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Use of Hydrazone Derivates as Inhibitors for the Corrosion of Nickel in Hydrochloric Acid Solution

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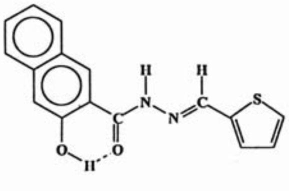
The influence of hydrazone derivatives on the corrosion of nickel in 2 mol L^{-1} hydrochloric acid solution has been studied using weight loss and galvanostatic polarization techniques. In general, at constant acid concentration, the inhibition efficiency increases with increasing the inhibitor concentration and decreases with increasing temperature. Polarization studies indicate that the compounds act as mixed- type inhibitors. The addition of iodide ions enhances the inhibition efficiency to a considerable extent .The effect of temperature on corrosion inhibition has been studied and activation energy has been calculated. Some thermodynamic parameters are calculated and discussed.

Keywords: Corrosion, nickel, hydrochloric acid, hydrazone derivatives, weight loss, polarization, potassium iodide.

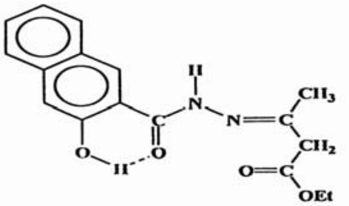
1. INTRODUCTION

The corrosion behavior of nickel in acid baths in plating, electrowinning and pickling process is of industrial concern. Although the mechanism of corrosion and inhibition of nickel has been extensively studied in a variety of media [1-5]. Tianging et al [6] studied the effect of surfactant of Triton x- 100, cetyltrimethyl ammonium bromide (CTAB), and sodium dodecyl sulfate (SDS) as corrosion inhibitors for nickel dissolution in hydrochloric acid solution. The results showed that the inhibition efficiency is decreased with increasing both HCl concentrations and temperature, and increased with increasing the concentrations of the surfactants. Essoufi et al [7] used 1- phenyl-5- mercapto-1,2,3,4- tetrazole as a corrosion inhibitor for nickel dissolution in H_2SO_4. The results showed that by increasing the concentration of this inhibitor , the inhibition efficiency increased and the corrosion current decreased. The aim of the present investigation is to assess the inhibitive properties of some hydrazone derivatives for nickel in 2 mol.L^{-1} HCl solution and to throw some light on the mechanism of inhibition by these inhibitors.

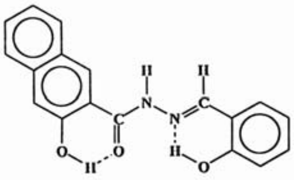
(1) **Thiophene-2-carboxaldehyde-[N-(3-hydroxy-2-naphthoyl)]hydrazone** ***(H$_2$THNH)***



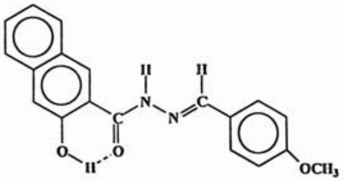
(2) **Ethylacetoacetate-[N-(3-hydroxy-2-naphthoyl)]hydrazone** ***(H$_2$EHNH)***



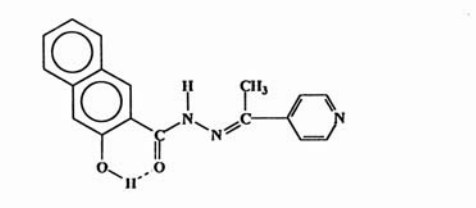
(3) **Salicylaldehyde-[N-(3-hydroxy-2-naphthoyl)]hydrazone** ***(H$_2$SHNH)***



(4) **_p_-Anisaldehyde-[N-(3-hydroxy-2-naphthoyl)]hydrazone** ***(H$_2$-p-AHNH)***



(5) 4-Acetylpyridine-[N-(3-hydroxy-2-naphthoyl)]hydrazone *(H_2APHNH)*



2. EXPERIMENTAL

2.1 Materials

Nickel sheets and wires were prepared from High – purity (BDH grade) nickel with the following compositions (in weight %) : Fe, 0.05; Al; 0.005; Co; 0.005; Mn; 0.005; Mg; 0.005 and Ti; 0.005. Specimens were first polished with different grades of emery paper ,in order to obtain a smooth surface, washed using bidistilled water and degreased with acetone in an ultrasonic bath. The samples were dried and stored in a vacuum desiccator.

The aggressive solutions were made of Analar grade (BDH) HCl. Appropriate concentrations of acid were prepared using bidistilled water. All chemicals used were of AR grade.

2.2. Methods

2.2.1 Corrosion weight loss tests

For weight loss measurements, rectangular nickel specimens of size 20x 20 x2 mm were immersed in 100 ml of inhibited and uninhibited solutions and allow to stand for several intervals (30 mins. For each) at 30°C in water thermostat for a period of 4 hrs. All experiments were repeated at least three times using different specimens to confirm the reproducibility of the results. The percentage inhibition (%P) of the inhibitor was calculated using the equation :

$$\% P = \left[\frac{(\text{wt. loss}_{\text{uninh}} - \text{wt. loss}_{\text{inh.}}) \times 100}{\text{wt . loss}_{\text{uninh.}}} \right] \qquad (1)$$

2.2.2 Electrochemical measurements

Galvanostatic polarization studies were carried out on nickel in 2 mol L^{-1} HCl solution without and with different concentrations of the inhibitors used at 30°C. Saturated calomel electrode (SCE) was used as reference electrode while a platinum wire as a counter electrode. All experiments were carried out at 30 ± 0.1°C. A 1 cm long cylindrical nickel electrode having a diameter of 1.25 mm was used as working electrode. The inhibition efficiency (%P) from this method is defined as:

$$\%P = \left(\frac{I_{corr} - I_{inh}}{I_{corr}} \right) \cdot 100 \qquad (2)$$

Where I_{corr}. and I_{inh}. are the uninhibited and inhibited corrosion current densities, respectively.

3. RESULTS AND DISCUSSION

Weight loss of nickel in 2 mol L^{-1} HCl was determined in the absence and presence of the tested hydrazone derivatives. The data in Table 1 showing the percentage inhibition for the various additives at the same concentration demonstrate that the efficiency varies with both the type and the concentration of the additives used. This indicates that the additives behave as inhibitors over the concentration range studied.

Table 1: Effect of inhibitors concentrations on the percentage inhibition efficiency of nickel in 2 mol L^{-1} HCl solutions from weight-loss.

Concentration of the additive mol L^{-1}	% Inhibition(%P)				
Inhibitor →	**1**	**2**	**3**	**4**	**5**
$1.5x10^{-5}$	36.9	32.0	30.0	26.1	23.3
$1.0x10^{-5}$	32.0	28.4	27.8	23.3	19.3
$1.5x10^{-6}$	28.4	27.1	26.2	20.5	14.8
$1.0x10^{-6}$	27.1	22.3	22.1	16.1	11.1
$1.0x10^{-7}$	23.3	18.2	16.1	10.1	4.8

Table 2: Effect of inhibitors concentrations on the percentage inhibition efficiency of nickel in 2 mol L^{-1} HCl in presence of $1x10^{-4}$ mol L^{-1} KI at 30°C as determined from weight - loss method.

Concentration of the additive mol L^{-1} / Inhibitor	% Inhibition(% P)				
	1	**2**	**3**	**4**	**5**
$1.5x10^{-5}$	66.0	56.3	54.0	51.6	49.2
$1.0x10^{-5}$	58.4	51.6	49.2	48.9	46.0
$1.5x10^{-6}$	46.6	43.8	43.2	40.8	40.0
$1.0x10^{-6}$	43.8	43.2	42.9	40.0	36.5
$1.0x10^{-7}$	40.0	39.5	40.0	37.5	32.8

The order of decreasing inhibition efficiency of hydrazone derivatives (Table 1) in 2 mol L^{-1} HCl is : 1 > 2 > 3 > 4 > 5.

As seen from Table 1, the percentage inhibition efficiency of the tested hydrazone derivatives is low, so in order to raise these values, we use KI (1x10^{-4} mol L^{-1}) with different concentrations of inhibitors (Table 2).

Also, we use certain concentration of inhibitors with different concentrations of KI (Table 3).

Table 3: Effect of KI concentrations on the percentage inhibition efficiency of nickel dissolution in 2 mol L^{-1} HCl as determined from weight- loss method in presence of 1.5x10^{-5} mol L^{-1} inhibitors at 30^{o}C.

Concentration of the additive mol. L^{-1} / Inhibitor	% Inhibition(%P)				
	1	**2**	**3**	**4**	**5**
1x10^{-3} KI	75.7	66.0	60.2	58.0	55.6
1x10^{-4} KI	66.0	56.3	54.0	51.6	49.2
1x10^{-5} KI	46.6	43.8	41.7	38.7	35.4

It can be seen from Table 2 and 3, that the addition of KI inhibits the corrosion of nickel to a large extent and by increasing the concentration of KI (1x 10^{-5} – 1 x 10^{-3} mol L^{-1}) the percentage inhibition increases in comparison to the percentage inhibition in absence of KI. This can be interpreted according to Schmitt and Bedbur [8], which proposed two types of joint adsorption namely competitive and cooperative. In competitive adsorption the anions and cations are adsorbed at different sites on the electrode surface, and in cooperative adsorption, the anions are chemisorbed on the surface and the cations are adsorbed on a layer of the anions, a part from the adsorption on the surface directly.

$$S_\theta = (1- \theta_{1+2}) / (1- \theta'_{1+2}) \quad (3)$$

where $\theta_{1+2} = \theta_1 + \theta_2 - \theta_1\theta_2$ (4)

θ'_{1+2} = measured surface coverage by the anion in combination with cation.

θ_1 and θ_2 = are the surface coverage for anions and cations, respectively.

Values of S_θ are given in Table 4.

Table 4 : Synergism parameter “ $\mathbf{S_\theta}$ ” calculated from weight -loss method for different concentrations of the additives.

Concentration of the additive mol L^{-1} / Inhibitor	**S_θ**				
	1	**2**	**3**	**4**	**5**
1.5x10^{-5}	1.3	1.1	1.1	1.1	1.!
1.0x10^{-5}	1.1	1.0	1.0	1.1	1.0
1.5x10^{-6}	0.9	0.9	0.9	0.9	1.0
1.0x10^{-6}	0.9	0.9	1.0	1.0	1.0
1.0x10^{-7}	0.9	0.9	1.0	1.0	1.0

Since most of these values of S_θ are about unity, the higher inhibition efficiencies of iodide and additives can be calculated as brought out by synergistic effect. Fig.1 demonstrates the variation of the degree of surface coverage with bulk concentration of the additives from weight loss technique.
The degree of surface coverage was calculated from [9].

$$\theta = 1 - [\text{wt. loss}_{\text{inh.}} / \text{wt. loss}_{\text{uninh.}}] \quad (5)$$

Assuming no change in the mechanism in presence and absence of hydrazone derivatives. Attempts were made to fit (θ) values to various isotherms. By far the best fit was obtained with Freundlich isotherm [10].

$$(\theta) = KC^n \quad (6)$$

$$\text{or} \quad \log(\theta) = \log K + n \log C \quad (7)$$

where K and C are the equilibrium constant of adsorption and additive concentration, respectively.

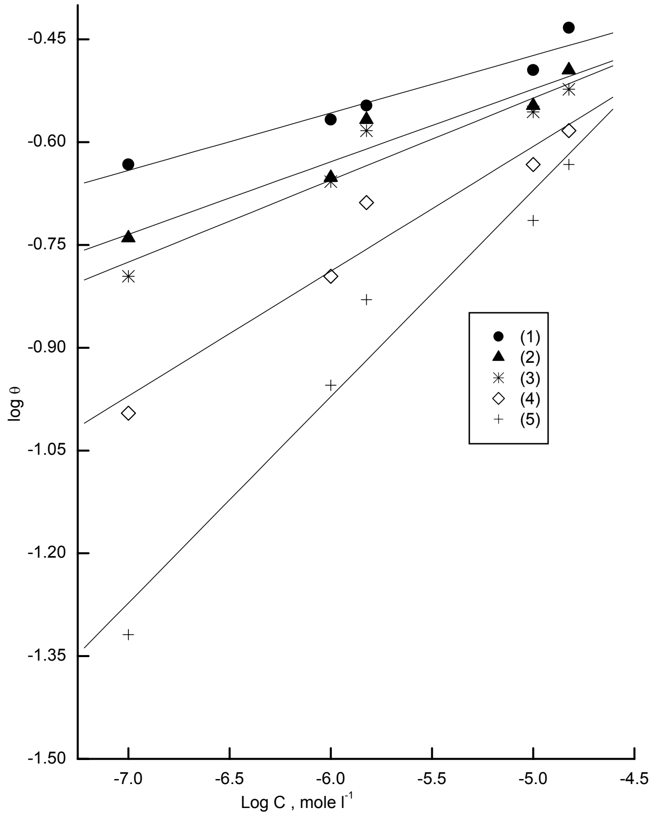


Figure 1. Effect of different concentrations on the degree of surface coverage for nickel in 2 mol L^{-1} HCl at 30 °C.

Assuming no change in the mechanism in presence and absence of hydrazone derivatives.

The equilibrium constant (K) is related to the standard free energy of adsorption by the relation [11,12] :

$$K = 1/55.5 \exp[-\Delta G^o_{ads}/RT] \quad (8)$$

Where R is the universal constant, the value of 55.5 is the concentration of water in the solution in moles and T **is** the absolute temperature.

Straight lines are obtained by plotting log θ against log C. This suggested that,Freundlich adsorption isotherm is obeyed. From Table 5 it is noted that $\Delta G^{o}_{ads.}$ have a negative sign indicating that the adsorption process proceeds spontaneously. The values of $-\Delta G^{o}_{ads.}$ increase as the percentage inhibition increases.

Table5: Equilibrium constant and adsorption free energy of the inhibitors adsorbed on the surface of nickel in 2 mol L^{-1} HCl at 30ºC.

Inhibitor type	**$-\Delta G^{o}_{ads}$, kJ mol^{-1}**	**K, mol $^{-1}$x10^{-2}**
Compound (1)	2.8	5.5
Compound (2)	2.9	5.7
Compound (3)	3.1	6.3
Compound (4)	7.1	30.4
Compound (5)	9.7	83.5

The effect of temperature (30-60^{o}C) on the performance of the inhibitor at a concentration of 1.5 x 10^{-5} mol L $^{-1}$ for nickel in 2 mol L $^{-1}$ HCl was studied using weight loss measurements. Plots of log k (corrosion rate) against 1/T (absolute temperature) Fig. 2 for nickel in 2 mol L^{-1} at constant concentration of all additives (1.5 x 10^{-5} mol L^{-1}), give straight lines.

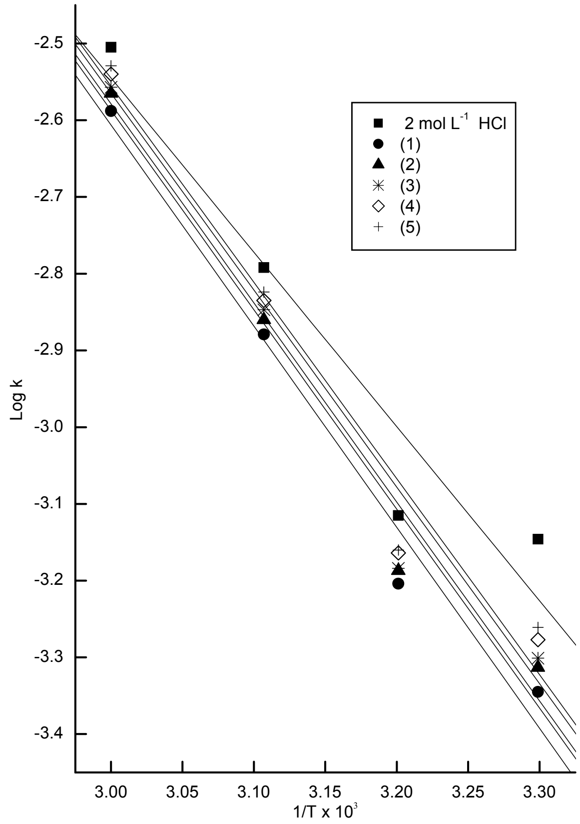


Figure 2. Log k-1/T curves for nickel corrosion in in 2 mol L^{-1} HCl in absence and presence of 1.5x10^{-5} mol L^{-1} of different compounds.

The values of the slopes obtained at different temperatures permit the calculation of Arrhenius activation energy (E_a). The activation energy values obtained from this Figure were found to be 43.44 kJ mol^{-1} for 2 mol L^{-1} and 50.14 – 49.00 kJ mol $^{-1}$ for acid containing inhibitors (Table 6).

Table 6 : Values of activation parameters for the dissolution reaction of nickel in the presence of different compounds in 2 mol L^{-1} HCl.

Inhibitor	**E_a, kJ mol^{-1}**	**ΔH^*, kJ mol^{-1}**	**- ΔS^*, J mol^{-1} K^{-1}**
Free acid	43.4	40.8	172.0
Compound (1)	50.1	47.7	152.4
Compound (2)	49.8	47.2	153.7
Compound (3)	49.6	46.8	154.8
Compound (4)	49.2	46.7	154.8
Compound (5)	49.0	46.3	155.7

Activation parameters for corrosion of nickel were calculated from Arrhenius – type plot:

$$k = A \exp (- E_a^* / RT) \quad (9)$$

and transition state – type equation [13] .

$$k = RT/NH \exp (\Delta S^*/R) \exp (-\Delta H^*/ RT) \quad (10)$$

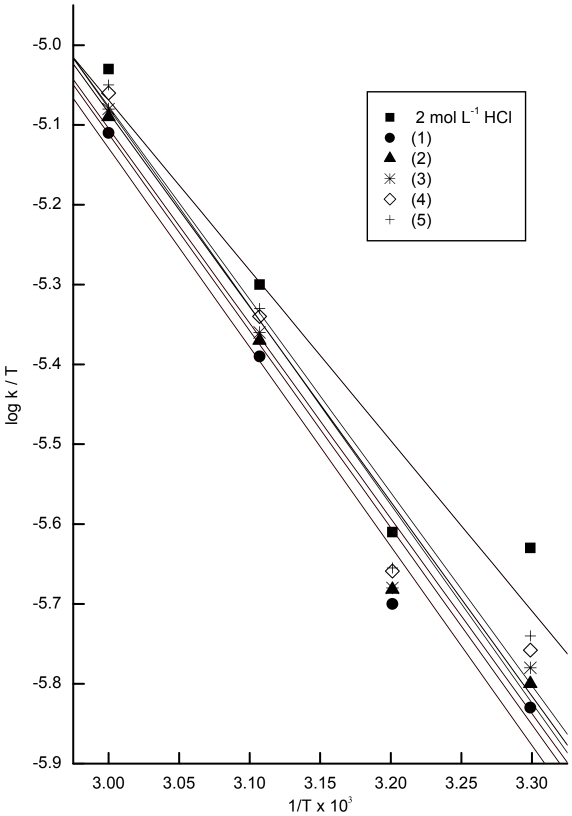


Figure 3. Log k/T-1/T curves for nickel corrosion in in 2 mol L^{-1} HCl in absence and presence of 1.5x10^{-5} mol L^{-1} of different compounds..

The relationship between log k/T vs. 1/T gives straight line, from its slope, ΔH* can be computed and from its intercept ΔS* can be computed Fig.3. Table 6 exhibits the values of apparent activation E_a*, ΔH* and ΔS* for the corrosion of nickel in 2 mol L^{-1} solution in absence and presence of 1.5 x 10^{-5} mol L^{-1} from different additives. The presence of hydrazone derivatives increases the activation energies of nickel dissolution indicating strong adsorption of the inhibitor molecules on the metal surface. The presence of these additives induce energy barrier for the corrosion reaction and this barrier increases with increasing the additive concentration. The higher values of ΔH* is explained on the basis, that the process of adsorption exhibits a rise in the enthalpy of the corrosion process. The calculated activation entropies, ΔS*, for nickel in HCl solution are large and negative. The presence of these additives lowers the values of ΔS*. The changes in ΔS* are directly proportional to the concentration of the additives. This phenomenon was discussed before as inhibitor- free acid solutions, the transition state of the rate determining step represents a more orderly arrangement relative to the initial state, and hence a negative values for ΔS* are produced. In the presence of inhibitor, the system passes from less orderly to a more random arrangement and hence an increase in the values of ΔS* is observed. Fig.4 shows the galvanostatic polarization curves (E vs. log I) of nickel dissolution in 2 mol L^{-1}, in presence of different concentrations of compound (1). An increase in the concentration of inhibitor shifts the polarization curves towards more negative potentials for cathodic Tafel lines, and towards more positive potentials for anodic Tafel lines. Polarization data suggest that the additives used act as mixed-type inhibitors ($\beta_a \simeq \beta_c$). The corrosion kinetic parameters such as corrosion current density ($I_{corr.}$), corrosion potential ($E_{corr.}$) , cathodic Tafel slope (β_c), anodic Tafel lines (β_a), degree of surface coverage (θ) and percentage inhibition were derived from the curves Fig. 4 are recorded in Table 7.

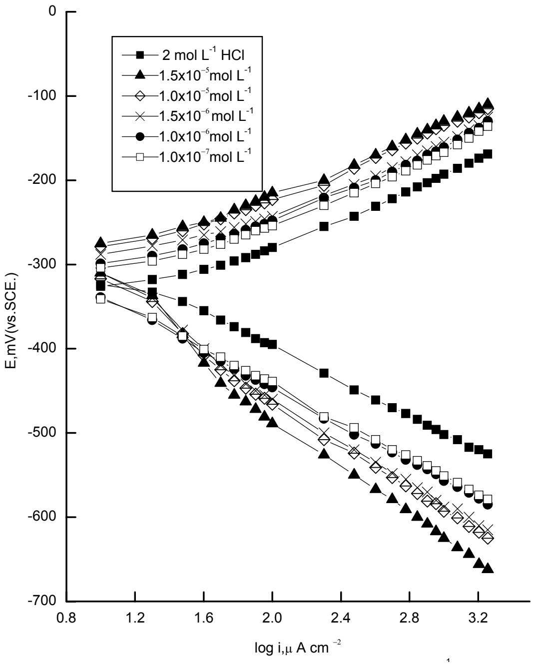


Figure 4. Galvanostatic polarization curves of nickel in 2 mol L^{-1} HCl alone and containing different concentrations of compound(1) at 30 °C.

Table 7. Data from galvanostatic polarization of nickel in 2 mol L^{-1} HCl containing different concentrations of compound (1) at 30°C.

Concentration mol L^{-1}	$-E_{corr.}$ mV	$I_{corr.}$ µA cm^{-2}	β_c $mVdec^{-1}$	β_a $mVdec^{-1}$	θ	%P
0.0	295	229.09	98.5	76.7	-	-
1.0×10^{-7}	285	190.50	107.8	80.0	0.169	16.9
1.0×10^{-6}	270	181.90	109.0	79.3	0.206	20.6
1.5×10^{-6}	260	151.40	125.0	76.3	0.339	33.9
1.0×10^{-5}	250	109.65	112.5	79.2	0.521	52.1
1.5×10^{-5}	275	93.33	100.0	79.6	0.593	59.3

The order of inhibition efficiency derived from this method is [Table 8]:

1>2>3>4>5

Table 8: Effect of inhibitors concentrations on the percentage inhibition efficiency of nickel in 2 mol L^{-1} HCl solution from polarization method at 30°C.

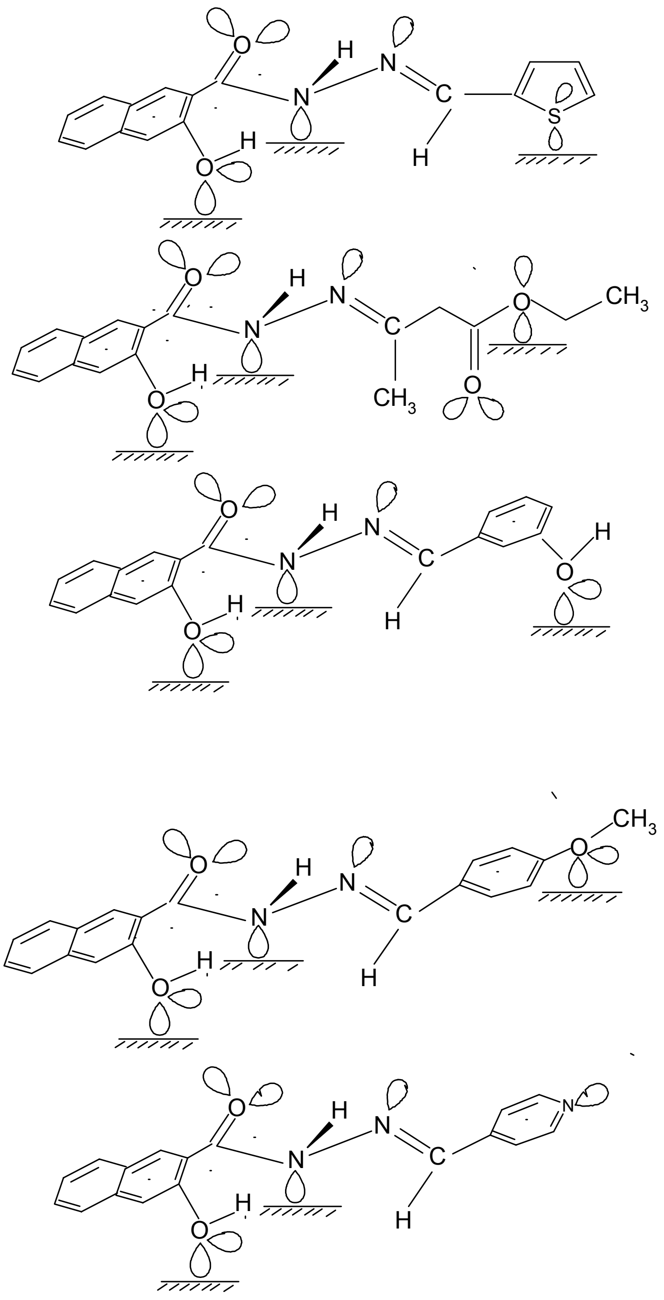
Concentration of the additive mol L^{-1}	% Inhibition(%P)				
Inhibitor →	**1**	**2**	**3**	**4**	**5**
1.5×10^{-5}	59.3	56.4	51.0	45.0	30.8
1.0×10^{-5}	52.1	51.0	30.8	30.8	20.6
1.5×10^{-6}	34.0	30.8	16.9	12.9	10.9
1.0×10^{-6}	20.6	16.8	12.9	8.8	6.7
1.0×10^{-7}	16.9	13.0	6.7	4.5	2.3

3.1 Mechanism of inhibition

Skeletal representation of the mode of adsorption of the compounds is shown in Fig. 5, and clearly indicates the active adsorption centers.

The order of decreasing inhibition efficiency of hydrazone derivatives in 2 mol L^{-1} HCl is: 1>2>3>4>5. The inhibition efficiency of the compounds depends on many factors [14], which include the number of adsorption active centers in the molecule and their charge density, molecular size, mode of adsorption, heat of hydrogenation and formation of metallic complexes.

The obtained results of the additives (Table 1) indicate that compound (5) gave a lower corrosion inhibition than that of the other compounds (1,2,3 and 4), this may be ascribed to its lower molecular size and its lesser number of active sites (two active centers). On the other hand compound (1) is the most efficient inhibitor due to the presence of three active adsorption centers and higher molecular size compared to the other compounds. Compound (2) comes next in spite of having three active adsorption centers as compound (1), but with lower molecular size than compound (1), also in compound (1), the sulfur atom is more basic than the oxygen atom in compound (2) and as known, the stronger coordinate bond formation (and hence stronger adsorption) by S and O atoms increases with increasing the electronegativity (O<N<S) [15&16].



(1)

(2)

(3)

(4)

(5)

Figure 5. Skeletal representation of the mode of adsorption of different additives.

Compounds (3) and (4) follow behind compound (2), in spite of having three active adsorption centers. This can be interpreted in terms of Hammet constant (σ) for – OH group (σ = -0.37), but for – OCH_3 group (σ = -0.27), so compound (3) is more efficient than compound (4).

4. CONCLUSIONS

1. All the additives studied are found to perform well as a corrosion inhibitor in hydrochloric acid solution and the inhibiting efficiency values of the examined compounds follow the order: 1>2>3>4>5 at all the studied concentrations range.
2. The compounds studied are found to act as mixed-type inhibitors.
3. The protection efficiency increases with a decrease in temperature or an increase in concentration of the studied compounds.
4. The adsorption of these compounds was found to follow Freundlich adsorption isotherm.
5. The addition of KI was found to increase the percentage inhibition due to synergistic effect.

References

1. W. Went, H. G. Z. Feller, *Metallik*, 61 (1970) 178
2. I. Garz, B. Glazer, *Corros. Sci*., 14 (1974) 353
3. M. Kesten, G. Sussek, *Werk. Korros*., 77(1976)
4. L.A. Barkalatsora, A. G. Pshenicknikov, *Electrochimiya*, 12 (1976) 42
5.K. Nobe, MITS Gov.Rep.Announce.Index US 75,71(1975)
6. Liu, Tianqing, Zou, Aihua and Guo, Rong, *Cailiaobaohu*, 33(5) (2000) 9
7. H. Essoufi, S. Kertit, B. Hammouti and M. Benkaddour, *Bull. Electrochem*., 16(5) (2000) 205
8. G. Schmitt, K. Bedbur and U. Werkst, *Korros.,* 36 (1985) 273
9. M. B. Abo El-Khair and I. A. Abdel Hamed, *Corros. Sci*., 16 (1976) 169
10.B. Berg, K.hn. C. Grijotheim and T.T. Torkiep, Light Metal proceeding of 105th Annual Meeting, 23 (1976).
11.M. Kliskic, J. Radosevic, S. Gndic ,*J. Appl. Electrochem*., 27 (1997) 947
12. M. Abdallah, *Bull.Electrochem*., 16(6) (2000) 258
13. A. C, Markrides and N. Hackerman, *Ind. Eng. Chem*., 46 (1954) 523
14. E. Blomgren, J. O' M. Bockris and C. Jesch, *J. Phys. Chem*., 65 (1961) 2000
15. Szkarska-Smialowska and B. Dus, *Corrosion*, 23 (1967) 130
16. A. S. Fouda, M. N. Moussa, F. I. Taha and A. I. Elneanaa, *Corros. Sci*., 26 (1986) 719