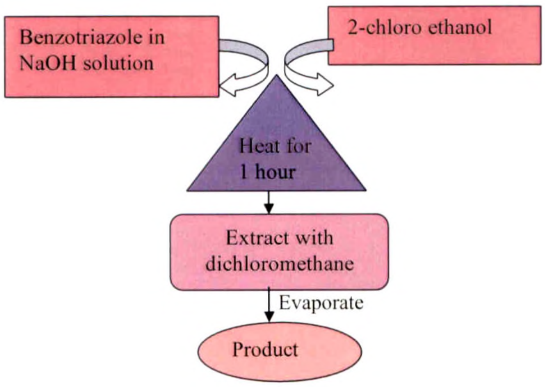
# *RESULTS AND DISCUSSION*

# 4. RESULTS AND DISCUSSION

The present investigation efforts are taken to synthesis BTA derivatives such as 2- Hydroxy ethyl benzotriazole (HEBTA), nitro benzotriazole (NBTA), and bromo benzotriazole (NBTA) and utilize the synthesized and characterized inhibitors for reducing the corrosion of Brass in 3 % NaCl.

## Synthesis of 2- Hydroxy ethyl benzotriazole (HEBTA)

To a solution of Benzotriazole (11.9g), in NaOH solution (4.8g in 70ml $H_2O$ ) added 2- chloro ethanol (6.7ml). The reaction mixture is heated for 100°c for 2 hours in a round bottomed flask fitted with a water condenser. It is cooled at room temperature and extracted with dichloromethane. The contents are dried over sodium sulphate and the solvent is evaporated. The residue is purified by recrystallization.



## Synthesis of Nitro benzotriazole (NBTA)

1.346 ml of concentrate $HNO_3$ is taken in a 100ml round bottomed flask and added in portions with shaking 1.538ml of concentrated $H_2SO_4$ acid in an efficient fume cupboard. The mixture is kept in ice. A thermometer is placed in the acid mixture. 1g of benzotriazole is introduced. A reflux condenser is filtered in the flask and heated it in a water bath maintained at 60°c for 40-45 minutes. The flask is removed and poured the contents of the flask into about 100ml of cold water in a beaker. Stirred the mixture well in order to wash out as much acid as possible from the nitro benzotriazole and allowed to stand and filtered. The products are filtered through a small fluted fitter paper and dried. A portion of the product obtained is recrystallised with benzene.

## Synthesis of Bromo benzotriazole (BBTA)

1g of benzotriazole and 0.1ml of dry pyridine (dried over potassium hydroxide pellets) is taken in a100ml round bottomed flask. A reflux condenser is attached to the flask and fitted a device for absorbing the hydrogen bromide gas subsequently evolved. The flask is immersed in a bath of cold water, partially supported upon a tripod and gauze carefully. 4ml of bromine is added through the condenser and immediately inserted the absorption device into the upper end of the condenser. A vigorous reaction soon occurs and HBr evolved is absorbed by the $H_2O$ in the beaker. The reaction is carried out in a water bath at a temperature of 25- 30°C for 1 hour. Finally the temperature is raised up to 65-70°C for further 45 minutes. The solid obtained is filtered and dried. A portion of the product obtained is recrystallised with benzene.

# CHARACTERIZATION OF HEBTA, BBTA, AND NBTA

To characterize BTA derivatives, FTIR spectra were taken for all the investigated and synthesized inhibitors. The following points are to be kept in mind in assigning and confirming the structure of the synthesized compounds, which are the out come of the literature survey.

1. The existence of an aromatic ring in a structure normally readily determine from C-H and C=C=C-C ring related vibrations. The C-H stretching occurs above 3000cm$^{-1}$ indicates the formation of hetero aromatic compounds. The frequency range of N-H stretching in hetero aromatic compounds are found to be in the range of 2000 to 3300 cm$^{-1}$
2. The free OH stretching frequency of hydroxy compounds is at the range of 3676-3584 cm.$^{-1}$ The hydroxy absorption is singly one of the important bands in the IR spectrum
3. The bromo substituted compounds shows the absorption in the range of 600cm$^{-1}$ to 500cm$^{-1}$ in the case of nitro substituted compounds the absorption peak are in the range of 1500-1510 cm$^{-1}$ for asymmetric and symmetric stretching based on the literature survey and Spectral analysis of BTA derivatives the characterization of all synthesized BTA derivatives are made.

Spectral analysis of BTA derivatives are presented in the Table (1-3). The presence of functional groups in benzotriazole compounds can be detected with a fair degree of certainty from its FT-IR spectrum. More over the number and positions of substituents on the ring can also be ascertained from the IR spectral data.

**TABLE-1**

**IR ABSORPTION DATA OF HEBTA**

| S.NO | HEBTA | Assignment |
|---|---|---|
| 1 | 3060.2 cm$^{-1}$ | C-H stretching in the aromatic ring |
| 2 | 1429.15,1456.16,1496,1568.2 and 1589.2 cm$^{-1}$ | C=C stretching in skeleton ring |
| 3 | 3109.04 C m-1,3456.2 cm$^{-1}$ | Free OH stretching |
| 4 | 2877.6,2929 and 2960 cm$^{-1}$ | CH2, CH stretching |

## TABLE-2

## IR ABSORPTION DATA OF BBTA

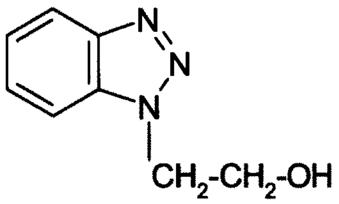
| S.NO | BBTA | Assignment |
|---|---|---|
| 1 | 2200-3300 $cm^{-1}$ | N-H stretching bands of heteroaromatic compounds |
| 2 | 3070 $cm^{-1}$ | C-H stretching in the aromatic ring |
| 3 | 1419.5,1458.08,1508.23 and 1595.02 $cm^{-1}$ | C=C stretching in skeleton ring |
| 4 | 536.17,590.18 $cm^{-1}$ | Bromo group |

## TABLE-3

## IR ABSORPTION DATA OF NBTA

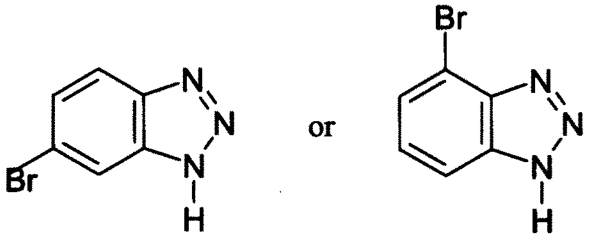
| S.NO | NBTA | Assignment |
|---|---|---|
| 1 | 2279-3471 $cm^{-1}$ | N-H stretching bands of heteroaromatic compounds |
| 2 | 3089.75 $cm^{-1}$ | C-H stretching in the hetero aromatic ring |
| 3 | 1436.87,1490.87and 1610 $cm^{-1}$ | C=C stretching in skeleton ring |
| 4 | 1527.52 $cm^{-1}$ | ($Ar-NO_2$) N-O Asymmetric stretching |
| 5 | 1344.29 $cm^{-1}$ | ($Ar-NO_2$) N-O Symmetric stretching |

a) IR spectrum of HEBTA was presented in the Figure (1). The formation of a strong and broad band at 3365.01 $cm^{-1}$ indicates the presence of the free OH stretching. A medium peak at 3040 $cm^{-1}$ is due to stretching from the hetero aromatic ring. The two or more peaks at 1589 $cm^{-1}$ and 1614 $cm^{-1}$are characteristic of N=N-N tri azo group and C=C stretching respectively. A peak 3087.82 $cm^{-1}$ infers the presence of hetero aromatic compounds. Band at 2860-2950 $cm^{-1}$ due to C-H stretching from methyl or methylene group. Other bands at 824.02 and 743 $cm^{-1}$ are due to the C-H def out of plane. Hence the structure of the compound.



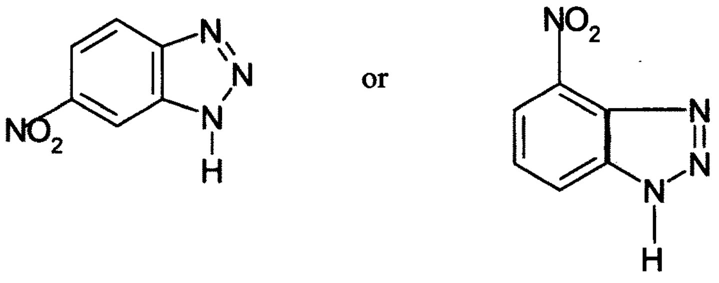
2-Hydroxy ethyl Benzotriazole

b) IR spectrum of bromo benzotriazole is depicted in Figure (2). The peak at 536.17 and 590-18 cm$^{-1}$ corresponding to the stretching frequency of Aromatic–Br bond. Mono substituted B-BTA was confirmed from absorption band in 750.28 cm$^{-1}$. The peaks at 2150 to 3332.7 cm$^{-1}$ are due to the presence of triazole. This was present in all the BTA derivatives. This is due to the hetero aromatic characteristic and the peak at 3070.46 cm$^{-1}$ exhibits the C-H stretching frequency.



Bromo Benzotriazole

c) Hetero aromatic compounds containing an >N-H group exhibit N-H stretching absorption in the region from 3100-3000 cm$^{-1}$and C=C and C=N stretching vibrations occur in the region 1436, 1496, 1610 cm$^{-1}$. The absorption at 1527.52 and 1344.29 cm$^{-1}$ are assigned respectively to asymmetric and symmetric Ar-$NO_2$ stretching vibrations of nitro group. The structure of the compounds is



Nitro Benzotriazole

# Figure-1 IR SPECTRUM OF HEBTA

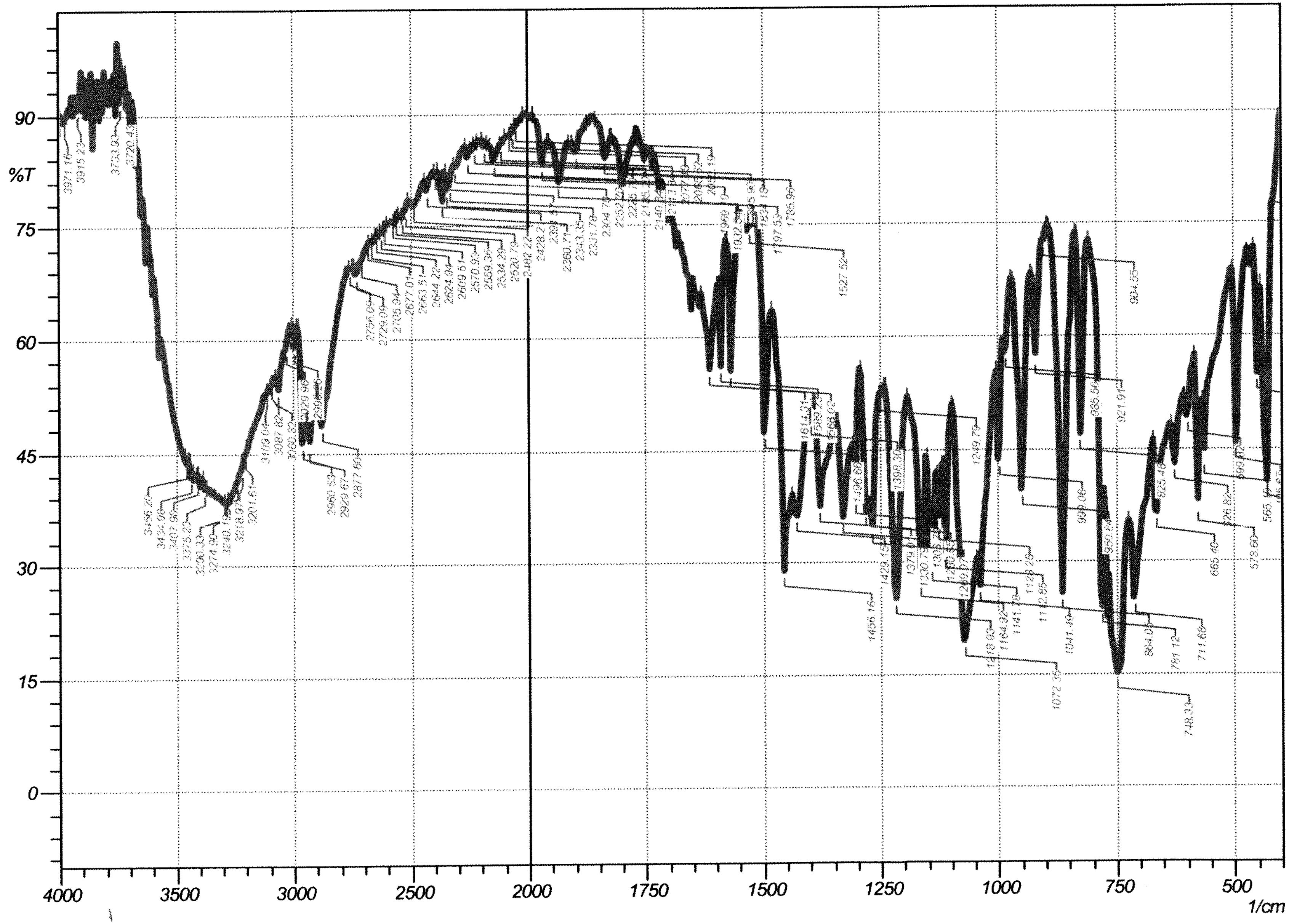
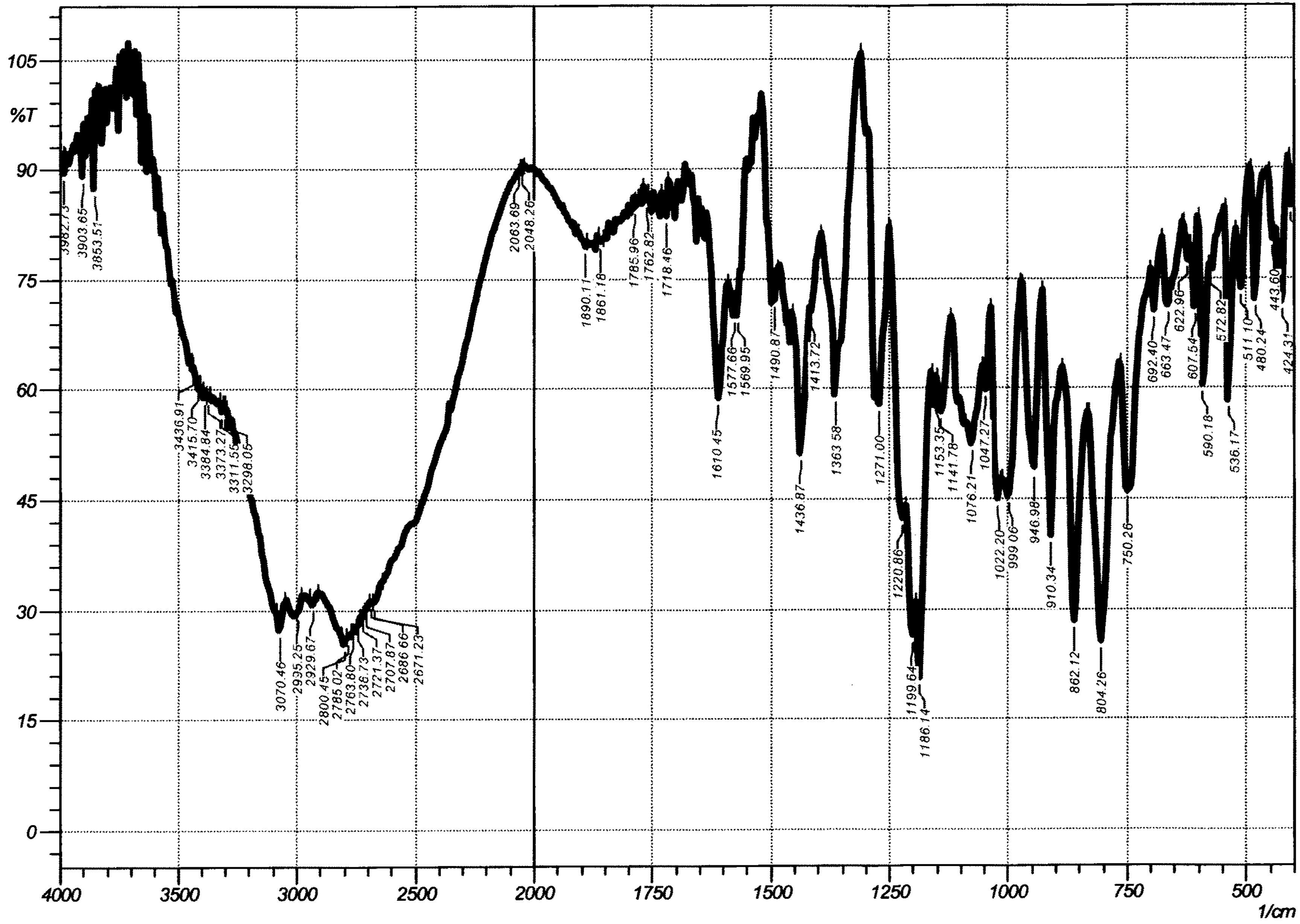
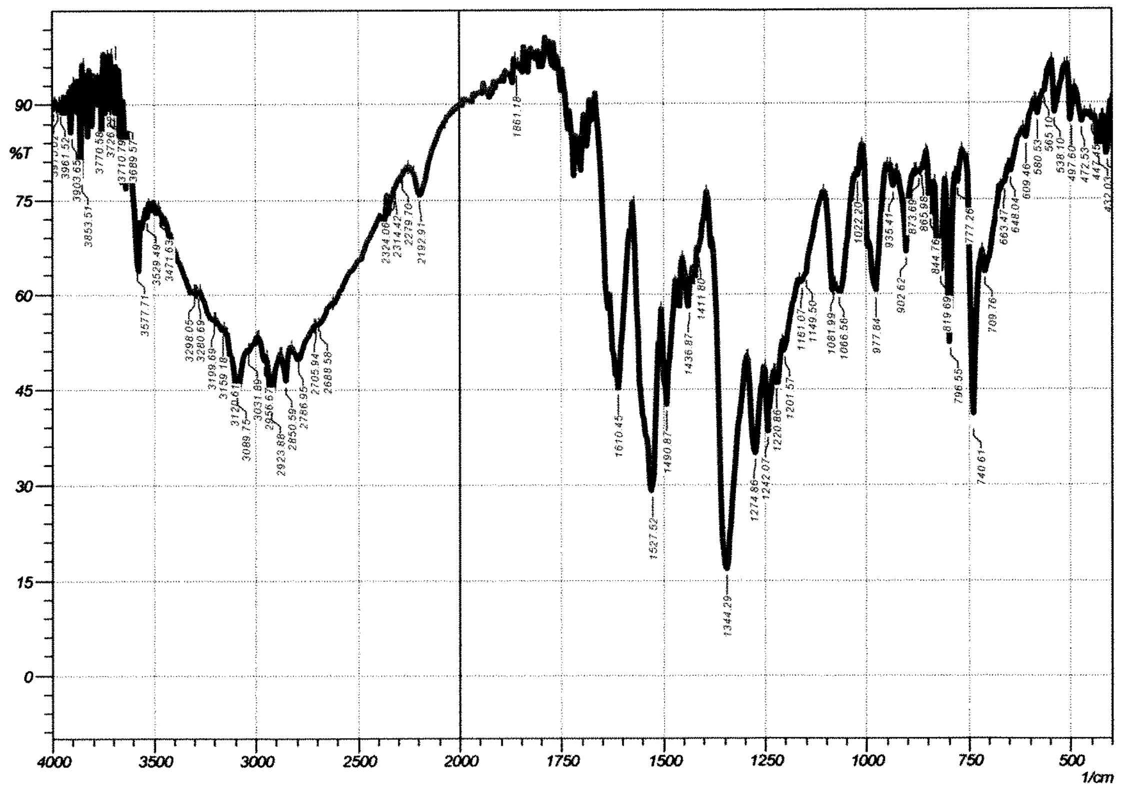


**Figure-2 IR SPECTRUM OF BBTA**



# Figure-3 IR SPECTRUM OF NBTA



The present investigation on **"Substituted benzotriazoles as corrosion inhibitors for brass in 3% NaCl"** are tabulated and discussed. Result of the present investigation are discussed under the following headings

1. Weight loss method
    - ✱ Effect of concentration (100ppm to 450ppm)
    - ✱ Effect of temperature (313K-353K)
    - ✱ Period of Exposure (duration in days 3,5,15, and 25 )
2. Electro chemical methods
    - ✱ Linear polarization techniques
    - ✱ Electrochemical impedance spectroscopy
    - ✱ Cyclic voltammetry
3. Surface analytical techniques
    - ✱ Optical electron microscopy
4. Mechanism of inhibition

## WEIGHT LOSS METHOD

In this method the effect of concentration of HEBTA, BBTA, and NBTA on corrosion inhibition of brass in 3% NaCl was studied at room temperature. Role of temperatures 313K, 323K, 33K, 343K and 353K on inhibition of brass was carried out. To find out effective time of immersion studies were carried out with time duration 3, 5, 15 and 25 days. Inhibition efficiency was calculated by varying the concentration of BTA, HEBTA, NBTA and BBTA at room temperature, at high temperature and at various periods of immersion.

## EFFECT OF CONCENTRATION OF HEBTA, BBTA, AND NBTA

The corrosion rate and inhibition efficiency of BTA, HEBTA, NBTA and BBTA on brass by weight loss measurements at different concentration of the inhibitors in 3% NaCl at room temperature are presented in Tables (4-6) and depicted in Figures (4-6). The corrosion rate was found to decrease with the increase in concentration of the inhibitors.

The experiments were also carried out by increasing the concentration of the inhibitors such as HEBTA, BBTA, and NBTA on brass. From the figures it is imperative that the efficiency of inhibition was found to increase with increase of concentration of these inhibitors and reaches the maximum values which were found to depend on the nature of substituted groups. In the presence case, inhibition efficiency was found to be 83.5% in HEBTA, 99.3% in BBTA, and 93% in NBTA at 450 ppm respectively. This behavior of increase of IE could be attributed to the increase in the surface area covered by the adsorbed molecules of HEBTA, BBTA and NBTA with the increase in concentrations.

Results indicate that the IE increases with increasing in concentration of the BTA derivatives, there by confirming the adsorption of the inhibitor molecules on brass surface Similar results were given by Mohammed. A. Amin, 2005, Subramanian. et. al., 2003 and Quraishi. M. A. et. al., 2005. Comparison of IE of HEBTA, BBTA, and NBTA inhibitors on brass corrosion in 3% NaCl is depicted in fig and represented in the Figures (7) and represented in the bar graph. The IE was determined using weight loss methods was found to be in the order BBTA>NBTA >HEBTA which is mainly due to the nature of the substituent and it position. It is well known that different substituents on the organic molecule polarize in a different manner. The presence of substituents may increase the polarity and adsorability of inhibitors on the surface of alloy.

Figure-4

**INFLUENCE OF CONCENTRATION ON IE OFHEBTA FOR BRASS IN 3% NaCl AT VARIOUS TIME OF IMMERSION**

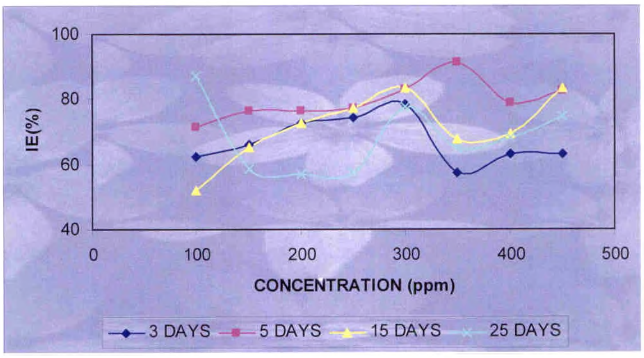


Figure-5

**EFFECT OF CONCENTRATION ON IE OF BBTA IN 3% NaCl ON BRASS**

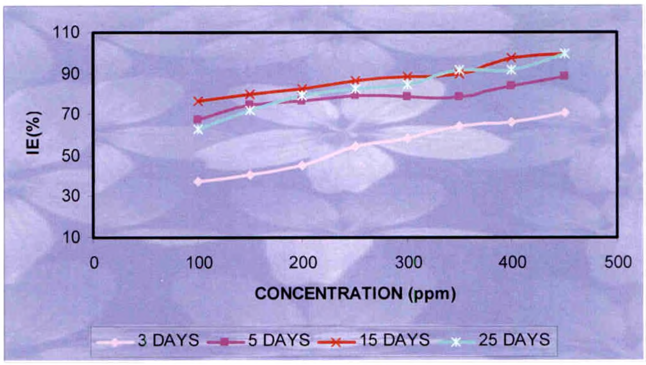


Figure-6

**VARIATION OF IE WITH TIME ON BRASS IN 3% NaCl AT VARIOUS CONCENTRATION OF NBTA**

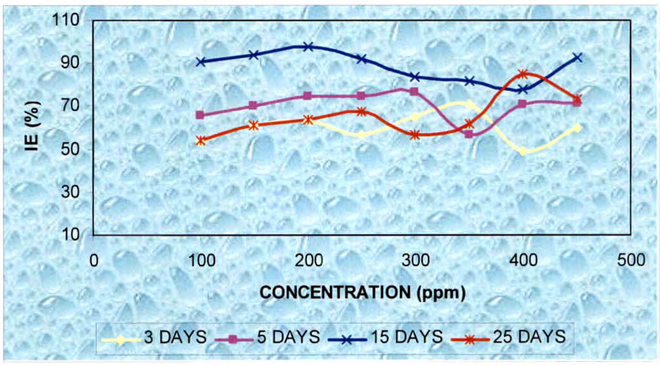
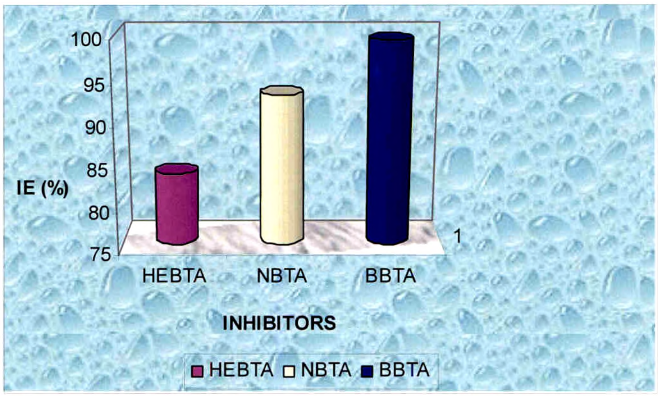


Figure-7

**COMPARISONS OF IE OBTAINED FOR DIFFERENT INHIBITORS ON BRASS IN 3% NaCl -15 DAYS STUDY**



## EFFECT OF EXPOSURE PERIOD

Measurements of weight changes were performed with brass coupons in 3% NaCl with and without the inhibitors and allowed to stand for 3, 5, 15 and 25 days. Results of the studies are tabulated in the Tables (4-6). Analysis of the tables infers that the IE increases with increasing in concentration of the studied inhibitors. IE was found to increase with exposure period for 3 days and 5 days in the case of HEBTA the IE was found to decrease after 15 days and 25 days. In the case of NBTA and BBTA the IE was low at 3 and 5 days and prolonged immersion (15 days and 25 days). IE was found to increase with exposure period. IE was pictorially presented in the Figures (8-10). The order of IE of the investigated inhibitors is in the order of BBTA > NBTA > HEBTA. Competitive adsorption of the inhibitor chloride ion in 3% NaCl in the presence of current inhibitors are represented in the bar diagram 3, 5, 15 and 25 days at maximum concentration.

The high IE at 3 days and 5 days exposure compared to 15 days and 25 days exposure time is due to the strong adsorption of the inhibitor on brass surface and later and prolonged immersion the desorption of the case of HEBTA. The reverse is observed in the case of NBTA and BBTA. This may be due to slow and steady adsorption inhibitors molecules.

Figure-8

VARIATION OF IE WITH TIMEOF IMMERSION (HEBTA ON BRASS IN 3% NaCl )

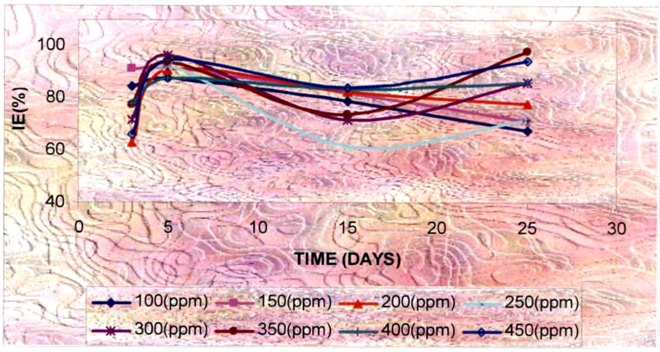


Figure-9

VARIATION OF INHIBITION EFFICIENCY AT VARIOUS TIME INTERVALS (NBTA IN 3% NaCl)

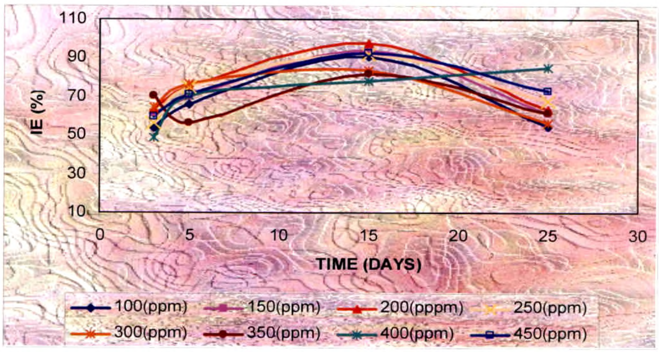
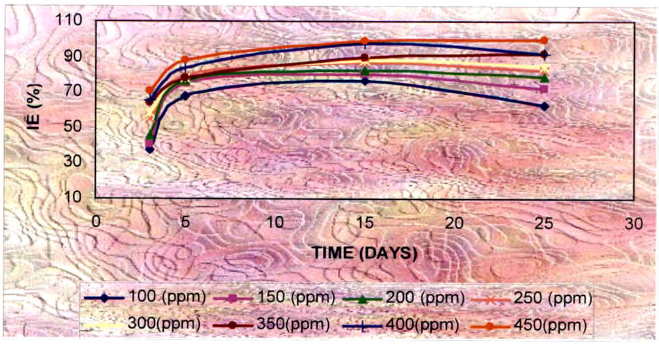


Figure-10

EFFECT OF CONCENTRATION ON IE OF BBTA IN 3% NaCl ON BRASS



## TABLE-4

## VARIATION OF CORROSION RATE WITH PEREIODS OF IMMERSSION ON CORROSION OF BRASS IN 3 % NaCl +HEBTA.

| S.NO | Concentration (ppm) | 3 DAYS | | 5 DAYS | | 15 DAYS | | 25 DAYS | |
|---|---|---|---|---|---|---|---|---|---|
| | | CR(mpy) | IE(%) | CR(mpy) | IE(%) | CR(mpy) | IE(%) | CR(mpy) | IE(%) |
| 1. | 100 | 0.225 | 62.2 | 0.165 | 71.3 | 0.171 | 52.2 | 0.0169 | 87.3 |
| 2. | 150 | 0.203 | 66.0 | 0.135 | 76.6 | 0.214 | 65.2 | 0.0554 | 58.5 |
| 3. | 200 | 0.163 | 72.6 | 0.2718 | 76.3 | 0.239 | 72.8 | 0.0571 | 57 |
| 4. | 250 | 0.152 | 74.5 | 0.132 | 77.2 | 0.253 | 77.3 | 0.0567 | 57.6 |
| 5. | 300 | 0.129 | 78.3 | 0.098 | 83.0 | 0.273 | 83.5 | 0.0297 | 77.7 |
| 6. | 350 | 0.253 | 57.5 | 0.050 | 91.2 | 0.222 | 67.7 | 0.0466 | 65 |
| 7. | 400 | 0.219 | 63.2 | 0.121 | 78.9 | 0.227 | 69.4 | 0.04256 | 68.1 |
| 8. | 450 | 0.219 | 63.2 | 0.101 | 82.4 | 0.273 | 83.5 | 0.0338 | 74.7 |

## TABLE-5

## TRENDS IN IE OF BBTA ON BRASS IN 3%NaCl MEDIUM

| S.NO | Concentration (ppm) | 3 DAYS | | 5 DAYS | | 15 DAYS | | 25 DAYS | |
|---|---|---|---|---|---|---|---|---|---|
| | | CR(mpy) | IE(%) | CR(mpy) | IE(%) | CR(mpy) | IE(%) | CR(mpy) | IE(%) |
| 1. | 100 | 0.371 | 37.7 | 0.185 | 67.8 | 0.076 | 76 | 0.049 | 63.1 |
| 2. | 150 | 0.355 | 40.6 | 0.148 | 74.9 | 0.065 | 80 | 0.0371 | 72.2 |
| 3. | 200 | 0.326 | 45.3 | 0.135 | 76.6 | 0.057 | 82.4 | 0.0277 | 79.2 |
| 4. | 250 | 0.270 | 54.7 | 0.118 | 79.5 | 0.044 | 86.6 | 0.0236 | 82.3 |
| 5. | 300 | 0.247 | 58.5 | 0.125 | 78.3 | 0.038 | 88.3 | 0.0209 | 84.3 |
| 6. | 350 | 0.214 | 64.2 | 0.125 | 78.3 | 0.034 | 89.7 | 0.0108 | 91.9 |
| 7. | 400 | 0.202 | 66 | 0.094 | 83.6 | 0.008 | 97.6 | 0.0108 | 91.9 |
| 8. | 450 | 0.174 | 70.8 | 0.067 | 88.3 | 0.002 | 99.3 | 0.0004 | 99.6 |

## TABLE-6

## TRENDS IN IE RANGE OVER IMMERSION PERIOD CONTAINING VARIOUS CONCENTRATION OF NBTA IN 3% NaCl ON BRASS

| S.NO | Concentration (ppm) | 3 DAYS | | 5 DAYS | | 15 DAYS | | 25 DAYS | |
|---|---|---|---|---|---|---|---|---|---|
| | | CR(mpy) | IE(%) | CR(mpy) | IE(%) | CR(mpy) | IE(%) | CR(mpy) | IE(%) |
| 1. | 100 | 0.276 | 53.8 | 0.195 | 66 | 0.298 | 90.7 | 0.061 | 54.5 |
| 2. | 150 | 0.230 | 61.3 | 0.169 | 70.7 | 0.307 | 93.8 | 0.078 | 61.6 |
| 3. | 200 | 0.219 | 63.2 | 0.145 | 74.8 | 0.319 | 97.59 | 0.126 | 63.6 |
| 4. | 250 | 0.258 | 56.6 | 0.145 | 74.8 | 0.319 | 92.9 | 0.104 | 67.67 |
| 5. | 300 | 0.208 | 65.1 | 0.135 | 76.6 | 0.278 | 84.88 | 0.077 | 56.56 |
| 6. | 350 | 0.174 | 70.7 | 0.250 | 56.7 | 0.271 | 82.8 | 0.513 | 61.61 |
| 7. | 400 | 0.304 | 49.0 | 0.172 | 70.17 | 0.257 | 78 | 0.574 | 84.9 |
| 8. | 450 | 0.236 | 60 | 0.166 | 71.3 | 0.305 | 93 | 0.358 | 73.2 |

## EFFECT OF TEMPERATURE

Radovici et. al., (1965) classified the inhibitors into three groups according to the temperature effects:

1. Inhibitors whose IE decreases with temperature increase. The value of the apparent activation energy Ea is greater than that in the uninhibited solution.
2. Inhibitors whose IE does not change with temperature variation. The apparent activation energy does not change with the presence or absence inhibitors.
3. Inhibitors in whose presence the IE increases with temperature increase while the value of Ea for the corrosion process is smaller than that obtained in the uninhibited solution. This is an indication, according to the author, for a specific type of adsorption of the inhibitors.

Machu et. al., (1988) also states that the corrosion process taking place in the presence of powerful inhibitors is characterized by an activation energy whose value is smaller than that of the uninhibited process. (Putilova. L. N. et. al., 1960).

To investigate the inhibition mechanism and to determine the activation energy and free energy of adsorption of the corrosion process weight loss measurements were taken in the temperatures ranging from 313K, 323K, 333Kand 353K in the absence and presence of various concentrations of HEBTA, NBTA and BBTA inhibitors. Inhibition efficiency in presence of HEBTA, BBTA, and NBTA at various temperatures are presented in Tables (7-9). It is notable that the change in IE with temperature and concentration. The result may be attributed to the high dissolution process of the brass measured at higher temperatures. Result revealed that the corrosion rate increases in the blank with rise in temperature but in the presence of inhibitors the dissolution is delayed.

However the values of inhibition efficiency in the presence of BTA, and HEBTA at (323K) higher temperatures is greater when compared to those in the presence of BBTA, second maximum inhibitor was observed in NBTA inhibitor. The maximum IE was found to be 98.97% for HEBTA at 323K in 200ppm concentration. Second highest IE- 98% of IE for NBTA (333K at 300ppm), 93% of IE for BBTA (323K at 450ppm). From this temperature studies that the nitro and hydroxyl compounds have a higher protective effect than the BBTA compound. Results furnished by Mohammed. A. Amin 2005 supported the present study. The inhibition efficiency decreases with rise in temperature. These results may be attributed to the decrease in strength of adsorption process at higher temperatures. The inhibition efficiency increases with increase in temperature upto323K after that there is a decline in IE at 333K. IE was found to increases after 333K. This may be due to desorption of inhibitors molecules at 333K and after that strong adsorption of inhibitors molecules at higher temperature. At higher concentration for all inhibitors involves higher inhibition.

The fact that IE increases with temperature is explained by Ammar. I. A. 1973 as the likely specific interaction between the metal surface and the inhibitor. Balezin (E. S. Ivanov. et. al., 1986) considers the increase of IE with temperature increase as the change in the nature of adsorption's the inhibitor is adsorbed physically at lower temperatures, while chemisorption is favoured as temperature increases. The same phenomenon is explained by others Putilova. L. N. et. al., (1960) as due to increase in the surface coverage by an inhibitor. Thus, at a high degree of coverage, the diffusion through the surface layer containing the inhibitor and corrosion products becomes the rate determining step of the metal dissolution process.

Similar results were obtained by Popova. A. et. al, (2003), Bentiss. F. et. al, (2001), Sankarapapavinasam. S. et. al, (1991) and Mahmoud. M. Saleh. and Asem. A. ATI (2006).

## TABLE-7

## INFLUENCE OF CONCENTRATION ON IE OF HEBTA ON BRASS AT 3% NaCl AT VARIOUS TEMPERATURES

| S.NO | Concentration (ppm) | 313K | | 323K | | 333K | | 343K | | 353K | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | CR(mpy) | IE(%) | CR(mpy) | IE(%) | CR(mpy) | IE(%) | CR(mpy) | IE(%) | CR(mpy) | IE(%) |
| 1. | B | 124.02 | | 158 | | 45.395 | | 116 | | 89 | |
| 2. | 100 | 29.18 | 76.4 | 11.3 | 92.8 | 17 | 61 | 17 | 85.4 | 31.6 | 64 |
| 3. | 150 | 28.3 | 77.1 | 9.73 | 93.8 | 15.5 | 62.5 | 13.7 | 88 | 17.02 | 81.08 |
| 4. | 200 | 31.6 | 74.5 | 1.62 | 98.97 | 14.6 | 66 | 11.34 | 90.2 | 11.3 | 87.3 |
| 5. | 250 | 25.13 | 79.7 | 16.2 | 89.7 | 27.5 | 37 | 12.9 | 88.88 | 3.2 | 96.2 |
| 6. | 300 | 22.7 | 81.7 | 15.4 | 90.2 | 25.72 | 42 | 12.9 | 88.88 | 2.4 | 97.2 |
| 7. | 400 | 85.11 | 85.11 | 8.9 | 94.3 | 18.6 | 57 | 18.6 | 84.02 | 22.69 | 74.77 |
| 8. | 450 | 14.59 | 14.59 | 5.1 | 96.76 | 28.3 | 35 | 12.1 | 89.58 | 16.2 | 81.98 |

## TABLE-8

## ROLE OF TEMPERATUREON THE IE OF BBTA ON BRASS IN 3% NaCl

| S.NO | Concentration (ppm) | 323K | | 333K | | 343K | | 353K | |
|---|---|---|---|---|---|---|---|---|---|
| | | CR(mpy) | IE% | CR(mpy) | IE% | CR(mpy) | IE% | CR(mpy) | IE% |
| 1. | B | 158 | | 45.395 | | 116 | | 89 | |
| 2. | 100 | 27.56 | 82 | 11.34 | 74 | 93.22 | 20.13 | 18.6 | 79 |
| 3. | 150 | 25.129 | 84 | 17.8 | 59.2 | 90.7 | 22 | 29.9 | 66.6 |
| 4. | 200 | 23.5 | 85 | 17.8 | 59.2 | 99.7 | 14.5 | 29.18 | 67.5 |
| 5. | 300 | 21 | 87.41 | 12.5 | 70.5 | 107 | 7.6 | 21.8 | 72.67 |
| 6. | 350 | 17 | 89 | 8 | 81.47 | 85.9 | 26.389 | 27.5 | 73.87 |
| 7. | 400 | 18.6 | 88 | 7.29 | 83.3 | 101.3 | 13.19 | 19.45 | 75.67 |
| 8. | 450 | 10.5 | 93 | 9.72 | 77.77 | 77.8 | 33.33 | 29.18 | 75.67 |

## TABLE-9

## INFLUENCE OF TEMPERATURE ON THE CORROSION RATE OF BRASS IN 3% NaCl IN NBTA.

| S.NO | CONCENTRATION (ppm) | 323K | | 333K | | 343K | | 353K | |
|---|---|---|---|---|---|---|---|---|---|
| | | CR(mpy) | IE% | CR(mpy) | IE% | CR(mpy) | IE% | CR(mpy) | IE% |
| 1. | B | 158 | | 45.395 | | 116 | | 89 | |
| 2. | 100 | 84 | 46 | 14.59 | 66.6 | 30.8 | 73.6 | 27.56 | 69 |
| 3. | 200 | 55.12 | 65 | 10.5 | 75.92 | 32.4 | 72.2 | 32.42 | 63.96 |
| 4. | 250 | 55165 | 13.8 | 9.7 | 77.77 | 26.3 | 76.9 | 22.679 | 74.77 |
| 5. | 350 | 5027 | 4.6 | 12.96 | 70.36 | 34.04 | 70.8 | 26.7 | 70.27 |
| 6. | 400 | 140.2 | 11.256 | 4.86 | 88.88 | 24.3 | 79.1 | 28.37 | 68.46 |
| 7. | 450 | 149.2 | 24.3 | 24.3 | 44.43 | 29.18 | 75 | 31.61 | 64.86 |

Figure-11

TRENDS IN INHIBITION EFFICIENCY AS A FUNCTION OF TEMPERATURE IN THE PRESENCE OF HEBTA ON BRASS IN 3% NaCl

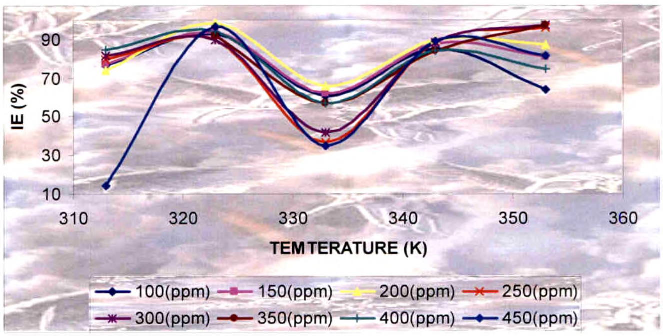


Figure-12

PICTORIAL REPRESENTATION OF IE Vs TEMPERATURE AS A FUNCTION OF CONCENTRATION OF NBTA IN 3 % NaCl

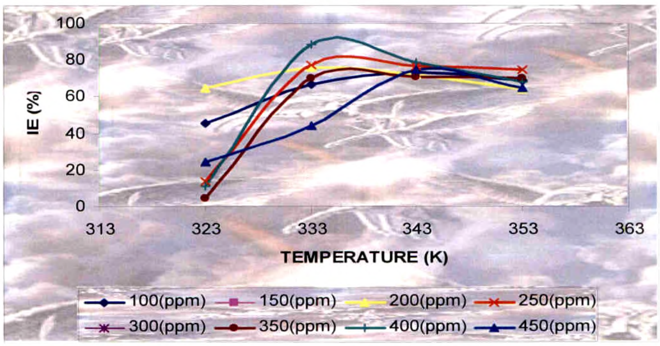
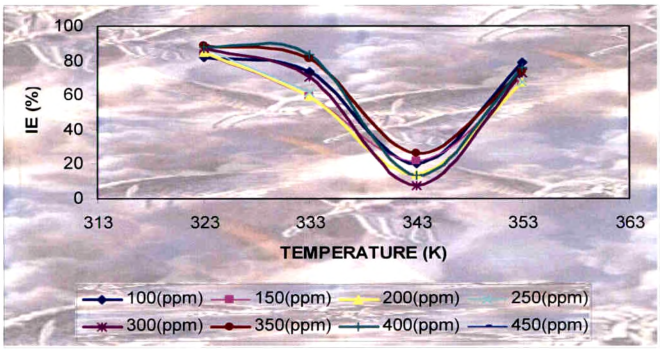


Figure-13

ROLE OF TEMPERATURE ON THE IE OF BBTA ON BRASS IN 3% NaCl



## ADSORPTION ISOTHERM

In the present study values of surface coverage (θ) were evaluated using, values of IE obtained from weight loss method 15 days immersion studies result were used for the adsorption isotherms. The υ values for different concentration of inhibitors from the neutral solution were tested graphically by fitting in to various isotherms like

Langmuir isotherm (log (θ /1-θ) Vs (log C)),
Temkin isotherm (θ Vs log C)

## LANGMUIR ISOTHERM

It was found from Figure (15) that a plot of log ((θ /1-θ) Vs log C gave a straight line with approximately unity suggesting that the adsorption of inhibitor on brass / neutral solution interface obeys Langmuir's adsorption isotherms. The deviation from unity may be explained on the basis of the interaction between the adsorbed species on the metal surface. It has been postulated in the derivation of Langmuir isotherm equation that the adsorbed molecules do not interact with each other. This is not true in the case of organic molecules having polar atoms or groups which are adsorbed on the anodic and cathodic species may interact by mutual repulsion or attraction.

## TEMKIN'S ISOTHERM

Temkin's adsorption isotherm was tested by plotting θ Vs log C where C is concentration of inhibitors in ppm. A straight line was obtained proving that the adsorption of these compounds on the surface of brass obeys Temkin's adsorption isotherms. The adsorption of the organic compounds can be described by two main types of interaction, physical adsorptions and chemisorptions. These are influenced by the nature and charge of the inhibitor and the type of electrolyte.

The data obtained by the weight loss method have been fitted in to various adsorption isotherms. Regressive co-efficients were obtained using various adsorption isotherms and are presented in the Table (10). From that table it is inferred that it follows Langmuir and Temkin adsorption isotherms.

**Figure -14**

**TEMKIN PLOTS FOR DIFFERENT INHIBITORS**

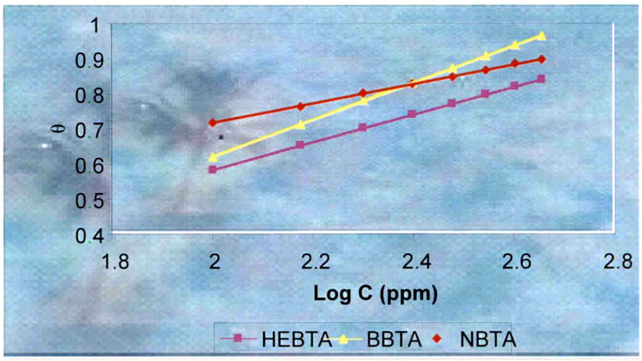


**Figure-15**

**LANGMUIR ADSORPTION ISOTHERMS PLOTS FOR BTA DERIVATIVES IN 3% NaCl MEDIUM ON BRASS.**

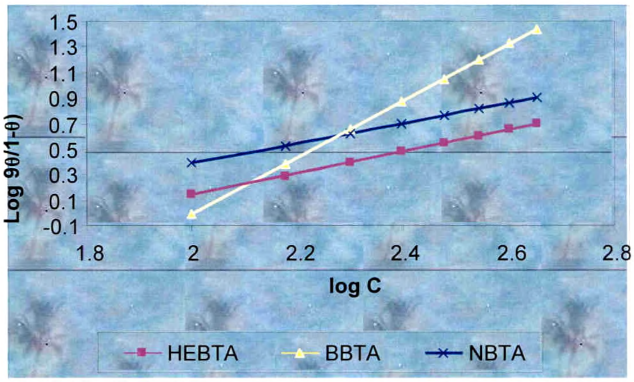


**TABLE-10**

**REGRESSION CO-EFFICIENTS OBTAINED USING VARIOUS ADSORPTION ISOTHERMS**

| INHIBITORS | LANGMUIR | | TEMKIN | |
|---|---|---|---|---|
| | R | SLOPE | R | SLOPE |
| NBTA | 0.970372 | 0.780114 | 0.952252 | 0.281429 |
| HEBTA | 0.812617 | 0.850841 | 0.817406 | 0.394477 |
| BBTA | 0.847656 | 2.209235 | 0.972534 | 0.531474 |

## THERMODYNAMIC PARAMETERS

Thermodynamic parameters including enthalpy of adsorption, free energy and entropy of adsorption are important in the elucidation of the inhibition mechanism.

The values of **ΔG** Adsorption at different temperatures were calculated from the equation

$$-\Delta G = 2.303 \times R \times T\,(1.74 + \log\theta\,(/1-\theta) - \log C)$$

Where R - 8.314 Joules/ mol
T - Temperature
C - Concentration of inhibitor

-**ΔG** against temperature gives a straight line, as shown in Figures (16-18). From the slope, entropy of adsorption (ΔS) and from the intercept enthalpy of adsorption (ΔH) were calculated and presented with Tables (11-13). The negative values of the free energy of adsorption indicate spontaneous adsorption of the inhibitor on the metal surface. Adsorption is stable in the temperature range up to 60°C and there is a change in IE after increase in temperature. Values of the -ΔG infers that the all the inhibitors are chemisorbed on the brass layer.

## ENTROPY

ΔS decreases with increasing inhibitor concentration. The trend of ΔS adsorption with inhibitor concentration may be due to replacement of water molecules from the surface during adsorption of inhibitor molecules, resulting in a decrease in disorderliness (Mohammed. A. Amin., 2005).

The negative values of ΔS ads (shown in Table) are expected as the adsorption process is accompanied by a decrease in the disorder of the system due to the adsorption of the free bulky BTA derivatives molecules onto the electrode surface.

## ENTHALPY

The absolute value of the adsorption enthalpy increases with increase in surface coverage due to the attractive interaction between the adsorption molecules Conway. B.,1965. The origin of the attractive forces is most probably the dipole-dipole interaction occurring between the neighboring adsorbed molecules (Martine. Z., et. al., 2003). The negativity of the enthalpy means that heat is released from the adsorption process. Generally an exothermic adsorption process signifies either physic or chemisorptions while an endothermic process is attributable clearly to chemisorptions (Mohammed. Amin., 2005)

Figure-16

CHANGE IN FREE ENERGY OF ADSORPTION WITH TEMPERATURE IN THE PRESENCE OF HEBTA ON BRASS

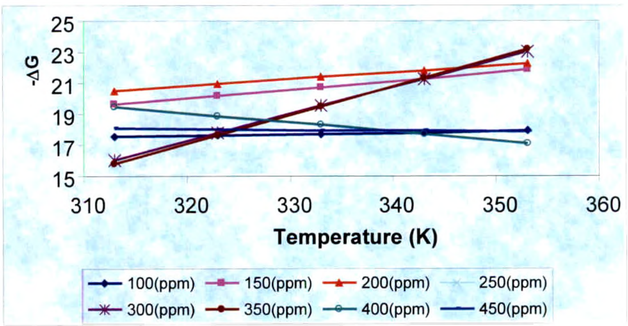


Figure-17

--ΔG AS A FUNCTION OF TEMPERATURE IN THE PRESENCE OF BBTA IN 3% NaCl.

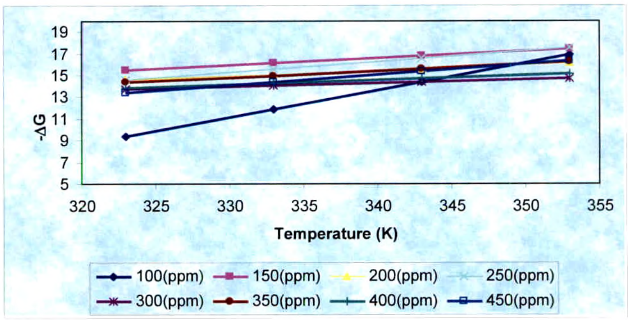
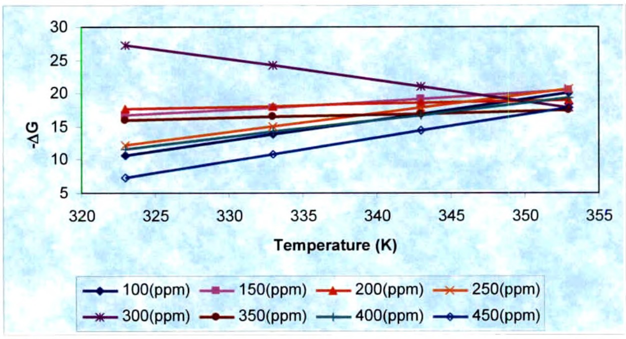


Figure-18

CHANGE IN FREE ENERGY OF ADSORPTION WITH TEMPERATURE IN THE PRESENCE OF NBTA ON BRASS



## TABLE-11

## THERMODYNAMIC PARAMETERS OF DISSOLUTION REACTION OF BRASS IN 3% NaCl IN THE PRESENCE OF HEBTA

| Concentration (ppm) | -ΔG Values KJ/mol | | | | | ΔS J/mol | -ΔH KJ/mol |
|---|---|---|---|---|---|---|---|
| | 313K | 323K | 333K | 343K | 353K | | |
| 100 | 19.5 | 23.8 | 1.9 | 23.1 | 20.3 | 9.06736 | 14.7 |
| 150 | 18.5 | 23.2 | 17.8 | 22.5 | 21.6 | 54.8013 | 2.5 |
| 200 | 17.4 | 27.3 | 17.5 | 22.4 | 22.2 | 45.4051 | 6.2 |
| 450 | 17.8 | 22.0 | 11.6 | 19.8 | 18.6 | -5.90752 | 19.9 |

## TABLE-12

## DEPENDENCE OF THERMODYNAMIC PARAMETERS ON TEMPERATURE IN THE PRESENCE OF NBTA IN 3% NaCl

| Concentration (ppm) | -ΔG Values KJ/mol | | | | ΔS J/mol | -ΔH KJ/mol |
|---|---|---|---|---|---|---|
| | 323K | 333K | 343K | 353K | | |
| 100 | 16.5 | 3.0 | -0.9 | 20.9 | 309.4 | 89.2 |
| 150 | 15.9 | 18.7 | 19.6 | 19.8 | 127.5 | 24.6 |
| 250 | 9.6 | 18.4 | 18.9 | 18.9 | 284.3 | 79.7 |
| 400 | 7.7 | 19.4 | 17.9 | 16.7 | 254.0 | 70.5 |
| 450 | 5.3 | 12.7 | 16.5 | 15.8 | 352.0 | 106.4 |

## TABLE -13

## VARIATIONS OF THERMODYNAMIC PARAMETERS WITH TEMPERATURE IN THE PRESENCE OF BBTA IN 3% NaCl

| Concentration (ppm) | -ΔG Values KJ/mol | | | | ΔS J/mol | -ΔH KJ/mol |
|---|---|---|---|---|---|---|
| | 323K | 333K | 343K | 353K | | |
| 100 | 16.9 | 0.6 | 14.0 | 20.8 | 251.2 | 71.8 |
| 150 | 15.8 | 17.4 | 13.3 | 19.4 | 65.0 | 5.5 |
| 200 | 15.0 | 16.6 | 11.0 | 18.6 | 51.5 | 2.1 |
| 250 | 14.5 | 16.2 | 15.4 | 17.9 | 97.9 | 17.1 |
| 350 | 13.6 | 18.1 | 11.5 | 17.9 | 64.2 | 6.4 |
| 400 | 13.2 | 18.1 | 8.7 | 17.8 | 43.5 | 0.3 |
| 450 | 12.9 | 16.8 | 11.8 | 17.9 | 99.7 | 18.9 |

## POTENTIODYNAMIC POLARIZATION STUDIES

The cathodic and anodic polarization curves of brass in 3% NaCl solution with various concentrations of HEBTA, NBTA and BBTA are shown in Figures 19-21. In the presence of inhibitor, the cathodic and anodic curves are shifted and the shift is dependent on inhibitor concentration.

Mamas. S. et. al., 2005 explained the kinetics and mechanism of anodic and cathodic dissolution and film formation of brass in neutral chloride solution. The mechanism of electrode dissolution and film formation on brass in NaCl is described by the following reactions. According to their concept the reaction outlined below.

Brass behaves passively because a ZnO film is formed in air. In chloride containing media with the reaction of

$$Cu + Cl^- \longrightarrow CuCl_{(ads)} + e \quad \text{------------ (1 )}$$

$$Cu + OH^- \longrightarrow CuOH_{(ads)} + e- \quad \text{------------ (2)}$$

$CuCl_{(ads)}$ and $CuOH_{(ads)}$ adsorbed layers are formed. Following this $CuOH_{(ads)}$ converts into stable $Cu_2O$ meanwhile in chloride media, copper ions can pass into the solution by the reaction of

$$Cu + 2Cl^- \longrightarrow CuCl_2 + e- \quad \text{------------- (3)}$$

In the $CuCl_{(ads)}$ formation potential, stable CuCl layer is also formed according to the following reactions.

$$Cu + CuCl_2^- \longrightarrow 2CuCl^- + e- \quad \text{------------ (4)}$$

If the polarization potential reaches the formation of CuO and $Cu(OH)_2$, these oxides can also be formed in CuCl pores. The same reactions can also occur in 3% NaCl solution, since Zn in brass is less noble than copper. A brass surface enriches by copper while being impoverished by zinc during corrosion because of the following reactions.

$$2(CuCl_2^-)\text{ surface} + Zn \longrightarrow 2Cu + Zn^{2+} + 4Cl^-$$

$$Cu_2O + Zn + 2Cl^- + H_2O \longrightarrow 2Cu + Zn(OH)_2Cl_2^{2-}$$

$$Cu_2O + Zn \longrightarrow ZnO + 2Cu$$

$$CuO + Zn + 2Cl^- + H_2O \longrightarrow Cu + Zn(OH)_2Cl_2^{2-}$$

$$CuO + Zn \longrightarrow ZnO + Cu$$

These reactions make the brass surfaces less resistance to copper increases the resemblance of copper and brass electrochemical properties in chloride containing media. It will be stressed that Saber and EI warraky consider in the first step of the mechanism of brass corrosion in NaCl the formation of $Cu_2O$ as well as ZnO and after the CuCl and further the $CuCl_2^-$. Conversely to the other authors that take the cuprous oxide as the results of a precipitation reaction. In the end of the experiment at open circuit potential, the colour of brass surface become reddish as a consequence of its enrichment by copper. This observation has been previously reported by several authors Smamar, 2005 Kabasakalogly 2002. They have attributed this behavior to the deposition of copper on brass surface electrode.

In the present study the presence of the BTA derivatives hinders aqueous attack on the brass. Hence increasing the inhibitor concentration gives rise to a consistent decrease in anodic and cathodic current densities, this infer that the inhibition process is taking place in the presence of benzotriazole derivatives such as HEBTA and BBTA. The presence of HEBTA, NBTA and BBTA inhibit the corrosion of brass by reducing the current densities. Polarization curves of brass in 3% NaCl in the presence of the investigated inhibitors are pictorially given in the figures. This infers that the inhibitors HEBTA and BBTA act as mixed type but NBTA inhibitor prevents the corrosion by mixed type, predominantly anodic control. The values of Tafel slope ba, bc, $I_{corr}$, $E_{corr}$ and IE of BTA derivatives are presented in the Tables (14-16). The values of Tafel slopes ba, bc for benzotriazole derivatives are found to change with inhibitor concentration. This indicates an increase in the energy barrier for proton discharge, leading to less gas evolution.

In the case of NBTA a large decrease in the anodic current density in comparison to the inhibitor-free solution was observed, which indicated that NBTA interacted with the brass (copper alloy) surface and inhibited the formation of zinc complex and cuprous complexes. From the equation (4) it is evident that in the presence of NBTA inhibitor, the cathodic and anodic curves were shifted towards positive potential region and the shift was found to be dependent on inhibitor concentration. Table illustrates the corresponding electrochemical parameters. The $E_{corr}$ values were marginally shifted in the presence NBTA inhibitor. This observation clearly indicated that the inhibitors control mainly the anodic reactions and thus act as mixed type predominantly anodic type inhibitors.

It is evident that in the presence of inhibitors, the cathodic and anodic curves were shifted towards positive potential region and the shift was found to be dependent on inhibitor concentration.

Table illustrates the corresponding electrochemical parameters. The $E_{corr}$ values were marginally shifted in the presence of NBTA this observation clearly indicated that the inhibitors control mainly the anodic reaction and thus act as anodic type inhibitors. The values of IE increases with increase in inhibitor concentration indicating that a higher surface coverage was obtained in solution with optimum concentration.

The inhibition efficiency was calculated from Icorr values. The values of IE increase with increase in inhibitor concentration, indicating that a higher surface coverage was obtained in a solution with maximum concentration of inhibitor. Analyzing the result presented in the table at which maximum IE obtained was found to be 450 ppm in all the investigated inhibitors HEBTA, NBTA and BBTA could afford a maximum of 89%, 97.17 and 99.7% of IE respectively at 450ppm concentration. Maximum inhibition efficiency indicates the higher coverage of the inhibitor molecules on the brass surface in 3% NaCl.

The presence of the heterocyclic ring and $\pi$ electron character is likely to induce an adsorption of the compound on the surface of copper in NaCl medium. In fact, the inhibition effect in presence of BTA derivatives could be explained by the formation of Cu- BTA derivative complexes at the electrode surface. Similar results were obtained for Cu- corrosion inhibition by BTA. It was suggested Fox. P. G. et. al, 1979 and Notoya. T. et. al., 1981 that the corrosion inhibition results from the precipitation of

Cu–complexes on the surface metal, thus producing a barrier to the corrosive environment. (M.AEL Morsi et.al, 1999). The polarization results obtained in the current studies are on par with the results furnished by Muralidharan. et. al., 2003 and Abd. S. et. al., 2000.

The IE as determined using Icorr values was found to be in the order BBTA > NBTA > HEBTA which is mainly due to the nature of the substituent and it position. It is well known that different substituents on the organic molecules polarize in a different manner. The presence of substituents may increase the polarity and adsorability of inhibitors on the surface of alloy.

## COMPARISON OF IE OBTAINED BY CONVENTIONAL WEIGHT LOSS METHOD AND ELECTROCHEMICAL METHODS

IE obtained using various benzotriazole derivatives such as HEBTA, NBTA and BBTA by weight loss and electrochemical methods are graphically represented in bar diagram (22) results are found to be quite comparable.

## TABLE - 14

## TABULATION OF $I_{corr}$, ba, bc AND $E_{corr}$ OF BRASS IN 3% NaCl IN THE PRESEANCE OF NBTA

| CONCENTRATION (ppm) | $I_{corr}$ $\mu Acm^{-2}$ | -E corr m/V | ba(mV/dec) | bc(mV/dec) | IE% |
|---|---|---|---|---|---|
| B | 5.2779 | 334.478 | 102.4 | 219.9 | |
| 100 | 1.5236 | 283.88 | 79.1 | 141.3 | 71.13 |
| 150 | 1.2964 | 296.92 | 56.8 | 127.6 | 75.43 |
| 350 | 1.2682 | 261.76 | 217.7 | 187.9 | 75.97 |
| 450 | 0.14924 | 262.14 | 67.52 | 86.52 | 97.17 |

## TABLE - 15

## POLARIZATION DATA OF BRASS IN 3% NaCl IN THE PRESENCE OF HEBTA

| CONCENTRATION (ppm) | $I_{corr}$ $\mu Acm^{-2}$ | -E corr m/V | ba(mV/dec) | bc(mV/dec) | IE% |
|---|---|---|---|---|---|
| B | 14.178 | 259.26 | 103.8 | 219 | |
| 100 | 5.42 | 237.62 | 51.572 | 103.7 | 96.17 |
| 200 | 5.0498 | 270.79 | 46.719 | 117.89 | 96.438 |
| 250 | 6.7593 | 315.22 | 87.06 | 321.61 | 95.23 |
| 300 | 8.2678 | 249.92 | 98.9 | 220.27 | 94.169 |
| 400 | 2.6087 | 298.23 | 108.19 | 365.59 | 81.60 |
| 450 | 1.4582 | 301.9 | 229.27 | 239.67 | 89.71 |

# TABLE - 16

# IE AS A FUNCTION OF $I_{corr}$, $E_{corr}$, ba AND bc, OF BRASS IN THE PRESENCE OF BBTA

| CONCENTRATION (ppm) | $I_{corr}$ $\mu Acm^{-2}$ | -E corr m/V | ba(mV/dec) | bc (mV/dec) | IE% |
|---|---|---|---|---|---|
| B | 14.178 | 276.8 | 102.3 | 219 | |
| 100 | 0.<br>034757 | 277.24 | 61 | 232 | 99.755 |
| 150 | 1.3592 | 319.28 | 185 | 783 | 90.413 |
| 200 | 6.4008 | 335.5 | 114 | 253 | 95.485 |
| 250 | 6.622 | 285.17 | 84 | 251 | 95.32 |
| 350 | 8.6491 | 292.2 | 97 | 226 | 93.899 |
| 450 | 9.6716 | 256.5 | 79 | 247 | 93.178 |

**Figure-19**
**POLARIZATION CURVES FOR BRASS IN THE PRESENCE OF EBTA IN 3% NaCl**

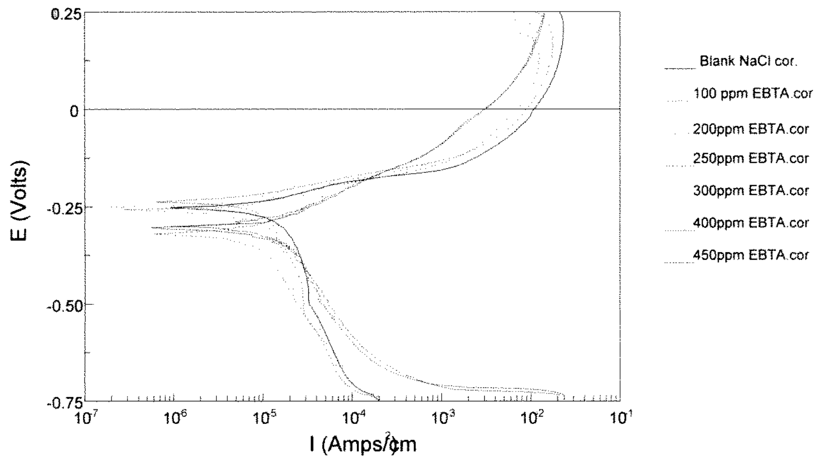
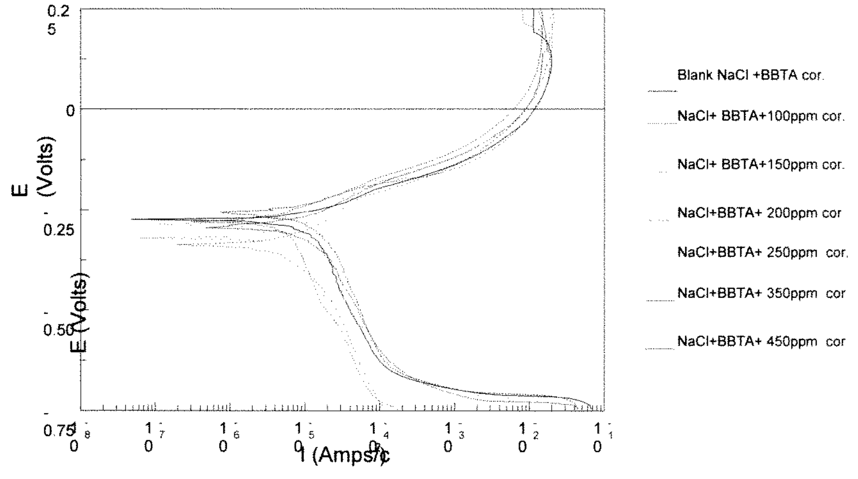
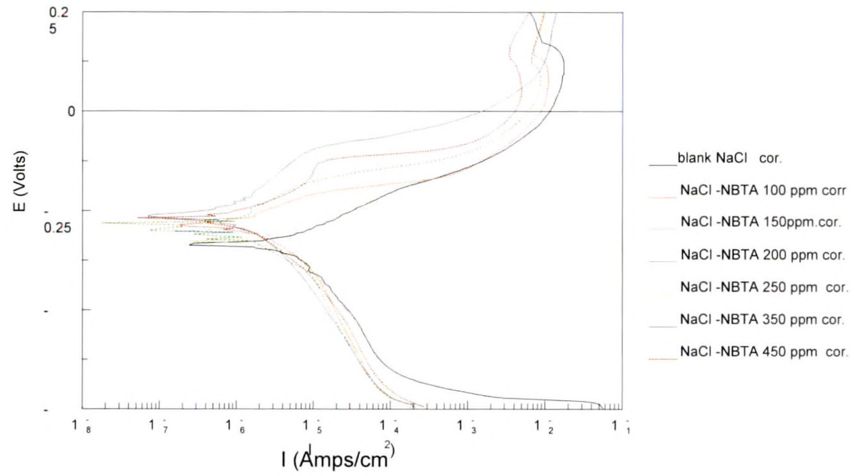


**Figure-20**
**POLARIZATION CURVES FOR BRASS IN THE PRESENCE OF BBTA IN 3% NaCl**



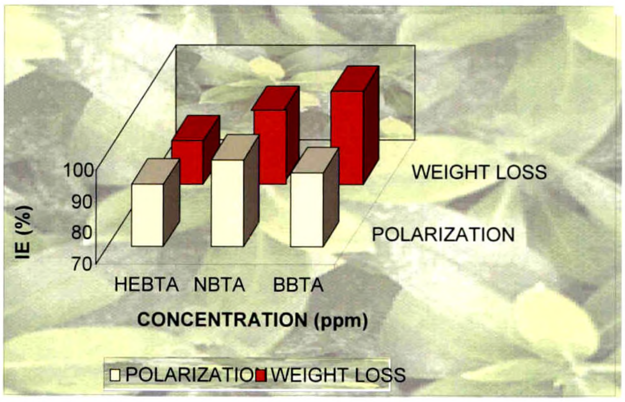
## Figure-21

## POLARIZATION CURVES OF BRASS IN THE PRESENCE OF NBTA IN 3% NaCl MEDIUM



## Figure – 22

## COMPARISONS OF IE OF BTA DERIVATIVE IN 3% NaCl BY VARIOUS METHODS

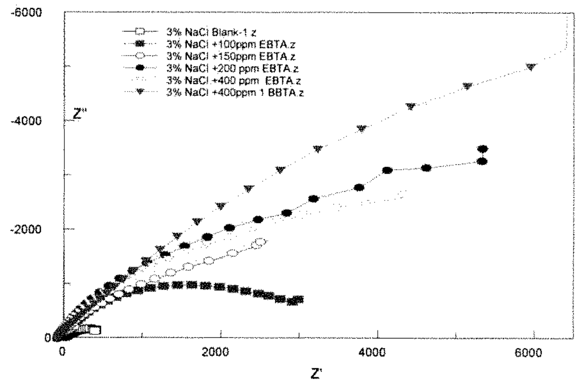


## ECTROCHEMICAL IMPEDANCE SPECTROSCOPIC MEASUREMENTS

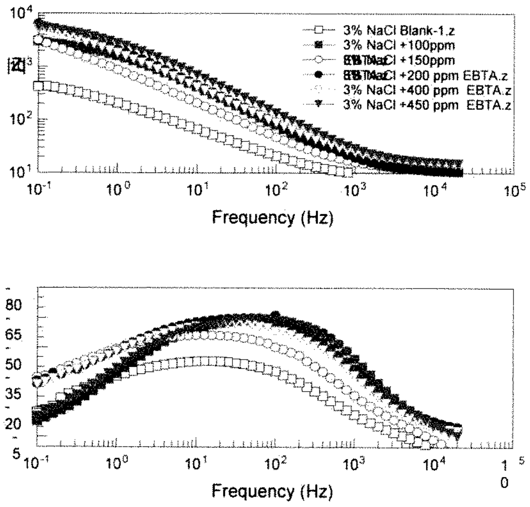
The electrochemical impedance spectroscopy provides an important mechanistic and kinetic information for an electrochemical system under investigation. The method was successfully employed to explain the corrosion and passivation phenomena on brass metal. Typical Nyquist impedance plot obtained for brass at open circuit potential in 3% NaCl solution and in the presence and absence of various concentrations of HEBTA, BBTA and NBTA are shown in Figures (23-28). It has been reported Ma. et. al., 2002 visualizing the Nyquist plot for brass in 3% NaCl solution and in the presence of the inhibitor. The Nyquist plots of brass in 3% NaCl and in the presence of investigated inhibitors at respective open circuit potential as shown in figures the shape of the curves in general indicates the semicircle. The size of the semicircle increase with increase in concentration of inhibitors. Similar curves were obtained by Kumar et al 2007.

The conclusion can be drawn as follows: the semicircles at high frequencies are generally associated with the relaxation of electrical double layer capacitors and the diameters of the high frequency capacitive loops can be considered has the charge transfer resistance. Similar observation were obtained by Ma et al 2002 and it has been reported by Ma et al that the semicircles at high frequencies are generally associated with the relaxation of electrical double layer capacitors and the diameters of the high frequency capacitive loops can be considered as the charge transfer resistance. The corrosion of brass in 3% NaCl from EIS measurements it controlled by charge transfer as well as mass transports that is the transport of $Cl^-$ ions to the electrode surface and $CuCl_2^-$ ions from the electrode.

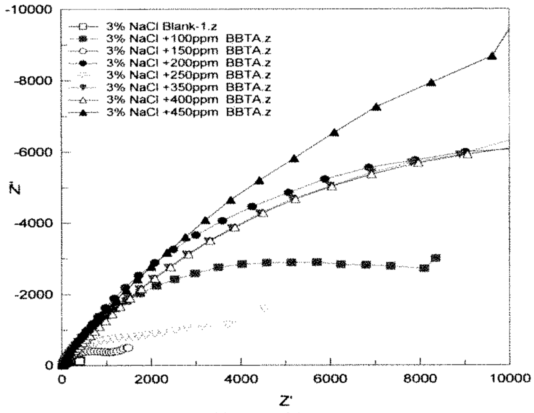
## Figure-23
## NYQUIST PLOTS FOR BRASS IN 3% NaCl IN THE PRESENCE OF HEBTA



## Figure-24
## BODE PLOT OF BRASS IN THE PRESENCE OF HEBTA IN 3% NaCl



## Figure-25
## NYQUIST PLOTS FOR BRASS IN 3% NaCl IN THE PRESENCE OF BBTA



## Figure-26
## BODE PLOT OF BRASS IN THE PRESENCE OF BBTA IN 3% NaCl

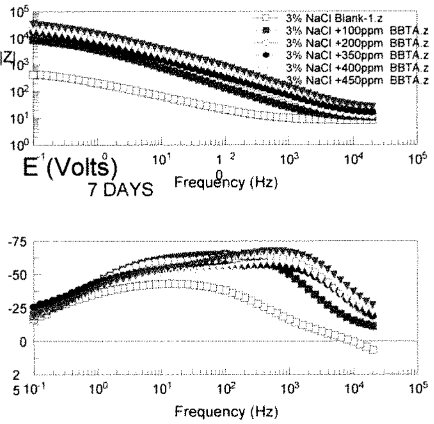


Figure-27
NYQUIST PLOTS FOR BRASS IN 3% NaCl IN THE PRESENCE OF NBTA

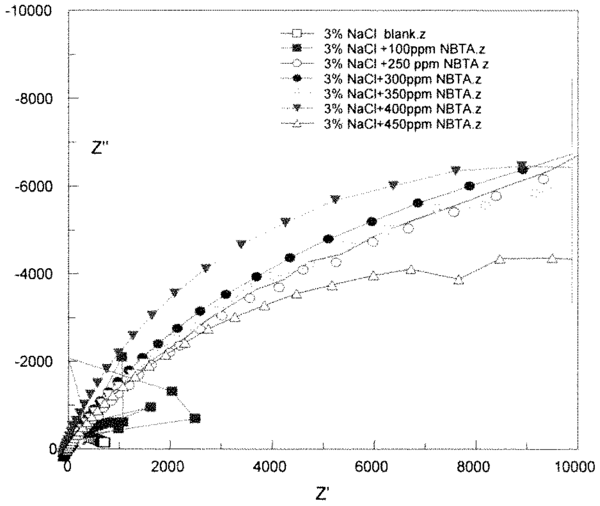
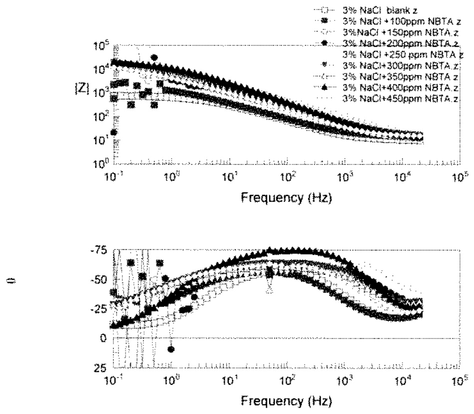


Figure-28
BODE PLOT OF BRASS IN THE PRESENCE OF NBTA IN 3% NaCl



# CYCLIC VOLTAMMETRY

The electro chemical behaviour of brass in 3% NaCl was studied by cyclic voltammetry. Measurements performed in the presence of investigated inhibitors such as 2-Hydroxy ethyl Benzotriazole (HEBTA), Nitro Benzotriazole (NBTA) and Bromo Benzotriazole (BBTA) in 3% NaCl are presented in the Figures (29-32). The maximum concentration at which maximum IE obtained using weight loss methods was selected for cyclic voltammetry studies. Cyclic voltammetry was recorded for brass starting from -0.75 V to 1 V with scan rate 10mV/s. The results of cyclic voltammetry are presented in the Table (17). It can be seen that the voltammograms present three anodic peaks and one cathodic peak in 3% NaCl solution and in the presence of the inhibitors. The voltammograms present two anodic peaks and always one cathodic peak It is noticed that the shape of the voltammogram is strongly influenced in the presence of the inhibitors. Similar results were obtained by Crousies et, al., (1988). They concluded both anodic peaks represent formation of $CuCl_2^-$ this behaviour can be explained according to the well accepted mechanism of brass dissolution in chloride media.

$$Cu + Cl^- \longrightarrow CuCl + e \text{ ------------- } (1)$$

$$Cu\,Cl + Cl^- \longrightarrow CuCl_2^- + e \text{ ------------- } (2)$$

According to this mechanism the first anodic peak (A1) is due to the formation of CuCl precipitate on the electrode surface. This layer is porous and electrochemical reactions continue through it and second anodic peak (A2) is observed this is due to the formation of $CuCl_2^-$

During anodic scan there is always a balance between CuCl and $CuCl_2^-$ (between film formation and film dissolution). The cathodic peak (C1) represents the reduction of $CuCl_2^-$ . The voltammetry obtained in the presence of the inhibitors strongly reduce both cathodic and anodic peaks values which are listed in the Table (17). From this voltammogram we can understand because of the increased $CuCl_2^-$ mass transfer towards the bulk solution, the concentration of the primary corrosion products near the electrode surface was reduced and an extensive local hydrolysis to $Cu_2O$ was prevented. It can be therefore concluded that the slowly and weakly bonded $CuCl_2^-$ is reduced in the presence of these inhibitors and the cathodic peak can also be attributed to the reduction of $CuCl_2^-$ but probably of those species which are more strongly bonded to the surface layer.

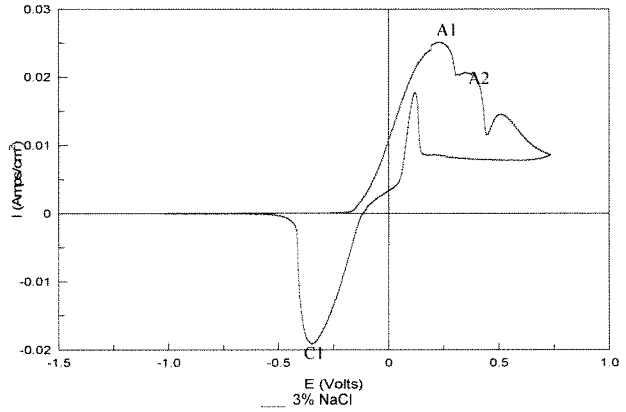
## TABLE-17

## TABULATION OF POTENTIAL AND CURRENT IN THE PRESENCE OF INHIBITORS.

| Inhibitors | Concentration (ppm) | Peak position | Cathodic peak | | Peak position | Cathodic peak | |
|---|---|---|---|---|---|---|---|
| | | | potential V | current Amps/Cm$^2$ | | potential V | current Amps/Cm$^2$ |
| **3% NaCl** | | C1 | -0.343 | -0.019 | A1 | 0.236 | -0.025 |
| | | | | | A2 | 0.382 | 0.021 |
| | | | | | A2 | 0.438 | 0.022 |
| **NBTA** | 450ppm | C1 | -0.384 | 0.0136 | A1 | 0.157 | 0.013 |
| | | | | | A2 | 0.456 | 0.149 |
| **HEBTA** | 450ppm | C1 | -0.514 | 0.0162 | A1 | 0.275 | 0.015 |
| | | | | | A2 | 0.480 | 0.009 |
| **BBTA** | 450ppm | C1 | -0.377 | 0.0144 | A1 | 0.110 | 0.011 |
| | | | | | A2 | 0.494 | 0.021 |

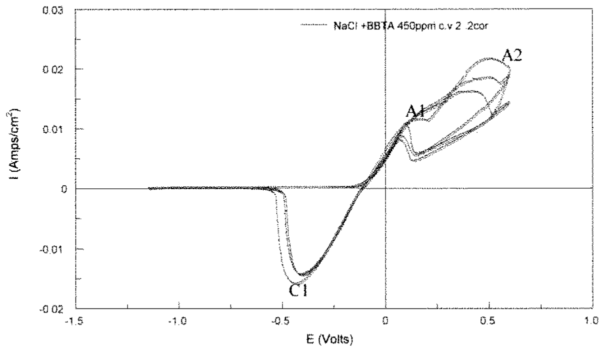
## Figure-29

## CYCLIC VOLTAMMOGRAM FOR BRASS IN THE PRESENCE OF 3% NaCl BLANK



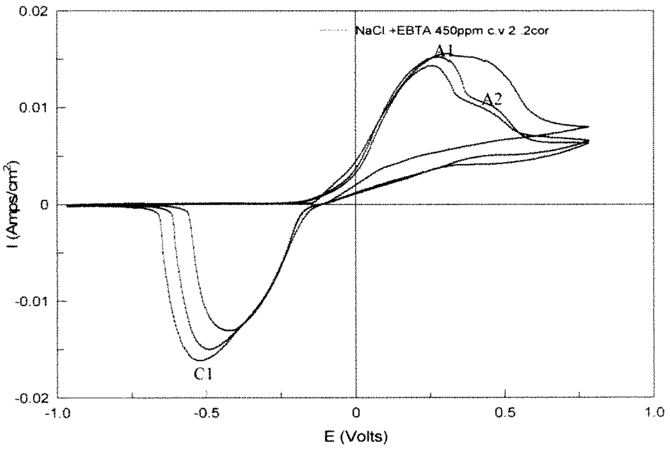
## Figure-30

## Cyclic voltammogram for brass in 3% NaCl and in the presence of BBTA



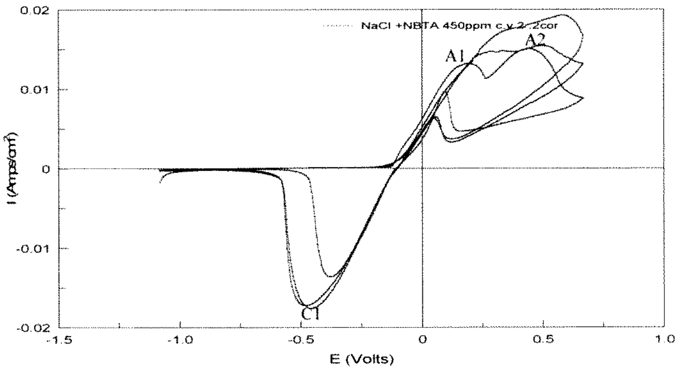
## Figure-31

## CYCLIC VOLTAMMOGRAMS FOR BRASS IN 3% NaCl AND IN THE PRESENCE OF HEBTA



## Figure-32

## CYCLIC VOLTAMMOGRAMS FOR BRASS IN 3% NaCl AND IN THE PRESENCE OF NBTA



## OPTICALELECTRON MICROGRAPH

The optical micrograph obtained for the brass surface in 3 % NaCl in the presence and absence of the investigated inhibitors is presented in Figures (33-34). It is seen that the inhibitors molecules are strongly covered the Brass surface the inhibitors are indeed strongly adsorbed on the surface this provides another confirmation on the ability of inhibitor molecules to be adsorbed on the brass surface and to prevent it from being corroded easily.

The brass surface was covered with a layer containing not only the carbon, but also the chloride. It can be concluded from this analysis that chlorides are incorporated in the inhibitor layer either as precipitate, or more likely, as a part of the protective layer. In the case of brass, the inhibitors morphology changes from globular to fibrillar like structure. (Otmacic, H., et, al., 2004)

BRASS-POLISHED SURFACE

BRASS- IN THE ABSENCE OF INHIBITORS

BRASS-IN THE PRESENCE OF HEBTA

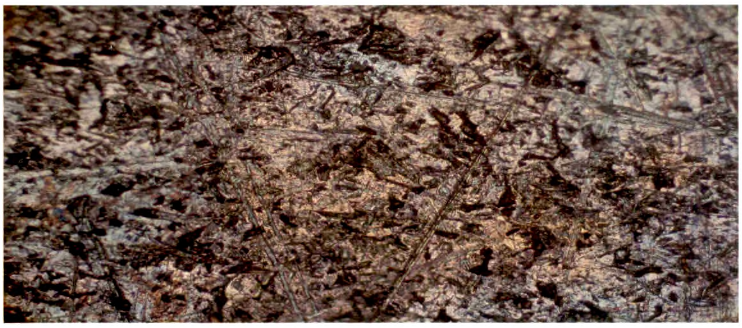


FIGURE-33 OPTICAL MICROGRAPH OF BRASS EXPOSED FOR 15 DAYS IN 3% NaCl IN THE PRESENCE OF HEBTA

**BRASS-POLISHED SURFACE**

**BRASS- IN THE ABSENCE OF INHIBITORS**

**BRASS-IN THE PRESENCE OF BBTA**

**FIGURE-34 OPTICAL MICROGRAPH OF BRASS EXPOSED FOR 15 DAYS IN 3% NaCl IN THE PRESENCE OF BBTA**

BRASS-POLISHED SURFACE

BRASS- IN THE ABSENCE OF INHIBITORS

BRASS-IN THE PRESENCE OF BBTA

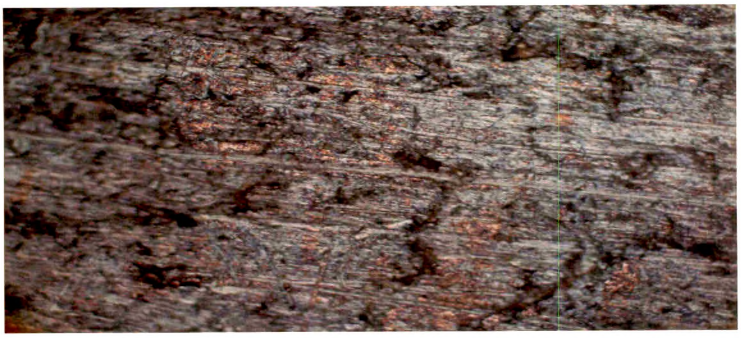


FIGURE-35 OPTICAL MICROGRAPH OF BRASS EXPOSED FOR 15 DAYS IN 3% NaCl IN THE PRESENCE OF BBTA

# MECHANISM OF CORROSION INHIBITION

It is well known that the inhibitive action of organic compounds containing N, S and /or O are 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 compounds, the effective electron density at the functional group can be varied by introducing different substituents in the ring leading to variation of the molecular structure. The inhibition efficiency of the benzotriazole compounds is due to donor-acceptor interactions between the $\pi$ electron of the inhibitor and the vacant d-orbital of copper surface or an interaction of inhibitor with already adsorbed chloride ions (Ravichandran.R.et.al, 2005).

## INHIBITION PROCESS OF INHIBITORS

BTA derivatives is strongly adsorbed on the brass surface as far as the inhibition process is concerned, it is generally assumed that the adsorption of the inhibitor at the metal/solution interface. Four types of adsorption may take place. Involving organic molecules at the metal /solution inter-face.

(i) Electrostatic attraction between charged molecules and the charged metal,
(ii) Interaction of unshared electron pairs in the molecule with the metal,
(iii) Interaction of $\pi$-electrons with the metal and
(iv) A combination of the above.

Chemisorption involves charge sharing or charge transfer from the inhibitor molecules to the surface to form a coordinate-type bond. In fact, electron transfer is typical for transition metals having vacant, low-energy electron orbitals. Electron transfer can be expected with compounds having relatively loosely bound electrons. Mansfeld. F., 1987.

Inhibition efficiency depends on several factors, such as the number of adsorption sites and their charge density, molecular size, heat of hydrogenation, mode of interaction with the metal surface and the formation metallic complexes. Most organic inhibitors contain atleast one polar group with an atom of nitrogen, sulphur or oxygen; each of them might be a chemisorptions centre. The inhibitive properties of such compounds depends on the electron densities around the chemisorption centre; the higher the electron density at the Centre. (Bentiss.F etal.2001 and Sankarapapavinasam, S. 1991)

According to the above argument, chemisorptions of the BTA derivatives on the brass surface, may take place through the donor–acceptor links between the electrons of the BTA ring and the empty d-orbital of the Zn and Cu atom. This mode of adsorption is shown in Figure. It corresponds to a planar orientation of the molecule on the surface. Since there is a strong adsorption of the organic molecules on the metal surface, another site may accentuate the adsorption capability of the inhibitor molecule. According to the literature, when an inhibited solution contains adsorbable anions, such as halide ions (Cl) ions in our case), these adsorb on the metal surface creating oriented dipoles. Consequently, this results in an increase in the adsorption capability of the inhibitor cations, BTA+ derivatives on the dipoles. The adsorption of the compound studied here can occur either directly through π-electrons and the d-orbitals of metal surface atoms or with additional interaction of the functional groups. Also, there is a possibility to promote inhibition by the chloride ions already adsorbed on the surface. By virtue of donor-acceptor interactions adsorption can occur directly through π-electrons of the benzotriazole and its derivatives and vacant d-orbitals of brass from the surface. Nitrogen atoms are available for interaction sharing their electrons. Thus, each compound is chemisorbed on the metal surface through the nitrogens from the triazole ring. These are some evidence which shows that hetero cyclic compounds are effective in preventing corrosion. (A.A. Atial and M.M. Saleh , 2002)

All the compounds studied performed excellently as inhibitors for the corrosion of brass in 3 % NaCl. The lower efficiency of NBTA (93%) and HEBTA (83.5%) compared with the BBTA may be attributed to the orientation of ethyl hydroxyl group and $NO_2$ group, which prevents the flat orientation of the metal surface by reducing adsorption and inhibition. A similar explanation has been given by Rengamani, et. al., 1994, concerning the discrepency in the inhibition efficiency of isomers of anisidine in a study of the inhibition of anions on the performance of anisidines as corrosion inhibitors for mild steel. Quraishi, et. al., 1997, has also given a similar argument on explaining the variationin the inhibition efficiencies of triazole derivatives for steel corrosion in boiling HCl.