



Protective Effect of 1-(Phenylthiomethyl)Benzotriazole and 1-(Benzylthiomethyl)Benzotriazole towards Corrosion of Brass in Polluted Natural Sea Water

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ABSTRACT

Benzotriazole derivatives, namely 1-(phenylthiomethyl)benzotriazole (PTBT) and 1-(benzylthiomethyl)benzotriazole (BMBT) were synthesized and their inhibition behaviour on brass in polluted natural sea water were investigated by weight-loss measurements, potentiodynamic polarization and electrochemical impedance techniques. Results obtained revealed that these compounds exhibited good inhibition efficiency in sulphide polluted natural sea water. Potentiodynamic polarization studies showed that the PTBT and BMBT behave as a mixed-type of inhibitors for brass in polluted natural sea water. 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.

1. Introduction

Copper-based alloys have a long history of service in marine environments. In general, they exhibit an attractive combination of properties, e.g., good machinability, good resistance to corrosion and bio-fouling and superior thermal and electrical conductivities [1, 2]. In view of their good machinability, they are available in a wide range of products [3]. The most prominent among the copper-based alloys is the Cu-Zn alloys, which are widely used for condenser and heat exchanger tubes in various cooling water systems [4]. Brass when suspended in neutral chloride media undergoes dezincification as well as general corrosion releasing copper and zinc ions. 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 [5].

Organic compounds containing an azole system have frequently been employed to inhibit corrosion of copper and brass mostly in acidic or neutral solution [6, 7]. Among these, benzotriazoles (BTA), a sub category of heterocyclic compounds is known as one of the best corrosion inhibitors for copper and its alloys in a wide range of environments [8]. Immersion of copper into a solution of BTA enables chemisorptions to occur on the surface and gave enhanced resistance to atmospheric oxidation of copper. Bag et al [9] investigated the protective action of azole derivatives on the corrosion and dezincification of 70/30 brass in ammonia solution and concluded that the inhibitors effectively control corrosion. The addition of BTA to acidic, neutral and alkaline solution is commonly used and has significantly reduced corrosion [10]. Frignani et al [11] investigated the influence of an alkyl chain on the protective effects of benzotriazole towards copper in acidic chloride solution. Qafsaoui et al [12] reported that the growth of a protective film on copper in the presence of triazole derivatives. Naguib and Mansfeld [13] studied the corrosion behavior of 26000 brasses in artificial seawater using EIS and ENA techniques. BTA, sodium salts of gluconic acid and polyphosphoric acid were evaluated as corrosion inhibitors. Otieno-Alego et al [14] made an electrochemical and SERS study of the effect of 1-[N, N-bis-(hydroxy ethyl) amionomethyl] benzotriazole on the acid corrosion and dezincification of 60-40 brass. Shukla and Pitre [15] studied the electrochemical behavior of brass and the inhibitive effect of imidazole in acid solution. Fenelon and Breslin [16]

studied the formation of BTA surface films on copper, Cu-Zn alloy and Zn in chloride solution.

2. Experimental Methods

2.1 Materials Preparation

The composition of brass used in the present study is given in Table 1. The brass alloy specimens were taken from the same brass sheet. The polluted natural sea water was collected near National Thermal Power Station (NTPC), Ennore, Chennai, India. The chemical composition of the polluted seawater was analyzed by analytical technique, whose composition was given in Table 2. The pH of the seawater is 6.6. The inhibitors 1-(phenylthiomethyl)benzotriazole (PTBT) and 1-(benzylthiomethyl)benzotriazole (BMBT) were synthesized according to the reported procedures [17] and their structures are shown in the Fig. 1.

Table 1 Chemical composition of 67-33 brass (in wt. %)

Alloy	Cu	Zn	Sn	Pb	Fe	Cr	Al
Composition	66.93	32.87	0.062	0.013	0.12	0.003	0.002

Table 2 Composition of polluted natural sea water

Species	Concentration (g/L)
Chloride	33.87
Sulphate	3.62
Bicarbonate	0.76
Phosphate	0.07
sulphide	1.53
Silicate	0.06
Nitrate	0.02
Nitrite	0.03
Bromide	0.14
Fluoride	0.008

2.2 Synthesis of Benzotriazole Derivatives

2.2.1 Synthesis of 1-(Phenylthiomethyl)benzotriazole (PTBT)

To an ice-cold solution of thiophenol (11.0 g, 0.1 mol) in methanol (100 mL) was added to sodium metal (2.1 g, 0.1 mol). On complete dissolution of metal, 1-(chloromethyl)benzotriazole (16.7 g, 0.1 mol) was added in

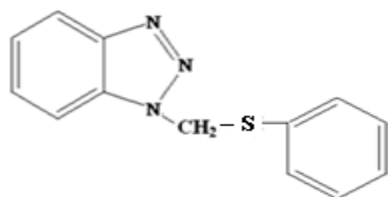
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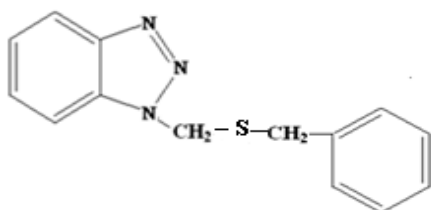
small portion over 10 minutes. The solution was allowed to warm to room temperature and stirred overnight. The solvent was removed under pressure giving a solid which was stirred with water and then filtered. The solid was washed with water and then ethanol–water mixture (30%) and dried in vacuum.

2.2.2 Synthesis of 1-(benzylthiomethyl)benzotriazole (BMBT)

To a preferred mixture of sodium methoxide (2.70 g, 50 mmol), toluene-thiol (6.2 g, 50 mmol) and methanol (30 mL) that had been refluxed for 2 hrs was added 1-(chloromethyl)benzotriazoles (8.35 g, 50 mmol). The mixture was stirred at overnight, filtered, and the solvent removed by evaporation. The residue was stirred for several hours with methanol (60 mL) and water (40 mL) containing 20 mmol KOH. The precipitate was filtered off and washed with 5 % NaOH. Drying in vacuum oven gave as a white solid.



1-(Phenyl thiomethyl)benzotriazole



1-(benzyl thiomethyl)benzotriazole

Fig. 1 Structure of organic inhibitors

2.3 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 (120–1200 grit), thoroughly washed with distilled water, degreased with acetone, rinsed with distilled water, dried and weighed. The specimens were immersed in 300 mL of polluted natural sea water, with and without inhibitors at 30 °C for 15 days.

For electrochemical studies, the working electrode with an area of 1 cm² 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.

Potentiodynamic 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 polluted natural sea water (open atmosphere) and allowed to stabilize for 30 minutes [18]. In each case a potential of -1.5 V 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*_{corr}). The frequency range of 100 kHz to 1 mHz was employed. All potentials are reported vs SCE.

3. Results and Discussion

3.1 Weight-Loss Method

The inhibition efficiency increases with increase in concentration of the inhibitors. The maximum IE% of each compound was achieved at 200 ppm and a further increase in concentration showed only a marginal change in

the performance of the inhibitor. The optimum concentration of the inhibitors was 200ppm and BMBT exhibited better inhibition efficiency than PTBT.

The corrosion rates and inhibition efficiencies of brass with different concentrations of PTBT and BMBT in polluted natural sea water at room temperature are given in Table 3. The inhibition efficiency (IE %) were calculated using the following equation [19],

$$IE\% = \frac{CR_{(bl)} - CR_{(inh)}}{CR_{(bl)}} \times 100$$

where *CR*_(inh) and *CR*_(bl) are the corrosion rate of brass in the presence and absence of inhibitors respectively. The inhibition efficiency increases with increase in concentration of the inhibitors. The maximum IE% of each compound was achieved at 200 ppm, 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 found to be 200 ppm and BMBT exhibited better inhibition efficiency than PTBT. The inhibition of corrosion by these compounds can be attributed to their adsorption on the metal surface because of the following interactions.

- The interaction between the π-electrons of the benzotriazole ring and the positively charged metal surface, and
- The interaction between the lone pair of electrons of the atoms of nitrogen and the positively charged metal surface

The order of inhibition shown by these compounds can be mainly attributed to the electron releasing tendencies (+I effect) of different substituents present in the benzotriazole derivatives. An increase in the size of the molecule of these compounds can lead to more surface coverage and thereby more corrosion inhibition.

Inhibition of corrosion of brass in polluted natural sea water can be explained in the following way. The adsorption of benzotriazole derivatives on the surface of brass leads to the formation of a protective layer of Cu(I) chloride-complex on the surface of brass. Actually the formation of a benzotriazole film starts with the chemisorption of the inhibitor molecule on to the slightly oxidized areas of the copper surface. The adsorption of benzotriazole molecules on the oxidized parts of the copper surface was found to occur much faster than on bare metal zones. The film formed in this way has a limited hydrophobic action, which succeeds in protecting brass in the corroding medium by blocking main reaction centres on the metal surface.

Table 3 Inhibition efficiency of different concentrations of benzotriazole derivatives for the corrosion of brass in polluted natural sea water by weight-loss method

Inhibitor	Inhibitor concentration / ppm	Corrosion Rate/ mpy	Inhibition Efficiency / %
Blank	-	10.34	-
PTBT	50	4.96	52.03
	100	2.71	73.79
	150	1.04	89.94
	200	0.46	95.56
BMBT	50	4.12	60.15
	100	2.37	77.08
	150	0.86	91.68
	200	0.27	97.39

3.2 Polarization Studies

The cathodic and anodic polarization curves of brass in polluted natural sea water containing different concentrations of PTBT and BMBT are shown in Figs. 2 and 3. Tables 4 illustrate the corresponding electrochemical parameters. The *E*_{corr} values were marginally shifted in the presence PTBT and BMBT, which clearly indicated that the inhibitors control the anodic and cathodic reactions and thus act as mixed-type inhibitors. The current density also decreased with increasing concentrations of the inhibitors. The corrosion rates were calculated from polarization curves using the following Equation [20].

$$CR = \frac{0.129 \times I_{corr} \times EW}{D}$$

$$IE\% = \frac{I_{corr} - I_{corr(inh)}}{I_{corr}} \times 100$$

where CR is the corrosion rate (mpy), D is the density (g cm⁻³), EW is the equivalent weight of the brass, IE is the inhibition efficiency and *I*_{corr} (inh) and *I*_{corr} are corrosion current density in the presence and absence of inhibitors respectively.

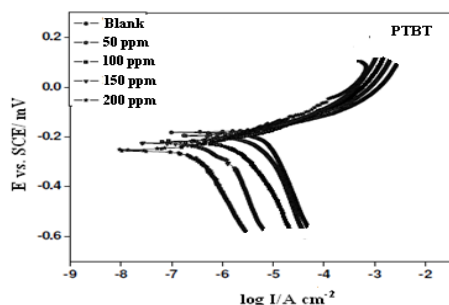


Fig. 2 Polarization curves of brass in polluted natural sea water with different concentrations of PTBT

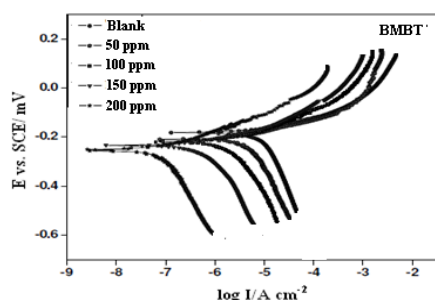


Fig. 3 Polarization curves of brass in polluted natural sea water with different concentrations of BMBT

Table 4 Electrochemical parameters and inhibition efficiency for corrosion of brass in polluted natural sea water containing different concentrations of PTBT and BMBT

Inhibitor	Inhibitor Concentration/ppm	$E_{corr}/$ mV vs SCE	$I_{corr}/$ $\mu\text{A cm}^{-2}$	β_a	β_c	Corrosion Rate/mpy	Inhibition Efficiency/ (%)
Blank	-	185	11.26	44	37	11.17	-
PTBT	50	198	5.62	56	53	5.58	50.08
	100	225	3.26	60	60	3.24	71.04
	150	232	1.34	67	67	1.33	88.10
	200	241	0.53	72	73	0.53	95.29
BMBT	50	213	4.78	65	56	4.74	57.55
	100	234	2.78	71	67	2.76	75.31
	150	245	1.08	87	85	1.07	90.41
	200	254	0.36	89	88	0.36	96.80

The values of cathodic Tafel slope (β_c) and anodic Tafel slope (β_a) of benzotriazole derivatives are found to change with inhibitor concentration, which clearly indicates that the inhibitors controlled both the reactions. The inhibition efficiency of PTBT and BMBT in polluted natural sea water attained a maximum value of 95.29% and 96.80% at 200 ppm concentration respectively. The values of inhibition efficiency increase with increasing concentration of inhibitor, indicating that a higher surface coverage was obtained in the solution with the optimum concentration of inhibitor. The corrosion rate of brass in polluted natural sea water was found to be 11.17 mpy and it was minimized by adding the inhibitors to a lower value of 0.53 mpy and 0.36 mpy due to the adsorption of PTBT and BMBT on the metal surface respectively. A comparison of the values of inhibition efficiency obtained by weight loss measurements and polarization studies bring out clearly the fact that there is a fairly good agreement between these values.

3.3 Electrochemical Impedance Spectroscopic Studies

The Nyquist plots of brass in polluted natural seawater in the presence and absence of PTBT and BMBT are shown in Figs. 4 and 5. The impedance spectra were measured at the corrosion potential for each inhibitor at different concentrations. The Nyquist plots are significantly changed on addition of inhibitors, the impedance of the inhibited system increased with inhibitor concentration. The parameters obtained by fitting the equivalent circuit and the calculated inhibition efficiency are listed in Table 5.

The most pronounced effect and highest charge-transfer resistance is for BMBT. R_{ct} increase with concentration for all inhibitors studied. The value of the double-layer capacitance depends on many variables including electrode potential, temperature, ionic concentrations, types of ions, oxide layers, electrode roughness, impurity adsorption, etc., [21]. It can be seen from the table that by increasing the concentration of benzotriazole derivatives, C_{dl} values tend to decrease and the inhibition

efficiency increases. The decrease in C_{dl} , which result from local dielectric constant decrease and/or an increase in the thickness of the electrical double layer, suggest that these molecules act by adsorption on the metal/solution interface. It is clear that R_{ct} increases and C_{dl} decreases as the inhibitor concentration increases. The decrease in C_{dl} could be attributed to the adsorption of the inhibitor, forming protective adsorption layer [22]. A large charge transfer resistance is associated with a slower corroding system [23].

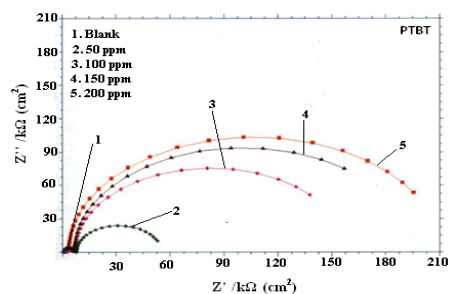


Fig. 4 Nyquist diagram of brass in polluted natural sea water with different concentrations of PTBT

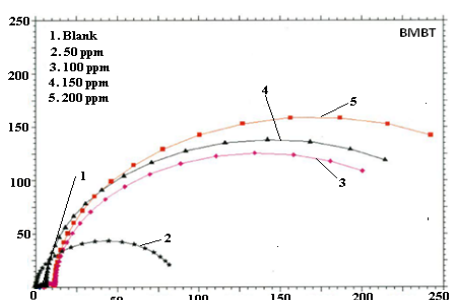


Fig. 5 Nyquist diagram of brass in polluted natural sea water with different concentrations of BMBT

Table 5 Electrochemical impedance data of brass in polluted natural sea water containing different concentrations of PTBT and BMBT

Inhibitor	Inhibitor concentration/ppm	R_{ct} $\times 10^4 / \Omega\text{cm}^2$	$C_{dl} / \mu\text{Fcm}^{-2}$	$R_F \times 10^4 / \Omega\text{cm}^2$	$C_F / \mu\text{Fcm}^{-2}$	IE/ %
Blank	-	0.76	43.68	0.97	42.35	-
PTBT	50	2.34	8.34	2.78	7.26	67.52
	100	4.27	1.36	5.46	2.15	82.20
	150	13.56	0.26	13.89	0.52	94.40
	200	23.82	0.04	18.93	0.10	96.81
BMBT	50	2.62	7.24	2.94	8.02	70.99
	100	4.87	1.32	5.97	2.46	84.4
	150	13.62	0.21	14.53	0.64	94.4
	200	24.76	0.02	19.28	0.09	96.9

Furthermore; better protection provided by an inhibitor can be associated with a decrease in capacitance of the metal. The faradaic resistance that linked to the redox process involving corrosion products increases with increase in concentration of all the studied inhibitors, whereas faradaic capacitance decreases simultaneously with increase in concentration of all the studied inhibitors. From this, it can be concluded that the corrosion products are less susceptible to redox process with increase of concentration of the inhibitors and give better protection efficiency to brass surface. It is seen from the table that R_F increased and C_F decreased. It may be due to the blocking of the electrode. The inhibition efficiency increases with increase in concentration. The IE % calculated from EIS show the same trend as those estimated from polarisation measurements. The investigations proved that the effectiveness of the BTA derivatives as corrosion inhibitors depends on their molecular structure, particularly on their molecular size and electronic effects of the substituent in the molecule.

4. Conclusion

Both PTBT and BMBT showed good inhibition efficiency in polluted natural sea water. The IE% of BMBT was higher than that of PTBT. Polarization studies indicated that PTBT and BMBT behave as mixed inhibitors for brass in polluted natural sea water. The inhibition efficiency

increases with increase in the concentration of the inhibitor. The corrosion current density decreases with increasing the concentration of the inhibitor. Impedance studies showed that the change in charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) values are related to the adsorption of PTBT and BMBT on the metal surface, leading to the formation of a protective film.

References

- [1] P.T. Gilbert, L.L. Shreir, Corrosion: Metal/environment Reactions, Newness-Butterworths, Vol. 1, 2nd Ed., London, 1976.
- [2] R. Gasparac, C.R. Martin, E. Stupnisek-Lisac, In situ studies of imidazole and its derivatives as copper corrosion inhibitors, *J. Electrochem. Soc.* 147 (2000) 548-551.
- [3] R.B. Ross, F.N. Spon, Metallic materials specifications hand book, 3rd Ed., London, 1968.
- [4] M.I. Abbas, Effects of temperature on dezincification and electrochemical behavior of 70-30 brass in sulphuric acid, *Br. Corros. J.* 26 (1991) 273-278.
- [5] R. Ravichandran, N. Rajendran, Influence of benzotriazole derivatives on the dezincification of 65-35 brass in sodium chloride solution, *Appl. Surf. Sci.* 239 (2005) 132-142.
- [6] S. Ramesh, S. Rajeswari, S. Maruthamuthu, Corrosion inhibition of copper by new triazole phosphonates, *Appl. Surf. Sci.* 229 (2004) 214-225.
- [7] F.M. Al-Kharafi, B.G. Ateya, Effect of sulphides on the electrochemical impedance of copper in benzotriazole-inhibited media, *J. Electrochem. Soc.* 149 (2002) 206-210.
- [8] A. Frignani, L. Tommesani, C. Monticelli, G. Brunoro, M. Fogagnolo, Influence of the alkyl chain on the protective effects of 1,2,3-benzotriazole towards copper corrosion Part I: Inhibition of the anodic and cathodic reactions, *Corros. Sci.* 41 (1999) 1205-1215.
- [9] S.K. Bag, S.B. Chakraborty, A. Roy, S.R. Chaudhuri, 2-aminobenzimidazole as corrosion inhibitor for 70-30 brass in ammonia, *Br. Corros. J.* 31 (1996) 207-212.
- [10] R. Walker, Aqueous corrosion of Tin-Bronze and inhibition by benzotriazole, *Corros.* 6 (2000) 1211-1219.
- [11] A. Frignani, M. Fonsati, C. Monticelli, G. Brunoro, Influence of the alkyl chain on the protective effects of 1,2,3-benzotriazole towards copper corrosion Part II: Formation and characterization of the protective films, *Corros. Sci.* 41 (1999) 1217-1227.
- [12] W. Qafsaoui, Ch. Blanc, J. Roques, N. Pebere, A. Shiri, et al, Pitting corrosion of copper in sulphate solutions: Inhibitive effect of different triazole derivative inhibitors, *J. Appl. Electrochem.* 31 (2001) 223-231.
- [13] A. Nagiub, F. Mansfeld, Evaluation of corrosion inhibition of brass in chloride media using EIS and ENA, *Corros. Sci.* 43 (2001) 2147-2171.
- [14] V. Otieno-Alego, G.A. Hope, T. Notoya, D.P. Schweinsberg, An electrochemical and SERS study of the effect of 1-[N,N-bis-(hydroxyl ethyl)amino methyl]-benzotriazole on the acid corrosion and dezincification of 60/40 brass, *Corros. Sci.* 38 (1996) 213-223.
- [15] J. Shukla, K.S. Pitre, Electrochemical behaviour of brass in acid solutions and the inhibitive effect of imidazole, *Corros. Rev.* 20 (2002) 217-228.
- [16] A.M. Fenelon, C.B. Breslin, An electrochemical study of the formation of benzotriazole surface films on copper, zinc and a copper-zinc alloy, *J. Appl. Electrochem.* 31 (2001) 509-516.
- [17] A. Katritzky, S. Rachwal, B. Rachwal, The chemistry of N-substituted benzotriazoles, *J. Chem. Soc. Perkin Trans. Part 1*: 17 (1987) 781-788.
- [18] R. Ravichandran, S. Nanjundan, N. Rajendran, Effect of benzotriazole derivatives on the corrosion and dezincification of brass in neutral chloride solution, *J. Appl. Electrochem.* 34 (2004) 1171-1176.
- [19] M.G. Fontana, Corrosion Engineering, McGraw Hill Book Company, 3rd Ed., Singapore, 1987.
- [20] B. Ramesh babu, R. Holze, Corrosion and hydrogen permeation inhibition for mild steel in HCl by isomers of organic compounds, *Br. Corros. Jour.* 35 (2000) 204-209.
- [21] P. Galicia, N. Batina, I. Gonzalez, The relationship between the surface composition and electrical properties of corrosion films formed on carbon steel in alkaline sour medium: An XPS and EIS study, *J. Phys. Chem. B* 110 (2006) 14398-14405.
- [22] H.H. Hassan, E. Abdelghani, M.A. Amin, Inhibition of mild steel corrosion in hydrochloric acid solution by triazole derivatives: Part I. polarization and EIS studies, *Electrochim. Acta* 52 (2007) 6359-6366.
- [23] K.F. Khaled, The inhibition of benzimidazole derivatives on corrosion of iron in 1 M HCl solutions, *Electrochim. Acta* 48 (2003) 2493-2503.