I) and in table (2) for alloy (II) in 0.5M H<sub>2</sub>SO<sub>4</sub> in absence and in presence of different concentrations of the investigated organic compounds (I, II, III, IV, V, VI). The values of surface coverage,  $\theta$ , and inhibition efficiency, I%, are calculated from the corrosion rate,  $R_w$  (mg/cm<sup>2</sup>.h), by using the following equations :

$$\theta = 1 - \frac{(R_w)_{inh.}}{(R_w)_{free}} \quad (1)$$

$$I\% = \left[ 1 - \frac{(R_w)_{inh.}}{(R_w)_{free}} \right] \times 100 \quad (2)$$

where  $(R_w)_{free}$  and  $(R_w)_{inh.}$  are the corrosion rate in absence and in presence of inhibitors, respectively. The calculated values of  $\theta$  and I% are listed in tables (1-2) for the investigated alloys (I, II) and inhibitors (I -VI).

Fig.(1) represents the variation of inhibition efficiency, I%, for alloy (I) as a function of concentration of the investigated organic compounds (I-VI). Fig.(2) represents the variation of inhibition efficiency, I% for alloy (II) as a function of the concentration of the investigated inhibitors

(I-VI). The plots of these figures (1,2) indicate that the inhibition efficiency of the investigated organic compounds increases with the increase of their concentration.

The results of Figs. (1,2) and tables (1,2) indicated that the investigated organic compounds have high inhibiting effect on the corrosion of alloy (I, II) in  $H_2SO_4$  solution. The inhibition efficiency, I%, of the investigated organic compounds increases according to the order :

$$I < II < III < IV < VI < V$$

## 2. Linear polarization measurements :

Figs.(3,4) represent the plots of potential, E, versus the current density, i, for the alloys (I,II), respectively, in 0.5 M  $H_2SO_4$  solution in absence and in presence of different concentrations of compound (I). Similar plots are obtained for the alloys (I,II) in presence of different concentrations of the other organic compounds (II, III, IV, V, VI) but not shown. The values of linear polarization resistance,  $R_p$ , are deduced from the slopes ( $\Delta E/\Delta i$ ) of straight lines of the plots of Figs. (3,4) and similar ones and listed in table (3) for alloy (I), and in table (4) for alloy (II). The values of surface coverage,  $\theta$ , and inhibition efficiency, I%, are calculated from  $R_p$  by using the following equations from :

$$\theta = 1 - \frac{(R_p)_{free}}{(R_p)_{inh}} \quad (3)$$

$$I\% = \left[ 1 - \frac{(R_p)_{free}}{(R_p)_{inh}} \right] \times 100 \quad (4)$$

where  $(R_p)_{free}$  and  $(R_p)_{inh.}$  are the linear polarization resistance in 0.5M  $H_2SO_4$  and in presence of inhibitor, respectively,. The calculated values of  $\theta$  and I% are listed in tables (3,4) for alloys (I, II) and in

presence of inhibitors (I – VI) in 0.5M H<sub>2</sub>SO<sub>4</sub> solution. The results of these tables indicate that the inhibition efficiency of the investigated organic compounds is high and increases according the order : I<II<III<IV<VI<V. This order is the same as that obtained from the weight-loss measurements.

### 3. Impedance measurements :

Figs. (5,6) represent the impedance diagrams (Nyquist plots) for the alloy (I, II), respectively, in 0.5M H<sub>2</sub>SO<sub>4</sub> in presence of different concentrations of compound (I). Similar plots are obtained for the other organic compounds (II, III, IV, V, VI) but not shown. These impedance diagrams are not perfect semicircles and has been attributed to frequencies dispersion [30,31].

The charge transfer resistance ( $R_t$ ) values are calculated from the difference in impedance at lower and higher frequency, as suggested previously [32-34].

The double layer capacitance,  $C_{dl}$ , was determined from the frequency,  $f$ , at which  $Z_i$ , was maximum, using the following relationship.

$$f(-Z_{i,max}) = (2\pi C_{dl} R_t)^{-1} \dots\dots\dots (5)$$

The inhibition efficiency,  $I\%$ , of the alloys is calculated from the charge transfer resistance,  $R_t$ , using following equation :

$$I\% = \frac{(R_{tcorr}^{-1} - R_{tcorr(inh.)}^{-1})}{(R_{tcorr}^{-1})} \times 100 \quad (6)$$

Where  $R_{tcorr}$  and  $R_{tcorr(inh)}$  are the charge transfer resistance values in absence and in presence of inhibitor, respectively. The impedance parameters derived form these investigations are given in table (5) for



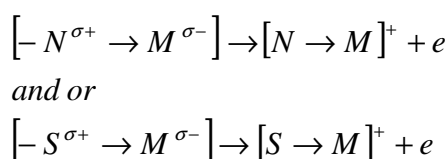
alloy (I), and in table (6) for alloy (II). The results of these tables indicate that as the inhibitor concentration increases the values of  $R_t$  and  $I\%$  increase, but the values of  $C_{dl}$  decrease. This indicates the occurrence of adsorption of the organic compounds on the alloys surface. Also, the inhibition efficiency,  $I\%$ , of the investigated organic compounds increases according to the order:  $I < II < III < IV < VI < V$ . This order is the same as those obtained by weight-loss and linear polarization measurements.

Fig.(7) represents the plots of variation of the values of  $R_t$  with the concentration of compound (I) for the alloys (I, II). Similar plots are obtained in presence of different concentrations of the other compounds (II, III, IV, V, VI), but not shown. The plots of Fig.(7) and similar ones indicate that the values of  $R_t$  increase with the increase of inhibitors concentration.

Fig.(8) represents of plots of variation of the values of  $C_{dl}$  as a function of concentration of compound (I) for alloys (I,II). Similar plots are obtained in presence of different concentrations of the other compounds (II, III, IV,V, VI) but not shown. The plots of Fig. (8) and similar ones indicate that the values of  $C_{dl}$  decrease with increasing inhibitors concentration. This indicates, as above mentioned, the occurrence of adsorption of inhibitors molecules, on the surface of the investigated alloys.

As suggested by Hoar and Holliday [35], there may be on the metal surface cathodic and anodic sites providing centers for cathodic and anodic reactions. The adsorption of an inhibitor takes place through physical and chemisorption [36]. At the cathodic site on the metal

discharge of  $H^+$  ions take place. The rate of cathodic reaction will be governed by the availability of electrons at the cathodic sites. Supply of the negative charge to cathodic sites can be only maintained through the energy produced from chelation of active centers of adsorption atom may be N-atoms and / or S-atoms of inhibitor molecule and metallic surface (M) thus :



The adsorption of an organic adsorbate on the surface of a metal can be regarded as a substitutional adsorption process between the organic compound in aqueous phase  $org_{(aq)}$  and water molecules adsorbed on the electrode surface  $H_2O_{(s)}$  [37].



Where (x) is the size ratio, which is the number of water molecules replaced by one molecule of organic adsorbate. The above process attains equilibrium when :

$$\mu_{org(aq)} + \mu_{xH_2O(s)} = \mu_{org(s)} + \mu_{xH_2O(aq)}$$

where ( $\mu$ ) is the chemical potential.

Experimental relationships for the adsorption of organic inhibitors from the aqueous solution on the metallic surface versus concentration follow either the adsorption isotherms of Langmiur, Temkin, Frumkin, Hill de Boer and Parsons [38-41] in which the molecular interaction parameter (a) is included or the adsorption isotherms of Flory-Huggins, Dhar- Flory – Huggins and Bockris – Swinkels. In the first case, the molecular interaction parameter (a) which depends on the molecular



interaction in the adsorption layer and on the degree of heterogeneity of the sample, is included. In the later isotherms the number of water molecules replaced by one molecule of organic adsorbate (x) is included .

All the above isotherms are essentially of the form [42, 43].

$$f(\theta, x) \exp (-a\theta) = KC \quad (7)$$

Where  $\theta$  is a surface coverage, it can be calculated by applying the above –mentioned equations (1,3), C is the inhibitor concentration in the bulk of solution and f ( $\theta$ , x) is the configurational factor that depends essentially on the physical model and assumptions underlying derivation of the isotherm [43]. Moreover, all the above expressions include the equilibrium constant of the adsorption process (K) which is related to the standard free energy of adsorption  $\Delta G^\circ_{ads}$  by:

$$K = \frac{1}{55.5} \exp \frac{-\Delta G^\circ_{ads}}{RT} \quad (8)$$

Equations (7, 8) have been used in this study to evaluate the most suitable isotherm describing the adsorption of the investigated organic compounds (I-VI) onto the alloys (I, II) surface. Upon rearrangement of equation (7), the following equation is obtained ;

$$\ln \frac{f(\theta, x)}{C} = a\theta + \ln K \quad (9)$$

The plots of  $\theta$  versus  $\ln C$  for the investigated inhibitors (I, VI) are depicted in Figs (9,10) for the alloys (I, II), respectively. The values of  $\theta$  and C were taken from the results listed in tables (1-2) for the weight – loss measurements. From these plots, it is found that Temkin's isotherm is the most suitable for the adsorption process of the investigated inhibitors onto the surface of the alloys and has the form :

$$2\theta a = \ln KC \quad (10)$$

$$\theta = \frac{1}{-2a} \ln K + \frac{1}{-2a} \ln C \quad (11)$$

The straight lines of Figs.(9-10) have slopes of  $(1/-2a)$  and an intercept of  $(1/-2a \ln K)$ . The values of  $(K)$  can be determined and from them the standard free energy  $(\Delta G^\circ_{\text{ads}})$  can be calculated using equation (8). Also, the values of  $(a)$  can be calculated from the slopes of obtained straight lines of Figs.(9-10). The values of  $(\Delta G^\circ_{\text{ads}})$  and  $(a)$  are listed in table (7).

The negative values of  $(\Delta G^\circ_{\text{ads}})$  indicate that the adsorption of the investigated organic compounds on the surface of the alloys (I, II) is a spontaneous process [44].

The inhibition efficiency of the additive compounds depends on many factors including : the number of adsorption sites and their charge density, molecular size, heat of hydrogenation, mode of interaction with the metal and formation of metallic complex [45].

The possibility correlating structural characteristics with the inhibitor properties of organic substances is justified by the fact that the metal- inhibitor interactions are based on chemisorption. The electron density of the organic function can be defined as the reaction center for the establishment of the adsorption bond is then obviously important, since it is possible to assume a bond of the Lewis acid-base type [46], generally with the inhibitor as the electron donor and metal as the electron acceptor. The strength of this bond depends on the characteristics of both the adsorbent and adsorbate.

Organic compounds containing lone pairs and/or multiple bonds are usually effective inhibitors. Thus organic inhibitors are compounds with at least one polar function, having atoms of nitrogen, sulphur, oxygen and in some cases selenium and phosphorus. In such a case the adsorption bond strength is determined by the electron density of the atom acting as the reaction center and the polarizability of the function atoms. The effectiveness of the function atoms with respect to the adsorption process, when the stabilities of the compounds are equal can be taken as being in the following sequence :  $\text{Se} > \text{S} > \text{N} > \text{O}$  [47-50].

The obtained results in the present studies indicate that the inhibition efficiency,  $I\%$ , of the investigated organic compounds increases according to the order :  $\text{I} < \text{II} < \text{III} < \text{IV} < \text{VI} < \text{V}$ . This may be attributed to that compound (V) (2-aminiotiazole) contains more than one adsorption center including nitrogen and sulphur atoms, state of which gives more strong adsorption bond between the organic compound and the metallic surface. The compound (VI) (3-methyl- 1-phenyl-2-pyrazolin-5-one) contains more than one adsorption centers including nitrogen and oxygen atoms and also benzene ring state of which gives strong adsorption bond between the compound and the metallic surface. For this reason the inhibition efficiency of compound VI is less than that of compound (V) and higher than that of other compounds (I, II, III, IV).

The inhibition efficiency,  $I\%$ , of compounds (I, II, III, IV) are less than that of compounds (VI) and (V). Also, the inhibition efficiency of this series of compounds, (I - IV) increases according to the order :  $\text{I} < \text{II} < \text{III} < \text{IV}$ . The structural formulae of these compounds can be written as :



- 3- The negative values of (  $\Delta G_{\text{ads}}^{\circ}$  ) indicate that the adsorption of the investigated organic compound on the surface of alloys ( I , II ) is a spontaneous process.

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Table(1): Data of weight loss measurements for alloy (I) in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution and containing concentrations of compounds (I-VI) at 25°C.

compound	Concentration (M)	R <sub>w</sub> mg/cm <sup>2</sup> .h	θ	I%
( I )	0.00	0.06	-	-
	10 <sup>-6</sup>	0.0432	0.28	28
	10 <sup>-5</sup>	0.039	0.35	35
	10 <sup>-4</sup>	0.030	0.50	50
	10 <sup>-3</sup>	0.024	0.60	60
	10 <sup>-2</sup>	0.0168	0.72	72
	10 <sup>-1</sup>	0.012	0.80	80
( II )	0.00	0.06	-	-
	10 <sup>-6</sup>	0.0408	0.32	32
	10 <sup>-5</sup>	0.0354	0.41	41
	10 <sup>-4</sup>	0.0285	0.525	52.5
	10 <sup>-3</sup>	0.0219	0.635	63.5
	10 <sup>-2</sup>	0.0156	0.74	74
	10 <sup>-1</sup>	0.0096	0.84	84
( III )	0.00	0.06	-	-
	10 <sup>-6</sup>	0.0393	0.345	34.5
	10 <sup>-5</sup>	0.033	0.45	45
	10 <sup>-4</sup>	0.0264	0.56	56
	10 <sup>-3</sup>	0.0198	0.67	67
	10 <sup>-2</sup>	0.0141	0.765	76.5
	10 <sup>-1</sup>	0.0078	0.87	87
( IV )	0.00	0.06	-	-
	10 <sup>-6</sup>	0.0378	0.37	37
	10 <sup>-5</sup>	0.0318	0.47	47
	10 <sup>-4</sup>	0.0255	0.575	57.5
	10 <sup>-3</sup>	0.0183	0.695	69.5
	10 <sup>-2</sup>	0.012	0.80	80
	10 <sup>-1</sup>	0.006	0.90	90
( V )	0.00	0.06	-	-
	10 <sup>-6</sup>	0.033	0.45	45
	10 <sup>-5</sup>	0.0276	0.54	54
	10 <sup>-4</sup>	0.0204	0.66	66
	10 <sup>-3</sup>	0.0144	0.76	76
	10 <sup>-2</sup>	0.0078	0.87	87
	10 <sup>-1</sup>	0.0024	0.96	96
( VI )	0.00	0.06	-	-
	10 <sup>-6</sup>	0.036	0.40	40
	10 <sup>-5</sup>	0.030	0.50	50
	10 <sup>-4</sup>	0.0228	0.62	62
	10 <sup>-3</sup>	0.0165	0.725	72.5
	10 <sup>-2</sup>	0.0105	0.825	82.5
	10 <sup>-1</sup>	0.0045	0.925	92.5

Table(2) : Data of weight loss measurements for alloy (II) in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution and containing different concentrations of compounds ( I-VI ) at 25°C .

compound	Concentration (M)	R <sub>w</sub> mg/cm <sup>2</sup> .h	θ	I%
( I )	0.00	0.12	-	-
	10 <sup>-6</sup>	0.00948	0.21	21
	10 <sup>-5</sup>	0.081	0.325	32.5
	10 <sup>-4</sup>	0.0684	0.43	43
	10 <sup>-3</sup>	0.0552	0.54	54
	10 <sup>-2</sup>	0.039	0.675	67.5
	10 <sup>-1</sup>	0.030	0.75	75
( II )	0.00	0.12	-	-
	10 <sup>-6</sup>	0.0888	0.26	26
	10 <sup>-5</sup>	0.0768	0.36	36
	10 <sup>-4</sup>	0.063	0.475	47.5
	10 <sup>-3</sup>	0.051	0.575	57.5
	10 <sup>-2</sup>	0.0348	0.71	71
	10 <sup>-1</sup>	0.0252	0.79	79
( III )	0.00	0.12	-	-
	10 <sup>-6</sup>	0.0852	0.29	29
	10 <sup>-5</sup>	0.072	0.40	40
	10 <sup>-4</sup>	0.060	0.50	50
	10 <sup>-3</sup>	0.0468	0.61	61
	10 <sup>-2</sup>	0.0312	0.74	74
	10 <sup>-1</sup>	0.021	0.825	82.5
( IV )	0.00	0.12	-	-
	10 <sup>-6</sup>	0.081	0.325	32.5
	10 <sup>-5</sup>	0.0666	0.445	44.5
	10 <sup>-4</sup>	0.0552	0.54	54
	10 <sup>-3</sup>	0.0432	0.64	64
	10 <sup>-2</sup>	0.027	0.775	77.5
	10 <sup>-1</sup>	0.0180	0.85	85
( V )	0.00	0.12	-	-
	10 <sup>-6</sup>	0.0744	0.38	38
	10 <sup>-5</sup>	0.0612	0.49	49
	10 <sup>-4</sup>	0.048	0.60	60
	10 <sup>-3</sup>	0.0348	0.71	71
	10 <sup>-2</sup>	0.0192	0.84	84
	10 <sup>-1</sup>	0.0096	0.92	92
( VI )	0.00	0.12	-	-
	10 <sup>-6</sup>	0.078	0.35	35
	10 <sup>-5</sup>	0.0642	0.465	46.5
	10 <sup>-4</sup>	0.051	0.575	57.5
	10 <sup>-3</sup>	0.0384	0.68	68
	10 <sup>-2</sup>	0.0228	0.81	81
	10 <sup>-1</sup>	0.0132	0.89	89

Table(3) : Data of linear polarization measurements for alloy (I) in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution and containing different concentrations of compounds (I-VI) at 25°C.

compound	Concentration (M)	R <sub>p</sub> Ω. cm <sup>2</sup>	θ	I%
( I )	0.00	750	-	-
	10 <sup>-6</sup>	1027.40	0.27	27
	10 <sup>-5</sup>	1136.36	0.34	34
	10 <sup>-4</sup>	1442.31	0.48	48
	10 <sup>-3</sup>	1875.0	0.60	60
	10 <sup>-2</sup>	2500	0.70	70
	10 <sup>-1</sup>	3571.43	0.79	79
( II )	0.00	750	-	-
	10 <sup>-6</sup>	1086.96	0.31	31
	10 <sup>-5</sup>	1250	0.40	40
	10 <sup>-4</sup>	1562.5	0.52	52
	10 <sup>-3</sup>	2027.03	0.63	63
	10 <sup>-2</sup>	2777.78	0.73	73
	10 <sup>-1</sup>	4545.45	0.835	83.5
( III )	0.00	750	-	-
	10 <sup>-6</sup>	1136.36	0.34	34
	10 <sup>-5</sup>	1351.35	0.445	44.5
	10 <sup>-4</sup>	1666.67	0.55	55
	10 <sup>-3</sup>	2205.88	0.66	66
	10 <sup>-2</sup>	3125	0.76	76
	10 <sup>-1</sup>	5357.14	0.86	86
(IV )	0.00	750	-	-
	10 <sup>-6</sup>	1181.1	0.365	36.5
	10 <sup>-5</sup>	1388.89	0.46	46
	10 <sup>-4</sup>	1744.19	0.57	57
	10 <sup>-3</sup>	2419.35	0.69	69
	10 <sup>-2</sup>	3750	0.8	80
	10 <sup>-1</sup>	6818.18	0.89	89
( V )	0.00	750	-	-
	10 <sup>-6</sup>	1339.29	0.44	44
	10 <sup>-5</sup>	1595.74	0.53	53
	10 <sup>-4</sup>	2142.86	0.65	65
	10 <sup>-3</sup>	3000	0.75	75
	10 <sup>-2</sup>	5357.14	0.86	86
	10 <sup>-1</sup>	15000	0.95	95
(VI )	0.00	750	-	-
	10 <sup>-6</sup>	1229.51	0.39	39
	10 <sup>-5</sup>	1470.59	0.49	49
	10 <sup>-4</sup>	1875	0.6	60
	10 <sup>-3</sup>	2678.57	0.72	72
	10 <sup>-2</sup>	4166.7	0.82	82
	10 <sup>-1</sup>	9375	0.92	92

Table( 4 ) :Data of linear polarization for alloy (II) in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution and containing different concentrations of compounds (I-VI) at 25°C.

compound	Concentration (M)	R <sub>p</sub> Ω. cm <sup>2</sup>	θ	I%
( I )	0.00	500	-	-
	10 <sup>-6</sup>	625	0.20	20
	10 <sup>-5</sup>	735.29	0.32	32
	10 <sup>-4</sup>	863.07	0.42	42
	10 <sup>-3</sup>	1083.83	0.53	53
	10 <sup>-2</sup>	1515.15	0.67	67
	10 <sup>-1</sup>	2000	0.75	75
( II )	0.00	500	-	-
	10 <sup>-6</sup>	671.14	0.255	25.5
	10 <sup>-5</sup>	769.23	0.35	35
	10 <sup>-4</sup>	943.396	0.47	47
	10 <sup>-3</sup>	1162.79	0.57	57
	10 <sup>-2</sup>	1666.67	0.7	70
	10 <sup>-1</sup>	2325.58	0.785	78.5
( III )	0.00	500	-	-
	10 <sup>-6</sup>	694.44	0.28	28
	10 <sup>-5</sup>	819.67	0.39	39
	10 <sup>-4</sup>	980.39	0.49	49
	10 <sup>-3</sup>	1250	0.6	60
	10 <sup>-2</sup>	1851.85	0.73	73
	10 <sup>-1</sup>	2777.78	0.82	82
(IV )	0.00	500	-	-
	10 <sup>-6</sup>	735.29	0.32	32
	10 <sup>-5</sup>	892.86	0.44	44
	10 <sup>-4</sup>	1063.83	0.53	53
	10 <sup>-3</sup>	1351.35	0.63	63
	10 <sup>-2</sup>	2173.9	0.77	77
	10 <sup>-1</sup>	3225.81	0.845	84.5
( V )	0.00	500	-	-
	10 <sup>-6</sup>	793.65	0.37	37
	10 <sup>-5</sup>	961.54	0.48	48
	10 <sup>-4</sup>	1250	0.60	60
	10 <sup>-3</sup>	1666.67	0.70	70
	10 <sup>-2</sup>	2941.18	0.83	83
	10 <sup>-1</sup>	5882.35	0.915	91.5
(VI )	0.00	500	-	-
	10 <sup>-6</sup>	757.58	0.34	34
	10 <sup>-5</sup>	925.93	0.46	46
	10 <sup>-4</sup>	1162.79	0.57	57
	10 <sup>-3</sup>	1515.15	0.67	67
	10 <sup>-2</sup>	2500	0.80	80
	10 <sup>-1</sup>	4166.67	0.88	88



Table (5): Data of impedance measurements for alloy (I) in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution and containing different concentrations of compounds(I-VI) at 25°C.

compound	Concentration (M)	R <sub>t</sub> Ω .cm <sup>2</sup>	C <sub>dl</sub> μF/ cm <sup>2</sup>	I%
( I )	0.00	150	1061.57	-
	10 <sup>-6</sup>	206.9	769.63	27.5
	10 <sup>-5</sup>	230.77	689.93	35
	10 <sup>-4</sup>	300	530.79	50
	10 <sup>-3</sup>	370.37	429.9	59.5
	10 <sup>-2</sup>	535.71	297.25	72
	10 <sup>-1</sup>	731.7	217.62	79.5
( II )	0.00	150	1061.57	-
	10 <sup>-6</sup>	220.59	721.83	32
	10 <sup>-5</sup>	250	636.94	40
	10 <sup>-4</sup>	319.15	497.7	53
	10 <sup>-3</sup>	416.67	381.9	64
	10 <sup>-2</sup>	576.92	275.98	74
	10 <sup>-1</sup>	967.74	164.5	84.5
( III )	0.00	150	1061.57	-
	10 <sup>-6</sup>	227.27	700.55	34
	10 <sup>-5</sup>	272.73	583.86	45
	10 <sup>-4</sup>	337.08	472.5	55.5
	10 <sup>-3</sup>	447.76	355.44	66.5
	10 <sup>-2</sup>	625	254.78	76
	10 <sup>-1</sup>	1200	132.7	87.5
(IV )	0.00	150	1061.57	-
	10 <sup>-6</sup>	236.22	674.1	36.5
	10 <sup>-5</sup>	283.02	562.67	47
	10 <sup>-4</sup>	348.84	456.3	57
	10 <sup>-3</sup>	488.87	329	69
	10 <sup>-2</sup>	750	212.31	80
	10 <sup>-1</sup>	1578.94	100.85	90.5
( V )	0.00	150	1061.57	-
	10 <sup>-6</sup>	270.27	589.17	44.5
	10 <sup>-5</sup>	326.09	488.45	54
	10 <sup>-4</sup>	434.78	366.06	65.5
	10 <sup>-3</sup>	600	265.39	75
	10 <sup>-2</sup>	1111.11	143.31	86.5
	10 <sup>-1</sup>	3000	53.08	95
(VI)	0.00	150	1061.57	-
	10 <sup>-6</sup>	250	636.94	40
	10 <sup>-5</sup>	300	530.78	50
	10 <sup>-4</sup>	389.61	408.3	61.5
	10 <sup>-3</sup>	535.71	297.08	72
	10 <sup>-2</sup>	833.33	191.08	82
	10 <sup>-1</sup>	1875	84.93	92

Table(6): Data of impedance measurements for alloy (II) in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution and containing different concentrations of compounds(I-VI) at 25°C.

compound	Concentration (M)	R <sub>t</sub> Ω .cm <sup>2</sup>	C <sub>dl</sub> μF/ cm <sup>2</sup>	I%
( I )	0.00	100	1592.36	-
	10 <sup>-6</sup>	125	1273.9	20
	10 <sup>-5</sup>	147	1083.24	32
	10 <sup>-4</sup>	175.44	907.32	43
	10 <sup>-3</sup>	215.5	738.9	53.5
	10 <sup>-2</sup>	303.03	525.53	67
	10 <sup>-1</sup>	392.16	406	74.5
( II )	0.00	100	1592.36	-
	10 <sup>-6</sup>	135.14	1178.3	26
	10 <sup>-5</sup>	153.85	1035	35
	10 <sup>-4</sup>	188.68	842.5	47
	10 <sup>-3</sup>	232.56	684.6	57
	10 <sup>-2</sup>	333.33	477.71	70
	10 <sup>-1</sup>	465.12	342.36	78.5
( III )	0.00	100	1592.36	-
	10 <sup>-6</sup>	138.88	1146.4	28
	10 <sup>-5</sup>	166.67	953.51	40
	10 <sup>-4</sup>	200	796.18	50
	10 <sup>-3</sup>	250	636.94	60
	10 <sup>-2</sup>	384.62	414.01	74
	10 <sup>-1</sup>	555.56	286.6	82
( IV )	0.00	100	1592.36	-
	10 <sup>-6</sup>	147.06	1083.24	32
	10 <sup>-5</sup>	178.57	889.58	44
	10 <sup>-4</sup>	217.39	732.45	54
	10 <sup>-3</sup>	277.78	573.2	64
	10 <sup>-2</sup>	370.37	429.94	77
	10 <sup>-1</sup>	625	254.78	84
( V )	0.00	100	1592.36	-
	10 <sup>-6</sup>	161.29	1012.96	38
	10 <sup>-5</sup>	192.31	828.02	48
	10 <sup>-4</sup>	243.9	652.87	59
	10 <sup>-3</sup>	333.33	477.71	70
	10 <sup>-2</sup>	606.6	262.51	83.5
	10 <sup>-1</sup>	1250	127.39	92
( VI )	0.00	100	1592.36	-
	10 <sup>-6</sup>	153.85	1034.67	35
	10 <sup>-5</sup>	185.19	859.8	46
	10 <sup>-4</sup>	232.56	684.6	57
	10 <sup>-3</sup>	307.69	517.5	67.5
	10 <sup>-2</sup>	500	318.98	80
	10 <sup>-1</sup>	833.33	191.1	88

Table (7): Standard free energy  $\Delta G_{\text{ads}}^{\circ}$  for alloy (I) and alloy (II) in 0.5 M  $\text{H}_2\text{SO}_4$  containing different concentrations of different inhibitors (I- VI) at 25°C.

Inhibitor	Alloy (I)		Alloy (II)	
	$\Delta G_{\text{ads}}^{\circ}$ ( KJ/mol )	a	$\Delta G_{\text{ads}}^{\circ}$ ( KJ/mol )	a
( I )	-55.477	-11.5	-50.485	-10.925
( II )	-49.048	-9.409	-54.899	-11.50
(III)	-57.40	-11.022	-56.892	-11.50
(IV)	-59.552	-11.138	-58.316	-11.50
( V )	-62.299	-11.02	-62.304	-11.50
(VI)	-58.822	-10.679	-60.595	-11.50

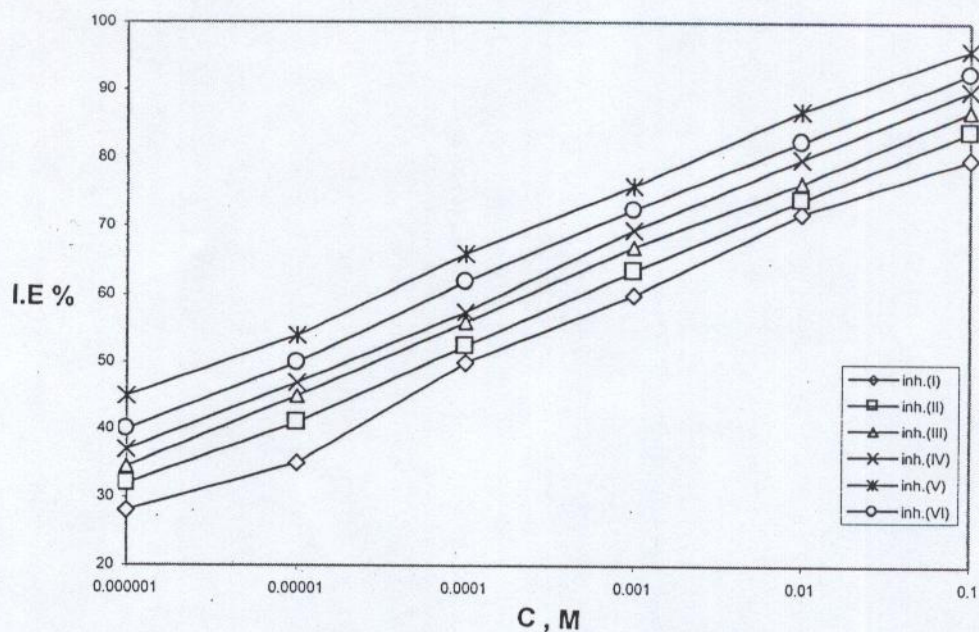


Fig.(1): Variation of inhibition efficiency with concentration for alloy (I) in 0.5M H<sub>2</sub>SO<sub>4</sub> solution containing different inhibitors ( I-VI) at 25°C.

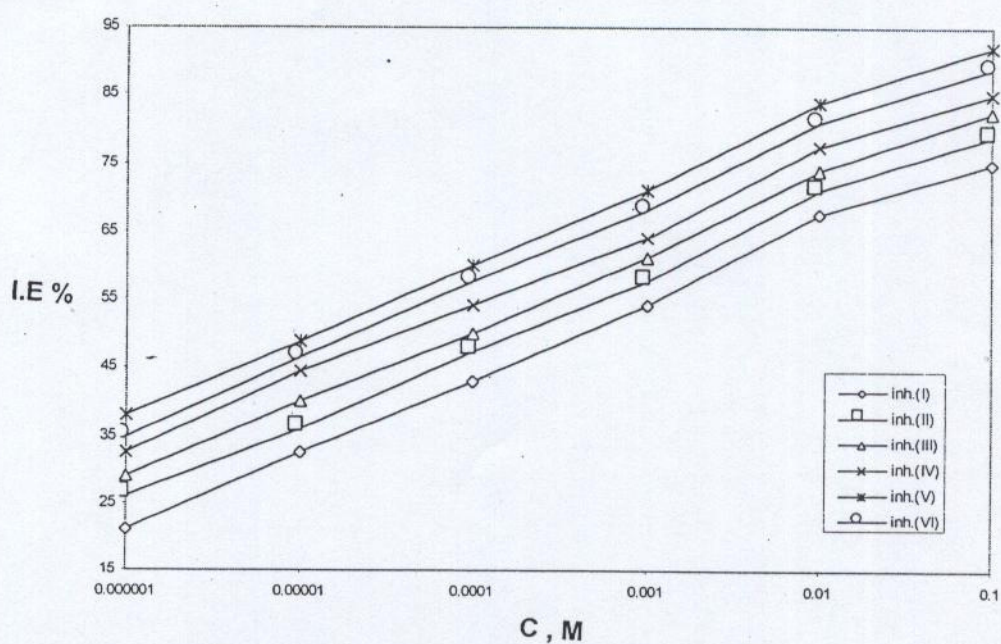


Fig.(2): Variation of inhibition efficiency with concentration for alloy (II) in 0.5M H<sub>2</sub>SO<sub>4</sub> solution containing different inhibitors ( I-VI) at 25°C.



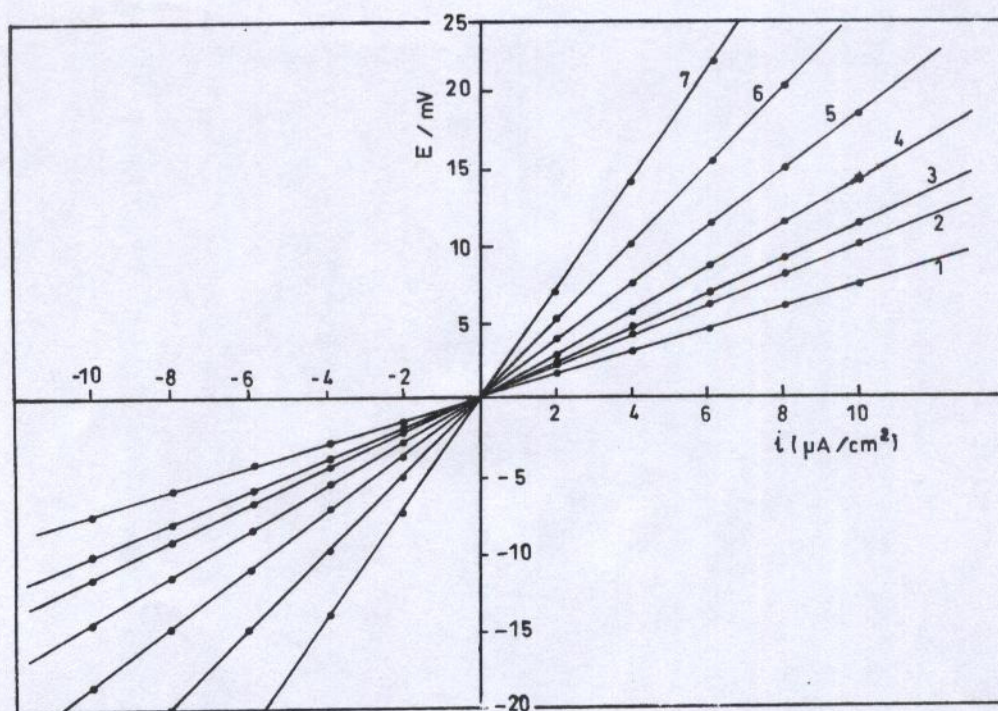


Fig.( 3 ) :linear polarization plots for alloy (I) in 0.5M  $H_2SO_4$  solution in absence and in presence of inhibitor (I) at 25°C. where 1=0.00M glycine , 2=  $10^{-6}$ M glycine, 3= $10^{-5}$ M glycine,4= $10^{-4}$  M glycine, 5= $10^{-3}$  M glycine, 6= $10^{-2}$  M glycine, 7= $10^{-1}$  M glycine.



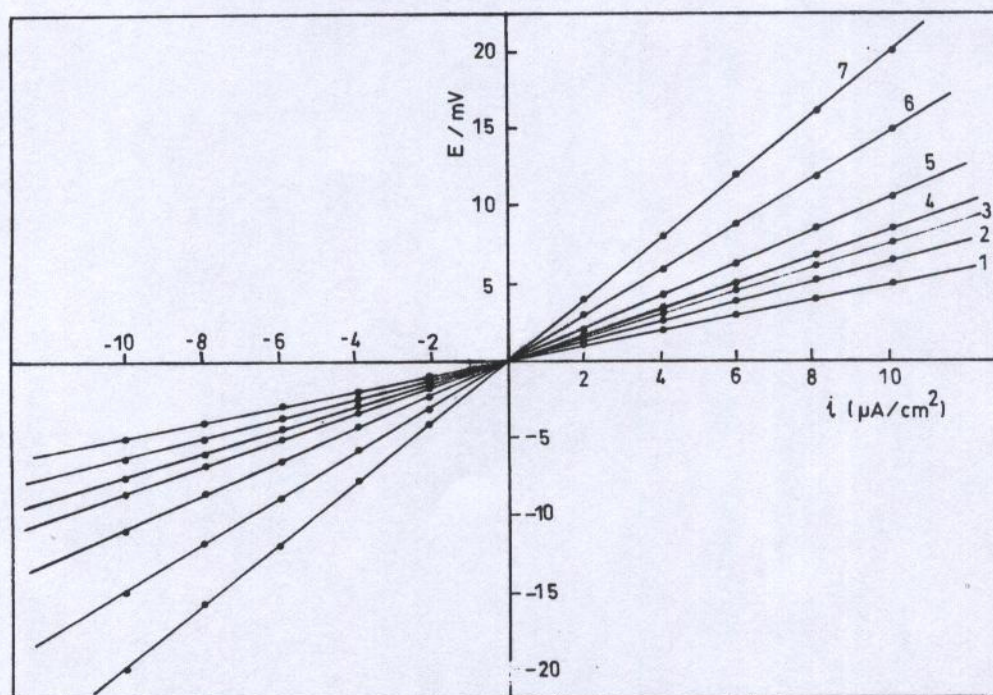


Fig.( 4 ) :linear polarization plots for alloy (II) in 0.5M  $H_2SO_4$  solution in absence and in presence of inhibitor (I) at 25°C. where 1=0.00M glycine , 2=  $10^{-6}$ M glycine, 3= $10^{-5}$ M glycine, 4= $10^{-4}$  M glycine, 5= $10^{-3}$  M glycine, 6= $10^{-2}$  M glycine, 7= $10^{-1}$  M glycine.

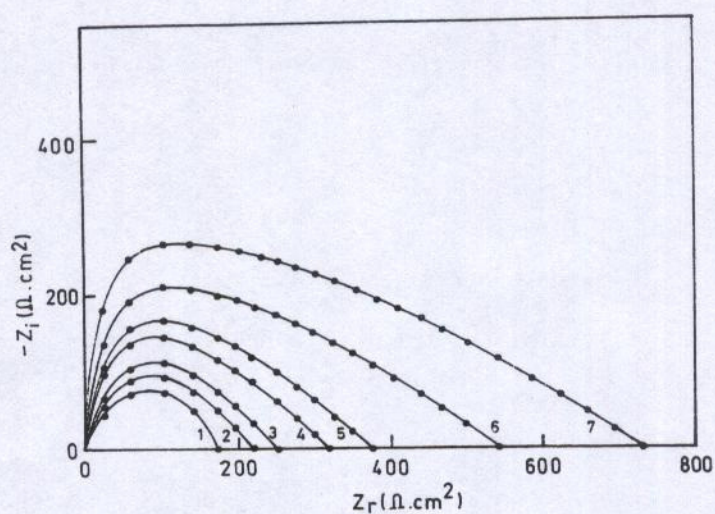


Fig.( 5 ) :Nyquist plots for alloy (I) in 0.5M H<sub>2</sub>SO<sub>4</sub> solution in absence and in presence of different concentrations of inhibitor (I) at 25°C.  
where 1=0.00M glycine , 2= 10<sup>-6</sup>M glycine, 3=10<sup>-5</sup>M glycine,  
4=10<sup>-4</sup> M glycine, 5=10<sup>-3</sup> M glycine, 6=10<sup>-2</sup> M glycine, 7=10<sup>-1</sup> M glycine.



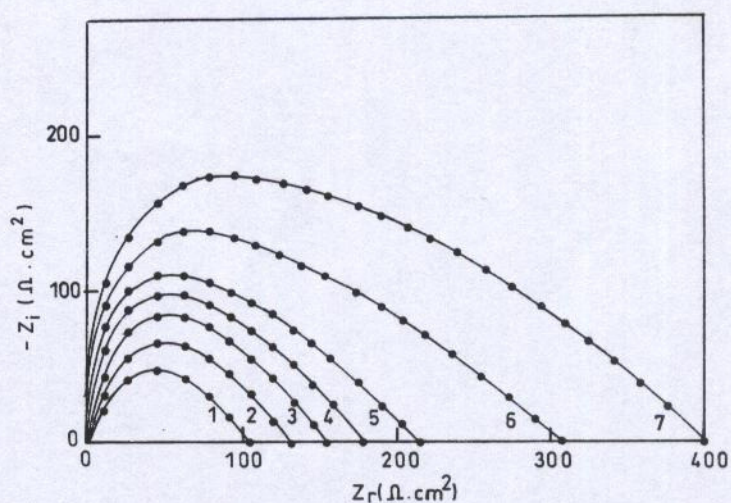


Fig.( 6 ) :Nyquist plots for alloy (II) in 0.5M  $H_2SO_4$  solution in absence and in presence of different concentrations of inhibitor (I) at 25°C. where 1=0.00M glycine , 2= $10^{-6}$ M glycine, 3= $10^{-5}$ M glycine, 4= $10^{-4}$  M glycine, 5= $10^{-3}$  M glycine, 6= $10^{-2}$  M glycine, 7= $10^{-1}$  M glycine.

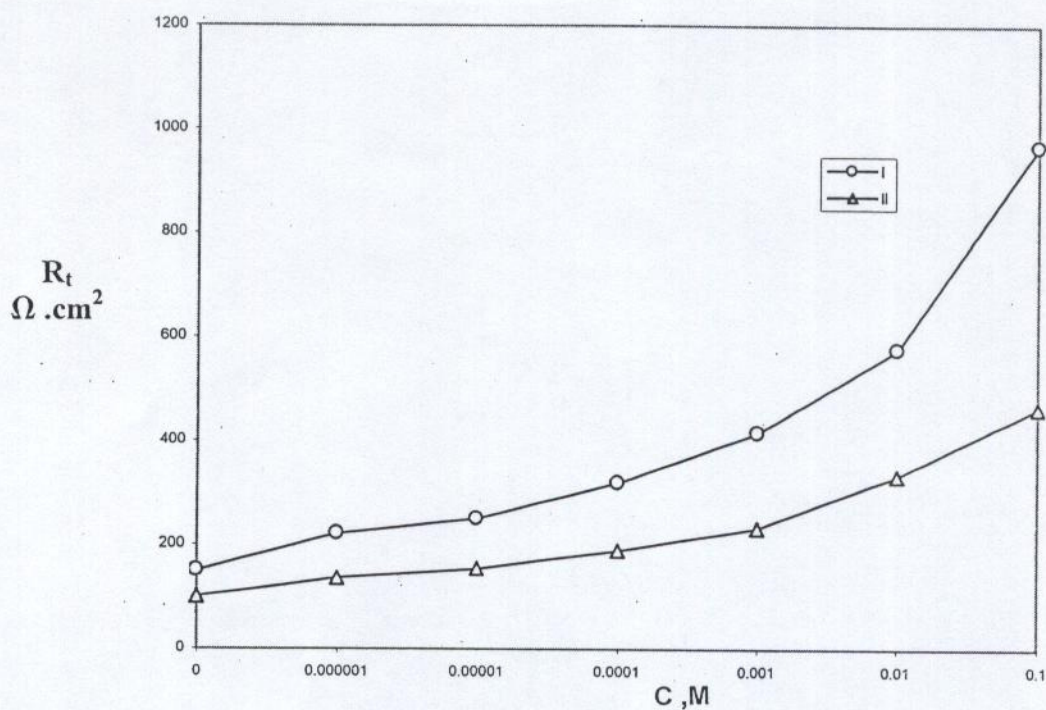


Fig.(7): variation of the charge transfer resistance with concentration of inhibitor (I) glycine for alloy (I) and alloy (II) in 0.5M  $\text{H}_2\text{SO}_4$  solution at 25°C.

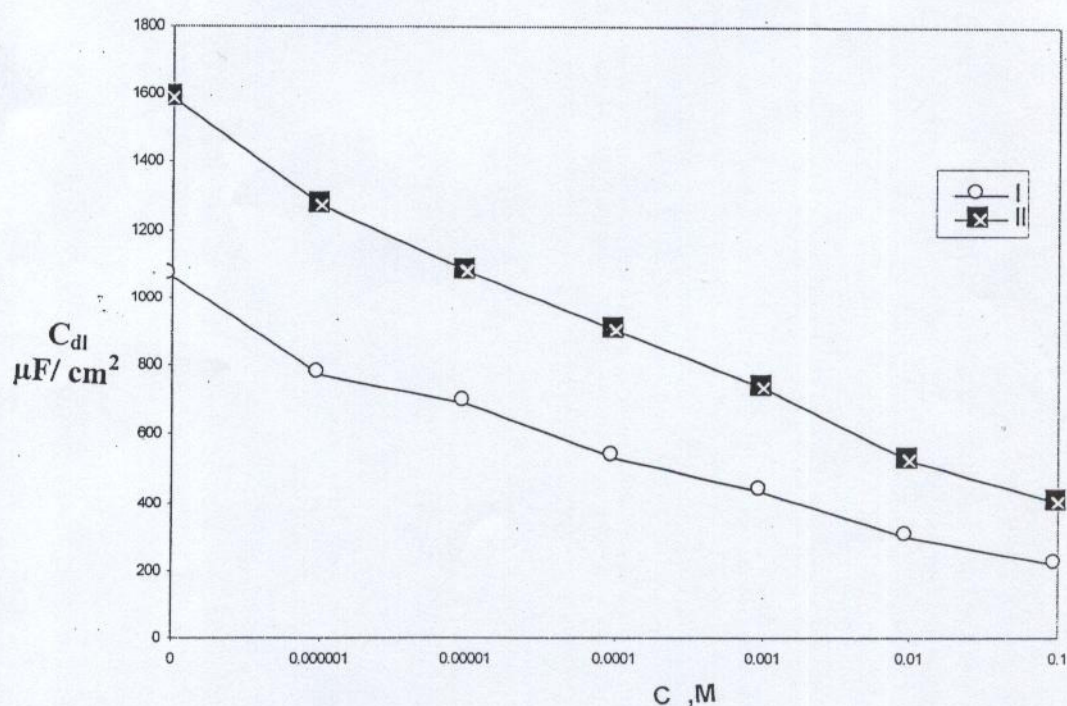


Fig.(8): variation of the double layer capacitance with concentration of inhibitor (I) glycine for alloy (I) and alloy (II) in 0.5M H<sub>2</sub>SO<sub>4</sub> solution at 25°C.



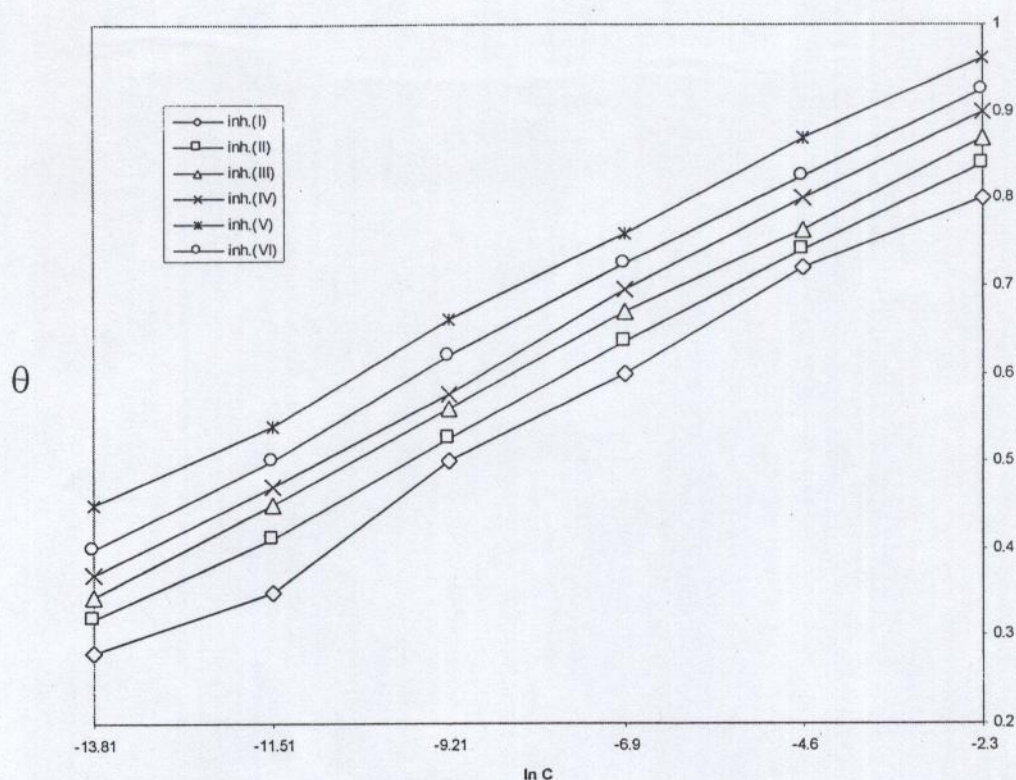


Fig.(9): variation of the surface coverage( $\theta$ ) with  $\ln(\text{concentration})$  for alloy (I) in 0.5M  $\text{H}_2\text{SO}_4$  solution containing different inhibitors (I-VI) at 25°C.



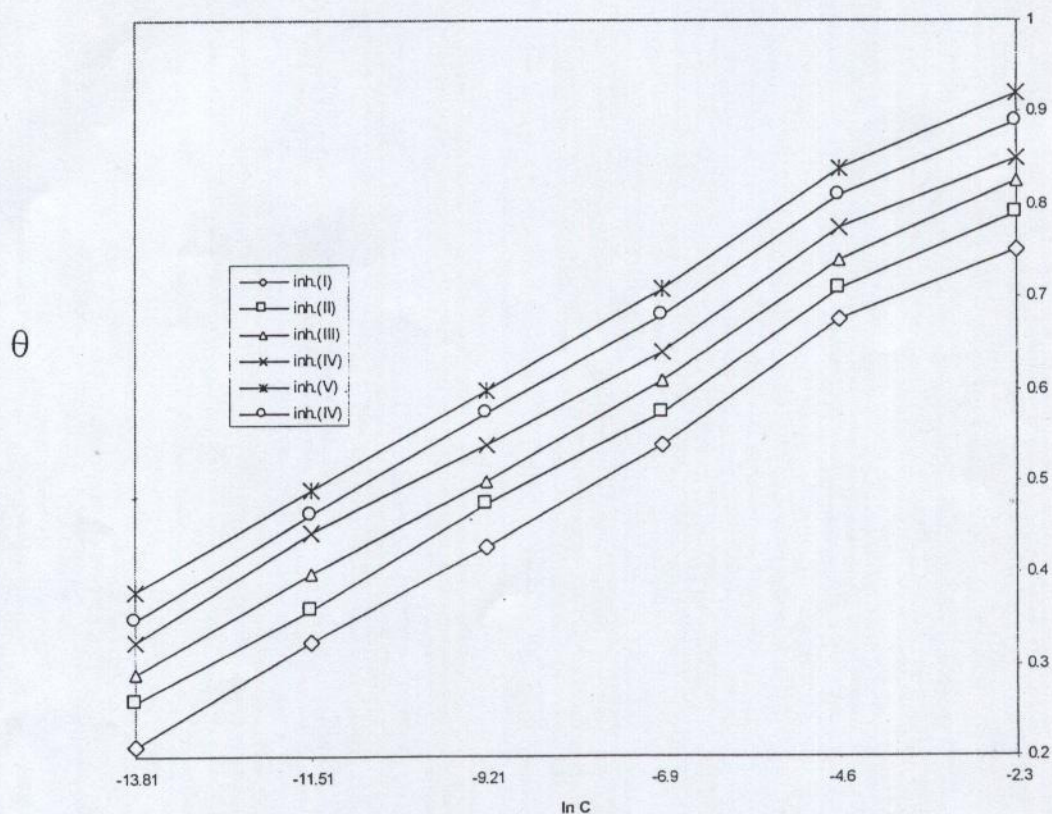


Fig.(10): variation of the surface coverage( $\theta$ ) with  $\ln(\text{concentration})$  for alloy (II) in 0.5M  $\text{H}_2\text{SO}_4$  solution containing different inhibitors (I-VI) at 25°C.





