2-Hydroxyacetophenone-aroyl Hydrazone Derivatives as Corrosion Inhibitors for Copper Dissolution in Nitric Acid Solution

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The effect of 2-hydroxyacetophenone-aroyl hydrazone derivatives on the inhibition of copper corrosion in 3N nitric acid solution at 303 K was investigated by galvanostatic polarization and thermometric techniques. A significant decrease in the corrosion rate of copper was observed in the presence of the investigated compounds. The corrosion rate was found to depend on the nature and concentrations of the inhibitors. The degree of surface coverage of the adsorbed inhibitors is determined from polarization measurements, and it was found that the results obey the Frumkin adsorption isotherm. The inhibitors acted as mixed-type inhibitors, but the cathode is more polarized. The relative inhibitive efficiency of these compounds has been explained on the basis of structure dependent electron donor properties of the inhibitors and the nature of the metal-inhibitor interaction at the surface. Also, some thermodynamic data for the adsorption process (ΔG_a^- and f) are calculated and discussed.

Introduction

Pickling in nitric acid is commonly practised in industry for finishing metal surfaces. The use of inhibitors during the pickling operation is of very recent origin. The mechanism of the action of inhibitors for nitric acid has not been studied exhaustively.[1]

Dilute nitric acid is one of the best sovlents for copper. According to Veley,[2] copper readily dissolves in nitrous acid, less readily in a mixture of nitrous and nitric acid and still less rapidly in nitric acid alone. The reaction of nitric acid on copper is conditioned by (1) concentration of the acid, 2) temperature 3) presence of nitrous acid, and 4) solubility of the reaction products in the acid.

Quinine and Strychnine.[3] Caffeine,[4] *n*-decylamine,[5] 2,4-dinitrophenyl hydrazine.[6] substituted phenols,[7] benzoyl benzaldehyde hydrazone derivatives[8] and ethylamine[9] have been used as effective corrosion inhibitors for copper. Copper is widely used in various industrial operations, therefore the study of the corrosion inhibition of copper is a subject of pronounced practical significance.

The purpose of the present contribution is to determine the influence of some 2-hydroxyacetophenone aroyl hydrazone derivatives towards the corrosion of copper in nitric acid, to throw some light on the mechanism of inhibition and to study the effect of the temperature on the rate of corrosion.

Experimental Section

The thermometric reaction vessel and the procedure for determining the rate of dissolution of copper in 3 N HNO₃ solution were the same as described elsewhere.[10] The study was carried out with test pieces made of sheets measuring $1 \times 10 \times 0.2$ cm³. Before being used, these were lightly abraded with emery papers of 1/0, 2/0, 3/0 and 4/0 grade then degreased by acetone. Each experiment was carried out with a new clean specimen and with 15 mL of the aggressive

solution. The variation of the temperature of the system was measured to ± 0.1 °C on a calibrated thermometer. All chemicals were of AR quality and were used without further purification.

The inhibiting efficiency was calculated from the percentage decrease in *RN*:

$$\text{Inhibition efficiency (\%)} = \frac{RN_{free} - RN_{inh}}{RN_{free}} \times 100 \qquad (1)$$

The reaction number RN is defined as.[11]

$$RN = \frac{T_m - T_i}{t} = \frac{\Delta T}{t} \, °C \, min^{-1}. \qquad (2)$$

where T_m and T_i are the maximum and initial temperatures respectively, and t is the time in minutes taken to reach T_m. All experiments were started at 30 ± 0.1 °C.

Copper in the form of wire (99.7%) in the case of polarization measurements, was fixed in glass tubing, such that only a surface area of 0.3 cm² was exposed to 100 mL of the corrosive medium. For polarization measurements, a saturated calomel electrode and a platinum wire were used as reference and auxiliary electrodes, respectively. Currents from constant current device measured with a multimeter with an accuracy of ± 4%. Corrosion potentials were recorded using a digital ionalizer device (Orion model 701A). The potential at any given current under similar experimental conditions was reproducible within 7%. The detailed experimental procedure has been given elsewhere.[12] The inhibitive efficiency was calculated employing the formula:

$$\%I_e = \left(1 - \frac{i_{inh}}{i_o}\right) \times 100 \qquad (3)$$

where i_o and i_{inh} are the corrosion current densities without and with inhibitor, respectively.

The additives used as inhibitors were prepared and crystallized several times according to the general procedure: To ethanolic solution of the appropriate aromatic aldehyde-2-

hydroxyacetophenone, the corresponding acid hydrazides were added. The reaction mixture was refluxed for 2-4 hours on a water bath for a time depending on the acid hydrazide used. The solution was evaporated till a precipitate is formed. The precipitate was washed with hot ethanol, diethyl-ether and dried. The structure of these compounds were identified by elementary, IR. m.p.. and NMR analysis. The structure of the inhibitors are listed below:
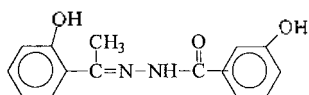
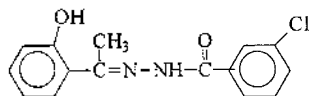1) 2-hydroxyacetophenone-3-aminobenzoyl hydrazone
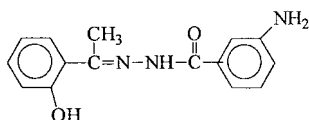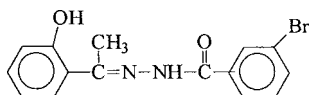
2) 2-hydroxyacetophenone-3-toloyl hydrazone
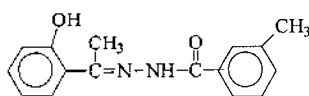
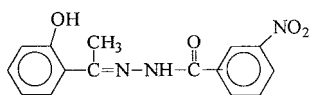3) 2-hydroxyacetophenone-3-hydroxybenzoyl hydrazone

4) 2-hydroxyacetophenone-3-chlorobenzoyl hydraozne

5) 2-hydroxyacetophenone-3-bromobenzoyl hydrazone

6) 2-hydroxyacetophenone-3-nitrobenzoyl hydrazone

Results and Discussion

Polarization measurements. Corrosion potentials. corrosion current densities determined by extrapolating the cathodic and anodic Tafel regions. the intersect is the corrosion current and corrosion potential. Figure 1 shows the galvanostatic polarization of copper in 3 N HNO₃ solution in the presence and in the absence of various concentrations of compound (1). As can seen, both the cathodic and the anodic reactions are inhibited and the inhibition increases as the inhibitor concentration increases, but the cathode is more polarized $(\beta_c > \beta_a)$. Similar results were obtained for other tested compounds. The order of decreasing inhibition efficiency was found to be: 1 > 2 > 3 > 4 > 5 > 6 (Table 2). Tafel lines of nearly equal slopes were obtained as can be seen from Table 1. This indicates[13] that the adsorbed molecules of compound (1) have no effect on the mechanism of either
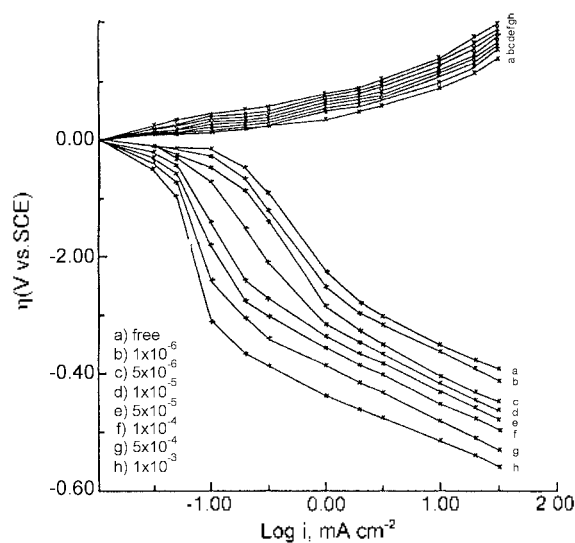

Figure 1. Galvanostatic polarization curves of copper in 3 N HNO₃ alone and containing different concentrations of compound (1).

Table 1. The effect of compound (1) concentrations on the free corrosion potential (E_{corr}), corrosion current density (i_{corr}), Tafel slopes $(\beta_a \& \beta_c)$, inhibition efficiency (Pi) and degree of surface coverage (θ) for polarization of copper in 3.0 N HNO₃ at 30 °C

Conc. (M/L)	E_{corr} (mV vs. SCE)	i_{corr} (mA/cm²)	β_a mV/current decade	β_c mV/current decade	%P_I	θ
0	50	16.0	60	120	–	–
1×10⁻⁶	50	9.0	50	110	43	0.43
5×10⁻⁶	55	6.2	60	105	61	0.61
1×10⁻⁵	55	4.7	60	100	70	0.70
5×10⁻⁵	50	3.4	50	95	78	0.78
1×10⁻⁴	55	2.3	50	85	86	0.86
5×10⁻⁴	60	1.5	60	85	90	0.90
1×10⁻³	65	0.9	60	95	95	0.95

copper dissolution or hydrogen evolution reaction.

The surface coverage (θ) of the adsorbed inhibitors was calculated[13] assuming no change in the mechanism of both the anodic and the cathodic reactions using the equation

$$\theta = \left[1 - \frac{i_{inh.}}{i_{free}}\right] \tag{4}$$

Figure 2 shows the plot of $\theta = f(\log C)$ which has the characteristic S-shape. In analysis the isotherms having the S-shape in the θ-log C system of co-ordinates, Frumkin's approach was considered. Frumkin isotherm has the formula:[14]

$$BC = \left(\frac{\theta}{1 - \theta}\right) \exp(-f\theta). \tag{5}$$

$$B = \exp\left(\frac{-\Delta G_a^o}{RT}\right) \frac{1}{55.5} \tag{6}$$

where C is the concentration of the adsorbed substance in the bulk of the solution and B is the modified equilibrium
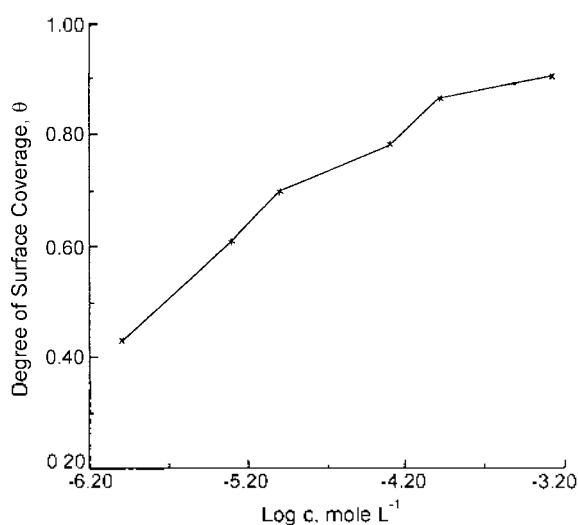
Figure 2. Effect of compound (1) concentration on the degree of surface coverage for copper in 3 N HNO₃.

constant of the adsorption process. In Eq. (5) f is a constant depending on the intermolecular interactions in the adsorption layer and on the heterogeneity of the metal surface. This parameter can either be positive or negative.

The values of B, ΔG_a^o and activation energy are shown in Table 2. The negative values of ΔG_a^o indicate the spontaneous adsorption of inhibitors on copper and also, indicate that molecular interactions are not predominant in the formation of a protective layer but the heterogeneity of the surface is the predominant in the formation of a protective layer of the inhibitor or its complexes which in turn reduce the corrosion rate of copper. One could expect that the degree of adsorption by these inhibitors on copper surface is in the order: 1 > 2 > 3 > 4 > 5 > 6. This is also in agreement with observed order of corrosion inhibition (Table 1).

The adsorption equilibrium constants (B) for the inhibitors decrease in the order: $1(2.33 \times 10^{-5}) > 2(2.23 \times 10^{-5}) > 3(1.94 \times 10^{-5}) > 4(1.70 \times 10^{-5}) > 5(1.44 \times 10^{-5}) > 6(1.27 \times 10^{-5})$ (Table 2) indicating increased adsorption with increasing the electron density on the molecules of inhibitors.

Thermometric measurements. The dissolution of copper in 3 N HNO₃ was accompanied by temperature change. This temperature change was followed in the absence and in the

Table 2. Values of thermodynamic parameters during adsorption of 2-hydroxyacetophenone-aroyl hydrazone derivatives (10^{-5} M) on copper in 3 N HNO₃ at 303 K

Inhibitor	B	$-\Delta G_a^o$ Kcal mol⁻¹	E_a^* Kcal mol⁻¹	% Inhibition
1	2.33×10^{-5}	9.90	12.89	70.0
2	2.23×10^{-5}	9.89	11.93	69.0
3	1.94×10^{-5}	9.81	11.05	66.0
4	1.70×10^{-5}	9.73	10.23	63.0
5	1.44×10^{-5}	9.63	9.48	59.0
6	1.27×10^{-5}	9.55	8.78	56.0
Free	–	–	7.33	–

Table 3. Efficiency of corrosion inhibition of 2-hydroxyacetophenon-aroyl hydrazone derivatives as determined by percentage reduction in reaction number in 3.0 N HNO₃

Concentration of the additive (M/L)	% Reduction in R.N.					
	1	2	3	4	5	6
1×10^{-6}	38.5	37.4	39.2	25.7	17.7	27.5
5×10^{-6}	44.1	44.1	43.0	38.8	28.0	35.4
1×10^{-5}	56.0	55.3	52.8	49.4	44.4	40.5
5×10^{-5}	76.6	73.3	74.1	66.4	59.9	57.5
1×10^{-4}	84.7	83.4	82.9	81.5	72.0	69.5

presence of different concentrations of the additives used.

In all cases the dissolution of copper in acid is characterized by initial slow rise in temperature followed by a sharp rise and finally decrease after attaining a maximum value. The maximum temperature (T_m) measured in the free acid is 39.8 °C and is attained after 50 min.. while the T_m in presence of the additives used are lower and are attained after a longer time. This indicates that additives behave as inhibitors for the dissolution of copper in 3 N HNO₃, presumably by their adsorption on the surface of the metal.

The present thermometric curves allow distinction between weak and strong adsorption.[15] Strong adsorption is noted for all additives used. The curves of Figure 3 represent this adsorption in the presence of compound (1).

The fact that the compounds studied bring about a decrease in RN indicates that these act as inhibitors. The results recorded in Table 3 reveal that the efficiency of corrosion inhibition as determined from the percentage reduction in RN varies with both concentration and the type of the additives used.

The inhibition efficiency of the additives decreases in the order: 1 > 2 > 3 > 4 > 5 > 6.

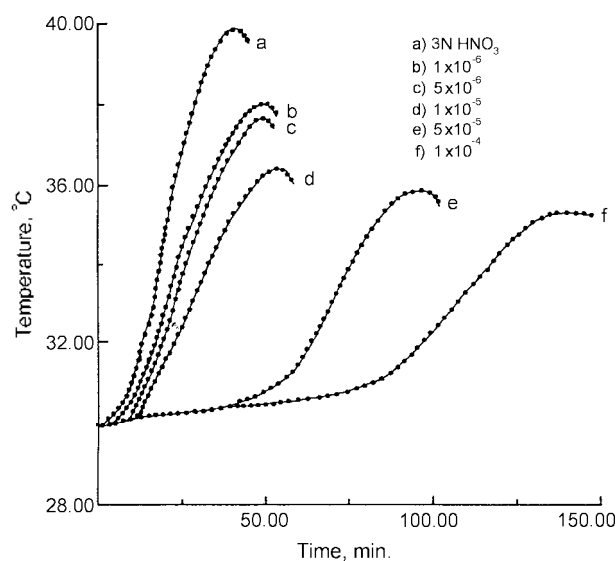**Effect of temperature.** Galvanostatic polarization of cop-

Figure 3. Temperature--time curves obtained in absence and presence of different concentrations of compound (1).
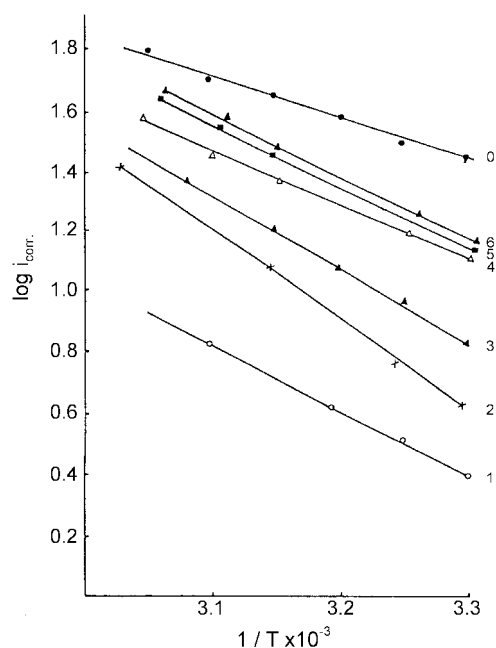
Figure 4. Log i_{corr} *vs.* $1/T$ curves for copper dissolution in the presence and absence of 5×10^{-5} M of different inhibitors.

Tafel lines to higher potential regions. 3) the variation in percentage reduction in reaction number with concentration of the inhibitors, and 4) the decrease in corrosion inhibition with increasing temperature indicate that the corrosion inhibition takes place by adsorption of the inhibitors at the electrode solution interface.[18] Inhibition efficiency was shown[19] to depend on the number of adsorption active centers in the molecule and their charge density.

Variation in structure of the inhibitors molecules (1-6) takes place through the benzoyl side chain. So. the inhibition efficiency will depend on this part of molecule.

Skeletal representation of the mode of adsorption of these compounds is shown by Figure 5.

Adsorbed molecules on the surface of the corroding metal interfere with cathodic and/or anodic reactions. Inhibition of
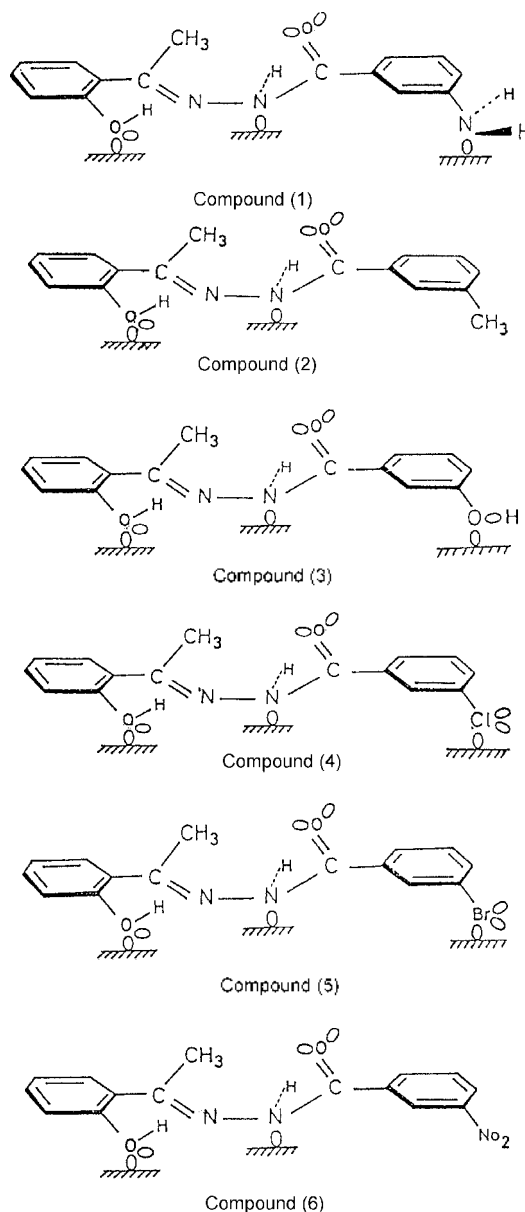
per in 3 N HNO₃ was studied in the temperature range 30-55 °C in absence and in presence of 10^{-4}-10^{-6} M of different additives. The rate of corrosion increases as the temperature increases *i.e.* the protection efficiency of the additives decreases with rise in temperature. This behaviour proves that the inhibition of copper dissolution occurs through physical adsorption of the additives on the metal surface.

Plots of log i_{corr} against $1/T$ for different additives at 5×10^{-5} M as shown in Figure 4 gave straight lines. The values of the slopes of these straight lines permit the calculation of the Arrhenius activation energy, E_a^*. [$\log i_{corr}$ = $(-E_a^*/2.303RT)$ + constant] (Table 2). The results reveal that the presence of inhibitors increase the activation energy of copper dissolution reaction. The activation energy of copper dissolution in absence of inhibitors was found to be 7.33 Kcal mol⁻¹. Fouda *et al.*[16] found that activation energy of 4.61 Kcal mol⁻¹ for copper corrosion in 3 N HNO₃. Also. Mostafa[15] found activation energy of 11.67 Kcal mol⁻¹ for corrosion of copper in 3 N HNO₃. This inconsistancy between the literature values of activation energy may be due to: (1) the nature and concentration of the electrolytes used and (2) the purity of copper electrode used in each case.

The order of decreasing inhibition efficiency of different additives for copper dissolution as gathered from the increase in activation energy is: 1 > 2 > 3 > 4 > 5 > 6.

Chemical structure and corrosion inhibition of copper. Inhibition of corrosion of copper in nitric acid by the investigated 2-hyroxyacetophenone-aroyl hydrazone derivatives as determined by galvanostatic polarization and thermometric measurements was found to depend on the concentration and nature of inhibitor. The observed corrosion data in the presence of inhibitors namely: 1) the decrease of corrosion rate with increase in concentration of the inhibitor. 2) the shift in

Figure 5. Skeletal representation of the mode of adsorption of these compounds is shown by Figure 5.

these reactions would obviously depend on the degree of surface coverage of the metal with the adsorbate. Competitive adsorption is assumed to occur on the surface of the metal between the aggressive NO_3^- ions on one hand and the inhibitor molecules on the other. The order of decreasing inhibition efficiency of the tested compounds is: $1 > 2 > 3 > 4 > 5 > 6$.

This order of decreased inhibition efficiency of the additives can be accounted for in terms of the polar effect[20] of the *m*-substituents on the benzoyl ring. Compound (1) is the most efficient inhibitor because of the presence of highly electron releasing *m*-NH_2 ($\sigma = -0.16$) which enhances the delocalized π-electrons on the active centers of the compound. where σ is the substituent constnat[21] and is a relative measure of the electron density at the reaction center. Moreover. the nitrogen of NH_2 can act as active center and increases the active centers into three. Compound (2) ($\sigma_{m\text{-}CH_3}= -0.07$) comes next in the sequence of decreased inhibition efficiency. This because *m*-CH_3 is lower in electron charge density than *m*-NH_2 and also this compound has two active centers only. Compound (3) ($\sigma_{m\text{-}OH}=-0.002$) follows suit despite the presence of the same number of adsorption centers as compound but OH is less basic than NH_2 and CH_3. respectively. Compounds (4) (*m*-Cl, $\sigma =0.37$). (5) (*m*-Br. $\sigma =0.39$) and (6) (*m*-NO_2, $\sigma =0.71$). occupy the rear and they decreased corrosion inhibition efficiency of copper parallels an increasing order of electron withdrawing (electrophilic) character. The *m*-NO_2 group with the highest electrophilic character imparts the lowest inhibition efficiency to inhibitor (6) which comes last among the additives used. Possible hydrogenation[19] of the NO_2 group in acid medium on the copper surface would also enhance decreased efficiency of inhibitor (6) as the released heat of hydrogenation would aid the desorption of the molecule.

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