

Effect of 5-Methylbenzotriazole on the Corrosion Inhibition of Brass in NaCl Solution

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Abstract: The corrosion behavior of brass in the presence of inhibitor namely 5-methyl benzotriazole (MBTA) has been investigated in 3% NaCl medium. The inhibition efficiency of MBTA was evaluated from chemical and electrochemical techniques. Experimental studies showed that MBTA reduces markedly the corrosion of brass in 3% NaCl solution and this reduction in corrosion rates enhances with increasing concentration of MBTA. Weight loss study revealed that the formulation consisting of 150 ppm of MBTA showed 71% inhibition efficiency. Polarization studies also revealed that the inhibitor act as mixed type for brass in chloride solution. The characterization of corrosion product on brass in presence of MBTA was analysed by FTIR.

Keywords: Brass, 5-Methylbenzotriazole, Impedance spectroscopy, Polarization studies, FTIR.

Introduction

Copper has a wide range of applications due to its good properties¹⁻³. Brass has been widely used as tubing material for condensers and heat exchangers in various cooling water system^{4,9}. Due to the electrodisolution of metal in chloride solutions, there is a growing interest in inhibitors, for the application of copper or its alloys in marine environments. *N*-heterocyclic compounds have been widely used as corrosion inhibitors. Among these azoles are known as one of the best corrosion inhibitors for copper and its alloys in a wide range of environments¹⁰⁻¹³. Benzotriazole is a good anodic inhibitor for copper in acidic conditions¹⁴ and in chloride solutions¹⁵. Frignani *et al.*¹⁶ investigated the influence of alkyl chain on the protective effects of benzotriazole towards copper in acidic chloride solution and concluded that the inhibitors effectively control corrosion.

Although there is an extensive literature on the corrosion properties of triazole such as aminotriazole and benzotriazole on steel and copper¹⁷⁻¹⁹, there are very few reports devoted to the various functional groups in BTA derivatives on the corrosion of brass. In the cases where these benzotriazole derivatives have been considered, they have first been introduced as effective corrosion inhibitors in cooling water systems.

The present work is devoted to the investigation of the corrosion behavior of brass in NaCl medium. Further, the study was extended to understand the effect of MBTA in the corrosion inhibition of brass. The effect of the addition of MBTA as inhibitor on the corrosion behavior of brass has been studied by the weight loss method and some electrochemical methods. The passive film characterization was carried by FTIR spectra.

Experimental

The chemical composition (weight percent) of the of the brass plate used in these tests was 65% Cu, 35% Zn, 0.1385% Fe, 0.0635% Sn and the rest Pb, Mn, Ni, Cr, As, Co, Al and Sr as analyzed by optical emission spectrophotometer. The brass specimens were polished mechanically with SiC papers (120 -1200 grit), washed with double distilled water and degreased in acetone²⁰. The solutions were prepared from AR chemicals using DD water. The structure of MBTA is given in Figure 1.

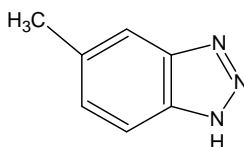


Figure 1. Structure of 5-methylbenzotriazole

Weight loss method

Weight loss measurements were carried out using brass specimen of size 4 x 1 x 0.4 cm. The specimens were immersed in 100 mL of 3% NaCl solution with and without inhibitors at room temperature for 24 h.

Potentiodynamic polarization study

The potentiodynamic polarization studies were carried out with brass strips having an exposed area of 1 cm². 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 potentiostat/galvanostat and the data obtained were analyzed.

The working electrode was immersed in a 3% NaCl solution and allowed to stabilize for half an hour²¹. Each electrode was immersed in a 3% NaCl solution in the presence and absence of optimum concentrations of the inhibitors to which a current of 1.5 mA cm⁻² was applied for 15 min to reduce oxides. The cathodic and anodic polarization curves for brass specimen in the test solution with and without inhibitor were recorded at a sweep rate of 1 mV s⁻¹. The inhibition efficiencies of the compounds were determined from corrosion currents using the Tafel extrapolation method.

Electrochemical AC impedance studies

AC impedance measurements were conducted at room temperature in the frequency range²² of 100 kHz to 1 mHz and the results were analysed.

FTIR spectra

The film that developed on the surface of brass during polarization measurements in the presence of the inhibitor was washed with water, dried and collected by scrapping from the surface of the alloy for subsequent spectral analysis and FTIR spectra were recorded²³.

Results and Discussion

Weight loss method

Table 1 shows the inhibition efficiency (IE) and corrosion rate (CR) of brass by weight loss measurements at different inhibitor concentrations in 3% NaCl at room temperature. The CR and IE were calculated using the following equation.

$$C = (534 \times W) / (D \times T \times A)$$

Table 1. Inhibition efficiency of MBTA on brass in 3% NaCl by weight loss method

Inhibitor concentration, ppm	Corrosion rate, mils year ⁻¹	Inhibition Efficiency, %
Blank	0.395	
MBTA 10	0.282	28.61
50	0.225	43.04
100	0.169	57.20
150	0.113	71.39
200	0.169	57.20
250	0.282	28.61
300	0.338	14.43

Where A is the area, T the immersion time, W the weight loss and D the density of the specimen. It has been observed that the IE increases and CR decreases with increase in concentration of inhibitors and the optimum efficiency was 71% at 150 ppm concentration. The percentage of IE for different concentration of MBTA (ppm) increases in the following order 10 < 50 < 100 < 150 and decreases at 200 ppm.

Potentiodynamic polarization studies

The cathodic and anodic polarization curves of brass in 3% NaCl solution and with optimum concentrations of MBTA are shown in Figure 2. It is evident that in the presence of inhibitor, the cathodic and anodic curves were shifted to more positive potential region and the shift was found dependent on concentration of the inhibitor. The CR and IE²⁴ were calculated from the following equations and the values were presented in the Table 2.

$$CR = (0.129 \times I_{corr} \times ED) / (D \times A)$$

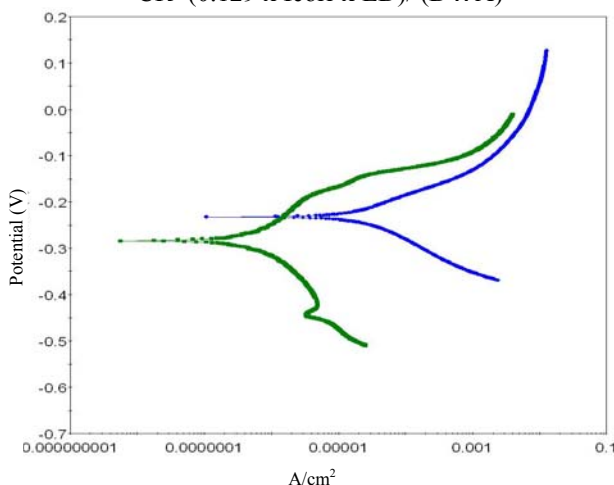


Figure 2. Polarisation curves for brass in 3% NaCl (O → blank, □ → 150 ppm MBTA)

Where EW is the equivalent weight (g), D the density (g cm^{-3}), A the area (cm^2) of the specimen and $I_{\text{corr}}(\text{inh})$ and I_{corr} are the corrosion current density values with and without inhibitors, respectively.

From the Table 2, it is observed that the E_{corr} values are shifted towards noble direction in the presence of optimum concentration of MBTA. This observation clearly shows that the MBTA control both cathodic and anodic reactions and thus acting as mixed type inhibitor.

Table 2. Electrochemical parameters and inhibition efficiency of brass in 3%NaCl solution containing optimum concentration of MBTA

Inhibitor concentration, ppm	I_{corr} μAcm^{-2}	Corrosion rate mils year^{-1}	Inhibition Efficiency, %
Blank	23.33	1.15	-
MBTA (150 ppm)	7.42	0.70	68.17

AC impedance studies

The corrosion behavior of brass in NaCl solution and with MBTA was investigated by electrochemical impedance spectroscopy at room temperature. Various impedance parameters such as charge transfer resistance (R_{ct}), and IE are given in Table 3. The (R_{ct}) were calculated from the difference in impedance at the lower and higher frequencies as suggested by Haruyama *et al.*,²⁵. Nyquist plots of brass in inhibited and uninhibited NaCl solution containing optimum concentrations of 150 ppm MBTA are shown in Figure 3. The IE% of corrosion of brass is calculated by the following equation:²⁶,

$$\text{IE \%} = \left[\frac{R_{\text{ct}} - R_{\text{ct}}(\text{inh})}{R_{\text{ct}}} \right] \times 100$$

Table 3. Impedance measurements and inhibition efficiency of brass in 3% NaCl containing optimum concentration of MBTA

Inhibitor concentration, ppm	R_{ct} Ω	Inhibition Efficiency, %
Blank	4977	-
MBTA (150 ppm)	13040	61.80

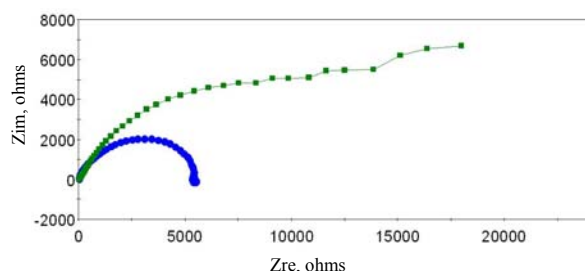
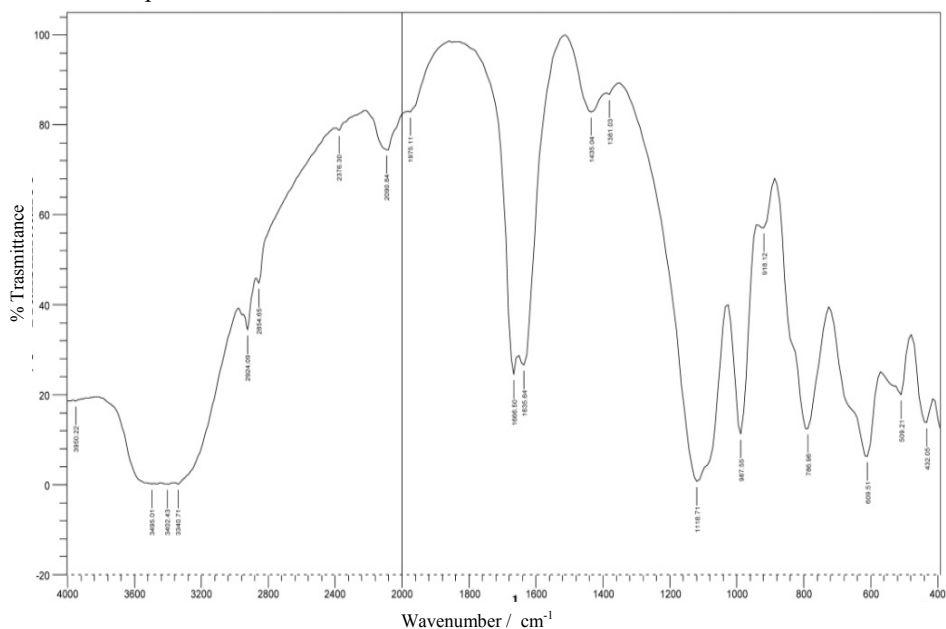


Figure 3. Nyquist diagram for brass in 3% NaCl (O \rightarrow blank, $\square \rightarrow$ 150 ppm MBTA)

Where $R_{\text{ct}}(\text{inh})$ and R_{ct} are charge transfer resistance values with and without inhibitors, respectively. In the presence of inhibitor, R_{ct} values increased. It suggests that the MBTA function by adsorption at the metal–solution interface. The change in R_{ct} values was caused by the gradual replacement of water molecules by the anions of the NaCl and adsorption of the organic molecules on the metal surface, reducing the extent of dissolution.

Analysis of FTIR spectra

The FTIR analysis of blank and MBTA- copper complex was carried out between 500 and 4000 cm^{-1} . The spectra are shown in Figure 4 and 5. The N–H stretching of MBTA showed a sharp intense peak around 3400 cm^{-1} . The aliphatic and aromatic C–H stretching produced a less intense peak between 2900 and 3100 cm^{-1} .



The N–H bends are shown around 1500–1600 cm^{-1} and the C–N stretching vibrations are shown with an intense peak around 1300–1450 cm^{-1} . The presence of MBTA over the oxide surface is well evidenced by the aromatic C–H stretch lying just above 3000 cm^{-1} . The peak around 1000 cm^{-1} in the MBTA-copper complex is due to O–Cu–O vibration. The spectral data confirmed the formation of Cu-MBTA inhibitive complex on the metal surface.

Conclusion

- Weight loss data shows quantitatively the inhibitor exhibit 71% IE on Brass in 3% NaCl solution.
- When the concentration of inhibitor increases IE also increases and reaches a maximum value at 150 ppm concentration.
- The potentiostatic polarization studies indicate that both cathodic and anodic processes are controlled equally and the inhibitor behaves as a mixed type.
- EIS studies confirms the formation of metal-inhibitor complex on the corroding sites.

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