

"THE USE OF CHALCONES AS CORROSION INHIBITORS FOR NICKEL CORROSION: IN NITRIC ACID SOLUTION"

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ABSTRACT

The influence of some chalcones on the corrosion of nickel in 1 N nitric acid solution has been studied using weight loss and galvanostatic polarization techniques. In general, at constant acid concentration, inhibitor efficiency increases with increase of concentration of inhibitor and decreases with rise in temperature. Polarization studies reveal that the compounds behave as cathodic inhibitors. The effect of temperature on corrosion inhibition has been studied and activation energy has been evaluated. The adsorption of the inhibitor on the nickel surface is found to obey the Frumkin adsorption isotherm. Some thermodynamic parameters are calculated and discussed.

Key words: Corrosion, nickel, nitric acid, chalcones.

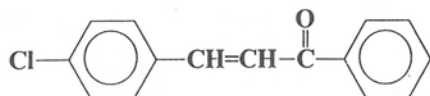
INTRODUCTION

Nickel finds applications in the handling of food products because of its ability to maintain product purity, and also in synthetic fibers and in structural applications where resistance to corrosion is of prime concern.

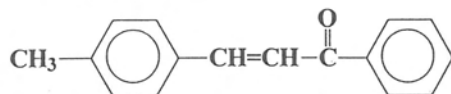
The anodic dissolution of nickel in different acid solutions in presence of organic and inorganic inhibitors have received recent attention by a large number of workers⁽¹⁻¹⁰⁾. Cheng et al.⁽¹¹⁾ studied the corrosion of nickel in acid solutions with H₂S and they reported that Ni dissolution is under both the acceleration effect of H₂S and the hindering effect of NiS layer. Abd El-Gulil et al.⁽¹²⁾ used 2,3,5-triphenyl tetrazolium chloride as a corrosion inhibitor for Ni in 5N H₂SO₄. Although there is a considerable activity on the correlation between inhibitor efficiency and molecular structure on the inhibitors in acid iron system, very few investigations have yet been done on the above with nickel. Polarization measurements afford information about the influence of inhibitors on the cathodic and anodic partial processes, in addition to the usual data which provide about corrosion rate.

The purpose of the present contribution is to determine the influence of nitric acid on the nickel corrosion in presence and in absence of the following chalcones:

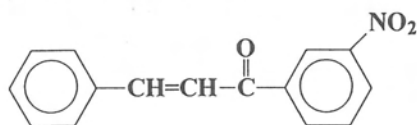
I) p-chlorobenzal acetophenone



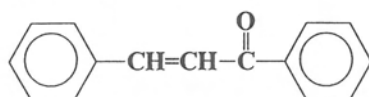
II) Anisal acetophenone



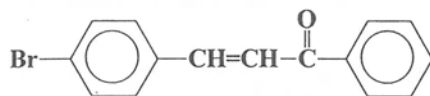
III) Benzal-m-nitroacetophenone



IV) Benzal acetophenone



V) p-Bromobenzal acetophenone



EXPERIMENTAL

High-purity BDH-produced nickel sheets and wires of the following composition (in weight %): Fe, 0.05; Al, 0.005; Co, 0.005; Mn, 0.005; Mg, 0.005 and Ti, 0.005 were used. Specimens were abraded successively with 1/0 and 0/0 papers. Then degreased in an ultrasonic bath, washed with water and then dried at room temperature.

The aggressive solutions were made of HNO₃. Appropriate concentrations of acid were prepared using bidistilled water. All chemical used were of AR grade.

Corrosion weight loss tests

For weight loss measurements, rectangular nickel specimens of size 20x20x2 mm were immersed in 100 ml of inhibited and uninhibited solutions and allow to

stand for several intervals at 25°C in water thermostat. the percentage protection (%P) of the inhibitor was calculated using the equation:

$$\%P = \frac{W_0 - W}{W_0} \times 100 \quad (1)$$

where *w* and *w*₀ are the weight loss of nickel with and without inhibitors, respectively.

Electrochemical measurements

Galvanostatic cathodic polarization studies were carried out on nickel in 1N HNO₃ solution without and with different concentrations of the inhibitors used at 25°C. Saturated calomel electrode (SCE) was used as reference electrode while a platinum wire as counter electrode. all experiments were carried out at 25±0.1°C. A cylindrical rod with a surface area of 0.72 cm² was used as working electrode. The inhibition efficiency (%P) is defined as:

$$\%P = \left(\frac{I_{\text{corr.}} - I_{\text{inh.}}}{I_{\text{corr.}}} \right) \times 100 \quad (2)$$

where *I*_{corr.} and *I*_{inh.} are the uninhibited and inhibited corrosion current densities, respectively.

RESULTS AND DISCUSSION

Table 1 gives values of inhibition efficiency obtained from the weight loss measurements for various concentrations of different inhibitors used at 25°C and 60 min. immersion. It is seen from this table that at low concentration of 5x10⁻⁷M the inhibition efficiency is found to be 60-64%, and reaches a maximum value of 73% at a concentration of 1x10⁻⁴M. The results of the table show that all compounds used inhibits the corrosion at all concentrations (1x10⁻⁴-5x10⁻⁷M) in 1N HNO₃. There is no gradual change of inhibition efficiency with increase in the concentration of the inhibitor test solutions. The change is found to be abrupt.

The effect of temperature (25-55°C) on the performance of the inhibitor at a concentration of 1x10⁻⁵M for nickel in 1N HNO₃ was studied using weight loss measurements. a plot of log *k* vs. 1/*T* was made for both the acid and inhibitors containing acid and the slope of the straight lines were evaluated (Figs. 1 & 2). The energy of activation obtained from these figures were found to be 76.55 KJ mol⁻¹ for 1N HNO₃ and 86-89 KJ mol⁻¹ for acid containing inhibitors (Table 2).

Table 1. Variation of % inhibition efficiency for different inhibitors with various concentrations at 25°C, and after 60 min. immersion.

	% Inhibition efficiency				
	I	II	III	IV	V
5×10^{-7}	64.00	60.74	60.8	60.55	61.20
1×10^{-6}	70.00	66.20	66.6	65.90	69.60
5×10^{-6}	71.10	69.00	69.8	68.70	70.53
1×10^{-5}	72.14	70.10	70.4	69.80	72.00
5×10^{-5}	72.70	71.00	71.9	70.70	72.30
1×10^{-4}	73.60	72.45	72.8	72.45	73.40

Table 2. Values of thermodynamical parameters, f, B, ΔG^* , ΔS^* and ΔH^* during adsorption of inhibitors ($10^{-5}M$) on nickel in 1N HNO₃ at 25°C.

Inhibitor	f	B	$-\Delta G^*$ kcal mol ⁻¹	ΔS^* cal K ⁻¹	ΔH^* kcal mol ⁻¹
I) p-chlorobenzal acetophenone	19.5	1.769×10^{-2}	10.9	6.4	8.99
II) Anisal acetophenone	24.0	1.7728×10^{-2}	9.7	15.0	5.23
III) Benzal-m-nitro acetophenone	20.6	1.7726×10^{-2}	9.6	53.3	6.28
IV) Benzal acetophenone	28.4	1.7737×10^{-2}	9.9	31.7	0.45
V) p-bromobenzal acetophenone	18.3	1.7701×10^{-2}	10.6	10.0	7.62

The almost similar values of E_A^* suggest that the inhibitors are similar in their mechanism of action and the order of efficiency may be related to the pre-exponential factor A by the equation:

$$\log k = \log A - E_A^*/RT \quad (3)$$

This is further related to concentration, steric effects, metal surface characteristics etc. The weight loss due to corrosion was found to increase with temperature and hence, the inhibitive efficiency of all inhibitors decrease with the rise in temperature from 25-55°C.

The efficiency of different compounds at the temperature range 25-55°C was found to decrease in the order: I > V > III > II > IV.

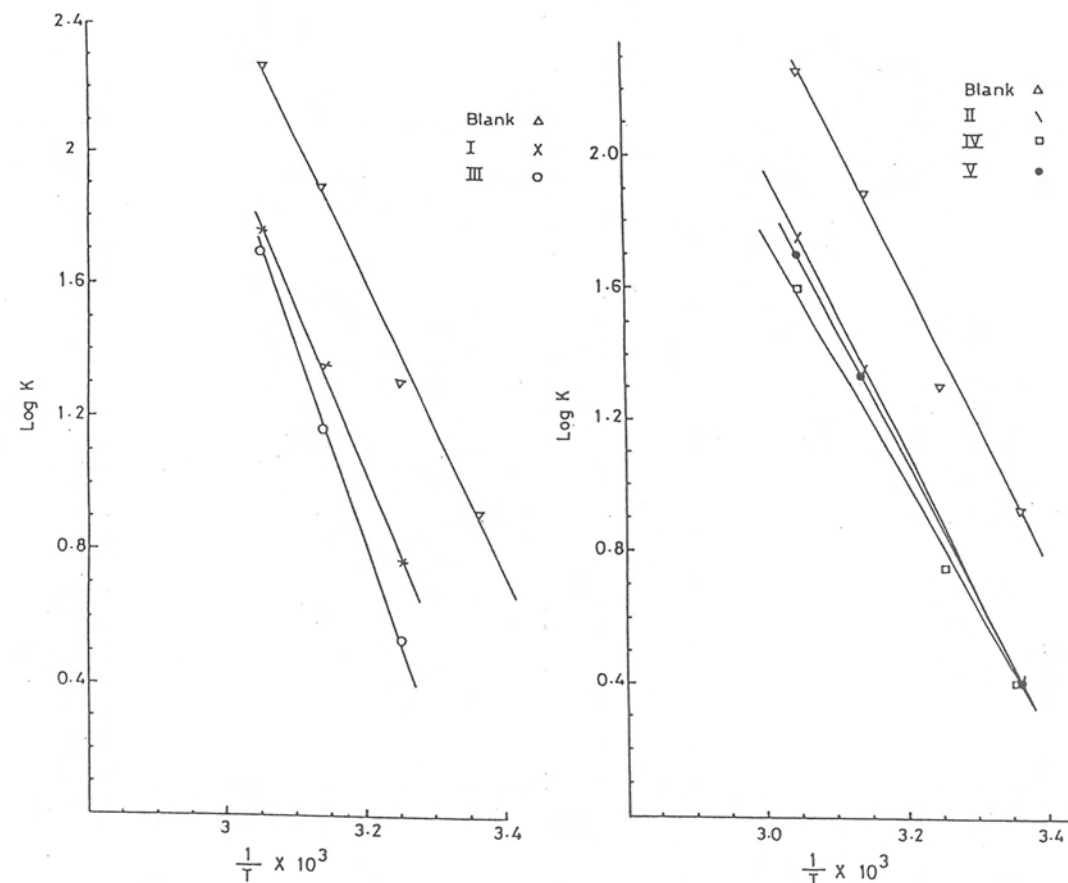


Fig. (1). Log k-1/T curves for nickel dissolution in presence and in absence of compounds I and III. Fig. (2). Log k-1/T curves for nickel dissolution in presence and in absence of compounds II, IV and V.

The nature of inhibitor interaction on the corroding surface during corrosion inhibition of metals has been deduced in terms of adsorption characteristics of the inhibitor⁽¹³⁾. The plot of θ ($\theta = 1-w/w_0$) degree of surface coverage vs. log C (inhibitor concentration) (Fig. 3) followed an S-type curve characteristic of the Frumkin adsorption isotherm⁽¹⁴⁾.

$$K_a C = \frac{\theta}{1-\theta} \exp(-f \theta) \quad (4)$$

where k_a is the equilibrium constant of the adsorption reaction, C the concentration, and f is a parameter related to the variation of the adsorption energy with coverage characterizing the interaction of adsorbed species between them and with surface atoms or ions of the metal.

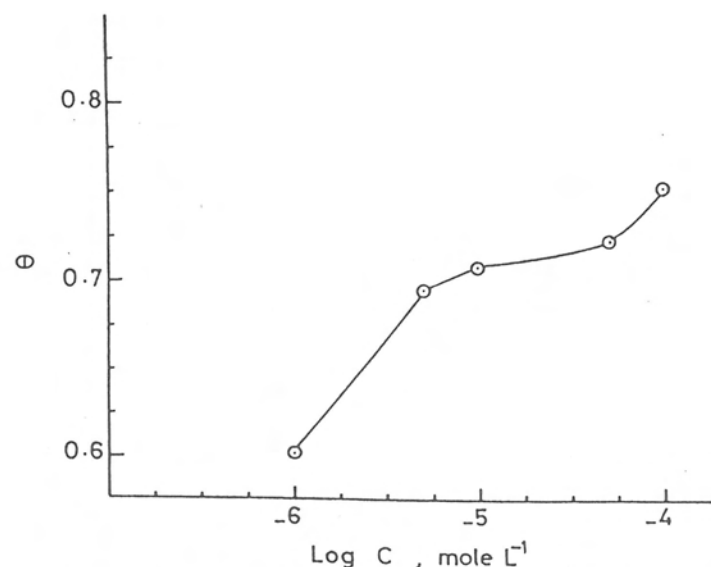


Fig. (3). Effect of compound (I) concentration on the degree of surface coverage for nickel in 1N HNO₃.

The constant K_a is related to the free energy of adsorption ΔG* by the relation:

$$k_a = \exp\left(\frac{\Delta G^*}{RT}\right) \frac{1}{55.5} \quad (5)$$

The value of 55.5 is the concentration of water in solution expressed in mol l⁻¹.

The values of ΔG* were calculated. The entropy of adsorption ΔS* was evaluated from the relation between ΔG* and T (Fig. 4). From values of ΔG* and ΔS*, the heat of adsorption ΔH*, is calculated. Thermodynamic parameters for the adsorption of inhibitors are given in Table 2, the negative values of ΔG* indicate the spontaneous adsorption of inhibitors on nickel surface.

Figure 5 shows the cathodic Tafel plots for nickel in 1N nitric acid and in presence of different concentrations of compound (1). An increase in the concentration of inhibitor shifted the polarization curves towards more negative potentials (Table 3). A cathodic Tafel slope of 190±10 mv per decade was obtained with and without inhibitors used. Polarization data suggest that in case of all chalcones used the cathode is preferentially polarized.

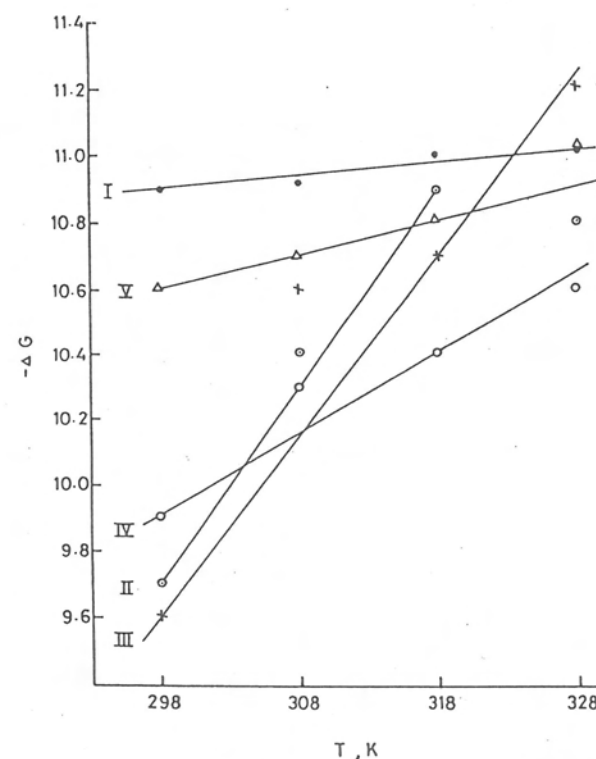


Fig. (4). ΔG* vs. T curves for chalcone derivatives

Table 3 reports the values of: Corrosion potential, E_{corr.}, cathodic Tafel slope, b_c, corrosion current density, I_{corr.}, degree of surface coverage, θ, and inhibition efficiency, 1% for different concentrations of compound (1).

The order of inhibition efficiency of the additives as determined by the polarization is: I > V > III > II > IV.

Mechanism of inhibition

According to Hackerman et al.⁽¹⁵⁾, the adsorption of the compounds over the nickel surface is not only by itself but that in some cases adsorption of inhibitor takes place through already adsorbed solution anions. So, NO₃⁻ anion already adsorbed on the metal surface, it interferes with the adsorption of the inhibitor molecules and come in competition with them. Owing to the acidity of the medium, these chalcones remain in the protonated form (enol form), at least at the moment of contact between metal and solution. So, the chalcones affect the course of the cathodic processes.

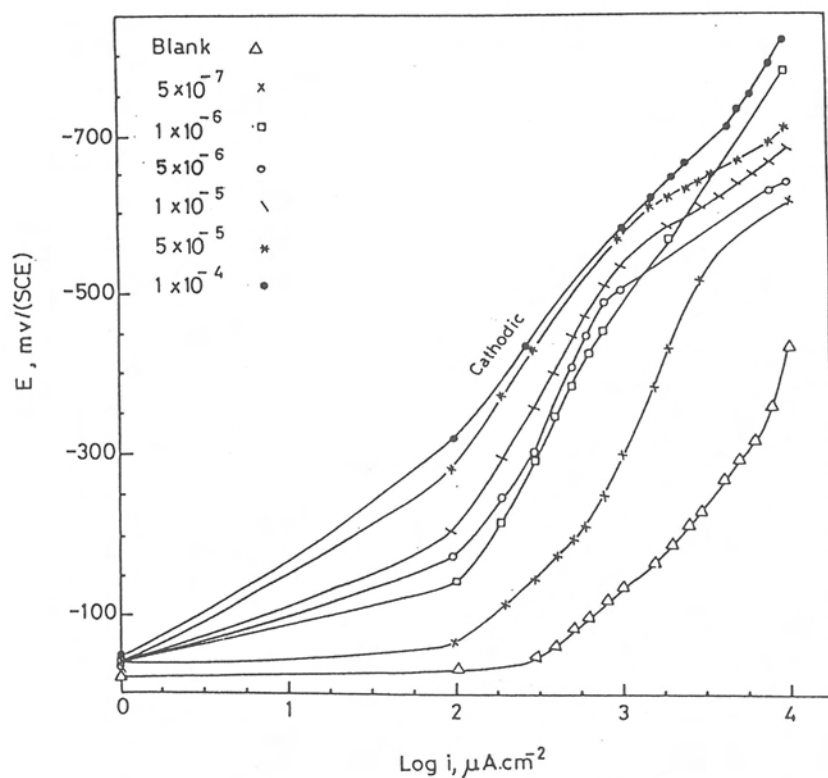
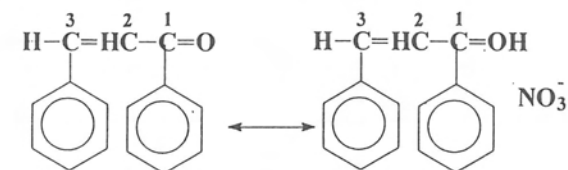


Fig. (5) Galvanostatic polarization curves of nickel in 1N HNO₃ alone and containing different concentrations of compound (I)

Table 3. Data from galvanostatic polarization of nickel in 1N HNO₃ containing different concentrations of compound (I) at 25°C.

Conc. M	-E _{corr.} mV	I _{corr.} μA cm ⁻²	b _c mV dec ⁻¹	%I	θ
0.0	20.0	316.23	190	-	-
5x10 ⁻⁷	53.2	89.12	170	71.80	0.72
1x10 ⁻⁶	43.0	39.80	170	87.40	0.87
5x10 ⁻⁶	42.3	28.20	170	91.00	0.91
1x10 ⁻⁵	45.0	19.95	180	93.60	0.94
5x10 ⁻⁵	45.0	10.60	180	96.60	0.97
1x10 ⁻⁴	48.0	7.94	180	97.50	0.98



Substitution of the hydrogen atom in the para position of the phenyl group at C-3 of compound (IV) by a chlorine atom (compound I) or by bromine atom (compound V) or by methyl group (compound II) or by substitution of hydrogen atom in meta position of the phenyl group at C-1 by nitro group (compound III) leads to an increase in protection efficiency. This behaviour can be discussed on the basis that introducing the nucleophilic group (-CH₃) to the molecule increases the electron density of the surface active center of the molecule (O-C) and gives strong adsorption.

Skeletal representation of the mode of adsorption of the compounds is shown by Fig. 6, and clearly indicates the active adsorption centers.

Compound I is the most efficient inhibitor, instead of it contains a chlorine atom at the para position in the phenyl group at C-3, which is an electrophilic group and reduces the electron density at the functional group (O=C), also leads to an increase in protection efficiency. This phenomenon has been reported previously⁽¹⁶⁾. This behaviour can be explained on the following basis^(17,18).

- Owing to either electrostatic forces due to the increase in dipole moment of the molecule or to a coordinate type of bonding, the substituent electrophilic group has a polar character interaction with the metal surface.
- Where adsorption of the protonated form of the inhibitor species occurs, the decrease in electron density of the functional group leads to an effective increase in the positive charge and hence stronger electrostatic force.

Compound (V) comes after compound (I) in protection efficiency instead of, it contains a bromine atom at the para position in the phenyl group at C-3. This may be due to the lower dipole moment of Br atom than the Cl atom. Compound III comes after compound (V) in protection efficiency instead of it contains nitro group in the meta position of the phenyl group at C=1. NO₂ group may add an additional center of adsorption to the molecule in addition to the center of adsorption due to the C=O and the rest of molecule protituted perpendicularly in the solution. Compounds II & IV come after that, but compound II comes before compound IV in protection efficiency.

This may be due to the CH₃ group is an electron donating group than H atom, so the CH₃-group increases the electron density on the active center and hence protection efficiency increases.

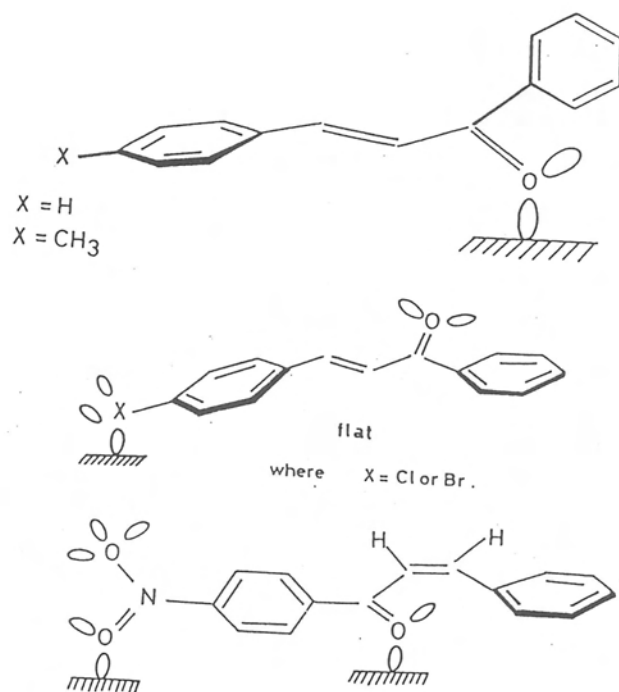


Fig. (6). Skeletal representation of the mode of adsorption of chalcone compounds.

CONCLUSIONS

1. All the chalcones studied are found to perform well as a corrosion inhibitor in nitric acid solution and the inhibiting efficiency values of the examined chalcones follows the order: I > V > III > II > IV at all the studied concentrations range.
2. The chalcones studied are found to act as cathodic inhibitors.

3. The protection efficiency increases with a decrease in temperature or an increase in concentration of the studied chalcones and depends on electrophilic and nucleophilic character of the substituted groups.

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