

13. R. N. Roy, J. J. Gibbons, J. K. Trower, G. A. Lee, J. J. Hartley and J. G. Mack, *J. Chem. Thermodynamics*, **14**, 473 (1982).
14. C. Y. Chan, Y. Weng and K. Sen, *J. Chem. Eng. Data*, **40**, 685 (1995).

THE INHIBITION EFFECT OF 4(2-PYRIDYL)-1-BENZALDEHYDE-3-THIOSEMICARBAZONE DERIVATIVES TOWARDS THE IRON CORROSION

by S.A. Abd El-Maksoud

Chemistry Department, Faculty of Education, Suez Canal University, El-Arish, Sinai, Egypt

ABSTRACT

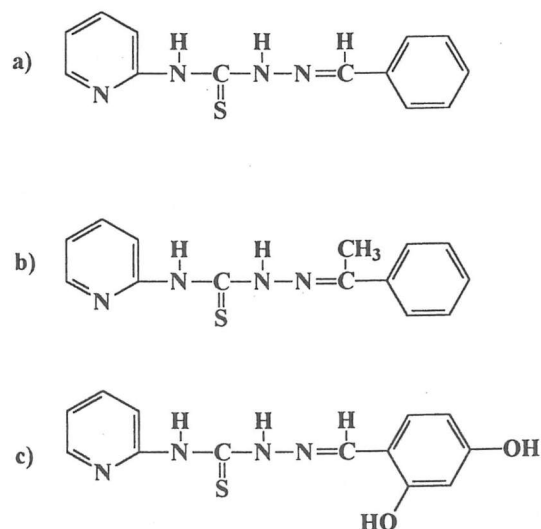
The effect of 4(2-pyridyl)-1-benzaldehyde-3-thiosemicarbazone derivatives towards the corrosion of iron in 1M HCl solution at 303K was investigated. Potentiodynamic and weight loss measurements show that compounds under investigation act as effective inhibitors for the corrosion of iron in 1 M HCl. The results show that these compounds behave as mixed type inhibitors. The corrosion rate was found to be a function of the nature and concentration of the inhibitors. The adsorption of the compounds on the iron surface is found to obey Temkin's adsorption isotherm.

Key words: Corrosion, inhibition, iron, potentiodynamic, weight loss.

INTRODUCTION

The inhibition of corrosion of iron in acidic media by different type of organic compounds has been widely studied[1-11]. The existing data show that most organic inhibitors act by adsorption on the iron surface. This phenomenon is influenced by the nature and surface charge of metal, by the type of aggressive electrolyte and by the chemical structure of inhibitors. Most organic inhibitors are substances with at least one functional group considered as the reaction centre for the adsorption process. The adsorption of inhibitor is related to the presence of hetero atoms as nitrogen, phosphorus and sulphur as well as triple bond or aromatic ring in their molecular structure. It has also been noted that the molecular area[12] and molecular weight[13] of the inhibitor play an important role.

In previous work, Sym. diphenylcarbazine, thiosemicarbazide and semicarbazide were studied as inhibitors for acid corrosion of aluminium[14] and zinc[15]. Thiosemicarbazone derivatives were used as inhibitors for the corrosion of iron in acidic medium[16]. The aim of the present work is to study the inhibition action of a new class of compounds of 4(2-pyridyl)-1-benzaldehyde-3-thiosemicarbazone derivatives towards the corrosion of iron. The choice of these compounds is based on the presence of an electron cloud on the aromatic ring, the electronegative nitrogen and the easily polarized sulphur which induce greater adsorption of the compounds on the surface of the iron, which can lead to effective inhibition. Compounds used in this study are shown below.



EXPERIMENTAL

Organic inhibitors were prepared as previously described.[17]. The potentiodynamic studies were carried out using Wenking potentiostat model LB 75H, Wenking function generator model VSG 72 and Philips PM 8271 xyt recorder. Iron test samples containing 0.016%C, 0.005%P, 0.25%Mn, 0.019%S, 0.04%Si, 0.055%Cr, 0.035%Ni and 0.07%Cu were used. For potentiodynamic measurement, circular wire of 0.53mm diameter and 1 cm length were used, the electrodes were polished with emery paper, cleaned with distilled water and degreased in acetone. Finally, they were washed with distilled water and dried between two filter papers. For weight loss experiments pieces with dimensions of 20x20x1 mm were used. Experiments were carried out with potential scan rate of 1mVs^{-1} in a double wall three compartment cell; reference and counter electrodes were saturated calomel (SCE) and platinum sheet electrode, respectively. Electrolytic solutions were prepared from analytical grade HCl and water obtained with a Megapure system (MP-A6 Corning). All experiments were carried out at $30\pm 0.2^\circ\text{C}$ using ultrathermostatic bath.

RESULTS AND DISCUSSION

A- Potentiodynamic studies:

Current density-potential curves for iron in 1M HCl in the absence and in the presence of compounds were studied. Before each measurement, open circuit potential, " $E_{o,p}$ " was allowed to stabilise for 20 min. immersion. The sweep rate was 1mVs^{-1} with holding time of 30 sec. at -660mV vs. SCE. Fig.1 shows the potentiodynamic

polarization curves of iron in 1M HCl in the absence and in the presence of different concentrations ($1\times 10^{-6}\text{M}$ — $1\times 10^{-4}\text{M}$) of inhibitor a. It is clearly observed that the presence of inhibitor a reduces the current value at constant potential, and this suppression in current increases as the inhibitor concentration increases.

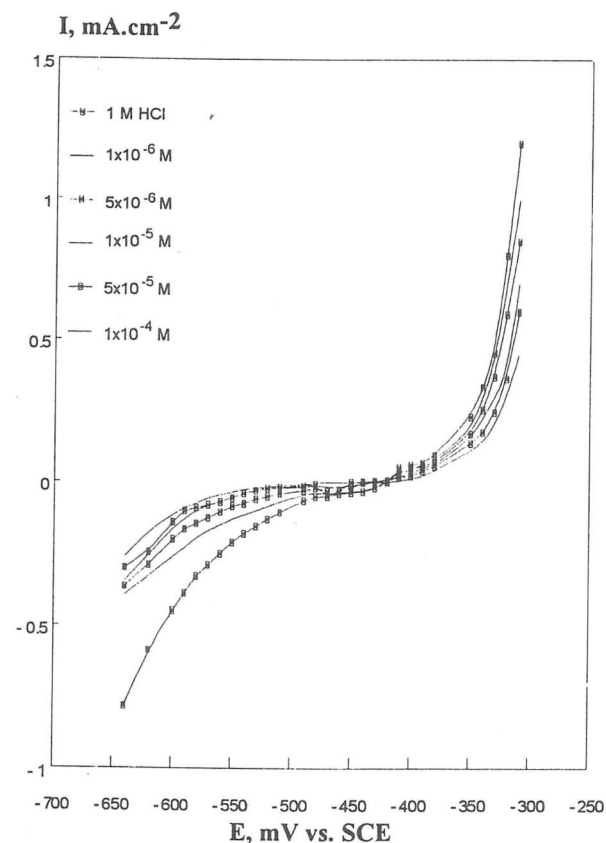


Fig.1: Potentiodynamic polarization curves of iron in 1M HCl in the absence and in the presence of different concentration of compound a., Scan rate = 1mV.s^{-1} at 30°C

Fig.2 shows the potentiodynamic polarization curves ($v = 1\text{mVs}^{-1}$) of iron in the absence and in the presence of $1\times 10^{-5}\text{M}$ of different inhibitors. From this figure one can conclude that the order of inhibition is $c > b > a$.

Tables 1 and 2 represent the electrochemical parameters for iron corrosion in 1M HCl containing different concentrations of compound a and $1\times 10^{-5}\text{M}$ of different compounds respectively. Table 1 shows the corrosion potential, E_{CORR} , the corrosion current density, I_{CORR} , Tafel slopes, B_c and B_a , and percentage inhibition, %I. From this table one can conclude that:

- 1) The inhibitors affect the cathodic reaction more than the anodic one, since $B_c > B_a$ and E_{corr} goes to more ϕ negative values.
- 2) The percentage inhibition increases with the increase of inhibitor concentration.
- 3) The corrosion current densities calculated by Tafel extrapolation decreases with the increase of concentrations of inhibitor a.

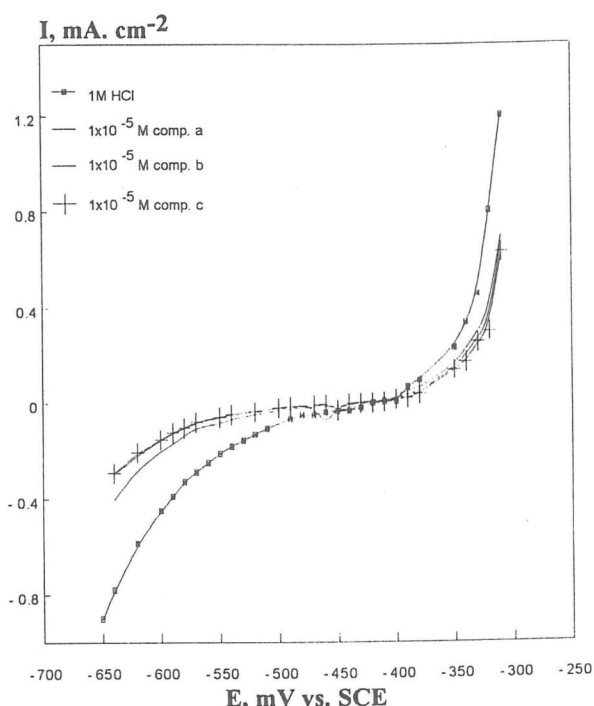


Fig.2: Potentiodynamic polarization curves of iron in 1M HCl in the absence and in the presence of 1×10^{-5} M concentration of different compounds., Scan rate = $1 \text{ mV} \cdot \text{s}^{-1}$ at 30°C

Table.1 Electrochemical parameters for iron corrosion in 1M HCl containing different concentrations of compound a.

	$-E_{corr.}$ mV(vs. SCE)	$I_{corr.}$ mA.cm ⁻²	B_c mV/decade	B_a mV/decade	%inh. % I
Free	429	20.7	98	65	—
$1 \times 10^{-6}\text{M}$	431	15.8	101	68	19.9
$5 \times 10^{-6}\text{M}$	433	8.9	108	69	57.2
$1 \times 10^{-5}\text{M}$	440	6.7	111	69	68.4
$5 \times 10^{-5}\text{M}$	445	4.3	114	70	79.3
$1 \times 10^{-4}\text{M}$	447	2.5	109	72	87.9

Table.2a: Electrochemical parameters for iron corrosion in 1M HCl containing $1 \times 10^{-5}\text{M}$ concentration of different compounds.

	$-E_{corr.}$, mV (vs. SCE)	$I_{corr.}$ mA.cm ⁻²	B_c mV/decade	B_a mV/decade	%inh. % I
Free	429	20.7	98	65	—
compound a	440	6.7	111	69	68.4
compound b	445	6.0	114	64	71.1
compound c	444	5.1	110	68	75.3

Table.2b- Electrochemical parameters for iron corrosion in 1M HCl containing $1 \times 10^{-4}\text{M}$ concentration of different compounds.

	$-E_{corr.}$, mV (vs. SCE)	$I_{corr.}$ mA.cm ⁻²	B_c mV/decade	B_a mV/decade	%inh. % I
Free	429	20.7	98	65	—
compound a	447	2.5	109	72	87.9
compound b	445	2.15	114	70	89.6
compound c	446	1.41	112	74	93.2

Table 2 (a and b) represent the effect of $1 \times 10^{-5}\text{M}$ and $1 \times 10^{-4}\text{M}$ from inhibitors under investigation. From the table, it is clear that the current densities decrease in the order $a > b > c$ and the order of inhibition efficiency is $c > b > a$. The values for the corrosion current densities and corrosion potentials were estimated from the intersection of the anodic and cathodic Tafel lines. Fig.3 shows experimental results from potentiodynamic polarization and Tafel lines at different concentrations ($1 \times 10^{-6}\text{M}$ — $1 \times 10^{-4}\text{M}$) from inhibitor a. It is observed that the value of $i_{corr.}$ decreases in the presence of different concentrations of compound a and the values of $i_{corr.}$ decreases with increasing of concentrations. Fig.4 shows the plot of Tafel lines at $1 \times 10^{-5}\text{M}$ of different inhibitors, the corrosion current densities for the substituted $1 \times 10^{-5}\text{M}$ of different inhibitors, the corrosion current densities for the substituted compounds decrease than the unsubstituted inhibitor and the decrease is in the order $a > b > c$. The inhibition efficiency (%I) was obtained from the corrosion current densities of the uninhibited (i_u) and inhibited electrodes (i) according to equation (1)

$$(\%I) = 100 (1 - i / i_u) \quad (1)$$

The inhibition efficiency varies in the order $c > b > a$.

B- Weight loss measurement.

Iron pieces were immersed in unstirred 1M HCl with different concentrations of the inhibitors at 30°C . Fig.5 is a plot of the weight loss (mg cm^{-2}) vs. the time of

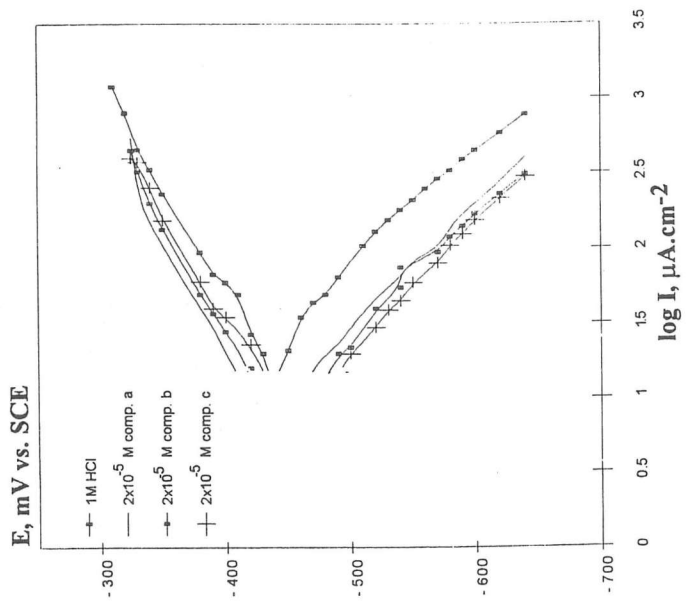


Fig. 4. Tafel lines for iron in 1M HCl at $1 \times 10^{-5}M$ of different compounds

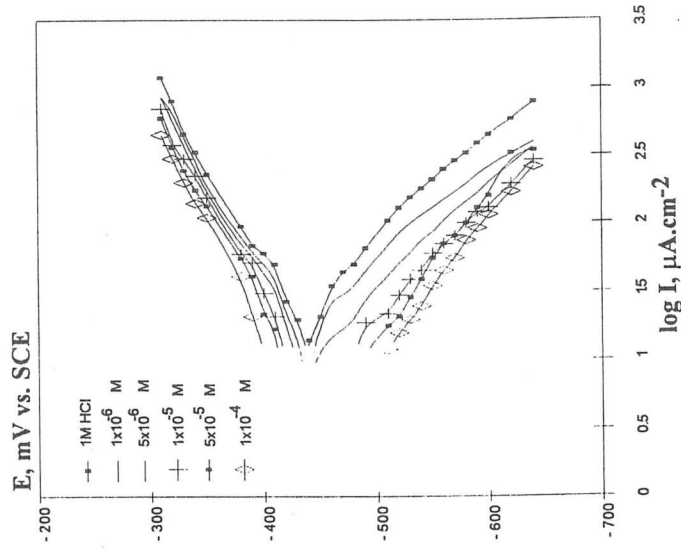


Fig. 3. Tafel lines for iron in 1M HCl at different concentrations of compound a

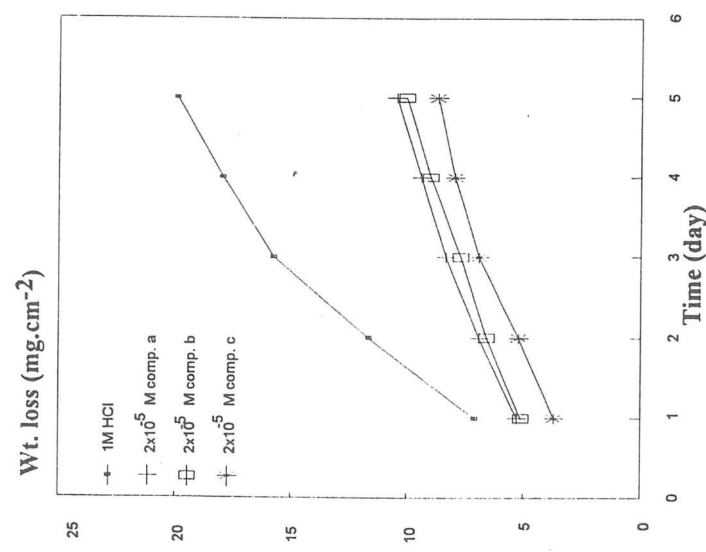


Fig. 6. Weight loss - time curves for iron in 1M HCl in the absence and in the presence of $2 \times 10^{-5}M$ concentration of different compounds

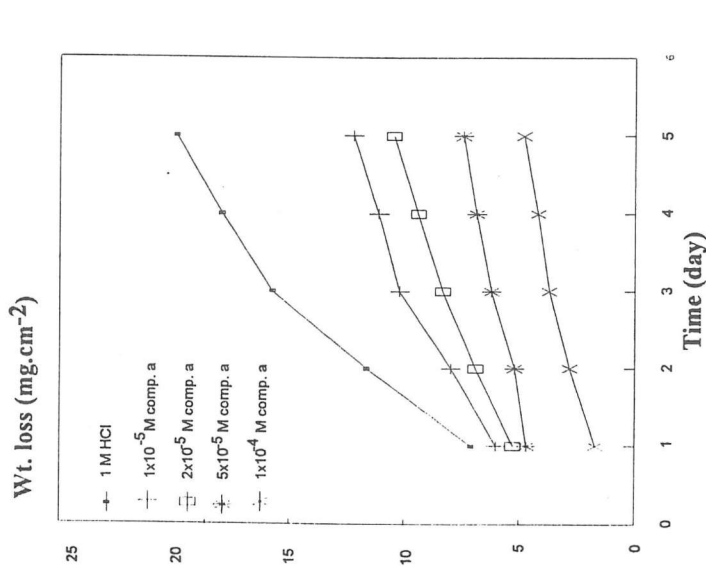


Fig. 5. Weight loss - time curves for iron in 1M HCl in the absence and in the presence of different concentrations of compound a

immersion (days) for iron in 1M HCl in the absence and in the presence of $2 \times 10^{-5} \text{M}$ of different inhibitors, and Fig.6 shows the weight loss vs. time curves in the absence and in the presence of different concentrations ($1 \times 10^{-5} \text{M}$ — $1 \times 10^{-4} \text{M}$) of compound a. Curves for all additives containing systems fall below that of the free acid. The efficiency of a certain corrosion inhibitor is measured by the percentage inhibition (%P) given by [18]

$$(\%P) = 100 (1 - W_2/W_1) \quad (2)$$

where W_1 and W_2 are the weight loss in the absence and the presence of inhibitor respectively.

As shown from Table 3, values of weight loss (mg cm^{-2}) decreases with increasing of inhibitor concentration and the percentage inhibition increases. Table 4(a and b) shows the effect of $2 \times 10^{-5} \text{M}$ and $1 \times 10^{-4} \text{M}$ of different derivatives on the percentage inhibition, the order of decreasing inhibition efficiency is $c > b > a$. This order is in agreement with that obtained from potentiodynamic studies. Moreover θ_{org} increases with increasing concentration of inhibitor a. (Table 3). The plot of θ vs. $\log C$ for inhibitor a, where $\theta = 1 - W_2/W_1$ is shown in fig.7, resulting in a linear correlation which is a characteristic of Temkin isotherm [19].

Table.3 Weight loss and inhibition efficiency of iron corrosion in 1M HCl solutions containing various concentrations of compound a.

concentration (M)	weight loss (mg.cm^{-2})	% Inhibition (%P)
Free	17.95	—
1×10^{-5}	11.44	36.26
2×10^{-5}	9.39	47.26
5×10^{-5}	7.04	60.78
1×10^{-4}	4.40	75.49

Table.4a- Weight loss and inhibition efficiency of corrosion of iron in 1M HCl solutions containing $2 \times 10^{-5} \text{M}$ concentration of different compounds.

Inhibitor	weight loss (mg.cm^{-2})	% Inhibition (%P)
Free	17.95	—
compound a	9.39	47.69
compound b	8.99	49.92
compound c	7.95	55.71

Table.4b- Weight loss and inhibition efficiency of corrosion of iron in 1M HCl solutions containing $1 \times 10^{-4} \text{M}$ concentration of different compounds.

Inhibitor	weight loss (mg.cm^{-2})	% Inhibition (%P)
Free	17.95	—
compound a	4.40	75.5
compound b	3.86	79.5
compound c	2.39	86.7

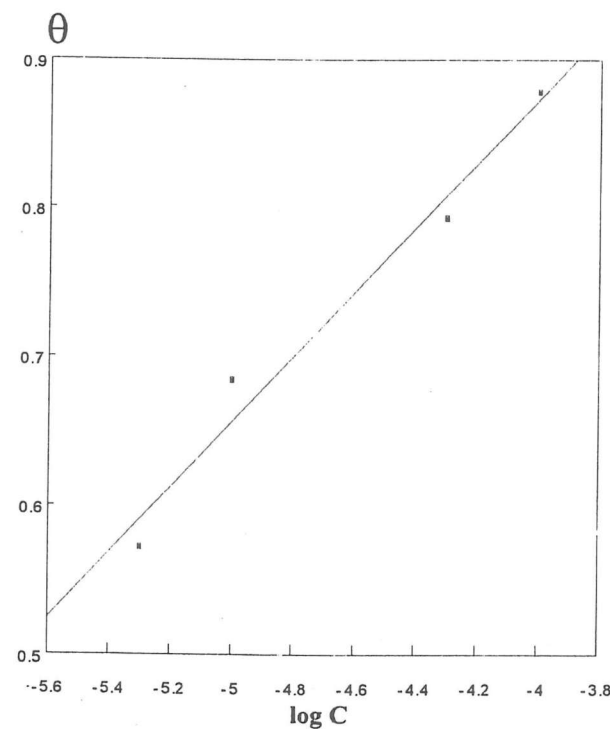


Fig.7: Relationship between θ vs. $\log C$ for compound a

Effect of chemical constitution on the inhibition efficiency.

Inhibition efficiency of the additives depends on many factors [20] including the number of adsorption centres in the molecule and their charge density, molecular size, mode of adsorption and formation of metallic complexes.

The obtained results, from potentiodynamic and weight loss techniques, indicate that the decrease in inhibition efficiency of the additives for iron in 1M HCl is in the order $c > b > a$. The basicity of the compounds will depend on the type of the substituent attached to the 4(2-pyridyl)-1-benzaldehyde-3-thiosemicarbazone part, which increases the charge density on the adsorption sites. Fig.8 shows the skeletal representation of the adsorption of compound c on the iron surface. It is clear that the N-atom of pyridine

ring, n-atom of -N-C=S, N-atom of -N-N=C and the two oxygen of the hydroxyl groups attached to the benzene ring are the probable centres for adsorption; thus compound c comes on the top of the compounds as an effective inhibitor. This may be due to i) the presence of five active centres; ii) the presence of two hydroxyl groups with high electron donating ability; iii) the highest molecular weight compared with compounds a and b; iv) the presence of the two oxygens of the hydroxyl groups on the surface, which make the benzene ring lies flat on the surface without any probability of rotation and thus the molecular area occupied by compound c is large compared with the molecular areas of compounds a and b. On the other hand compound b comes after compound c in the percentage inhibition. This may be attributed to the presence of three centres of adsorption as compared with five in compound c and also to the presence of CH₃ which is less electron donating than OH in compound c. Compound a is the last compound in the percentage inhibition; this may be due to its smallest size among the compounds under investigation and the absence of any electron donating substituents.

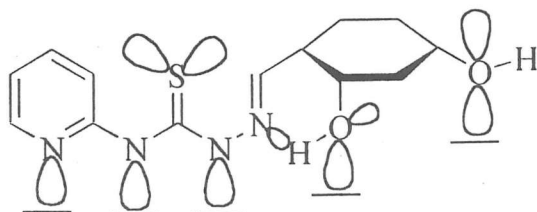


Fig.8. Skeletal representation of the adsorption of compound c.

REFERENCES

- 1- B.Sathianandhan, K.Balahrishnan and N.Subramyan, *Br. Corros.J.*, **5**, (1970), 270 .
- 2- F.Zucchi, G.Trabanelli and G.Brunoro, *Corros.Sci.*, **33**, (1992), 1135.
- 3- J.Uhrea and K.Aramaki, *J.Electrochem.Soc.*, **138**, (1991), 3245.
- 4- J.O'M.Bockris and B.Yang, *J.Electrochem.Soc.*, **138**, (1991), 2237.
- 5- G.Banerjand S.N.Malhotra, *Corrosion*, **48**,(1992),10 .
- 6- S.Kertit, A.Elkholy, J.Arife, A.Shriri, A.Ben-Bachir and M.Etman, *J.Appl. Electrochem.*, **19**, (1989), 83.
- 7- M.Elachouri, M.S.Hajji, S.Kertit, E.M.Essassi, M.Salem and R.Coudert, *Corros. Sci.*, **37**, (1995), 381.
- 8- A.S.Fouda, M.N.Moussa, H.A.Moustafa, *Korrosion (Dresden)*, **18**, (1978), 28.
- 9- J.Vosta, S.M.Pelikanj, *Werkst.Korr.*, **25**, (1974), 750.
- 10-R.Narayan, K.Pillai, *Trans. Soc.Adv.Electrochem.Sci.Technol.*, **7**, (1972), 117.
- 11-G.L.Nemehaninova and N.G.Klyuchnikov, *Inhibitory Korros. Met.*, **20**, (1992), 117.
- 12-D.C.Trivedi and S.K.Dhawan, in *Frontier of polymer Research* (Edited by J.K.Nigam), p. 419 plenum press, New York (1991).
- 13-A.Kitani, J.Yano and K.Saski, *J. Electroanal. Chem.*, **209**, (1986), 227.
- 14-A.S.Fouda, L.H.Madkour, A.A.El-Shafei and A.H.Elaskalany, *Mat-wiss-u. Werkstofftech.*, **26**, (1995), 342.
- 15-14-A.S.Fouda, L.H.Madkour, A.A.El-Shafei and S.A.Abd El-Maksoud, *Bull. Korean Chem. Soc.*, **16**, (1995), 454.
- 16-S.A.Abd El-Maksoud, A.A.El-Shafei, and A.S.Fouda, *Mat-wiss-u. Werkstofftech.*, **28**, (1997), 7.
- 17-G.M.Abu El-Reash, I.M.Kenawy, U.El-Ayaan and M.A.Khattab, *Indian J. Chem.*, **33A**, (1994), 914.
- 18-G.Trabanelli, V.Carassiti, In "*Advances in Corrosion Science and Technology*" (Eds.M.G.Fontana & R.W.Staehle) vol., p.147, Plenum Press, N.Y.,1970.
- 19-A.K.Mohamed, S.A.Abd El-Maksoud and A.S.Fouda, *Portugaliae Electrochimica Acta*, **15**, (1997) 27
- 20-A.S.Fouda, M.N.Moussa, F.I.Taha and A.I.Elneanaa, *Corros. Sci.*, **26**, (1986), 719.

Received, January 24, 1998
 Revised, June 2, 1998