

# **Inhibitive Effect of 2-(1H-benzotriazol-1-yl)phenylacetohydrazide and 2-(1H-benzotriazol-1-yl) acetopyrazolidine dione for the control of corrosion of admiralty brass in Natural Sea water**

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## **Abstract**

New corrosion inhibitors, namely 2-(1H-benzotriazol-1-yl)phenylacetohydrazide(BTPH) and 2-(1H-benzotriazol-1-yl) acetopyrazolidine dione(BTAP) were synthesised and their action on corrosion control of admiralty brass in natural sea water has been studied. Weight loss, potentio - dynamic polarisation measurement and electrochemical impedance spectroscopy (EIS) has been employed to analyse their inhibition behaviour. Polarization measurements showed that the organic compounds investigated are mixed type inhibitors, inhibiting the corrosion of brass by blocking the active sites of the metal surface. Changes in the impedance parameters (charge transfer resistance ( $R_{ct}$ ) and double layer capacitance ( $C_{dl}$ )) are related to adsorption of organic inhibitors on the metal surface, leading to the formation of a protective film. BTAP showed better protection over the other inhibitor used. The dissolution of copper and zinc in presence of BTAP and BTPH is negligible compared to blank. A combination of electrochemical methods and surface examination techniques are used to investigate the protective film and explain the mechanistic aspects of corrosion inhibition.

**Key words:** Admiralty brass, natural sea water, polarization, impedance spectroscopy, BTA derivatives, dezincification..

**1. INTRODUCTION**

Copper and copper alloys are widely used in industrial equipments. These alloys offer a particularly beneficial combination of electrical and/or thermal conductivity, corrosion resistance, strength and wear resistance[1,2] They are widely used for water cooling systems, desalination plants, shipboard condensers, power plant condensers and heat exchangers [3,4]. Admiralty brass is used industries as evaporator tubing, heat exchanger tubing, condenser tube plates, distiller tubes, oil well pump liner, ferrules, bourdon tubes, condenser tubes.

Copper and its alloys are subjected to corrosion in different environments; especially marine environments. The corrosion of copper and many of its alloys in marine environments has been extensively studied [5-11]. Dezincification of brass is one of the well-known and common processes by means of which brass loses its valuable physical and mechanical properties leading to structural failure[12].

Organic compounds containing an “azole nucleus” have frequently been employed to inhibit corrosion of copper and brass mostly in acidic or neutral solution [13,14]. Benzotriazole and other azoles are the well known corrosion inhibitors of copper and many of its alloys. The excellent inhibiting efficiency of benzotriazole is attributed to the formation of a protective film of Cu(I)BTA on the copper surface [15-19]. Immersion of copper into a solution of BTA enables chemisorption to occur on the surface and gave enhanced resistance to atmospheric oxidation of copper [20]. Brusic et al [21] showed that a polymerized network formed and gave significant protection in many environments; the enhanced protection was retained even when the copper was removed from the BTA solution. BTA to acidic, neutral and alkaline solution is commonly used and has significantly reduced corrosion [22]. It may be adsorbed only onto the oxide on the surface of copper [23,24] or function on oxide free surfaces [25]. Frignani et al [26] investigated the influence of alkyl chain on the protective effects of benzotriazole towards copper in acidic chloride solution. Huynh et al [27] have studied the corrosion protection of octyl esters of carboxy benzotriazole on copper in an aerated acidic sulphate solution. Qafsaoui et al [28] also reported that the growth of protective film on copper in the presence triazole derivatives. Although there is an extensive literature on the corrosion properties of triazoles such as aminotriazole and benzotriazole on steel and copper [29-31], there remains little information on

corrosion and dezincification of brass alloys using BTA derivatives. Based on this, the above inhibitors have been considered and synthesized according to the previous report.

Hence, it was proposed to investigate the effect of synthesized compounds namely 2-(1H-benzotriazol-1-yl)phenylacetohydrazide and 2-(1H-benzotriazol-1-yl) acetopyrazolidine dione as corrosion inhibitors for brass in natural sea water. The influence of these compounds on the corrosion and dezincification of brass has been studied by the weight-loss method and by two electrochemical methods, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The percentage composition of the brass surface was analyzed using energy dispersive X-ray analysis (EDAX). Dezincification of brass was analyzed using inductively coupled argon plasma-atomic emission spectroscopy (ICPAES).

## 2. Experimental

### 2.1 Materials

The material used for this study was admiralty brass supplied in the form of sheet and the chemical composition (weight percent) of the admiralty brass was 70.34% Cu, 28.53% Zn, 0.92% Sn, 0.069% Pb, 0.058% Fe and traces of Mn, Ni & As, as analyzed by optical emission spectrophotometry. The natural sea water was collected nearby the Thermal Power Station, Tuticorin, India. The inhibitors 2-(1H-benzotriazol-1-yl)phenyl acetohydrazides(BTAH), 2-(1H-benzotriazol-1-yl)acetopyrazolidine dione (BTAP) were synthesized according to the reported procedures [32] and their structures are shown in the scheme 1.

## 2. Experimental details

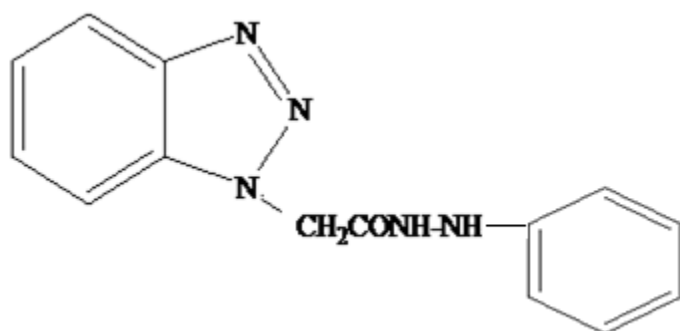
### Synthesis of 2-(1H-benzotriazol-1-yl)phenyl acetohydrazides:

In a 250ml iodine flask, an ethanolic solution of ethyl 1-H benzotriazol-1-yl acetate (0.01M) and phenyl hydrazine hydrate (20 ml) was stirred for 4 hours at room temperature and then refluxed on a water bath for 3 hours in a 250 ml round bottom flask, the solution was kept overnight in a 250 ml beaker and then excess solvent was removed under reduced pressure. The solid mass so obtained was washed with cold water and recrystallised from ethanol. (Yield – 78.13%)

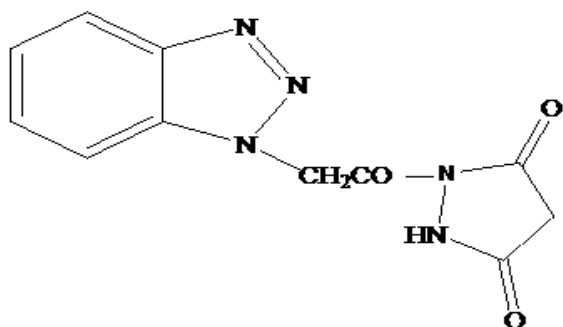
## Synthesis of 2-(1H-benzotriazol-1-yl) acetohydrazides pyrazolidine dione:

In a 250ml round bottomed flask, 2-(1-H-benzotriazol-1-yl) aceto hydrazide (0.01M) was dissolved in ethanol (50ml) and diethyl propanedioate (0.01M), glacial acetic acid (2-3 drops) were added. The reaction mixture was refluxed for 6 hours. Then the reaction mixture was kept in an open china dish for 3 days. The so obtained crystals were filtered and recrystallised from ethanol. (Yield-82.56%)

**Scheme 1.**



### 2-(1H-benzotriazol-1-yl)phenyl acetohydrazide (BTPH)



### 2-(1H-benzotriazol-1-yl) acetohydrazides pyrazolidine dione (BTAP)

#### 2.2 Methods

For the weight-loss method, the brass specimens (4 cm x 2.5 cm x 0.2 cm) were abraded with silicon carbide papers (120-1200grit), thoroughly washed with distilled water, degreased with

acetone, rinsed with distilled water, dried and weighed. The specimens were immersed in 300 ml of natural sea water, with and without inhibitors at 30°C for 45 days.

For electrochemical studies, the working electrode with an area of 1 cm<sup>2</sup> was embedded in epoxy resin in a Teflon holder. The electrode was abraded mechanically with silicon carbide papers from 120 to 1200 grit followed by polishing with 5 µm diamond paste. The electrode was thoroughly washed with double distilled water, degreased in acetone for 15 minutes using ultrasonic vibration, rinsed with distilled water and dried. The cell assembly consisted of brass as working electrode, a platinum foil as counter electrode and a saturated calomel electrode (SCE) as a reference electrode with a Luggin capillary bridge.

Polarization studies were carried out using a Vibrant potentiostat/ galvanostat model No. VSM/CS/30 at a scan rate of 1 mV/s.. The working electrode was immersed in natural sea water (open atmosphere) and allowed to stabilize for 30 minutes [33]. In each case a potential of -1500 mV was then applied for 15 minutes to reduce oxides. The cathodic and anodic polarization curves for brass specimen in the test solution with and without inhibitors were recorded between -500 to 500 mV at a scan rate of 1 mV/s. The inhibition efficiencies of the compounds were determined from corrosion current density using the Tafel extrapolation method. A.C. impedance measurements were conducted at room temperature using an AUTOLAB with Frequency Response Analyzer (FRA), which included a Potentiostatic model "Autolab PGSTAT 12". An ac sinusoid of ±10 mV was applied at the corrosion potential ( $E_{\text{corr}}$ ). The frequency range of 100 kHz to 1 mHz was employed. All potentials are reported Vs SCE.

During the anodic polarization, metal dissolution takes place releasing considerable amounts of metal ions from the material. Hence, the solutions were analyzed to determine the leaching characteristics of the brass alloys. The solution left after polarization measurement was analyzed for copper and zinc by inductively coupled argon plasma-atomic emission spectroscopy (ICP-AES). Solutions containing the optimum concentration of the inhibitor were chosen and a blank was also analyzed for comparison purposes. The composition of the brass surface after polarization measurements was analyzed using JOEL<sup>R</sup> JSM 35C SEM combined EDAX[33].

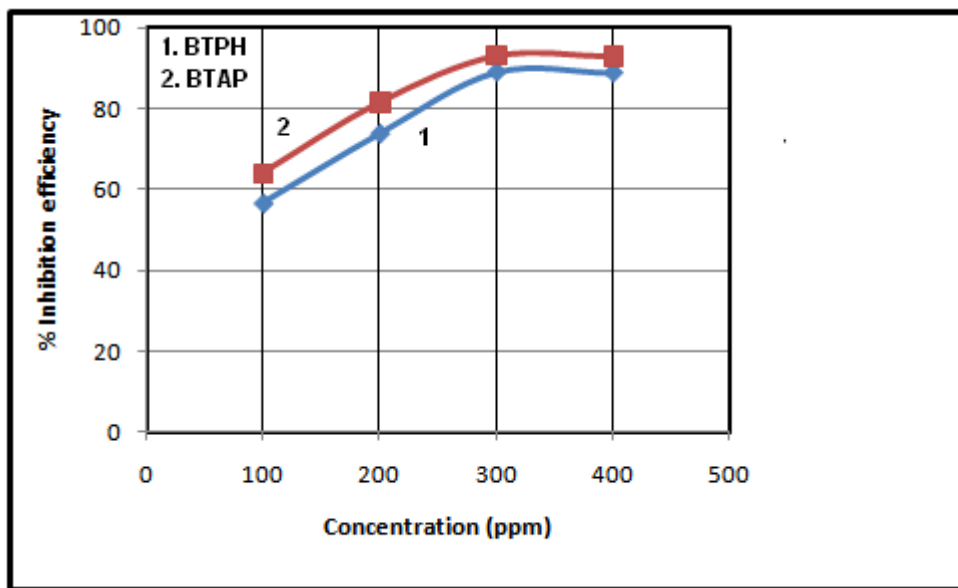
### 3. Results and discussion

#### 3.1. Weight-loss method

The variation of inhibition efficiency (IE %) with inhibitor concentration is shown in Figure 1. The inhibition efficiency increases with increase in concentration of the inhibitors. The maximum IE% of each compound was achieved at 300ppm, and a further increase in concentration showed only a marginal change in the performance of the inhibitor. The optimum of concentration of the inhibitors was 300ppm and BTAP was superior to BTPH.

**Table 1. Inhibition efficiency at different concentrations of BTPH and BTAP of admiralty brass in natural sea water**

Inhibitor concentration (ppm)	Corrosion rate x 10 <sup>-2</sup> (mm yr <sup>-1</sup> )	Inhibition efficiency (%)
<b>Blank</b>	12.14	-
<b>BTPH</b>		
100	5.26	56.67
200	3.17	73.89
300	1.32	89.12
400	1.34	88.96
<b>BTAP</b>		
100	4.36	64.08
200	2.23	81.63
300	0.83	93.16
400	0.85	93.00



**Fig. 1: Effect of different concentrations of the inhibitors on the inhibition efficiency of admiralty brass in natural sea water.**

### *Mechanism of corrosion inhibition*

The dissolution and film formation of brass in natural sea water takes place via the reactions outlined below.

In the initial corrosion stage, zinc forms ZnO as a result of



and copper forms Cu<sub>2</sub>O as a result of



Thus a passive oxide film consisting of both Cu<sub>2</sub>O and ZnO covers the surface. However, CuCl is formed on the surface (in the presence of chloride) by the reaction

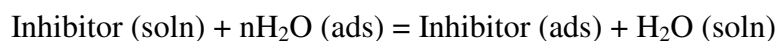


which may ultimately result in the formation of CuCl<sub>2</sub> complex via



The effectiveness of BTA derivatives as corrosion inhibitors for brass can be gauged from the electrochemical behaviour of brass in natural sea water.

The nature of the interaction of inhibitor on the metal surface during corrosion inhibition has been deduced in terms of the adsorption characteristics. In most cases the adsorption of inhibitor from the corrosive medium is a quasi-substitution process.



The BTA derivatives are chemisorbed on the metal surface and that this chemisorbed layer prevents adsorption of oxygen and oxide formation. The protective film is a 1:1 complex of Cu (I) and BTA. The film is probably polymeric, in which BTA bridges two copper atoms via  $\text{N}_1$  and  $\text{N}_3$  and the aromatic ring is aligned parallel to the metal surface. Formation Cu (II) complexes also can occur, but they do not be protective. Chadwick et al concluded that zinc is also incorporated into the surface film in significant quantities.

BTA derivatives inhibits by a two-fold mechanism. The chemisorbed film has a hydrophobic backbone that limits the transport of hydrated aggressive ions to the metal surface. Once formed, the film stabilized Cu (I) ions by means of an electronic effect, network formation or both.

It is well known that the inhibitive action of organic compound containing S, N and/or O is due to the formation of a co-ordinate type of bond between the metal and the lone pair of electrons present in the additive. The tendency to form co-ordinate bond and hence the extent of inhibition can be enhanced by increasing the effective electron density at the functional group of the additive. In aromatic or heterocyclic ring compounds, the effective electron density at the functional group can be varied by introducing different substituents in the ring leading to variations of the molecular structure.

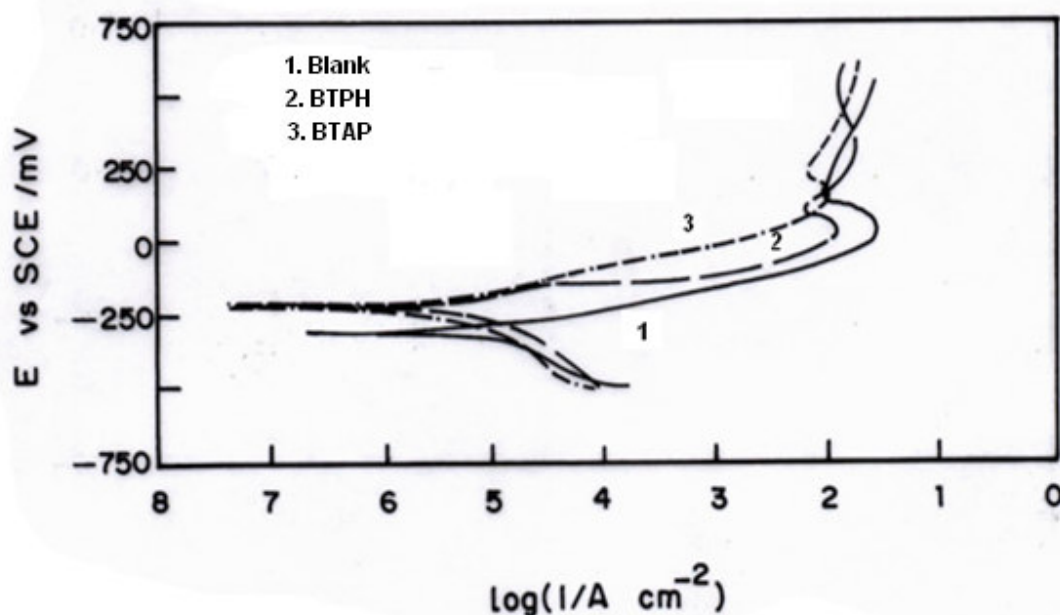
Based on the results, both BTPH and BTAP showed better inhibition efficiencies, due to the presence of heteroatom such as N and  $\pi$  electrons on aromatic nuclei. When compared to BTPH, BTAP showed highest inhibition efficiency, which may be due to high molecular weight possessed by the BTAP molecule. In the BTPH molecule, though the phenyl groups strongly



reduce their solubility, the  $\pi$  electron delocalization is greater, hence it possess moderate inhibition efficiency. The higher inhibition efficiency of the organic compounds are due to the basis of donor-acceptor interactions between the  $\pi$  electrons of the inhibitor and the vacant d-orbital of copper surface or an interaction of inhibitor with already adsorbed chloride ions [34,35].

### 3.2 Potentiodynamic polarization studies

The cathodic and anodic polarization curves of brass in natural sea water with optimum concentrations of BTPH and BTAP are shown in Figure 2. From the figure, as the potential increases in the noble direction, the current density increases (active region), at a particular stage, the current density remains constant indicates the maximum rate of corrosion occurs. On further



**Fig. 2. . Polarization curves of admiralty brass in natural sea water containing optimum concentrations of BTPH and BTAP.**

increase of potential, the current density decreased which showed the formation of passive film. In the presence of different concentrations of inhibitors, the current density decreased significantly. This behavior is due to the chemisorptions of organic molecules on the surface of

**Table 2. Electrochemical parameters and inhibition efficiency for corrosion of admiralty brass in natural sea water containing different concentrations of BTPH and BTAP.**

<b>Inhibitor Concentration  / ppm</b>	<b>E<sub>corr</sub> (mV vs. SCE)</b>	<b>I<sub>corr</sub>  /μA cm<sup>-2</sup></b>	<b>Corrosion Rate  / mmyear<sup>-1</sup>  x 10<sup>-2</sup></b>	<b>Inhibition Efficiency  / %</b>
Blank	-321	9.18	12.20	-
BTPH				
100	-261	3.98	6.09	56.64
200	-238	2.86	4.05	68.84
300	-219	1.09	1.69	88.13
400	-220	1.10	1.73	88.02
BTAP				
100	-254	3.63	5.32	60.46
200	-231	2.28	3.62	75.16
300	-210	0.74	1.24	91.93
400	-211	0.76	1.28	90.95

the brass. Besides, the similar behavior is observed for cathodic Tafel region, which is attributed to the reduction of oxygen on the brass surface.

It is also observed that in the presence of inhibitor, the corrosion potential is shifted in the positive direction and the shift was found to be dependent on concentration of the inhibitor. The extrapolation curves indicate that the inhibitors retard both the cathodic and anodic reactions and thus act as mixed type inhibitors. The current density calculated from the cathodic Tafel slope also decreased with increasing concentrations of the inhibitors. The inhibition efficiency was calculated from I<sub>corr</sub> values [36].

$$\text{I.E.}\% = \frac{I_{\text{corr}} - I_{\text{corr(inh)}}}{I_{\text{corr}}} \times 100$$

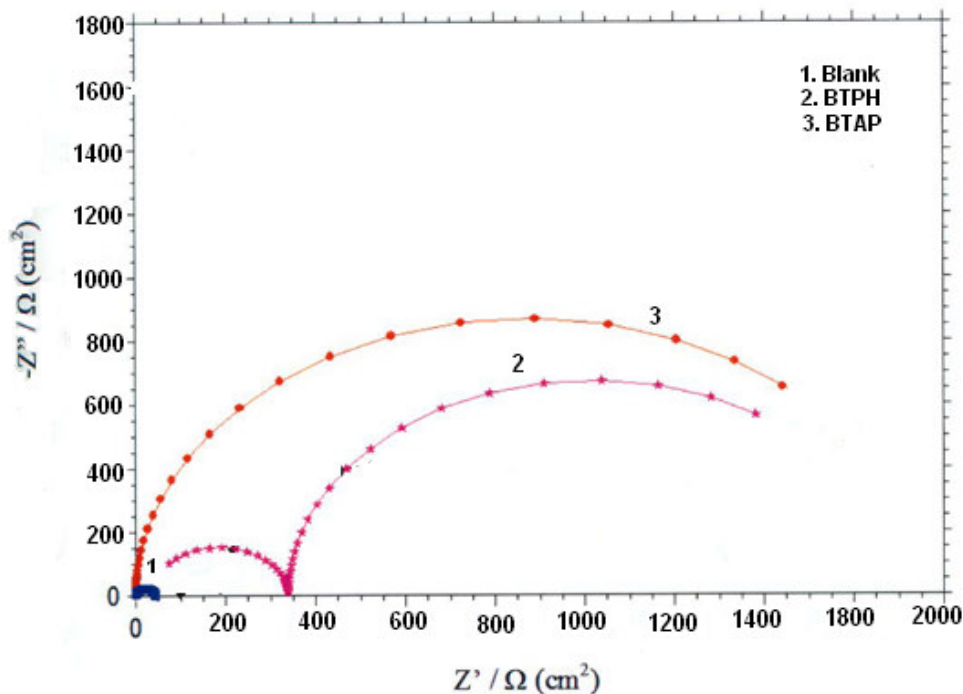
Where  $I_{\text{corr(inh)}}$  and  $I_{\text{corr}}$  are corrosion current density in the presence and absence of inhibitors respectively. The values of the cathodic Tafel slope ( $b_c$ ) and anodic Tafel slope ( $b_a$ ) of the benzotriazole derivatives are found to change with inhibitor concentration, which clearly indicates that the inhibitors controlled both reactions. The inhibition efficiency of BTPH and BTAP attained a maximum value of 88.13 and 91.93 at 300ppm concentration respectively. The values of inhibition efficiency increase with increasing concentration of inhibitor, indicating that a higher surface coverage was obtained in a solution with the optimum concentration of inhibitor. The results obtained from the polarization measurements are in good agreement with the weight-loss measurements in natural sea water.

### 3.3 A.C. Impedance studies

The corrosion behaviour of brass in natural sea water in the presence of benzotriazole derivatives was investigated by EIS method at room temperature. Nyquist plots of brass in inhibited and uninhibited sea water containing optimum concentrations of BTPH and BTAP after immersion of 120 hrs is shown in Figure 3.. The percent inhibition efficiency (IE %) of corrosion brass was calculated as follows [37]:

$$\text{I.E \%} = \frac{(R_{\text{ct}})^{-1} - R_{\text{ct(inh)}}^{-1}}{(R_{\text{ct}})^{-1}} \times 100$$

where,  $R_{\text{ct inh}}$  and  $R_{\text{ct}}$  are the charge-transfer resistance values with and without inhibitors respectively. IE% attained 96.70 after 120 hrs immersions with optimum concentration of BTAP, which was comparatively higher than that of BTPH in sea water. This behaviour was attributed to more surface coverage of BTAP on the brass surface from sea water. The inhibition efficiency values determined using the polarization curves were lower than those determined by EIS experiments, this difference was probably due the shorter immersion time in the case of the polarization measurements [38]. Impedance parameters derived from these investigations are given in Table 2. In the presence of optimum concentration of inhibitors,  $R_{\text{ct}}$  values increased, whereas  $C_{\text{dl}}$  values tended to decrease. The term ( $C_{\text{dl}}$ ) is voltage dependant and in aqueous media this capacitance is typically a few tens of microfarads per square centimeter, and the measured value can be used to estimate the effective area of a corroding electrode. The decrease in  $C_{\text{dl}}$



**Fig.3 Nyquist diagram of admiralty brass in natural sea water containing optimum concentration of BTPH and BTAP after immersion of 120 hours.**

**Table 3. Impedance measurements and inhibition efficiency of admiralty brass in natural sea water containing optimum concentrations of BTPH and BTAP after 120 hrs immersion.**

Inhibitors	$R_{ct} \times 10^4 (\text{ohm cm}^2)$	$C_{dl} (\mu \text{Fcm}^{-2})$	Inhibition efficiency (%)
Blank	0.83	0.921	
BTPH	18.43	0.096	95.50
BTAP	25.16	0.074	96.70

values was caused by adsorption of benzotriazole derivatives on the metal surface.  $R_{ct}$  values for brass in sea water increased with increase in immersion time while  $C_{dl}$  values are decreased with increase in immersion time. The tendency to decrease in  $C_{dl}$ , which can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that the benzotriazole derivatives function by adsorption at the metal-solution interface

[39]. The change in  $R_{ct}$  and  $C_{dl}$  values was caused by the gradual replacement of water molecules by the chloride ions of the sea water and adsorption of the substituted BTA molecules on the metal surface, reducing the extent of dissolution [40].

### 3.4 Surface composition analysis

The surface composition (wt.%) of the alloy in the presence and absence of inhibitors after polarization are given in Table 3. In the absence of inhibitors, the % of Cu and Zn are present in the surface were reduced due to the leaching of metal ions in sea water. Moreover, the higher concentration of chloride ions on the surface shows the penetration of  $Cl^-$  ions from the electrolyte. However, in the presence of BTBA and DBCH, the % of Cu & Zn is closer to that of the bulk composition of the alloy. Based on the surface analysis, these inhibitors exhibited excellent inhibition efficiency in natural sea water.

**Table 4. Surface composition (%) of admiralty brass in natural seawater after polarization with optimum concentration of inhibitors.**

Inhibitors	Cu / %	Zn / %	Cl / %
Alloy	70.34	28.53	-
Blank	63.47	19.36	17.24
BTPH	68.56	26.78	4.62
BTAP	69.81	28.09	2.08

### 3.5 Accelerated leaching studies (ICP-AES)

The results of solution analysis and the corresponding dezincification factor (z) in the presence and absence of benzotriazole derivatives at their optimum concentration level in natural sea water for brass are given in Table 4. The dezincification factor (z) was calculated using the relation.

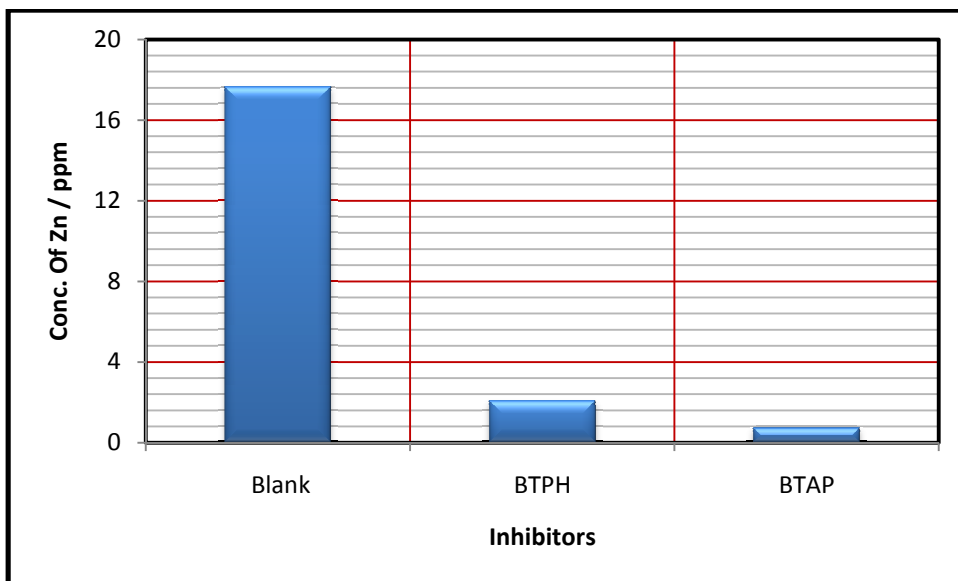
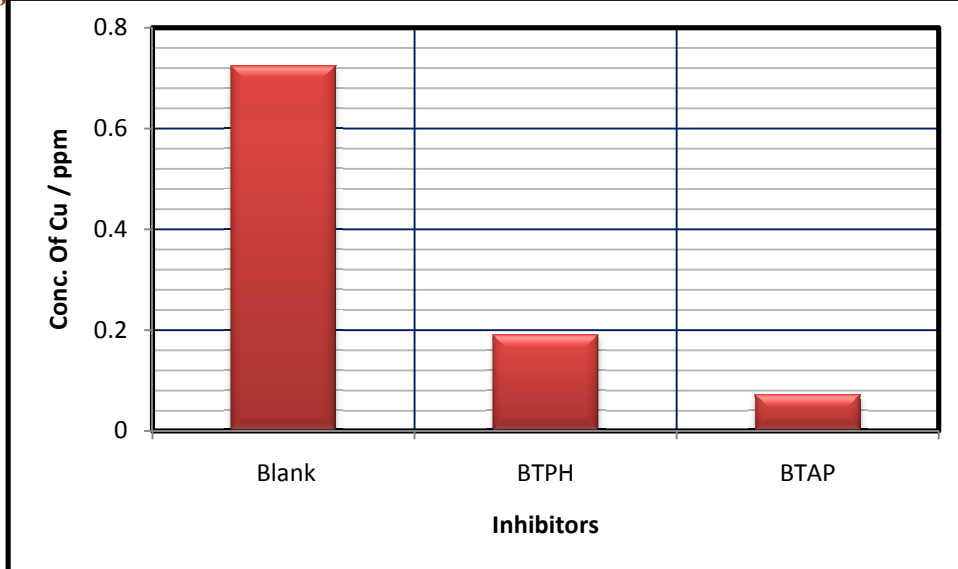
$$z = \frac{(\text{Zn/Cu})_{\text{sol}}}{(\text{Zn/Cu})_{\text{alloy}}}$$

Where, the ratio  $(Zn/Cu)_{sol}$  is determined from solution analysis and  $(Zn/Cu)_{alloy}$  is the ratio of weight-percent in the alloy [41].

Figure 4 represent the effect of inhibitors on the dissolution of brass in natural sea water. From the figure, it can be observed that both copper and zinc were present in the solution whereas in the presence of inhibitors, which are able to minimize the dissolution of both copper and zinc. The data recorded in tables illustrate that the percent inhibition efficiency against the dissolution of zinc was correspondingly high as compared to the dissolution of copper. This indicates the excellent inhibition efficiency of inhibitors to prevent the dezincification of brass in natural sea water, which is also reflected in the values of dezincification factor. Among the inhibitors studied, BTAP shows highest inhibition efficiency in the dissolution of brass in natural sea water. The percent inhibition efficiency against the dissolution of Zn was correspondingly high i.e. 95.86% can be achieved in the presence of BTAP containing natural sea water for brass, indicating that the preferential dissolution of zinc was almost completely minimized.

**Table 5. Effect of optimum concentrations of BTPH and BTAP on the dezincification of admiralty brass in natural sea water.**

Inhibitors	Solution analysis		Dezincification factor (z)	Percent inhibition	
	Cu (ppm)	Zn (ppm)		Cu (%)	Zn (%)
Blank	0.724	17.65	60.10	-	-
BTPH	0.19	2.08	26.99	73.75	88.22
BTAP	0.072	0.73	25.12	90.05	95.86



**Fig. 4: Concentration of copper and zinc leached out from brass in natural sea water containing optimum concentration BTPH and BTAP.**



1. Both BTPH and BTAP show good inhibition efficiency in natural sea water. The %IE of BTAP was higher than that of BTPH.
2. The polarization data indicate suppression of both the partial corrosion processes in the presence of BTBA and DBCH. These inhibitors behave as mixed type. They decrease the anodic reaction rate more strongly than the cathodic reaction rate and renders the open circuits potential of brass more positive in natural sea water.
3. The inhibitors easily adsorb on the brass surface at the corrosion potential and form a protective complex with the Cu (I) ion, controlling brass from corrosion.
4. Electrochemical impedance spectroscopy shows that  $R_{ct}$  values increase, while  $C_{dl}$  values decrease in the presence of BTPH and BTAP.
5. Solution analysis reveals that the BTPH and BTAP excellently prevent the dezincification of brass in natural sea water.

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