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Dezincification of Brass in Sulfide Polluted Sodium Chloride Medium: Evaluation of the Effectiveness of 2-Mercaptobenzothiazole

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The present paper addresses the effectiveness of 2-mercaptobenzothiazole (MBT) in preventing the dezincification of brass in sulfide polluted 3.5% NaCl solution. The dezincification behaviour of brass in 3.5% NaCl solution containing 100-1000 ppm of sulfide ions and 1×10^{-6} to 1×10^{-3} M MBT was studied by potentiodynamic polarization, electrochemical impedance spectroscopy, current-time transient and accelerated leaching studies. The presence of sulfide ions in 3.5% NaCl solution has caused a significant increase in the extent of corrosion attack on brass. The inhibiting effect of MBT is markedly reduced in the presence of sulfide ions in the medium. The easy replacement of Cu-MBT complex by Cu_2S film on the surface of brass is responsible for the inability of MBT to prevent corrosion attack in the presence of sulfide ions. The study concludes that the effectiveness of MBT in preventing the dezincification of brass is dependent on the concentration of the sulfide ions in the medium and the effectiveness is nullified at higher concentrations of sulfide ions.

Keywords: Dezincification, brass, sulfide, 2-mercaptobezothiazole

1. INTRODUCTION

Brass possesses attractive properties, namely, good corrosion resistance, good machinability, high thermal and electrical conductivity and better resistance to biofouling. Hence, it finds extensive use in water distribution systems, water treatment units, condensers, desalination, petrochemical and heat exchangers in oil and chemical industries, processing plants for electricity generation and desalination plants [1-4]. However, brass is susceptible for dezincification. Dezincification of brass involves preferential dissolution of zinc leaving a porous copper layer, resulting in either a plug type or uniform type corrosion [5-7]. The dezincification process leads to serious deterioration of the surface and mechanical properties of the remaining alloy. Thus, studies on the mechanism of dezincification and the possible ways of preventing this type of corrosion failure have attracted many researchers. Selvaraj et al. [8] have recently reviewed the types of dezincification of brass, the effect of various pollutants, the mechanism of dezincification and its control. Alloying of brass with elements like arsenic and/or phosphorous is reported to decrease the dezincification attack [9, 10]. The use of inhibitors, such as azole compounds is another approach. These inhibitors due to their adsorption and their ability to form a chelating compound enable the formation of a physical blocking barrier that prevents dezincification of brass [11]. Among the azole compounds, benzotriazole (BTA) and 2-mercaptobenzothiazole (MBT) have been shown to be very efficient in various environments [12-20]. However, the effectiveness of these inhibitors in preventing the dezincification of brass in sulfide polluted environments is a matter of concern.

Sulfide pollution of seawater at the coastal areas can occur from industrial waste discharge, biological and bacteriological process in seawater (seaweed, marine organisms or microorganisms, sulfide reducing bacteria), which promotes aqueous corrosion of copper and its alloys [21]. It has been reported that corrosion rate of copper alloys increases by a factor of 10-30 when seawater contains sulfur compounds as impurities [22]. Sayed et al. [23] have studied the effect of dealloying of Cu-Ni alloys in chloride environment containing 500 and 1000 ppm of sulfide and showed the strong dependence of the extent of corrosion attack of Cu-Ni alloys on the concentration of sulfide ions. The presence of sulfide ions in seawater is found to influence the fatigue strength and fatigue life of Al-brass and Cu-10Ni alloys [24], the susceptibility of Al-bronze to stress corrosion cracking [25, 26], the corrosive wear of copper alloys [27]. Increase in sulfide ion concentration in the medium is reported to decrease the fatigue strength of Al-brass and Cu-10Ni alloys, reduce the maximum stress and change the morphology of the fracture from ductile to brittle feature of Al-bronze at anodic potentials and, accelerate the corrosive wear due to the surface embrittlement induced by the sulfide ions [24-27].

The effectiveness of BTA in sulfide polluted salt water has been studied earlier [28-30]. Allam et al. [30] have suggested that the addition of benzotriazole is capable of preventing the corrosion of Cu-10Ni alloy in 3.4% NaCl solution containing 2 ppm of sulfide ions. Al-Kharafiz and Ateya [29] have observed that the addition of 40 ppm (1.25×10^{-3} M) of the sulfide ions to a benzotriazole inhibited (at 5×10^{-3} M BTAH) sodium chloride solution leads to an immediate and profound deterioration of the passivity of the Cu-NaCl interface. It has been shown that the competitive adsorption of protective benzotriazole film and the corrosion promoting sulfide on the alloy surface determines the effectiveness. Gupta et al. [31, 32] have suggested that MBT offers better inhibition towards the corrosion of 70/30 brass than BTA in ammonia as well as in sulphuric acid medium. Subramanian and Laskshminarayanan [33] have reported that MBT has a strong affinity for copper in alkaline medium and forms a rigid, thicker and non-permeable film compared to BTA. The effectiveness of MBT in sulfide polluted medium has not yet been studied.

At lower concentrations of sulfide ions of the order of 1-2 ppm, azole compounds are found to be effective in inhibiting the corrosion of copper alloys. BTA is capable of preventing the corrosion of

Cu-10Ni alloy in 3.4% NaCl solution containing 2 ppm of sulfide ions [30]. Laachach et al. [34] have observed higher inhibition efficiency for aminotriazole in presence of 1 ppm of sulfide ions towards the corrosion of Cu-Ni alloy and suggest that a synergistic effect is likely to exist between sulfide ions and aminotriazole. The major concern is the deleterious effect caused by higher concentration of sulfide ions and hence it is important to ascertain whether the azole type inhibitors are effective at higher concentrations of sulfide ions. In this perspective the present study intends to evaluate the effectiveness of MBT in preventing the dezincification of brass in 3.5% NaCl solution containing 100-1000 ppm of sulfide ions.

2. EXPERIMENTAL DETAILS

The electrodes used for corrosion studies were cut from a 2 mm thick sheet of 65-35 brass. They were polished using 60 grit silicon carbide paper followed by 220, 400, 600, 1/0, 2/0, 3/0 and 4/0 grades of emery paper, degreased with acetone and rinsed with deionized water. The electrochemical measurements were performed using a potentiostat/galvanostat/frequency response analyzer (ACM instruments, UK) and a flat cell. A 3.5% NaCl solution (dissolved oxygen concentration: 6 ppm; pH 6.5) was used as the electrolyte medium in which varying concentrations of MBT (1×10^{-6} to 1×10^{-3} M) and sulfide (100, 200, 500 and 1000 ppm) ions were added to study the dezincification behaviour of brass. Only 1 cm^2 of the brass electrode was exposed to the electrolyte solution. A graphite rod and saturated calomel electrode (SCE) served as the counter and reference electrodes, respectively. All experiments were performed at 27±1°C. Potentiodynamic polarization measurements were made at a potential scan rate of 100 mV/min. The corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were determined using the Tafel extrapolation method. Electrochemical impedance (EIS) studies were carried out in the frequency range between 10,000 Hz and 0.01 Hz. The charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) were determined from the Nyquist plot by fitting the data using Boukamp software. The current-time transients were recorded at different impressed potentials, namely, -250, -200, -150, -100, -50 and 0 mV vs. SCE. The amount of copper and zinc ions leached out from the alloy at these potentials were analyzed using atomic absorption spectrometer (GBC-Avanta). Based on the amount of copper and zinc ions leached into the solution, the dezincification factor (z) was calculated using the relation:

$$\text{Dezincification factor (z)} = [C_{Zn}/C_{Cu}]_{solution} / [C_{Zn}/C_{Cu}]_{alloy}$$

where C_{Zn} and C_{Cu} represents the contents of zinc and copper, respectively, in a designated phase.

3. RESULTS AND DISCUSSION

3.1 Effect of Na_2S on the corrosion of brass in 3.5% NaCl solution

The potentiodynamic polarization curve of brass in 3.5% NaCl solution containing 0, 100, 200, 500 and 1000 ppm of Na_2S is shown in Fig. 1. The corrosion potential (E_{corr}) and corrosion current density (i_{corr}), calculated using the Tafel extrapolation method are given in Table 1. It is evident from Fig. 1 and Table 1 that the addition of Na_2S shifts the E_{corr} towards more negative values and increases the i_{corr}. The extent of shift in E_{corr} and the increase in i_{corr} is found to be a function of the concentration of Na_2S; higher the concentration of Na_2S, higher the shift in E_{corr} and larger the increase in i_{corr} values. The corrosion rate increases from 8.73 to 34.05 mils/year when the concentration of Na_2S is increased from 0 to 1000 ppm.

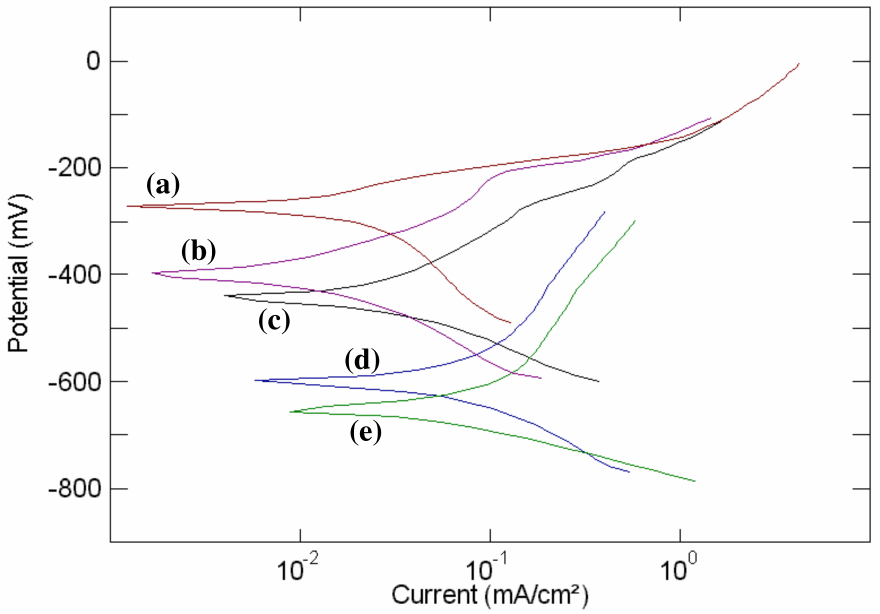

Figure 1. Potentiodynamic polarization curve of brass in 3.5% NaCl solution containing varying concentrations of Na_2S: (a) 0 ppm Na_2S; (b) 100 ppm Na_2S; (c) 200 ppm Na_2S; (d) 500 ppm Na_2S; and (e) 1000 ppm Na_2S

Table 1: Effect of varying concentrations of Na_2S on the corrosion behaviour of brass in 3.5% NaCl solution evaluated by polarization and EIS studies

Electrolyte used	E_{corr} (mV) vs. SCE	i_{corr} ($\mu A/cm^2$)	R_{ct} ($Ohm.cm^2$)	C_{dl} (F)
3.5%NaCl	-271	17.53	743	4.837×10^{-4}
3.5% NaCl with 100 ppm of Na_2S	-438	23.92	376	2.265×10^{-4}
3.5% NaCl with 200 ppm of Na_2S	-480	32.63	281	1.101×10^{-4}
3.5% NaCl with 500 ppm of Na_2S	-598	45.76	188	1.132×10^{-4}
3.5% NaCl with 1000 ppm of Na_2S	-656	68.41	101	1.150×10^{-3}

The Nyquist plot of brass in 3.5% NaCl containing 0, 100, 200, 500 and 1000 ppm of Na_2S is shown in Fig. 2. In the absence of Na_2S only a single semicircle is observed whereas a semi-circle followed by a diffusion tail is observed in presence of Na_2S. The size of the semicircle decreases with increase in Na_2S concentration in the medium, indicating a decrease in corrosion resistance of brass with the increase in Na_2S concentration (100-1000 ppm). The appearance of Warburg diffusion tail suggests that the corrosion of brass in 3.5% NaCl medium containing Na_2S is diffusion controlled. The charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) values, calculated after fitting the data using Boukamp software, are given in Table 1. The decrease in R_{ct} and increase in C_{dl} values with increase in Na_2S concentration in the medium suggest an increase in rate of corrosion of brass in presence of Na_2S and support the observations made in the potentiodynamic polarizations studies.

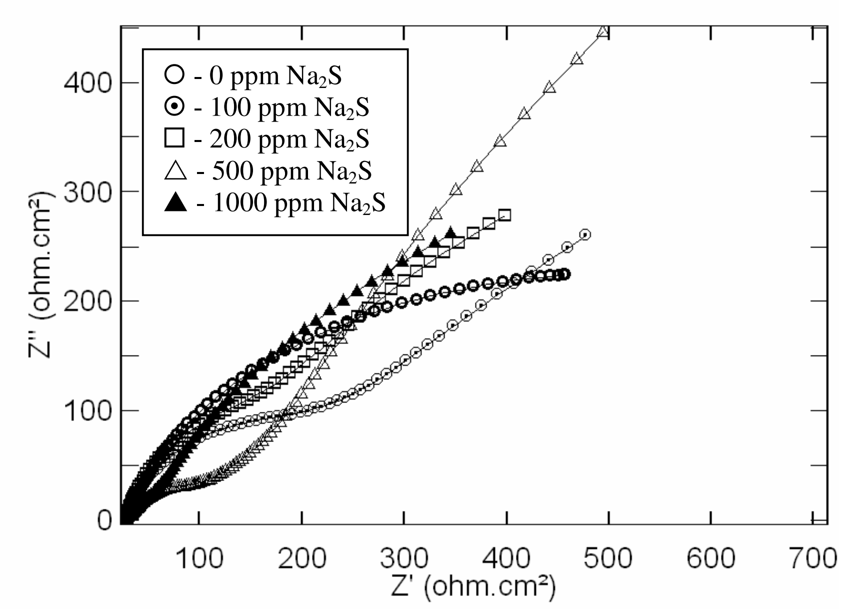

Figure 2. Nyquist plot of brass in 3.5% NaCl solution containing varying concentrations of Na_2S.

Current-time transient studies are performed at different impressed potentials, in the range of - 250 mV to 0 mV vs. SCE, anodic to the E_{corr} of brass in 3.5% NaCl solution. Representative curves of current-time transients of brass in 3.5% NaCl solution containing 0 and 100 ppm of Na_2S are shown in Fig. 3. The steady state current density values obtained at different impressed potentials (Table 2) reflect the corrosion behaviour of brass in 3.5% NaCl solution containing varying concentrations of Na_2S. The current density values obtained from this study strongly supports the observations made by potentiodynamic polarization and EIS studies; the addition of Na_2S (100-1000 ppm) increased the current density values.

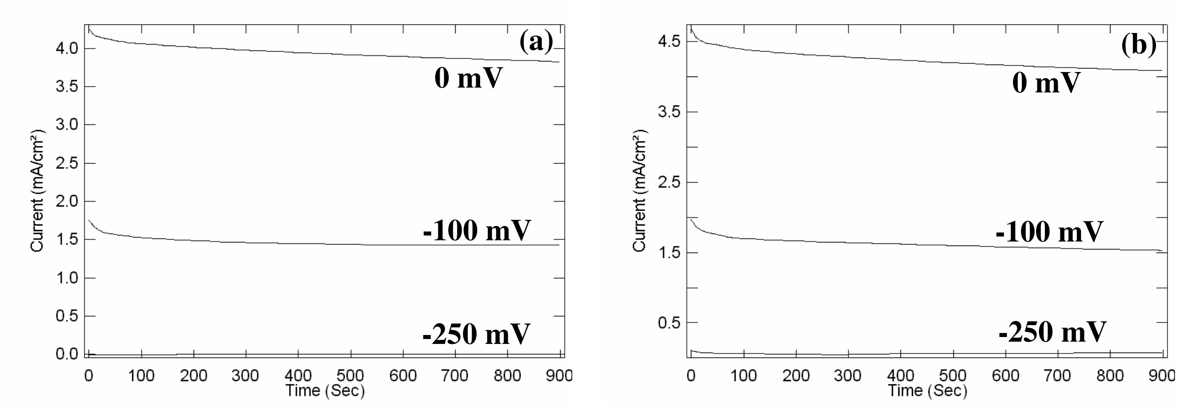

Figure 3. Current-time transient curves of brass in 3.5% NaCl solution at different impressed potentials (vs. SCE) (a) 3.5% NaCl with 0 ppm Na_2S; and (b) 3.5% NaCl with 100 ppm Na_2S.

Table 2. Steady state current densities of brass in 3.5% NaCl solution containing 0, 100 and 1000 ppm of Na_2S at different impressed potentials (vs. SCE)

Electrolyte used	Steady state current density at different impressed potentials (mA/cm^2)					
	-250 mV	-200 mV	-150 mV	-100 mV	-50 mV	0 mV
3.5 % NaCl	0.008	0.14	0.62	1.52	2.30	4.00
3.5 % NaCl with 100 ppm Na_2S	0.058	0.25	0.75	1.60	2.75	4.30
3.5 % NaCl with 1000 ppm Na_2S	0.180	0.34	0.85	1.75	3.00	4.60

Dezincification of brass in 3.5% NaCl solution involves dissolution of both zinc and copper from the alloy and re-deposition of copper. However, in sulfide containing 3.5% NaCl solution, the nature of surface film formed by the sulfide ions would influence the dezincification behaviour of brass. Hence, accelerated electrochemical leaching studies are performed at three different potentials, namely, -250, -100 and 0 mV vs. SCE. The former is closer to the E_{corr} of brass in 3.5% NaCl solution whereas the latter two are anodic to E_{corr} of brass. The amount of copper and zinc ions leached into the solution and dezincification factor (z) of brass in 3.5% NaCl solution containing 100 and 1000 ppm of N_2S obtained at -250 mV, -100 mV and 0 mV vs. SCE are given in Table 3. It is evident from Table 3 that addition of Na_2S increased the amount of copper and zinc ions leached into the solution. The extent of leaching is very high when the concentration of Na_2S is increased to 1000 ppm.

Table 3. The extent of leaching of copper and zinc and the dezincification factor of brass in 3.5% NaCl solution containing 100 and 1000 ppm of Na_2S obtained from accelerated leaching studies at -250 mV, -100 mV and 0 mV vs. SCE

Electrolyte used	Solution analysis		Dezincification factor (Z)
	Cu (mg)	Zn (mg)	
At - 250 mV vs. SCE			
3.5 % NaCl	0.0115	0.0372	5.87
3.5 % NaCl with 100 ppm Na_2S	0.0241	0.1486	11.19
3.5 % NaCl with 1000 ppm Na_2S	0.2593	1.8212	12.75
At -100 mV vs. SCE			
3.5 % NaCl	0.0120	0.0435	6.58
3.5 % NaCl with 100 ppm Na_2S	0.0448	0.2873	11.64
3.5 % NaCl with 1000 ppm Na_2S	0.3831	2.7530	13.05
At 0 mV vs. SCE			
3.5 % NaCl	0.0124	0.0435	6.37
3.5 % NaCl with 100 ppm Na_2S	0.0650	0.4238	11.84
3.5 % NaCl with 1000 ppm Na_2S	0.4868	3.7100	13.84

The results of potentiodynamic polarization, EIS, current-time transient and accelerated electrochemical leaching studies reveal that the presence of sulfide ions in 3.5% NaCl solution increases the extent of corrosion attack of brass. The increase in the extent of corrosion attack of copper alloys in the presence of sulfide ions is also observed by many researchers [21, 23, 35-40]. The observed negative shift in the E_{corr} in presence of sulfide ions and the increase in the extent of negative shift with increase in concentration of sulfide ions (Fig. 1 and Table 1) suggest that the corrosion of brass in sulfide containing 3.5% NaCl solution is under anodic control. The negative shift in E_{corr} and the increase in i_{corr} in the presence of sulfide ions are considered to be due to the change in nature of surface films on brass. In the absence of sulfide ions, the surface layers are mainly composed of oxides of the alloying elements [35, 41-46]. In the presence of sulfide ions, the surface film that forms on brass in 3.5% NaCl solution will be primarily composed of Cu_2S, although CuS, Cu_2O, and non-stoichiometric copper sulfide species such as $Cu_{1.8}S$ [36-40]. In presence of sulfide ions in the medium the Cu_2O oxide layer becomes defective [47]. This defective surface layer consists of Cu_2O and Cu_2S that permit rapid ionic and electronic transport through it and causes an increase in the corrosion rate. The Cu_2S film is porous, non protective and catalyzes the corrosion reaction [21, 23, 34, 43, 48-51]. Hence, the observed increase in the corrosion rate of brass in 3.5% NaCl solution containing 100-1000 ppm of Na_2S is due to the porous nature of the Cu_2S film formed on the surface of brass and the ability of the sulfide ions to catalyze the corrosion process.

3.2 Effect of MBT on the corrosion of brass in 3.5% NaCl solution containing varying concentrations of Na_2S

The effect of addition of 1 x 10^{-6} M and 1 x 10^{-3}M MBT on the corrosion behaviour of brass in 3.5% NaCl solution containing varying concentrations of Na_2S (100, 200, 500 and 1000 ppm) is assessed by potentiodynamic polarization and EIS studies. The polarization curve of brass in 3.5% NaCl solution obtained in presence of 1 x 10^{-3} M MBT and varying concentrations of Na_2S is given in Fig. 4. The corrosion potential (E_{corr}) and corrosion current density (i_{corr}), calculated using the Tafel extrapolation method are given in Table 4. It is evident from Fig. 4 and Table 4 that MBT could offer some inhibition towards the corrosion of brass only when the concentration of Na_2S is low of the order of 100 ppm. The effectiveness of MBT is decreased when the concentration of Na_2S is increased beyond 100 ppm and it is nullified at 1000 ppm of Na_2S. In 3.5% NaCl containing 1000 ppm of Na_2S, addition of 1 x 10^{-3} M of MBT could decrease the corrosion rate only from 34.05 to 23.21 mils/year. This observation suggests the inability of the MBT to prevent corrosion of brass in 3.5% NaCl medium containing higher concentrations of Na_2S.

The Nyquist plot of brass in 3.5% NaCl solution in presence of 1 x 10^{-3} M MBT and varying concentrations of Na_2S is shown in Fig. 5. In all the cases, a semicircle followed by a Warburg diffusion tail is observed. A comparison of Figs. 2 and 5 reveals that the shape of the curves is similar. However, the size of the semicircle is relatively bigger when the solution contains MBT along with sulfide ions. This observation suggests that addition of 1 x 10^{-3} M of MBT is able to reduce the corrosive attack of brass induced by the sulfide ions only to a limited extent. The charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) values, calculated after fitting the data using

Boukamp software, are given in Table 5. It is evident from Table 5 that that the addition of MBT could decrease the extent of corrosion of brass in 3.5% NaCl solution only to a limited extent. The effectiveness of MBT is decreased when the concentration of Na_2S is increased beyond 100 ppm and it is nullified at 1000 ppm of Na_2S.

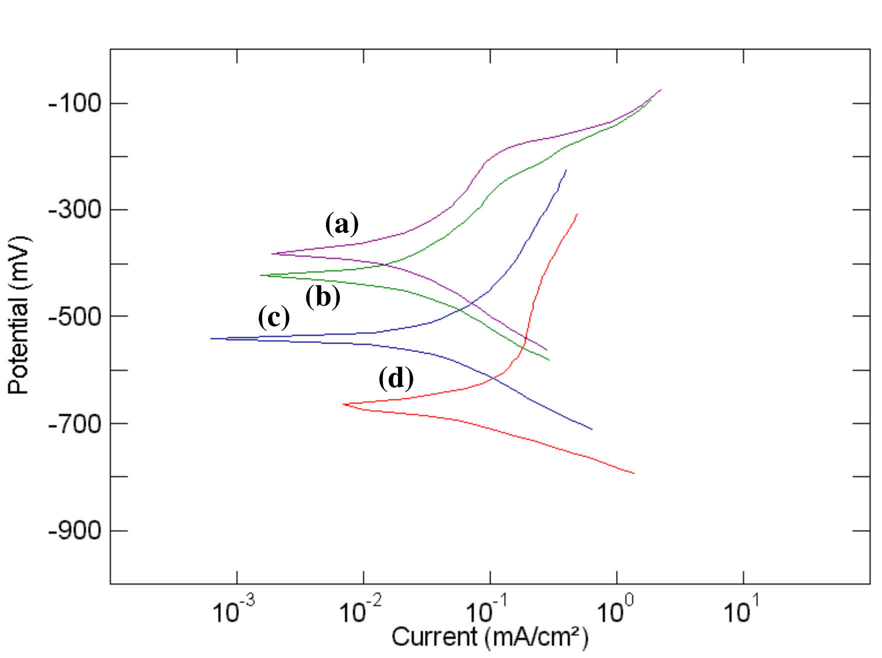

Figure 4. Potentiodynamic polarization curve of brass in 3.5% NaCl solution in presence of 1 x 10^{-3} M MBT and varying concentrations of Na_2S: (a) 100 ppm Na_2S; (b) 200 ppm Na_2S; (c) 500 ppm Na_2S; and (d) 1000 ppm Na_2S.

Table 4. Effect of MBT on the corrosion behaviour of brass in 3.5% NaCl containing varying concentrations of Na_2S evaluated by polarization studies

Electrolyte used	Corrosion potential (E_{corr}) (mV Vs. SCE)	Corrosion current density (i_{corr}) (µA/cm^2)
3.5% NaCl with 1000 ppm Na_2S	-656	68.41
3.5% NaCl with 1000 ppm Na_2S and 1 x 10^{-6}M MBT	-650	59.24
3.5% NaCl with 1000 ppm Na_2S and 1 x 10^{-3}M MBT	-602	46.63
3.5% NaCl with 500 ppm Na_2S	-598	45.76
3.5% NaCl with 500 ppm Na_2S and 1 x 10^{-6}M MBT	-587	37.19
3.5% NaCl with 500 ppm Na_2S and 1 x 10^{-3}M MBT	-541	26.08
3.5% NaCl with 200 ppm Na_2S	-480	32.63
3.5% NaCl with 200 ppm Na_2S and 1 x 10^{-6}M MBT	-479	26.49
3.5% NaCl with 200 ppm Na_2S and 1 x 10^{-3}M MBT	-423	16.18
3.5% NaCl with 100 ppm Na_2S	-438	23.92
3.5% NaCl with 100 ppm $Na_2S$and 1 x 10^{-6}M MBT	-413	18.28
3.5% NaCl with 100 ppm $Na_2S$and 1 x 10^{-3}M MBT	-381	13.35

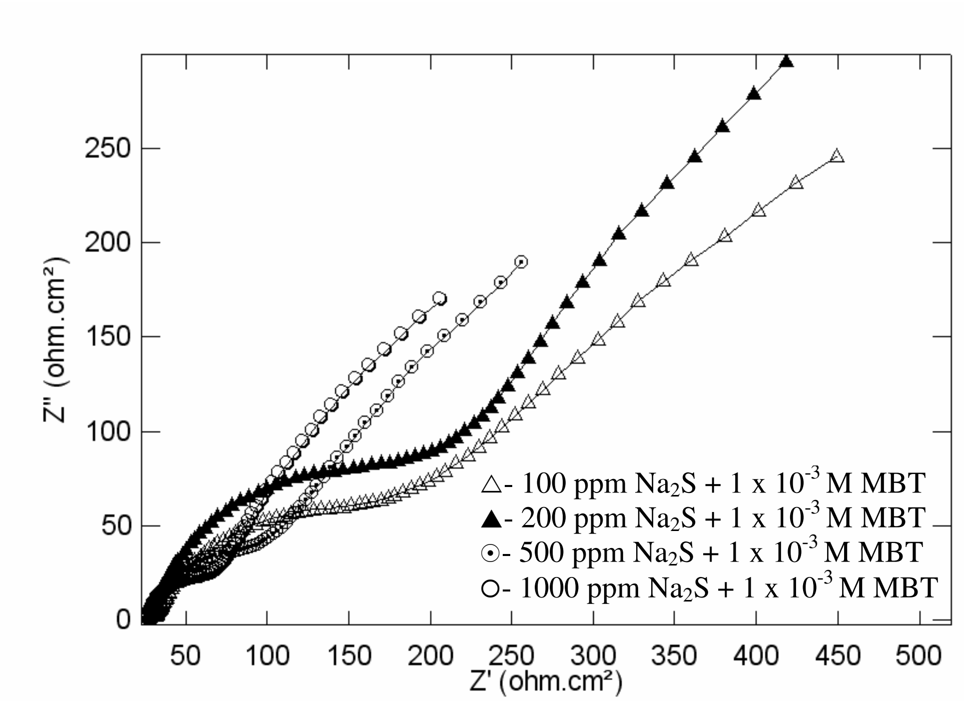

Figure 5. Nyquist plot of brass in 3.5% NaCl solution in presence of 1 x 10^{-3} M MBT and different concentrations of Na_2S.

Table 5. Effect of varying concentrations of MBT on the corrosion behaviour of brass in 3.5% NaCl containing varying concentrations of Na_2S evaluated by polarization and EIS studies

Electrolyte used	Charge Transfer Resistance (R_{ct}) Ohm.cm^2	Double Layer Capacitance (C_{dl}) F
3.5% NaCl with 1000 ppm Na_2S	101	1.150 x 10^{-3}
3.5% NaCl with 1000 ppm Na_2S and 1 x 10^{-3}M MBT	161	1.010 x 10^{-4}
3.5% NaCl with 500 ppm Na_2S	188	1.132 x 10^{-4}
3.5% NaCl with 500 ppm Na_2S and 1 x 10^{-3}M MBT	239	5.875 x 10^{-4}
3.5% NaCl with 200 ppm Na_2S	281	1.101 x 10^{-4}
3.5% NaCl with 200 ppm Na_2S and 1 x 10^{-3}M MBT	328	6.842 x 10^{-4}
3.5% NaCl with 100 ppm Na_2S	376	2.265 x 10^{-4}
3.5% NaCl with 100 ppm Na_2S and 1 x 10^{-3}M MBT	473	4.530 x 10^{-4}

Representative curves of current-time transients of brass in 3.5% NaCl solution containing 1 x 10^{-3}M MBT in presence of 0 and 100 ppm of Na_2S are shown are shown in Fig. 6. The steady state current density values obtained at different impressed potentials (Table 6) reflect the corrosion behaviour of brass in 3.5% NaCl solution containing varying concentrations of MBT and Na_2S. The current density values obtained from this study strongly supports the observations made by potentiodynamic polarization and EIS studies; the addition of MBT in sulfide containing 3.5% NaCl medium could sustain the corrosion attack only when the concentration of Na_2S is low of the order of 100 ppm.

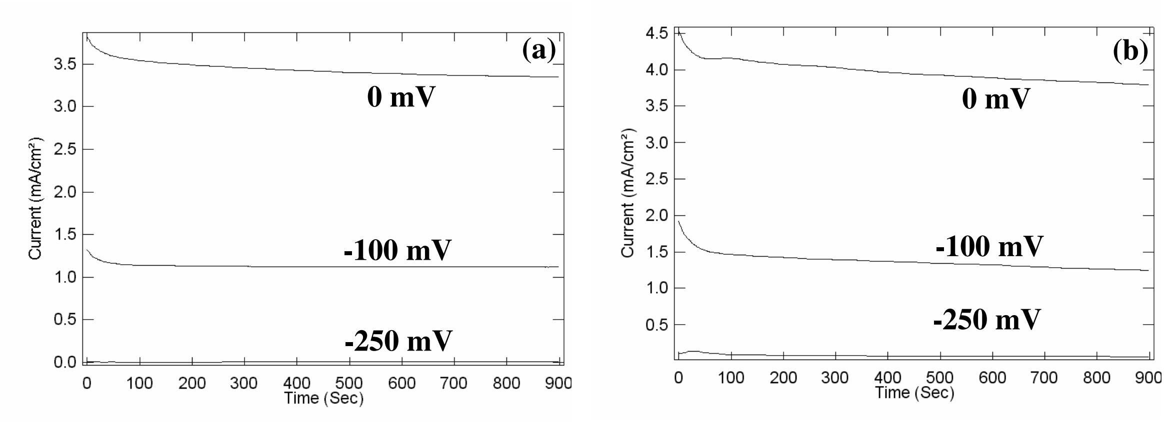

Figure 6. Current-time transient curves of brass in 3.5% NaCl solution at different impressed potentials (vs. SCE) both in presence and absence of Na_2S and MBT: (a) 3.5% NaCl with 1 x 10^{-3} M MBT; and (b) 3.5% NaCl with 100 ppm Na_2S and 1 x 10^{-3}M MBT.

Table 6. Steady state current densities at different impressed potentials in presence of 100 and 1000 ppm of Na_2S and 10^{-6} and 10^{-3} M MBT obtained from current-time transient studies

Electrolyte used	Steady state current density at different impressed potentials (mA/cm^2)					
	-250 mV	-200 mV	-150 mV	-100 mV	-50 mV	0 mV
3.5 % NaCl with 100 ppm Na_2S	0.058	0.25	0.75	1.60	2.75	4.30
3.5 % NaCl with 100 ppm Na_2S and 1 x 10^{-6} M MBT	0.040	0.16	0.55	1.46	2.68	4.10
3.5 % NaCl with 100 ppm Na_2S and 1 x 10^{-3} M MBT	0.030	0.15	0.45	1.35	2.60	3.80
3.5 % NaCl with 1000 ppm Na_2S	0.180	0.34	0.85	1.75	3.00	4.60
3.5 % NaCl with 1000 ppm Na_2S and 1 x 10^{-6} M MBT	0.110	0.24	0.72	1.3	2.65	3.75
3.5 % NaCl with 1000 ppm Na_2S and 1 x 10^{-3} M MBT	0.050	0.12	0.60	1.2	2.25	3.60

Accelerated electrochemical leaching studies performed at -250, -100 and 0 mV vs. SCE reveals that the addition of MBT in sulfide containing 3.5% NaCl medium decreases the amount of copper and zinc ions leached into the solution. However, the extent of inhibition offered by MBT is not sufficient to prevent the corrosion attack of brass in 3.5% NaCl solution containing higher concentrations of Na_2S (Table 7).

Table 7. The extent of leaching of copper and zinc and the dezincification factor of brass in 3.5% NaCl solution containing 100 and 1000 ppm of N_2S and 1 x 10^{-3} M MBT obtained from accelerated leaching studies at -250 mV, -100 mV and 0 mV vs. SCE

Electrolyte used	Solution analysis		Dezincification factor (Z)
	Cu (mg)	Zn (mg)	
At - 250 mV vs. SCE			
3.5 % NaCl with 1 x 10^{-3} M MBT and 100 ppm Na_2S	0.0125	0.0413	6.00
3.5 % NaCl with 1 x 10^{-3} M MBT and 1000 ppm Na_2S	0.0675	0.4192	11.28
At -100 mV vs. SCE			
3.5 % NaCl with 1 x 10^{-3} M MBT and 100 ppm Na_2S	0.0141	0.0721	9.28
3.5 % NaCl with 1 x 10^{-3} M MBT and 1000 ppm Na_2S	0.0863	0.5494	11.56
At 0 mV vs. SCE			
3.5 % NaCl with 1 x 10^{-3} M MBT and 100 ppm Na_2S	0.0186	0.0989	9.60
3.5 % NaCl with 1 x 10^{-3} M MBT and 1000 ppm Na_2S	0.1066	0.7016	11.95

It is evident from the results of potentiodynamic polarization, EIS, current-time transient and accelerated electrochemical leaching studies that the inhibition efficiency offered by MBT is very low in presence of Na_2S in 3.5% NaCl solution. The chemical nature of MBT in the corrosive medium decides its mode of adsorption and ability to form a surface complex. MBT has a pKa value of 6.93 (at 20°C) [52]. This implies that MBT will exist in the unionized protonated form in acidic media whereas in alkaline media it will be in the ionized form, in which the negative charge is concentrated on the exocyclic S atom [32, 53, 54]. Besides the chemical nature of MBT, the orientation of the adsorbed MBT molecule could also influence the inhibition efficiency. It has been reported that MBT forms a polymeric film of mercaptobenzothiazolato-Cu(I) (Cu(I)-MBT) on Cu (Fig. 7) by a surface reaction between the cuprous ion and the adsorbed MBT [18]. Chadwick and Hashemi [55] have reported that the film thickness of Cu-MBT polymeric film is closely related to the pH of the medium. Subramanian and Laskshminarayanan [33] have reported that the presence of 1 mM of MBT has effected an almost complete suppression of both the anodic and cathodic peaks of copper in 0.1 M NaOH due to the formation of a rigid, thick and non-permeable Cu-MBT film on the surface of copper. The pH of 3.5% NaCl solution used in this study is 6.5. At this pH, MBT is likely to exist in the unionized form. Hence it is presumed that the adsorption of MBT will be relatively weak and the Cu-MBT polymeric film will be a thin layer.

When both Na_2S and MBT are added to the 3.5% NaCl solution, the sulfide ions will compete with MBT for adsorption on the surface of brass. Hence, the formation of Cu-MBT or Cu_2S will be determined by the concentrations of sulfide ions and MBT in the medium. However, the formation of Cu_2S has a much higher equilibrium constant of the order of 10^{47} [56]. Since the stability of Cu_2S is much higher, the sulfide ions will extract the Cu(I) ions from the Cu(I)-MBT polymer film. This will result in the disintegration of the Cu-MBT film and lead to the exposure of the brass surface to the aggressive sulfide species which by virtue of their adsorption catalyze the corrosion process [21, 35, 38, 49]. Hence, the observed corrosion behaviour of brass in 3.5% NaCl solution in presence of both

Na_2S and MBT could be attributed to the breakdown of the Cu-MBT polymer film and adsorption of sulfide ions which catalyses the corrosion process. The presence of sulfides in 3.5% NaCl solution eliminates the inhibiting effects of MBT and promotes the corrosion of brass. The deleterious effect of sulfide ions on the corrosion of copper alloys is also observed in sulfide polluted corrosive media containing BTA [28-30, 57-60]. Hegazy et al. [28] and Allam et al. [30] have reported that in salt water containing sulfides, an increase in BTA concentration decreases the degree of the brass and Cu-10Ni alloy surface covered with sulfide ions and decrease the corrosion rate. However, they have used a very low sulfide ion concentration of 2 ppm. Though Subramanian and Laskshminarayanan [33] have reported that MBT could form a rigid, thick and non-permeable Cu-MBT film on the surface of copper than that of Cu-BTA, they have observed such an effect in 0.1 M NaOH (alkaline medium). In our study the sulfide ion concentrations are very high compared to that used by Hegazy et al. [28] and Allam et al. [30] and, the pH of the 3.5% NaCl solution is 6.5 and not alkaline as that of Subramanian and Laskshminarayanan [33]. Hence, the Cu-MBT film formed by MBT under the experimental conditions of the present study is expected to be thin and less protective. When both MBT and sulfide ions are present in the 3.5% NaCl solution, the sulfide ions extract the Cu(I) ions from the Cu(I)-MBT polymer film, causing disintegration of the Cu-MBT film and catalyzing the corrosion process.

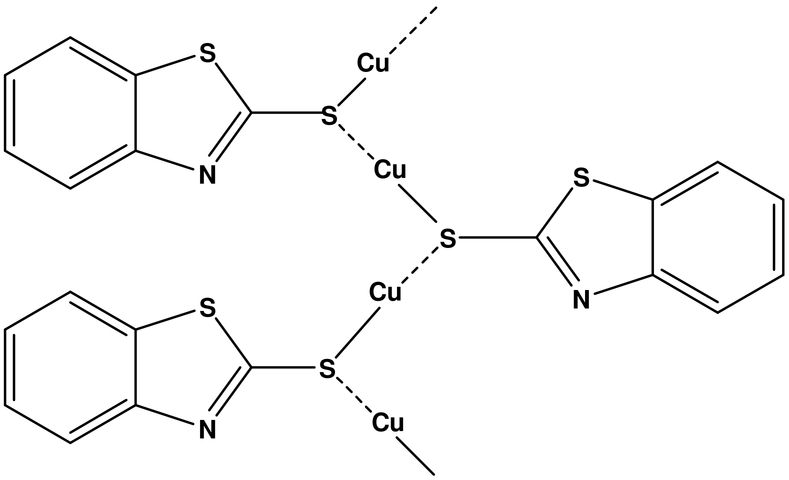

Figure 7. Structure of the Cu-MBT polymeric film.

4. CONCLUSION

The presence of sulfide ions in 3.5% NaCl cause a significant increase in the extent of corrosion attack on brass. The porous nature of the Cu_2S film and the catalyzing ability of the sulfide ions are responsible for the increased corrosion attack. The existence of MBT in 3.5% NaCl solution (pH 6.5) in the unionized form could not able to form a rigid, thick and non-permeable Cu-MBT polymeric film. Hence, in the presence of sulfide ions in the medium, the Cu-MBT film is easily replaced by the Cu_2S and this results in a significant decrease in the inhibition effect offered by MBT. The effectiveness of MBT in preventing the dezincification of brass is dependent on the concentration of the sulfide ions in the medium and the effectiveness is nullified at higher concentrations of sulfide ions.

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