Effect Of Sodium Gluconate And Benzotriazole Derivative As Synergist on Inhibition Efficiency of Brass Corrosion In 3% Nacl Solution

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Abstract- *The corrosion inhibition of brass in 3% NaCl has been investigated with 5-methyl 1-H Benzotriazole (5MBTA) and sodium gluconate (SG) using mass loss method, electrochemical techniques, SEM, and EDAX Analysis. Analysis of results revealed that of BT inhibits 71% at optimum concentration (150 ppm). The addition of SG with 5MBTA enhanced the inhibitive effect upto 87% and showed a synergism of inhibition. Potentiodynamic polarization results suggested that the mixture of BT and SM behave as mixed type inhibitors.SEM and EDAX analysis were used to determine the nature of the protective film formed on the brass surface.*

Keywords- Brass, 5-methyl 1-H Benzotriazole, sodium gluconate, electrochemical techniques, SEM and EDAX .

I. INTRODUCTION

Brass are widely used in industry because of their excellent electrical and thermal conductivity and are often used in heating and cooling system[1,2]. Brass is susceptible to corrosion process known as dezincification by means of which brass loses its valuable physical and mechanical properties leading to structural failure and this tendency increases with increasing zinc content of the brass[3]. Many techniques have been used to minimize the dezincification and corrosion of brass. One of the most important methods in corrosion protection is to use inhibitors. Benzotriazole is known as one of the best corrosion inhibitors for copper and its alloys like brass in wide range of environments[4-7].

The good chelating properties of gluconates[8] are also exploited e.g., in preventing incrustation in boilers and heat exchangers. These properties suggest that the gluconate anion itself has inhibitive properties; especially sodium and ammonium gluconate appear to suppress corrosion.

The combination of different inhibitors, in order to take advantage of their synergistic effects seems a promising way to increase the protection while reducing the dosage of inhibitor and, therefore, the possible health or environmental risks[9]. Sodium gluconate is an excellent co-inhibitor for both open and closed systems, for environmentally safe products.

The present investigation deals with the effect of sodium gluconate (SG) on the inhibition efficiency of 5-methyl 1-H Benzotriazole (5MBTA) on the corrosion inhibition of Brass in 3% NaCl solution by weight-loss, electrochemical, SEM and EDAX methods.

II.EXPERIMENTAL METHODS

2.1. Materials

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 acetone.The solutions were prepared from AR chemicals using DD water. The structure of 5MBTA is given in Fig.1and the structure of SG is given in Fig.2.

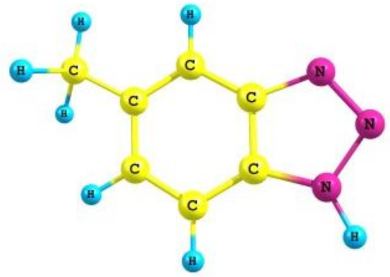

Fig.1 methyl 1-H benzotriazole (5MBTA)

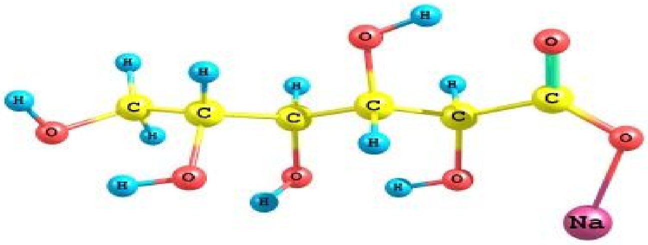

Fig .2 Sodium gluconate (SG)

2.2 Weight loss method

Weight-loss measurements were carried out using brass specimen of size 4 cm x 1 cm 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.

2.3 Potentiodynamic polarization study

The potentiodynamic polarization studies were carried out with brass strips having anexposed 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 referenceelectrode 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 hour[10-1]. 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.

2.4 Electrochemical AC impedance studies

AC impedance measurements were conducted at room temperature in the frequency range[11-2] of 100 kHz to 1 mHz and the results were analysed.

2.4. Scanning electron microscope (SEM)

Surface examination[12] of brass specimens were carried out to examine the surface morphology of brass in 3% NaCl solution in the presence and absence of inhibitor using JEOL-Scanning electron microscope model JSM6309.

III. RESULTS AND DISCUSSION

3.1 Analysis of the results of weight–loss method

The corrosion rates (CR) and the inhibition efficiencies (IE) calculated for brass in 3% NaCl solution with and without and different concentration of sodium gluconate (SG) at 303K, for 24 hrs time of immersion, at pH 7 by weight-loss method are given in Table 1. It is found that SG shows a slight IE 21% even at 350 ppm concentration. Table 2 shows the enhanced synergistic influence of SG with the inhibitor 5MBTA in controlling corrosion of Brass in aqueous environment at pH 7.

Table 1. CR and IE for various concentration of SG for the corrosion of brass in 3% NaCl obtained by weight loss method at room temperature, pH : 7, period of immersion : 24 hrs

Conc. of SG (ppm)	Corrosion rate (mpy)	Inhibition Efficiency (%)
0	0.395	--
150	0.349	12
200	0.340	14
250	0.325	18
300	0.315	20
350	**0.311**	**21**
400	0.345	13
450	0.338	14

It is observed from the Table 1, SG shows the maximum inhibition efficiency of 21% at 350 ppm concentration. The same methodology and environment is carried out for various concentration of SG with 150 ppm of 5MBTA and is in Table 2. It shows 87% for 350 ppm of SG + 150 ppm 5MBTA. The CR decreases and IE increases with increase in concentration of inhibitor system and is shown in Fig.1. This reveals the combined influence of SG (21%) on 5MBTA 150 ppm (71%). Thus a synergistic effect of SG proves that the inhibitive film may consist of complex of 5MBTA+SG with brass surface.

Table 2. CR and IE for various concentration of 5MBAT+SG for the corrosion of brass in 3% NaCl obtained by weight loss method at room temperature, pH : 7, period of immersion : 24 hrs

Conc. of 5MBTA (ppm)	Conc. of SG (ppm)	Corrosion Rate (mpy)	Surface Coverage (θ)	Inhibition Efficiency %
0	0	0.395	-	-
150	0	0.113	0.714	71
150	150	0.102	0.742	74
150	200	0.090	0.772	77
150	250	0.079	0.800	80
150	300	0.065	0.835	83
150	**350**	**0.050**	**0.873**	**87**
150	400	0.078	0.803	80
150	450	0.094	0.762	76

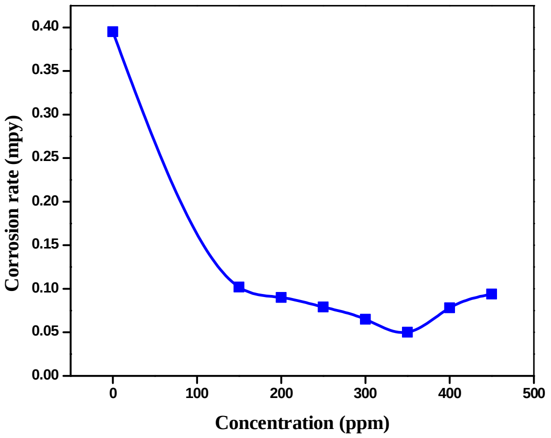

Fig.1 Plot of corrosion rate with various concentration of the inhibitor system 5MBTA+SG

3.2 Influence of duration of immersion on the inhibition efficiency of 5MBTA+SG

The influence of different concentration of SG with optimum concentration (150ppm) of 5MBTA on brass at different time intervals of 24, 48, 72, 96 and 120 hrs is studied in 3% NaCl environment given in Table 8.3.

Table 8.3. CR and IE for various concentration of 5MBTA+SG for the corrosion of brass in 3% NaCl obtained by weight loss method, at room temperature, pH : 7, period of immersion : 24, 48, 72, 96, 120hrs

Conc. of 5MBTA (ppm)	Conc. of SG (ppm)	Effect of Immersion Time on IE and CR									
		24 hrs		48 hrs		72 hrs		96 hrs		120 hrs	
		CR (mpy)	IE %	CR (mpy)	IE %	CR (mpy)	IE %	CR (mpy)	IE %	CR (mpy)	IE %
0	0	0.395	-	0.424	-	0.455	-	0.489	-	0.510	-
150	150	0.102	74	0.103	76	0.091	80	0.086	82	0.077	85
150	200	0.090	77	0.083	80	0.071	85	0.068	86	0.056	89
150	250	0.079	80	0.075	82	0.055	88	0.047	90	0.044	91
150	300	0.065	83	0.056	87	0.044	90	0.034	93	0.030	94
150	**350**	**0.050**	**87**	**0.046**	**90**	**0.037**	**92**	**0.029**	**94**	**0.023**	**95**
150	400	0.078	80	0.066	84	0.050	89	0.047	90	0.054	91
150	450	0.094	76	0.093	78	0.076	83	0.062	87	0.057	89

Fig.2 shows the inhibition efficiency with concentration of inhibitor system 5MBTA+SG. From this Table 8.3, it is shown that the IE increases with time. The system (5MBTA+SG) shows 95% IE even upto 120 hrs time of immersion (Table 3). In the presence of synergist SG, the exposure time and IE are increased due to the rich electron centre provided by the combined effect of SG and 5MBTA. Thus the synergist prolonged the IE of the inhibitor for longer time.

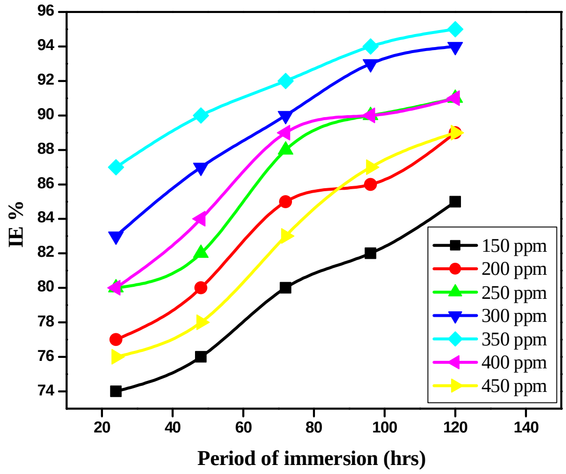

Fig 2 Plot between inhibition efficiency and period of immersion shows the effect of immersion time on IE of 5MBTA+SG

3.3 Influence of pH on 5MBTA+SG system

Effect of pH on the CR of brass in 3% NaCl solution and in the presence of various concentration of SG with optimum concentration (150 ppm) of 5MBTA was studied in the pH range of 4, 5, 9,10 using weight loss method (Table 4). It is seen from the Table 4 that at pH 7, the system of 150 ppm 5MBTA+350ppm SG has 87% IE. When pH is lowered to 4 ,5 by addition of acid, the IE decreased to 71% ,77% respectively. When pH is increased to 9, 10 by addition of NaOH, IE increased to 89% , 91% respectively. Fig 3 shows that when pH of the solution increases, IE of inhibitor increases.

Table 4. CR and IE for various concentration of 5MBTA+SG for the corrosion of brass in 3% NaCl obtained by weight loss method, at room temperature, pH : 4,5,9,10 , period of immersion : 24hrs

Conc. of 5MBTA (ppm)	Conc. of SG (ppm)	pH									
		4		5		7		9		10	
		CR (mpy)	IE %	CR (mpy)	IE %	CR (mpy)	IE %	CR (mpy)	IE%	CR (mpy)	IE %
0	0	0.845		0.676		0.395	-	0.338		0.282	
150	150	0.291	65	0.225	67	0.102	74	0.072	79	0.050	82
150	200	0.282	67	0.208	69	0.090	77	0.056	83	0.047	85
150	250	0.273	68	0.188	72	0.079	80	0.050	85	0.036	87
150	300	0.262	69	0.169	75	0.065	83	0.043	87	0.031	89
150	**350**	**0.248**	**71**	**0.153**	**77**	**0.050**	**87**	**0.037**	**89**	**0.026**	**91**
150	400	0.266	69	0.169	75	0.078	80	0.049	86	0.038	87
150	450	0.282	67	0.180	73	0.094	76	0.058	83	0.047	85

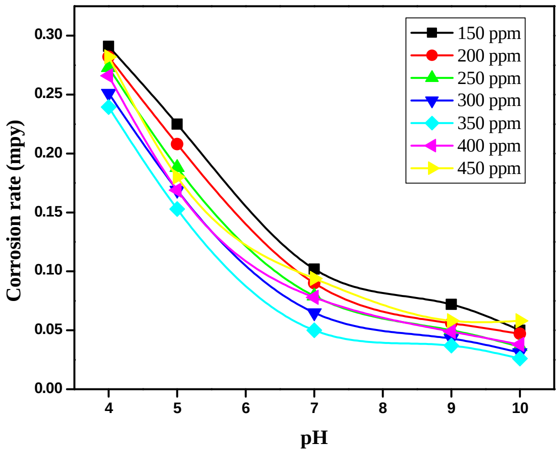

Fig.3 Plot between corrosion rate with pH level

In acidic pH environment (4,5), dissolution of brass is high and in alkaline pH (9,10) the metal surface is inhibited by 5MBTA+SG complex contains film on the brass surface. It is observed that in acidic[13-16] medium, IE decreases due to metal dissolution. However in alkaline medium, dezincified zinc ions present in the system is converted into $Zn(OH)_2$ which carries more and more of inhibitor from solution phase to metal surface. Hence IE increases in alkaline medium. This analysis reveals that in neutral and in alkaline medium 5MBTA+SG show good IE.

3.4 Synergism parameters (S_I)

The synergism parameters[17-19] for the inhibitor system (5MBTA + SG) calculated by equation no(7) are given in Table 5. It can be seen from Table 5, the values of synergism parameters of investigated compound are greater than unity[17], which suggests that the enhanced IE is caused by the addition of SG to 5MBTA mainly due to the synergistic effect.

Table 5 Synergism parameters of 5MBTA+SG inhibitor system

Conc. of SG (ppm)	IE (%) I_1	Conc. of 5MBTA (ppm)	IE (%) I_2	Combined IE I'_{1+2}	Synergism, S_I
250	11	150	71	74	27.8082
300	14	150	71	77	24.8684
350	18	150	71	80	17.7215
400	21	150	71	83	13.6585
450	20	150	71	87	9.7674
500	13	150	71	80	7.9747
550	14	150	71	76	4.6667

3.5 Analysis of F-Test

Analysis of variance has been used to establish whether the synergistic effect existing between two inhibitor systems is statistically significant[18]. The F-value calculated for 5MBTA-+SG system is 19.8 (Table 6). This is greater than the critical

F-value (4.74) for 1,12 degrees of freedom at 0.05 level of significance. Hence it is concluded that the synergistic effect exist between 5MBTA+SG is statistically significant.

Table 6 Distribution of F-value between the inhibition efficiencies of 5MBTA and 5MBTA+SG systems

Source of variance	Sum of squares	Degree of Freedom	Mean square	F Value	Level of significance of F
Between	4500	1	4500	19.8	$p>0.05$
Within samples	2727	12	227		

3.6 Adsorption isotherm

The adsorption depends on the chemical structure of the inhibitor, chemical composition of the solution, nature of the metal surface, temperature and electrochemical potential at the metal – solution interface. The values of surface coverage (θ) corresponding to different concentrations of inhibitors are used to obtain the best adsorption isotherm. Data are tested graphically by fitting to various isotherms namely Tempkin, Flory-Huggin. The plot of C/θ against the inhibitor concentration C yields a straight line (Fig.4) with correlation coefficient equal to unity and a slope is equal to 1. The linear regressions are calculated, and the parameters are given in Table 7. The strong correlation shows that 5MBTA+SG is adsorbed on the brass surface according to langmuir isotherm[19]. It indicates that adsorption of 5MBTA+SG obeys the Langmuir adsorption isotherm.

Table 7 Parameters of the linear regression between log C/θ and logC

Linear correlation coefficient (R)	K	SLOPE
0.93512	0.2575	1.0095

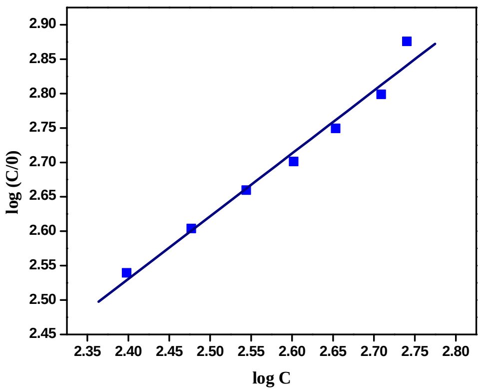

Fig 4 Langmuir adsorption isotherm for the inhibitor system consisting of 5MBTA+SG in 3% NaCl

3.7 Analysis of potentiostatic polarisation study

The corrosion parameters of brass in various test solutions are given in Table 8. The polarization curves are shown in Fig.5. When brass is immersed in NaCl, the corrosion potential for blank solution is -232 mV vs SCE and is shifted to -255 mV vs SCE with 5MBTA+SG. Potential change in such a case is smaller and its direction is determined by the relative size of the anodic and cathodic effects. The values of anodic Tafel slope b_a and cathodic Tafel slope b_c are found to change with inhibitor concentration from 112 mV/dec to 109 mV /dec and 192 mv/dec to 195mV /dec respectively. I_{corr} value is decreased from 7.34 µA / cm^2 (blank solution) to 1.068 µA / cm^2 indicate the inhibitive effect of this formulation.

This shows that this formulation functions as a mixed inhibitor in controlling anodic and cathodic reaction almost equally. The mixed nature of inhibitor can be explained in terms of a change in E_{corr} values in presence of inhibitor. If the displacement of E_{corr} value in presence of inhibitor is more than ±85 mV/SCE related to E_{corr} of blank, the inhibitor can be considered as cathodic and anodic[20].

Table 8. Electrochemical parameters and inhibition efficiency of brass in 3% NaCl solution containing optimum concentration of 5MBTA+SG

Conc. of inhibitor (ppm)	I_{corr} (µAcm^{-2})	E_{corr} (mV/SCE)	b_a (mV/dec)	b_c (mV/dec)	Corrosion rate (mpy)	Inhibition Efficiency (%)
Blank	7.34	-232	112	192	3.6532	-
150 ppm 5MBTA +350 ppm SG	1.068	-255	109	195	1.0680	**85**

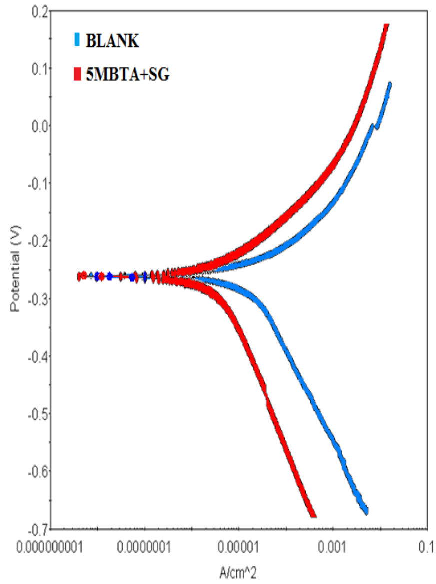

Fig.5 Polarization for brass in 3% NaCl containing 5MBTA+SG

If the change in E_{corr} is less than ±85mV/SCE[21], the corrosion inhibitor may be considered as a mixed type inhibitor. The maximum displacement in the present investigation is 23 mV/SCE which indicates 5MBTA+SG act as mixed type inhibitor. The CR and IE are calculated from I_{corr} values. CR is decreased from 3.653 to 1.068 and IE of (150ppm of 5MBTA+350 ppm of SG) system attained a value 85% which indicates that a higher surface coverage is obtained in a solution with the optimum concentration of inhibitor. The inhibition efficiency calculated from polarization study is 85% and is an excellent agreement with the value (87%) obtained from weight loss measurement. The slight variation in value is due to the long exposure of brass specimen in weight loss measurement but in electrochemical study is instantaneous.

3.8 Analysis of the results of AC impedance spectra

Nyquist plots of brass in inhibited (3% NaCl) and uninhibited solution of (150 ppm 5MBTA+350 ppm SG + 3%NaCl) are shown in Fig 6

The AC impedance parameters calculated for brass immersed in various test solutions and percentage of inhibition efficiency (IE%) of corrosion of brass is calculated[22] are given in Table 9. When brass is immersed in an aqueous solution containing 3% NaCl, the charge transfer resistance (R_{ct}) is found to be 4990 Ω and the double layer capacitance (C_{dl}) is found to be 154 µF/cm^2. When inhibitor solution, namely 150 ppm of 5MBTA+ 350 ppm of SG is added to the above solution, the R_{ct} value increases from 4990 Ω to 35636

Ω and the C_{dl} value decreases from 154 µF/cm^2 to 65 µF/ cm^2. The data obtained (Table 9) from the EIS shows the compared values of the R_{ct} and the corresponding percentage of inhibition efficiency 86% confirms the good protection. Thus AC impedance spectra of the present study reveal that a protective film is formed on the brass surface. The IE calculated from R_{ct} value is 86% and is in good agreement with potentiostatic polarization (85%) and mass loss method (87%). It indicates that the corrosion of brass is mainly controlled by charge transfer process[23].

Table 9 Impedance measurements and inhibition efficiency of brass in 3% NaCl solution containing optimum concentration of 5MBTA+SG

Conc. of Inhibitor (ppm)	R_{ct} (Ω cm^2)	C_{dl} µF/cm^{-2}	Inhibition Efficiency (%)
Blank	4990	154	-
150 ppm 5MBTA + 350 ppmSG	35636	65	**86**

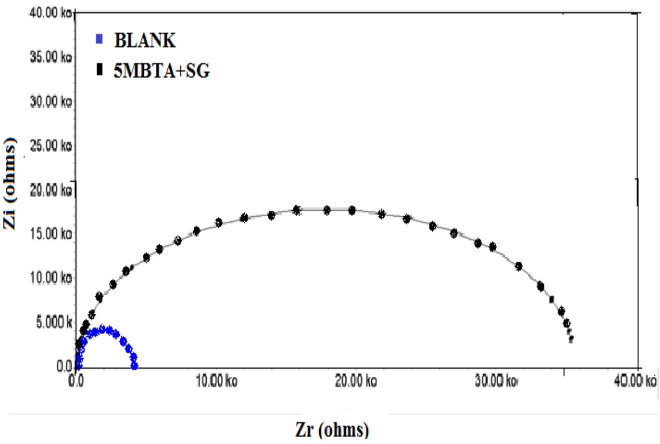

Fig.6 Nyquist plots of brass in 3% NaCl containing 5MBTA+SG

3.9 Scanning Electron Microscopy

Surface examination using SEM was carried out to study the effect of inhibitor (150ppm 5MBTA+350 ppm SG) on the surface morphology of brass Fig 7.a shows SEM image of brass surface after immersion in 3%NaCl solution without inhibitor.

It shows pits on the whole surface of the sample. In Fig.7.b, the surface is smoother than blank surface indicating a protective layer of adsorbed inhibitor preventing corrosion attack[24-25].

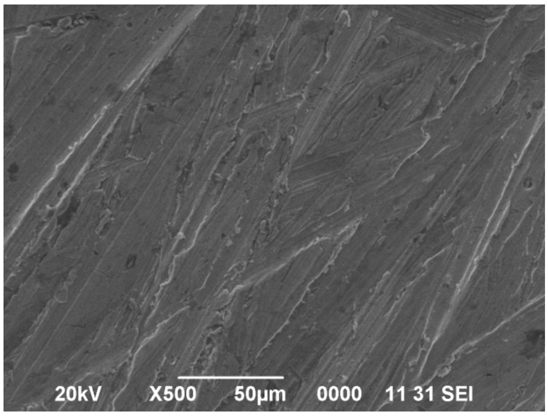

Fig.7.a BLANK

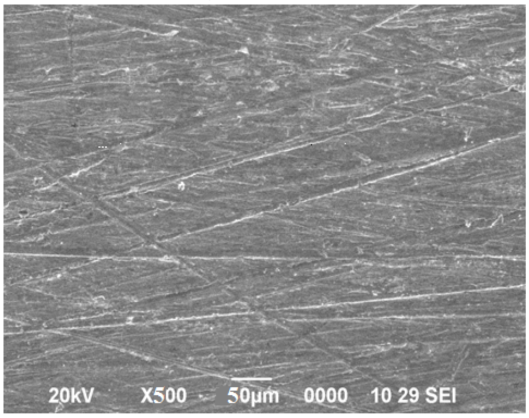

Fig.7.b (5MBTA+SG)

Fig.7.a-b Scanning electron microscopy photographs in the absence and
presence of inhibitor 5MBTA+SG

3.10 Analysis of Energy dispersive X-ray analysis (EDAX)

EDAX spectrum of brass in 3% NaCl solution in the presence and absence of optimum concentration of inhibitor (150 ppm 5MBTA+350 ppm SG) are shown in Fig 8.a-b. From these Figures, it is observed that the intensity of Cu and Zn peak are considerably increased while chloride ion peak is reduced in the presence of inhibitor which is also reflected in values of surface composition of brass.

The surface composition (wt%) of the alloy in the presence and absence of inhibitor obtained from the spectra is presented in the Table 10. In the absence of inhibitor, the weight percentage (wt%) of Cu (57.86%) and Zn (24.82 %) in brass are reduced due to the leaching of ions in 3% NaCl solution. Moreover, the higher concentration of chloride ions (17.02) on the surface shows penetration of Cl^- ions into the alloy. However, in the presence of 5MBTA+SG, the (wt%) of Cu (64.89%) and Zn (33.57%) is closer to the bulk composition of the alloy. This observation proves that the inhibitor is strongly adsorbed on the brass surface and thus rapidly reacts with the metal ions on or around the brass surface forming insoluble and tightly adherent brass – inhibitor complex[26]. These complexes protect the active sites at the brass surface from aggressive chloride ions. Thus, the corrosion of brass in 3% NaCl solution containing inhibitor (150 ppm 5MBTA+350 ppm SG) is strongly inhibited and thus effectively controls the corrosion of brass in sodium chloride solution.

Table 10. EDAX data for surface composition of brass in 3%NaCl with the optimum concentration of 5MBTA+SG

Experimental system	Cu %	Zn %	Cl%
Alloy	65.3	34.4	-
Blank	57.86	24.82	17.02
5MBTA+SG	64.89	33.57	1.24

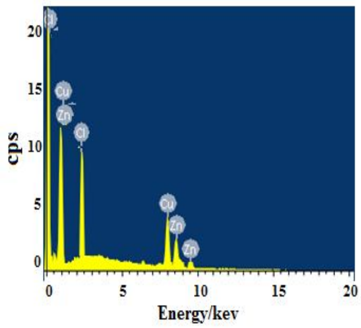

Fig.8.15.a Blank

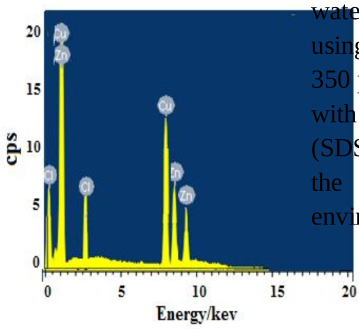

Fig.8.15.b 5MBTA + SG

Fig.8.a-b EDAX spectra for brass in 3% NaCl in the absence and presence of inhibitor 5MBTA+SG

IV. CONCLUSION

- Results of the weight-loss method reveal that the formulation consisting of 150 ppm of 5MBTA and 350 ppm of SG as synergist offers accompanied inhibition efficiency of 87% for 24 hrs time of immersion at 303K and at pH 7.
- The inhibition efficiency for 5MBTA+SG is found to increase with increasing concentration, pH. The inhibition efficiency is found to increase (95%) with period of immersion upto 120 hrs at room temperature level.
- Statistical analysis (ANOVA) showed that the variation of inhibition efficiency of (5MBTA+SG) in 3% NaCl is significant at 5% level.
- Polarization study reveals that this formulation functions as a mixed inhibitor.
- AC impedance spectra reveal the presence of a protective film on the brass surface.
- SEM micrographs of brass specimen show that the inhibitor molecule forms a good protective film on the brass surface.
- EDAX mapping of brass immersed in 3% NaCl with inhibitor system proves that very low amount of copper and zinc ions are leached out from brass which is revealed by the low intensity of Cu and Zn peak in the spectrum, that is due to the formation of an insoluble stable film through the process of complexation of 5MBTA+SG.
- It is concluded that SG acts as a good synergist along with 5MBTA for inhibiting the corrosion of brass in 3%NaCl medium.
- Synergism parameter also confirms this conclusion.

Based on these investigation, the synergistic inhibitive action of SG along with 5MBTA on the corrosion inhibition of brass in 3% NaCl usually encountered in cooling water systems has 87% inhibition efficiency achieved by using the formulation consisting of 150 ppm of 5MBTA + 350 ppm of SG for 24hrs period of immersion at pH 7. Along with this formulation of inhibitor, cationic (CPC) and anionic (SDS) surfactants has 100% biocidal efficiency, which show the ability to destroy microbial bacteria in aqueous environment.

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