

A near-infrared FT-Raman (SERS) and electrochemical study of the synergistic effect of 1-[(1',2'-dicarboxy)ethyl]-benzotriazole and KI on the dissolution of copper in aerated sulfuric acid

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The adsorption on copper in aerated 0.5 M sulphuric acid (30°C) of 1-[(1',2'-dicarboxy)ethyl]-benzotriazole (BTM) has been investigated by means of surface enhanced Raman scattering (SERS) techniques. The inhibition efficiency in aerated acid increased with increasing BTM concentration to a maximum (52%) at the 1×10^{-3} M level. Benzotriazole (BTAH) was found to be about 20% more efficient as an inhibitor for copper corrosion under the same conditions. BTM (1×10^{-3} M) showed increased inhibition with increasing pH reaching a maximum value of 78.3% at pH 8. Polarization studies showed that BTM suppressed both the cathodic and anodic corrosion reactions. The SERS studies suggest that, like BTAH, BTM inhibits copper corrosion by adsorption through the azole nitrogen. This study also showed that the performance of BTM can be significantly improved by adding KI. SERS indicates that the iodide ions displace the protonated BTM on the copper surface and this is followed by an overlayer of protonated BTM molecules.

1. Introduction

Organic compounds have been used as corrosion inhibitors for copper and copper-based alloys in various corrosive environments. Of these, triazole compounds have shown the greater inhibitive efficiency [1–4]. Many studies have postulated that the corrosion-inhibiting effect of triazoles is due to either (a) the formation of a protective film of copper-triazole polymeric complex (at high pH and potential values) or (b) their adsorption on the copper surface (at low pH and less noble potentials) [5]. These compounds, like many other effective organic inhibitors for corrosion of metals have functional groups containing hetero-atoms (O, N, S, P) which can donate a lone pair of electrons. In an acidic medium certain triazoles can be protonated to form organic cations. For example, benzotriazole (BTAH) exists predominantly as a protonated species BTAH_2^+ at pH < 1 [6]. The surface of a metal can be assumed to be positively charged in acidic media [7] and the protonated species would be less strongly adsorbed on the metal surface (like charges are weakly adsorbed). This results in reduced inhibition efficiencies of most organic inhibitors in acid solu-

tions. Thus, despite extensive studies on inhibitors, there is still a need for compounds suitable for the protection of metals in acidic media.

The addition of halide ions has been observed to increase the adsorption of organic cations and this can greatly enhance the inhibiting action of an organic compound in acid environments [2, 7]. For example, Wu *et al.* [2] have shown that a synergistic effect exists when BTAH and KI are used together to prevent the corrosion of copper in aerated sulfuric acid. Controversy exists, however, on the actual role of the iodide ions in relation to the improved organic cation adsorption. Conventionally, it is thought that the adsorption of the iodide occurs such that the negative ends of the iodide-metal dipole is oriented towards the solution thereby facilitating the attraction of the organic cations to the metal surface [2, 7]. Other investigators have proposed a molecular theory for explaining this phenomena. Accordingly, improved adsorption of the organic cations is due to the formation of a covalent bond between a nonionized molecule of the inhibitor and the adsorbed iodide molecule [2, 7]. Another explanation for this behaviour has been given in terms of the zero-charge potential. With regard to this theory, addition of iodide ions causes a positive shift in the zero-charge potential and this makes the overall charge on the metal

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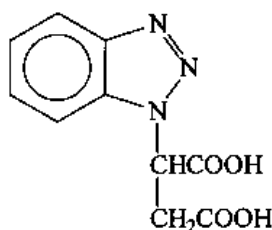


Fig. 1. Structural formula of 1-[(1',2'-dicarboxy)ethyl]-benzotriazole (BTM).

surface more negative. This favours the adsorption of the positively charged species [2, 7].

The present study investigates the adsorption and inhibitive action of 1-[(1',2'-dicarboxy)ethyl]-benzotriazole (BTM) (Fig. 1), a new derivative of BTAH, for the retardation of copper dissolution in aqueous aerated H_2SO_4 solutions with and without iodide ions. Surface enhanced Raman scattering (SERS) spectroscopy was used to examine the initial interaction of these compounds with the copper surface. The polarization behaviour was also established and the inhibition efficiencies were determined by coupon tests.

2. Experimental details

2.1. Materials

The working electrode (WE) for potentiodynamic and SERS measurements was pure copper (99.99%) and was prepared as previously described [8]. The WEs were abraded with silicon carbide paper (grade P1200), degreased with AR grade acetone and rinsed with deionized water before use. Coupons for the metal dissolution measurements were cut from AR grade copper sheet (3 cm \times 1 cm \times 0.01 cm). BTM (supplied by Johoku R&D Co. Ltd., Japan) was used as received. All other chemicals were AR grade and the solutions were prepared using deionized water (ELGA maximum ultrapure water). Solutions for the polarization runs were purged with high purity nitrogen. The pH of 0.5 M H_2SO_4 was adjusted to 1, 3, 5 and 8 with NaOH.

2.2. Apparatus

Metal dissolution determinations were carried out by placing the coupons in large test tubes (15 cm \times 2.5 cm dia.) suspended in a thermostatted water bath (30°C). Dissolved copper was determined using an inductively coupled plasma-atomic emission spectrometer (ICP-AES). Polarization runs were conducted in a PAR corrosion cell using an EG&G PAR potentiostat/galvanostat (model 273A) and software package 352/252 SoftCorr II. The potential of the WE was measured against a saturated calomel electrode (SCE) and two platinum electrodes were used as the counter electrodes. *In situ* SERS measurements were conducted using a Perkin Elmer 2000 FT-Raman spectrometer (1064 nm radiation from a Nd^{3+} : YAG laser) as previously described [9].

2.3. Procedures

2.3.1. Metal Dissolution Measurements. The coupons were degreased in acetone, etched in 1:1 HNO_3 , washed thoroughly in distilled water and then fully immersed in the quiescent 0.5 M H_2SO_4 test solutions containing different levels of BTM (1×10^{-5} – 5×10^{-3}) for 48 h at 30°C. The test tubes were open to air. Previous studies with some azoles showed that maximum inhibition efficiency was reached after this immersion period [10]. Studies were also done in solutions of different pH (0–8) and KI concentration (20–1000 ppm) containing 1×10^{-3} M BTM for 48 h. At the conclusion of a run the corrosion products were stripped from the coupons by immersion in a pickling solution (deaerated 1:2 HCl) for 2 min*. They were then washed with deionized water and the washings, combined with the HCl solutions, were transferred to 200 mL volumetric flasks. The weight losses experienced by the coupons and subsequent mean corrosion rates over 48 h period were calculated from ICP-AES measurements of the concentrations of copper in solution. The inhibition efficiencies (IE) were then calculated from the following equation:

$$IE \% = \left(1 - \frac{w_s}{w_b}\right) \times 100 \quad (1)$$

where w_s and w_b are the coupon weight losses in acid with and without inhibitor, respectively.

2.3.2. Potentiodynamic measurements. Previous to all polarization runs the test solutions were purged with nitrogen for 30 min. Gas bubbling was then maintained throughout the experiments. This procedure reduced the amount of dissolved oxygen in solution to about 0.1 ppm [8]. The degreased WE was inserted into the solution and immediately cathodically polarized (–1.0 V vs SCE) for 1 min to reduce any oxides on the copper surface. The corrosion potential (E_{corr}) was then monitored until stable. The electrode was then polarized cathodically and this was followed by the anodic scan after E_{corr} had again stabilized. The scan rate was 20 mV min^{-1} .

2.3.3. SERS and FT-Raman measurements. The copper electrode was polished, etched in 1:1 HNO_3 and then washed thoroughly with deionized water before placement in the cell. No nitrogen purging was carried out. The copper surface was then immediately activated using oxidation–reduction cycles (o.r.c) by directly switching the potential between +0.3 V and –0.3 V (Ag/AgCl). Three cycles were performed and potentials were held for 20 s before reversing the polarity. Cycling may be carried out either in the presence or absence of the inhibitor. In this work the former procedure was used. The SERS spectrum was

*ASTM G1–90, Standard Practice for Preparing, Cleaning and Evaluating Corrosion Test Specimens.

measured in 0.5 M H_2SO_4 solution containing (a) 1×10^{-3} M BTM, (b) 1×10^{-3} M BTM + varying KI and in H_2SO_4 solutions of pH 3.5 and 8 containing 1×10^{-3} M BTM. Each spectrum recorded was the average of 200 scans at a resolution of 8 cm^{-1} and a laser power of 400 mW. FT-Raman spectra of solids and solutions were obtained using standard sample holders at the same laser power.

3. Results and discussions

3.1. Metal dissolution measurements

From the calculated weight losses of the coupons the inhibition efficiency (IE) at each BTM concentration was calculated according to Equation 1. The results are shown in Fig. 2. Increasing the concentration of BTM increases IE up to a maximum value (52%) at 1×10^{-3} M level, above which it starts to decrease. This behaviour is consistent with results obtained for other azole compounds in acidic media and is attributed to dissolution of the complex protective film [10]. It was thought desirable to compare the inhibitive properties of BTM with those of BTAH and tests were conducted with BTAH concentrations in the range from 1×10^{-4} to 5×10^{-3} M. The IE data obtained for BTAH at these levels are also shown in Fig. 2. BTAH is seen to be about 20% more efficient as an inhibitor for copper in 0.5 M H_2SO_4 . Both BTAH and BTM are thought to inhibit corrosion by adsorption on the metal and subsequent coordination through the azole nitrogen atoms. Neither compounds are particularly good inhibitors in strong acid and the inferior action of BTM may be attributed to a slight electron withdrawing effect of the carboxyl

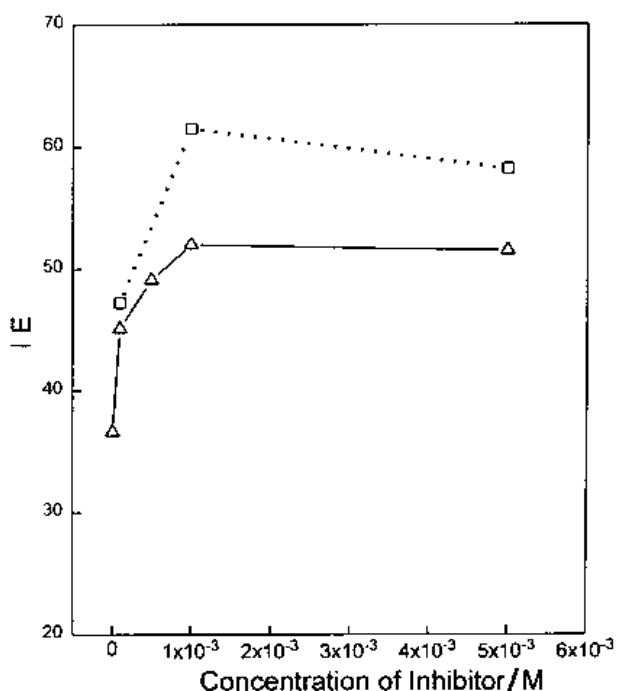


Fig. 2. Variation of IE with concentration of inhibitor: a(— Δ —) BTM, b(---□---) BTAH.

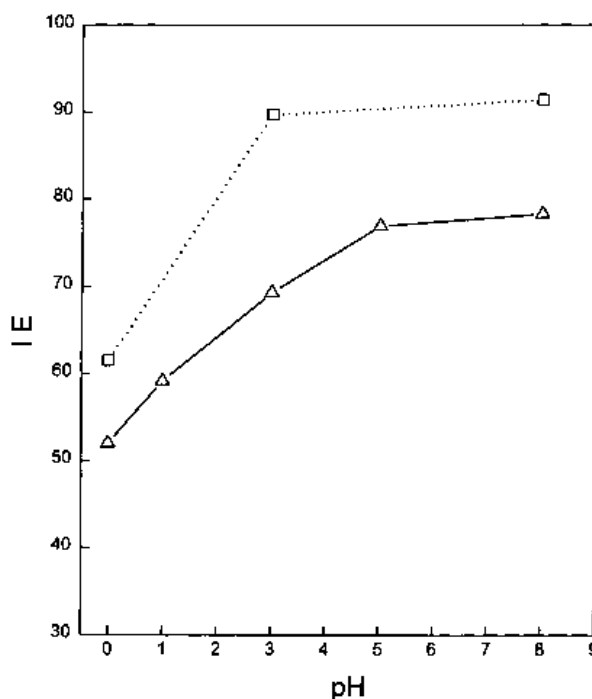


Fig. 3. Effect of pH on IE of 1×10^{-3} M inhibitor level: a(— Δ —) BTM, b(---□---) BTAH.

group [11] in addition to a steric effect which may lead to blockage of the coordination sites on the molecule.

BTAH is known to be a good inhibitor for the corrosion of copper in neutral/alkaline solution and it was decided, therefore, to establish the effect of pH on the inhibition efficiency of BTM. The dissolution rate of copper was determined in aqueous H_2SO_4 solutions of pH 0, 1, 3, 5 and 8 and containing 1×10^{-3} M BTM. The results are presented in Fig. 3, together with some BTAH data for comparison. BTM showed increased inhibition with increasing pH reaching a maximum level of 78.3% at pH 8. BTAH exhibited the same trend and the IE at pH 8 was 91.4%. BTAH is still more efficient at the 1×10^{-3} M level over the pH range studied. The high inhibition efficiency of BTAH is thought to result from the formation of complex polymer films on the copper surface [5]. These polymeric films become more stable as the activity of H^+ decreases (high pH) and the increased IE observed here for BTM may also be due to the formation of these types of films on the copper surface. Fig. 3 shows any complex polymer formed by BTM is inferior to that formed by BTAH.

3.2. Effect of mixtures of BTM and KI on metal dissolution

A further series of tests was carried out in 0.5 M H_2SO_4 containing 1×10^{-3} M BTM (optimum concentration) and different concentrations of KI. Figure 4 shows that an addition of KI increases the IE of BTM and that the efficiency continues to increase with increasing KI concentration. Mixtures of 1×10^{-3} M BTM and a KI concentration ≥ 500 ppm

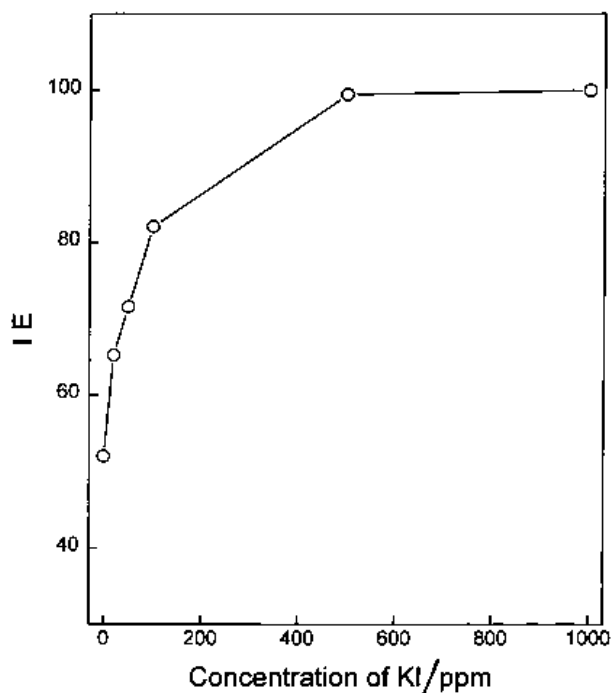
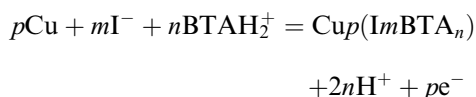


Fig. 4. Effect of [KI] on IE of 1×10^{-3} M BTM solution.

provided almost complete protection (IEs greater than 98.5% were observed) for copper dissolution in 0.5 M H_2SO_4 . Wu *et al.* [2] observed a similar marked decrease in the corrosion rate of copper in sulfuric acid for mixtures of BTAH and KI. They proposed a mechanism of synergism in which adsorbed iodide ions on the copper surface preferentially adsorbed an overlayer of protonated BTAH $_2^+$ to form a polymeric Cu-iodide-BTAH complex as follows:



where $m + n = p$. It is reasonable to assume that in the present study, the improved corrosion inhibition on the addition of KI is also due to the formation of a much more compact and corrosion resisting polymeric Cu-iodide-BTM complex. It appears from Fig. 4 that the quality of this film improves with increasing KI concentration. Further tests were conducted with 1×10^{-3} M BTM and 100 ppm KI at different solution pH. The results are shown in Fig. 5. The data show that inhibition efficiencies obtained in the solution containing both BTM and KI are significantly higher (over all the pH ranges studied) than those obtained in solutions containing BTM alone. As with BTM alone, IE increases as the pH increases. In the case of BTM + KI mixture, no corrosion was detected at pH values above 3.

3.3. Polarization measurements

Figure 6 shows typical polarization curves for copper in 0.5 M H_2SO_4 containing approximately 0.1 ppm oxygen. The oxygen promotes copper dissolution and in all cases the cathodic curve observed near E_{corr} is

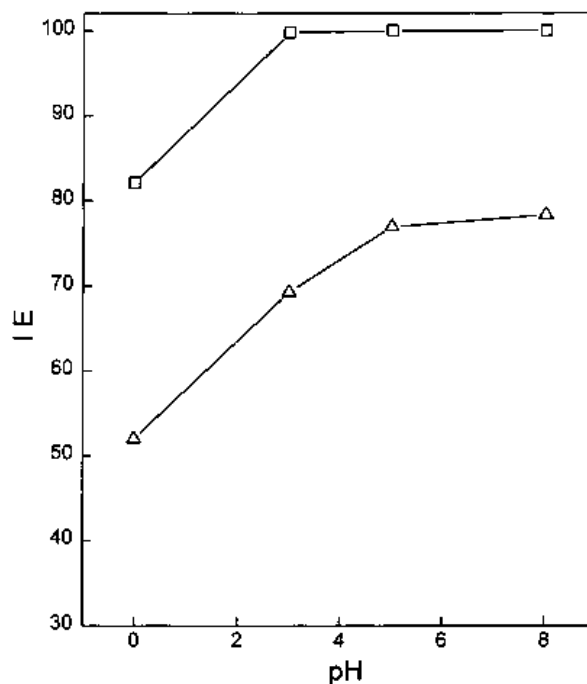


Fig. 5. Effect of pH on IE of: a(— Δ —) 1×10^{-3} M BTM, b(— \square —) 1×10^{-3} M BTM + 100 ppm KI.

indicative of the reduction of oxygen [12]. The cathodic curve observed at potentials more negative than -124 mV vs SCE (up to about -280 mV vs SCE) has been ascribed to combined oxygen and Cu^{2+} ion reduction whilst at more negative potentials hydrogen evolution occurs [12].

BTM alone acts to suppress both the copper dissolution and oxygen reduction corrosion reactions indicating that it is a mixed inhibitor (E_{corr} is marginally more positive). The addition of 500 ppm KI

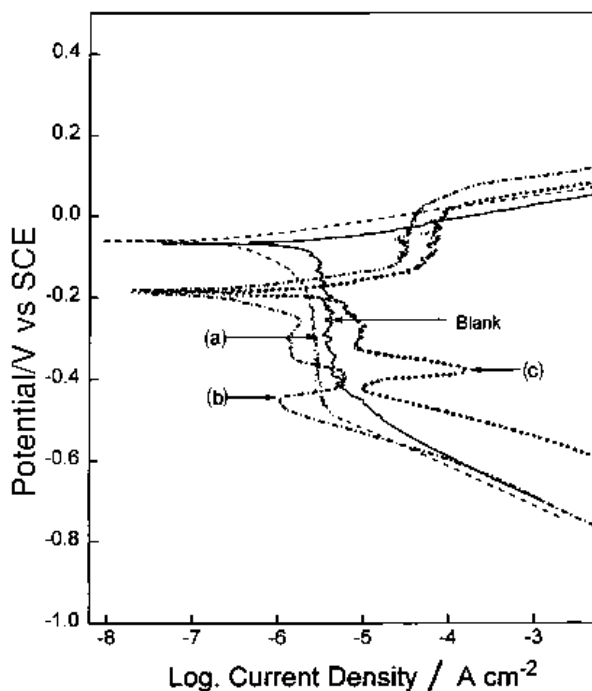


Fig. 6. Representative polarization curves for Cu in N_2 purged 0.5 M H_2SO_4 (30 °C) containing: (a) 1×10^{-3} M BTM, (b) 1×10^{-3} M BTM + 500 ppm KI, (c) 500 ppm KI.

alone to the acid renders E_{corr} more negative (by about -90 mV vs SCE). This behaviour was observed by Wu *et al.* [2]. They also reported that in the presence of 0.01 M KI the corrosion rate of copper increased. In the present study a limiting anodic current was also observed on polarization at about -100 mV vs SCE which can be attributed to formation of CuI film on the metal. At more positive potentials the film breaks down leading to an increased metal dissolution rate [2].

The recorded cathodic curves in the presence of KI showed a peak at about -380 mV vs SCE and this is most likely due to the reduction of I_2 [13] which spontaneously forms when iodide ions react with dissolved oxygen [14]. With respect to solution containing both BTM and KI, the shape of the cathodic curve was similar to that observed for KI alone. This is consistent with previous work [2] and shows that BTM and KI do not react with each other to form new phases. The presence of BTM, however, shifted both the anodic and cathodic curves to a lower current density region. The magnitude of the cathodic peak was also depressed in BTM + KI solutions.

3.4. SERS and FT-Raman measurements

The FT-Raman spectrum of solid BTM in the frequency range 1800 – 200 cm^{-1} is shown in Fig. 7(a). The SERS spectrum of 1×10^{-3} M BTM in 0.5 M H_2SO_4 on a roughened copper surface at -0.7 V vs Ag/AgCl is also shown (Fig. 7(b)). At this concentration no Raman spectrum of BTM was observed. In previous work using 2 M H_2SO_4 the SERS spectrum of SO_4^{2-} and HSO_4^- ions adsorbed at the copper were observed [9]. In this study, at the 0.5 M level, these bands were too weak to be assigned. Proposed assignments of the significant peaks are

listed in Table 1 together with those for solid BTAH [15, 16]. For solid BTM, weak carboxylic C=O stretches (1723 , 1720 and 1666 cm^{-1}), C–OH stretch (1175 cm^{-1}) and C–OH out of plane OH bending (932 cm^{-1}) were assigned in addition to bands which would be characteristic of the parent BTAH molecule (Table 1). As with previous work on the SERS of BTAH on copper [9], distinct frequencies were observed below 1600 cm^{-1} . The frequencies observed in the SERS spectrum were attributed mainly to the triazole portion of the molecule (Table 1) except for the peaks at 1590 , 786 and 431 cm^{-1} which are assigned to benzene ring stretching, breathing and bending modes, respectively.

Comparison of the solid Raman and SERS spectra of BTM shows some differences which are a result of the SERS interaction. Characteristic triazole modes in the solid at 1390 , 637 and 551 cm^{-1} are enhanced but shifts to 1388 , 631 and 548 cm^{-1} , respectively, are not conclusive in view of the resolution used in the experiment (8 cm^{-1}). This portion of the molecule may be closest to the copper surface. This is also supported by the fact that the relative intensities of the bands due to the benzene part of the molecule (1594 , 1373 and 783 cm^{-1}) are decreased in comparison to those observed in the solid Raman spectrum. When BTM is dissolved in acid the molecule may be protonated at the nitrogen atom in the 2 or 3 position on the triazole ring. The new SERS band observed at approximately 1162 cm^{-1} can be assigned to $\delta(\text{N-H})$ mode in the protonated molecule. In addition, the SERS spectrum also shows a broad peak at approximately 230 cm^{-1} , and this has been attributed to the Cu – N stretching mode [9] resulting from the adsorption of BTM on the metal surface.

The dependence of the SERS spectrum on applied potential was examined (Fig. 8). In earlier work on

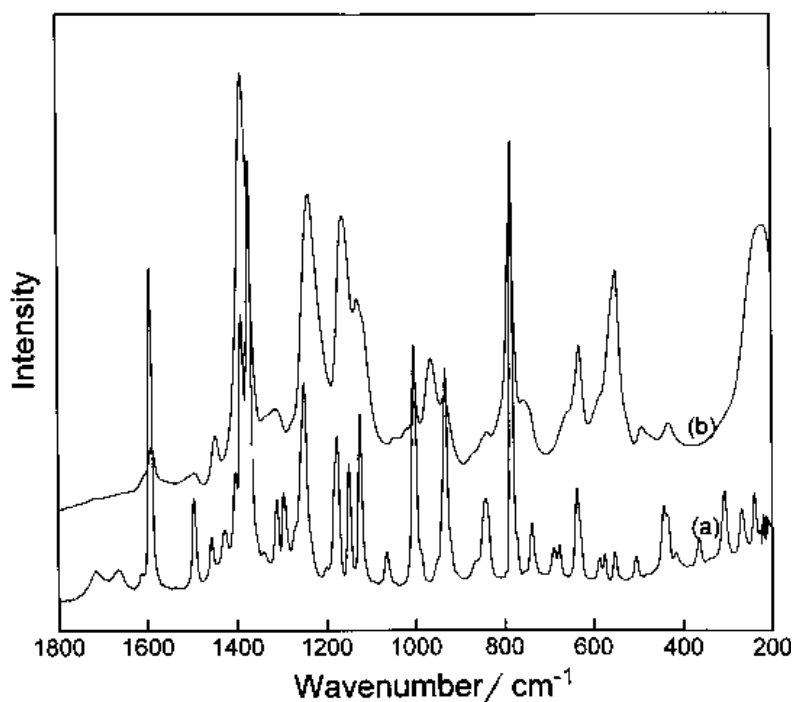


Fig. 7. (a) FT-Raman of solid BTM, (b) SERS spectrum of 1×10^{-3} M BTM on Cu in 0.5 M H_2SO_4 at -0.7 V.

Table 1. Proposed assignments for significant peaks in the solid FT-Raman of BTAH and BTM, and SERS solution spectra of BTM

BTAH solid (Raman)		BTM solid (Raman)		1×10^{-3} M BTM in 0.5 M H_2SO_4 SERS on copper substrate	
Frequency	Assignment	Frequency	Assignment	Frequency	Assignment
437 w	bz ring bend	443 w	bz ring bend	230 m,br	Cu-N stretch
539 w	tz ring torsion	551 w	tz ring torsion	431 w	bz ring bend
552 w	tz ring torsion	637 w	tz ring bend	548 m	tz ring torsion
632 w	tz ring bend	783 vs	bz ring breathing	631 w	tz ring bend
781 vs	bz ring breathing	932 m	C – OH bending	784 s	bz ring breathing
1007 m	bz in plane ring bend	1002 m	bz in plane ring bend	964 w	C – OH bending
1096 w	bz ring vibration	1064 w	bz ring vibration	1128 m	tz mode
1128 m	tz mode	1122 m	tz mode	1162 m	N-H deformation
1210 m	tz ring breathing	1148 m	CH ₂ wag and twist	1238 s	tz ring breathing
1280 m	CH in plane bend	1175 m	C – OH stretch	1388 vs	tz ring stretch
1372 m	bz ring stretch	1248 m	tz ring breathing	1590 w	bz ring stretch
1387 vs	tz ring stretch	1294 w	CH in plane bend		
1499 w	bz ring stretch	1373 vs	bz ring stretch		
1594 s	bz ring stretch	1390 m	tz ring stretch		
		1496 w	bz ring stretch		
		1594 s	bz ring stretch		
		1666 w	C=O stretch		
		1720 w	C=O stretch		

tz = triazole; bz = benzene; m = medium; w = weak; s = strong; vs = very strong; br = broad

the SERS of BTAH on copper in 2 M H_2SO_4 [9], the relative intensities of the peaks increased as the electrode potential was made more negative. Protonation of BTM results in a molecule with a net positive charge and making the electrode more negative increases physical adsorption of the positively charged species. This accounts for the enhancement observed.

The effect of acid concentration on the SERS spectrum for the copper electrode polarized at -700 mV vs Ag/AgCl in solutions containing 1×10^{-3} M BTM is shown in Fig. 9. Lowering the acid concentration had a significant effect on the relative intensity of the peaks; in general the intensities

of the bands decreased. This may be due to the higher pH favouring the formation of a polymeric complex. Additionally, at the higher pH BTM is less protonated and $\delta(N-H)$ deformation at 1162 cm^{-1} would be expected to decrease in relative intensity (e.g., to the benzene ring breathing mode at 786 cm^{-1}) and this was observed in practice.

When KI was added to 0.5 M H_2SO_4 no SERS spectrum was observed over a range of applied potentials (-0.7 to $+0.05$ V vs Ag/AgCl). No evidence of the Cu – I vibrational band was observed. Figure 10 shows that with increasing concentration of KI the SERS spectrum of 1×10^{-3} M BTM decreases in

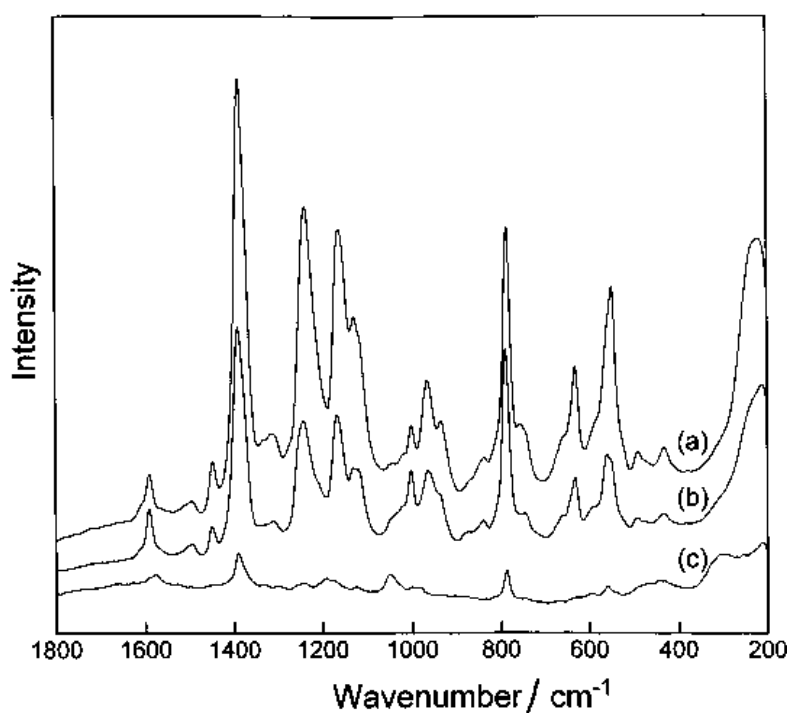


Fig. 8. SERS spectra for 1×10^{-3} M BTM on Cu in 0.5 M H_2SO_4 at (a) -0.7 (b) -0.4 and (c) $+0.05$ V.

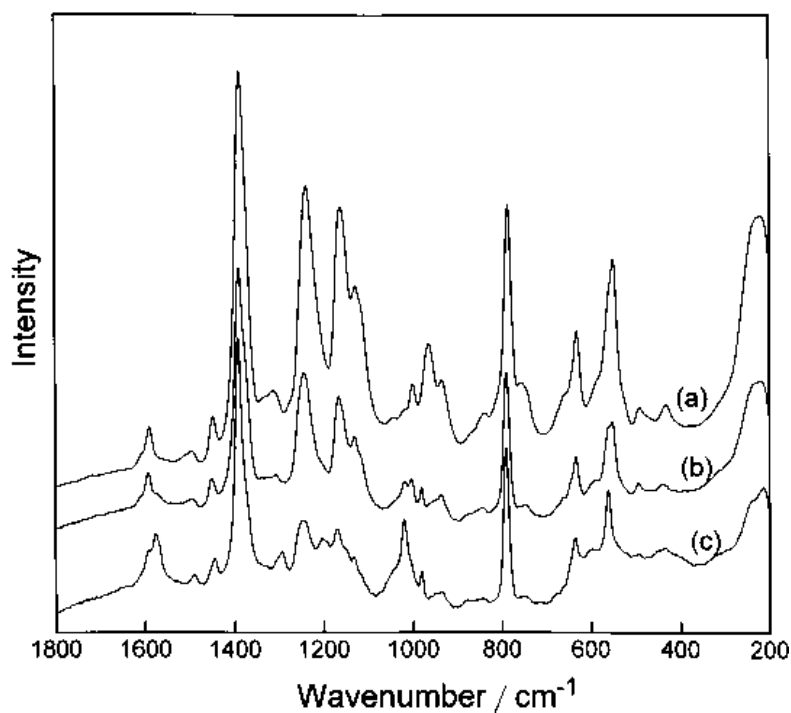


Fig. 9. Effect of pH on SERS spectrum of 1×10^{-3} M BTM on Cu in 0.5 M H_2SO_4 at -0.7V : (a) pH 0, (b) pH 3.5 and (c) pH 8.

quality. The intensities of the peaks also decrease. Upon addition of 200 ppm KI the SERS spectrum was completely extinguished. This suggests increased contact adsorption of iodide ions at the copper with no direct metal-BTM interaction. These observations further support the enhanced inhibition observed in BTM-iodide solutions as being first due to adsorption of iodide, followed by an overlayer of protonated BTM.

4. Conclusions

- (i) Substitution of the H-atom in the triazole ring of BTAH with $-\text{C}(\text{CH}_2\text{COO})\text{COOH}_2$ significantly decreased the inhibition efficiency. This group decreases the electron density of the triazole moiety of the molecule with resultant decreased chemisorption through nitrogen. The carboxyl group may also sterically hinder the N coordination sites.
- (ii) Mixtures of BTM and KI improve the IE with almost complete protection for 1×10^{-3} M BTM

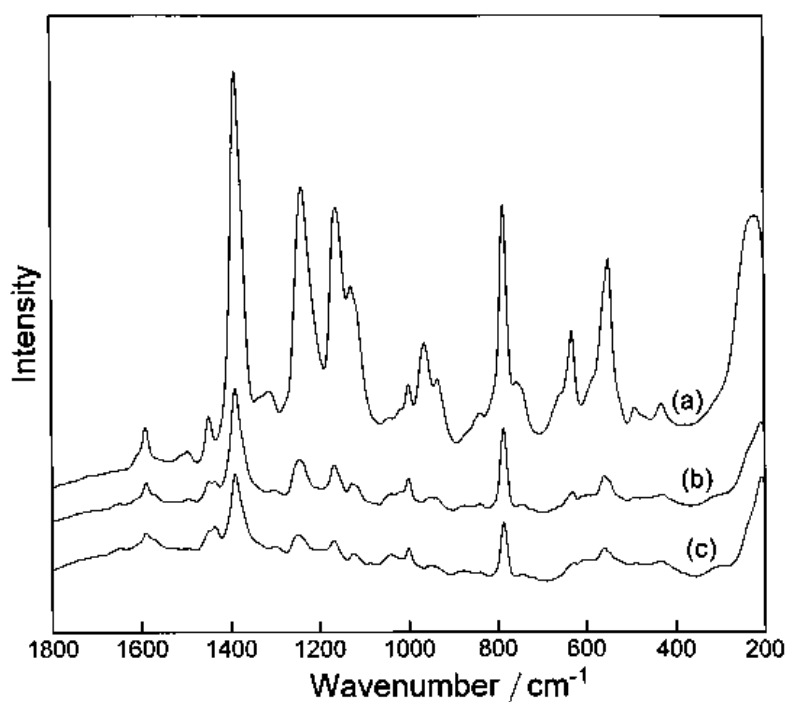


Fig. 10. Effect of [KI] on SERS spectrum of 1×10^{-3} M BTM on Cu in 0.5 M H_2SO_4 at -0.7V : (a) 0 ppm KI, (b) 20 ppm KI and (c) 50 ppm KI.

and $[KI] \geq 500$ ppm. This synergistic effect results from initial contact adsorption of iodide ions on the copper surface, followed by a decrease in the positive charge on the metal, thereby facilitating the adsorption of protonated BTM.

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