Review

Inhibition of copper corrosion by 1,2,3-benzotriazole: A review

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A B S T R A C T

Benzotriazole (BTAH) has been known for more than sixty years to be a very effective inhibitor of corrosion for copper and its alloys. In spite of numerous studies devoted to the investigation of BTAH action, the mechanism of its action is still not completely understood. The aim of this review is to summarize important work in the field of BTAH as a copper corrosion inhibitor, from the early discoveries to the present time. Special attention is given to the BTAH surface structure. The disagreement between findings and mechanisms is discussed.

1. Introduction

Corrosion plays a very important role in diverse fields of industry and, consequently, in economics. The protection of metals and alloys is thus of particular interest. The goal of studying the processes of corrosion is to find methods of minimizing or preventing it. One approach is the use of corrosion inhibitors. The mechanism of how organic corrosion inhibitors work is usually not known. In most cases, empirical testing has provided information on the effectiveness of a particular molecule as a corrosion inhibitor for a certain substrate in a certain medium. Knowledge of the surface chemistry of adsorbed organics is important for elucidating the mechanism of inhibitor action and, to achieve this, surface analytical techniques are required.
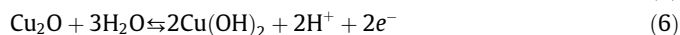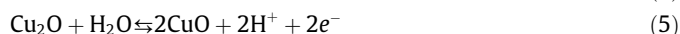
Copper is one of the most important nonferrous materials, with long life properties in neutral water solution, such as in water distribution networks. Strehblow and Titze [1] showed that the Cu passive layer consists of a duplex structure of oxides, with an inner cuprous oxide and an outer cupric hydroxide. Copper will not corrode in non-oxidizing acidic environments, since hydrogen evolution is not a part of its corrosion process. However, when oxygen or other oxidants such as Fe^{3+} and NO_3^- ions are present, corrosion becomes important. Copper oxides are stable only in the pH range of 8–12 [2], but not in acidic solutions (Eqs. (1) and (2)) in which surface roughening can occur:

$$Cu_2O + 2H^+ \leftrightarrows 2Cu^+ + H_2O \qquad (1)$$

$$CuO + 2H^+ \leftrightarrows Cu^{2+} + H_2O \qquad (2)$$

Moreover, Cu^+ ions can undergo disproportionation according to Eq. (3) [3].

$$2Cu^+ \leftrightarrows Cu^{2+} + Cu \qquad (3)$$

The potentiodynamic behaviour of pure Cu in near neutral and slightly alkaline solutions exhibits three anodic peaks associated with the formation of Cu_2O, CuO and $Cu(OH)_2$. Cu_2O is first formed (Eq. (4)), which subsequently oxidizes to CuO (Eq. (5)) or, at more positive potentials, to $Cu(OH)_2$ (Eq. (6)) [1,4].

$$2Cu + H_2O \leftrightarrows Cu_2O + 2H^+ + 2e^- \qquad (4)$$

$$Cu_2O + H_2O \leftrightarrows 2CuO + 2H^+ + 2e^- \qquad (5)$$

$$Cu_2O + 3H_2O \leftrightarrows 2Cu(OH)_2 + 2H^+ + 2e^- \qquad (6)$$

It has been known since 1947 [5] that 1,2,3-benzotriazole (BTAH, $C_6H_5N_3$) is an effective corrosion inhibitor for copper and its alloys by preventing undesirable surface reactions. Since then BTAH has been included in a number of patents ([6,7] and references therein). BTAH prevents discoloration of copper surfaces under atmospheric and immersed conditions. It has been used to protect artefacts of archaeological and historical concern [8–10]. It is known that a protective barrier layer, consisting of a complex between copper and BTAH, is formed when Cu is immersed in a solution containing BTAH. However, contradictory mechanisms and models of its action have been proposed. The reason probably lies in the insolubility of Cu-BTAH complexes in aqueous and many organic solutions, which precludes detailed structural and chemical studies that could lead to better understanding of its surface behaviour. The mechanism by which BTAH becomes connected to the surface on copper is also not completely understood, in spite of the application of various techniques. Powerful *in situ* techniques with high surface sensitivity are thus required to provide specific molecular information concerning the metal surfaces.

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The most important application of BTAH is to protect copper and its alloys under immersed conditions. However, BTAH can also be adsorbed from the gas phase (then the surface chemistry is different [11,12]) and, due to its low vapour pressure (8×10^{-6} torr), it can be used as a vapour phase inhibitor. It can also be used as an important additive for Cu plating baths [13].

BTAH (CAS RN 95–14-7) is a heterocyclic organic compound with a molar mass of 119.124 g/mol (Fig. 1), produced by reaction of orthophenylenediamine with sodium nitrite and acetic acid (Eq. (7)) [14], giving a whitish powder at room temperature.

$$(7)$$
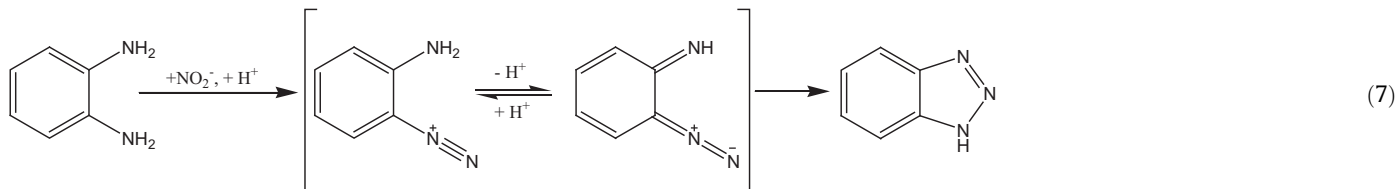
It is sufficiently soluble in water solutions for use as a corrosion inhibitor. The melting and boiling points of BTAH are around 100 °C and 350 °C. It is only slightly toxic – the oral LD_{50} value in white rats is quoted as 560 mg/kg [9] – so it does not constitute a major environmental hazard. The form of the molecule in aqueous solution depends on the pH and can be either neutral (BTAH), negatively charged (BTA⁻) or protonated (BTAH$_2^+$) [15–17].

$$BTAH_2^+ \leftrightharpoons BTAH + H^+, \quad pK_1 \approx 1 \tag{8}$$
$$BTAH \leftrightharpoons BTA^- + H^+, \quad pK_2 = 8.2 \tag{9}$$
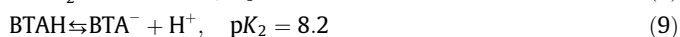
In slightly acidic environments benzotriazole is present mainly in the undissociated form as BTAH, whilst at alkaline pH the molecule is predominantly present in the BTA⁻ form.

In this review Cu-complexes will be designated as Cu(I)BTAH and Cu(II)BTAH when there is no clear evidence for removal of the N–H hydrogen from the BTAH molecule. Cu(I)BTA and Cu(II)BTA represent complexes with known Cu oxidation state and not involving this hydrogen atom. Cu-BTA refers to the molecule with no N–H hydrogen atom, but with unknown Cu oxidation state. Finally, the term Cu-BTAH is used when the structure of the complex is not a matter of discussion. We have followed studies of BTAH action from the early studies up to the present, drawing attention to differences in interpretation. The pioneering studies are described, followed by an account of the most important results concerning the structure, composition, mechanism, inhibitory effectiveness, synergistic effects of BTAH and the impact of benzotriazole derivatives. The most important models and mechanisms proposed for the BTAH action are presented.

2. Pioneering research on benzotriazole as a corrosion inhibitor for copper

Cotton and his co-workers [18–20] pioneered research in the field of BTAH as a copper corrosion inhibitor. They showed that the Cu surface pretreated with BTAH induces long-lasting prevention of staining. Dugdale and Cotton [19] explained the BTAH inhibitory action in terms of a physical barrier, i.e. a surface complex of Cu-BTAH. It was proposed that this structure was formed
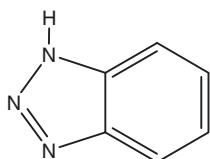
on immersion of copper in BTAH containing solution, where soluble copper ions were produced. This surface layer was characterized as a mixed type inhibitor since it retarded both oxygen reduction (cathodic reaction) and oxidation of the metal (anodic reaction). The authors claimed that this surface film was unable to diminish the hydrogen evolution reaction, which, as will be seen later, was at variance with the conclusions of other authors. Cotton and Scholes [20] showed that BTAH forms a water insoluble precipitate with both cuprous and cupric ions. With cuprous ions, crystalline Cu(I)BTA was observed, which they found to be amorphous or mono-crystalline. They also claimed that this structure might contain some coordinated water molecules. Their conclusions about the Cu(II)BTAH structure were less certain. It was only proposed that it should contain some stabilizing elements – chlorine, oxygen or water. For the complex chemisorbed on the Cu surface, Cotton [18] postulated that it is polymeric with a linear structure, as in Fig. 2, in which copper was bonded by coordination involving a lone pair of electrons from one nitrogen atom and a covalent link formed by replacement of the H atom from the N-H group. Alternate copper atoms and BTA⁻ thus form a polymeric chain. According to Cotton and Scholes [20] this layer is less than 50 Å thick.

Wall and Davies [21] showed that, in the presence of BTAH, dissolution of copper and pick-up of copper ions from the solution is reduced in closed-circuit systems containing copper, such as water-cooled stators used in power industry. The authors claimed that BTAH forms an insoluble and invisible chelate on the Cu surface that is responsible for reducing corrosion attack. Hansen et al. [22] determined the pK_2 for the ionization of the N–H group on benzotriazole, Eq. (9), to be 8.38 ± 0.03. This value is slightly higher than that determined by Fagel and Ewing, $pK_2 = 8.2$ [15].

Poling [23] confirmed the linear polymeric Cu(I)BTA structure proposed by Cotton [18] (Fig. 2) and stated more decisively that this structure contains Cu(I) ions. The formation of Cu(I)BTA was not limited to a monolayer, but could grow further to form films up to several thousand Å thick, unlike the conclusion of Cotton and Scholes [20]. It was proposed that the growth of the Cu(I)BTA film is controlled by the transport of Cu(I) ions from the matrix
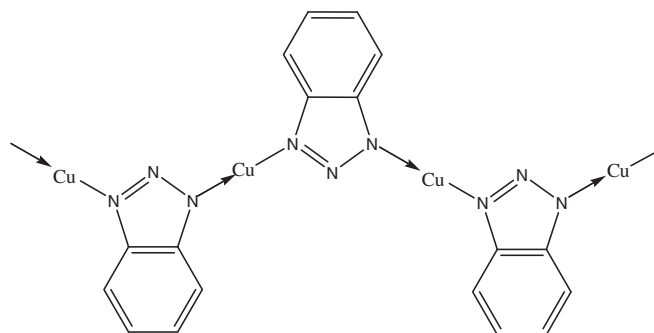

Fig. 1. Chemical structure of benzotriazole.

Fig. 2. Cu-BTA complex chemisorbed on the Cu surface as postulated by Cotton [18].

copper metal through the surface film. Cuprous ions, once transferred through the surface film, react with physisorbed BTAH molecules and form an insoluble polymeric complex. Thus, in corrosive medium or under anodic polarization, in which the amount of Cu(I) ions is higher than that from, for example, Cu immersed in distilled water, much thicker Cu(I)BTA films were observed. Change in the exposure time, temperature, pH and BTAH concentration did not affect the structure of the Cu(I)BTA complex, as shown by the IR spectra. Poling [23] suggested that the inhibitory effectiveness, IE, of the Cu(I)BTA layer increases with increasing thickness. It was proposed that the Cu(I)BTA surface film inhibits hydrogen evolution more effectively than the reduction of O_2, which was later supported [24–26] but differed from the previous investigation [19].

Morito and Suëtaka [27–29] proposed a pH-dependent mechanism for the corrosion of Cu in 3% NaCl solution containing BTAH, Eq. (10). It was based on the reduced ionization of copper atoms at the interface copper-surface film, due to the formed Cu(I)BTA complex [28]. This mechanism was later completed by Youda et al. [30] by including the potential dependence. Morito and Suëtaka suggested that the plane of the Cu(I)BTA surface complex is aligned parallel to the Cu surface [27] and that the Cu protection is based on the formation of a Cu(I)BTA surface film and not due to a film of chemisorbed BTAH [29].

$$Cu(I) + BTAH \leftrightharpoons Cu(I)BTA + H^+ \qquad (10)$$

Mansfeld et al. [31] found that BTAH is an excellent inhibitor for Cu immersed in 5% NaCl solution only when present in the solution during the course of the experiment, but was ineffective in preventing corrosion when the specimen was only dipped into the inhibitor containing solution and later exposed to 5% NaCl. These results were not in agreement with previous observations reported by Dugdale and Cotton [19] and later by Walker [7] and by Hollander and May [32]. Based on ellipsometry results, Mansfeld et al. [33] concluded that BTAH chemisorbs only on a copper surface covered with oxides (Morito and Suëtaka excluded chemisorption [29]). This chemisorbed layer then prevents corrosion by blocking adsorption of oxygen.

Roberts [34] confirmed that the nature of copper oxide substrates (Cu_2O or CuO) influences the adsorption of BTAH, which forms multilayer films. The adsorption was fast on Cu_2O and very slow on CuO. It was proposed that, after Cu(I)BTA forms on the Cu_2O substrate in water solution at the elevated temperature (60 °C), it gradually oxidizes to Cu(II)-BTAH. This was the first suggestion that a Cu(II)-BTAH surface complex is formed. The structure of the Cu(II)-BTAH complex may differ depending on the substrate (Cu_2O or CuO). Subsequent studies revealed, however, that the formation of the Cu(II)-BTAH complex was not due to partial oxidation of Cu(I)BTA film but due to the atmospheric oxidation of the sample during the transfer to the spectrometer [35–37].

3. Surface structure and composition of the BTAH treated Cu

Chadwick and Hashemi [35,36] showed that the Cu(I)BTA complex, whether adsorbed on the Cu surface or synthesized as a Cu(I)BTA crystal, is unstable when exposed to air and starts to oxidize to Cu(II)BTA. In contrast to the previous observations of Roberts [34], only Cu(I)BTA complex was formed during longer immersion in acidic chloride solution. Cu(II) species were formed only after removal from the liquid phase. Based on X-ray Photoelectron Spectroscopy (XPS) depth profiling, it was suggested that either oxygen or water molecules could be involved in this surface complex. Alternatively, it was suggested that BTAH may be sandwiched between the Cu_2O layers.

Similarly, using XPS, Fox et al. [37] observed that only Cu(I)BTA is formed on Cu_2O substrate, and not mixed Cu(I)BTA/Cu(II)BTA complexes. Our recent work also showed that no Cu(II) species are formed by immersion of Cu in BTAH solution containing 3% NaCl [38]. Fox et al. [37] suggested that the synthesized Cu(II)BTA complex comprised incorporated hydroxides or water, similar to the proposal of Cotton and Scholes [20]. The centre of the N 1s XPS peak of the synthesized Cu(II)BTA complex was shifted by 1 eV to lower binding energy (*BE*) than that of the Cu(I)BTA structure formed on Cu_2O in solution. This shift indicated an increased electron density on the valence orbitals of the N atoms in the former complex. The thickness of the Cu(I)BTA surface film on Cu was between 1 and 3 nm [39], in accordance with Ref. [34].

The investigation of the film composition was continued by Hashemi and Hogarth [3] who used Auger Cu LMM and XPS signals to characterize the BTAH treated Cu_2O substrate. A new feature was recognized in Cu LMM spectra located at 4.0 eV and 1.4 eV higher binding energies than for the peaks for Cu and Cu_2O, respectively. For the Cu(I)BTA surface complex the full width at half maximum, FWHM, of the XPS N 1s peak was significantly narrower than for pure BTAH (2.7 eV in contrast to 6.1 eV), but located at higher *BE* in the case of the Cu(I)BTA surface complex. A narrow N 1s peak indicated that the charge is evenly distributed by the conjugated π structure delocalized over the three N atoms in the complex, thus implying a similar chemical environment. The adsorption of BTAH on an oxide-free copper surface was said to be either unlikely, or to occur by the formation of an extremely thin layer of the complex, consistent with the work of Poling [23]. Hashemi and Hoghart [3] performed synthesis of crystals in KCl aqueous solution containing CuCl and BTAH, which resulted in the formation of a complex with the ratio Cu:Cl:BTA of 2:1:1, suggesting a new structure different from the one described earlier [18,20,23]. A structure was proposed with copper in the monovalent state and coordination number of 2, with chlorine bridging [40] (Fig. 3). The authors believed that the formation of the Cu_2Cl–BTA surface complex was related to the existence of the CuCl interlayer.

In the case of BTAH adsorption on copper oxides, Roberts [34], using XPS, revealed that the Cu(I)BTA surface structure contained nitrogen with the N 1s peak located at a similar binding energy but narrower than that in pure BTAH (a shift was noted by Hashemi and Hogarth [3]). Fig. 4 shows the tautomery of BTAH. Due to the different environments of N atoms, three distinct peaks (deconvoluted) are expected in the high resolution N 1s XPS spectra for the left tautomeric form and two peaks in the case of the right tautomeric form. Moreover, BTAH, as a nitrogen-containing molecule, is considered to be an electron donating ligand. Coordi-
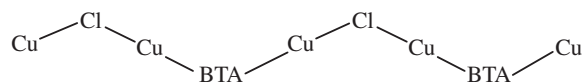
Fig. 3. Cu(I)-Cl-BTA structure formed in chloride media as proposed by Hashemi and Hogarth [3].
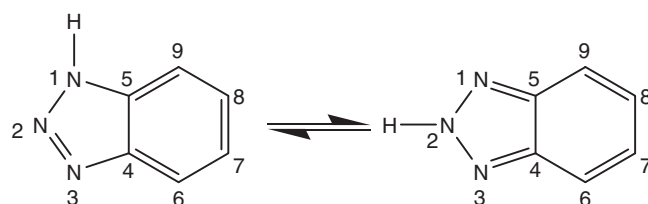
Fig. 4. BTAH tautomeric forms.

nation of copper ions by N1 and N3 of BTAH is therefore likely to decrease the electron density on the Cu-bonded N atoms relative to the N atoms of the free ligand, which causes a shift of the XPS N 1s peak to higher *BE* (if the surface structure corresponds to the one proposed by Cotton and Scholes [20]). However, Roberts [34] observed only a narrower N 1s peak in the case of surface structure compared to the pure BTAH, but not a significant shift in *BE*. Since the common coordination of Cu(I) ion is four in the tetrahedral array [41], Roberts suggested that for the first BTAH layer on the Cu$_2$O substrate, Cu(I) ions could be connected by two bonds to the two oxygen atoms in the Cu$_2$O lattice, and the remaining two to the deprotonated BTAH molecules. A structure according to the proposal of Roberts is given in Fig. 5.

Kester et al. [42] were the first to use Surface Enhanced Raman Scattering (SERS) to study the structure of adsorbed BTAH on the Cu surface. Direct evidence was obtained for a Cu-BTAH connection, and the authors proposed that the first monolayer of BTAH on Cu is not polymerized. The advantage of SERS, compared to other *in situ* vibrational spectroscopic techniques, is the possibility of obtaining useful information in the low-frequency region. It also solves the problem of strong absorption of light in aqueous systems, in contrast to IR spectroscopy. However, intense spectra from organic adsorbates can be obtained only on roughed surfaces of noble metals [43]. Rubim et al. [44,45] also employed SERS to study the interaction of BTAH on Cu surfaces. They proposed an improved Cu(I)BTA model [44] based on the structure proposed by Cotton [20] (Fig. 6). In this model the π-electrons of the 5- and 6-membered rings are completely delocalized and the N1 and N3 atoms are equivalent. Formation of a Cu–N bond was explained by overlapping of the Cu sp-hybrid atomic orbital with the N-hybridized lone-pair atomic orbitals. SERS spectra obtained for the Cu treated with a solution containing 5 mM BTAH and 0.1 M KCl were similar to the Raman spectrum of the synthesized [Cu(I)BTA]$_n$ complex, indicating that the latter structure was formed on the Cu surface. At potentials more negative than –0.4 V *vs.* SCE and the addition of HCl (1 mM) to this medium led to the formation of a proposed new structure on the Cu surface, [Cu(I)Cl(BTAH)]$_4$. Da Costa et al. [45] distinguished [Cu(I)BTA]$_n$ from [Cu(I)Cl(BTAH)]$_4$ based on their characteristic bands in Raman spectra at 1020 cm^{-1} and 1050 cm^{-1}.

Ito and Takahashi [46] claimed that the structure of the film grown on BTAH treated Cu in methanol solution containing CuCl is similar to that of the Cu$_2$Cl$_6$(BTA)$_6$ complex. They suggested that this structure could be closely related to the films formed on Cu surfaces in aqueous solutions.

BTAH is persistent once adsorbed on Cu surfaces and subsequently exposed to simulated cooling water conditions, i.e. dynamic flowing systems, as demonstrated by Hollander and May [32] (consistent with Refs. [7,19], but in disagreement with Ref. [31]). For the Cu(I)BTA surface complex, the authors [32] proposed
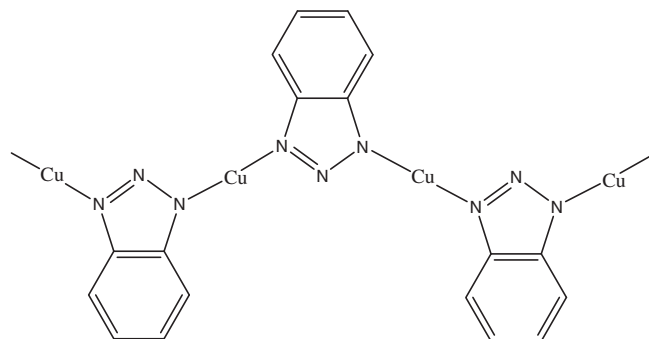
Fig. 6. An improved Cu-BTA complex (postulated by Cotton [18]) proposed by Rubim et al. [44].

a model involving d-π* interactions between Cu(I) ions and the triazole ring, the plane of the BTAH molecule being parallel to the metal. This model was in agreement with that of Morito and Suëtaka [27], but strongly contradicted in subsequent studies [11,12]. Ten years later, d–π* bonding between Cu(I) and benzotriazole anion was again suggested by Johnson and Lu [47]. In contrast with the previous hypothesis [32], however, they suggested that bonding is through the carbon rather than the nitrogen ring of the benzotriazole anion. Hollander and May [32] also studied reactions between chlorine and BTAH or Cu(I)BTA. Chlorine reacted with BTAH forming 4,5,6,7-tetrachlorobenzotriazole, but not with the Cu(I)BTA surface complex.

Quite different BTAH bonding for the very first chemisorbed layer was proposed by Fang et al. [11]. However, BTAH adsorption was performed by vapour deposition in the absence of hydrated Cu(I) ions on the surface, which may be the cause for the difference. They claimed that copper oxides do not play an important role in the bonding of the vapour-deposited BTAH. The first chemisorbed BTAH layer was proposed to be connected to the copper or copper oxide surface through the nitrogen lone pairs (Fig. 7). Moreover, no proton removal from the N1-H group of the BTAH molecule was proposed, in contrast to [2,12,20,23,48]. It was suggested that BTAH is oriented almost perpendicular to the surface and stabilized by hydrogen bonding between N1 of the BTAH molecule and H5 of the next one. However, this kind of hydrogen bonding is expected to be extremely weak [49]. The distance between N1 and H5 on adjacent BTAH molecules would then be only 0.7 Å, which is impossible. To overcome this problem, the authors proposed an alternative tilting of molecules by 9° above and below the plane (Fig. 7 and Fig. 8), thus resulting in the distance of 1.2 Å. This structure is presented in Fig. 8 and was constructed using XCrySDen software developed in our group [50].

Similarly to Fang et al. [11], Nilsson et al. [12] introduced BTAH onto sputter-cleaned Cu and onto cuprous oxide surfaces by ther-
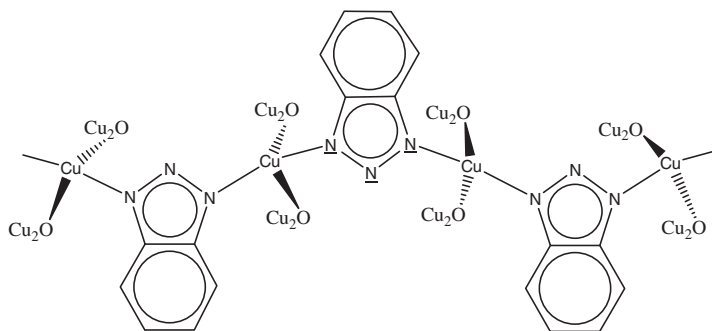
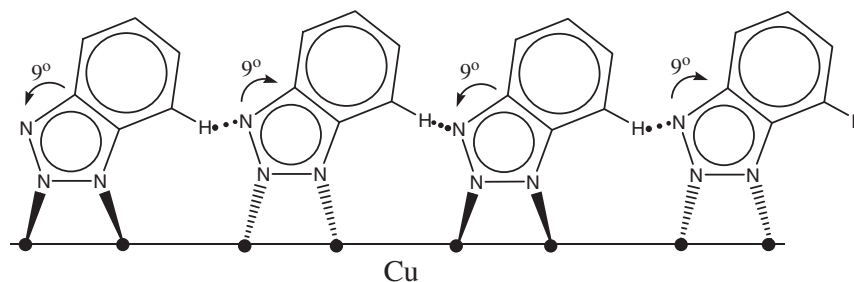**Fig. 5.** Cu(I)BTA structure on Cu$_2$O as proposed by Roberts [34].

Fig. 7. Structure of the first chemisorbed layer, proposed by Fang et al. [11].
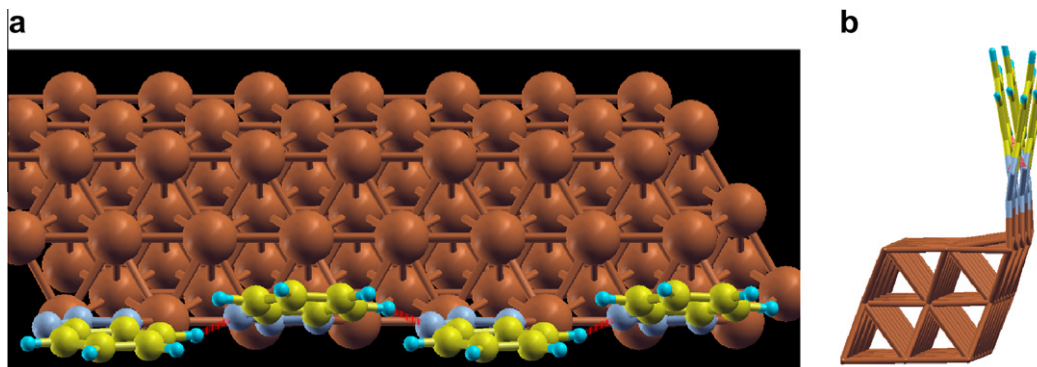

Fig. 8. Fang model [11]: a) top and b) side view. Copper is brown, carbon is yellow, nitrogen is violet, hydrogen is blue and hydrogen bond is red. Pictures were constructed by XCrySDen software [50].

mal evaporation. The investigation was based on XPS and IR measurements. The thickness of the BTAH layer formed was smaller on the clean copper substrate than on the copper oxides (the same trend as for the treatment in solution [3,36]). The XPS N 1s peak shifted to the high *BE* side in the case of the bulk BTAH, in contrast to the BTAH adsorbed on Cu or Cu_2O. This result differed from that reported by Hashemi and Hogarth [3], as explained above. Nilsson et al. [12] showed that the triazole ring is pointed towards the Cu/Cu_2O surface. The presence of BTA⁻ instead of molecular BTAH in the synthesized Cu(I)BTA complex and in the structure formed on the Cu surface was confirmed by IR spectroscopy (as in Refs. [23,44,51]). The authors suggested that BTAH is neither lying on nor perpendicular to the surface, but it is somehow tilted in between these two orientations.

Xue and Ding [52] studied the adsorption mechanism of BTAH on Cu in acetate-buffered solution (pH 6). They claimed that different surface films are formed, depending on whether the Cu sample is immersed in stagnant or dynamic solution. Under stationary conditions, adsorption rather than complex formation was suggested, whereas under dynamic conditions the formation of mixed Cu(I)BTA and Cu(II)(BTA)$_2$ polymeric complexes was proposed. The proposed structure of the Cu(II)(BTA)$_2$ complex is shown in Fig. 9.

Brusic et al. [2] used ellipsometry to observe different growth kinetics of BTAH on Cu within the single adsorption process that could indicate the formation of at least two different structures. A possible explanation is the adsorption of molecular BTAH forming the first chemisorbed layer, with subsequent loading of the Cu(I)BTA complex on top. By employing Time of Flight Secondary ion mass spectrometry (TOF-SIMS), they proved the existence of the Cu(I)BTA surface polymer complex, thus providing direct evidence of its formation.

The formation of two BTA⁻ forms in the surface polymer was proposed by Carron et al. [53], based on the shoulder of the band at 780 cm⁻¹ in the SER spectrum. The ratio between these two forms was suggested to be 1:3, comprising a nearly planar array
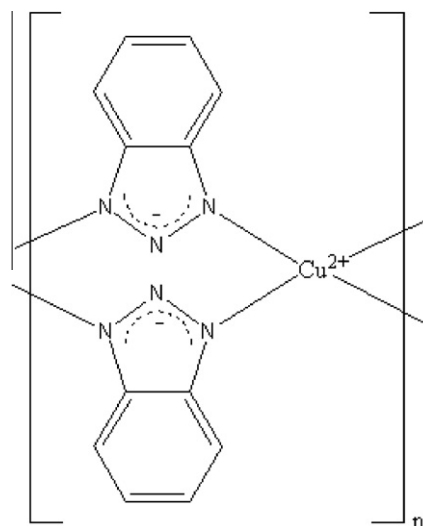

Fig. 9. Cu(II)(BTA)$_2$ structure proposed by Xue and Ding [52].

of BTA⁻ bonded to a copper through each of its nitrogen atoms. These structures are bridged with the second BTA⁻ form, which serves as the connection for the subsequent parallel layers. Therefore, copper possesses a disordered tetrahedral coordination, which is common for Cu(I)-complexes [41]. Even though the proposed structure has not been confirmed analytically, it could explain the controversy between the previous and subsequent studies, in which perpendicular or parallel orientation was observed.

Ling et al. [54] examined adsorption of BTAH on Cu in aerated H_2SO_4 solution at pH 1 and 2. They proposed initial BTA⁻ adsorption on the positively charged Cu_2O surface by electrostatic interaction, followed by formation of the Cu(I)BTA complex. The authors

claimed that after the initial stage, continuous growth of the complex occurs in the direction to the bulk solution and is controlled by the diffusion of Cu(I) ions from the Cu₂O surface. The suggested surface structure is given in Fig. 10. It appears that the authors did not take into account the instability of Cu_2O in acidic solutions [2].

In the 1990s the development of surface sensitive techniques such as AFM (Atomic Force Microscopy) and STM (Scanning Tunneling Microscopy) was important in revealing the details of BTAH action as a corrosion inhibitor [55–62]. Using ex-situ STM, Cho et al. [56,57] showed that BTAH adsorption can take place on an oxide-free Cu(1 1 0) surface, forming a well-oriented superstructure corresponding to the flat adsorption scheme with π-d interactions (in agreement with [27,32,47], but contradictory to [11,12]). A distance between BTAH molecules of 6.2 Å was reported. BTAH adsorption was significantly greater on oxidized Cu(1 1 0) than on oxide-free surfaces, and formed a random amorphous-like structure. Later, a new adsorption mechanism on Cu(1 1 0) was proposed involving at least two structures [58]. BTAH molecules in the first adsorption layer lie flat on the surface while the second layer is polymerized, with BTAH standing vertically. These findings could confirm the observation made earlier by Kester et al. [42] about the first layer not being polymerized.

Vogt et al. [59,60] were the first to report an in situ STM study of BTAH adsorption on Cu(1 0 0) in sulphate [59] and chloride [60] med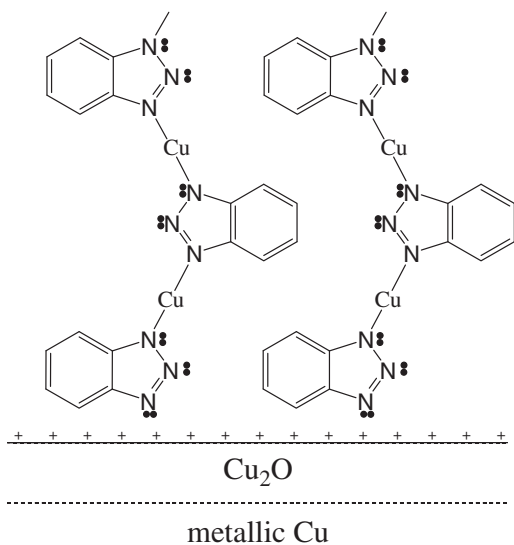ia. Three surface structures were observed. At low electrode potentials, a flat adsorption geometry of the BTAH molecules was observed, followed by parallel stacking of BTAH molecules to form chain-like structures, with the molecular plane perpendicular or slightly tilted with respect to the surface. This fits well with the results of the investigation of Park et al. [58], who suggested that at least two BTAH surface structures exist. A third structure of Cu(I)BTA complex, with poor electrical conductivity and large thickness, was observed at more positive potentials. It was next found [61] that anodic dissolution of Cu(1 1 1) in pure H_2SO_4 solution containing 10 mM BTAH led to the formation of parallel chain-like structures with a distance of ~4 Å between neighbouring BTAH molecules along the chain.

Using the near-edge X-ray absorption fine structure (NEXAFS) technique, in combination with ab initio calculations, Walsh et al. [63] studied the orientation of BTAH molecules on the Cu(1 0 0) surface. At sub-monolayer coverage they proposed a 75° tilt of the BTAH molecular plane relative to the substrate plane and, at multilayer coverage, a 40° tilt angle. Based on the results reported by Walsh et al. [63], we constructed the model. At low coverage, three structural models were envisaged (Fig. 11). One (A), two (B) or three (C) N atoms are involved in the adsorption process. In model C the terminal N is bound to the second Cu layer and the other two N atoms to the first Cu layer (an "arrowhead" type of bonding). Regarding the crystal structure proposed by Escande et al. [64] and assuming that Cu atom rearrangement of the substrate at room temperature is possible [65], the authors proposed that model C could be the binding centre of the whole Cu-BTA complex.

Based on electrochemical [66,67] and surface analytical [38] studies, combined with calculations based on density functional theory (DFT) [67], we recently proposed a tentative model for the first layer formed on a Cu surface immersed in 3% NaCl solution containing BTAH (Fig. 12). In this model the molecular structure is planar, which is suitable for intermolecular bond formation (e.g. H-bonds or BTA–Cu–BTA). Electrochemically synthesized Cu-BTAH structures were amorphous [66]. However, using XPS we observed that BTAH molecules on the Cu surface (either in the Cu(I)BTA complex or in the molecular form) were directed toward the Cu surface through triazole N atoms, and we proposed that the very first layer could be the molecular form of BTAH (uncomplexed) [38].

4. Mechanism of benzotriazole inhibition

Evans [68] sought to explain the inhibition by BTAH in chloride solutions by the formation of basic copper chloride on the Cu surface that interacts with BTAH molecules. This blocking substance would thus be responsible for the high degree of inhibition.

Fig. 10. Adsorption of Cu(I)BTA complex on the Cu₂O under-layer as proposed by Ling et al. [54].
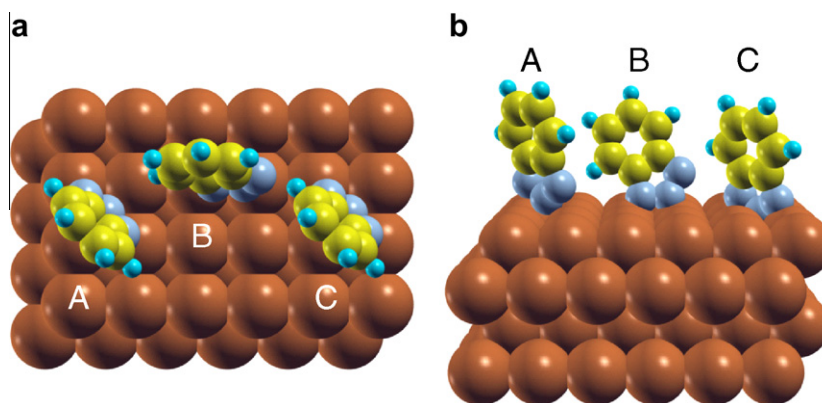

Fig. 11. Orientation at sub-monolayer coverage as predicted by Walsh et al. [63] (tilt angle of 75°). a) top-view and b) side-view. Pictures were constructed by XCrySDen software [50].
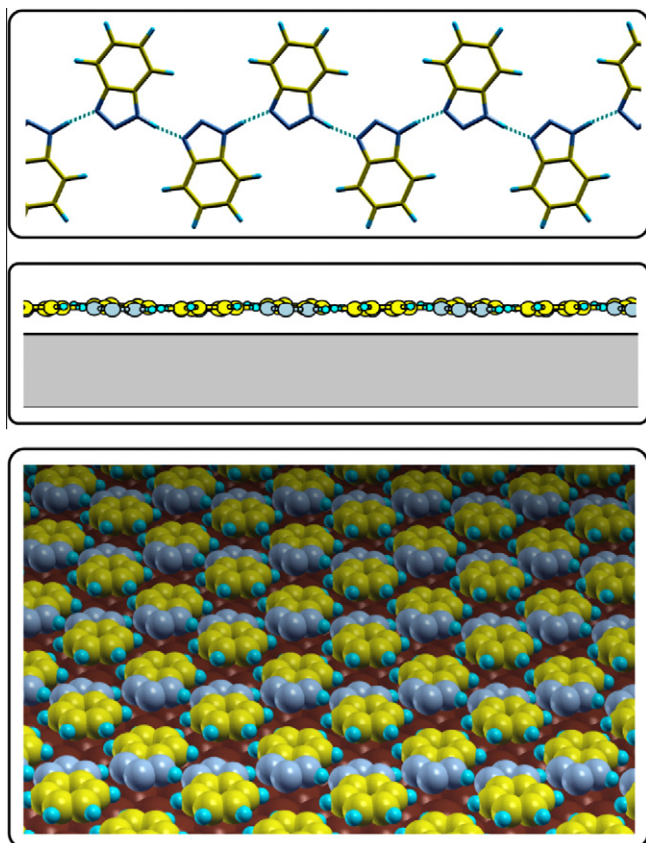
Fig. 12. Tentative model of BTAH adsorbed on Cu surface [38].

According to this theory BTAH would not be effective in other solutions, or the mechanism for corrosion inhibition should change when chlorides are not present.

Ogle and Poling [69] classified the formation of naturally growing thin and thick Cu(I)BTA films according to the pH limit (pH$_L$), which they found to be $4 > pH_L > 3.5$. In near neutral pH solution (above pH$_L$) a thin compact multilayer of Cu(I)BTA was formed on top of the Cu$_2$O interlayer. In more acidic environments, in which Cu$_2$O is unstable (pH < 3.5), a thick film of acicular Cu(I)BTA crystallites grew on the surface. Pretreatment of Cu by anodic film growth in the presence of BTAH resulted in the formation of a Cu(I)BTA film that was more compact than those naturally grown, but the inhibitory effectiveness of those films did not differ significantly. It was claimed that the Cu(I)BTA surface film acts as a physical barrier to the inward diffusion of aggressive ions. Notoya and Poling [70] demonstrated the surface topographies of the Cu-BTAH films adsorbed on Cu$_2$O under-layer with different thicknesses. Cu-BTAH crystallites were formed on both thin and thick Cu$_2$O substrates, but the structure was different. On thin Cu$_2$O substrates ($\sim$20 Å) crystallites adopt star-like structures composed of large needle-like crystallites, whereas on thick Cu$_2$O substrates ($\sim$1700 Å) finer and denser crystallites were formed. The latter structure was more protective. The thickness and IE increased with increasing the temperature of the film formation process, reaching 98.7% for structures formed at 100 °C in 3% NaCl solution containing 20 mM BTAH [71]. The higher IE obtained at higher temperature was ascribed to the reduced number of defect sites within the protective film.

By using electrochemical impedance spectroscopy (EIS), Lewis [72] studied the adsorption of BTAH on a Cu$_2$O covered Cu surface in 0.51 M NaCl. He suggested that adsorption of BTAH is under mixed control, by the diffusion of the molecule in solution and by its heterogeneous adsorption onto the surface. In his subsequent work, Lewis [73] examined adsorption isotherms of BTAH in 0.2 M NH$_4$Cl by employing a weight-loss test (calculation of relative surface coverage according to Eq. (11), where ΔW and ΔW_0 stand for the mass changes of Cu immersed in inhibited and uninhibited solutions, respectively).

$$\theta = 1 - \frac{\Delta W}{\Delta W_0} \qquad (11)$$

A sigmoidal-shaped adsorption isotherm (surface coverage vs. concentration) was found and the experimental results were best fitted using the Frumkin isotherm. On that basis, chemisorption of the organics was proposed, which agrees with Mansfeld et al. [33], but not with Morito and Suëtaka [29]. Since the surface coverage achieved a constant value above a concentration of 0.01 M, he proposed that this concentration is the limit for the transition from chemisorption (molecular adsorption) to the complex formation mechanism. This concentration limit was quite close to the 7.5×10^{-3} M previously found by Mayanna and Setty [74] in 0.1 N H$_2$SO$_4$ solution.

Pergola et al. [75] and Foresti et al. [76], employing polarography and chronocoulometry, studied the oxidation of copper on a dipping amalgam electrode in perchloride solutions containing BTAH. They showed the presence of an adsorbed [–Cu(I)–BTA$^-$]$_n$ film on the electrode surface, which was formed by electro-reduction of Cu(II) ions or electro-oxidation of Cu(0)(Hg). The authors claimed that this film consists of a polymeric chain in zigzag disposition, with the BTA$^-$–Cu–BTA$^-$ bond angle, regarding both BTA$^-$ molecules, deviating slightly from 180° [75]. McCrory-Joy and Rosamilia [77], employing cyclic voltammetry (CV) and chronocoulometry, studied the adsorption of BTAH on the Cu electrode. They reported that, at sufficiently positive or negative potentials relative to the metal's potential of zero charge (PZC), neutral BTAH molecules are replaced by more polar water molecules oriented approximately at the charged electrode surface. It is generally believed that maximum adsorption of organics occurs at the PZC. According to most data in the literature, PZC for Cu ranges from –0.15 to –0.3 V vs. SCE [78].

Heakal and Haruyama [79] carried out an electrochemical study in 3% NaCl solution. They showed that the Cu-BTAH film acts primarily as an anodic inhibitor. Using EIS they demonstrated that this surface film has a dielectric character with a dielectric constant of around 20. They also found that the Cu-BTAH film thickness increased asymptotically with time in the first 1000 min. From a study of BTAH action on different brasses in aerated and de-aerated H$_2$SO$_4$ solution, Da Costa et al. [80] concluded that BTAH adsorption constant increases with increasing copper content in the alloy.

Youda et al. [51] confirmed a surface complex previously proposed by Rubim et al. [44]. However, they stated that this complex is formed only in neutral or acidic solution at potentials more positive than –0.3 V vs. SCE. On the other hand, in acidic sulphate solution at potentials more negative than –0.3 V vs. SCE, they proposed that BTAH molecules adsorb to the Cu surface by the coordination of the lone pair electrons of the triazole nitrogen atom, without forming a complex polymer. Using SERS, on the basis of the deuteration induced shift, they postulated a band at 1140 cm^{-1} to a δ(N–H) in-plane bending mode of the molecular BTAH adsorbed on the Cu. In the following work [30] they found the BTAH adsorption to be pH dependent. Those results suggested an equilibrium between the adsorption and the complex formation according to Eq. (12):

$$n(BTAH)_{ads} + nCu \leftrightarrows [Cu(BTA)]_n + nH^+ + ne^- \qquad (12)$$
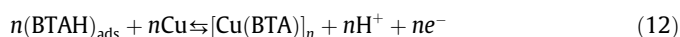
It was deduced that the complex formation is unfavourable at low BTAH concentration because of decrease of the (BTAH)$_{ads}$ parameter. Moreover, as seen from Eq. (12), at low pH and negative potential, adsorption rather than complex formation would occur. Equation (12) is basically an improved form of Eq. (10) developed by Morito and Suëtaka [28], that includes potential dependence. These findings were later confirmed by Hope et al. [81]. Moreover, the potential limit for the transition adsorption/complex formation in sulphate solution at pH greater than 2, determined by Chan and Weaver [82], was 0.1 V more positive than that determined by Youda et al. [51]. Moretti et al. [83] determined this potential limit at −0.2 V *vs*. SCE in H$_2$SO$_4$ at pH 1.7. The equilibrium in Eq. (12) could thus explain the major disagreement between different research groups as to whether molecular adsorption or polymeric complex formation takes place.

Alkire and Cangellari [84] studied the mechanism of Cu dissolution in the presence of BTAH in 1 N H$_2$SO$_4$ by rotating disc electrode. They suggested that a dual layer forms on the surface, with a thin inner, highly resistive barrier layer and an outer porous Cu(I)BTA complex layer. This could confirm the previous observation made by Kester et al. [42] that the first adsorbed layer is not polymerized and is thus different from the outer layer. Moreover, this would also confirm the theory of Fang et al. [11], who claimed that the very first chemisorbed layer is in fact composed of BTAH in molecular form.

Infrared–visible sum frequency generation spectroscopy (SFG) was used by Schultz et al. [85] to investigate adsorption of BTAH on Cu(1 0 0) and Cu(1 1 1) surfaces in acidic solution. They showed that BTAH (as BTA⁻) is in well-oriented mode on Cu(1 0 0) over a wide potential range. However, structural rearrangements, caused by sweeping the potential in the anodic direction, had been observed previously [30,51,82,83, 86]. The discrepancy could arise because latter authors used a polycrystalline Cu substrate. In contrast to Cu(1 0 0), Schultz et al. [85] showed that BTAH molecules are disordered on Cu(1 1 1) surface at negative potentials. The ability of Cu(1 0 0) to retain a more ordered ad-layer could explain why it is more resistant to corrosion in BTAH containing solutions than Cu(1 1 1) [59–61,74].

Theoretical calculations made by Jiang and Adams [87], using first principle density functional theory (DFT), pointed out that physisorption (<0.1 eV) or weak chemisorption (∼0.43 eV) of BTAH on Cu(1 1 1) can take place and that chemical bonds are formed through nitrogen sp^2 lone pairs. The authors excluded the option that the driving force for the BTAH polymerization can be via C–H···N hydrogen bonding, and thus discarded the model proposed by Fang et al. [11].
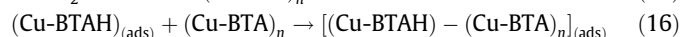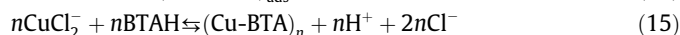
The effect of the applied potential on the adsorption process on phosphorous-deoxidized (DHP) [88] and oxide-free dehydrated (OF-HC) [89] copper surfaces in Na$_2$SO$_4$ solution has been studied by Mansikkamäki et al., using scanning electrochemical microscopy (SECM) [88,89]. As in previous studies [30,51,83, 90], SECM results confirmed that the formation of insulating Cu(I)BTA films is faster at more positive potentials, at which thicker layers are

formed. This can be accounted for by the level of disposable Cu(I) ions, which increases at more positive potentials [23]. In their next work [91] they showed that dissolved oxygen plays a crucial role in Cu(I)BTA film formation. The importance of oxygen was emphasized also by Xue et al. [92]. They suggest that copper immersed in a medium that is in contact with air, adsorbs O$_2$ ((Cu)O$_2$(ads)). This co-adsorbed oxygen has more basic and oxidizing properties than oxygen in the air or dissolved in the solution [93]. With the aim of co-adsorbed O$_2$, Cu is oxidized to Cu(I) and BTAH is deprotonated to BTA⁻, leading to the formation of Cu(I)BTA complex. The proposed mechanism is depicted in Fig. 13. When the same solution was purged with N$_2$, the reaction did not take place. In contrast to other authors [2,3,12,20,23,33–36,57], Xue et al. [92] claimed that BTAH reacts with clean Cu much faster and forms a more protective layer than a surface covered with copper oxides. Thus, according to this theory dissolved oxygen is responsible for the Cu(I)BTA complex formation. Chan and Weaver [82] also claimed that the presence of O$_2$ molecules are required for complex formation in both aqueous and damp environments (Eq. (13)).

$$4Cu + 4BTAH_{(ads)} + O_2 \leftrightarrows 4Cu(I)BTA + 2H_2O \quad (13)$$

Metikoš-Huković et al. [4,94] studied BTAH adsorption phenomena on Cu in sodium acetate solutions at pH 5.8 and 10.0. At 1–5 mM BTAH concentration and immersion time 30–180 min, the diffusion coefficient and concentration of Cu(I) mobile species in the Cu(I)BTA ad-layer were of the order of 10^{-14} cm s^{-1} and 10^{-6} mol cm^{-3}. At low BTAH concentrations (<0.5 mM), the adsorption followed the Flory–Huggins isotherm [94]. It was suggested that BTAH forms a multilayer structure of Cu/Cu$_2$O–Cu(I)BTA on the Cu electrode surface (pH 5.8), but only when the concentration of the inhibitor exceeds 1 mM. At lower concentrations, chemical adsorption of the BTAH molecules was proposed [95]. These findings fitted the theory put forward by Youda et al. [30].

Tromans and Sun [16] showed that a Cu-BTA protective layer can be formed on a metallic oxide-free copper surface in chloride solution containing BTAH. Based on electrochemical experiments they proposed the following mechanism of inhibition:

$$Cu + BTAH \rightarrow (Cu-BTAH)_{ads} \quad (14)$$

$$nCuCl_2^- + nBTAH \leftrightarrows (Cu-BTA)_n + nH^+ + 2nCl^- \quad (15)$$

$$(Cu-BTAH)_{(ads)} + (Cu-BTA)_n \rightarrow [(Cu-BTAH) - (Cu-BTA)_n]_{(ads)} \quad (16)$$

The adsorption of BTAH in Eq. (14) was time and potential dependent. The interaction between BTAH and Cu was fastest at 40 mV vs. SCE, being completed in less than 20s. This potential was related to the potential of zero charge, PZC, where organic molecules are readily adsorbed [77]. The Cu-BTA complex is formed in the diffusion layer from CuCl$_2^-$ (Eq. (15)). When it is adsorbed on the initial (Cu-BTAH)ads monolayer on the Cu surface (Eq. (16)), it forms a polymeric film. Evans [68] also claimed that chlorides are required for the formation of a protective layer. The fact that the BTAH was effective Cu corrosion inhibitor at pH > 3, but not at pH 1 [16], indicated that solubility of the Cu-BTA film in-
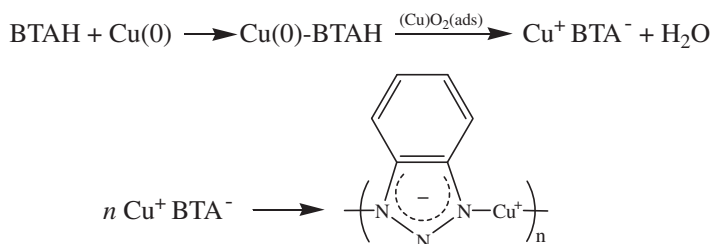

Fig. 13. Mechanism of formation of Cu(I)BTA complex proposed by Xue et al. [92].

creased at higher proton concentrations (Eq. (15)). Tromans [96] constructed E–pH diagrams for the Cu–BTAH–H$_2$O and Cu–BTAH–Cl–H$_2$O systems to indicate the stability region of Cu-BTA films. Thermodynamic predictions were consistent with findings of corrosion inhibition performance at different pHs and applied potentials. Similarly to Tromans and Sun [16], Modestov et al. [97] proposed a reversible mechanism of BTAH action on Cu in chloride media, according to Eqs. (17) and (18). At the early stage, the growth of a Cu-BTA film is controlled by the diffusion of CuCl$_2^-$ into the pores of the film. This reaction is accompanied by the formation of a Cu$_2$O under-layer. Later, the film growth is controlled by the volume diffusion of Cu(I) ions through the film. The enhanced corrosion resistance of Cu in the presence of BTAH was attributed to the stabilizing action and maintenance of purity of the Cu$_2$O by the Cu-BTA over-layer (like a membrane) and not because of the Cu-BTA action alone. They claimed that this surface film prevents the doping of Cu$_2$O by Cl$^-$ ions that leads to solid CuCl formation.

$$Cu^0 + 2Cl^- - e^- \leftrightarrows CuCl_2^- \tag{17}$$

$$CuCl_2^- + BTAH \leftrightarrows Cu\text{-}BTA + 2Cl^- + H^+ \tag{18}$$
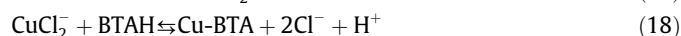
Vogt et al. [59,60] suggested the following mechanism of inhibition in chloride media. At $E < -0.6$ V vs. SCE, BTAH is adsorbed to the surface; at -0.6 V $< E < -0.35$ V BTAH molecules are replaced by chloride ions; at $E > -0.35$ V CuCl$_2^-$ is formed that reacts with BTAH in the solution to form Cu(I)BTA, thus covering the electrode surface. This mechanism agrees well with the results of Tromans and Sun [16] and Modestov et al. [97]. In BTAH-containing H$_2$SO$_4$ solution, however, the chemisorbed BTAH ad-layer is transformed directly to Cu(I)BTA complex by increasing the electrode potential [60]. The differences in mechanisms of inhibition account for the lower inhibitory effectiveness in chloride than in sulphate solutions.
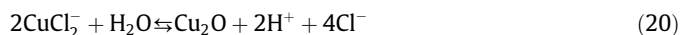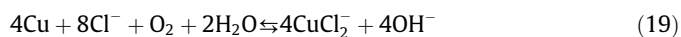
Cao et al. [86] also proposed that the structure of the Cu(I)BTA film formed in 0.1 M KCl is potential dependent. At negative potentials the [Cu(I)BTA]$_n$ polymeric film was remodelled to a [Cu(I)BTAH]$_4$ structure. Therefore the coordinated BTA$^-$ anion may take up a proton. It was explained that the source of H$^+$ ions increases at lower potentials, leading to the diffusion of protons towards the electrode and consequently to decomposition of the polymer [Cu(I)BTA]$_n$ and formation of [Cu(I)BTAH]$_4$. On the contrary, BTAH adsorption at negative electrode potential in the molecular (uncomplexed) form, rather than remodelled complex formation, has been proposed by other authors [30,51,82,83].

In alkaline KOH solution at pH 12, BTAH adsorbed on oxide-free Cu(0), Cu$_2$O and CuO surfaces [98]. A logarithmic thickness vs. time relationship was found in the initial stages of BTAH adsorption on Cu$_2$O and CuO, which supported a previous investigation [28]. The thinnest film was formed on the Cu(0) (limited to 5–7 Å), a slightly larger thickness on CuO, while thicker films had been established on Cu$_2$O. Presumably a single monolayer, and not a Cu-BTA complex, was formed on the Cu(0) and CuO surfaces by perpendicular or slightly tilted orientation of the BTAH molecules relative to the surface (consistent with Refs. [11,12]).

Xu et al. [48] showed that adsorption was much faster on Cu$_2$O than on CuO. Logarithmic growth kinetics was observed in both cases, similarly to those already reported [28,98]. Using UV transmission methodology, the authors confirmed the existence of BTA$^-$ species in the surface complex adsorbed on the Cu$_2$O surface [12,23,44,51]. From the AES measurements of the Cu$_2$O sample immersed for 120 s in 3.5 mM BTAH/H$_2$O, a surface density of 2.7×10^{14} BTA/cm^2 was established. On the other hand, a higher surface density of $(6.3 \pm 0.2) \times 10^{14}$ BTA/cm^2 was obtained when they performed adsorption in aqueous solution containing 30 mM BTAH [99]. They reported an average BTA$^-$ angle of 62° and this angle was independent of BTA$^-$ surface concentration.

Chen et al. [100] studied the growth kinetics on electroplated Cu in NaCl solution of BTAH at pH 9, using an electrochemical quartz crystal microbalance. In uninhibited medium, a linear mass increment vs. time was found, indicating continuous ion movement through the poorly protective surface film, leading to Cu$_2$O formation. This mechanism was described by Eqs. (19) and (20).

$$4Cu + 8Cl^- + O_2 + 2H_2O \leftrightarrows 4CuCl_2^- + 4OH^- \tag{19}$$

$$2CuCl_2^- + H_2O \leftrightarrows Cu_2O + 2H^+ + 4Cl^- \tag{20}$$

The growth kinetics changed after the addition of BTAH. At low BTAH concentrations (<0.17 mM), a parabolic growth curve was observed whereas, at higher concentrations ($\geqslant 0.17$ mM), growth was logarithmic, in agreement with previous findings [28,48,98]. The dependence of the growth kinetics on BTAH concentration indicates the formation of different surface film structures. At low BTAH concentrations patchy BTAH adsorption was observed, leading to the formation of some CuO on top of the Cu surface, as previously demonstrated [36]. At higher BTAH concentrations this effect was not observed, probably due to the fact that the inhibitor entirely covered the surface [100].

Results relating to the role of surface oxides in BTAH adsorption are controversial. Whereas several research groups concluded that surface oxides are important [2,3,12,20,23,33–37,57], others doubted their role [11,92, 101]. Moreover, we explored the influence of BTAH on the thickness of the Cu$_2$O oxide layer formed on a Cu immersed in 3% NaCl solution by reconstructing the X-ray induced Auger Cu L$_3$M$_{4,5}$M$_{4,5}$ spectra using angle resolved XPS [102]. The spectra were reconstructed with the Monte Carlo algorithm. The relative contributions of Cu, Cu$_2$O and Cu(I)BTA constituents to the composite Cu L$_3$M$_{4,5}$M$_{4,5}$ spectra measured at different emission angles were then used to estimate the thickness of the Cu$_2$O oxide layer. The results showed that the presence of BTAH substantially reduces the thickness of the Cu$_2$O oxide layer formed on Cu in chloride media. The average thickness of the Cu$_2$O layer below the Cu(I)BTA was estimated to be about 1.3 nm, while the Cu$_2$O thickness of the non-inhibited sample was about 2.3 nm.

5. Inhibitory effectiveness of benzotriazole

The effectiveness of inhibition of corrosion by BTAH, using various conditions and procedures, is summarized in Table 1.

Ross and Berry [24] investigated BTAH action on Cu in 10% H$_2$SO$_4$ solution under dynamic conditions. At low flow rates (Reynolds number < 500) they reported maximum IE at 10 mM BTAH. IE was not dependent on aeration of the solution. On the other hand, at higher flow rates (Reynolds number of 10,000) the presence of O$_2$ increased the corrosion rate.

Walker [7] showed that 0.12 g/L BTAH, in medium containing ammonium hydroxide or ferric chloride or hydrogen peroxide, promoted Cu corrosion. However, in these media, when a copper plate was first dipped into a hot aqueous solution of BTAH (5 g/L), the BTAH film formed was effective in preventing corrosion. This was attributed to the reinforcing of the copper oxides by BTAH in the pretreatment solution. On the other hand, corrosion by BTAH was significantly reduced in acetic, hydrochloric, nitric and sulphuric acids, solutions of ammonium or sodium chloride, and solutions with dissolved carbon dioxide and sulphuric dioxide. In addition, BTAH imparted increasing protection for Cu in sulphuric acid as the pH rises (Table 1).

Hobbins and Roberts [103] used ellipsometry to explore differences in thickness and growth rate of surface layers between BTAH and benzimidazole (BIMDA) on Cu/Cu$_2$O substrate in aqueous solu-

Table 1
The inhibitory effectiveness of BTAH against Cu corrosion in various media as a function of pH and treatment procedure.

Medium	Reported pH	BTAH concentration	Special treatment/test conditions	Effective or IE	Reference
3% NaCl	–	NG	Pretreated with BTAH	yes	[19]
3% NaCl	3	20 mM	H_2 purged or air exposed test solution, 26° C	yes	[23]
3% NaCl	3–5.3	20 mM	H_2 or air purged test solution	63–95%	[69]*
3% NaCl	3–5.8	20 mM	Pretreated for 1 or 5 min at various temp.	5.3–98.7	[71]*
5% NaCl	–	1%	BTAH present	yes	[31]
5% NaCl	–	2%, 3%, saturated	if only BTAH pretreated	no	[31]
3% NaCl	3	20 mM	Up to 200° C	yes	[28]
3% NaCl	3	20 mM	Above 250° C	no	[28]
1 M NaCl	1	1 g/L	–	no	[16]*
1 M NaCl	3	1 g/L	–	yes	[16]*
1 M NaCl	6	1 g/L	–	yes	[16]*
3% NaCl	–	0.1–10 mM	–	75.4–89.3%	[67]
0.1 M NaCl	–	0.5 mM	–	93%	[123]
1 M KCl	7	1 mM	Aerated solution	yes	[43]
1 M KCl	2 and 7	1 mM, 10 mM	–	21–98%	[105]
0.1 M KCl	–	0.1 mM	–	70.4%	[86]
10% (w) H_2SO_4	–	10 mM	23–28° C, without O_2	95%	[24]
1 N H_2SO_4	0.3–2.8	up to 16.7 mM	–	yes	[25]
0.1 N H_2SO_4	–	> 7.5 mM	Test at 30° C, IE depended on Cu crystallographic orientation	yes	[74]*
0.5 M H_2SO_4	–	10 mM	N_2 purged test solution	yes	[30,51,124]
0.5 M Na_2SO_4	7	10 mM	N_2 purged test solution	yes	[30,51,124]
1 N H_2SO_4	–	various	Fluid flow test	yes	[84]
0.5 M H_2SO_4	–	0.2 mM	–	yes	[115]
0.5 M H_2SO_4	–	20 mM	–	yes	[55]
0.5 M H_2SO_4	–	10 mM and 20 mM	–	yes	[112]
H_2SO_4	1 and 2	0.01–1 mM	Aerated solution	yes	[54]
0.0667 M Na_2SO_4	–	0.333 mM	DHP Cu or OF-HC Cu substrates	yes	[88,89,91]
0.5 M Na_2SO_4 + 0.05 M H_2SO_4	1.1	5 mM	Test at 23 ±1° C	yes	[116]
0.55 M Na_2SO_4	6.4	5 mM	Test at 23 ±1° C	yes	[116]
0.1 M HCl	–	75 mM	Cu(100) and Cu(111) substrates	yes	[104]
0.1 M H_2SO_4	–	75 mM	Cu(100) and Cu(m) substrates	yes	[104]
0.1 M Na_2SO_4	2.5	> 10^{-6} M	Test at 30° C, OFHC Cu used	yes	[128,129]
0.1 M NaCl	2.5	> 10^{-6} M	Test at 30° C, OFHC Cu used	yes	[128,129]
1 N H_2SO_4 + 3.5% NaCl	–	4.16 mM	–	yes	[26]*
General use	–	0.25% (w)	Pretreated at 60° C for 2 min	yes	[20]
General use	–	2% (w)	Wrapped in BTAH impregnated paper	yes	[20]
Simulated cooling water	7	100 mg/L	Pretreated Cu at 49° C for 48 h, test in recirculating solution	yes	[32]*
Water	–	20–100 ppm	Test in closed circuit	yes	[21]
0.1 N sea water	7.5–8	1 mM	Immersed Cu	100%	[122]*
0.1 N $NaNO_2$	6.5–6.6	1 mM	Immersed Cu	100%	[122]*
0.1 N NaCl	4.8–6.1	1 mM	Immersed Cu	100%	[122]*
0.1 N NH_4Cl	4.7–7.1	1 mM	Immersed Cu	59%	[122]*
0.1 N $(NH_4)_2SO_4$	4.8–5.4	1 mM	Immersed Cu	100%	[122]*
0.1 N NaCN	–	1 mM	Immersed Cu	2%	[122]*
0.1 N CH_3COOH	2.8–3.0	1 mM	Immersed Cu	93%	[122]*
0.1 N $CH_2ClCOOH$	2.1–2.3	1 mM	Immersed Cu	60%	[122]*
0.1 N $CHCl_2COOH$	1.4–1.5	1 mM	Immersed Cu	85%	[122]*
0.1 N CCl_3COOH	1.3–1.6	1 mM	Immersed Cu	89%	[122]*
0.1 N HNO_3	1.0–1.2	1 mM	Immersed Cu	79%	[122]*
0.1 N H_3PO_4	2.0–2.1	1 mM	Immersed Cu	33%	[122]*
0.1 N H_2SO_4	1.2–1.8	1 mM	Immersed Cu	32%	[122]*
0.1 N HCl	1.5–4.0	1 mM	Immersed Cu	10%	[122]*
SO_2 saturated H_2O	0.7–1.3	1 mM	Immersed Cu	66%	[122]*
CO_2 saturated H_2O	2.8–3.0	1 mM	Immersed Cu	65%	[122]*
0.1 N H_2O_2	3.8–7.7	1 mM	Immersed Cu	no	[7,122]*
0.1 N NH_4OH	10.8–11.8	1 mM	Immersed Cu	no	[7,122]*
0.1 N $FeCl_3$	2.0 –3.8	1 mM	Immersed Cu	no	[7,122]*
0.2 M NH_4Cl	-	Various	Stagnant or stirred test solution at 25° C	yes	[37,73]
Acetate-buffered	3, 4.5 and 6	Various	–	yes	[77]
Acetate-buffered	6	1–100 mM	Pretreated in BTAH-EtOH, N_2 purged solution	yes	[52]
1 M acetate solution	4–10	> 10^{-5} M	–	yes	[4,94,95]
0.1 M KCl + 1 mM HCl	–	5 mM	–	yes	[44]
0.1 M KBr + 1 mM HNO_3	–	5 mM	–	yes	[44]
0.1 M $NaClO_4$	3.8	5 mM	O_2 + CO_2 saturated test solution	yes	[125]*
0.1 M $NaClO_4$	6	5 mM	N_2 saturated test solution	yes	[125]*
3.5% NaCl	2.5	0.2 mM	Pretreated in BTAH solution at 80° C	yes	[127]*
3.5% NaCl	7	0.2 mM	Pretreated in BTAH solution at 80° C	yes	[127]*
0.1 M $NaClO_4$	7	0.2 mM	Pretreated in BTAH solution at 80° C	yes	[127]*
0.01 M $NaHCO_3$	8.4	0.2 mM	–	yes	[62]
0.01 M H_3BO_3 + 0.01 M $Na_2B_4O_7$ + 0.2 M chloride	9	0.1 mM, 10 mM	Test at 22° C	yes	[108]
0.01 M H_3BO_3 + 0.01 M $Na_2B_4O_7$ + 0.01 M sulphate	9	> 10^{-6} M	Test at 22° C	yes	[109]
0.5 M Na_2SO_4 + 0.05 M H_2SO_4 + 1.25 mM Na_2S	1.1	5 mM	Test at 23 ± 1° C	no	[116]
0.55 M Na_2SO_4 + 1.25 mM Na_2S	6.4	5 mM	Test at 23 ± 1° C	no	[116]
3.5% NaCl + 1.25 mM Na_2S	–	5 mM, 10 mM	Test at 25 ± 1° C	no	[118]

* More data in the text, NG – not given, IE – inhibitory effectiveness.

tion. Although BTAH formed an approximately 5 times thinner surface film than BIMDA, it was more effective at preventing Cu corrosion. It was concluded that the BTAH surface film was less porous.

The effect of crystallographic orientation of Cu on the efficacy of BTAH inhibition in 0.1 N H_2SO_4 was investigated by Mayanna and Setty [74]. They demonstrated that the relative stability of the crystal planes was in the order of Cu(1 1 1) < Cu(1 1 0) < Cu(1 0 0). They also suggested that 7.5×10^{-3} M BTAH, where maximum inhibition was observed, marks the limit for the transition from adsorption to Cu-BTAH film formation. However, Biggin and Gewirth [104] reported that cyclic voltammograms accompanying Cu(I)BTA surface complex formation are not affected by crystallographic orientation, seen from the same electrochemical behaviour.

Musiani et al. [105] showed that BTAH is less effective in acidic solution, which was at variance with previous investigations [7, 106]. Brusic et al. [2] showed that the degree of Cu(I)BTA polymerization was pH dependent, being greater at high pH where copper oxides are stable. The degree of polymerization correlated positively with inhibitory effectiveness but negatively with thermal stability.

Using NMR, Sutter et al. [107] showed that synthesized Cu(I)BTA exhibits complex-like behaviour, with partial charge transfer from the ligand to the metal. By comparing different synthesized Cu(I)–organic complexes of known inhibitors, they concluded that the nature of binding between Cu(I) and organic molecules (formation of complexes or corresponding salts on the surface) cannot be exactly correlated with inhibitory efficacy.
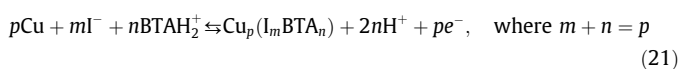
Qafsaoui et al. [108–110] studied inhibition by BTAH of localized corrosion of pre-passivated copper in 0.2 M chloride [108] and 0.01 M sulphate [109] containing borate buffer. In the presence of chlorides, BTAH acted as pitting inhibitor only at higher concentrations (>0.5 mM), whereas in the presence of sulphate ions, BTAH countered pitting, even at low concentrations (>10^{-6} M).

Da Costa et al. [45] reported that BTAH at concentrations higher than 10 mM acts as an effective corrosion inhibitor for Cu in 1.0 M HCl containing ~5 mM Fe^{3+}. The corrosion rate for this process was controlled by the diffusion of the Fe(III) ions to the Cu surface.

6. Synergistic and accelerating effects

A synergistic effect of benzylamine and BTAH for Cu protection was reported by Fleischmann et al. [111]. The layer formed in the BTAH/benzylamine solution was thought to be composed mainly of a [Cu(II)BTA$_2$]$_n$ polymeric network. The layer was more protective when formed at anodic potentials.

Wu et al. [112] reported that iodide ions and BTAH together improve corrosion protection of Cu in sulphuric acid. It was suggested that adsorbed iodide ions on the Cu surface preferentially adsorb an over-layer of protonated BTAH$_2^+$ and form a new Cu(I)BTA polymeric complex film (Eq. (21)). This film is much thicker and has a higher degree of polymerization than the one formed in sulphuric acid solution containing only BTAH. As shown before, a higher degree of polymerization correlates with higher inhibitory effectiveness [2].

$$p\mathrm{Cu} + m\mathrm{I}^- + n\mathrm{BTAH}_2^+ \leftrightarrows \mathrm{Cu}_p(\mathrm{I}_m\mathrm{BTA}_n) + 2n\mathrm{H}^+ + pe^-, \quad \text{where } m+n=p \tag{21}$$

This synergistic effect was also found for iron [113]. Another synergistic effect with halogen ions was reported by Souto et al. who showed that a combination of BTAH and ethyl xanthate inhibits corrosion, but only in the presence of chloride [114].

A synergistic effect was observed between sodium dodecylsulphate (SDS) and BTAH on corrosion inhibition of Cu in 0.5 M H_2SO_4 [115]. Based on SERS observations it was suggested that BTAH at low pH exists mainly in the BTAH$_2^+$ form (Eq. (8)). In this form it is adsorbed to the Cu surface, together with the anionic dodecylsulphate, forming an ion pair. This combined adsorption is more effective than that of BTAH alone.

Yao et al. [90] investigated the role of triphenylphosphine (pph$_3$) on the formation of Cu-BTAH surface complex in acetonitrile solution. In the presence of pph$_3$, the formation of Cu(I)BTA complex was suppressed and the dissolution of Cu was accelerated, presumably due to the formation of soluble Cu(pph$_3$)$^+$.

In spite of the fact that BTAH is a superior inhibitor for copper and brasses in a number of corrosive media, it is far less effective in sulphate [116] and chloride solutions [117–121] containing sulphide ions. The latter are thought to extract Cu(I) ions from the Cu(I)BTA surface film, leading to its decomposition according to Eq. (22) [116,117], and loss of inhibitory activity.

$$n\mathrm{HS}^- + 2[\mathrm{Cu(I)BTA}]_n \rightarrow n\mathrm{Cu}_2\mathrm{S}_{(s)} + n\mathrm{BTA}^- + n\mathrm{BTAH} \tag{22}$$
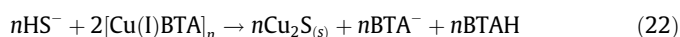
HS$^-$ ions were suggested to compete with BTAH molecules for adsorption at the same site on the Cu surface [119,120]. The sulphide ions were reported not only to destroy the inhibitory ability of BTAH but, above certain concentrations, actually to promote corrosion compared to the BTAH-free sulphide solution [118,120]. In the case of corrosion of Cu-10Ni alloy in 3.4% NaCl, concentrations of sulphide ions as low as 2 ppm eliminated the BTAH inhibitory activity [121]. This alloy can otherwise be protected at substantially higher BTAH concentrations (>5×10^{-4} M).

7. Derivatives of benzotriazole

Fleishmann et al. [43] showed that BTAH in 1 M KCl completely displaces 1-hydroxybenzotriazole (BTAOH) from the Cu surface after prolonged exposure, indicating its higher inhibitory potential. Musiani et al. [105] demonstrated that BTAH is displaced by the more protective inhibitor, 2-mercaptobenzothiazole, in chloride solution at pH 1. Naphthotriazole is more effective than benzotriazole against Cu corrosion [122], but its use is precluded by the fact that it is far more expensive.

Törnkvist et al. [123] investigated a number of monosubstituted methyl-benzotriazoles as Cu corrosion inhibitors in 0.1 M NaCl. While 1-Me-BTA and 2-Me-BTA were ineffective in preventing Cu corrosion, 4-Me-BTAH and 5-Me-BTAH were even more strongly protective than the non-substituted BTAH, presumably due to their increased hydrophobic character. Methyl groups on the triazole ring are believed to decrease the ability of the molecule to coordinate to the Cu surface, because of steric effects, but not if substituted on the benzene ring.

Aramaki et al. [124] studied the E–pH mechanism of adsorption and complex formation for 5-substituted BTAH derivatives, 5-Cl-BTAH, 5-Me-BTAH and 5-NO$_2$-BTAH in sulphate medium. All these derivatives readily formed protective complex polymers at high pH and noble potential. At low pH and less noble potentials, they were chemisorbed on the copper surface. Thus, an adsorption/complex mechanism, similar to that proposed for the non-substituted BTAH, was concluded to be operative [30,51] (Eq. (12)). The inhibitory effectiveness of these derivatives decreased in the order 5-Cl-BTAH > 5-Me-BTAH, BTAH > 5-NO$_2$-BTAH.

Similar studies were also performed in other media. In 0.1 M NaClO$_4$ solution, Brunoro et al. [125] showed that 5-hexyl-BTAH inhibited corrosion of pre-filmed, oxygen-free high conductivity (OFHC) Cu was better than non-substituted BTAH. 5-hexyl-BTAH also showed high inhibitory effectiveness under simulated heat-exchange conditions in 0.1 M NaCl [126]. The inhibitory effective-

ness for Cu of the 5-alkyl-BTAH derivatives, methyl-, butyl- and hexyl-, in 3.5% NaCl at pH 2.5 and pH 7 increased with increasing alkyl chain length, attributed to the increasing hydrophobicity [127]. Frignani et al. [128] also studied other 5-alkyl-substituted BTAH molecules, methyl-, butyl-, hexyl-, octyl- and dodecyl-, as OFHC copper corrosion inhibitors in 0.1 M Na$_2$SO$_4$ and 0.1 M NaCl. As noted by Tommesani et al. [127], the inhibitory effectiveness in sulphate medium increased with increasing alkyl chain length. In 0.1 M NaCl medium, however, only 5-butyl-BTAH and 5-hexyl-BTAH were more effective than the non-substituted BTAH. The improved inhibition was attributed to the formation of more hydrophobic and more resistant surface films, with fewer defects [129].

The reason why BTAH is more effective than BTAOH was elucidated using calculations based on density functional theory (DFT) [67]. Electronic parameters of these inhibitors were related to their IE. Introduction of the –OH group into the benzotriazole molecules does not change their electronic parameters significantly, either in the gas phase or in the presence of water solvent. Other parameters, therefore, affect the inhibitory effectiveness. In particular, the interplay of planar molecular structure, adsorption and intermolecular H-bonding, which cooperatively may result in the formation of a thin, protective film, are responsible for the superior effectiveness of BTAH. The BTAH surface layer formed after 1 h of immersion was thin, 1.5 ± 0.3 nm, but still three times thicker than the BTAOH layer formed under the same conditions [38]. The thickness was determined according to the Tougaard method [130,131], used for the first time to deduce the thickness of the inhibitor layer. Moreover, the porosity of surface layers formed in BTAH or BTAOH solution plays an important role [132]. Porous acicular crystallites, whose shapes depend on whether they are formed under stationary or dynamic conditions, were composed of BTAOH molecules. In BTAH containing solutions, non-porous, roundish and acicular structures, or plates a few hundred nanometres thick, were composed of BTAH.

8. Conclusions

Benzotriazole (BTAH) is one of the best corrosion inhibitors for Cu and its alloys. It is effective in preventing copper corrosion under stationary as well as dynamic conditions. Its inhibitory effectiveness increases with increased concentration and time of immersion. It was shown that BTAH acts as a mixed type inhibitor, but its predominant effect is on inhibition of anodic reaction. The Cu(I)BTA surface complex, involving Cu–N bonds, is well recognized, but the exact structure of the complex and its mode of binding on the metal surface are still being discussed. The question as to whether complex formation takes place at the surface–solution interface or in the solution followed by precipitation on the surface, remains open. The problem is aggravated by the fact that determination of the exact surface structure of the Cu(I)BTA complex has shown it to differ from that of the synthesized one. Discussions in the literature concerning the orientation of the BTAH surface structure have sometimes been controversial. The Cu(I)BTA surface complex has been proposed to be oriented with the BTAH perpendicular, tilted, or parallel relative to the Cu metal surface. A zigzag structure of the Cu(I)BTA polymer was postulated in the sixties by Cotton [19]. However, the use of surface sensitive techniques has suggested that parallel stacking of the BTAH molecules, making a chain-like structure, is more likely. BTAH has been reported to adsorb only on copper oxide surface, to adsorb faster on copper oxides than on pure Cu, and to adsorb only on a clean Cu surface.

CuCl$_2^-$ is reported to control Cu(I)BTA film formation. Evidence exists that the thickness of the Cu-BTA protective layer is greater on a Cu$_2$O substrate than on CuO and, particularly, on metallic Cu. Formation of the BTAH surface film has mostly been found to follow a logarithmic growth law. Benzotriazole is more effective at higher pH values, which fits perfectly the mechanism proposed by Morito and Suëtaka [29] and improved by Youda et al. [30], where the reaction between Cu and BTAH is shifted to the formation of the Cu(I)BTA surface complex. This complex is therefore held to be responsible for the improved corrosion inhibition, and not chemisorbed BTAH itself. However, at higher pH, copper oxides are more stable and BTAH action could be hindered. BTAH concentration and electrode potential also play a role in the complex formation. At low BTAH concentration and more negative potentials, adsorption of molecules, rather than complex formation, is favoured. Inhibitory effectiveness on Cu substrates is reported to be in the order of Cu(1 0 0) > Cu(1 1 0) > Cu(1 1 1).

Substituted BTAH derivatives were found to be effective Cu corrosion inhibitors when functional groups are present on the benzene ring, but not the triazole ring. Moreover, sodium dodecylsulphate, benzylamine, iodine ions and ethyl xanthate show synergistic effects in combination with BTAH, while sulphide ions and triphenylphosphine promote corrosion.

It is clear from this review that the exact mechanism of BTAH action on copper materials still remains to be elucidated. It is important to clarify why BTAH, and not other organic molecules with similar electronic structure, imparts corrosion protection. The answer to this question will provide the basis for predicting new and more effective corrosion inhibitors.

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