4-Amino-4'-nitroazobenzene Derivates as Corrosion Inhibitors for Copper in HNO₃ solution

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Summary

The effect of some 4-amino-4'-nitroazobenzene derivatives as corrosion inhibitors for copper in nitric acid solution at 30 °C was investigated using thermometric and polarization techniques. The corrosion rate was found to be a function of the nature, of inhibitor and temperature of the medium. The calculated degree of concentration surface coverage was used to evaluate the free energy of adsorption (ΔG^o_a) of the process. All the inhibitors follow the Frunkin adsorption isotherm.

The mechanism of inhibitor action has been discussed on the basis of adsorption and molecular polarizability of the inhibitors. The observed experimental data indicate that these compounds act as mixed inhibitors. Some thermodynamic function were calculated and discussed.

Key words: Corrosion, inhibitors, acid solution, copper, dyes.

Introduction

Copper is widely used in various industrial operations and the study of corrosion of copper and its inhibition is a subject of practical significance.

The use of nitrogen-containing compounds as corrosion inhibitors is widespread for many metals and alloys. Several mechanisms have been proposed, due to the complexity of the process of the inhibition by the use of inhibitors, to explain the function of corrosion inhibitors of which the adsorption theory is the most pertinent [1]. The reaction of corrosion inhibitors at the metal-solution interface has been evaluated by adsorption characteristics and also by the

thermodynamics of adsorption [2-4]. Many compounds are known to retard the corrosion of copper in nitric acid [5-8].

The corrosion attack of HNO_3 on copper is mainly due to the HNO_2 formed during the reaction. It follows that a substance which would prevent the autocatalytic cycle of formation of HNO_2 would retard the corrosion of copper and brass in HNO_3 [9].

Aromatic amines react with HNO_2 to form diazo compounds according to the reaction:

$$R-NH_2 + OH-NO + HX \rightarrow R-N=N-X + 2H_2O$$
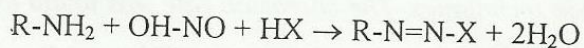
Where R=aryl group , X=CI , Br , I , SO_4 or NO_3

The present study was undertaken to investigate the inhibition of these 4-amino -4'-nitroazobenzene derivatives which when condensed with 2-methyl quinazol-4-one in presence of acetic acid or fused sodium acetate solution gives dyes that have good affinity for synthetic fibers, showing good levelness and depth of shade.

Experimental

Chemicals used were of AR grade (BDH). The solutions were prepared using double distilled water. Copper (Prolabo 99.9% grade) in the form of wire with an area of $0.13 \ cm^2$ was used for the corrosion rate determination.

Polarization was carried out in three compartment cell with a fine Luggin capillary to avoid ohmic polarization. A galvanostatic condition was maintained using an Amel galvanostat-potentiostat (Model 549). A silver-silver chloride and platinum electrode were used as reference and auxiliary electrodes, respectively. Experiments were carried out in 2M HNO_3 without and with various concentrations of inhibitors, at $30 \pm 1 \ °C$. Copper test pieces measuring $0.1 \times 10 \times 50mm$ were used for thermometric measurements. The copper surface was mechanically polished with 2/0 emery papers, degreased, washed and dried

between filter papers. The percentage inhibition efficiency was calculated from the following equations:

$$\% \ I_e = [1 - (i_{inh.}/i_o)] \times 100 \qquad (1)$$

$$\text{and} \ \% \ I_e = [1 - (RN_{inh.}/RN_o)] \times 100 \qquad (2)$$

Where RN is defined as :

$$RN = \frac{(T_{max.} - T_i)}{t} \quad °C \ min^{-1} \qquad (3)$$

Where i_o and $i_{inh.}$ are the corrosion current densities in the absence and presence of additives. RN_o and $RN_{inh.}$ are the reduction in reaction number in the absence and presence of additives, and $T_{max.}$ and T_i are the maximum and initial temperatures, respectively, and t is the time (in minutes) required to reach the maximum temperature.

The additives used as inhibitors (4-amino-4'-nitroazobenzene derivatives) were prepared and crystallized several times according to Fadda et al. [10]. The structures of the inhibitors are listed below :
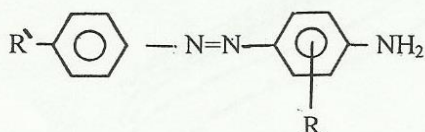
Where   R = H   R′ = H   (I)
          = 2-OCH$_3$ = 4-NO$_2$ (IV)
          = 2-Cl   = 4-NO$_2$ (V)
          = 3-OCH$_3$ = 4-NO$_2$ (II)
          = 3-CH$_3$ = 4-NO$_2$ (III)

Results and Discussion

Fig.1 shows the galvanostatic polarization of copper in 2 M HNO$_3$ solution in the presence and in the absence of various concentrations of compound II. As can be seen, both the cathodic and the anodic reactions are inhibited and the inhibition increases as the inhibitor concentration increases. Similar results were

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obtained for other compounds. Also from the curves of polarization, one can conclude that for the same inhibitor concentration the lowering of potential to less negative value with substituted group increases in the following order: $CH_3 >$ $OCH_3 >$ Cl. Tafel lines of nearly equal slopes were obtained as can be seen from Table 1. This indicates that the adsorbed molecules of compound II have no effect on the mechanism of either copper dissolution or hydrogen evolution reaction.
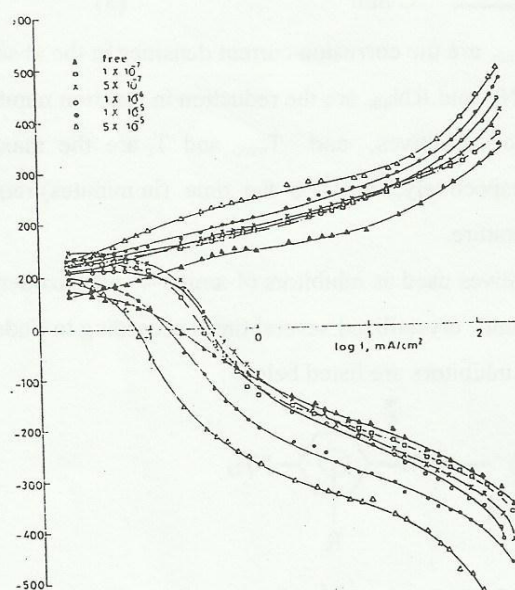

Fig 1 Galvanostatic polarization of copper in 2 M HNO₃ alone and containing different concentrations of compound (II)

The results of Table 1, show also that, E_{corr} shifts to more negative values in case of cathodic polarization and to more positive values in case of anodic polarization. The magnitude of such shifts increased with increase of the inhibitor concentrations.

Table 1. *The effect of various concentration of compound II on anodic and cathodic Tafel slops, inhibitor efficiency and corrosion current density for copper in 2M HNO$_3$ at 303 K*

Conc. of inh., M	$-E_{corr}$ mV	I_{corr} $\mu A C m^{-2}$	B_a mVdecade^{-1}	B_c mVdecd^{-1}	% I_e
0.00	90	25	65	96	---
1x10^{-7}	90	14.3	80	80	43.2
5x10^{-7}	80	12.3	80	85	50.8
1x10^{-6}	100	10.5	65	95	58.0
1x10^{-5}	90	9.5	75	90	61.6
5x10^{-5}	120	8.0	65	90	68.0

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

$$\theta = [1 - (i_{inh.} / i_o)] \qquad (4)$$

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

$$Bc = (\theta/1-\theta)exp (-f\theta) \qquad (5)$$
$$B = exp (\Delta G^{\circ} ads. / RT) \; 1/55.5 \qquad (6)$$

Where c is the concentration of the adsorbed substance in the bulk of the solution and B is the modified equilibrium constant of the adsorption process.
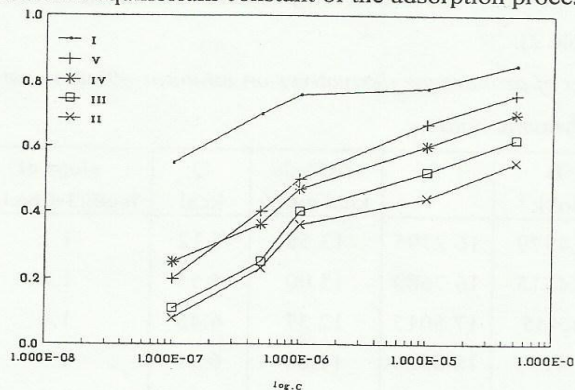

Fig.2 The dependence of the degree of coverage of copper surface in 2 M HNO$_3$ 30°C on the concentration of adsorbing substance.

In equation (5) f is a constant depending on 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 and f were calculated (Table 2) by choosing values of θ in the range (0.4 - 0.9) and corresponding values of c and then solving the two simultaneous equations. The values of f indicate [11] that molecular interactions are not predominant in the adsorption layer (due to the very small values). This may be attributed to the influence of the heterogeneity of the copper surface.

The values of free energy of adsorption for each concentration of inhibitors are calculated from the equation :

$$\Delta G^{\circ}a/2.303RT = \log c - \log \frac{\theta}{(1-\theta)} - 1.74 \qquad (7)$$

The negative values of $\Delta G^{\circ}a$ 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: I > V > IV > II > III. This is also in agreement with observed order of corrosion inhibition (Table 2).

Table 2. *Effect of azobenzene derivatives on inhibitor efficiency at 1×10^{-5} and some thermodynamic data.*

Inhibitor	B mol k^{-1}	f	-ΔG°ads kcal mol^{-1}	Q kcal	slope of logθ/(1-θ)vs 1/T	% I$_e$
I	1.4979	16.2795	13.59	5.12	1.1	75.0
V	1.4715	16.7680	13.00	5.53	1.2	72.0
IV	1.445	17.5015	12.37	6.45	1.4	67.6
II	1.4153	18.8020	11.68	6.91	1.5	61.6
III	1.3974	20.1092	11.26	7.37	1.6	57.2

Nature of adsorption

The effect of temperature on the corrosion rate (R_{corr}) of copper in free and inhibited acids was studied. The corrosion rate increased with increasing temperature in free and inhibited acids and hence, the values of % I_e decreased with increasing temperature. These results are characterizing for the physical adsorption. Also, the above results can be proved from the magnitude of the heat of adsorption Q. The latter was estimated by the relation:

$$- Q/2.303R = [\, d \log (\theta/1-\theta) \, /d \, (1/T) \,] \qquad (8)$$

which has been found to be 5-7 kcal mole^{-1}. deg^{-1}. These values of Q lie in the range which characterizing physical adsorption. So, the adsorption of the additives on the surface of copper is likely to be of a physical nature. From the results of Table 2 it may be generalized that the more efficient inhibitor the less value of Q it has and vice versa, i.e. the order of increasing inhibition efficiency is: I > V > IV > II > III.

The energies of activation, E_a , for the corrosion process in free and inhibited acid evaluated from the slops of log corrosion rate againest 1/T (Arrhenius plots are given in Fig3.) were found to equal to 33.6 kJ mol^{-1}. (8 k cal mol^{-1}). Fouda et al [12] found that activation energy of 19.36 k J mol^{-1} (4.61kcal mol^{-1}) for copper in 3 M HNO$_3$ solution. Also, Mostafa [13] found that activation energy for copper in 3 M HNO$_3$ solution was 49 kJ mol^{-1}. (11.67 kcal mol^{-1}). Generally, one can say that the nature and concentration of the electrolyte greatly affect the activation energy for the corrosion process. For 1×10^{-5} and 1×10^{-6} M compound II solutions, the calculated values of the apparent activation energies are 9.72 and 9.15 kcal mol^{-1}, respectively, these differences are not considered to be significant. Therefore, the presence of compound II does not affect the activation energy of the corrosion process. These results indicate also that compound II does not change the mechanism of the rate-determining step of the corrosion, although it significantly reduces its rate.
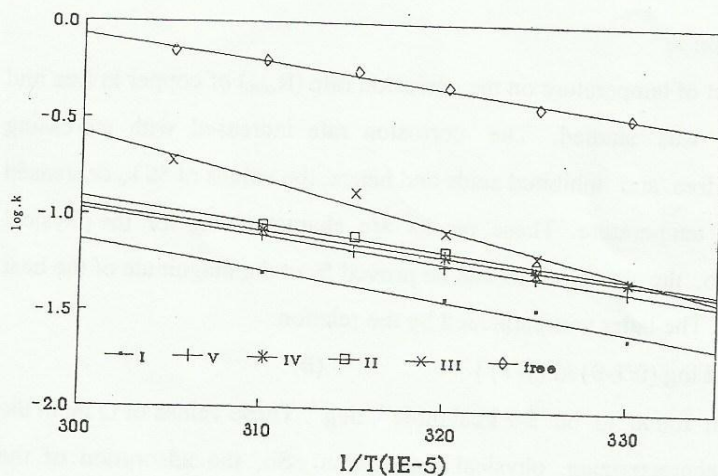
Fig.3 Log k vs. 1/T curves for copper in 2 M HNO₃ in absence and presence of 1×10⁻⁵M of additives used.

From Fig.3, the calculated value of the apparent activation energy is ranging from 8-10.5 kcal mol⁻¹. These values are also of the order of the activation energies encountered for the hydrogen evolution reaction.

Thermometric measurements

In this method the temperature change of the system involving copper in 5 M HNO₃ was followed in the absence of and in the presence of different concentrations of inhibitors used. Fig.4 shows the effect of compound II concentration on thermometric curves for copper in 5 M HNO₃. The maximum temperature measured in acid solution is 32 °C and is attained after 32 min. This corresponds to an RN of 0.2813 °C min⁻¹. On increasing the concentration of the inhibitors the time required to reach T$_{max}$ increases. This indicates that the additives retard the dissolution of copper in HNO₃, presumably by adsorption onto the surface of the metal. The extent of retardation for inhibition depends on the degree of coverage of the metal with the adsorbate, and the temperature-time curves provide a means of differentiating between weak and storage adsorption [25]. Strong adsorption is noted since a simultaneous increase in t and a diminution in T$_{max}$ takes place, and both factors cause a large decrease in the RN of the system. The results recorded in Table 3 reveal that the efficiency of inhibition of corrosion increases with the concentration of the inhibitors.
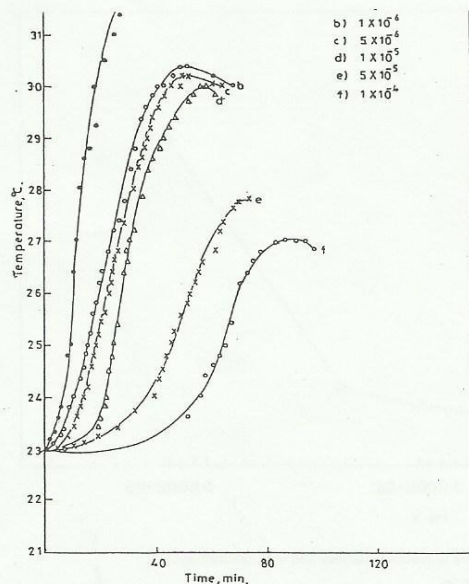
Fig.4 Temperature-time curves obtained in the absence and presence of varying concentrations of compound (I I).

Table3. *Effect of compound II concentration on the parameters of the thermometric curves for copper in 5 M HNO_3 solution.*

Compound II conc., M	T_i °C	T_{max} °C	t min	RN °C min^{-1}	% I_e
0.00	23.0	32.0	32	0.2813	---
1×10^{-6}	23.0	31.4	40	0.2000	28.90
5×10^{-6}	23.0	29.6	53	0.1886	33.00
1×10^{-5}	23.0	29.4	40	0.1600	43.15
5×10^{-5}	23.0	29.0	55	0.1091	61.26
1×10^{-4}	23.0	28.8	85	0.0800	71.60

Fig.5 relates to the reduction in the reaction number (RN), with log concentration of compound II for copper in HNO_3. One inflection point was observed, indicating perhaps that compound II forms a monolayer on the surface of copper, in accordance with Frumkin's isotherm [26].
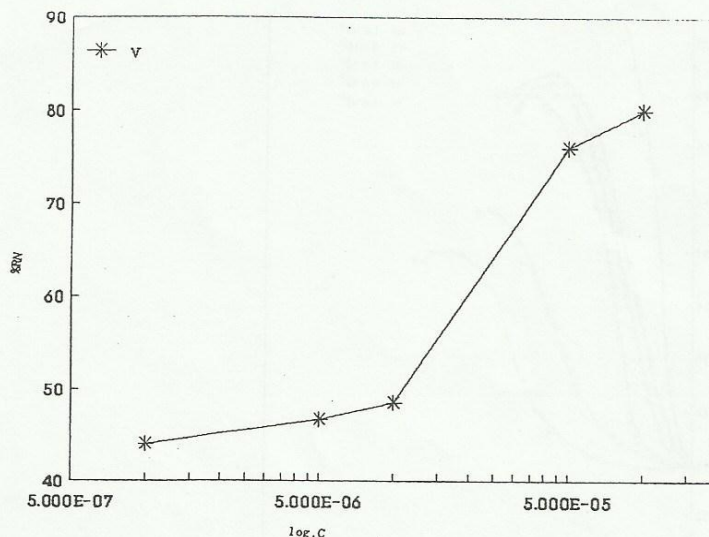
Fig.5 Relation between the % reduction in reaction number and log concentration
of compound (I I) for copper in 5 M HNO₃.

The percentage reduction in RN decreases in the order:

I > V > IV > II > III.

It should be noted that the two different techniques demonstrated the agreement and conformity of the experimental results as to the type of inhibition of the corrosion of copper in HNO_3. Nevertheless, they showed small difference in absolute values for the inhibition efficiency. However, this observed discrepancy could be attributed to the different experimental conditions under which each technique was carried out.

Mechanism of inhibition

It is known that the corrosion of copper in HNO_3 is autocatalytic, involving HNO_2 as the intermediate product [9,15,16]. The stability of HNO_2 in the solution depends on the concentration of HNO_3. In dilute HNO_3 (< 1.0 M) HNO_2 may decompose into nitric oxide [17], which evolves at the electrode surface, in concentrated HNO_3 (> 1.0 M), which in our case, HNO_2 becomes stable and is effective during the corrosion process.

HNO_2 increases the rate of dissolution of Cu in HNO_3 by a process involving NO_2 as an intermediate product [15.18], and it has been reported

before [19] that substances capable of interaction with HNO_2 formed in this way could inhibit the rate of dissolution of Cu in the acid. This assumption has been used to explain the inhibiting effect of aromatic amines and amino acids in inhibiting the dissolution of brass [20], and that of substituted phenols [8] on the dissolution of Cu in the acid medium. The mechanism assumed is that of breaking the autocatalytic cycle by destruction of HNO_2. In this case, there is a significant possibility of a chemical reaction occurring between the 4-amino-4'-nitroazobenzene derivatives and HNO_2 at 30 °C, which causes the destruction of the acid, and leads to the retardation of Cu dissolution. The dual effect (removal of HNO_2 and formation of diazonium compounds) of 4-amino-4'-nitroazobenzene derivatives causes, at a certain concentration, the complete inhibition of the reaction of Cu and HNO_3.

It has been reported that substituents increase the velocity of the diazotization in the following order:

p-OCH_3 > p-CH_3 > o-OCH_3 > o-CH_3 > m-OCH_3 > m-CH_3 > -H > m-Cl > o-Cl.

This order depends on both the resonance R and the inductive effect (I) of the group attached to the aniline ring also on their position (o^-, m^-, p^-). This chemical transformation occurs in the electrolyte or on the electrode surface, and they are the secondary products (the corresponding diazonium compounds) rather than the primary substances which have actual inhibiting effect.

The foregoing results indicate that the inhibition efficiency is influenced to some extent by the electronic character of the substituent in the aniline and nitrophenyl rings. Compound I has the comparatively-better efficiency with respect to the other tested compounds. This is due to the absence of: a)the NO_2-group which is the electron-withdrawing group and b)steric crowding , i.e. absence of o-substituent with respect to aniline or nitrophenyl rings. Compound V comes after compound I in inhibition efficiency. This may be due to the presence of an electron withdrawing group in the p-position in the nitrophenyl ring and also

the presence of Cl atom in the o-position with respect to -N=N- group. The presence of Cl atom adds a new active centre but on the other hand the substitution in the o-position exercises some steric crowing and this influences its effect on the inhibition efficiency [21.22]. So, the chloro derivatives have dual effect [23,24]. Compound IV like compound V but the OCH_3- group in the o-position with respect to -N=N- group is a bulky group compared to the CI- atom, so the steric crowding is more in compound IV than in compound V. This leads to the lowering of the inhibition efficiency of compound IV than of compound V.

As known the NH_2 group is o- and p- directing group, so in compound II and III the substituent in the o-position with respect to NH_2 group has a great effect on the NH_2- reaction center , i.e. increase the diazotization reaction. But on the other hand both OCH_3- and CH_3-groups exercise some steric crowding and this influences its effect on inhibition efficiency [21.22]. In compound II the OCH_3-group adds a new active center, but still bulky group compared to the CH_3-group, so compound II comes before compound III in the order of inhibition efficiency.

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