



An Extraordinary Effect of Benzotriazole and Sulfide Ions on the Corrosion of Copper

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While benzotriazole (BTAH) is an excellent inhibitor for the corrosion of copper in unpolluted media, it promotes corrosion in sulfide-polluted salt water. BTAH loses its remarkable inhibiting efficiency in the unpolluted medium and allows corrosion rates that are greater than those in the absence of BTAH. Scanning electron microscopy images revealed extensive general corrosion. On the other hand BTAH inhibited the anodic dissolution of copper at more noble potentials in the polluted medium. The results are discussed in terms of competition between the sulfide ions and BTAH for adsorption on the surface and for complex formation with copper ions.

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Benzotriazole (C₆H₅N₃, BTAH) is widely used as a corrosion inhibitor for copper and its alloys in many industries, e.g., petrochemical industries,¹⁻³ desalination,⁴ chemical mechanical polishing,⁵⁻¹⁰ and refrigeration.^{4,11} The remarkable inhibiting efficiency of BTAH is attributed to the formation of a polymeric film of Cu(I)BTA¹²⁻²³ on the surface, which inhibits the anodic dissolution reaction. The mechanism of inhibition involves adsorption of BTAH.^{12-16,24-31} The adsorption process can be represented by



where Cu:BTAH_(ads) refers to BTAH adsorbed on the copper surface. The degree of coverage of the surface with BTAH, θ_{BTAH} , can be expressed for a Langmuir isotherm by

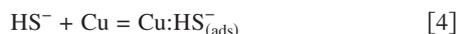
$$\theta_{\text{BTAH}} = K[\text{BTAH}]/(1 + K[\text{BTAH}]) \quad [2]$$

where K is the equilibrium constant of Reaction 1. Under anodic potentials, this adsorbed species can be oxidized to give the complex Cu(I) BTA,³² i.e.



Reaction 3 is an equilibrium between the adsorbed BTAH and that involved in complex formation. In principle, some of BTAH remains adsorbed on the surface while the rest is involved in complex formation. Increases in the pH of the medium and in the potential in the noble direction favor the formation of the complex Cu(I)BTA, while the adsorbed species, Cu:BTAH, is favored at more active potentials and in more acidic electrolytes.

The above mechanisms are well-accepted in clean (unpolluted) media. It is now widely recognized that many natural water bodies and industrial water streams are polluted. For example, formation waters in sour oil and gas wells are heavily contaminated with hydrogen sulfide which promotes metallic corrosion.³³ In such environments, copper and its alloys serve in media that are inhibited by BTAH and polluted with sulfide ions. Sulfide ions are known to promote the corrosion of copper.³⁴⁻⁴² This is believed to be via an adsorption step that can be represented by



where Cu:HS_(ads)⁻ refers to an adsorbed HS⁻ ion on the copper surface. The sulfide covered copper is oxidized to give CuS, i.e.,



The aim of this work is to study the effects of sulfide ions on the inhibition efficiency of BTAH against the corrosion of Cu in a chloride medium. In addition to its considerable industrial and environmental significance, this point raises interesting questions about the interaction of BTAH and HS⁻ ions on the surface of copper in a

corrosive environment. Several electrochemical and surface characterization techniques were used to address this point.

Experimental

Electrodes were prepared from Cu (99.9%) obtained from Goodfellow. The Cu electrodes (disks of area 0.2 cm²) were polished using SiC papers successively down to 2400 grits, followed by 0.3 μm alumina to acquire a mirror-like finish. A conventional three-electrode cell was used with an Ag/AgCl reference electrode, $E = 0.197$ V SHE, and a Pt sheet counter electrode. Solutions were prepared using deionized water, BTAH from Aldrich, AnalaR Na₂S, and NaCl from Fluka.

Potentiodynamic polarization curves were measured on the Cu electrode (at 2 mV s⁻¹) in 3.5% NaCl containing various concentrations of sodium sulfide and BTAH. The potential was controlled using a Gamry potentiostat. Potential scanning started from the less to the more noble potentials. Measurements were performed at 25 ± 1 °C while the electrolyte was stirred using a magnetic stirrer. The electrodes were preimmersed for 15 min in the chloride BTAH solution before measuring the polarization curves.

Electrochemical impedance spectroscopy (EIS) measurements were carried out under the open circuit potential within a frequency range of 100 kHz to 0.1 Hz using a Gamry potentiostat with impedance software.

The surfaces of the electrodes were examined using X-ray photoelectron spectroscopy (XPS), VG Scientific 200 spectrometer (U.K.), using Mg Kα radiation (1253.6 eV) operating at 300 W, 13 kV, and 23 mA, and a scanning electron microscope (SEM, JSM-6300 JEOL).

Results and Discussion

Effect of BTAH.—Figure 1 illustrates the effects of BTAH and HS⁻ ions on the polarization curve of copper in the chloride medium (3.5% NaCl). In the absence of sulfide ions, BTAH has a profound effect on the rate of anodic dissolution of copper. Comparison of curves a (3.5% NaCl) and b (3.5% NaCl + 1 × 10⁻³ M BTAH) reveals that a concentration of 5 × 10⁻³ M BTAH passivates the copper surface considerably. It decreases the rate of copper dissolution by two to three orders of magnitude over a broad range of potential that extends for about 600 mV starting from the free corrosion potential. The SEM images obtained on the copper surface in this region show that it is indeed passive (see Fig. 3). Under these potentials, the protection of the copper surface is attributed to the formation of the Cu(I)BTA complex (Eq. 3). A 700 mV wide passive region was reported for copper in a medium containing 0.2 mM BTAH in 0.01 M NaHCO₃.⁴³ A much narrower (300 mV) passive region was reported for copper in 0.5 M H₂SO₄ in the presence of 20 mM BTAH.⁴⁴ Across this passive region, the inhibited copper supports residual currents of the order of a fraction of a microampere, as shown in Fig. 1. Note that the effect of BTAH on the

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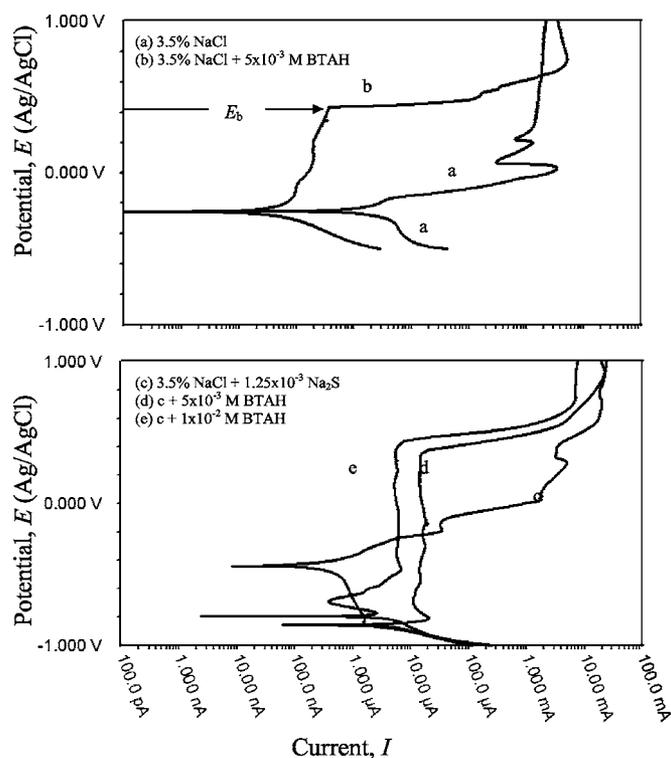


Figure 1. Effect of BTAH on the polarization curves of Cu electrodes (0.2 cm^2) in the unpolled (curves a and b) and in the sulfide-polluted electrolytes (curves c, d, and e): (a) 3.5% NaCl, (b) 3.5% NaCl + $5 \times 10^{-3} \text{ M}$ BTAH, (c) $1.25 \times 10^{-3} \text{ M}$ Na_2S , (d) 3.5% NaCl + $5 \times 10^{-3} \text{ M}$ BTAH + $1.25 \times 10^{-3} \text{ M}$ Na_2S , and (e) 3.5% NaCl + $1 \times 10^{-2} \text{ M}$ BTAH + $1.25 \times 10^{-3} \text{ M}$ Na_2S .

cathodic partial reaction is much less pronounced than on the anodic reaction, which indicates that BTAH acts as an anodic inhibitor.

Beyond the passive region, the current increases rapidly with an increase in potential indicating a breakdown in the protective film. This occurs at a potential defined as the breakdown potential, E_b . The value of this breakdown potential, E_p , is 435 mV (Ag/AgCl) for a concentration of 5 mM BTAH in a medium of 3.5% NaCl. One can detect a more subtle breakdown potential in the uninhibited medium at a potential of about -160 mV (Ag/AgCl). This value is about 600 mV more active than that in the inhibited medium and only about 75 mV more noble than the free corrosion potential.

Effect of sulfide ions.—Curves c, d, and e in Fig. 1, represent the corresponding results obtained in the sulfide-polluted medium. The presence of BTAH in the sulfide-polluted medium produces a much more complex behavior, curves d and e. The results suggest that BTAH inhibits the anodic dissolution of copper in the sulfide-polluted medium at high potentials while it promotes the reaction around the free corrosion potential. This leads to the appearance of a limiting current over a broad potential region that ends at the breakdown potential, E_a (curves d and e). The effects of different concentrations of BTAH on the polarization curve of copper in the sulfide-polluted medium, 3.5% NaCl + $1.25 \times 10^{-3} \text{ M}$ Na_2S (c) are shown in curves d and e. A higher concentration of BTAH decreases the magnitude of the limiting current and shifts the breakdown potential in the noble direction (compare curves d and e which show limiting currents of 17 and 6 μA , respectively).

Figure 2 compares the polarization curves of copper in the chloride medium inhibited with $5 \times 10^{-3} \text{ M}$ BTAH in the absence and in the presence of 1.25 mM HS^- ion. The figure reveals the following changes for a certain concentration of BTAH: (i) the limiting current in the sulfide-polluted medium is about two orders of magnitude

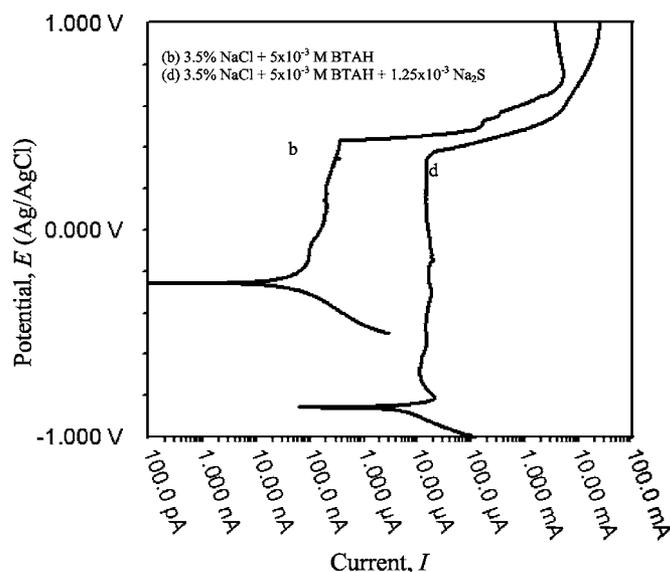
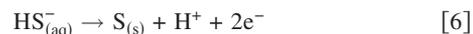


Figure 2. Effect of sulfide ions on the polarization curves of Cu electrodes (0.2 cm^2) in the presence of various concentrations of BTAH: (b) 3.5% NaCl + $5 \times 10^{-3} \text{ M}$ BTAH and (d) 3.5% NaCl + $5 \times 10^{-3} \text{ M}$ BTAH + $1.25 \times 10^{-3} \text{ M}$ Na_2S .

greater than the passive current in the unpolled medium; (ii) the free corrosion potential in the sulfide-polluted medium is shifted by about 500 mV in the active direction compared to that in the unpolled medium; and (iii) the breakdown potential, E_b , decreases by 55 mV from 435 to 380 mV. The increase in the limiting current caused by the presence of sulfide ions may be attributed to deterioration of the properties of the protection film and/or the anodic oxidation of the sulfide ions, i.e.



It is shown elsewhere^{45,46} that the limiting current of Reaction 6 is an order of magnitude greater than the limiting current shown in Fig. 2 (curve d). Furthermore, the XPS spectrum of the copper surface polarized in the presence of HS^- ions (see Fig. 6) reveals the absence of elemental sulfur (which has an XPS peak at a binding energy of 164.0 eV).

These findings show that the presence of $1.25 \times 10^{-3} \text{ M}$ Na_2S in the electrolyte leads to considerable deterioration in the protection efficiency of the Cu(I) BTA complex against the dissolution of copper. This is further substantiated by the SEM micrographs shown in Fig. 3 for copper surfaces polarized for 3 h at 0.2 V (Ag/AgCl). The SEM image in (a) was obtained after treatment in 3.5% NaCl + $5 \times 10^{-3} \text{ M}$ BTAH. It shows some inactive pits and defects in an otherwise passive surface. On the other hand, the image in (b), which is taken at the same magnification as that in (a), shows the effect of sulfide ions on the morphology of the corroded surface. Note the extensive general corrosion caused by the sulfide ions. The image in (c) displays an area that is fivefold greater than that in (b) for otherwise the same conditions.

Figure 4 shows current transients obtained on a copper electrode in the inhibited medium at a potential of 0.2 V (in the passive region) in the absence (a) and in the presence (b) of sulfide ions. Note the decay of current with time in both media. The quasistationary current in the polluted medium (after about 1 h) is more than an order of magnitude greater than that in the unpolled medium. Note the frequent current spikes caused by the sulfide ions in curve (b) which might be caused by localized corrosion cells that are re-passivated. This points to the promoting effects of sulfide ions on the anodic dissolution of copper in the presence of BTAH.

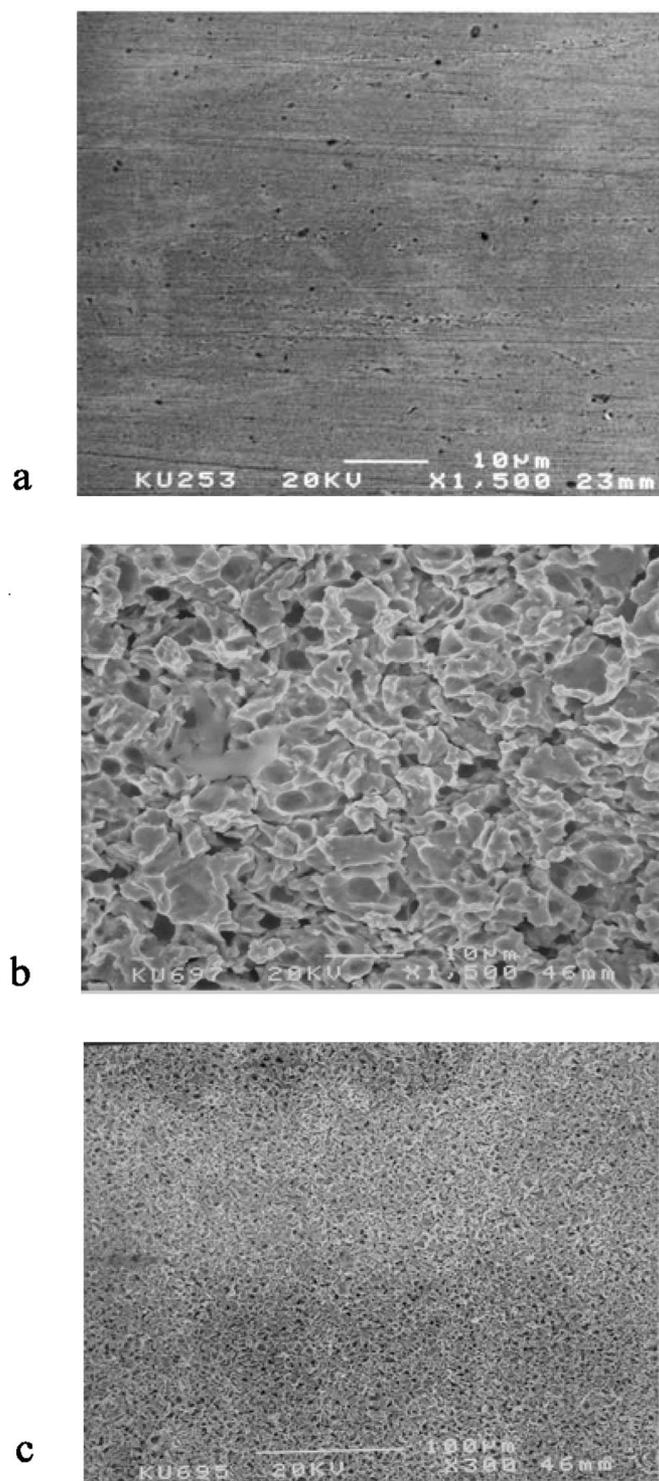


Figure 3. SEM micrographs of copper electrodes after being polarized for 3 h at 0.2 V Ag/AgCl in electrolytes containing: (a) 3.5% NaCl + 5×10^{-3} M BTAH and (b) 3.5% NaCl + 5×10^{-3} M BTAH + 1.25×10^{-3} M Na₂S. The magnification in image (c) is fivefold smaller than in (b) and otherwise the same condition.

Electrochemical impedance spectroscopy.—Measurements were carried out to monitor the changes in the polarization resistance (R_p) and in the double-layer capacitance (C) of the Cu/electrolyte interface in the presence of various concentrations of BTAH and sulfide ions under the free corrosion potential. Figure 5a is an

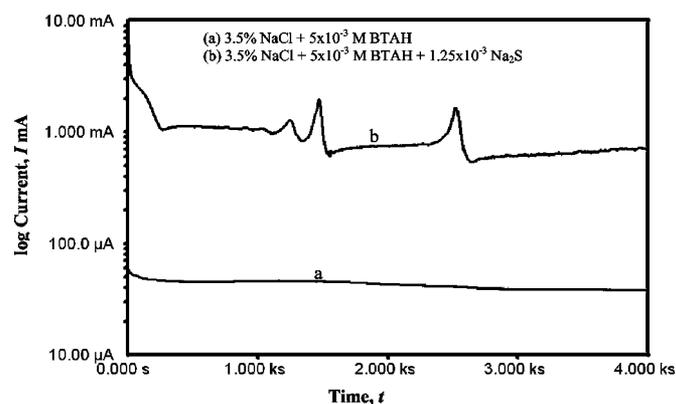


Figure 4. Current transients supported by Cu electrodes (0.2 cm^2) polarized at 0.2 V Ag/AgCl in electrolytes containing: (a) 3.5% NaCl + 5×10^{-3} M BTAH and (b) 3.5% NaCl + 5×10^{-3} M BTAH + 1.25×10^{-3} M Na₂S.

illustrative example of a Bode plot of the Cu electrode in the presence of electrolytes containing: (a) 3.5% NaCl, (b) 3.5% NaCl + 5×10^{-3} M BTAH, and (c) 3.5% NaCl + 5×10^{-3} M BTAH + 1.25×10^{-3} M Na₂S. It shows the variation of the impedance of the interface, Z , and the phase angle Φ^0 with the frequency of the signal (f). Many such figures were measured under various conditions.

Such results are frequently analyzed by fitting the plots to the behavior of equivalent circuits of the form shown in Fig. 5b,⁴⁷ where R_s is the resistance of the electrolyte, C is the capacitance of the electrical double layer, and Z is an impedance term.⁴⁷ Depending on the number of parallel or consecutive steps involved in the corrosion reaction, such as charge-transfer, diffusion, adsorption, etc., and the homogeneity of the surface, Z is simulated using a number of resistive and capacitive components connected in series or in parallel.⁴⁸ The simplest form of this equivalent circuit is obtained when the impedance of the interface is caused primarily by the

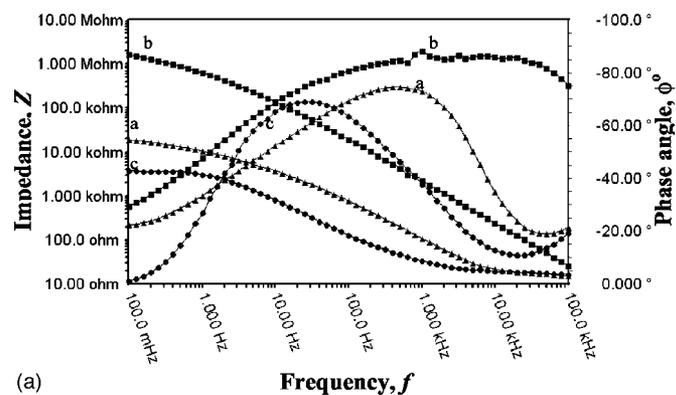


Figure 5. (a) Bode plot of a Cu electrode (0.2 cm^2) in electrolytes containing: (a) 3.5% NaCl, (b) 3.5% NaCl + 5×10^{-3} M BTAH, and (c) 3.5% NaCl + 5×10^{-3} M BTAH + 1.25×10^{-3} M HS⁻. (b) Equivalent circuit of the interface, R_s is the resistance of the electrolyte, C is the double-layer capacitance, and Z is the impedance to the faradaic reaction, see text.

Table I. Effects of the concentrations of BTAH and HS⁻ ions on the polarization resistance (R_p) and the double-layer capacitance (C) of the Cu/electrolyte interfaces in 3.5% NaCl, and the slope of the linear region (n), see Fig. 5a.

Solutions	EIS parameter	
	R_p (k Ω)	C (μ F)
a	18.7	2.0
b	4.0×10^3	0.13
c	7.0	41.0
d	3.6	23.0
e	16.7	15.0

^a 3.5% NaCl.

^b 3.5%NaCl + 5×10^{-3} M BTAH.

^c 3.5%NaCl + 1.25×10^{-3} M Na₂S.

^d 3.5%NaCl + 5×10^{-3} M BTAH + 1.25×10^{-3} M Na₂S.

^e 3.5%NaCl + 5×10^{-3} M BTAH + 1.25×10^{-1} M Na₂S.

charge-transfer step, in which case the $Z \approx R_p$ where R_p is the polarization (or charge-transfer) resistance of the interface.

These results were analyzed to obtain the impedance parameters in the light of the above equivalent circuit using Gamry software (Echem Analyst version 1.30). Table I lists the impedance parameters obtained under various concentrations of BTAH and sulfide ions. Note that R_p is a measure of the resistance of the interface to charge-transfer across the double-layer while C is a measure of the corroding area. The polarization resistance is inversely proportional to the corrosion current, i_{corr} ,⁴⁹ i.e.

$$R_p = \frac{b_a b_c}{2.3(b_a + b_c)i_{\text{corr}}} \quad [7]$$

where b_a and b_c are the anodic and cathodic Tafel slopes. Note that the very large value of R_p under condition b is associated with a small value of C . This is compatible with a large fraction of the surface being protected by the inhibitor and hence the corrosion rate is small.

The effect of BTAH in the unpolluted medium becomes evident upon comparing the results obtained under conditions (a) and (b) in Table I. The protection efficiency (% P) caused by 5×10^{-3} M BTAH against the corrosion of copper is given by

$$\%P = [1 - (R_p/R_{p(\text{BTAH})})] \times 100 \quad [8]$$

where R_p and $R_{p(\text{BTAH})}$ refer to the polarization resistance in the absence and in the presence of BTAH, respectively. Using the values of R_p in Table I for conditions (a) and (b) (18.7 and 4.0×10^3 k Ω , respectively) one finds that the protection efficiency is 99% for 5×10^{-3} M BTAH in the unpolluted medium.

A comparison of the data in b, d, and e in Table I reveals the large damaging effects of sulfide ions on the polarization resistance of the interface and hence on the inhibiting efficiency of BTAH. A sulfide concentration of 1.25×10^{-3} M HS⁻, in the absence of BTAH, increases the corrosion rate by more than twofold (compare the values of R_p of 18.7 and 7 k Ω in the absence and in the presence of HS⁻, respectively). On the other hand, in the presence of 5×10^{-3} M BTAH, the effect of HS⁻ is much more profound. Under this condition, a concentration of 1.25×10^{-3} M HS⁻ decreases the polarization resistance by several hundredfold from 4.0×10^3 to 3.6 k Ω . It is also noteworthy that the polarization resistance in the presence of both 5×10^{-3} M BTAH and 1.25×10^{-3} M HS⁻ (3.6 k Ω) is significantly lower than that in the absence of BTAH (7.0 k Ω). These findings suggest that the presence of sulfide ions (at 1.25×10^{-3} M) under this condition not only eliminates the 99% inhibiting efficiency of BTAH (at 5×10^{-3} M) but also promotes the corrosion reaction to a greater extent than in the absence of BTAH. A similar finding was reported by Fiaud and

Ghimouz⁵⁰ who studied the effect of hydrogen sulfide on the atmospheric corrosion of copper preconditioned in BTAH. While Fiaud and Ghimouz used a micromolar concentration of hydrogen sulfide in the gas phase without defining a concentration of BTAH, our results were obtained in the presence of millimolar amounts of both BTAH and sulfide ions in an aqueous salt solution. These authors have also shown a remarkable promoting effect of water vapor on the rate of growth of Cu₂S on copper which was preconditioned in BTAH.

Competition between HS⁻ and BTAH.—The detrimental effects of sulfide ions on the inhibiting efficiency of BTAH can be rationalized, for both cases of adsorption of BTAH (Eq. 1) and formation of the Cu(I)BTA complex (Eq. 3). In the presence of both HS⁻ and BTAH in the same medium, the above results suggest that HS⁻ competes with BTAH for adsorption on the same active sites on the copper surface, that is⁴²



Reaction 9 is shifted more in the forward direction with the increase in the concentration of HS⁻ in the medium, HS_(aq)⁻. For such a competitive adsorption process and assuming the applicability of the Langmuir isotherm, the degree of coverage of the surface with each species is given by

$$\theta_{\text{HS}^-} = K_{\text{HS}^-}[\text{HS}^-]/(1 + K_{\text{HS}^-}[\text{HS}^-] + K_{\text{BTAH}}[\text{BTAH}]) \quad [10]$$

$$\theta_{\text{BTAH}} = K_{\text{BTAH}}[\text{BTAH}]/(1 + K_{\text{HS}^-}[\text{HS}^-] + K_{\text{BTAH}}[\text{BTAH}]) \quad [11]$$

where K refers to the equilibrium constant of adsorption of the particular species, see Eq. 1. Equations 10 and 11 indicate that an increase in the concentration of HS⁻ ions in the medium increases θ_{HS^-} and hence the rate of Reaction 5. Furthermore, it decreases θ_{BTAH} and hence the rate of Reaction 3, thus retarding the formation of the protective film Cu(I)BTA.

Alternatively, for the regions covered with the protective Cu(I)BTA complex, HS⁻ ions extract the Cu(I) ions from the complex leading to its deterioration,⁵¹ i.e.



Reaction 12 proceeds in the forward direction as the concentration of HS⁻ ions increase. This reaction leads to the breakdown of the Cu(I)BTA complex and the formation of Cu₂S. The driving force for reaction 12 results from the large difference in the stability constants of Cu (I) BTA²² ($\sim 10^2$) and Cu₂S⁵² ($\sim 10^{47}$).

X-ray photoelectron spectroscopy.—Figure 6a shows the N 1s signal in the XPS spectra obtained on copper electrodes after being polarized for 3 h at 0.2 V Ag/AgCl in 3.5% NaCl + 5×10^{-3} M BTAH in the absence and in the presence of 1.25×10^{-3} M HS⁻ ions. The signal has a peak at a binding energy of 399.5 eV which is characteristic for nitrogen.⁵³ It reveals the existence of BTAH on the electrode surface in the presence and in the absence of sulfide ions. On the other hand, Fig. 6b shows the S 2p signal that was obtained from the surface of the electrode treated in the presence of sulfide ions. The peak of the signal occurs at a binding energy of 162.5 eV which is characteristic of copper sulfide.⁵⁴⁻⁵⁷ The spectrum also revealed the existence of the Cu₂p_{3/2} at 932.3 eV which is characteristic of copper sulfides.⁵⁸ The fact that the N 1s signal was also detected on the sulfide-treated surface indicates that BTAH coexists with the sulfide ions on the electrode surface. It is interesting to note here that Fiaud and Ghimouz⁵⁰ also suggested the formation of Cu₂S, as indicated by peak reduction potentials.

Conclusions

Sulfide ions show a damaging effect on the remarkable inhibiting efficiency of benzotriazole against the corrosion of copper in salt water. In fact, under some conditions, sulfide ions not only eliminate

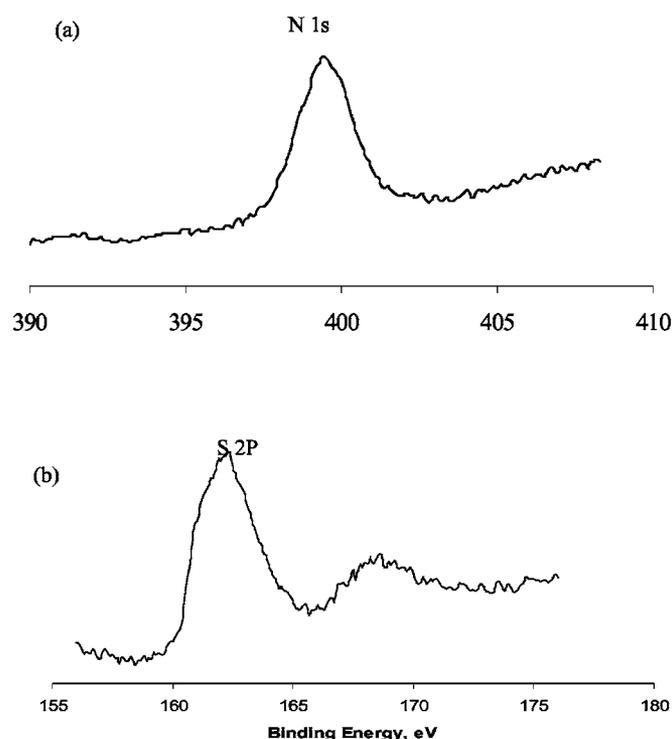


Figure 6. Segments of the XPS spectra of the copper electrode after being polarized for 3 h at 0.2 V Ag/AgCl in 3.5% NaCl + 5×10^{-3} M BTAH with and without sulfide ions: (a) N 1s signal obtained in the absence and in the presence of sulfide ions and (b) is the S 2p signal obtained in the presence of sulfide ions.

the inhibiting effects of BTAH but also promote the corrosion reaction to a greater extent than in the absence of BTAH. This suggests the existence of a form of interaction between HS^- ions and BTAH under this condition that needs further investigation. The loss of efficiency of BTAH under the effect of HS^- ions can be rationalized on the basis of competition between the HS^- ions and BTAH for adsorption on the copper surface and for complex formation with the copper ions.

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