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Bis-triazole as a new corrosion inhibitor for copper in sulfate solution. A model for synergistic inhibition action

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Bis-[4H-5 hydroxy-1, 2, 4-triazol-3-yl] methane "BHTAM" was tested as a promising new inhibitor for copper corrosion in 0.5 M Na_2SO_4 solutions using open – circuit potentials and galvanostatic polarization techniques. The results show that, BHTAM is an efficient inhibitor for copper corrosion in neutral medium. The anodic polarization is strongly affected by the presence of BHTAM compound as well as the cathodic polarization but to a lesser extent. The surface condition plays a significant role in the protection of copper. The pre-formed surface cuprous oxide films facilitate inhibitor adsorption as well as precipitation of insoluble [Cu (I) – BHTAM] complex. © *2000 Kluwer Academic Publishers*

1. Introduction

Copper is one of the most commonly used metals that have extensive applications in various industrial processes. Numerous heterocyclic compounds containing nitrogen have been examined for use as inhibitors for its corrosion. Benzotriazole "BTA" proved to be the most effective class of inhibitors for copper and copper base alloys in many aqueous environments. However, in comparison to the large volume of literature on this subject, little basic work was devoted to the understanding of the basic mechanism of its action. However, controversy exists among the various authors.

Early studies [1–3] suggested "BTA" chemisorbed on a copper oxide surface layer forming cuprous benzotriazole [Cu(I) – BTA] complex. Cuprous oxide was claimed to be essentially for the formation of [Cu(I) – BTA] film. On the other hand, recent studies [1, 4–6] seem to disagree with this claim on the basis that [Cu(I) – BTA] forms also on oxide free – surface (bare surface). Formation of polymeric complexes with cuprous ion $[Cu(I) – BTA]_n$ has been suggested [2, 3, 7–10] and that it is underlaid with cuprous oxide layer forming a bi – layer structure [7, 11, 12]. The importance of the initial oxide layer has been concluded by using various analytical surface studies [2, 8–11].

The purpose of the present study is (a) to assess the inhibition efficiency of the suggested bis-[4H-5 hydroxy-1, 2, 4-triazol-3-yl] methane "BHTAM" as a new and promising corrosion inhibitor for copper in neutral solution and (b) to give an insight on the controversy exists about the presence of surface cuprous oxide layer.

2. Experimental

Bis-[4H-5 hydroxy-1, 2, 4-triazol-3-yl] methane (2) "BHTAM" was synthesized according to the published methods [13–15] (Fig. 1) as follows: A mixture from malonic acid dihydrazide (0.1 mol) and ethylchloroformate (0.2 mol) was refluxed in an oil bath at 120 °C for 3 hours. The solid separated after cooling was recrystallized from ethanol to give bis-[5-hydroxy-1, 3, 4-oxadiazol-2-yl] methane (1) "BHOAM" in 95% yield. IR data of compound (1) "BHOAM" showed absorption bands (cm^{-1}) near 3244(OH), 3041(NH), 1753(C=O), 1697(C=N), and 1248, 1068(C-O-C). The mass spectrum showed molecular ion peak at $m/e = 184$ $[M]^+$.

Fusion of (0.1 mol) of compound (1) with (0.2 mol) of formamide at 180 °C for 4 hours gave the corresponding bis-[4H-5 hydroxy-1, 2, 4-triazol-3-yl] methane (2) "BHTAM". The solid was re-crystallized from ethanol with 80% yield. The structure of compound (2) "BHTAM" was established by IR – spectrum with absorption bands (cm^{-1}) at 3132(OH), 3043(NH), 1747(C=O), 1651(C=N) and 1400(CH_2) while its mass spectrum revealed molecular ion peak at $m/e = 182$ $[M]^+$.

The solutions used in the electrochemical measurements were 0.5 M Na_2SO_4 without and with different concentrations from BHTAM. 0.5 M Na_2SO_4 was prepared from high – grade chemicals (Merck) with re-distilled water. The BHTAM inhibitor was dissolved into 0.5 M Na_2SO_4 solutions at various concentrations.

A copper rod (Aldrich Chemicals, purity 99.998%) was soldered into bright copper wire, introduced into pyrex glass tubing and fixed in position by means of Araldite. Before each experiment, the surface of the copper electrode was polished with emery paper, degreased with re-distilled water and acetone.

The present study was carried out using open – circuit potential and galvanostatic polarization measurements. All the measurements were carried out in glass cell containing the working copper electrode, a platinum counter electrode (separated from the cell solution by a sintered glass frit) and a saturated calomel

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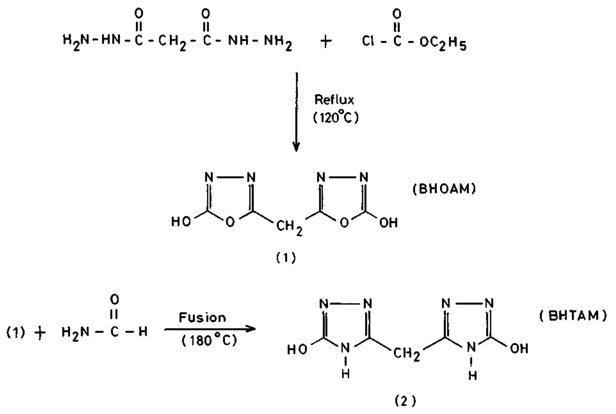

Figure 1 Schematic diagram illustrating the reaction steps involved in the preparation of BHTAM.

electrode (SCE). The trends of the open – circuit potentials, as a function of time, were recorded to the nearest mV on a Wenking Potentiometer, Type C. G. 822, relative to the saturated calomel electrode. The steady – state values were considered valid when the potential not changing more than 1 mV in 20 minutes. The current – polarization curves were measured galvanostatically using a model 363 Potentiostat/Galvanostat (EG & G Prinecton Applied Research – USA). The potentials were recorded using digital multimeter. However, the corrosion product that formed on the copper surface was analyzed using some basic chemical qualitative analysis and FT–IR spectroscopic methods.

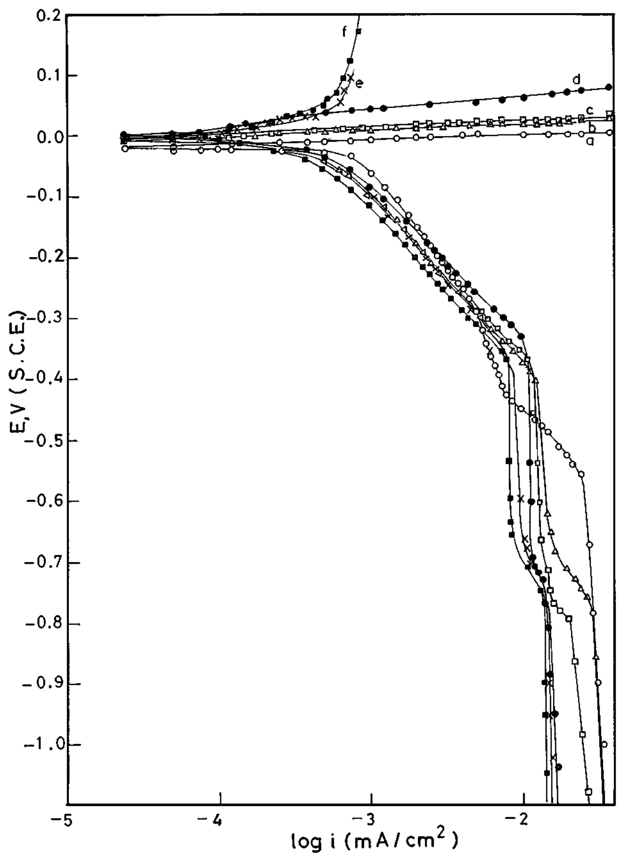

Figure 2 Polarization curves of the copper substrates in 0.5 M Na_2SO_4 solutions without and with different concentrations from BHTAM (a) free inhibitor; (b) 1.0 × 10^{-3} M; (c) 2.5 × 10^{-3} M; (d) 5.0 × 10^{-3} M; (e) 7.5 × 10^{-3} M; (f) 1.0 × 10^{-2} M.

3. Results and discussion

3.1. Galvanostatic polarization measurements

The results of cathodic and anodic polarization measurements on copper substrates in aerated 0.5 M Na_2SO_4 aqueous solutions containing different concentrations of BHTAM compound ranging between 10^{-3}–10^{-2} M at 25 °C are shown in Fig. 2 as Tafel plots. The characteristic basic potentials and the corrosion parameters are summarized in Table I. Polarization curves indicate that the anodic polarization is strongly affected by the presence of the BHTAM compound as well as the cathodic polarization but to a lesser extent. The overall reaction involves the dissolution of the metal and the reduction of the dissolved oxygen. Increasing the concentration of the BHTAM compound leads to shifting the corrosion potential to a more positive value relative to the blank and to decreasing current densities up to a limiting concentration of 7.5 × 10^{-3} M. Above this critical value, both values of corrosion potential and current density remain constant. The results demonstrate the efficiency of BHTAM compound as a corrosion inhibitor, which strongly affects the anodic oxidation of copper as well as the cathodic oxygen reduction but to a lesser degree.

Inspection of the cathodic polarization curves in Fig. 2 reveals that the cathodic reaction process is a chemical activation and concentration polarization characterized by two consequence limiting currents. This would indicate that the cathodic reaction is kinetically and diffusion controlled. The reduction of oxygen is by far the major cathodic process, which takes place via hydrogen peroxide. It is of interest to remark that, in Fig. 3 the two limiting cathodic currents are

TABLE I Characteristic basic potentials and corrosion parameters obtained for copper substrates immersed in 0.5 M Na_2SO_4 solutions without and with different concentrations from BHTAM at 25 °C

Inh. Conc. (M)	E_{corr}, SCE. (mV)	Cathodic Tafel slope (mV)	$I_{corr} \times 10^{-4}$ (mA/cm^2)	I.E (%)	Limiting current densities (mA/cm^2) $I_{L1} \times 10^{-3}$	$I_{L2} \times 10^{-3}$
0.00	−20	310.5	9.6	0.0	7.59	44.67
1.0 × 10^{-3}	−15	277.5	5.0	47.9	12.01	41.69
2.5 × 10^{-3}	−3	275.0	4.6	52.1	10.96	19.95
5.0 × 10^{-3}	0	265.5	4.4	54.2	10.47	14.45
7.5 × 10^{-3}	+2	285.2	2.9	69.8	8.32	13.80
1.0 × 10^{-2}	+2	275.8	2.8	70.8	7.94	13.80

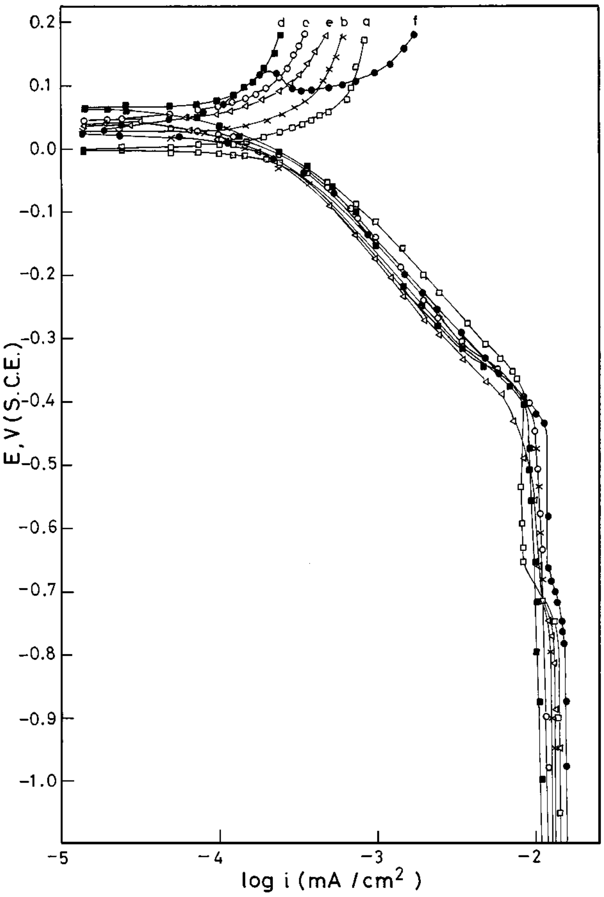

Figure 3 Polarization curves of the copper substrates in 0.5 M Na_2SO_4 solutions containing 1.0×10^{-2} M BHTAM. Results based on keeping the cleaned copper substrates exposed to air for a various number of hours prior measurements (a) zero hr; (b) 3 hr; (c) 6 hr; (d) 12 hr; (e) 24 hr; (f) 48 hr.

closer together to the extent that they analogous to one limiting. In contrast to the anodic polarization curves, the corrosion current densities were evaluated from the extrapolation of the cathodic Tafel line to the experimentally measured free corrosion potentials.

The degree of surface coverage (θ) and the percentage inhibition efficiency (I.E) were calculated using the following two equations [16–19]:

$$\theta = \left[1 - \frac{I_{\text{inh}}}{I_{\text{corr}}}\right] \rightarrow 1$$

$$\text{I.E}\,(\%) = \theta \times 100 \rightarrow 2$$

where I_{inh} and I_{corr} are the corrosion current densities in presence and in absence of inhibitor, respectively. However, the only requirement for equation 1 to hold is that the cathodic Tafel slope is constant [16] a condition closely approximated by the present results (Table I).

The anodic polarization curves (Fig. 2) reveal the presence of two different types of anodic behaviors. Results indicate that below concentration of 7.5×10^{-3} M, the anodic polarization is very small as indicated by the small change in potential with current over a range of current density. On the other hand, at and above this critical inhibitor concentration, the anodic polarization is strongly affected as indicated by a kind of limiting current that is being approached. This could be attributed to polarization resistance through the thin layer of the adsorbed inhibitor over the anodic areas which blocks a large fraction of electrode surface and hence reduce the corrosion rate.

In order to shed some light on the controversy problem on the role of surface cuprous oxide film, another set of experiments was carried out by keeping the copper substrate exposed to air for various periods of time (namely 3, 6, 12, 24 and 48 houres) as a pre-treatment prior to immersion of copper substrate in the test solution (namely 0.5 M $Na_2SO_4 + 0.01$ M BHTAM) for anodic and cathodic polarization measurements. Results are shown in Fig. 3 and the characteristic basic potentials as well as the corrosion parameters are summarized in Table II. The present results reveal that the pre-exposure period of copper samples in air has a significant effect on the anodic polarization and to a lesser extent on the cathodic polarization measurements. Increasing the pre-exposure time of copper in air lead to shifting the corrosion potential to a more positive values until a maximum is reached at about 12 hour after which it reverses its direction to a decrease in the potential but still in the positive region.

3.2. Open – circuit potential (O.C.P.) of copper substrate in 0.5 M Na_2SO_4 solutions with and without 0.01 M BHTAM

The way in which a metal changes its O.C.P. with time upon immersion in a solution could be taken as indicative to the measure of reactions taking place at the metal solution interphase. In general, whilst a shift of potential towards positive direction denotes a passivation

TABLE II Characteristic basic potentials and corrosion parameters obtained for copper substrates immersed in 0.5 M Na_2SO_4 solutions containing 1.0×10^{-2} M BHTAM at 25 °C. Results based on keeping the cleaned copper substrates exposed to air for a various number of hours prior to measurements

Pre-exposure time in air (hr)	E_{corr}, SCE. (mV)	Cathodic Tafel slope (mV)	$I_{\text{corr}} \times 10^{-4}$ (mA/cm^2)	I.E (%)	Limiting current densities (mA/cm^2) $I_{L1} \times 10^{-3}$	 $I_{L2} \times 10^{-3}$
Blank	+2	275.8	2.8	70.8	7.94	13.80
3.0	+22	284.1	2.5	74.0	11.48	—
6.0	+42	294.6	2.2	77.1	10.47	—
12.0	+62	290.2	1.8	81.3	9.12	—
24.0	+36	283.3	2.1	78.1	6.92	13.18
48.0	+29	277.3	2.3	76.0	11.48	15.14

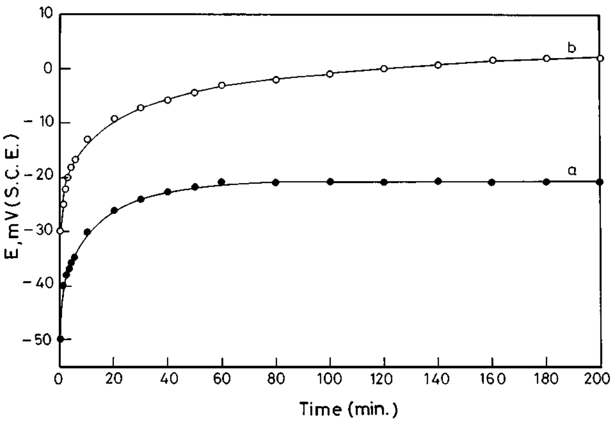

Figure 4 Variation of the O.C.P. as a function of time for copper substrates in 0.5 M Na_2SO_4 solutions without and with 1.0×10^{-2} M BHTAM (a) free inhibitor; (b) 1.0×10^{-2} M BHTAM.

behavior, a shift in the negative direction signifies an activation behavior.

Fig. 4 shows the O.C.P. versus time of the freshly cleaned copper substrate immediately immersed in the aerated 0.5 M Na_2SO_4 aqueous solutions at 25 °C with and without 0.01 M BHTAM compound until reaching a final steady state potential. In the absence of the inhibitor (Fig. 4a), an initial gradual changes in the potential in the noble direction was observed over about an hour time, followed by a slight continuous rise to reach a stabilized steady state value. Such a passive behavior could be most probably attributed to the chemisorption of the dissolved oxygen and its reduction together with possible formation of surface cuprous oxide film on copper substrate. The presence of 0.01 M BHTAM (Fig. 4b) shifted the potential – time curve over the whole range in potential in the positive direction in a parallel form. Moreover, the free corrosion potential shifted from −21 mV to +2 mV.

3.2.1. Effect of cuprous oxide film

To elucidate the possible influence of surface cuprous oxide film, copper substrates were kept exposed to air for different periods of time just before immersion in the test solution for electrochemical measurements.

A set of experiments was carried out, keeping the freshly cleaned copper electrodes standing in air for various periods of time (namely 3, 6, 12, 24 and 48 hours) followed by immediately dipping them in the test solution (0.5 M Na_2SO_4 + 0.01 M BHTAM) for tracing potential – time relationships. Results are shown plotted in Fig. 5 and the distinct features are summarized in Table III. Inspection of Fig. 5 reveals the presence of two distinct types of behavior depending on the pertreatment period in air. Curves c, d and e, which corresponds to pre-treatment 3, 6 and 12 hours respectively, are characterized by an initial rapid shift of potential in the active direction within the initial few minutes followed by a continuous rise in potential leading finally to a steady state value. On the other hand, curves f and g, which corresponds to pre-treatment 24 and 48 hours respectively, are characterized by an initial rapid rise in potential within the first few minutes followed by a nearly steady state value. This would indicate that air – formed – oxide film is sufficient to impart passivation immediately on dipping electrode in the test solution. It could be conclude that the air formed film during pre-exposure period plays a significant role and may be of vital importance with regard to the efficiency of the inhibitor.

TABLE III Characteristic open circuit potentials obtained for copper substrates immersed in 0.5 M Na_2SO_4 solutions containing 1.0×10^{-2} M BHTAM at 25 °C. Results based on keeping the cleaned copper substrates exposed to air for a various number of hours prior to measurements

	Characteristic open circuit potentials, SCE. (mV)	
Pre-exposure time in air (hr)	E_{initial}	E_{final}
blank	−30	+2
3.0	−22	+22
6.0	+36	+43
12.0	+55	+62
24.0	+11	+32
48.0	+5	+27

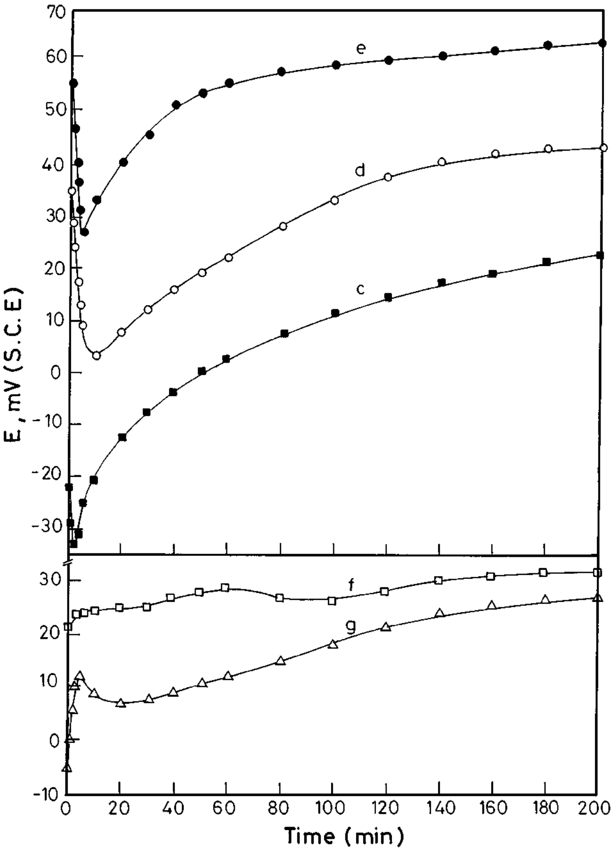

Figure 5 The O.C.P. as a function of time for the copper substrates in 0.5 M Na_2SO_4 solutions containing 1.0×10^{-2} M BHTAM. Results based on keeping the cleaned copper substrates exposed to air for a various number of hours prior measurements (c) 3 hr; (d) 6 hr; (e) 12 hr; (f) 24 hr; (g) 48 hr.

Fig. 6 illustrates how the open circuit potential (both the initial immersion and final steady state) vary with the number of hours during which the copper electrodes have been exposed to air prior to electrochemical measurements in the test solution. Curve a corresponds

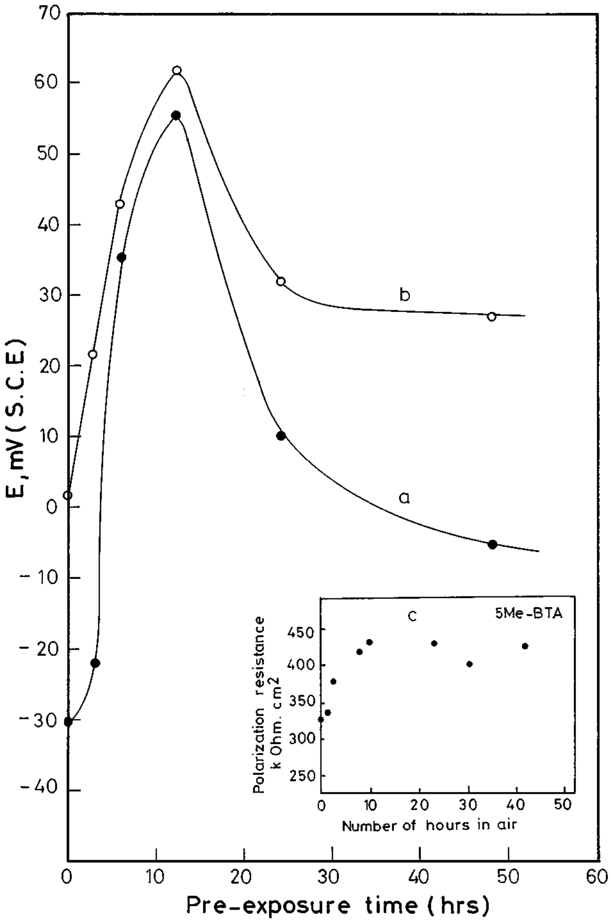

Figure 6 Variations of both the initial and final potentials with pre-exposure time of the copper substrates in air. Results based on 0.5 M Na_2SO_4 solutions containing 1.0×10^{-2} M BHTAM (a) initial potentials; (b) final potentials; (c) variation of the polarization resistance with pre-exposure time of the copper substrates in air. Results are based on 5.0×10^{-4} M 5 Me-BTA in 0.01 M NaCl (taken from reference 2 for comparison propose).

to the instantaneous initial potentials while curve b corresponds to the final steady state potentials. It is of interest to remark that the two curves are quite similar and run nearly parallel to each other. As inferred from Fig. 6 both curves a and b exhibit a continuous increase with exposure time in air until a maximum is reached after about 12 hour followed by a continuous decrease with a tendency to level up. In this respect, it is of utmost importance to refer to Tornkvist *et al.* [2] variation of polarization resistance measurements with pre-exposure time of copper substrates in air based on 0.0005 M 5 Me-BTA in 0.01 M NaCl. Tornkvist *et al.* exact results are included in Fig. 6 for comparison proposes. It exhibits a continuous increase with exposure in air until a maximum is reached after about 10 hour. The striking similarity between the present work and that of Tornkvist *et al.* could be taken as a support of the present work, further evidence for the importance of air – formed – film and the close correlation with oxide – film growth. Moreover, a possible interpretation of pattern of Fig. 6 could be given in terms of polarization resistance. The descending portion could be attributed to change in surface morphology. Further more, the final leveling up of the curve would indicate that an equilibrium steady state has been reached.

3.3. Analysis of the corrosion product

At the end of the corrosion experiment, copper samples were carefully withdrawn from the test solution (0.5 M Na_2SO_4 + 0.01 M BHTAM), washed by redistilled water and dried. The corrosion product (green precipitate) is then removed from the copper surface for carrying out some of the basic chemical qualitative analysis as well as IR – spectrum.

3.3.1. Basic chemical qualitative analysis

According to the well-known methods used for chemical analysis [20] it was found that Cu(I) ions are included in the green precipitate (corrosion product) and not Cu(II) ions. Also, it was found that the sulfate group (provided from the aqueous medium) is present as a ligand coordinated to Cu(I) ion of the corrosion product and not as a sulfate ionic group.

3.3.2. IR - spectrum

The IR – spectrum for both the BHTAM inhibitor and the green precipitate (corrosion product) are shown in Fig. 7 (a and b), and the more prominent bands are summarized and tentatively assigned in Table IV. Careful inspection of the IR – spectrum of BHTAM (Fig. 7a) and the data of Table IV reveal that, the strong band at 3132 cm^{-1} is due to the strongly hydrogen bonded OH group probably involving OH and N of heteroring from another molecule through dimmeric or polymeric structures. The band at 3043 cm^{-1} is due to υ_{NH} while the two medium bands at 1747 cm^{-1} and 1651 cm^{-1} are due to $\upsilon_{C=O}$ (keto – enol tautomerism) and $\upsilon_{C=N}$, respectively. The strong band at 1400 cm^{-1} is assigned for the stretching vibration of the CH_2.

The IR – spectrum of the corrosion product (Fig. 7b and Table IV) shows that the υ_{OH} is shifted to higher frequency relative to the υ_{OH} of the corresponding free BHTAM inhibitor. Thus, it is suggest that the hydrogen bond is absent. In the mean time, a new band is appeared at 1610 cm^{-1} which assigned to the $\upsilon_{C=N}$ (chelated). This behavior give a strong indication for the participation of the C=N group in bond formation with Cu(I) ion. This further confirmed from the appearance of a new band in the far IR region at 486 cm^{-1}, which assigned to the $\upsilon_{Cu\text{-}N}$. Also, the strong shift of the stretching vibration of the CH_2 band in case of free BHTAM inhibitor

TABLE IV Infrared frequencies (cm^{-1}) and assignments for both BHTAM and corrosion product (green precipitate)

cm^{-1}		
BHTAM	Corrosion product	Assignments
3132	3386	OH
3043	3200	NH
1747	—	C=O (keto – enol tautomerism)
1651	1650	C=N (free)
—	1610	C=N (chelated)
1400	1122	CH_2
—	987, 945, 875	SO_4^{-2} (coordinated)
—	601	Cu-O (oxygen from sulfate)
—	486	Cu-N

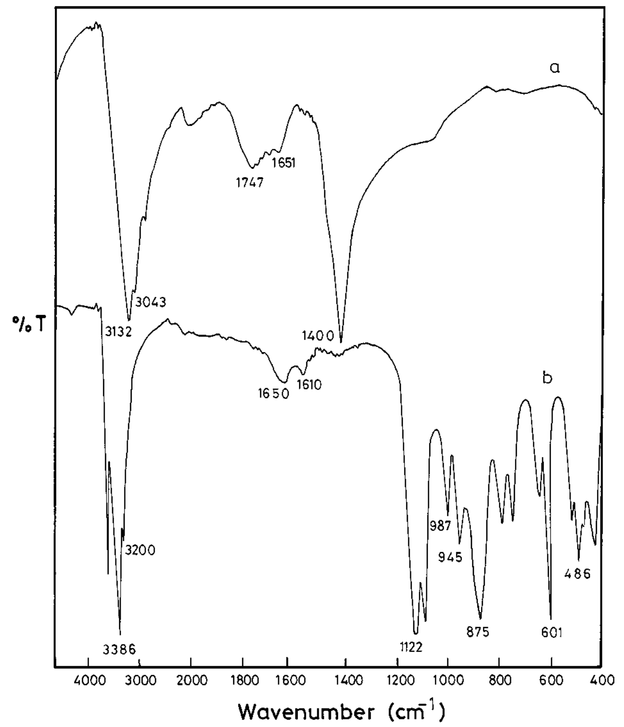

Figure 7 Infrared spectra of (a) BHTAM compound; (b) corrosion product (green precipitate).

to a lower frequency in case of corrosion product could be probably due to the contribution of this group in the ring structure of the complex formed. Moreover, the IR – spectrum of the corrosion product (Fig. 7b and Table IV) demonstrated a three medium – strong bands at 987, 945 and 875 cm^{-1}, which assigned for bridging sulfate anion via two oxygen atoms [21]. So it is proposed that the sulfate anion (provided from the aqueous medium) be contributed in the complex formation. This is further confirmed by the appearance of the strong band at 601 cm^{-1}, which is assigned to $\upsilon_{Cu\text{-}O}$ (oxygen of coordinated sulfate).

The foregoing results of both chemical qualitative analysis and IR – spectroscopic methods would indicate that the corrosion product (green precipitate) formed on the copper metal surface immersed in 0.5 M Na_2SO_4 solution containing BHTAM inhibitor is probably a complex compound, which is most probably as $\{[Cu(I)]_2\ [SO_4]_1\ [BHTAM]_2\}$.

3.4. Proposed mechanism for synergistic inhibition

The predication of the precise mechanism is rather a difficult problem because of the complexity of the present system as well as the many variables involved. However, a simple descriptive could be deduced as a qualitative attempt to account for the present experimental study that would help with understanding of the different factors and variables involved. As a starting point the mechanism could be visualized (Fig. 8) as occurring in two subsequential stages namely:

(A) Atmospheric corrosion (stage I)
(B) Solution inhibition (stage II)

The first stage involves activities happening when the copper substrate is kept in air for a pre-exposure period. On the other hand, the second stage involves activities happening in the test solution on the bases of chemisorbed inhibitor molecules.

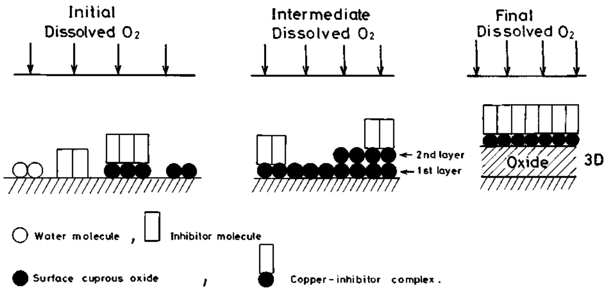

Figure 8 Simplified schematic diagrams for the proposed model for the interphase structure during the different stages.

Stage I (atmospheric corrosion): If an oxide – free copper surface is exposed to air, there is a rapid initial adsorption of oxygen followed by interaction with the metal forming a chemisorbed surface oxide film. Thus the surface oxide film is the result of the initial chemisorption of oxygen producing two – dimensional interface layer changing gradually to a three – dimensional and multi layers. This chemical oxidation of metal exhibit characteristic not generally met in simple reaction. The oxide, as it growth, shuts of metal more and more from oxygen. The initial rapid process slow down although it does not entirely ceased. This rate of growth is often controlled, not by the chemical reaction but most probably by the outward passage of metal cations and/or the inward oxygen anion through oxide film.

It is of interest to remark that [2] on copper at room temperature in clean, ambient, air there is observed a rapid initial growth in the film thickness to 30–40 Å where as after about 10 hour of exposure the film growth rate becomes almost negligible. There is a great deal of evidence in the literature that, depending on time of exposure, the copper substrate is partially or completely covered predominately with cuprous oxide.

Stage II (solution inhibition): Copper samples which, have been exposed to air are partially or completely covered with surface cuprous oxide patches, which have a certain degree of protection. On dipping in the test solution, the inhibitor molecules are chemisorbed on and reacted with cuprous oxide forming a stable and protective barrier film. The developed instantaneous open circuit potentials of the substrate on dipping into test solution reflect happenings during stage I, while the developed steady – state open circuit potentials reflect the happening in both stages I and II (Fig. 6). As referred from Figs 5 and 6, the admixing effect is continuous increase with exposure in air until a maximum is reached at about 12 hours.

The pre-formed surface cuprous oxide dipoles facilitate the adsorption as well as the formation of insoluble [Cu(I) – BHTAM] complex. The adsorbed cuprous oxide forms a bridge that links parts of the metal surface with reactive inhibitor molecules. The cuprous oxide film acts as a source of cuprous ions at the interface [2]. Thus the accessible amount of cuprous ions seems to be very essential to achieve a rapid film of surface complex. The inhibition efficiency is strongly developed on the extent and properties of the pre-formed surface oxide film. Moreover, the high inhibition efficiency is due to the formation of barrier complex layer, Cu(I) – inhibitor complex film, underlaid by cuprous oxide layer. Generally, the possibility of inhibitors interaction on oxide – covered metal surfaces and the availability of cuprous ions from cuprous oxide surface formed film has been demonstrated [2, 22, 23]. In conclusion, the high inhibition efficiency is due to the formation of a protective barrier layer, which is strongly dependent on time of exposure of copper substrate to air prior immersion in the test solution.

4. Conclusions

(1) BHTAM compound shows inhibiting effect on copper corrosion in 0.5 M Na_2SO_4 solution. 7.5×10^{-3} M inhibitor concentration is considered as a critical concentration at which the anodic polarization is strongly affected.

(2) The inhibitor is of mixed inhibitor type with predominant anodic effectiveness.

(3) The inhibition efficiency is strongly dependent on the extent and the properties of the surface cuprous oxide film. The pre-formed surface oxide film in air facilitates the adsorption of the BHTAM molecules as well as formation of insoluble Cu(I) complex containing BHTAM molecules.

(4) Depending on the experimental results, a proposed mechanism for synergistic inhibition action of copper corrosion in 0.5 M Na_2SO_4 solution containing BHTAM compound was discussed.

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