CORROSION INHIBITION OF NICKEL IN HCl SOLUTION BY SOME INDOLE DERIVATIVES

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ABSTRACT

Some indole derivatives are investigated as corrosion inhibitors for nickel in 0.5 M HCl solution using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. A significant decrease in the corrosion rate of nickel was observed in the presence of investigated indole derivatives. Polarization curves indicate that these compounds are mixed-type inhibitors, affecting both cathodic and anodic corrosion processes. The adsorption of the inhibitors on nickel surface in 0.5 M HCl was found to follow Frumkin adsorption isotherm. Thermodynamic adsorption parameters (K_{ads}, ΔG°_{ads}) of investigated compounds were calculated from the linear form of Frumkin adsorption isotherm. Activation parameters of the corrosion process such as activation energies, E^{*}_{a}, activation enthalpies, ΔH^{*}, and activation entropies, ΔS^{*} were calculated and discussed. EIS was used to investigate the mechanism of corrosion inhibition. Correlation between the inhibition efficiency and the structure of these compounds are presented.

Keywords: Nickel, HCl, Indole derivatives, EIS.

INTRODUCTION

Nickel is one of the most important metals and it used in a large number of applications. The pure nickel has a good corrosion resistance. Nickel is used as alloying element with other metals. Also, nickel plays an important role in repair or replacement of the diseased bone tissue. The corrosion resistance of nickel is due to the formation of

a passive film on its surface upon exposure to the corrosive media. Nevertheless, nickel could be attacked by acidic media in a considerable rate. Because nickel is frequently used in contact with acidic solutions, its corrosion rate must be controlled. One of the useful methods of controlling the corrosion process is the addition of corrosion inhibitors The use of inhibitors is one of the most practical methods for protection against metallic corrosion, especially in acidic media [Fouda *et al.,* (2005)]. The action of inhibition of nickel and its alloys in acidic media by various organic compounds has been widely studied [Fouda *et al.,(*2002); Fouda et al.,(2003); Schmit, (1984); Lewis, (1982); **Rengamani** *et al.,(*1993); Stern *et al.,(*1957) and Maayta *et al.,(*2004)]. Inhibitors find application in pickling, cleaning and acid descaling processes. In general, organic compounds such as amines, acetylenic alcohols and heterocyclic compounds, have found use as inhibitors in industrial applications [Fouda *et al.,(*2008) and Tsuru *et al.,* (1978)].
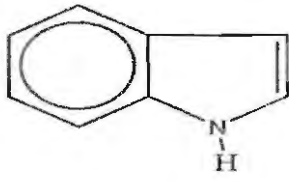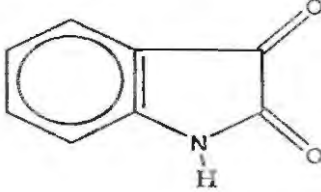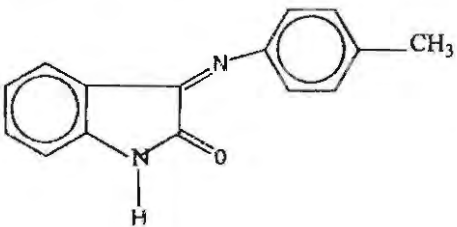
The present work was designed to study the corrosion inhibition of nickel in 0.5 M HCl solution using some indole derivatives as corrosion inhibitors by electrochemical techniques. The synergistic effect brought about by combination of the inhibitors with KI, KBr and KCl was examined and explained. Also, the effect of temperature on the corrosion behavior was investigated.

EXPERIMENTAL METHODS

1 Materials and chemicals :

The corrosion tests were performed on nickel rods with a composition (in wt. %): Fe 0.05; Al 0.005; Co 0.005; Mn 0.005, Ti 0.05 and nickel balance. These rods were mounted in Teflon. An epoxy resin was used to fill the space between Teflon and Ni electrode. Rods with an exposed length of 1 cm (φ = 1.25 mm) were used for all electrochemical measurements. Prior to experiments, all of the electrodes were gradually abraded with different grit emery papers up to 4/0 grit size, in order to obtain a smooth surface, followed by cleaning with bidistilled water and degreasing with acetone, and finally dried with cool air and stored in a vacuum desiccator. The aggressive solutions, 0.5 M HCl were prepared by dilution of analytical grade 37% HCl with bidistilled water. All experiments were carried out under static conditions. The investigated compounds were purchased from SIGMA-ALDRICH and used as inhibitors; stock solutions (1×10^{-3} M) were made in ethanol to ensure solubility. These stock solutions were used for all experimental purposes. Table (1) shows the molecular structure of investigated compounds. It is evident that these investigated compounds are heterocyclic compounds containing nitrogen and oxygen atoms, which could easily be protonated in acidic solution, and several π-electrons exist in these molecules.

Table (1) the structures of indole derivatives.

Inhibitor and Mol.Formula	structure	Mol. Wt.
indole $C_8 H_7 N$		117
isatin $C_8 H_5 N O_2$		147
3-p-tolylimino -1,3-dihydro - indole -2-one $C_{15} H_{12} N_2 O$		237

2 Methods :

Before starting the experiments, the working electrodes were immersed in the test solution for 30 min. until a steady potential reached, then the electrochemical measurements were carried out in a conventional three electrodes cylindrical glass cell with a capacity of 100 ml. A saturated calomel electrode (SCE) and a platinum electrode were used as reference and auxiliary electrode, respectively. The reference electrode was connected to a Luggin capillary to minimize IR drop. The polarization curves were obtained potentiodynamically in potential range -800 mV to + 800 mV versus open circuit potential (OCP) with the scan rate 5 mV s^{-1}.

The inhibition efficiency and surface coverage (θ) were calculated from the following equations:

$$\% \text{ IE} = [1 - (i_{corr\ (inh)} / i_{corr\ (free)}] \times 100 \quad (1)$$

$$\theta = [1 - (i_{corr\ (inh)} / i_{corr\ (free)})] \quad (2)$$

where ($i_{corr\ (free)}$) and ($i_{corr\ (inh)}$) are the corrosion current densities in the absence and presence of inhibitors, respectively.

The electrochemical impedance experiments were performed in the frequency range of 10^5 Hz to 0.5 Hz using a perturbation of 10 mV amplitude at OCP. The polarization and EIS Values of the double layer capacitance (C_{dl}) were calculated from the frequency at which the impedance imaginary component ($-Z_{img}$) was maximum. Using the following equation:

$$f(-Z_{(img)}\ max.) = 1/2\pi c_{dl}R_{ct} \quad (3)$$

% IE was calculated using the following equation:

$$\% \text{ IE} = [(1/R_{ct}) - (1/R'_{ct}) /(1/R'_{ct})] \times 100 \quad (4)$$

where R'_{ct} & R_{ct} are the charge transfer resistance values in the absence and presence of the inhibitors, respectively.

All experiments were conducted at 30 $\pm$ °C. Measurements were performed using Gamry PCI 300/4 Instrument Potentiostat/Galvanostat/ZRA. This includes Gamry Framework system based on the ESA400, Gamry applications that include dc 105 for dc corrosion measurements and EIS300 for electrochemical impedance spectroscopy along with a computer for collecting data. Echem Analyst 5.58 software was used for plotting, graphing and fitting data. All the potentials reported are referred to SCE.

RESULTS AND DISSCUSION

1 Potentiodynamic polarization measurements :

Figure (1) shows typical polarization curves for nickel in 0.5 M HCl solution with and without different concentrations of inhibitor (III) at 30 °C. Similar curves were obtained for other two indole derivatives (not shown). It is clear that the anodic and cathodic reactions of nickel electrode corrosion were inhibited after addition of inhibitor to the acidic solution, and this inhibition became more pronounced with increasing inhibitors concentration. This result indicates that the addition of inhibitor reduces nickel dissolution and also retards the hydrogen ions reduction. Table (2) collect the associated corrosion electrochemical parameters, i.e. corrosion potential (E_{corr}), corrosion current density (j_{corr}), anodic and cathodic Tafel slopes (β_a & β_c) derived from polarization curves by extrapolation, the degree of surface coverage (θ), as well as the percentage inhibition efficiency (% IE).

It is evident that the increasing concentration of the inhibitor resulted in a decrease in corrosion current densities and an increase in % IE, suggesting that the adsorption

protective film tends to be more complete and stable on nickel surface. The presence of inhibitors resulted in a slight shift of corrosion potential towards the noble direction compared to that in the absence of inhibitors, however, the slight displacement in E_{corr} can be defined as mixed-type inhibitors with predominantly control of anodic reaction [Ferreira *et al*, (2004), Vracar *et al*, (2002) and Li *et al*, (2008)]. The higher values of % IE indicate the higher surface coverage, due to the adsorption of inhibitors on the metal surface. The order of decreasing inhibition efficiency of the investigated indole derivatives is as follows:

$$III > II > I.$$

Table (2) The effect of concentration of the investigated compounds on the degree of surface coverage (θ), the inhibition efficiency (% IE) and corrosion rate for the corrosion of nickel in 0.5 M HCl at 30 °C

| Comp.	Conc. M	$-E_{corr}$, mV vs SCE	i_{corr} x10^{-4} A cm^{-2}	β_a, mV dec^{-1}	β_c, mV dec^{-1}	θ	% IE	C.R. mmy^{-1}
III	0	317	4.548	261	254	----	——	5.32
	3 x 10^{-6}	210	2.715	207	285	0.408	40.8	3.13
	6 x 10^{-6}	180	2.249	229	259	0.509	50.9	2.65
	3x 10^{-5}	242	2.243	224	284	0.511	51.1	2.60
	6 x 10^{-5}	236	1.747	204	278	0.619	61.9	2.03
	3 x 10^{-4}	256	1.262	236	278	0.725	72.5	1.47
	6 x 10^{-4}	222	3.960	238	260	0.914	91.4	0.46
II	3 x 10^{-6}	254	2.804	242	284	0.388	38.8	3.26
	6 x 10^{-6}	212	2.340	256	327	0.490	49.0	2.72
	3x 10^{-5}	295	2.312	222	274	0.496	49.6	2.68
	6 x 10^{-5}	259	1.806	268	285	0.606	60.6	2.10
	3 x 10^{-4}	206	1.713	247	280	0.626	62.6	1.99
	6 x 10^{-4}	199	1.027	233	273	0.869	86.9	0.70
I	3 x 10^{-6}	239	2.998	217	272	0.346	34.6	3.48
	6 x 10^{-6}	181	2.416	235	260	0.473	47.3	2.81
	3x 10^{-5}	217	2.317	232	265	0.495	49.5	2.69
	6 x 10^{-5}	137	1.865	192	270	0.593	59.3	2.16
	3 x 10^{-4}	208	1.734	190	283	0.622	62.2	2.01
	6x10^{-4}	318	1.559	291	291	0.660	66.0	1.81
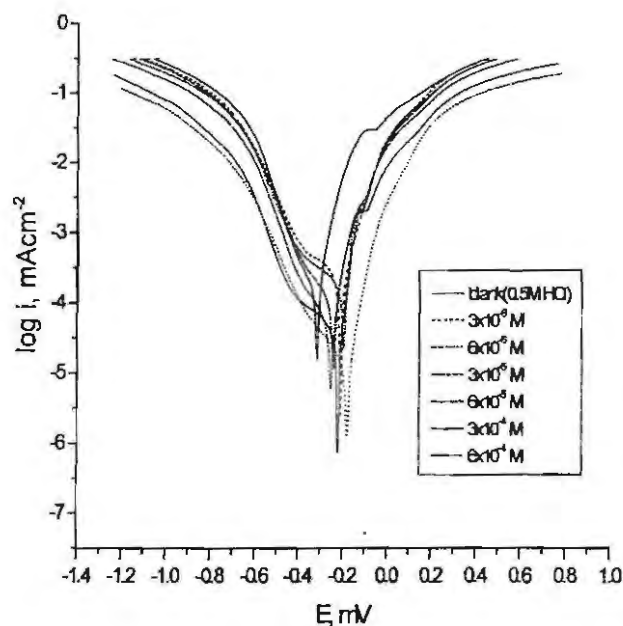
Fig. (1) The potentiodynamic polarization curves for the corrosion of nickel in 0.5 M HCl in   absence and presence of different concentration of compound (III) at 30 °C.

2 Electrochemical impedance spectroscopy (EIS) :

The corrosion behavior of nickel in 0.5 M HCl solution in absence and presence of different concentrations of the investigated compounds was investigated by the EIS method at 30 °C. **Fig. (3)** shows the Nyquist plots for nickel in 0.5 M HCl solution in the absence and presence of different concentrations of the compound (III) at 30 °C. The existence of a single semicircle in each plot shows that there was only single charge transfer process during the anodic dissolution of nickel and remained unaffected in the presence of inhibitive molecules of the inhibitors added in acid. The obtained Nyquist impedance diagrams in most cases doesn't show perfect semicircle, generally attributed to the frequency dispersion [**Paskossy, (1994)**] as a result of roughness and in homogenates of the electrode surface. The data reveal that, each impedance diagram consists of a large capacitive loop with low frequencies dispersion (inductive arc) which is generally attributed to anodic adsorbed intermediates controlling the anodic process [**Bessone et al.,(1983); Caprani et al, (1975) and   Epelboin et al, (1972)**]. By following this, inductive arc was disregarded. In 0.5 M HCl solution and presence of various concentrations of inhibitors, the impedance diagram shows the same trend (one

capacitive loop), however, the diameter of this capacitive loop increases with increasing concentration, due to the increase in the number of inhibitive molecules of inhibitors when the concentration was raised.. From the analysis of Nyquist diagram, the main parameters are the resistance of charge transfer R_{ct}, and the capacity of double layer C_{dl} which is defined as:

$$C_{dl} = 1/(2\pi f_{max} R_{ct}) \tag{5}$$

The surface coverage (θ) and the inhibition efficiencies (%IE) are defined by the following equations:

$$\theta = [1 - (R^{o}_{ct}/R_{ct})] \tag{6}$$

$$IE\% = [1 - (R^{o}_{ct}/R_{ct})] \times 100 \tag{7}$$

where R^{o}_{ct} & R_{ct} are the charge transfer resistance in the absence and presence of inhibitor respectively. The associated parameters with the impedance diagrams are given in **Table (3)**.

From the impedance results we found that the value of C_{dl} decreases with the increase in the concentration of the inhibitors. This considerable change indicated that the inhibitive molecules of the inhibitors have been adsorbed on nickel surface and decreased the roughness of the nickel surface. The % IE obtained from EIS measurements are close to those deduced from polarization method. The order of inhibition efficiency obtained from EIS measurements decreases as follows:

III > II > I

Table (3) Electrochemical Kinetic parameters obtained by EIS technique for Ni in 0.5 M HCl without and with various concentrations of compounds (I- III)

| Compound	Conc., (M)	C_{dl} $\mu F\ cm^{-2}$	R_{ct} Ohm cm^2	θ	% IE
III	0.5 M HCl	16.34	12.62	-	-
	3×10^{-5}	10.04	59.87	0.789	78.9
	6×10^{-5}	8.47	85.51	0.852	85.2
	3×10^{-4}	6.98	144.5	0.913	91.3
	6×10^{-4}	4.79	239.4	0.947	94.7
II	0.5 M HCl	16.34	12.62	-	-
	3×10^{-5}	14.64	22.80	0.446	44.6
	6×10^{-5}	13.27	32.17	0.608	60.8
	3×10^{-4}	10.33	37.71	0.665	66.5
	6×10^{-4}	8.87	43.18	0.708	70.8
I	0.5M HCl	16.34	12.62	-	-
	3×10^{-5}	17.00	20.21	0.376	37.6
	6×10^{-5}	12.56	24.66	0.488	48.8
	3×10^{-4}	11.11	31.24	0.596	59.6
	6×10^{-4}	10.98	38.57	0.673	67.3
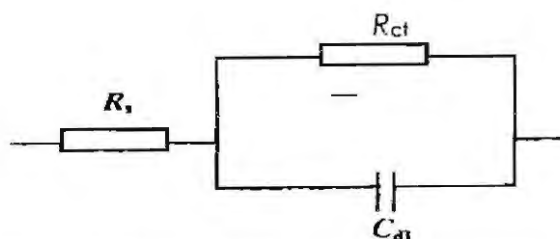
Fig. (2) Equivalent circuit model used in the fitting of the impedance data Ni
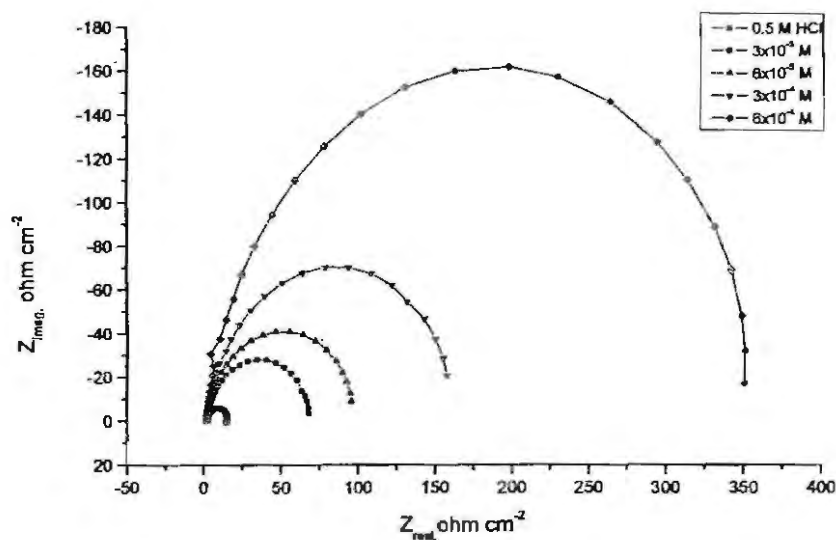
Fig. (3) Nyquist plots for nickel in 0.5 M HCl without and with various concentrations of compound (III) in 0.5 M HCl without and with various concentrations of compound (III).

3 Synergistic effects :

The corrosion behavior of Ni in 0.5 M HCl solution in the presence of 10^{-2} M KI, KBr and KCl at different concentrations of the investigated inhibitors was studied. From the results of Table (4), it is observed that % IE of the inhibitors increases on addition of these halides due to synergistic effect of the halide anions and the cationic form of the inhibitors. This may be attributed to the stabilization of adsorbed halide ions by means of electrostatic interactions with the inhibitor, which leads to greater surface coverage [Meaitra *et al*, (1983), Gomma, (1998)]. Halide ions are strongly adsorbed on metal surfaces, where the chemisorbed ions enter the metallic part of the double layer and the charge of ions become part of the charge of the metal surface [Meaitra *et al*, (1983)]. Thus, the inhibitor is not adsorbed directly on metal surface itself, but rather by coulombic attraction to the adsorbed halide ions on the metal surface. The data in Table (4) indicates that this co-operative effect increased in the order: $Cl^- < Br^- < I^-$, suggesting a possible role by the radii of the halide ions which also increase in the order: Cl^- (0.09 nm) $< Br^-$ (0.114 nm) $< I^-$ (0.135 nm).

Table (4) The effect of concentration of compound (III) on the free corrosion potential (E_{corr}), corrosion current density (i_{corr}), Tafel slopes (β_a & β_c), inhibition efficiency (%)IE, degree of surface coverage (θ) and corrosion rate for the corrosion of nickel in 0.5M HCl + 1×10^{-2} M KI, KBr and KCl at 30°C.

anion	Conc,M	$-E_{corr}$,mV.	i_{corr} ,A cm^{-2}	β_a, mVdec^{-1}	β_c, mVdec^{-1}	θ	IE%	C.R. mmy^{-1}
I$^-$	0	328	7.660×10^{-7}	227	324	----	-----	0.087
	3×10^{-6}	119	2.286×10^{-7}	237	212	0.969	96.9	0.003
	6×10^{-6}	189	1.660×10^{-7}	185	212	0.978	97.8	0.002
	3×10^{-5}	142	1.294×10^{-7}	184	198	0.983	98.3	0.002
	6×10^{-5}	143	1.190×10^{-7}	192	185	0.984	98.4	0.002
	3×10^{-4}	127	0.504×10^{-7}	186	180	0.993	99.3	0.001
	6×10^{-4}	107	0.453×10^{-7}	179	175	0.994	99.4	0.001
Br$^-$	0	263	8.012×10^{-6}	291.5	341.3	----	----	0.093
	3×10^{-6}	170	2.726×10^{-6}	254.8	272.3	0.660	66.0	0.032
	6×10^{-6}	178	2.320×10^{-6}	254.2	266.5	0.710	71.0	0.027
	3×10^{-5}	182	1.508×10^{-6}	233.9	258.0	0.812	81.2	0.018
	6×10^{-5}	196	1.473×10^{-6}	227.8	244.1	0.816	81.6	0.017
	3×10^{-4}	170	0.929×10^{-6}	240.3	247.0	0.884	88.4	0.012
	6×10^{-4}	197	0.532×10^{-6}	243.5	241.2	0.934	93.4	0.011
Cl$^-$	0	202	9.943×10^{-6}	266.8	300.3	----	----	1.015
	3×10^{-6}	277	3.878×10^{-6}	278.3	256.5	0.610	61.0	0.045
	6×10^{-6}	266	3.061×10^{-6}	259.8	259.1	0.692	69.2	0.036
	3×10^{-5}	290	2.753×10^{-6}	257.9	249.4	0.723	72.3	0.032
	6×10^{-5}	275	2.625×10^{-6}	255.6	247.4	0.736	73.6	0.031
	3×10^{-4}	253	1.283×10^{-6}	250.3	249.1	0.871	87.1	0.023
	6×10^{-4}	264	0.744×10^{-6}	254.2	251.9	0.925	92.5	0.019

4 Adsorption isotherm :

It is generally assumed that the adsorption of the inhibitors on the metal surface is the essential step in the inhibition mechanism [Asan et al (2005)]. To determine the adsorption mode, various isotherms were tested and the Frumkin mode should be the best. Plots of $\ln[\theta/(1-\theta)C]$ vs. θ where θ is the surface coverage and C is the concentrations of the inhibitors for the adsorption of investigated compounds on the surface of Ni in 0.5 M HCl acid at 30° C are shown in Fig. (4). This Frumkin model has been used for other inhibitor systems [Fouda et al (2010), Fouda et al (1990)]. According to this isotherm θ is related to inhibitor concentration via:

$$[\theta \quad / \quad (1-\theta) \quad \exp(-2a\theta) \quad = \quad KC] \tag{8}$$

Or its linear form:

$$Ln \quad [\theta / \quad (1-\theta)C] \qquad = \quad \ln K_{ads} + 2a\theta \tag{9}$$

where a is the interaction parameter between molecules adsorbed on the metal surface and K_{ads} the equilibrium constant of adsorption. From Fig. (4), straight lines were obtained for all investigated compounds. The equilibrium constant (K_{ads}) is related to the free energy of adsorption (ΔG°_{ads}) by:

$$K_{ads} \qquad = \qquad (1/55.5) \exp(-\Delta G^{\circ}_{ads}/RT) \tag{10}$$

where 55.5 is the molar concentration of water in solution in mol L^{-1}. The slope of the linear fitting of Frumkin gave the values of (a) and the intercepts gave the values of K_{ads} for all the investigated compounds (Table (5)). The negative values of (a) indicates the presence of repulsive forces between the adsorbed species of the investigated compounds and the increasing values of K_{ads} from I to III reflects the increasing capability, due to structural formation, on the metal surface [Da Costa *et al*, (1990)]. The calculated ΔG°_{ads} values, using Eq.10, were also given in Table (5). The large negative values of ΔG°_{ads} ensure the spontaneity of the adsorption process and the stability of the adsorbed layer on Ni surface [Tang *et al*, (2006), Tebbji *et al*, (2007)] as well as a strong interaction between inhibitors molecules and the metal surface [Mu *et al*, (2005)].

Generally, absolute values of ΔG°_{ads} up to 20 kJ mol^{-1} are consistent with physisorption, while those around 40 kJ mol^{-1} or higher are associated with chemisorptions as a result of the sharing or transfer of electrons from organic molecules to the metal surface to form a coordinate type of metal bond [Outirite *et al*, (2010)]. Here the calculated ΔG°_{ads} values are ranging from -52.2 and -46.4 kJ mol^{-1} , indicating that the adsorption mechanism of the inhibitors on Ni in 0.5 M HCl solution at the studied temperatures is both electrostatic-adsorption (ionic) and chemisorptions (molecular) [Ali *et al*, (2008)]. The decrease of % IE with rise in temperature indicates that the physisorption has the major contribution while the chemisorptions have the minor contribution in the inhibition mechanism [Noor *et al*, (2006)].

Table (5) Interaction parameters (a), adsorption equilibrium constant(K),free energy (ΔG°_{ads}) of Ni dissolution in 0.5 M HCl in the presence of investigated compounds at 30 °C.

Inhibitor	-a	$K \times 10^{-6}$ M^{-1}	$- \Delta G^{\circ}_{ads}$ kJ mol^{-1}
III	3.3	25.3	52.2
II	4.0	4.0	47.6
I	6.6	2.4	46.4
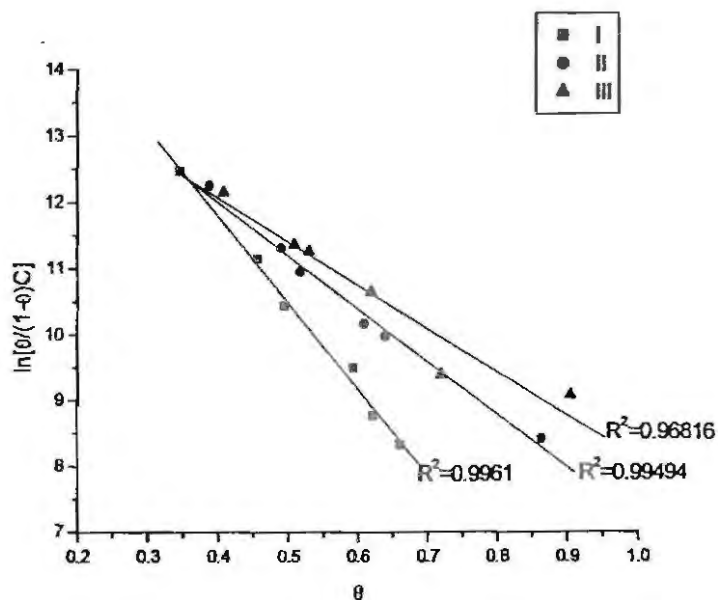
Fig. (4) The linear form of Frumkin adsorption isotherm of investigated compounds on Ni surface in 0.5 M HCl solution.

3.5 Effect of temperature

The influence of solution temperature on the inhibition performance of investigated compounds for nickel in 0.5 M HCl solution in the absence and presence of 6×10^{-4} M concentration at temperature ranging from 30 to 60 °C was studied using polarization measurements. The results are presented in **Table (6)**. The results of Table (6) show the increase in solution temperature causes E_{corr} to shift in the positive direction and enhances both the anodic and cathodic reactions. This may be attributed to the fact that an increase in temperature usually accelerates corrosion processes, giving rise to higher metal dissolution rates and a possible shift of the adsorption -- desorption equilibrium towards desorption .This as well as roughening of the metal surface as a result of enhanced corrosion, may also reduce the ability of the inhibitor to be adsorbed on the metal surface. The observed decrease in the strength of the adsorption at higher temperatures suggests that physical adsorption may be the main type of adsorption of indolederivatives.

Table (6) : The effect of 6×10^{-4} M of the investigated compounds on the free corrosion potential (E_{corr}), corrosion current density (i_{corr}), Tafel slopes (β_a & β_c), inhibition efficiency (% IE) ,degree of surface coverage (θ) and corrosion rate for the corrosion of nickel in 0.5M HCl at different temperatures.

Temp., °C	Conc. M	$-E_{corr.}$, mV vs. SCE	$i_{corr.} \times 10^{-4}$ A cm^{-2}	β_a, mV dec^{-1}	β_c, mV dec^{-1}	θ	% IE	C.R. mmy^{-1}
30	Blank	317	4.55	261	254	----	-----	5.32
	I	318	1.56	291	291	0.660	66.0	1.80
	II	199	6.03	233	273	0.869	86.9	0.70
	III	222	3.96	238	260	0.914	91.4	0.46
40	Blank	271	6.18	286	280	---	---	6.27
	I	247	2.53	256	256	0.586	58.6	3.25
	II	276	2.42	249	256	0.604	60.4	2.84
	III	247	2.37	252	257	0.610	61.0	2.80
50	Blank	206	6.51	297	249	---	---	6.45
	I	251	5.07	304	272	0.220	22.0	6.02
	II	277	4.82	249	283	0.259	25.9	5.72
	III	253	3.71	340	324	0.430	43.0	4.31
60	Blank	287	7.22	310	287	---	---	6.86
	I	307	5.91	305	331	0.182	18.2	6.21
	II	290	5.51	286	274	0.237	23.7	6.17
	III	321	5.17	293	279	0.285	28.5	6.10

6 Activation parameters of inhibition process :

Plot of logarithm of corrosion rate (log k), with reciprocal of absolute temperature (1/T) for Ni in 0.5 M HCl at 6×10^{-4}M for the investigated compounds is shown in **Figure (5)**. As shown from this Figure, straight lines with slope of $-E_a^*/2.303R$ and intercept of A were obtained according to Arrhenius-type equation:

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

(11)

where k is the corrosion rate, A is a constant depends on a metal type and electrolyte, E_a^* is the apparent activation energy, R is the universal gas constant and T is the absolute temperature.

Plot of log (corrosion rate/ T) vs. 1/ T for Ni in 0.5 M HCl at 6×10^{-4}M for the investigated compounds is shown in **Figure (6)**. As shown from this Figure, straight lines with slope of $(-\Delta H^*/2.303R)$ and intercept of (log R/ Nh + $\Delta S^*/2.303R$) were obtained according to transition state equation:

$$\text{Rate} = RT/Nh \exp(\Delta S^*/R) \exp(-\Delta H^*/RT)$$

(12)

where h is Planck's constant, N is Avogadro's number, ΔH^* is the activation enthalpy and ΔS^* is the activation entropy. The calculated values of the apparent activation energy, E_a^*, activation enthalpies, ΔH^* and activation entropies, ΔS^* are given in **Table (7)**. The linear regression coefficients (R^2) are close to unity, indicating that the corrosion of nickel in 0.5 M HCl solution may be elucidated using the kinetic model. These values indicate that the presence of the additives increases the activation energy, E_a^* and the activation enthalpy, ΔH^* and decreases the activation entropy, ΔS^* for the corrosion process. The higher values of, E_a^*, suggest that dissolution of nickel is slow in presence of inhibitors. It is clear from Eq.5 that the higher values of E_a^* lead to the lower corrosion rate. Also, the increase in the, E_a^*, indicates strong adsorption of the inhibitor molecules on Ni surface and the presence of energy barrier caused by the adsorption of the additive molecules on Ni surface. The increase in the activation enthalpy (ΔH^*) in the presence of the inhibitors implies that the addition of the inhibitors to the acid solution increases the height of the energy barrier of the corrosion reaction to an extent depends on the type and concentration of the present inhibitor. The positive sign of (ΔH^*) indicates the endothermic behavior of these compounds at activated states. The entropy of activation (ΔS^*) in the blank and inhibited solutions is large and negative indicating that the activated complex represents association rather than dissociation step [Gomma *et al.,* (1995) and Soliman *et al.,* (1995)]. The order of increasing inhibition efficiency, as observed from the increase in activation energy, is as follows:

$$I < II < III$$

than dissociation step [**Gomma** *et aL,* **(1995) and Soliman** *et aL,* (1995)]. The order of increasing inhibition efficiency, as observed from the increase in activation energy, is as follows:

$$I < II < III$$

Table (7) Thermodynamic activation parameters for the dissolution of Ni in the presence and absence of 6 x10^{-4}M of the investigated compounds in 0.5 M HCl

Inhibitor	Activation parameters		
	E^{*}_{a}, kJ mol^{-1}	ΔH^{*} kJ mol^{-1}	$-\Delta S^{*}$ J mol^{-1} k^{-1}
0.5 M HCl	17.4	6.5	177.7
I	30.1	10.2	158.5
II	32.7	10.5	154.7
III	35.9	11.1	145.1
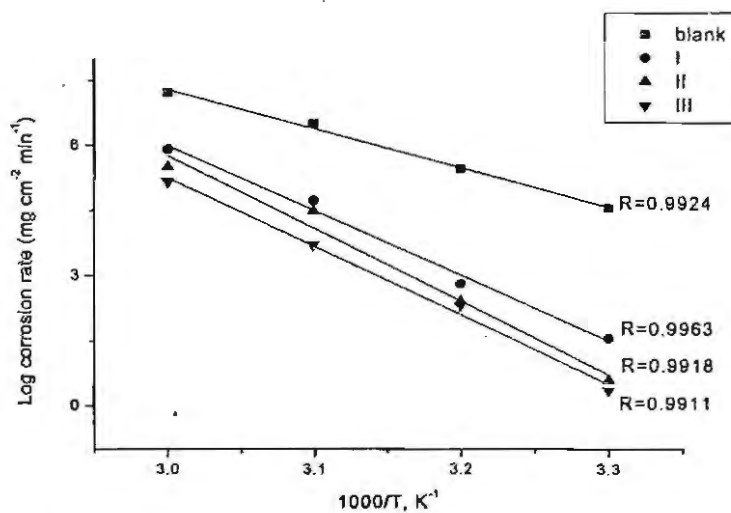
Fig. (5) log corrosion rate vs. 1/T curves for the corrosion of Ni in 0.5M HCl at 6x10^{-4}M for the investigated compounds.
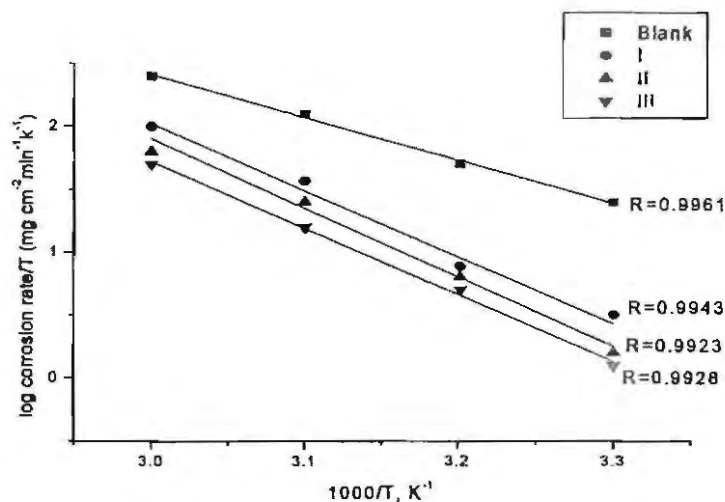
Fig. (6) log corrosion rate/T vs. 1/T curves for the corrosion of Ni in 0.5 M HCl at
6×10^{-4}M
investigated compounds.

7. Mechanism of corrosion inhibition :

Corrosion inhibition of Ni in 0.5 M HCl solution by the investigated indole
derivatives as indicated from potentiodynamic polarization and impedance (EIS)
techniques was found to depend on the concentration and the nature of the inhibitors.

It is generally, assumed that adsorption of the inhibitor at the metal / solution
interface is the first step in the action mechanism of the inhibitors in aggressive acid
media. Four types of adsorption may take place during inhibition involving organic
molecules at the metal / solution interface [Schweinsgerg *et al* , (1988)]

1) Electrostatic attraction between charged molecules and charged metal.
2) Interaction of unshared electrons pairs in the molecule with the metal.
3) Interaction of π electrons with the metal.
4) A combination of the above.

Concerning inhibitors, the inhibition efficiency depends on several factors; such
as: (i) the number of adsorption sites and their charge density, (ii) molecular size, heat
of hydrogenation, (iii) mode of interaction with the metal surface, and (iv) the formation
metallic complexes [Fouda *et al* , (1986)]. Most organic inhibitors contain at least one
polar group with an atom of nitrogen, sulfur or oxygen, each of them in principle
representing an adsorption center. The inhibitive properties of such compounds depend
on the electron densities surrounding the adsorption centers: the higher the electron
density at the center, the more the effective the inhibitor.

In the aqueous acidic solutions, most of organic compounds containing N atoms
exist either as neutral molecules or in the form of cations (protonated). In general two

modes of adsorption could be considered. In our case, the neutral form may adsorb on the Ni surface via the chemisorption mechanism, involving the displacement of water molecules from the metal surface and the sharing electrons between the N, and O atoms and Ni.

The order of increased inhibition efficiency for indole derivatives is: III > II > I as indicated from the different methods.

Compound (III) is the most efficient inhibitor. This is due to the larger molecular size, the presence of two N atoms, O atom and CH_3 in the p-position which has higher electron donation character. On the other hand, compound (I) has the least effective inhibitor in this series. This is due to the presence of one N atom and it has the lowest molecular size. Compound (II) comes after compound (III) in the inhibition efficiency. This is due to the presence of one N atom, two O atoms and lower molecular size than compound (III)

CONCLUSIONS

The investigated compounds are found to be good inhibitors for nickel in 0.5 M HCl. The inhibition is accomplished by adsorption of these compound molecules onto the nickel surface without changing the mechanism of partial corrosion reactions. Potentiodynamic polarization studies show that these compounds are mixed-type inhibitors. EIS measurements indicate the single charge transfer process controlling the corrosion of nickel. The synergistic effect between indole derivatives and halide ions was studied using potentiodynamic polarization method. The data obtained from the different methods namely potentiodynamic polarization and electrochemical impedance spectroscopy are in good agreement.

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الملخص العربى

تثبيط تآكل النيكل فى محلول الهيدروكلوريك بواسطة بعض مشتقات الاندول

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تم دراسة تآكل النيكل فى محلول الهيدروكلوريك وتثبيط هذا التآكل فى وجود تركيزات مختلفة من بعض مشتقات الاندول بواسطة استخدام ثلاث مشتقات مختلفة من الاندول وذلك باستخدام عدة طرق كهربية مختلفه (الاستقطاب البوتنشوديناميكى والمعاوقه الكهربيه). وقد دلت النتائج من كلا الطريقتين ان هذه المركبات تعمل كمثبطات مختلطه واان نسبة الكفاءة التثبيطيه لهذه المركبات تزداد بزيادة التركيز وتقل بارتفاع درجة الحراره وقد وجد ايضا ان هذه المشتقات يحدث لها ادمصاص على سطح معدن النيكل تابع للايزوثيرم فريمكن وقد تم حساب بعض الدوال الثيرموديناميكيه لعملية التآكل ووجد ان كفاءة التثبيط تعتمد على المجموعات المستبدله فى الجزيئات والوزن الكتلى للمثبطات المستخدمه.