Polarization of Copper in 4.0M HNO₃ Solutions Containing Organic Inhibitors

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ABSTRACT

The electrochemical behavior of copper in 4.0M HNO₃ solutions without and with different concentrations from two organic compounds were studied using both galvanostatic polarization and cyclic voltammetric techniques. These two organic compounds (namely: bis [4-amino-5-hydroxy-1,2,4-triazol-3-yl] methane "compound D_1" and bis [4-amino-5-hydroxy-1,2,4-triazol-3-yl] butane "compound D_2") acted as mixed inhibitor type with predominate cathodic effectiveness. Their high inhibition efficiency (>99%) may be due to adsorption of the additive itself and its further interference with the two partial processes. The results obtained from galvanostatic polarization technique are in consistent with that obtained from cyclic voltammetric measurements.

Key words: Electrochemical behavior, copper, nitric acid, organic inhibitors

INTRODUCTION

The kinetics of copper corrosion in nitric acid solutions have been studied in the past [1 - 4]. It is generally agreed that autocatalytic mechanism would account for the copper corrosion in concentrated HNO₃ solutions. The rate of production of HNO₂ and its retention in solution determine the overall rate of metal dissolution. Different classes of organic compounds were suggested to inhibit copper corrosion in HNO₃ solutions [5 - 18]. The inhibition observed following the addition of some amino compounds has been attributed to their destruction of HNO₂ which would retard the autocatalytic propagation [12 - 18]. However, most investigations on copper corrosion in concentrated nitric acid solutions without and with inhibitor did not give clear understanding about the characteristics of the corrosion reaction as a whole.

In a previous paper by the author [19], it was shown (using weight loss method) that bis [4-amino-5-hydroxy-1, 2, 4-triazol-3-yl] methane " compound D_1 "

and bis [4-amino-5-hydroxy-1, 2, 4-triazol-3-yl] butane " compound D_2 " are effective inhibitors for copper corrosion in 4.0M HNO₃ solutions. In the present study the electrochemical behavior of copper in 4.0M HNO₃ solutions without and with different concentrations of compounds D_1 and D_2 were investigated using both the galvanostatic polarization and cyclic voltammetic techniques. The inhibition mechanism of these inhibitors is discussed on the basis of the polarization data.

EXPERIMENTAL DETAILS

Bis [4-amino-5-hydroxy-1, 2, 4-triazol-3-yl] methane " compound D_1 " and bis [4-amino-5-hydroxy-1, 2, 4-triazole-3-yl] butane " compound D_2 " were used as inhibitors. These two organic compounds " D_1 and D_2 " were prepared according to the methods described elsewhere [20 - 23]. Their structures were characterized on the basis of the infrared spectral and chemical analysis data as following:

" Compound D_1 "   " Compound D_2 "
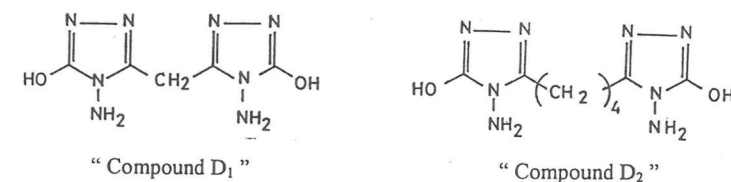
Copper electrodes were cut from a rod of spec pure copper (99.998%, Aldrich Chemicals) and embedded in Araldite adhesive with an exposed surface area of 0.25 cm². The electrodes were mechanically abraded to different grades of emery papers, degreased with acetone, washed with running doubly distilled water and finally dried with filter paper before use. All solutions were prepared from doubly distilled water. The nitric acid used was of analar grade chemical (Merck).

Galvanostatic cathodic and anodic polarization curves were measured by a model 363 potentiostat / galvanostat (EG&G Prinecton Applied Research – USA), using a three – compartment glass cell equipped with a Pt wire counter electrode (separated from the cell solution by a sintered glass frit) and a saturated calomel electrode (inside a luggin's capillary probe) as reference. The surface of the working copper electrode was always kept in close touch with the luggin capillary tip to minimize the IR drop through the cell. Galvanostatic polarization measurements were performed by the direct technique at regular intervals. The duration of potential

stabilization at each current density value was between (3 – 5) minutes. Cyclic voltammetry was performed for copper electrode in 4.0M HNO₃ solutions without and with three different selected concentrations from the two inhibitors under study (compounds D_1 and D_2) at 25°C and at a scan rate of 25mv/sec. In these experiments, polarization measurements were carried out from an initial very negative potential (-1.0V, SCE) relative to the steady-state open-circuit potential in the forward (anodic) direction up to a very high positive potential (+1.5V) and was then reversed back in the cathodic direction to the same initial negative potential. The potential of the working electrode was controlled using a wenking potentioscan (type pos.73) and the current density - potential curves were recorded on X-Y recorder (type pL 3).

The percentage of inhibitor efficiency (%I.E) was calculated from the galvanostatic polarization measurements using the following equation:

$$\%I.E = [1 - (I_{inh} / I_{corr})] \times 100$$

where I_{inh} and I_{corr} are the current densities with and without inhibitor respectively. The corrosion current densities were determined by extrapolating the cathodic Tafel line to the free corrosion potential (E_{corr}).

RESULTS AND DISCUSSION

I – Galvanostatic Measurements

a – General Features

The results of the cathodic and anodic polarization measurements on copper electrodes in 4.0M HNO₃ solution at 25 °C in absence and presence of the two organic compounds (D_1 and D_2) are shown in Figures 1 and 2, respectively. It is quite clear, that the two sets of curves in the two figures are very similar and that both compounds D_1 and D_2 have strong inhibiting effects on both the cathodic and anodic processes. As the inhibitor – concentration increases, both the corrosion potential as well as the cathodic polarization curves are shifted toward more negative potentials relative to the blank solution. In the mean time, corrosion current density decreases. This behavior suggests that although the two inhibitors are of the mixed type, they be predominantly of cathodic effectiveness.

The cathodic polarization curves are less complicated than the anodic polarization curves. It is quite clear, that all the cathodic curves are of the
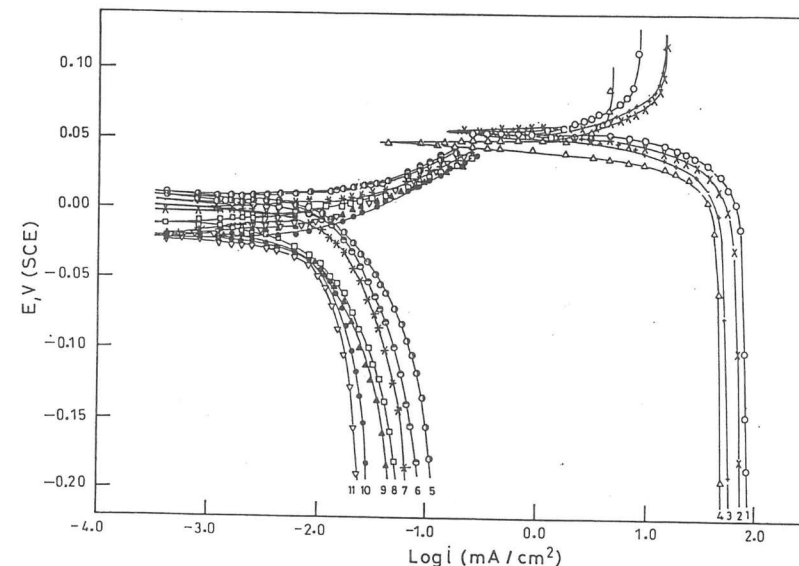

Fig.1. Polarization curves of copper in 4.0M HNO₃ for increasing compound D_1. (1) 0.0M, (2) 2.5×10^{-4}M, (3) 3.5×10^{-4}M, (4) 4.5×10^{-4}M, (5) 5.0×10^{-4}M, (6) 7.5×10^{-4}M, (7) 1.0×10^{-3}M, (8) 2.5×10^{-3}M, (9) 5.0×10^{-3}M, (10) 7.5×10^{-3}M, (11) 1.0×10^{-2}M.
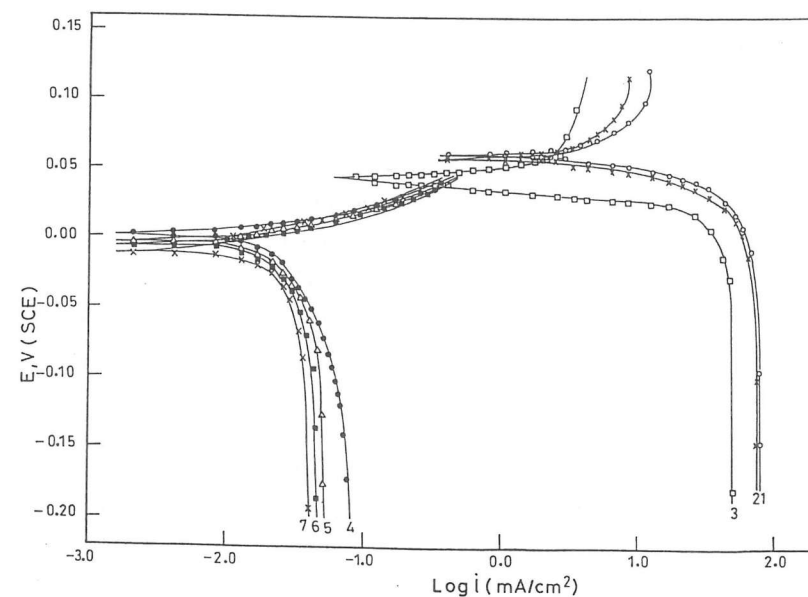
Fig.2. Polarization curves of copper in 4.0M HNO₃ for compound D_2. (1) 0.0M, (2) 1.0×10^{-3}M, (3) 1.5×10^{-3}M, (4) 2.5×10^{-3}M, (5) 5.0×10^{-3}M, (6) 7.5×10^{-3}M, (7) 1.0×10^{-2}M.

concentration - polarization type with its characteristic diffusion – controlled limiting current density (I_L). The percentage of the inhibition efficiency (% I.E) which were computed from these curves are given in Tables 1 and 2.

On the other hand, the anodic polarization curves are more complicated than the cathodic ones. Detailed consideration of the anodic behavior will be given latter but would be only briefly mentioned here. Depending upon the inhibitor concentration, the anodic curves are of different types (see Figures 1&2 and Tables 1&2). Thus, at low inhibitor – concentration, including the blank solution, the anodic polarization curves are characterized by a sudden rise in potential at a certain critical (limiting) current density (I_{cc}). Since no oxygen evolution and / or no surface layer formation were observed, the sudden rise in potential could be attributed to the anolyte which could form an obstructive film at the interface that can retard metal dissolution and cause a type of ohmic overpotential to the movement of copper ions into the solution. On the other hand, at high inhibitor - concentration, the anodic curves are of the activation polarization type with their characteristic Tafel slopes (b). The basic electrochemical parameters, which were computed from the polarization curves, are summarized in Tables 1 and 2 for the two inhibitors D_1 and D_2 respectively.

Table 1. E_{corr}, I_{cc}, anodic Tafel slope (b), I_L and %I.E of copper in 4.0M HNO_3 solutions without and with compound D_1, at 25°C.

Medium type	Inh. conc. (M)	E_{corr} SCE. (mV)	Anodic polarization		Cathodic polarization	
			I_{cc} (mA / cm²)	b (- mV)	I_L (mA / cm²)	%LE
Blank	0.0	+ 59	12.59	-	79.43	-
Low inhibitor	2.5×10^{-2}	+ 58	10.59	-	67.61	15.0
Concentration	3.5×10^{-4}	+ 55	7.08	-	58.88	26.0
	4.5×10^{-4}	+ 48	3.75	-	47.32	41.0
Medium and	5.0×10^{-4}	+ 10	-	38.0	0.09	99.9
High inhibitor	7.5×10^{-4}	+ 5	-	40.0	0.08	99.9
Concentration	1.0×10^{-3}	0	-	38.5	0.07	99.9
	2.5×10^{-3}	- 12	-	41.8	0.05	99.9
	5.0×10^{-3}	- 20	-	42.0	0.04	99.9
	7.5×10^{-3}	- 23	-	42.0	0.03	99.9
	1.0×10^{-2}	- 27	-	42.2	0.02	99.9

Table 2. E_{corr}, I_{cc}, anodic Tafel slope (b), I_L, and %I.E of copper in 4.0M HNO_3 solutions without and with compound D_2, at 25 °C.

Medium type	Inh. conc. (M)	E_{corr} SCE. (mV)	Anodic polarization		Cathodic polarization	
			I_{cc} (mA / cm²)	b (- mV)	I_L (mA / cm²)	%LE
Blank	0.0	+ 59	12.59	-	79.43	-
Low inhibitor	1.0×10^{-3}	+ 58	7.94	-	69.18	13.0
concentration	1.5×10^{-3}	+ 46	3.63	-	47.86	39.0
Medium and	2.5×10^{-3}	0	-	38.3	0.08	99.9
high inhibitor	5.0×10^{-3}	- 3	-	38.7	0.05	99.9
concentration	7.5×10^{-3}	- 5	-	39.0	0.04	99.9
	1.0×10^{-2}	- 7	-	39.7	0.03	99.9

The effects of the inhibitor – concentration on both (E_{corr}) and (I_L) for the two inhibitors are shown in Figures 3 and 4 respectively. It is of interest to remark that the curves in Figures 3 and 4 are characterized by two linear – portions separated by sudden change in both E_{corr} and I_L for both inhibitors. The critical inhibitor concentration, at which the sudden change in the values of E_{corr} and I_L took place, was found to be 4.8×10^{-4}M and 1.8×10^{-3}M for the two compounds D_1 and D_2 respectively. This is in consistent with the above mention fact that there is a significant difference in the behavior of the anodic polarization curves at low and at both medium and high inhibitor concentration (see Figures 3 and 4).

The parallelism between the effects of the two inhibitors on the corrosion behavior of copper in 4.0M HNO_3 solutions is quite clear from Figures 1 and 2 as well as from data in Tables 1 and 2. For this reason, a detailed discussion is given for compound D_1 (i.e. Figure 1 and Table 1) while predications and correlations for the case of compound D_2 (i.e. figure 2 and table 2) could be achieved by similarity. In order to have an insight on the corrosion mechanism of copper and to elucidate the inhibition effect, details discussion is needed. Apart from the blank curve, the polarization curves (see Figures 1 and 2) can be separated into two distinct classes namely: the low inhibitor concentration region and the medium and high inhibitor concentration region.

b – Blank Curve (Figure 1 – Curve 1)

Starting from the free corrosion potential (i.e. E = + 59 mV) the cathodic polarization curve is of concentration polarization type with its characteristic limiting current density (i.e. I_L = 79.43 mA/cm²). This suggests that a diffusion process control the corrosion rate of the system. In aerated solutions, oxygen reduction would be the most common cathodic processes. However, the reduction of nitric acid is thermodynamically and kinetically cathodic reaction more feasible than oxygen – reduction [1]. Moreover, it has been generally accepted that the most probable basic cathodic reaction in nitric acid solution is the autocatalytic reduction of nitric acid involving the production of HNO_2 and its retention in solution [1, 10, 15] as follow:

$$3 H^+ + NO_3^- + 2 e \rightarrow HNO_2 + H_2O$$

The anodic polarization curve is characterized by a sudden rise in potential to a high positive value at a certain critical current density (i.e. I_{cc} = 12.59 mA/cm²). Since no oxygen evolution was observed and no possible oxide layer could be formed, this sudden increase in current density could be most probably attributed to the mass transport effects of surface layer at the interface, which could be either easy to dissolve or loosely adhering to the surface of the electrode. It is thus a limiting anolyte phenomenon. It is worth remarking that such a potential – jump region could not be easily investigated under the present galvanostatic conditions. To make measurements
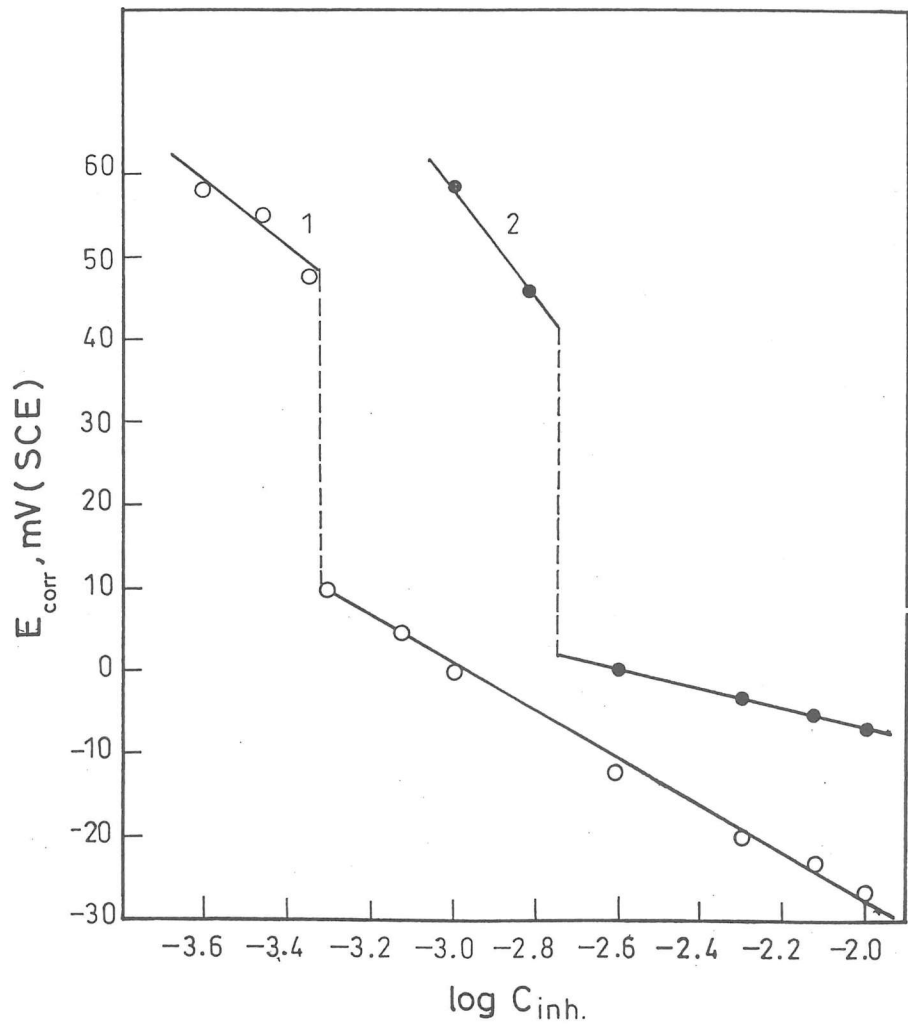
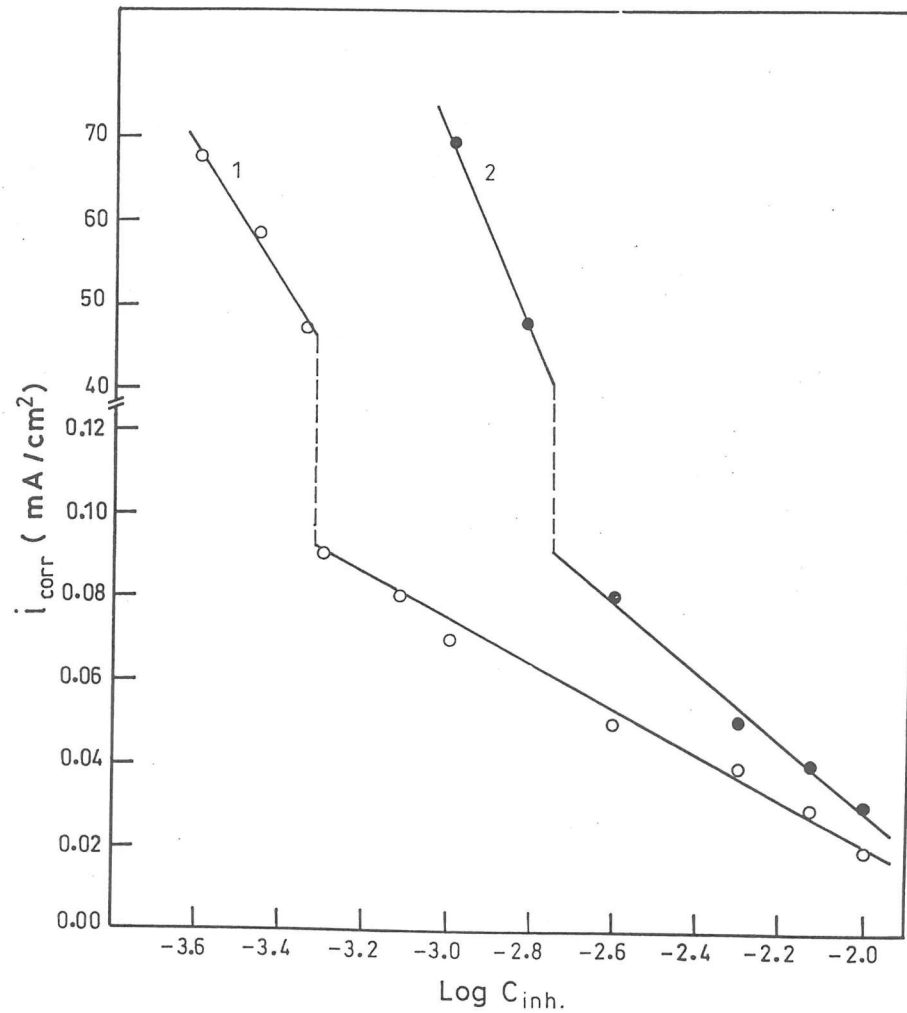Fig.3. Corrosion potential of copper in 4.0M HNO_3 vs concentrations of (1) compound D_1 and (2) compound D_2.

Fig.4. Corrosion current density of copper in 4.0M HNO_3 vs concentrations of (1) compound D_1 and (2) compound D_2.

within this region, it would be to control potential rather than to control current.

c – Low – Concentration Inhibitor Region

Compound D_1 ($\leq 4.5 \times 10^{-4}M$), Compound D_2 ($\leq 1.5 \times 10^{-3}M$)

Table 1 shows the effect of inhibitor low – concentration on the main corrosion parameters relative to the blank. Low – inhibitor concentration ($\leq 4.5 \times 10^{-4}M$), has a moderate inhibition effect.

The inhibition efficiency of the applied inhibitor could be explained as follows: as the inhibitor molecules approach the electrode surface, the high electric field of the double layer increases their polarization and thus enhancing the adsorption of the inhibitor molecules. The two inhibitors D_1 and D_2 attain an optimum inhibition of 41% at concentration of $4.5 \times 10^{-4}M$ and 39% at concentration of $1.5 \times 10^{-3}M$, for compounds D_1 and D_2, respectively (see Tables 1 and 2).

d – Medium and High – Concentration Inhibitor Region

Compound D_1 (5.0×10^{-4}-$1.0 \times 10^{-2}M$), Compound D_2 (2.5×10^{-3}-$1.0 \times 10^{-2}M$)

This set of polarization curves within the high concentration region are quite similar and close to each others but they are significantly separated from the corresponding set at low inhibitor concentration region. It shows (i.e. Figure 1, curves 5 – 11) the effect of medium and high inhibitor concentrations on the corrosion behavior of copper in 4.0M HNO$_3$ solutions at 25 °C. Polarization curves display an inhibition effect which is much higher than that at low inhibitor concentration. Table1 shows that within this region of concentration, increasing the inhibitor concentration gives rise to the following effects relative to the blank:

(i) a significance decrease in I_L.

(ii) a large shift in E_{corr} in the negative direction.

(iii) constant values of the inhibitor efficiency (%I.E) greater than 99%.

This reveals that medium and high inhibitor concentrations have a stronger effect on both the cathodic and anodic processes in comparison with low inhibitor concentrations.

II – Cyclic Voltammetric Measurements

Cyclic voltammetry was carried out to complement the galvanostatic studies and to throw more light and to give an insight on the cathodic and anodic partial reactions.

a- General Features

The cyclic voltammograms obtained for copper in 4.0M HNO$_3$ solutions without and with some selected inhibitor concentrations (low, medium and high inhibitor concentrations) from compounds D_1 and D_2 are given in figures 5 and 6 respectively. Voltammograms have the same general outlook namely two linear sections separated by a short current arrest at potential near the basic line.
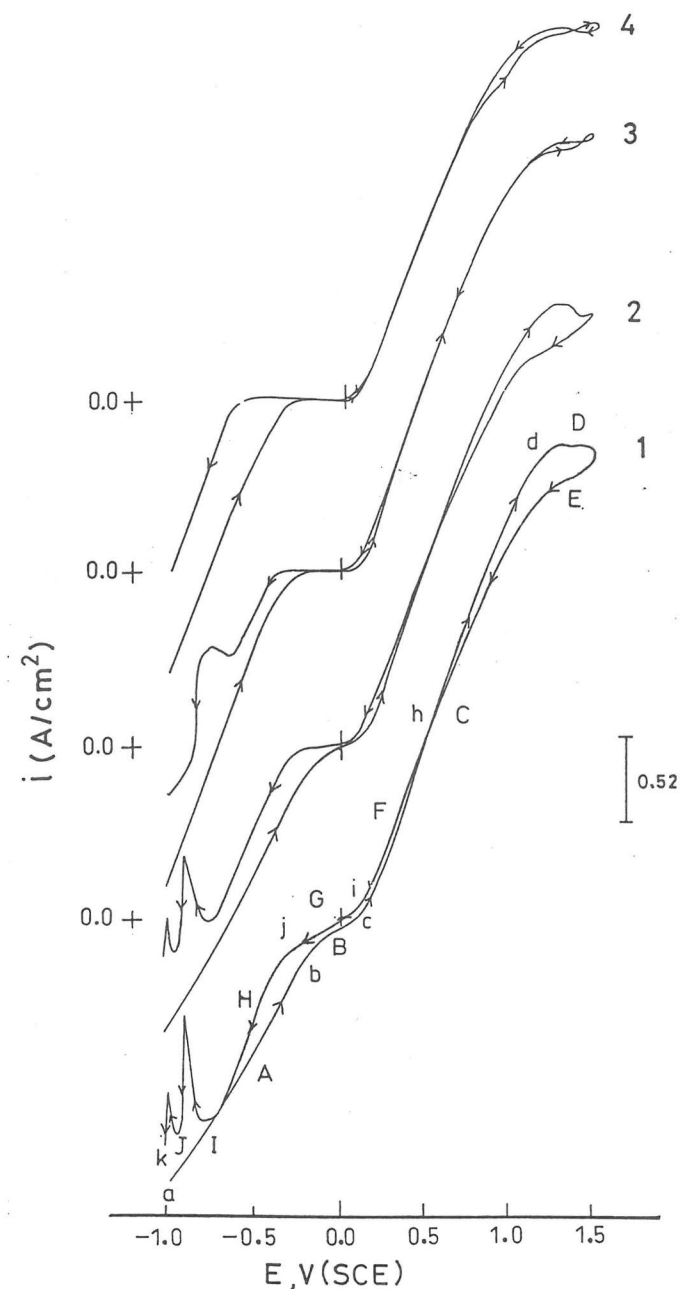
Fig.5. Cyclic voltammograms of copper in 4.0M HNO$_3$ for compound D_1 (1) 0.0M, (2) 4.5×10^{-4}M, (3) 5.0×10^{-4}M, (4) 1.0×10^{-2}M.
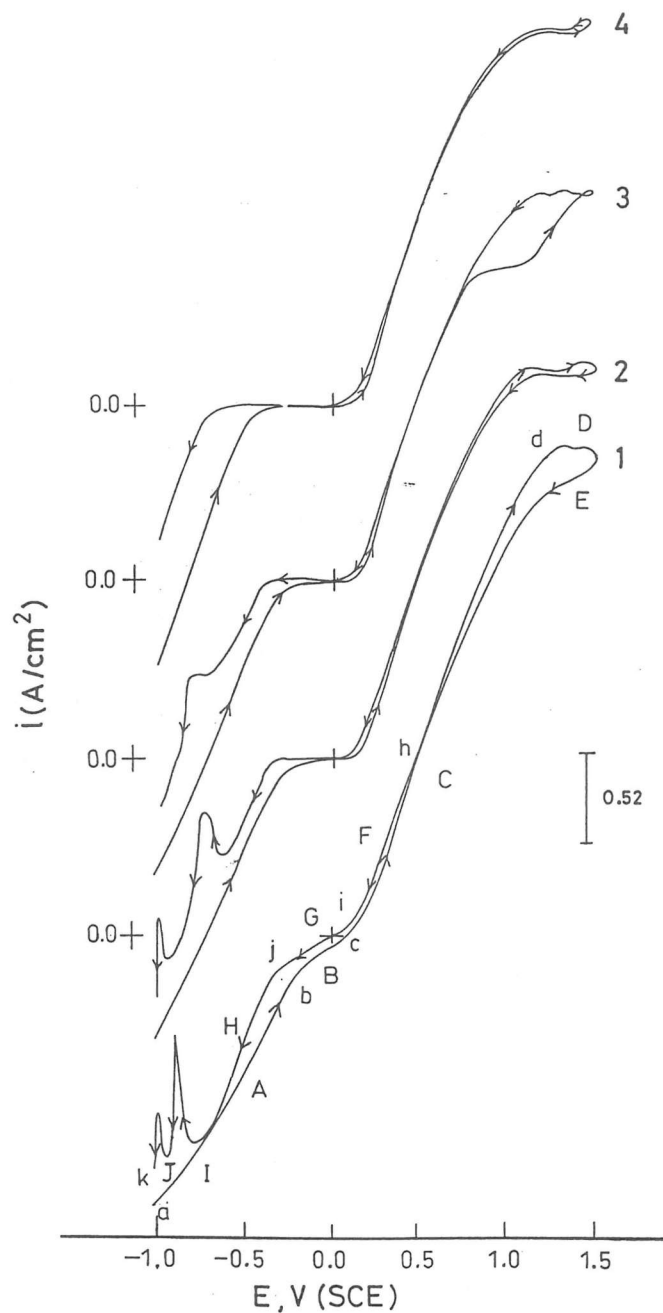
Fig.6. Cyclic voltammograms of copper in 4.0M HNO₃ for compound D₂ (1) 0.0M, (2) 1.5×10⁻³M, (3) 2.5×10⁻³M, (4) 1.0×10⁻²M.

b- Blank Curve (Figure 5 – Curve 1)

Complete cyclic voltammogram is characterized by several features marked by "A, B, C and D" on the forward (anodic) half-cycle and by "E, F, G, H, I and J" on the backward (cathodic) half-cycle.

Forward Half-Cycle (Regions A, B, C and D)

It begins at a very high negative potential (-1.0V, point a) and scanned in the anodic direction to a very high positive potential (+1.5V). An initial sharp rise in current density (region A) leading to a short current arrest (region B) is observed. In region A, the current is pure cathodic. By analogy with similar studies, region A could be due to the decay of any cathodic processes, to the reduction of any traces, to the activation of the electrode...etc.). The short current arrest (region B) could be also identically described as a residual current which is mainly due to the charging of the electrode double layer. The capacitative current will flow along region B until the potential becomes positive enough to affect the beginning of the main anodic dissolution process. Potential at point c was found to be +0.062V (SCE).

Beyond point c, the anodic current density rises sharply (region C) up to point d (potential = +1.25V and anodic current density = 2.73A/cm²) and eventually leading to an anodic shoulder (i.e. the forward surface of the anodic loop at region D). In other words, the current changes direction instead of continuing to rise.

Region C could be attributed to the main anodic dissolution process. According to Pourbaix diagrams of copper electrode in acidic medium [24], the thermodynamically stable oxidation product is copper ions. Moreover, no copper oxides or hydroxides are thermodynamically stable under this condition at all potentials. Thus region C could be attributed to metal dissolution with the formation of copper ions at appreciable rise in the anodic current density. This conclusion is further supported by the fact that the solution acquired faint blue colouration along region C.

Following region C and by analogy with similar studies, non-of the normally and generally associated processes which are normally expected was observed. Instead, a short forward surface of an anodic loop (anodic shoulder) at region D at about potential = +1.32V and anodic current density = 2.86A/cm² was obtained. It is of important to remark that on reversing the sweep, the current remained high. This would indicate that any film (or layer) that is previously formed is either immediately

dissolved or in poor contact with the electrode surface. Moreover, no reduction process corresponding to the reduction of this anodic shoulder (region D) was observed on the reverse backward of the voltammogram. These characteristics would suggest the presence of a limiting phenomenon of a surface solution layer at the interface. Thus, the most probable explanation of the anodic shoulder at region D is that, the slow diffusion process is unable to remove the accumulated copper ions formed away from the interface fast enough to keep up with the rapidly increasing potential. Thus the forward anodic shoulder at region D may be due to a saturated solution layer of accumulated copper ions at the interface leading to limiting shoulder diffusion controlled.

At the end of the forward half-cycle no oxygen evolution or surface film formation was observed. Solution acquired faint blue colour and surface appeared as if it is slightly etched.

### Backward Half-Cycle (Regions E, F, G, H, I and J)

On reversing the scan at the vertex potential (+1.5V), the cathodic branch was produced. At its beginning, an initial anodic shoulder (i.e. the backward surface of the anodic loop at region E) was observed followed by a rapid decrease in the anodic current density (region F) until it reaches the current arrest at potential near base line. This backward half – cycle crosses forward half-cycle at point h. It is of importance to point out that the backward anodic shoulder (region E) is similar to the forward anodic shoulder (region D) but shifted to more negative potential. This would indicate that when the scan was reversed, there were still some accumulated products of the electrolysis at the interface.

In region F, the anodic current density decreases sharply down to point i (potential = +0.03V) and eventually leading to the short current arrest (region G). The current arrest at region G obtained for the backward direction falls above that of the forward direction (region B) and longer than it. Capacitative current flew along region G until potential become negative enough at point j (-0.32V) to affect beginning of the main cathodic process. Beyond point j, a sharp rise in the cathodic current density along region H up to point k (-1.0V) leading to two well-defined cathodic peaks (I and J) at potentials −0.780V and −0.935V respectively. At the end (at point k), copper ions were cathodically deposited and solution became colourless.

The former cathodic peak I could be attributed to nitric acid reduction rather than hydrogen evolution as follows:

$$H^+ + e \rightarrow H$$

$$H + HNO_3 \rightarrow NO_2 + H_2O$$
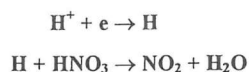
The second cathodic peak J that followed the former could be assigned for the chain reaction propagation as follow:

$$NO_2 + e \rightarrow NO_2^-$$

$$NO_2^- + H^+ \rightarrow HNO_2$$

$$HNO_2 + HNO_3 \rightarrow 2\ NO_2 + H_2O$$
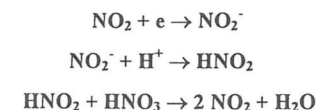
This self-stimulating reduction of nitric acid is identical to the autocatalytic reaction as has been generally proposed by Evans [1].

c- Effect of Inhibitor

Curves 2 – 4 shown in figures 5 and 6 represent the cyclic voltammograms obtained for copper electrode between −1.0V and +1.5V at voltage scan rate of 25mv/sec. in 4.0M HNO_3 solutions containing three selected concentrations form compounds D_1 and D_2 (namely: low, medium and high inhibitor concentrations). Inspection of these curves reveals that, increasing inhibitor concentrations affect markediy both peak potentials and current densities relative to the blank one (see figure 5, curve 1).

The currents of the forward surface of the anodic loop (anodic shoulder) at region D as well as the currents of the two cathodic peaks (I and J) are shifted to a lower values in presence of low inhibitor concentration (namely: $4.5 \times 10^{-4}M$ and $1.5 \times 10^{-3}M$ from compounds D_1 and D_2 respectively). In the mean time the potential of the anodic shoulder at region D is slightly shifted into more positive value. On the other hand, the potential of the first cathodic peak I is shifted to a less negative value while no marked change in the potential of the second cathodic peak J. These experimental findings would suggest that, low inhibitor concentration from compounds D_1 and D_2 has a moderate inhibition effect on copper corrosion in 4.0M HNO_3 solutions. This inhibition effect could be attributed to the adsorption of the inhibitor molecules on the metal surface. The adsorbed inhibitor molecules can retard both the anodic copper dissolution and the cathodic HNO_3 acid reduction by blocking the active metal sites. Moreover, the results indicate that compounds D_1 and D_2 are of mixed inhibitor type.

The current density of the anodic shoulder at region D is shifted to a lower value in presence of medium inhibitor concentration ($5.0 \times 10^{-4}M$ and $2.5 \times 10^{-3}M$ from compounds D_1 and D_2 respectively) while the two cathodic peaks (I and J) become ill

defined peaks (see figures 5 and 6). Addition of $1.0 \times 10^{-2}M$ from compounds D_1 and D_2 (high inhibitor concentration) lead to shift the anodic shoulder at region D to a lower value. In the mean time the two cathodic peaks (I and J) disappeared completely. These results would suggest that medium and high concentrations from compounds D_1 and D_2 lead to remove HNO_2 from the sphere of reaction through its consumption with the adsorbed inhibitor amines group at the cathodic sites. Consequently, the reduction of nitric acid is prevented. So it is concluded that medium and high concentrations from compounds D_1 and D_2 have a stronger inhibition effect on copper corrosion in 4.0M HNO_3 solutions.

It is of interest to remark that, in presence of medium and high inhibitor concentrations (see figures 5 and 6) the forward surface of the anodic loop at region D has a relatively lower anodic current density than the reverse surface of the loop at region E. The reverse situation happens in presence of low inhibitor concentration. This behavior could be attributed whether the copper ion – inhibitor complex occurs in solution and / or chemisorbed on the surface. In other words, the formed complex has two opposing effects leading to either retardation or acceleration over a short potential range. This would suggest that the effect of the inhibitors be most probably due to the chemical interaction between the adsorbed inhibitor molecules and the copper ions in solution and / or at the surface formed during polarization at the interface. Complicated surface processes involving both inhibitor molecules and copper ions would contribute to surface kinetics processes rather than diffusion controlled processes. This supports the probability of chemical reactions coupled with electrode processes (EC – mechanism) and thus the secondary products rather than the primary substance, which have the actual inhibiting effect.

Further inspection of figures 5 and 6 revels that increasing of inhibitor concentration has a marked effect on the potentials at which the two – electrochemical reactions are beginning (i.e. the potentials at point c and j). It is obvious that the potential at the beginning of the anodic reaction (point c) is shifted to more positive values relative to the blank while the potentials at which the cathodic reaction is starting (point j) is shifted to more negative values. Consequently, the length of the current arrests at regions B and G obtained for both forward and backward directions are increased. This behavior may be due the increasing of capacity for the adsorbed inhibitor molecules in the double layer at the metal – solution interface. Moreover and

as illustrated from figures 5 and 6 that the length of the current arrest at region B in case of forward direction is shorter than that in case of backward direction (region G). This behavior would indicate that the inhibitors under study (compounds D_1 and D_2) have a higher inhibition effect on the cathodic sites than that on the anodic sites. This conclusion supports the idea that compounds D_1 and D_2 are have mixed inhibitor type with a predominant cathodic effectiveness.

In conclusion, there is a good agreement between the results obtained from both galvanostatic polarization and cyclic voltammetric techniques.

CONCLUSIONS

1. The present galvanostatic polarization measurements indicate that in absence of inhibitor, the anodic metal dissolution and the cathodic nitric acid reduction are basic electrodics of corrosion – reaction of copper in 4.0M HNO_3 solution. In addition, the accumulated copper ions immediately adjacent to the electrode forms an obstructive layer at interface, which acts as a barrier for mass transport. Moreover, it indicates that the two organic compounds (D_1 and D_2) under study are good inhibitors of mixed type with cathodic predominate and that they act via general adsorption.

2. Cyclic voltammetric studies show that in absence of inhibitors, the anodic process is characterized by an initial rapid rise in the anodic current density starting at potential +0.062V, followed by anodic loop at the vertex potential. The cathodic process is characterized by an initial sharp rise in cathodic current density at potential –0.032V leading to two well - developed cathodic peaks at the negative potential end of the voltammogram. These two cathodic peaks are attributed to the reduction of nitric acid and the chain propagation reaction.

3. In presence of inhibitors (compounds D_1 and D_2), cyclic voltammetric studies show that inhibitors have significant inhibition effects on the two main features at the two extreme potentials of the voltammogram.

4. A parallelism between the results obtained from both galvanostatic polarization and cyclic voltammetric techniques is revealed.

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