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Physicochemical aspects of metal protection by azoles as corrosion inhibitors

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Abstract. The state of the art of studies dealing with development and perfection of methods for metal protection against corrosion by azole heterocycles is considered. The composition and the key mechanisms of formation of ultrathin (nanosized) protective layers on the surface of various metals by these inhibitors are discussed. The bibliography includes 155 references.

I. Introduction

Efficient methods of anticorrosive protection of metals and alloys are searched for because of the great technological and economical damage due to corrosion.[1] The deterioration of ecological situation due to the ingress of corrosion products [2] or toxic reagents resulting from corrosion of equipment at chemical plants and pipelines into the environment is no less harmful.[3] The use of corrosion inhibitors (hereinafter inhibitors), *i.e.*, chemical compounds or their mixtures that retard or even suppress corrosion of a metal when added to a system without changing considerably the content of corrosive constituents, is among the most efficient chemical methods used to prevent corrosion. Its position among other methods of corrosion protection should not be judged by comparing the overall production of corrosion inhibitors and the funding of activities on the implementation of the corresponding measures because the consumption of inhibitors (or anti-corrosion pigments based on them) is very small, in contrast, *e.g.*, with the consumption of paint coatings; in most cases, it is sufficient to add a small amount of an inhibitor for efficient protection of metal surfaces.

An important position among inhibitors belongs to organic compounds that can form compounds hardly soluble in water with cations of the metal being protected.[4–7] Interactions of inhibitors with the surface often result in ultrathin protective layers ($\leqslant$10 nm thick) that are resistant against effects of the corrosive medium (humid atmosphere, aqueous solutions of salts and even certain acids). Inhibitors can be used as independent protective means against metal corrosion, as well as in formulations with oils, in combination with cathodic protection, paints and conversion coatings.[4–10] The reagents commonly attributed to complex-forming inhibitors can be divided into two groups that are most extensively studied and used in practice.[6] One of these groups includes chelating agents, complexes with cations of various metals and formulations based on them. The leading role in this group belongs to phosphonates; the mechanism and specific features of action of these compounds have been repeatedly discussed in literature, including a monograph [4] and a number of reviews.[6, 11, 12]

The other group, which appears to be even more abundant, includes heterocyclic compounds; the interest in these compounds has not abated for over half a century.[13] However, more than 30 years have passed since the publication of the review by Kuznetsov and Podgornova [14] that dealt with the protective effects of heterocyclic chelating reagents, whereas later papers [15–17] only covered a narrow subject, *i.e.*, copper protection against corrosion by triazoles, mainly benzotriazole (BTA), the most popular inhibitor of this class. Meanwhile, over the last decade, not only the specific features of the mechanism have been studied in more detail for known inhibitors of this type, but also the range of objects that can be protected has been expanded and new efficient inhibitors and protection methods for various metals and alloys have appeared that are promising for modern industries, including nanotechnologies.

The efficiency of inhibitors is usually studied by gravimetric and electrochemical methods, whereas the thickness, composition and structure of protective layers, as well as the type of metal–inhibitor bonds, are studied using surface analysis methods, such as X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES), secondary-ion mass spectrometry (SIMS) and laser mass spectrometry (LMS).[18] Of numerous modern methods of microscopy to study the surfaces of solids, scanning tunnelling microscopy (STM) [19, 20] and atomic force microscopy (AFM) [21] are evolving most quickly.

A promising method for studying metal surfaces interacting with corrosion inhibitors is provided by surface-enhanced

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Raman spectroscopy (SERS). Irrespective of the mechanism, which has been considered elsewhere,[22,23] the increase in the intensity of SERS bands depends on the substrate nature (commonly used materials include silver, gold and copper), surface roughness and the size and shape of particles that are no larger than nanostructures.

One of the recent trends of studies in corrosion inhibition is the use of molecular simulation methods for computation of electronic properties and for explanation of inhibition mechanisms. Studies on the possible orientation of a molecule, favourable configuration, steric and electronic effects would be useful for better understanding of the inhibitor's efficiency. The frontier orbital theory is used to predict the probable adsorption centres of an inhibitor molecule that are responsible for interaction with metal surface atoms. In systems where corrosion occurs, an organic inhibitor and a metal behave as a Lewis base and a Lewis acid, respectively. Data obtained in corrosion studies were used for various correlations that took into account the type of electron density on the donor atom, ionisation potential, electron affinity, pK_a value, steric effects, the Hammett constants, dipole moments and portion of the electron density (ΔN) transferred from the molecule. Correlations of this kind may provide useful information about the reactivity, electronegativity or atomic charge. However, the effects of solution components and competing surface reactions are still neglected. A quantitative analysis of structure–activity relationships may favour the development of new inhibitors with higher efficiency.[23]

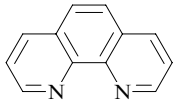
This review mainly focuses on azoles, the class of popular heterocyclic inhibitors that are studied most comprehensively. The potential of nanolayers of, and thicker conversion coatings modified by, these compounds for metal protection are discussed.

II. Nitrogen-containing heterocyclic inhibitors of metal corrosion

In an earlier review,[14] we mentioned the ability of a nitrogen-containing heterocyclic compound, namely pyridine, to form complex compounds on the surfaces of certain metals in aqueous solutions. However, the efficiency of corrosion protection with pyridine is considerably lower than with its derivatives containing additional amino groups, *e.g.*, in position 2 or 4. It was assumed that if the inhibitor molecule contains a second reaction centre, then, under certain conditions, it may form chelates with cations of the metal being protected, resulting in considerable enhancement in stability of the protective layer on the surface. This possibility can be implemented in case of polymerisation of a heterocyclic base, such as vinylpyridine. Strengthening of the bond with the metal is achieved not only due to the bond with the heteroatom, but also due to the π-electronic interaction of the aromatic ring with the surface, which was also used to explain the ability of quinoline and its derivatives to form a thin hardly soluble film of a complex with the metal, which protected iron, copper and zinc in aqueous solutions at pH $\geqslant$ 5.0. The protection of copper with polycyclic N-containing heterocycles (acridine, phenazine and xanthine) was explained in a similar way.[24] The most popular heterocyclic inhibitors include various azoles that are considered in our review. A common specific feature of many heterocycles should be noted, namely, the pronounced dependence of their orientation in the adsorption on a metal surface on the metal potential.

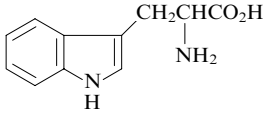
In fact, Diao *et al.*,[25] who studied the adsorption of 2,2′-bipyridyl (BP) on copper(111) in 0.1 M $HClO_4$ by cyclic voltammetry, electrochemical STM and SERS as a function of the electrode potential, found that doubly protonated BP is adsorbed as planar cations arranged along the surface in a well-ordered monolayer. However, at negative potentials ($E = -0.36$ V), BP is reduced to give dimers that create a well-ordered structure oriented vertically to the surface.

It has been shown using STM that in 0.1 M $HClO_4$ phenanthroline



is adsorbed in such a way that its molecules are oriented vertically to the Cu(111) surface at $E = 0.1$ to -0.15 V.[26] Owing to the π-interaction between the benzene rings, adsorbate species are packed in parallel rows. However, this orientation is violated at $E < -0.2$ V due to the mobility of inhibitor molecules, whereas at $E < -0.3$ V, adsorption ceases.

Of note is the specific adsorption behaviour of 2-amino-3-(indol-3-yl)propionic acid (tryptophane)



on copper.[27] It is often believed that amino acids are adsorbed on the surface through carboxy groups; and the molecules of amino acids are perpendicular to the surface. However, in the case of tryptophane, the molecule of which is non-planar and contains an indole fragment, it has been found that, along with the carboxy group, the nitrogen atom of the heterocycle is bound to the surface. The complex structure of the molecule predetermines the formation of various surface structures and different coverages of the copper surface; intermolecular hydrogen bonds may be the key factor responsible for the stability of superstructures.

III. Azoles as corrosion inhibitors

1. Imidazoles

Imidazole (1,3-diazole) is almost never used as an inhibitor because of its low surface activity caused by high solubility in water (hydrophilicity) and apparently insufficient reactivity of its heteroatoms (the pK_a for imidazole as an NH-acid is 14.2 and its pK_a as a base is 7.03–7.25).[28] However, it can form complexes with copper and retard its corrosion, *e.g.* in 1 M HNO_3.[29] In this case, according to XPS data, a film is formed on the metal surface, the inner layer of which is enriched with oxygen (oxide), whereas the outer layer consists of a copper–imidazole complex. This slows down the cathodic reaction on copper and metal corrosion. On the other hand, even for copper that is protected with imidazole most efficiently, the latter is one of the weakest inhibitors among azoles.[30]

It is known that 2-mercaptoimidazole manifests reasonably good inhibitory properties, at least in acidic media.[13] Based on this inhibitor, a new type of insulating film was obtained on copper in neutral salt solutions; in this case, electrochemical oxidation of 2-mercaptoimidazole results in the disulfide anion. Presumably, a polymeric film is formed on the surface, since mass-spectrometric data suggest the formation of tri- and tetrameric imidazole fragments.[31]

In an H_2SO_4 solution, 2-mercapto-4(5)-phenylimidazole is an even more efficient inhibitor, evidently due to an increase in its surface activity because of introduction of a hydrophobic substituent, that is, a benzene ring. In a 3% aerated NaCl solution, copper is well protected with small amounts (< 1 mmol litre^{-1}) of 2-mercapto-1-methylimidazole.[32]

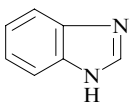
Higher alkylimidazoles with an optimum number of carbon atoms in the alkyl substituent ($n_C = 11$) are good corrosion inhibitors of low-carbon steel (high inhibitor concentrations are required for efficient protection at $n_C \leqslant 8$).[33] It should be noted that an increase in the efficiency of iron protection in 1 M HCl with an increase in alkyl group length in imidazole was observed back in the late 1960s, as discussed in our review.[14] The efficiency of copper protection in 0.5 M HCl with 4-methyl-1-(*p*-tolyl)imidazole[34] or 4-methyl-1-phenylimidazole[35] is also considerably higher than with imidazole. This effect can be explained by an increase in the inhibitor hydrophobicity. However, as mass spectrometric and XPS studies show, this inhibitor, which slows down both electrode reactions on copper, is adsorbed only physically (no nitrogen atoms are found on the surface), but its adsorption from water may result in formation of complex compounds with the metal.

A number of azoles, namely, indazole, imidazole, 4-bromo- and 4-methylimidazoles, pyrazole, 4-sulfo- and 4-nitropyrazoles, were studied as corrosion inhibitors of iron in 1 M HCl.[35,36] According to electrochemical impedance data, the charge transfer resistance was higher in the presence of these inhibitors (except for the last-mentioned compound) than without them. It increased with an increase in the inhibitor concentration and duration of electrode exposure to the solution. Structural and electronic parameters of azoles were studied. XPS data confirmed that inhibitor molecules were present in the surface film.

The partial shift of electrons from heteroatoms to surface metal atoms may be considered as formation of a coordination bond.[37,38] Such a shift of the electron density from the nitrogen atom in the heterocyclic ring might become the basis for strong adsorption and corrosion inhibition. However, nitrogen atoms in azoles are protonated in acidic media, which restricts their interaction with the surface. On the other hand, in acidic media, the double electrical layer is recharged due to chemisorption of anions, *e.g.* Cl^-, and the surface acquires a negative charge, which favours the adsorption of heterocycle's organic cations. This results in corrosion inhibition.

In neutral media or in the case of adsorption from a gas-vapour phase, protonation may exert no effect on the adsorption mechanism. As shown for zinc,[39] semiempirical calculations of stability of complexes of imidazole derivatives with metals may show a fairly good correlation with the inhibitory ability of organic compounds.

Of imidazole derivatives, the most popular corrosion inhibitor is benzimidazole (BI)



which has pK_a 13.2 and 5.53 at 25 °C in water.[28] It manifests protective properties in acidic, neutral and alkaline media, particularly for copper and zinc, which form rather stable complex compounds with BI.[40] Benzimidazole and its derivatives are known as inhibitors of general[41,42] and selective corrosion (dezincification)[43] of brass in aqueous solutions. Perhaps, 2-mercaptobenzimidazole (2-MBI) is the inhibitor that is used most widely; it is more efficient than BI in protection of copper and its alloys and is known as an antioxidant[44] and antiseptic agent.[45] It is interesting that in alkaline media where 2-MBI is used most widely, it exists as anions $(2\text{-MBI})^-$ and $(2\text{-MBI})^{2-}$ (in the latter case, one charge is localised on the sulfur atom, whereas the other one, in the azole ring). These anions are readily adsorbed, including adsorption on gold and silver with which they form salts at elevated temperature, *e.g.*, $Ag^+(2\text{-MBI})^-$ (Ref. 44). According to data published by Wang,[46] 2-MBI can be a good inhibitor for low-carbon steel in a wide range of phosphoric acid concentrations. In protection of brass (60 Cu/40 Zn) in 0.1 M NH_4Cl at pH 9.2 with 2-MBI, each surface atom of copper is bound to two ligands to form a polymeric film that slows down both electrode reactions.[42]

No wonder that substituted BIs attracted attention of physicochemists who studied the effect of chemical structure of inhibitors on the efficiency of corrosion protection of various metals (in particular, copper and zinc) with these inhibitors. It has been shown[14,47] that the inhibition coefficient of metal dissolution

$$\gamma = \frac{i_0}{i_{in}},$$

where i_0 and i_{in} are anodic current densities in 0.5 M $NaH_2PO_4 \cdot 2\,H_2O$ without and with an inhibitor, respectively (0.5 mmol litre^{-1} for copper or 1 mmol litre^{-1} for zinc), is adequately described by the following equations at a constant potential [$E = 0.14$ V (Cu) or -1.0 V (Zn)] for nineteen 2-substituted BIs studied:

for copper

$$\log\gamma = 0.650 + 2.319\,\sigma_I,\ r = 0.97; \quad (1a)$$

for zinc

$$\log\gamma = 1.189 - 1.468\,\sigma_I,\ r = 0.98. \quad (1b)$$

In these equations, σ_I is the induction constant of substituent R in the inhibitor molecule[48] and r is the correlation coefficient.

Similar relationships were obtained by processing the results of direct corrosion tests in which the minimum concentration of an inhibitor (c_{pr}) that provided full suppression of metal corrosion in the same phosphate solution was determined:

for copper

$$\log c_{pr} = -2.546 - 2.212\,\sigma_I,\ r = 0.92; \quad (2a)$$

for zinc

$$\log c_{pr} = -2.654 + 3.298\,\sigma_I,\ r = 0.91. \quad (2b)$$

It follows from these equations that electron-donating substituents increase the protection of zinc, whereas electron-withdrawing substituents increase that of copper. Similar relationships were found[49] in protection of the same metals with 2-substituted 5(6)-nitrobenzimidazoles (Fig. 1):

for copper

$$\log\gamma = 0.78 + 1.90\,\sigma_I,\ r = 0.98; \quad (3a)$$

for zinc

$$\log\gamma = 1.15 - 1.14\,\sigma_I,\ r = 0.98. \quad (3b)$$

As expected, 5(6)-nitrobenzimidazole is a markedly more efficient inhibitor of copper but a weaker inhibitor of zinc. The opposite types of substituents' effect on the efficiency of inhibitors in both reaction series with respect to copper and zinc protection is due to differences in the ability of both metals

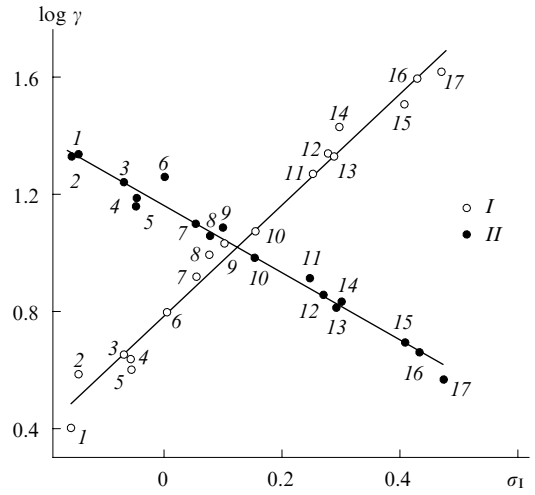


Figure 1. Dependence of $\log \gamma$ on σ_I obtained for copper (*I*) and zinc (*II*) in 0.5 M solution of $NaH_2PO_4 \cdot 2H_2O$ in the presence of 5(6)-nitro-2-R-substituted BIs.
Inhibitor concentration: 0.5 (*I*) and 1 mmol litre^{-1} (*II*); pH 11.7; the potentials are 0.14 (*I*) and -1.0 V (*II*). Substituents R: (*1*) OH, (*2*) COO^-, (*3*) Pr^n, (*4*) Me, (*5*) Et, (*6*) H, (*7*) CH_2OH, (*8*) Ph, (*9*) NH_2, (*10*) NHEt, (*11*) SH, (*12*) OEt, (*13*) COMe, (*14*) OMe, (*15*) CCl_3, (*16*) CF_3, (*17*) Cl.

to form σ- and π-bonds in complexes. Strengthening of the π-bond is most important for stability of copper complexes, whereas strengthening of the σ-bond is most important for zinc complexes.

On the other hand, the enhancement of the protective properties of BIs containing nitro groups in the case of copper and the opposite effect in the case of zinc is caused, to some extent, by an increase of dissociation of the N—H bond. These compounds are weak NH acids. Electron-withdrawing substituents increase the acidity of BIs.[50,51] Nitrogen-containing electron-withdrawing substituents in position 5(6) of a BI molecule affect acidity most strongly. It is likely that the considerable enhancement of the protective properties of substituted nitrobenzimidazoles with respect to copper in comparison with other BI derivatives is only due to an increase in the degree of dissociation of the inhibitor as a result of introduction of an NO_2 group in the benzene ring [$\gamma = 3.2$ for BI and 6.4 for 5(6)-nitrobenzimidazole].

Electron-withdrawing substituents introduced in 5(6)-nitrobenzimidazole increase the degree of dissociation even stronger since they decrease the electron density on the pyrrole nitrogen atom and hence weaken the N—H bond in the imidazole ring. The simultaneous effects of an NO_2 group and electrophilic substituents on the N—H bond should facilitate considerably the formation of an ionic bond between a copper cation and the inhibitor in the formation of a protective layer of the complex compound on the metal surface. Introduction of electron-donating substituents in a 5(6)-nitrobenzimidazole molecule increases the electron density on the heteroatom and hinders the inhibitor dissociation. However, nitro-substituted BIs are more strongly dissociated in solution than their analogues due to the presence of an NO_2 group in the benzene ring. Because of this, the participation of the pyrrole nitrogen atom in complexation is hindered; however, the formation of an ionic bond may not be ruled out. Perhaps that is why the inhibitory effect of substituted 5(6)-nitrobenzimidazoles is higher than that of 2-substituted BIs.

Similar reasoning in the case of zinc protection with nitrobenzimidazoles containing electron-donating substituents suggests that in this case the increase in the inhibitory effect can be explained on the assumption that a stronger σ-bond is formed in complexes than in non-substituted 5(6)-nitrobenzimidazoles. The weakening of the protective properties of compounds with an enhancement of electron-withdrawing properties of the ligand also suggests that there is no ionic bond between the zinc cation and nitrobenzimidazole or other BI derivatives. This is further supported by the fact that nitration of BI derivatives, which favours their dissociation, weakened the protective properties of these heterocyclic inhibitors.

However, it is not sufficient to take into account only the inhibitor dissociation to describe the protection of copper and zinc with this type of compounds. Without the assumption about dative π-bonds, it is difficult to explain the weakening of the protective properties of compounds with respect to zinc and their enhancement with respect to copper upon introduction of electron-withdrawing substituents in 5(6)-nitrobenzimidazole, as well as the opposite effect observed with electron-donating substituents.

Analysis of results of XPS studies of BI adsorption on copper surfaces in phosphate solutions, combined with electrochemical measurements of anodic reaction orders with respect to the phosphate anion and the inhibitor, brought us to the conclusion that copper protection is due to the formation of surface complexes. Taking into account the position and width of the peak of N1s electrons in the spectra of these compounds, it is assumed that copper—nitrogen bonds are formed [50] where copper exists in the oxidation state +1 and the copper : BI ratio is 1 : 2. The surface layer of the complex may be as thick as 3.5 nm.

Kuznetsov *et al.*[47,52] studied the effect of hydrodynamic conditions and BI concentration in 0.5 M $NaH_2PO_4 \cdot 2H_2O$ solution with pH 9.5 on the composition of the protective film on zinc surface. Since the positions of the XPS peaks $Zn2p_{3/2}$ are almost the same for zinc and zinc oxide (1023.0 eV), we used the position of the Auger line for the transition $ZnL_3M_{4.5}M_{4.5}$, which is shifted by ~ 6 eV for ZnO with respect to the line for metallic zinc. We failed to obtain direct evidence that BI and zinc form complex compounds; however, it was shown that exposure of samples in solutions containing BI resulted in considerable accumulation of nitrogen and carbon atoms on the surface. Taking into account that XPS analysis was performed after thorough washing of the surface with distilled water, it can be asserted that BI (or its complex with zinc) is strongly adsorbed on the electrode surface. Electrochemical measurements showed that interaction of zinc with BI resulted in the complex $[Zn \cdot 2\,BI]^+$. The layer of this complex may be up to 3.15 nm thick. Adsorption of BI affects the content of phosphates in the protective film. In fact, the P : Zn ratio reaches ~ 0.5 upon exposure of an electrode in a phosphate buffer solution, but is reduced to 0.1 in the presence of 4 mmol litre^{-1} of the inhibitor. Hence, BI displaces phosphates from the zinc surface. This is also supported by the data on the phosphorus content in the surface layer *vs.* inhibitor concentration in the solution. The P : Zn ratio in the surface film decreases abruptly as the inhibitor concentration increases to 4 mmol litre^{-1}.

Thus, XPS analysis of surfaces showed that formation of the external passivating layer on both metals resulted from BI chemisorption, whereas its thickness depended on the inhibitor concentration in the solution.

Benzimidazole can passivate zinc not only in alkaline phosphate solutions, but also in neutral borate buffers; it behaves as an adsorption-blocking type inhibitor on a uniform surface.[53] At a certain concentration $c_{BI} \geqslant c_c$, the free corrosion potential of zinc (E_{cor}) increases abruptly as the passivation current density (i_p) decreases below the limiting diffusion current density of the coupled cathodic reaction. Presumably, such a passivation is due to the formation of a chemisorption layer of benzimidazole on the zinc surface, which followed from a considerable aftereffect of the inhibitor observed after transfer of the zinc sample into pure borate buffer.

Benzimidazole and its derivatives have been extensively studied as inhibitors of iron and steel dissolution in aqueous media. Popova,[54] who studied the protection of low-carbon steel with BI and thirteen BI derivatives in 1.0–5.0 M HCl, recommended 1,2-dibenzylbenzimidazole as the most efficient acid pickling inhibitor. Even in 4.0 and 5.0 M HCl solutions, 0.5 mmol litre^{-1} of the inhibitor provides the degree of protection Z = 98.6% and 99.3%, respectively. 1-Benzylbenzimidazole inhibits steel corrosion somewhat less efficiently: $Z = 98.4\%$ and 99.0% at 1 mmol litre^{-1} of the inhibitor, respectively, whereas BI itself cannot provide $Z = 70\%$ even at a higher concentration (3 mmol litre^{-1}). 1,2-Dibenzylbenzimidazole is characterised by the highest hydrophobicity, hence no wonder that its adsorption hinders both cathodic and anodic electrode reactions on steel.

Quaternary salts of 2-(4-quinolyl)benzimidazole have been recommended as corrosion inhibitors not only in acids, but also in media containing hydrogen sulfide.[55]

The corrosion protection of steels with BI and its derivatives in neutral media has been studied to a lesser extent. However, it has been shown [56, 57] that addition of BI to a borate buffer with pH 7.4 only slightly affects the anodic behaviour of iron, whereas in a sulfate solution, it causes primary passivation of the surface. It was noted that the presence of BI decreased the number of pits that appeared due to the activating effect of the sulfate anions.

The dissolution of iron in 0.05 M Na_2SO_4 in the presence of 2-R-substituted BIs as inhibitors, where R = H, Me, Et, Pr^n, Pr^i, CH_2OH, NH_2 or NHOH, slowed down with an increase in the electron-donating properties of the substituents reflected by their σ_I.[56] Considering this fact as a consequence of inhibitor chemisorption that occurs due to nucleophilic substitution of inhibitor species for activator species on the metal surface, Ekilik *et al.*[57] noted the existence of linear correlations between σ_I and values that characterise (*cf.* Ref. 4) the reactivity of the nucleophile in similar reactions, that is, the logarithm of molar refraction and the π-constants of atoms or groups of the constituent atoms of the nucleophile. The involvement of the pyridine nitrogen atom in chemisorption is believed to play the decisive role in iron passivation.

The stability of BI makes it possible to use it as an additive (5 g litre^{-1}) to 13% NH_4OH solution in order to decrease the corrosion rate of low-carbon steel by a factor of ~6 (even at 150 °C).[58] Mixtures of BI with salts of undecenoic acid can passivate steel in this solution at smaller concentrations of the heterocyclic inhibitor.

Many studies deal with the mutual effects of BI (or its derivatives) and other inhibitors on metal protection. Thus the quantitative criteria of synergism in iron protection in 1 M H_2SO_4 were established for mixtures of 2-(2-pyridyl)benzimidazole with NaCl and NaCNS.[59, 60] This is of considerable importance for the inhibition theory in general, as we have emphasised in an earlier review.[6] It should be noted here that by combining anionic surfactants, *e.g.*, sodium dodecylbenzenesulfonate, with 2-MBI it is possible to enhance the protection of a metal (copper) in 1 M H_2SO_4.[61] It is believed that this enhancement is due to electrostatic interactions between the adsorbate ions, since 2-MBI exists as a cation in acidic media. Synergism of inhibitors, *viz.*, KI, BI, 4-methyl-1-(*p*-tolyl)-imidazole or 4-methyl-1-phenylimidazole, was also observed for copper protection in 0.5 M HCl; these azoles predominantly hinder the cathodic reaction (unlike BTA, which predominantly hinders the anodic dissolution of the metal).[62]

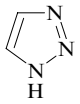
In neutral solutions, the ability of 2-aryl-substituted and especially 2-alkyl-substituted BIs to enhance the protective effect of anionic surfactants (sulfonated mustard-seed oil) was discovered and a composition was developed on this basis. It was recommended as a corrosion and biofouling inhibitor for recirculating systems in chemical and pharmaceutical industries.[63, 64]

It is also of note that 2-MBI can undergo electrochemical polymerisation that may be used to obtain protective films on copper or iron surfaces. Thus it has been shown [31] that the polymeric film obtained on a copper anode in an alkaline water-methanol solution well protects copper during its subsequent exposure in aerated 0.5 M NaCl solution. Chemical analysis of the film as well as IR spectroscopy and mass spectrometry revealed that anodic polarisation resulted not only in copper oxidation and formation of its complex with 2-MBI, but also in the inhibitor oxidation following its dimerisation, which involves C–S coupling reactions.

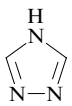
Assouli *et al.*[65, 66] obtained a protective film on brass in alkaline (pH 12.5) 0.1 M solution of 2-MBI in methanol by cyclic polarisation of the electrode at potentials within 0.2–2.4 V. The peak of the monomer oxidation on the voltammogram disappeared starting from the second cycle. This suggests the start of polymerisation and film formation, which was also confirmed by analysing the IR spectra of the reaction products. This film provided a fairly good corrosion protection of brass in 3% NaCl ($Z = 95\%$). On the other hand, it was shown that 2-MBI itself inhibited brass more efficiently in ammonia solution (pH 9.2) than an electroplated poly(2-mercaptobenzimidazole) coating pre-deposited on the surface.[42]

2. Triazoles

Studies on the inhibitory properties of 1,2,3-triazole (ozotriazole)



started much later than those of its most famous derivative, *viz.*, benzotriazole. Both 1,2,3-triazole and its isomer, 1,2,4-triazole (pyrrodiazole)



act as corrosion inhibitors of many metals and alloys (Al, Fe, Cu, brass, Ag, Ni) in aqueous solutions, but their efficiency is generally inferior to that of BTA.[14] On the other hand, a lot of quite efficient inhibitors have been found among substituted triazoles over the last decade.

In copper protection, which is a traditional application area of azoles, 3-amino-1,2,4-triazole (AT) was found to be

more efficient than BTA or 1-hydroxybenzotriazole in protection from pitting in a borate buffer solution containing chloride and sulfate ions.[67,68] According to Srhiri *et al.*,[69] it efficiently protects copper in 0.5 M NaCl by forming a thinner and less penetrable film on copper than that formed by 2-MBI. It was found earlier that this inhibitor can reliably protect copper–nickel alloys as well.[70] However, AT is unable to passivate iron in a borate buffer with pH 7.4 often used to simulate a neutral medium in studies on the passivation of metals and effects of various inhibitors on it.[71] This was explained by the insufficient hydrophobicity of AT that is much smaller than that of *e.g.* BTA, which favours passivation in the same solution.

An increase in the inhibitor surface activity due to AT alkylation increases its protective properties. A washing formulation patented in Germany for protection of metals, promarily silver items, contains 0.5 %–10% of 3-amino-5-R-1,2,4-triazole, where R is an alkyl, alkenyl or aryl.[72] Efficient corrosion protection of copper in 3% NaCl may be reached using 3-amino-4-decyl-1,2,4-triazole,[73] whereas brass dezincification is inhibited by 1 mmol litre^{-1}) of 3-phenyl-1,2,4-triazole-5-thione.[74]

In aqueous solutions of sodium sulfate, 5-amino-, 5-mercapto- and 3,5-diamino-1,2,4-triazoles inhibit corrosion of not only copper, but also of low-carbon steel, whereas nitro-1,2,4-triazoles facilitate steel passivation and have been recommended for use in combination with anodic protection.[75] It has been found [76] that 3,5-diamino-1,2,4-triazole also protects iron in 1 M HCl more efficiently than BTA. In hydrochloric acid solutions, these inhibitors predominantly hinder the cathodic reaction of hydrogen evolution on iron. According to the results by Salghi *et al.*,[77] 3,5-diamino-1,2,4-triazole efficiently protects aluminium alloy 3003 (Al—Mg—Si—Mn) from corrosion in carbonate-chloride solutions with pH 8 in the temperature range from 25 to 70 °C; adsorption on the alloy is described by the Langmuir isotherm, and the inhibition efficiency decreases with an increase in the temperature.

In an acidic medium (10% HCl), the inhibition factor of steel corrosion with 1,2,4-triazoles increases as their pK_a values increase [78]

$$\log\gamma = 0.98 + 0.25\,\mathrm{p}K_a\,. \qquad (4)$$

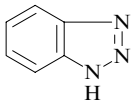
However, the electronic effects alone are often insufficient to describe the inhibitory effect of these compounds. In particular, this follows from the fact that relationship (4) is not met for the cyclohexyl substituent.[78] Subsequent studies showed conclusively that the introduction of hydrophobic substituents in the inhibitor molecule beneficially affects the efficiency of protection of different metals with such triazoles. Thus tolyltriazole is an efficient corrosion inhibitor of aluminium copper-containing alloys not only in neutral (1 M NaCl) but also in acidic medium (1 M HCl).[79] The efficiency of iron protection in 1 M hydrochloric or sulfuric acids also increases if the triazole contains a hydrophobic substituent, as shown for 4-amino-3,5-ditolyl-1,2,4-triazole (DTAT),[80,81] 4-amino-5-mercapto-3-n-propyl- (Ref. 82) or 4-dodecyl-1,2,4-triazole.[83] Quraishi and Ansari [84] found that in 20% formic acid, even at elevated temperatures, certain 5-substituted 4-phenyl-4*H*-1,2,4-triazole-3-thiols provide high level of protection of low-carbon steel at a concentration as low as 25 mg litre^{-1}.

A series of papers by Lagrenée and co-workers.[80,81,85–89] is likely to be the most thorough study of the inhibitory effect of aryl pyrrodiazoles and AT with respect to low-carbon steel in 1 M HCl and in 0.5 M H_2SO_4 . Not only corrosion tests in which the efficiency of the inhibitors was assessed from the mass loss of samples were performed and polarisation curves on steel were recorded, but the electrochemical impedance of electrodes was also measured. This allowed tracing the changes of the electrical capacitance of the double layer depending on the inhibitor concentration and to determination of the adsorption isotherms of the inhibitors.

It was found that in both acids the adsorption of 2-[5-(2-pyridyl)-1,2,4-triazol-3-yl]phenol [85] or DTAT [85,86] obeyed Langmuir's isotherm much better than Frumkin's or Temkin's isotherms. The efficiency of protection with DTAT depends on the position of the methyl group in the aromatic rings, and the best inhibitor, 4-DTAT, hinders both electrode reactions. Similar results were obtained in a study on 4-amino-3,5-di(*p*-methoxyphenyl)-1,2,4-triazole.[88]

Quantum chemical calculations were carried out for triazole and its derivatives in order to determine the efficiency of corrosion protection.[87,89] Analysis of structure–inhibition efficiency relationships showed that changes in the inhibiting ability can be explained by changes in the inhibitor electronic properties, which include such parameters as the difference between the highest occupied and lowest unoccupied molecular orbitals, as well as the calculated dipole moment of the inhibitor molecule.

As noted above, the protective properties of BTA



were studied in numerous works. This is due to not only the commercial availability of this very weak NH-acid (pK_a 8.11 ± 0.17 in a solution with ionic strength of 0.4), but also its fairly high solubility in water and water–ethanol solutions, high stability (m.p. 100 °C, b.p. 201–204 °C/15 Torr) and ability to form poorly soluble compounds with cations of many metals (Ag, Cu, Zn, Ni, Co, Pb).[14] BTA is especially popular for protection of copper and its alloys and to a smaller extent for protection of zinc, aluminium alloys, iron and low-carbon steels. Benzotriazole can prevent dissolution of not only copper itself, but also its corrosion products, which is used to preserve patina-coated copper items.[90] It should be noted that BTA solutions can passivate the alloy Cu—26 Zn—4 Al, which has a shape memory effect, and to increase its resistance against crevice corrosion.[91]

Benzotriazole is often added to various cooling systems and antifreezes due to its ability to hinder the corrosion of copper alloys in solutions with a wide range of salt content and pH, even at elevated temperatures.[4,12,13] It is believed [92] that BTA added to natural water not only does not impair the stabilising effect of phosphonate-type complexons, *e.g.* 1-hydroxyethane-1,1-diphosphonic acid (HEDP) at pH 9, but also hinder itself calcite crystallisation at pH 7.0; therefore, BTA can be used both as a metal corrosion inhibitor and a scaling inhibitor. According to the available data,[43] BTA is a more efficient inhibitor of brass dezincification than BI or 1-vinyl-2-phenylbenzimidazole in neutral and weakly acidic chloride solutions. However, it has been shown [93] that even small amounts of sodium sulfide (< 0.5 mmol litre^{-1}) can destroy the protective polymeric film formed by the inhibitor on the metal surface according to the reaction

$$2\,[\mathrm{Cu(I)-BTA}]_n + n\,S^{2-} \longrightarrow n\,Cu_2S + 2n\,\mathrm{BTA}^-. \qquad (5)$$

Although the equilibrium vapour pressure of BTA is low ($\sim 10^{-5}$ Torr at 25 °C), it can be used as a volatile corrosion inhibitor.[94] BTA alone is seldom used for this purpose. How-

ever, it is well compatible with other volatile inhibitors in compositions, which makes it possible to improve the protection of non-ferrous metals and alloys from outdoor corrosion with such compositions.[95]

Corrosion inhibition of copper with BTA and electrochemical reactions causing copper corrosion were studied in aqueous solutions with various compositions over a wide range of pH. For example, a study of copper behaviour in 1 M AcONa with pH 4–10 by voltammetry and electrochemical impedance[96] showed that restructuring of the surface copper oxide on metallic copper in the presence of BTA rapidly occurs in a weakly alkaline solution but is slower in neutral and weakly acidic solutions; such solutions require higher inhibitor concentrations. The free energy of BTA adsorption varies from -30 to 39 kJ mol^{-1} depending on pH. It was concluded that the protective film was a dielectric and its inhibitory effect increased with an increase in pH and BTA concentration.

The ability of BTA to inhibit pit corrosion of copper in aqueous solutions has been known for a long time, but it was found[97] that low concentrations (<0.05 mmol litre^{-1}) of this inhibitor itself could cause pit formation in pure borate buffer with pH 7.4. These pits were very small and readily underwent repassivation; they did not appear at higher BTA concentrations. This effect of BTA on initial stages of copper depassivation was explained by formation of complex compounds with various compositions. At low BTA concentrations, a protective polymeric film cannot yet be formed on the surface of oxidised copper, whereas formation of a soluble complex, *e.g.*, with Cu(II), produces small pits shaped as etching holes. However, this feature of BTA does not prevent its usage as a pit corrosion inhibitor of very thin films of copper deposited onto polished Si(100) wafers.[98] Owing to the formation of a superfine inhibitor film, the pitting potential of copper increases by 0.7 V, which is evidence of its reliable protection from local depassivation.

Of considerable importance are studies related to BTA adsorption on oxide-free metal surfaces (specific crystal planes), especially studies employing methods with atomic resolution such as STM or AFM. These studies make it possible to better understand the mechanism involved in the formation of protective films on metal surfaces. For example, the adsorption of BTA on various planes of a copper single crystal in aqueous solutions of mineral acids was studied.[99] The results obtained by STM suggest that BTA molecules adsorbed on the Cu(100) plane in 0.1 M $HClO_4$ form 'head to tail' parallel chains (Fig. 2*a*). On the Cu(110) plane, these chains have an antiparallel orientation (Fig. 2*b*). In the case of Cu(111), the molecular planes are perpendicular to the copper

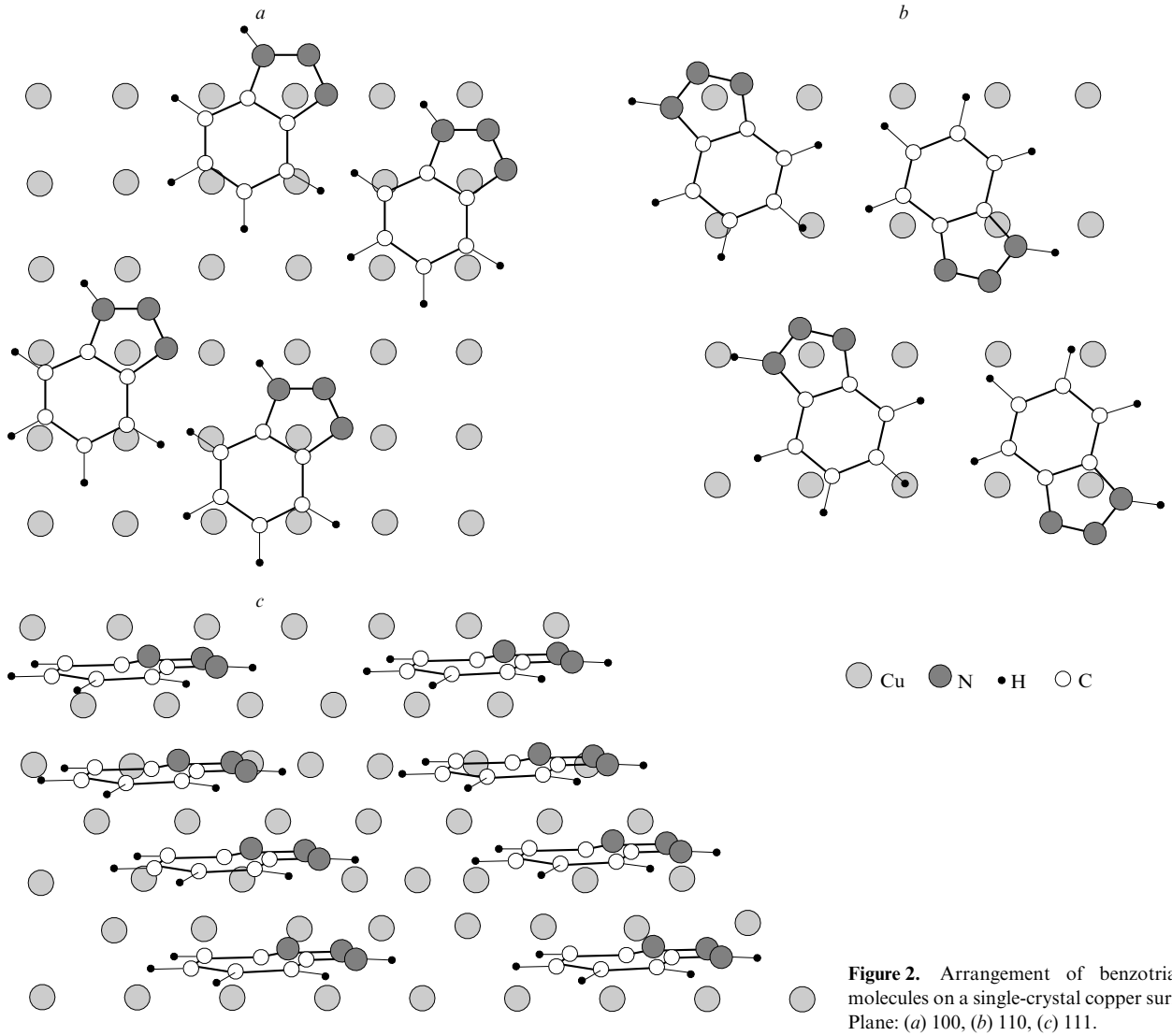


Figure 2. Arrangement of benzotriazole molecules on a single-crystal copper surface. Plane: (*a*) 100, (*b*) 110, (*c*) 111.

surface; they are arranged as if sideways to give ordered parallel rows (Fig. 2 *c*). As follows from the voltammograms, the orientation of the plane almost does not affect the cathodic current in the potential range from −0.3 to +0.2 V. The anodic current of metal dissolution appears at a potential of 0.25 V. The cathodic peak related to copper electrodeposition from the copper ions formed at positive potentials is detected at about −0.3 V. Below this value, hydrogen evolution occurs. Addition of 1 mol litre^{-1} BTA shifts the potential of copper dissolution by 0.2 V, irrespective of the plane orientation. Presumably, a multilayer film of the Cu−BTA complex is deposited in this case. On the other hand, the plane orientation affects markedly the hydrogen evolution potential: it decreases by 0.05 and 0.2 V, respectively, for the Cu(100) and Cu(110) planes, but remains unchanged for Cu(111). It should be noted that in the latter case, shifting the potential to −0.3 V results in destruction of the rows of adsorbed molecules. In view of this, it was assumed [99] that BTA molecules are either desorbed or become highly mobile. A similar behaviour was observed in the adsorption of other heterocyclic compounds, *e.g.* phenanthroline.[26] For other copper planes, shifting the potential to negative values did not result in the blurring of STM images. This suggests that the copper surface binds rather strongly the BTA molecules arranged in a planar way. The differences in the orientation of BTA molecules may be explained by differences in the force of molecule–substrate and molecule–molecule interactions due to the contribution of π-interactions. The latter exist in the case of such ordering where the rows of molecules are oriented vertically. At positive potentials, disordering of surface structures starts on all planes; it is presumably related to the formation of a polymeric Cu−BTA complex.

Based on STM data on the BTA adsorption from 0.1 M HCl solution on the Cu(100) surface at potentials more negative than −0.6 V, it was concluded that a chemisorbed layer of vertical (or slightly tilted) BTA rows was formed on the copper surface.[100] As the potential is increased, adsorbed BTA molecules are replaced by a monolayer of chlorides. At potentials above −0.35 V, a Cu(I)–BTA complex is formed that builds a protective film. This mechanism differs from that observed in sulfuric acid; in the latter case, a chemisorbed BTA layer is directly converted to give a Cu(I)–BTA phase. This may explain why the efficiency of copper inhibition in hydrochloric acid is lower than that in sulfuric acid.

In pure sulfuric acid, an adsorbed sulfate layer is formed on the surface of the Cu(111) plane, but addition of BTA results in sulfate displacement and formation of a monolayer of the triazole (though poorly ordered and defective), which includes short chain-like molecular structures.[101] The BTA molecules in such structures are oriented normally to the surface; as a result, the copper dissolution stage is hindered and the potential where copper dissolution starts is increased by 0.050–0.30 V, depending on the BTA concentration and surface coverage. At more positive potentials, metal dissolution occurs *via* nucleation and growth of very small pits, which increases the surface roughness.

Theoretical analysis of BTA adsorption in molecular and anionic forms on Cu(111) planes performed by Jiang and Adams [102] confirmed that not only physical adsorption of BTA but also chemisorption through sp^2 hybrid orbitals of nitrogen in the triazole ring is possible. Chemisorption of a BTA molecule can be stabilised due to interaction with the adjacent protophilic radical to give an intermolecular hydrogen bond and two chemisorption bonds on the surface. It was also concluded that C−H···N bonds could not be formed since the driving force for polymerisation on copper surface was not provided. However, it is possible that an N−H···N bond exists between two adsorbates, which creates a network film structure involving segments of the 1 : 1 Cu(I)–BTA complex with a bidentate structure.

The adsorption of BTA on oxidised Cu(110) surface has been studied by various methods, including STM.[103] On oxide-free Cu(110) surface, BTA is adsorbed on active sites (ledges, grain boundaries), with molecules arranged horizontally to form well-ordered structures, whereas a disordered structure several monolayers thick is formed on an oxidised surface.

On the other hand, STM data for polycrystalline copper foil show [104] that Cu–BTA complexes have the shape of oblong rectangles that are presumably two- rather than three-dimensional. The copper surface becomes more even, smoother and less rough, which favours protection. However, numerous grooves remain between the polymeric chains, through which corrosion can occur.

A study on the effect of oxygen on copper corrosion inhibition with BTA by scanning electron microscopy [105] showed that the growth of the passivating film of the Cu(I)−BTA complex in sulfate solution was hindered considerably as the oxygen concentration decreased (the solutions and chamber were deoxygenated with purified nitrogen). It was found that even with oxygen content in the solution lower than 90 μg litre^{-1}, the complex gradually formed a film that had dielectric properties; the film was no thicker than 5 nm even after 4 h, whereas without deoxygenation, it was about six times thicker. It was concluded that the formation of a film of the complex does not require a primary oxide Cu_2O to exist on the surface, but at least trace amount of oxygen is required in the corrosive medium.

Currently, the interest of researchers in corrosion inhibition of other metals with BTA and hence the formation of protective nano-sized layers increased. For example, Cao *et al.*[106] used polarisation measurements and Raman spectroscopy for *in situ* studies of the electrochemical behaviour of copper, iron and nickel in 0.1 M KCl solution. It is believed that protective films on the corresponding metals are formed by polymeric complexes $[Cu(I)–BTA]_n$ and $[(Fe(II))_n–(BTA)_m]_p$. In the case of iron, the formation of Fe−N coordination bonds and deprotonation of a BTA molecule can occur upon direct interaction of the organic compound with an iron surface. Poor protection was observed for nickel, though the possibility of formation of a surface Ni−BTA complex was not ruled out. Presumably, the dependence of Raman spectra on the potential in corrosion inhibition of copper and iron shows that BTA ions in the surface complexes can undergo protonation at more negative potentials, with a resultant decrease in the protection efficiency.

It has been found [107] that the surface enhancement factor of Raman scattering on an iron electrode free from oxides can vary by two to three orders of magnitude, depending on the surface roughness. Techniques for iron electrode pretreatment were elaborated in order to obtain optimum surfaces for SERS. Using these techniques, SERS can be successfully used to study practically important iron electrodes. A study on the formation of films and BTA inhibition effect in iron protection has shown that BTA interacts with the surface through two nitrogen atoms of the triazole ring to give a surface polymer $[Fe_n(BTA)_p]_m$ that can suppress iron dissolution and oxidation. It has also been shown that decreasing the pH from 7.0 to 1.8 (by adding sulfuric acid) degrades the complex due to BTA protonation, therefore the inhibition efficiency decreases. On the other hand, it is known that the addition of the I^- anions to

the solution suppresses the anodic process, which results in the positive shift of the corrosion potential, whereas the addition of BTA suppresses both the anodic and cathodic reactions. Data on the joint use of BTA and I^- in 0.5 M H_2SO_4 suggest a noticeable synergistic anticorrosion effect. Presumably, I^- is adsorbed on iron and modifies the surface, which then readily adsorbs protonated BTA molecules without formation of bonds between BTA and iron cations.

The interaction of BTA with copper, iron, nickel, silver, gold, chromium and zinc surfaces in neutral solutions containing NaCl (0.1 mol litre^{-1}) and BTA (0.01 mol litre^{-1}) was studied by time-of-flight secondary-ion mass spectrometry (TOF-SIMS).[108] The results were discussed in terms of the relationship between the efficiency of corrosion protection (as determined by polarisation resistance measurements) and the degree of polymerisation of BTA complexes on the surface. It was found that the maximum number of polymeric chains was observed for copper, especially at pH 6 where the highest protective effect is observed. The protective effect for zinc and nickel is very small, and no TOF-SIMS spectra were observed for chromium and iron at all. It was therefore assumed that iron did not form complexes with BTA under the conditions studied (possibly, BTA was not adsorbed on iron).

This conclusion disagrees with data of a number of studies that reported not only adsorption but also the formation of a Fe—BTA complex, which probably had a polymeric structure. For example, our XPS data [109] show that exposure of iron at the free corrosion potential in borate buffer (pH 7.36) containing 2.5×10^{-3} mol litre^{-1} of BTA resulted in a thin film on the iron electrode ($\sim$3 nm thick).

On AISI 304 stainless steel, at least in 1.0 M HCl solution, BTA does not affect the kinetics of anodic dissolution in the active potential range but considerably hinders cathodic processes.[110] This inhibits the corrosion cracking of steel, increases the critical stress intensity factor for corrosion cracking and decreases the crevice growth rate. Pickering and co-workers [111] found that BTA efficiently inhibited both hydrogen absorption on iron and hydrogen evolution. An increase in the BTA concentration in a deoxygenated aqueous solution of 0.1 N H_2SO_4 + 0.69 N Na_2SO_4 decreases the steady-state current of hydrogen penetration through an iron membrane, and its content in the metal decreases.

Iron can be protected with not only BTA itself, but also its complexes with metal cations. In fact, a synergistic effect of BTA and small amounts (no more than 5×10^{-6} mol litre^{-1}) of copper ions was observed [112] for iron protection in 0.5 M H_2SO_4. Presumably, this enhancement of corrosion inhibition results from the formation of a polymeric Cu(I)-BTA complex on the metal surface, which hinders the cathodic reaction on iron.

The regularities of copper and iron protection noted above were also observed for other, less thoroughly studied metals. As in the case of iron, BTA can slow down the corrosion of cobalt in aqueous solutions in a wide pH range.[113] In this case, BTA forms a coordination bond with the metal through nitrogen atoms, as well as an ionic bond with the anion formed due to inhibitor dissociation as an NH-acid. Naturally, such bonds are more readily formed in alkaline media where the passivating film includes cobalt oxide and BTA anions.

It was concluded from XPS and ellipsometric data [114] that the Zn(II)–2 BTA complex is formed on the surface of a zinc foil exposed to a solution of BTA in ethanol (10 g per 100 ml) and then washed. This complex is characterised by a noticeable shift of the $Zn2p_{3/2}$ peak (+0.8 eV) in comparison with the peak typical of zinc oxide; taking this into account, two peaks were resolved in the XPS spectrum and the thicknesses of the layers were determined. It was concluded that a layer of the complex 0.4 nm thick is formed atop a zinc oxide layer 0.6 nm thick; this agrees with ellipsometric results.

The protection mechanisms of the same metal with substituted BTAs may either be similar or have distinctive features. This depends to a considerable extent on the chemical structure of the inhibitors and on the composition of the corrosive medium. For example, the inhibition mechanisms of copper corrosion in 0.5 M H_2SO_4 with BTA and 4-carboxybenzotriazole are almost the same and consist of adsorption of the inhibitors *via* a triazole ring.[115] However, in borate buffer solution with pH 9.2, anodic polarisation of copper in the presence of the same inhibitors results in films of different types.[116] The film has n-conductivity in the former case and p-conductivity in the latter.

To find a corrosion inhibitor for copper and its alloys that is more efficient than BTA, Chinese scientists studied mixtures of BTA with comparatively simple derivatives. For example, in 3% sodium chloride solution, 4-carboxybenzotriazole not only fails to improve the inhibitory effect of BTA, but also creates steric hindrance of inhibitor interaction with the copper surface owing to the constituent CO_2H group.[117] Conversely, a mixture of BTA with carboxymethylbenzotriazole in the same solution features a mutual enhancement of copper protection by the components of the inhibiting mixture.[118]

Alkyl benzotriazole-4- or -5-carboxylates containing long-chain (*e.g.*, octyl) substituents are even more efficient in the corrosion protection of copper in acidic sulfate solutions (pH 0).[119] This is explained not only by the possibility of inhibitor chemisorption through protonated nitrogen atoms in the triazole ring, but also by an increase in physical adsorption. The authors believe that an important role belongs to van der Waals attraction forces between the substituents oriented in the direction away from the metal. An increase in pH (to 8) results in replacement of this structure by a sterically hindered polymeric film with poorer protective properties. Based on computer simulations for corrosion inhibition, it was concluded [120] that the energy of bonding of each ester with the surface regularly increases with an increase in the length of the alkyl chain. A quantum-chemical study of BTA and alkyl esters of carboxybenzotriazole performed using the Lee–Young–Parr functional revealed a linear relationship between the inhibitor's efficiency, the factor of charge distribution and the polarisability of the inhibitor molecule.[121]

Experimental studies carried out over the past 10–12 years have shown conclusively that alkylated BTA derivatives are quite efficient corrosion inhibitors of metals. For example, 5-n-hexylbenzotriazole inhibits copper corrosion more efficiently than BTA in cooled neutral water; in this case, according to data from XPS and SIMS, an intricate polymeric complex is formed on its surface.[122] Trabanelli and co-workers [123] have shown that at elevated temperatures under heat transfer conditions (with the wall and solution temperatures differing by 60 °C), 5-n-hexylbenzotriazole protects copper from corrosion more efficiently than 5-methyl- and 5-chlorobenzotriazoles or 2-amino-5-mercaptothiodiazole.

Tommesani *et al.*[124] used corrosion and electrochemical methods in a comparative study of protective films formed on copper at 80 °C upon exposure of samples for 1 h in a solution containing 0.2 mmol litre^{-1} of BTA or its derivatives. The following substituted BTA were used: 5-methyl-, 5-butyl- and 5-hexylbenzotriazole, as well as 5-dodecylbenzotriazole (a saturated solution of the latter was used due to its low

solubility). The studies were carried out at 30 °C in 3.5% neutral (pH 7.0) and acidic (pH 2.5) solutions. It was found that in the neutral solution, the protective effect of the films increased with an increase in the length of the alkyl chain in the inhibitor molecule and in the duration of copper pretreatment. However, the efficiency of 5-dodecylbenzotriazole is inferior to that of 5-butyl- and especially 5-hexylbenzotriazole. In the acidic solution, which is more corrosive, only the films formed by 5-hexylbenzotriazole ensure high protection, but this requires that the duration of pretreatment in the inhibitor solution be increased to 16 h. Using impedance measurements, the authors assessed the thicknesses (d) of the protective films and found that the growth rate of these films was much smaller in the presence of BTA than with 5-hexylbenzotriazole. In fact, pretreatment of a copper surface for 1 h in a BTA solution resulted in a film thickness of 2.6 nm, whereas treatment with a 5-hexylbenzotriazole solution gave a film $\sim$100 nm thick. In general, the presence of inhibitor films decreases the oxygen reduction rate; anodic dissolution is hindered only by 5-hexylbenzotriazole, which was found to be the most efficient inhibitor of all the compounds studied. It was also found that treatment of a copper surface with a solution of 5-hexylbenzotriazole makes it somewhat more hydrophobic (the contact wetting angle is 15° larger than that after similar surface treatment with the BTA solution). Brunoro *et al.*[125] showed that the protective films formed by BTA derivatives with long alkyl groups, especially the films formed by 5-octylbenzotriazole, prevent corrosion of not only copper but also bronze with a composition similar to ancient bronzes, in media simulating acid and neutral rains. Later, the efficiency of adding a BTA + 5-hexylbenzotriazole mixture to the wax widely used to protect bronze monuments was proved.[126]

Frignani *et al.*[127,128] studied the inhibiting effect of BTA and its 5-alkyl derivatives in 0.1 M Na_2SO_4 and NaCl solutions at pH 2.5 and 30 °C in order to minimise the oxide formation on a copper surface. The inhibitor concentration was varied from 10^{-3} to 10 mmol litre^{-1}. It was found that inhibition of copper dissolution in sulfate solutions increases in the series BTA < 5-methylbenzotriazole < 5-butylbenzotriazole < 5-hexylbenzotriazole $\approx$ 5-octylbenzotriazole. However, 5-dodecylbenzotriazole did not show any considerable inhibiting effect on the anodic reaction because of its low solubility. In chloride solutions, which are much more corrosive than sulfate solutions, neither BTA nor 5-methylbenzotriazole (0.1 mmol litre^{-1}) showed inhibiting properties. It was only alkyl derivatives of BTA containing four or six carbon atoms in the alkyl chain that hindered both the anodic and cathodic reactions on copper. Taking into account the results of electrochemical impedance measurements and nanoweighing on a quartz crystal with a copper layer obtained by electrolytic plating (after preliminary sputter-deposition of gold), it was concluded that at concentrations of the inhibitors that ensure complete suppression of copper dissolution, the molecules of BTA, 5-methylbenzotriazole and probably 5-butyl- and 5-hexylbenzotriazoles are oriented almost parallel to the metal surface plane.

Frignani *et al.*[129] studied 5-alkyl-substituted BTA as corrosion inhibitors of iron in acidic solutions (1 N H_2SO_4 and 1 N HCl). In sulfuric acid, the iron inhibition factor (Z) with BTA was 36%; 5-hexylbenzotriazole is the most efficient inhibitor (Z = 76%). In hydrochloric acid, these compounds inhibit the corrosion of iron more efficiently than that of copper: Z = 79% at 0.25 mmol litre^{-1} of BTA; the most efficient inhibitors include 5-hexyl- (Z = 95%) and 5-octylbenzotriazoles (Z = 97%), whereas for 5-dodecylbenzotriazole, Z = 66%. The logical assumption was made that the enhancement in the protective properties of inhibitors is due to the ability of chloride to recharge the surface making it negatively charged and thus enhancing the physical adsorption of the inhibitor cations.

Other BTA derivatives containing hydrophobic substituents were also studied in acidic media, but they did not show high protective properties toward iron, at least in sulfuric acid. For example, Selvi *et al.*[130] studied *N*-[1-(benzotriazol-1-yl)alkyl]arylamines and *N*-[(1-benzotriazol-1-yl)aryl]arylamines as corrosion inhibitors of low-carbon steel in 0.5 M H_2SO_4; the efficiency of these compounds was inferior to that of 1-hydroxymethylbenzotriazole (Z = 95%). Conversely, in hydrochloric acid, BTA derivatives are often much more efficient corrosion inhibitors of iron. For example, quinonoid BTA derivatives obtained in the reaction of 2,3-bis(benzotriazol-1-yl)-1,4-naphthoquinone and diethylenetriamine (or β-hydroxyethylidenediamine) decreased the corrosion rate of steel in 12% HCl at 60 °C by a factor of 36.8 (or 29.3). This is much higher than the corresponding value for BTA.[131]

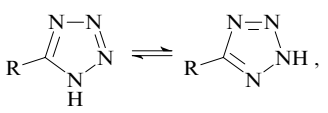
Copper and its alloys can also be efficiently protected with similar BTA derivatives in 0.5 M H_2SO_4 solutions, as shown, *e.g.*, in a study[132] on the corrosion protection of brass with 1-[*N*,*N*-bis(hydroxyethyl)aminomethyl]benzotriazole. This inhibitor is markedly more efficient than BTA in acidic medium, but its protective effect decreases as pH increases.

An interesting feature of adsorption on copper was found:[133,134] not only the protective effect but also the Raman spectra and electrochemical impedance spectra obtained after exposure of copper in a 1.0 M AcONa solution containing BTA or [bis(benzotriazol-1-yl)methyl]octylamine are almost totally identical. Presumably, the BTA derivative loses the aliphatic chain upon adsorption and, like BTA, forms a protective film with a multilayer structure: Cu/Cu_2O/Cu(I)—inhibitor. The film has dielectric properties; its thickness and protective effect increase with an increase in the inhibitor concentration and in the duration of copper exposure to the solution. At low concentrations of the BTA derivative and shorter immersion times, the inhibitor is chemically adsorbed on the electrode surface. Its adsorption behaviour can be formally described by the Frumkin isotherm with a free adsorption energy of -19.5 kJ mol^{-1} (Ref. 135).

BTA derivatives as corrosion inhibitors for aluminium alloys are less studied. However, it has been found that in 0.1 M HCl, the efficiency of corrosion protection of pure aluminium with substituted BTA (at a concentration of 10^{-4} mol litre^{-1}) increases in the series BTA < 5-chlorobenzotriazole < 5-methylbenzotriazole < 5-nitrobenzotriazole. This allows one to hope that a fairly efficient inhibitor will be found among these compounds.[136] The compounds studied are cathodic inhibitors, and the mechanism of their action is related to adsorption on the metal surface. Presumably, at low concentrations their molecules are arranged horizontally. At high concentration of nitrobenzotriazole, its molecules are oriented normally to the aluminium surface and the nitro group can be reduced to amino group.

3. Tetrazoles

Tetrazole (TA), which exists in two tautomeric forms



is a strong NH-acid (pK_a 2.68) well soluble in water.[137]

Tetrazoles are relatively little studied as corrosion inhibitors. It is likely that tetrazoles have been first patented for this purpose in 1984 in the USA,[138] but their high reactivity was well known by that time, including complexation with metals, relatively low toxicity, fungicide, bactericide and antioxidant properties.[139] Thermal cleavage of the tetrazole ring will not necessarily occur upon heating to 200 °C, therefore many tetrazoles withstand processing together with molten plastics. For this reason, they were studied as promising compounds for addition to polymeric films that find use in anti-corrosion packaging of metal items.[140]

5-Substituted tetrazoles were studied by recording polarisation curves on St10kp low-carbon steel and M3 copper in 0.5 M Na_2SO_4 solutions. Tetrazole itself was found to be a less efficient inhibitor than BTA. This may be because it is a stronger acid than BTA and the solution is acidified upon addition of tetrazole. Since the solution was not buffered, it is small wonder that introduction of a strong electron acceptor (CCl_3) to the tetrazole molecule increases its acidity, hence corrosion of steel is intensified. With electron-donating substituents (Me, NH_2), the protective effect of the inhibitors increases (5-aminotetrazole protects both metals more efficiently than BTA). The best protection, especially that of steel, was provided by the sodium salt of 5-phenyltetrazole. It is believed that 5-substituted tetrazoles, which form insoluble complexes with Fe(II) and Cu(II), give films a few nanometres thick on metal surfaces; here the electron density localised on two nitrogen atoms (or between them) partially overlaps with the d orbitals of the metal atom.

The involvement of tetrazoles in the formation of a protective film on steel was studied by IR spectroscopy and XPS,[141] the surface morphology was studied by scanning electron microscopy and atomic force microscopy.[142] Based on the data obtained, it was concluded that complex compounds with the composition $Fe(TA)_2(H_2O)_2$ and polymeric network structure are formed on the surface of low-carbon steel due to adsorption from an aqueous corrosive medium (0.05 M Na_2SO_4 solution) containing TA (0.06 mol litre^{-1}). The adsorbed layer may be as thick as 7–8 nm.

The efficiency of 5-phenyltetrazole was confirmed by Trabanelli *et al.*[143] who studied the protection of copper with tetrazole and six tetrazole derivatives in 0.1 M NaCl solution at 40 and 80 °C. If the pH was not fixed, it decreased to 2.7–3.6 upon addition of 1 mmol litre^{-1} of the compounds in question; tetrazole was poor inhibitor under these conditions. However, at pH 4.0 or 8.0, the protection was improved markedly (at 40 °C, $Z = 97.6\%$ or 98.6%, respectively). In all cases, 5-phenyltetrazole showed excellent protective properties ($Z = 98.6\% - 99.5\%$). The efficiency of this inhibitor decreases markedly with an increase in temperature, though it remains higher than the efficiency of tetrazole.

Even better inhibiting properties were first noted[144] for 5-mercapto-1-phenyltetrazole (MPT), the most popular corrosion inhibitor of copper among tetrazoles. It was shown that MPT passivates copper in deoxygenated 0.1 M NaCl solution and inhibits somewhat its local depassivation. This rather strong SH-acid (pK_a 2.9 ± 0.1) forms a hardly soluble compound with copper cations, mainly due to the bond of the metal with the sulfur anion. Though MPT has a hydrophobic substituent, it is fairly well soluble in water. It is believed[143,145–148] that MPT is the best tetrazole-type corrosion inhibitor for copper in acidic media.

Piezoquartz weighing was used to determine the inhibiting effect of MPT with respect to copper in acidified 0.1 M solutions of NaCl (Ref. 149) and Na_2SO_4 (Refs 146 and 150). High protective properties of MPT were confirmed in both cases, and it was shown that the protective film could last for a few hours after the electrode had been moved to the corrosive chloride solution containing no inhibitor. It was found that MPT is an anodic inhibitor in sulfate solution where no more than one monolayer of the compound is deposited on the copper electrode.[146]

The adsorption of MPT on the surface of a Cu(111) single crystal was studied in a sulfuric acid solution using surface-sensitive methods (STM, XPS and AES) that allowed the formation of the inhibitor film to be monitored.[150,151] High-resolution STM imaging provided details of the adsorbed layer and of the structure of separate molecules. Copper dissolution in a pure sulfate solution starts with Cu(111) crystal steps, whereas it occurs on terraces in the inhibitor-containing media since MPT blocks the step edges. STM data and quantum chemical calculations provided information on the size of the MPT molecule and its symmetry.

According to Brunoro *et al.*,[152] MPT is an efficient corrosion inhibitor of copper not only in sulfate solutions, but also in perchlorate and nitrate solutions with pH 3.4–5.3, through its protective efficiency is inferior to that of 5-butylbenzotriazole in a similar chloride medium.

The high efficiency of MPT in copper protection prompted scientists to use it for bronze protection. It was shown[147] that the efficiency of bronze corrosion inhibition in nitrate solutions decreased in the series MPT > 1-phenyltetrazole > 5-aminotetrazole > tetrazole. Chinese researchers[153] found that mixtures of MPT with BTA[148] or 2-mercaptobenzotriazole[153] in chloride solutions could be even more efficient for bronze protection than MPT or BTA.

Regrettably, the protection of steel against corrosion with tetrazole and its derivatives in chloride solutions has almost never been studied. It is only known that 1-(acridin-9-yl)-5-(4-chlorophenyl)tetrazole provides efficient protection of steel ($Z > 92\%$) in 1.0 M HCl solution at 30–60 °C.[154]

IV. Conclusion

Azoles can serve as corrosion inhibitors of ferrous and non-ferrous metals that provide efficient protection in various corrosive media. The mechanism of copper corrosion inhibition has been studied most thoroughly; on copper surface, many azoles form protective nano-sized coatings that consist of a polymeric complex of the inhibitor with the metal cation. The mechanism of iron corrosion inhibition has been studied in much less detail, though there are reasons to believe that azoles can provide reliable protection of this metal in media with broad pH range as well.

The efficiency of metal protection with substituted azoles is determined by not only electronic effects of substituents, but also their hydrophobicity. The solubility of organic inhibitors in aqueous media decreases in the case of hydrophobic substituents, but one can achieve very high protective properties of an inhibitor toward many metals by optimising the chemical structure of the azole. Of corrosion inhibitors discussed above, 5-substituted benzotriazoles deserve special attention as they have high complexing ability and high surface activity. Tetrazoles are relatively little studied as corrosion inhibitors; the high reactivity and fairly good thermal stability of these compounds allow us to hope that success in finding compounds of this class that are capable of corrosion protection of metals will be achieved in the future.

In comparison with other classes of compounds, the prospects of enhancing the corrosion protection efficiency of

azoles by combining them with other corrosion inhibitors or special additives have not been studied as thoroughly. However, the ability of many azoles to create ultrathin layers on the surface opens up new prospects for targeted construction of nano-sized protective films, as recently demonstrated by means of layer-by-layer adsorption of alkyl carboxylates and aromatic amino acids on an iron surface.[155]

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