

INFLUENCE OF BIOCIDES ON CORROSION INHIBITION EFFICIENCIES OF INHIBITOR SYSTEM ON BRASS IN NEUTRAL MEDIUM

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ABSTRACT

The inhibition efficiencies of sodium potassium tartrate(SPT) ,5-methyl 1-H benzotriazole(5MBTA) system on brass in 3% NaCl solution have been assessed. The inhibition efficiencies and biocidal efficiencies of biocides namely cetyl pyridinium chloride (CPC), sodium dodecyl sulphate (SDS) on inhibitor (SPT-5MBTA) system are studied. On comparing the biocidal efficiency of the biocides, CPC is found to be the best among the two biocides which controls the growth of microbes in the solution.

KEY WORDS: Brass, synergistic effect, ANOVA test, SEM, XRD, biocidal efficiency.

1. INTRODUCTION

Brass is widely used in industry especially in heating cooling systems because of their high thermal and electrical conductivities^[1,2]. However, as the zinc content of brass increases, the corrosion rate of the alloy is observed to show a marked increase due to the preferential dissolution of zinc from brass; such phenomenon is termed as dezincification.^[3,4] Recently many methods have been developed aiming to reduce the rate of dezincification of brass involving the use of some inhibitors; e.g., benzotriazole derivatives^[5,6] or development of novel brasses to resist dezincification^[7].

Furthermore, the foremost problems in cooling systems are not only corrosion but scaling or encrustation and biological fouling phenomena as well. which involves deterioration of metallic surfaces by the aggressive medium, decreases thermal efficiency exchange and microbiologically influenced corrosion (MIC) called also biocorrosion. These processes, occurring simultaneously, greatly affect the normal industrial production and have numerous economic impacts. Thus this issue has become a significant area of scientific and technological research.

To overcome the above shortcomings, literature reports point out that microorganisms tend to attach themselves onto surface, colonize, and proliferate to form a biofilm. The biofilm induces changes in the electrochemical conditions at the metal/ medium interface, and thereby microorganisms can easily accelerate corrosion. The use of quaternary ammonium compounds (surfactants) as non-oxidizing biocides has proven efficacy and performance in microbial control for various industrial applications^[8]. The antimicrobial effect is a function of the N-alkyl chain length, which confers lipophilicity^[9]. Moreover, it is well

known that the antimicrobial activity involves an association between the positively charged quaternary nitrogen of biocide and the negatively charged head groups of acidic phospholipids in bacterial membranes^[10]. These biocides are effective at low concentration, stable, and fast-acting in the inhibition of microbial growth and metabolism, aside being capable of controlling biofilm development.

The hydrocarbon chains align themselves to form an inner hydrophobic part while the polar head groups are located at the hydrocarbon-water interface. Depending on the nature of the head group these aggregates can be cationic, anionic and nonionic.

Surfactants have also been used as corrosion inhibitors^[11,12] or in combination with other compounds such as azoles^[13], organophosphonates^[14], trans-cinnamaldehyde^[15] and 1-phenyl-2-propyne-1-ol^[16] to enhance their performance as inhibitors.

The addition of organic and inorganic compounds to inhibitor mixture increases the corrosion inhibition efficiency by combined effect and also reduces the requirement of azoles and metal cations^[17]. Gunasekaran^[18] et al., studied enhancement of corrosion inhibition efficiency of 2-carboxy ethyl phosphonic acid (2CEPA) + Zn²⁺ system on mild steel from 40% to 96% by the addition of tartrate ions as an organic synergist in neutral aqueous system.

The present work is undertaken to evaluate effect of sodium potassium tartrate (SPT) and of 5-methyl 1-H benzotriazole (5MBTA) on the corrosion inhibition of brass in aqueous environment by weight-loss,

electrochemical methods and also to calculate the biocidal efficiency of cationic surfactant N-cetylpyridiniumchloride[19,20,] (CPC) and anionic surfactant sodium dodecyl sulphate^[21] (SDS), in controlling corrosion of brass immersed in 3% NaCl solution containing of sodium potassium tartrate (SPT) and 5-methyl 1-H benzotriazole (5MBTA) inhibitor solution using zobell medium and calculating the number of colony forming units per ml using a bacterial colony counter. Brass surface are analyzed by SEM, XRD.

2. 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.1 and the structure of SPT is given in Fig.2.

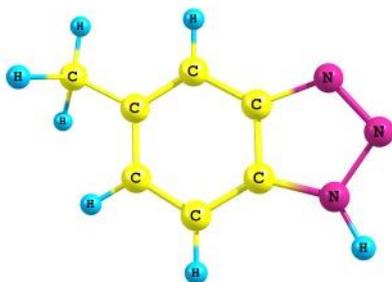


Fig. 1: 5-methyl 1-H benzotriazole(5MBTA).

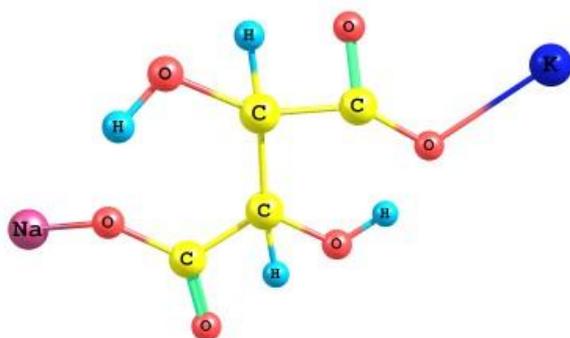


Fig. 2: Sodium potassium tartrate (SPT).

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. Determination of corrosion rate

The corrosion rates were calculated using the following relationship^[22]:

$$CR = \frac{534.W}{D.A.T}$$

where the corrosion rate (CR) is expressed in mpy units (mpy= mills per year), W is weight Loss in mgs, D is Density, A is Surface Area in square inch and T is Time in hrs.

2.4. Efficiency of Inhibitor

Corrosion inhibition efficiency (IE.) was then calculated using the equation^[23]:

$$IE \% = \frac{CR_0 - CR_{inh}}{CR_0} * 100$$

where CR_0 is corrosion rate in the absence of inhibitor and CR_{inh} is corrosion rate in the presence of inhibitor.

2.5 Scanning electron microscope (SEM)

Surface examination^[24] 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.

2.6 Surface analysis by X-ray diffraction (XRD)

The XRD[25] patterns were recorded by using a computer controlled X-ray powder diffractometer XRD-6000 (Shimadzu) operated at a voltage of 40 kV and a current of 30 mA with Cu $K\alpha$ radiation. The spectral datas are correlated with the use of software JCPD 25-0322.

2.7 Preparation of Zobell medium

Zobell medium^[26] was prepared by dissolving 5 g of peptone, 1 g of yeast extract, 0.1 g of potassium dihydrogen phosphate and 15 g of agar-agar in 1 liter of double distilled water. The medium was sterilized by applying 15 pounds per square inch for 15 minutes in an autoclave.

2.8 Determination of biocidal efficiency of the system

The biocidal efficiency of SPT+5MBTA formulation that offered the best corrosion inhibition efficiency was selected. The biocidal efficiencies of CPC and SDS in the presence and absence of the inhibitor formulation and also the effect of the biocides on the corrosion inhibition efficiency of SPT+5MBTA were determined. The biocidal efficiencies (BE) of the biocides at various concentrations in the presence and absence of the inhibitor system SPT+5MBTA were determined after immersing the specimens for 120hrs in test solutions. Inhibitor system that offered the best corrosion inhibition efficiency was selected. After 5 days, one ml each of test solutions from environments was pipetted out into sterile petri dishes each containing about 20 ml of the sterilized zobell medium. The petri dishes were then kept in a sterilized environment inside the laminar flow system fabricated and supplied by CEERI- Pilani, for 24 hrs. The total viable heterotropic bacterial colonies were counted using a bacterial colony counter.

3. RESULTS AND DISCUSSION

3.1 Analysis of the results of weight-loss method

The calculated value of corrosion rates (CR) and inhibition efficiencies (IE) of brass in 3% NaCl solution with and without different concentration of sodium potassium tartrate (SPT) for 24 hrs immersion, at 303 K, at pH 7 by weight-loss method are given in Table 1. The corresponding IE is also displayed as a function of inhibitor concentration in Fig. 3. It is observed from the Table 1, SPT shows the maximum inhibition efficiency of 29% at 400 ppm concentration. Further increase of

SPT concentration shows less IE. Table 2 shows that 400 ppm of SPT with 150 ppm of 5MBTA in the same environment shows 88%. It is evident from Fig. 3, Fig. 4.

This reveals the combined influence of SPT on 5MBTA. Thus a synergistic effect of SPT proves that the inhibitive film may consist of complex on brass surface. Further 5MBTA forms insoluble, inhibitive and adsorptive complexes with SPT, as a result corrosion is controlled by the formation of complex between inhibitor- brass surface.

Table 1: Corrosion rate and inhibition efficiency of SPT for the corrosion of brass in 3% NaCl.

Conc. of SPT (ppm)	Corrosion rate (mpy)	Inhibition Efficiency (%)
0	0.395	-
200	0.350	11
250	0.335	15
300	0.325	18
350	0.315	20
400	0.282	29
450	0.331	16
500	0.338	14

Table 2: Corrosion rate and inhibition efficiency of (5MBTA+SPT) for corrosion of brass in 3% NaCl.

Conc. of 5MBTA (ppm)	Conc. of SPT (ppm)	Corrosion Rate (mpy)	Inhibition Efficiency %
0	0	0.395	-
150	0	0.113	71
150	200	0.100	74
150	250	0.084	78
150	300	0.071	82
150	350	0.058	85
150	400	0.046	88
150	450	0.098	75
150	500	0.110	72

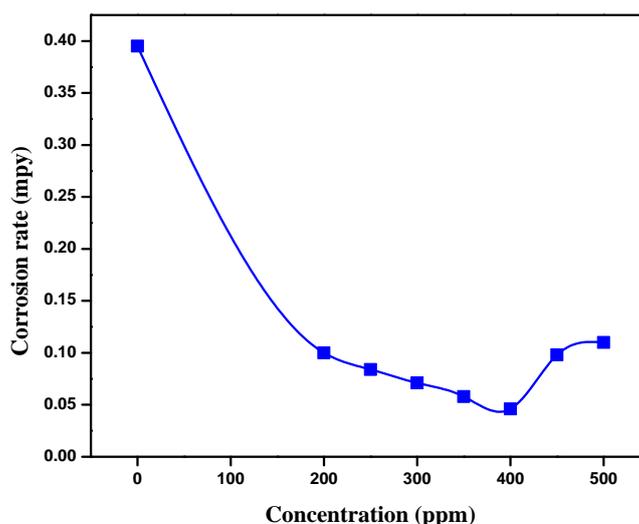


Fig. 3: Plot of corrosion rate with various concentration of the inhibitor system 5MBTA+SPT.

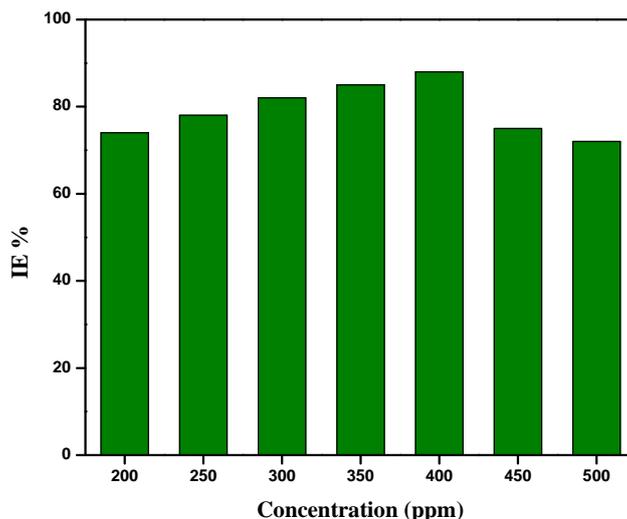


Fig.4 Plot of inhibition efficiency with various concentration of inhibitor 5MBTA+SPT.

3.2 Synergism parameters (S_I)

Synergism parameters have been used to confirm the synergistic effect existing between two inhibitor system^[27]. The synergism parameters calculated for the corrosion inhibitor system of 5MBTA+SPT on brass are

given in Table 3. The synergism parameters (S_I) calculated from surface coverage are found to be more than unity^[28]. This result clearly shows the synergistic effect between 5MBTA and SPT.

Table 3: Synergism parameters (S_I) of (5MBTA +SPT) inhibitor system.

Conc. of SPT (ppm)	IE (%) I_1	Conc. of 5MBTA (ppm)	I.E. (%) I_2	Combined I.E. I'_{1+2}	Synergism, S_I
200	11	150	71	74	41.80
250	18	150	71	78	34.53
300	20	150	71	82	21.41
350	15	150	71	85	14.94
400	16	150	71	88	13.33
450	29	150	71	75	6.12
500	14	150	71	75	3.88

3.3 Analysis of F-Test (ANOVA test)

Analysis of variance has been used to establish whether the synergistic effect existing between two inhibitor systems is statistically significant or not^[27,28]. The F-value calculated for 5MBTA-SPT system is 19 (Table 4).

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 exists between 5MBTA and SPT is statistically significant.

Table 4: Distribution of F-value between the inhibition efficiencies of 5MBTA and 5MBTA+SPT system.

Source of variance	Sum of squares	Degree of Freedom	Mean square	F Value	Level of significance of F
Between	4393	1	4393	19	$p > 0.05$
With in samples	2826	12	236		

3.4 Scanning Electron Microscopy

SEM micrographs of brass specimen exposed to 3% NaCl solution with and without optimum concentration of inhibitor (150ppm 5MBTA+400 ppm SPT) is given in Fig.5.a,b shows that brass surface is damaged in absence of inhibitor.

It shows pits on the whole surface of the sample. In Fig.5.a,b the surface is free from pits^[29], the surface of the brass remains smooth and bright, with accumulation of inhibitor over the brass surface^[30]. The accumulation of these particles over the surface provides better corrosion resistance.

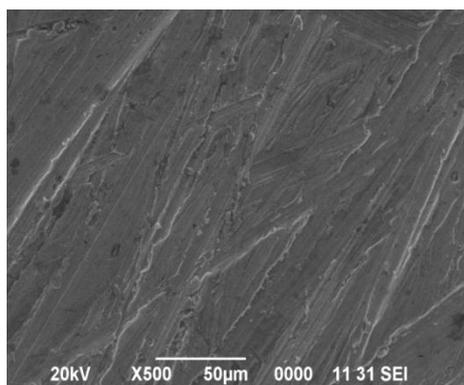


Fig.5.a BLANK

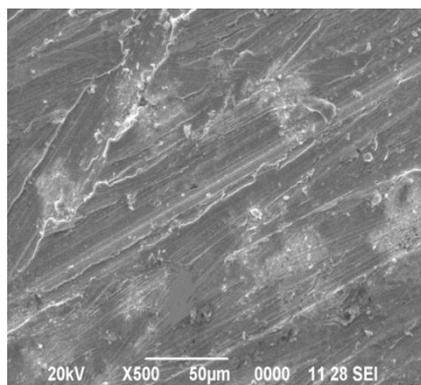


Fig.5.b (5MBTA+SPT)

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

3.5 Analysis of the X-ray diffraction patterns

The X-ray diffraction (XRD) patterns of the films formed on the surfaces of the brass immersed in various solutions are given in Fig.6,7. The various diffraction parameters such as the glancing angle (2θ), the interplanar spacing (d), intensity of the peaks (I) and relative intensities of the peaks (I/I_0) are given in Table 5.

The peaks due to the presence of usual corrosion products namely ZnO, CuCl and the shift of these peaks in the inhibitor systems are shown clearly in these figures. XRD pattern for brass immersed in 3% NaCl solution is shown in Fig. 6. The peaks due to CuCl appear^[7] at $2\theta = 31.13^\circ$, ZnO appear^[31] at $2\theta = 36.13^\circ, 47.20^\circ$ and 62.35° in addition to brass peaks at 42.97° and 49.70° . This indicates that in the chloride

environment, brass specimen has undergone corrosion due to the aggressive chloride ions leading to the formation of corrosion products.

The XRD pattern of surface of the brass immersed 3% NaCl solution containing 150 ppm 5MBTA+400 ppm SPT is shown in Fig.7. The peaks at $2\theta = 35.01^\circ, 37.92^\circ, 42.76^\circ, 43.80^\circ, 49.40^\circ, 62.09^\circ, 72.60^\circ$ and 79.32° match with standard peaks for brass taken from JCPD 25-0322. The peaks due to corrosive product $36.13^\circ, 47.20^\circ$ and 62.35° are shifted to $35.01^\circ, 49.40^\circ$ and 62.09° values because of inhibitive thin film^[32,33] formation of 5MBTA+SPT on the brass surface. The XRD pattern reveals that shifted values may due to the complexation reaction takes place between the brass surface and the inhibitor formulation.

Table 5: XRD pattern of brass surface immersed in various environment.

Experimental system	Peak No.	Glancing angle, 2θ , Degree	Interplanar Spacing d , Å	Intensity I, CPS	Relative Intensity, I/I_0
Blank	1	31.13	2.870	184	964
	2	36.13	2.484	285	1278
	3	42.97	2.103	464	4269
	4	47.20	1.924	29	179
	5	49.70	1.833	34	470
	6	62.35	1.488	734	9310
150 ppm 5MBTA + 400 ppm SPT	1	42.02	2.149	1010	5787
	2	43.03	2.100	770	5671
	3	49.90	1.826	32	233
	4	62.37	1.488	680	6281
	5	72.60	1.301	30	514
	6	79.70	1.202	70	385
	7	86.30	1.119	136	1043

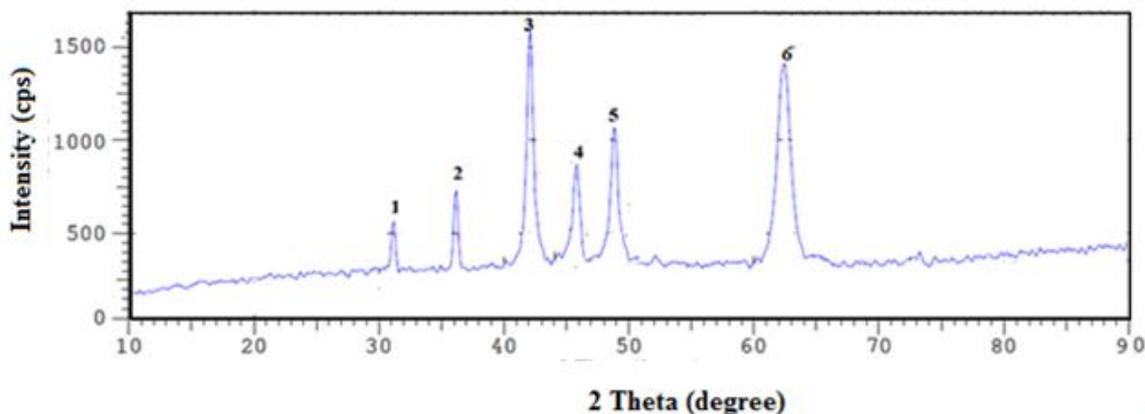


Fig. 6: XRD patterns of brass surface immersed in 3% NaCl.

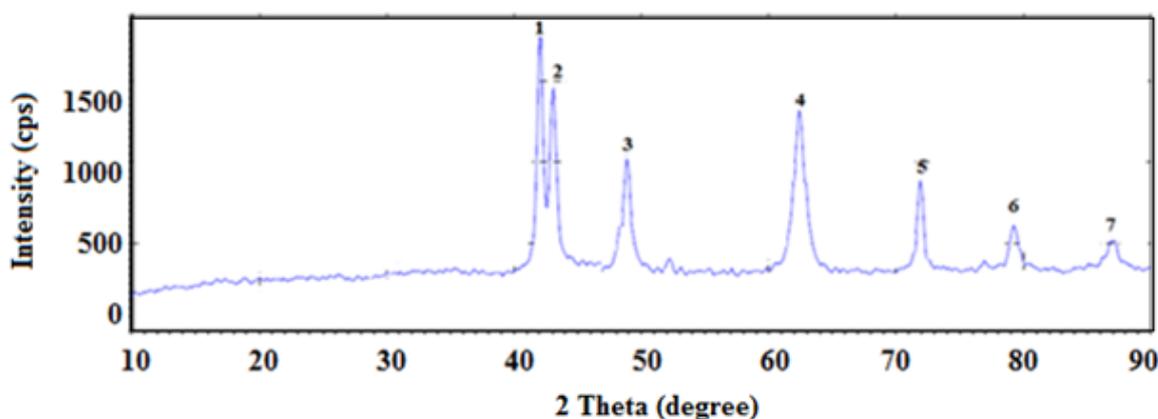


Fig. 7: XRD patterns of brass surface immersed in 3% NaCl containing 5MBTA+SPT.

3.6 Effect of CPC on the inhibition efficiency of 5MBTA+SPT system

The formulation consisting of 150 ppm 5MBTA+400 ppm SPT offers IE of 88% to the brass specimen immersed in 3% NaCl for 24 hrs solution is discussed under section 3.1. The CR and IE of brass in 3% NaCl solution containing 150 ppm 5MBTA+ 400 ppm SPT with various concentration of CPC obtained by weight loss method are given in Table 6. IE are also shown as a function of the concentration of the biocide CPC in Fig.8.

It is observed from the Table 6 that the concentration of CPC increases, IE increases and attains a maximum of 98% and then decreases. Hence the best formulation for the mutual influence of CPC on IE of 5MBTA+SPT is 50 ppm CPC + 150 ppm 5MBTA+400 ppm SPT in 3% NaCl. A miscelle would have been formed at this concentration. This formulation may find application in cooling water system, tubular piping system where corrosion of the metal is caused by aggressive Cl^- ions and also by microorganism present in cooling water system.

Table 6: Influence of CPC on corrosion rate and inhibition efficiency of (5MBTA+SPT) for the corrosion of brass in 3% NaCl.

Conc. of 5MBTA (ppm)	Conc. of SPT (ppm)	Conc. of CPC (ppm)	Corrosion rate (mpy)	IE %
0	0	0	0.510	-
150	0	0	0.098	81
150	400	0	0.018	96
150	400	10	0.015	97
150	400	50	0.006	98
150	400	100	0.006	98
150	400	150	0.018	96
150	400	200	0.023	95
150	400	250	0.023	95

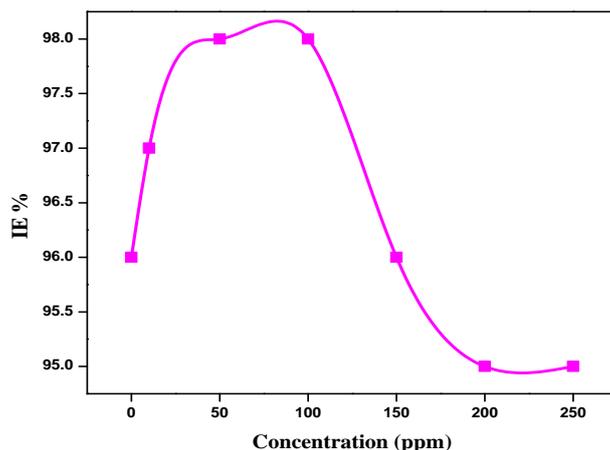


Fig.8 Effect of CPC on IE of 5MBTA+SPT

3.7 Effect of 5MBTA+SPT system on the biocidal efficiency of CPC

The influence of 5MBTA+SPT system on the biocidal efficiency of cationic surfactant CPC is given in Table 7. The number of colony forming units is shown in Fig.10 and the effect of concentration of CPC in the presence of 5MBTA+SPT system is shown in Fig. 9. When 10 ppm of CPC is added, the total number of bacterial count CFU/ml is 1×10^4 . When 50ppm of CPC is added, no bacteria count can be traced, which implies, the biocidal efficiency is 100% at the level. Hence, the optimum

concentration of CPC is ≥ 50 ppm. Thus it can be seen from the Table 6 that the formulation consisting of 150 ppm of 5MBTA+400 ppm of SPT+50 ppm of CPC has 100% biocidal efficiency. The 100% biocidal efficiency as evidenced by reported results prove that the cationic surfactant CPC along with other organic and inorganic inhibitors may be applied as an excellent biocide in cooling water systems. Aggregations of CPC with the inhibitors give resistance to the brass surface from microbial corrosion in neutral aqueous medium.

Table 7: Biocidal efficiencies of 5MBTA+SPT with various concentration of CPC.

Conc. of 5MBTA (ppm)	Conc. of SPT (ppm)	Conc. of CPC (ppm)	Colony Forming Units/ml (CFU/ml)	Biocidal Efficiency %
0	0	0	1×10^7	-
150	0	0	1×10^6	90
150	400	0	2.4×10^5	99
150	400	10	1.0×10^4	99
150	400	50	Nil	100
150	400	100	Nil	100
150	400	150	Nil	100
150	400	200	Nil	100
150	400	250	Nil	100

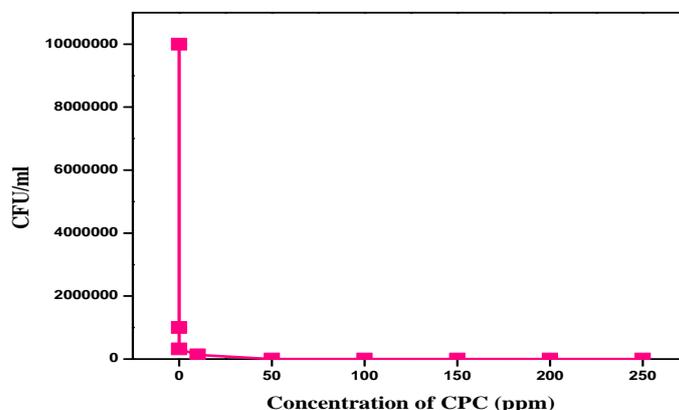


Fig.9 Biocidal Efficiency of CPC as a function of number of colony forming units in relating to concentration of biocide CPC

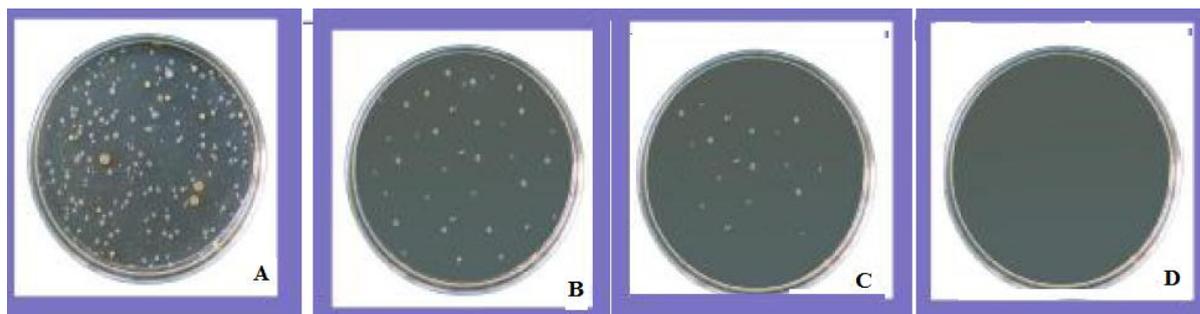


Fig.10 Bacterial colonies formed in various environments

(A-3%NaCl, B-150 ppm 5MBTA+400 ppm SPT in 3%NaCl, C-150 ppm 5MBTA+400 ppm SPT +10 ppm CPC in 3%NaCl, D-150 ppm 5MBTA+400 ppm SPT +50 ppm CPC in 3%NaCl)

3.8 Effect of SDS on the inhibition efficiency of 5MBTA+SPT system

The formulation consisting of 150 ppm 5MBTA-400 ppm SPT offers IE of 88% to the brass specimen immersed in 3% NaCl solution for 24 hrs is discussed under section 3.1. The CR and IE of brass in 3% NaCl solution containing inhibitor system (150 ppm 5MBTA+400 ppm SPT) with various concentration of SDS for 120 hrs, at 303K, at pH 7 obtained by weight loss method are given in Table 8. IE is also shown as a function of the concentration of the SDS in Fig.11.

It is observed from the Table 7 that the concentration of SDS increases, IE also increases upto 99% and then decreases. Hence the best formulation for the mutual influence of SDS on IE of 5MBTA is 50 SDS + 150 5MBTA +400 ppm SPT in 3% NaCl. A miscelle would have been formed at this concentration which prevents corrosion of metal^[34]. This formulation may find application in cooling water system, tubular piping system where corrosion of the metal is caused by aggressive Cl⁻ ions and also by microorganism present in cooling water system.

Table 8: Influence of SDS on corrosion rate and inhibition efficiency of (5MBTA+SPT) for the corrosion of brass in 3% NaCl

Conc.of 5MBTA (ppm)	Conc. of SPT (ppm)	Conc. of SDS (ppm)	CR (mpy)	IE%
0	0	0	0.510	-
150	0	0	0.098	81
150	400	0	0.035	96
150	400	10	0.012	98
150	400	50	0.006	99
150	400	100	0.006	99
150	400	150	0.006	99
150	400	200	0.018	97
150	400	250	0.030	94

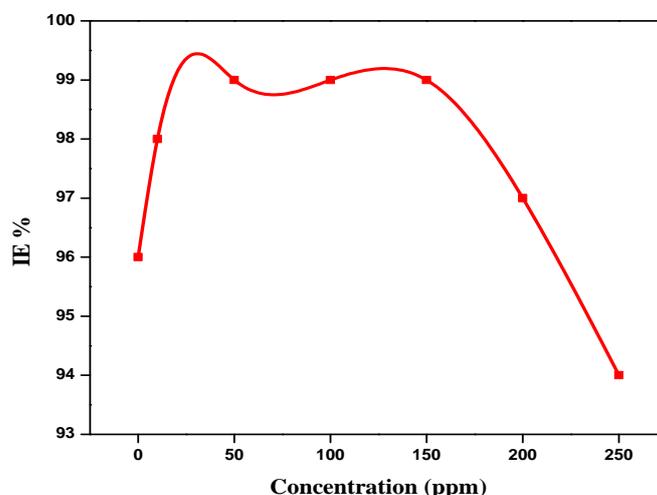


Fig.11 Effect of SDS on IE of 5MBTA+SPT.

3.9 Influence of 5MBTA+SPT system on the biocidal efficiency of SDS

The influence of 5MBTA+SPT system on the biocidal efficiency of SDS is shown in Table 9. The number of bacteria colony forming units as a function of concentration of SDS in the presence of 5MBTA+SPT system is shown in Fig.12. When 10 ppm of SDS is added, the total number of bacterial count CFU/ml is 2.6×10^4 . This is an unacceptable value in cooling water

systems. When 50 ppm of SDS is added, no bacterial colony is found, inferring the biocidal efficiency is 100%. Further, it is seen from the Table 8 that the formulation consisting of 150 ppm of 5MBTA+ 400 ppm of SPT+50 ppm of SDS in 3% NaCl solution shows 100% biocidal efficiency. This is due to the fact that at this concentration SDS aggregates with inhibitor system and inhibits (bio corrosion) microorganisms in the medium.

Table 9: Biocidal efficiencies of 5MBTA+SPT with various concentration of CPC.

Conc. of 5MBTA (ppm)	Conc. of SPT (ppm)	Conc. of SDS (ppm)	Colony Forming Units/ml (CFU/ml)	Biocidal Efficiency %
0	0	0	1×10^7	-
150	0	0	1×10^6	90
150	400	0	1.2×10^5	99
150	400	10	2.6×10^4	99
150	400	50	Nil	100
150	400	100	Nil	100
150	400	150	Nil	100
150	400	200	Nil	100
150	400	250	Nil	100

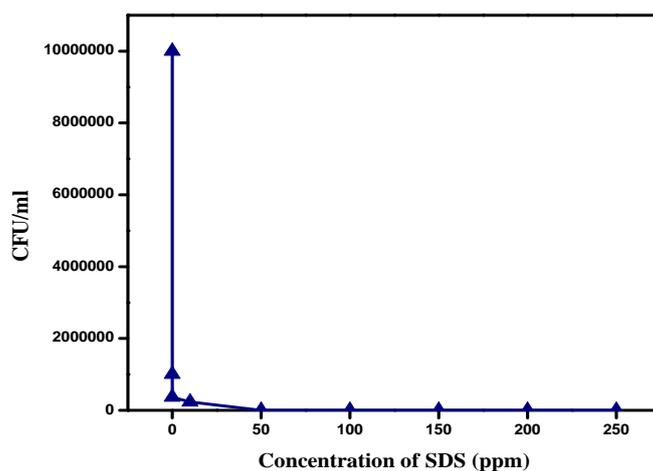


Fig.12 Biocidal Efficiency of SDS as a function of number of colony forming units in relating to concentration of biocide SDS

3.10 Comparative study of biocidal efficiencies of CPC and SDS on brass in 3% NaCl solution containing 5MBTA+SPT inhibitor system

The cationic surfactant of N-cetyl pridium chloride (CPC) (50 ppm) offers 98% IE with 5MBTA+SPT in aqueous medium. It shows the synergistic influence of CPC on IE of 5MBTA+SPT and 50 ppm of CPC provides 100% biocidal efficiency.

The anionic surfactant sodium dodecyl sulphate (SDS) (50 ppm) offers 99% IE reveals the synergistic influence of SDS on IE of 5MBTA+SPT. However 50 ppm of SDS provides 100% biocidal efficiency.

The SDS has more synergistic effect than CPC. However both have 100% biocidal efficiency at 50 ppm. Both the

surfactants have regarded as excellent inhibition and biocidal efficiency.

4. CONCLUSION

- ❖ Results of the weight-loss method reveal that the formulation consisting of 150 ppm of 5MBTA+400 ppm of SPT as synergist offers accompanied inhibition efficiency of 88% for 24 hrs immersion period, at 303 K, at pH 7.
- ❖ Synergism parameter also confirms this conclusion.
- ❖ Statistical analysis (ANOVA) show that the variation of inhibition efficiency of (5MBTA+SPT) in 3% NaCl is significant at 5% level.
- ❖ FTIR spectra show that complex formed are present on the inhibited brass surface.

- ❖ SEM micrographs of brass specimen show that the inhibitor molecule forms a good protective film on the metal surface.
- ❖ XRD patterns of the protective film correspond to absence of peak (Cu₂O and ZnO) and presence of brass peak.
- ❖ Microbial corrosion is prevented by biocidal efficiency of cationic (CPC) and anodic (SDS) surfactants.
- ❖ It is concluded that SPT acts as a good synergist along with 5MBTA for inhibiting the corrosion of brass in 3%NaCl medium.

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