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Research Article

A GREEN CHEMICAL FOR THE MICROBIAL ACTION AND INHIBITION OF CORROSION OF CARBON STEEL IN CHLORIDE ION ENVIRONMENT

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ABSTRACT

The aim of the present work is to study the inhibition efficiencies of the green biocide namely benzyl triethyl ammonium chloride (BTAC) in the presence and absence of various inhibitor systems carboxy methyl cellulose–Zn2+, caffeine–Zn2+, polyvinyl alcohol–Zn2+, sodium meta silicate–Zn2+ in 60 ppm of chloride ion solution. Classical weight loss method and FTIR spectroscopic technique are adopted. BTAC shows synergistic effect with CMC, PVA and SMS–Zn2+ systems at low concentrations while caffeine–Zn2+shows antagonistic effect with BTAC at all concentrations. FTIR spectra do not show any characteristic peaks for BTAC and BTAC reacts only with electrolyte and is responsible for the change in environment thereby changing the mechanism of electrode reaction.

Keywords: Inhibition efficiency, Inhibitor system, Biocide.

INTRODUCTION

Corrosion is a costly and severe material science problem. It manifests itself in multifarious forms in our daily lives. Whatever be the results of corrosion, remedial work may be costly in terms of finance, time and man power. In heat transfer systems, bacterially induced corrosion processes damaged the parts of the system. The bacteria, which seem to be most common in such systems, are Preudomonas, Nitrosomas, Thiobacillus, Desulfovibro, Gallioneella and some others. They are not directly involved in the corrosion processes, but through the consumption of inhibitors and in some cases the conversion of protecting inhibitors to other aggressive compounds, they will induce corrosion attacks. Detailed studies of such systems have shown that the inhibitor concentration can decrease in a very short time to very low values. The reason for this is related to bacterial activity. So, the logical step to protect the inhibitors from being consumed by bacteria is to add some types of bactericides to the system water.

Biocide is a chemical agent capable of killing organisms responsible for microbial degradation. Biocides are used for the long-term control of microbiological activity. The frequency and quantity of additions will depend on the microbiological activity of the system. Biocides can also be added to other materials to protect material biological infestation and growth. There are two types of biocides namely oxidizing and non-oxidizing biocides. Agents capable of oxidizing organic matter, e.g. cell material enzymes or proteins that are associated with microbiological populations resulting in death of micro-organism. And non-oxidizing biocide is one that functions by mechanisms other than oxidation including interference with cell metabolism and structure. Amines are effective surfactants that can act as biocide due to their ability to kill micro-organisms. They can enhance the biocidal effect of chlorinated phenolics, when they are applied in water.

Quaternary ammonium salts are surface active chemicals that consist generally of one nitrogen atom, surrounded by substitutes containing eight to twenty five carbon atoms on four sides of the nitrogen atom. These compounds are generally most effective against microorganisms in alkaline pH ranges. They are positively charged and will bond to the negatively charged sites on the bacterial cell wall. These electrostatic bonds will cause the bacteria to die of stresses in the cell wall. Quaternary ammonium salts also known for their corrosion inhibiting property. The present study aims at testing a quaternary ammonium salt for its inhibiting and biocidal activity.

Quaternary ammonium salts are surfactants which are used as corrosion inhibitors as well as biocides. Review of literature clearly reveals the usage of many quaternary ammonium salts as corrosion inhibitors and as biocides. Karpagavalli and Rajeswari [1] have reported the application of CTAB as inhibitor for the corrosion of brass in ground water. Soror and El-Ziady [2] have studied the effect of CTAB on the corrosion of carbon steel in acid. Lalitha et al. [3] have shown the existence of synergistic effect between SDS, CTAB with triazoles for the corrosion inhibitions of copper in acid medium. Free [4] has related the corrosion inhibition of mild steel in acidic medium by surfactant molecules cetyl pyridinium chloride and cetyltrimethylammonium bromide to the surfactant's ability to aggregate at interfaces and in solution. Wang et al. [5] have shown that both 2-mercaptothiazoline and cetylpyridinium chloride functions as effective inhibitors for low carbon steel over a wide concentration range of aqueous phosphoric acid solution.

Need, objective and scope of the present study

There are two important problems encountered in cooling water systems, they are corrosion and biofouling due to microbes. The most efficient corrosion inhibitors known are based upon the element s carbon, phosphorous, nitrogen, and sulphur. Bacteria on the other hand are completely dependent on their elements for their metabolism and survival. Sudden and apparently unjustified breaks down of inhibitors in technical water based systems are observed due to bacterial activity in the waters. Bacteria also induce corrosion by the formation of biofilms. Hence, it is important to add a chemical which functions as a biocide as well as corrosion inhibitors. As it is difficult to control both corrosion and microbial growth by a single chemical, it is important to develop an inhibitor system which includes a biocide.

Review of literature reveals that BTAC in combination with other organic chemicals are effective in controlling the corrosion of many metals in various environments and also as an excellent biocide. Hence, the present study investigate the possibility of using BTAC as a second synergist along with few well known inhibitors and Zn2+ combination and also as a biocide for the corrosion of carbon steel in 60 ppm of chloride ion solution.

The inhibitors chosen for the present study are:

1. Carboxymethyl cellulose (CMC), a common viscosifier.
2. Polyvinyl alcohol (PVA), a binder in adhesive formulations.
3. Caffeine, a naturally occurring purine derivative.
4. Sodium meta silicate (SMS), a base for detergent.

CMC is useful in a wide variety of applications in foods, drugs and cosmetics as a viscosifier, emulsion stabilizer, thickener and to improve texture. In textile warp sizing, adhesives, latex paints and polishes and paper processing and also in detergent as an antiredeposition agent [1,2].

Polyvinyl alcohol is highly resistant to solvent, oil and grease. It forms tough, clean film that has high tensile strength and abrasion resistance. Although usually amorphous, it can be drawn into a semi crystalline fibre. Polyvinyl alcohol is used in industries as: (1) binder in adhesive formulations and in textile sizing, (2) joint cement for building construction, water-soluble film for hospital-laundry bags, emulsifiers in cosmetics, soil binder to prevent erosion, intermediate in the production of polyvinyl butyral, and adhesive interlayer in laminated safety glass.

Caffeine is an alkaloid, found naturally in foods such as coffee beans, tea cacao beans and kola nuts. It is well known for its characteristic intense, bitter taste, and as a stimulant of the central nervous system, heart and respiration. It is also diuretic. It is added to some soft drink such as Colas and Mountain Dew. It is an alkaloid of the methylxanthine family [20]. Since Caffeine is a non-toxic material, it is chosen as the corrosion inhibitor for this present study along with zinc ions as the corrosion inhibitor.

Sodium meta silicate is used in laundry and for cleaning. It is also used as a base for detergent. It is a raw material for making silica gel. And in paper industry it is used for deinking.

BTAC: The molecular formula is $C_6H_5CH_2N(C_2H_5)_3Cl$. It is white to off-white crystalline powder and it is stable under ordinary conditions.

Objectives:

1. To investigate the influence of BTAC on the inhibiton efficency of PVA–Zn2+, CMC–Zn2+, SMS–Zn2+in 60 ppm of chloride ion solution.
2. To investigate the nature of the protective film formed on the surface of carbon steel by surface analysis techniques such as Fourier Transform Infra Red spectra (FTIR).

2. Preparation of the specimens

Carbon steel specimens were chosen from the same sheet of the following composition: 0.1% C, 0.03% S, 0.05% P, 0.5% Mn and balance Fe. Carbon steel specimens of the dimensions 1.0 × 4.0 × 0.2 cm were polished to mirror finish, degreased with trichloroethylene and used for weight-loss and surface examination studies. For Electrochemical studies, the surface area of metal surface was 1 cm2.

METHODS AND MATERIALS

Weight loss method

Weight loss experiments were carried out for a period of one day. Three carbon steel specimens were immersed in 100 ml of the solutions containing chloride as corrosive medium (120 ppm) and various concentrations of the inhibitor in the absence and presence of Zn2+ (ZnSO4.7H2O) of different products were cleaned with Clarke's solution [21]. The weights of the specimens before and after immersion were determined using a Shimadzu balance AY62. Inhibition efficiency (IE) was calculated from the relationship

$$IE = 100\,[1 - W_2/W_1]\ \text{percent}$$

Where: W1 is the corrosion rate in the absence of inhibitor and W2 is corrosion rate in the presence of inhibitor.

Surface examination study

Surface analysis by FTIR spectroscopic study

FTIR spectra (KBr pellet) were recorded using Perkin–Elmer 1600 FTIR spectrophotometer. After immersion period of one day in various test solutions, the specimens were removed and dried. The film formed on the surface of the metal surface was scratched carefully and it was thoroughly mixed so as to make it uniform throughout.

RESULTS AND DISCUSSION

Table 1 presents the corrosion rate and IE various concentrations of Zn ions, CMC and BTAC. Perusal of the table shows that the 50 ppm of Zn ions give an IE of 32% and 200 ppm of CMC gives 22% of IE, but their combination exhibits 76% IE. This clearly shows the existence of synergism between CMC and Zn ions in controlling the corrosion of carbon steel in Cl ion solution. The function of Zn ions is to carry the CMC molecules from the bulk of the solution to the surface of the metal.

The addition of 50 ppm of BTAC to 60 ppm of Cl ion solution containing of 200 ppm of CMC and 50 ppm of Zn ions enhances the IE of 76–84.6% .Further addition does not alter the IE much. Hence BTAC shows synergistic effect with CMC + Zn2+ system even at very low concentration of BTAC.

According to Table 2, 50 ppm of Zn2+ alone gives an IE of 32% and 200ppm of PVA gives 17% of IE, but their combination exhibits 60% IE. This clearly shows the existence of synergism between PVA–Zn2+ in controlling the corrosion of carbon steel in Cl- ion solution. The function of Zn2+ ion is to carry the PVA molecules from the bulk of the solution to the surface of the metal.

When 50 ppm of BTAC is added to the combination of 200 ppm of PVA and 50 ppm of Zn ions in 60 ppm of Cl- ion solution, the IE is found to increase from 60% to 69.2 %. Further addition of BTAC, increases the IE upto 150 ppm of BTAC beyond which again the IE falls. The fall in IE may be due to the fact that the monomers of BTAC are responsible for the corrosion inhibition and it acts synergistically with PVA–Zn2+ system in controlling the corrosion of carbon steel. At higher concentration of BTAC micelles is formed which are not effective in controlling the corrosion .hence the IE falls beyond 150 ppm of BTAC.

The IE of Zn2+, caffeine , caffeine + Zn2+, and caffeine + Zn2+ with various concentrations of BTAC are presented in Table 3.

This table indicates that 50 ppm of Zn2+ alone gives 32% IE and 200 ppm of caffeine gives 6% of IE, but their combination exhibits 52% IE. This clearly shows the existence of synergism between caffeine–Zn2+ in controlling the corrosion of carbon steel in Cl- ion solution. The function of Zn

Table 1. The influence of BTAC on the inhibition efficiency of carboxy methyl cellulose–Zn^{2+}, in controlling the corrosion of carbon steel in 60 ppm of chloride ion solution is given in Table 1. Inhibitor system:CMC+ Zn^{2+}+ BTAC

S. No	Zn^{2+} (ppm)	CMC (ppm)	BTAC (ppm)	CR (mdd)	IE (%)
1	0	0	0	28.79	–
2	50	0	0	19.58	32
3	0	200	0	22.46	22
4	50	200	0	6.91	76
5	50	200	50	4.43	84.6
6	50	200	100	4.26	85.2
7	50	200	150	4.35	84.9
8	50	200	200	4.20	85.4
9	50	200	250	4.46	84.5
10	50	200	300	4.58	84.1

Table 2. The influence of BTAC on the inhibition efficiency of poly vinyl alcohol–Zn2+, in controlling the corrosion of carbon steel in 60 ppm of chloride ion solution is given in Table 2. Inhibitor system: PVA + Zn2+ + BTAC

S. No	Zn^{2+} (ppm)	PVA (ppm)	BTAC (ppm)	CR (mdd)	IE (%)
1	0	0	0	28.79	–
2	50	0	0	19.58	32
3	0	200	0	23.59	17
4	50	200	0	11.56	60
5	50	200	50	8.87	69.2
6	50	200	100	5.07	82.4
7	50	200	150	1.87	93.5
8	50	200	200	3.94	86.3
9	50	200	250	6.99	75.7
10	50	200	300	10.19	64.6

Table 3. Inhibitor system: caffeine + Zn2++ BTAC.

S. No	Zn^{2+} (ppm)	Caffeine (ppm)	BTAC (ppm)	CR (mdd)	IE (%)
1	0	0	0	28.79	–
2	50	0	0	19.58	32
3	0	200	0	27.06	6
4	50	200	0	13.82	52
5	50	200	50	13.88	48.2
6	50	200	100	14.99	47.9
7	50	200	150	15.81	45.1
8	50	200	200	16.29	43.4
9	50	200	250	16.44	42.9
10	50	200	300	16.76	41.8

Table 4. Inhibitor system: SMS+ Zn2++ BTAC

S. No	Zn^{2+} (ppm)	SMS (ppm)	BTAC (ppm)	CR (mdd)	IE (%)
1	0	0	0	28.79	–
2	50	0	0	19.58	32
3	0	200	0	18.71	35
4	50	200	0	7.77	73
5	50	200	50	5.01	83
6	50	200	100	3.69	87.23
7	50	200	150	2.19	92.4
8	50	200	200	0	100
9	50	200	250	0	100
10	50	200	300	0	100

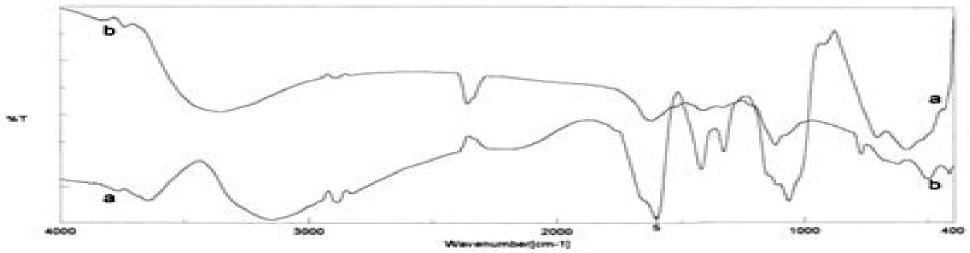

Fig. 1 FTIR spectra of CMC+Zn2+ +BTAC system. (a) FTIR spectra of CMC, (b) FTIR spectra of CMC+Zn2+ + BTAC.

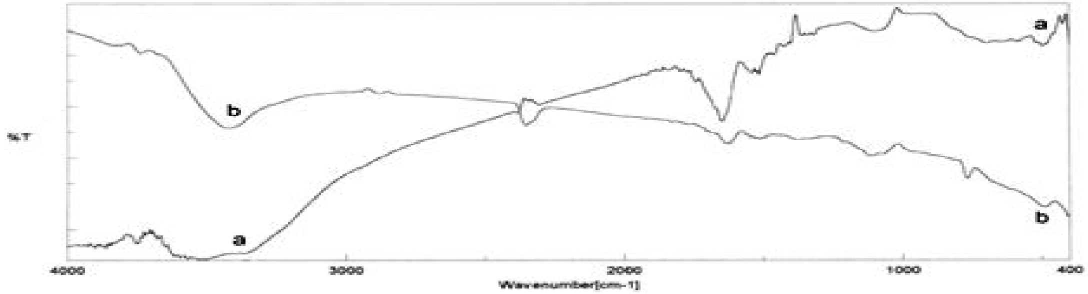

Fig. 2 (a) FTIR spectra of PVA; (b) FTIR spectra of PVA + Zn^{2++} BTAC

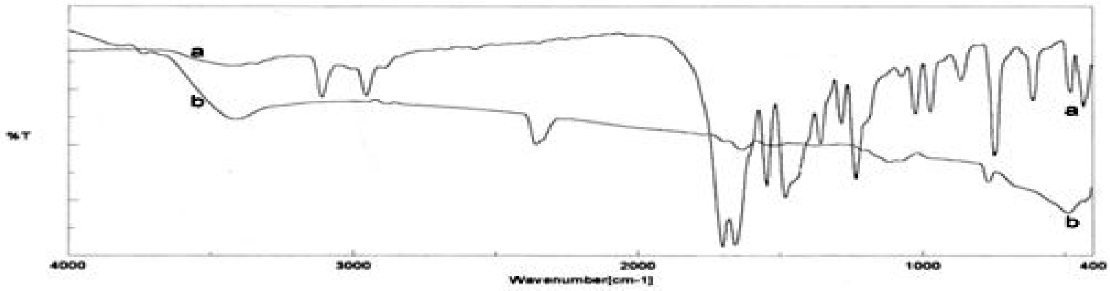

Fig. 3 (a) FTIR spectra of Caffeine; (b) FTIR spectra of caffeine + Zn2+ + BTAC

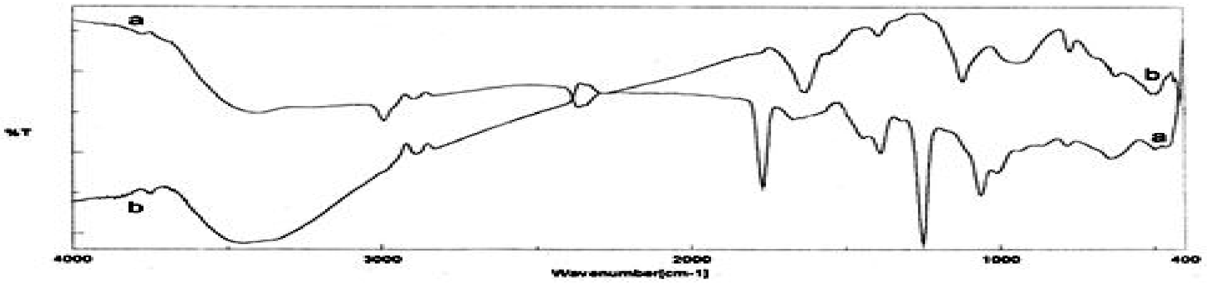

Fig. 4 FTIR spectra of SMS+Zn2++BTAC.

ions is to carry the caffeine molecules from the bulk of the solution to the surface to the metal.

In Table 4 corrosion rates and inhibition efficiencies of various concentrations of Zn2+, SMS + Zn2+ and SMS + Zn2+ + BTAC are given.

This table indicates that 50 ppm of Zn2+ alone gives 32% IE and 200 ppm of SMS gives 35% of IE, but their combination exhibits 73% IE. This clearly shows the existence of synergism between SMS–Zn2+ in controlling the corrosion of carbon steel in Cl- ion solution. The function of Zn ions is to carry the SMS molecules from the bulk of the solution to the surface to the metal. The addition of 50 ppm of BTAC to Cl- ion solution containing 50 ppm of Zn2+, 200 ppm of SMS increases the IE from 73% to 83% and the IE is found to increase with increase in the concentration of BTAC. A combination of 50 ppm of Zn2+ions, 200 ppm of SMS and 200 ppm of BTAC gives the maximum IE of 100% .This shows that SMS + Zn2+ and BTAC behave synergistically in controlling the corrosion of carbon steel.

SURFACE ANALYSIS BY FTIR SPECTRA

FTIR spectrum (KBr) of the thin film formed on the surface of the carbon steel immersed in 120 ppm of chloride solution containing 50 ppm of Zn2+ and 200 ppm of CMC and 50 ppm of BTAC is given in Figure 1. FTIR spectrum of pure CMC shows the characteristic –C–O–C– band at 1066.44 cm-1. The bands at 1598.70 cm-1 and 1419.35 cm-1 in the FTIR spectrum of CMC are due to the free COO-1 ion [6]. These bands are shifted to 1614.13 cm-1 and 1415.46 cm-1 respectively in the FTIR spectrum of the thin film. This shows that a strong covalent bond is formed between COO- and the metal that proves the formation of the complex [7]. FTIR spectrum of the thin film also shows a band at 773.32 cm-1, which may be due to Zn–O bending mode of vibration [8]. The band at 3737.37 cm-1 is due to –O–H stretching frequency of Zn(OH)2 [9]. The band at 497.54 cm-1 may be due to Fe–O stretching vibration [10]. However the spectrum does not show any characteristic peak of BTAC. So it is obvious that BTAC reacts only with the electrolyte and responsible for the change in the environment there by changing the mechanism of electrode reaction.

FTIR spectra of thin film formed on the surface of the metal after immersing the specimens in Cl- ion solution containing the inhibitor formulation 50 ppm of Zn2+, 200 ppm of PVA and 150 ppm of BTAC for one day is given in Figure 2. 3423.03 cm-1 is due to The –OH stretching frequency . The band due to asymmetric –C–C–O– stretching is at 1072.23 cm-1. The band at 754.03 cm-1 may be due to Zn–O stretching vibration [10]. The band at 1344.14 may be due to in-plane vibration of –O–H group in Zn(OH)2 [11]. The band at 495.62 cm-1 may be due to Fe–O stretching vibration [12]. This clearly shows that the PVA is absorbed on the surface of the metal. However the spectrum does not show any characteristic peak of BTAC. So it is obvious that BTAC reacts only with the electrolyte and responsible for the change in the environment there by changing the mechanism of electrode reaction.

ANALYSIS OF FTIR SPECTRA

FTIR spectra (KBr) of pure caffeine and the thin film formed on the surface of the carbon steel immersed in 120 ppm chloride solution in the presence of the inhibitor formulation containing 200 ppm of caffeine, 50 ppm of Zn2+ and 50 ppm of BTAC are shown in Figure 3. FTIR spectrum of caffeine shows a broad peak at 3428.81 cm-1 due to –N–H stretching vibration and two sharp peaks at 1700.91 cm-1 and 1656.55 cm-1 due to –C=O and –C=N [10] stretching frequencies respectively [13]. In the spectrum of the film formed on the surface of the carbon steel, these bands are shifted to 3411.46 cm-1, 1691.27 cm-1 and 1637.27 cm-1 respectively. The bands at 765.6 cm-1 may be due to Zn–O stretching frequency [11]. The band at 1394 cm-1 may be due to the in-plane vibration of O–H in Zn(OH)2 [11,6]. The bands at 655.6 cm-1 and 489.83 cm-1 are due to the metal –N/O bonds [14]. All the above bands clearly indicate the formation of a complex between zinc ions and caffeine.

This clearly shows that the caffeine is absorbed on the surface of the metal. However the spectrum does not show any characteristic peak of BTAC. So it is obvious that BTAC reacts only with the electrolyte and responsible for the change in the environment there by changing the mechanism of electrode reaction.

FTIR spectrum (KBr) of pure SMS and the film formed on the surface of the carbon electrode immersed in the solution containing 50 ppm of Zn2+, 200 ppm of SMS and 50 ppm of BTAC are shown in Figure 4. The band at 3432.67 cm-1 represents the characteristic group frequency of –OH group. The peaks observed at 1241.93 cm-1 and at 1054.87 cm-1 are due to –Si–O stretching vibrations. The water of crystallization produces bands at 3432.67 cm-1, 1764.55 cm-1 and at 1378.85 cm-1 [15-18]. The two –Si–O stretching frequencies observed in the pure SMS have merged into one and appear at 1116.58 cm-1 in the spectrum of the thin film. This clearly shows the involvement of silicate ions in the complex formation. The bands at 3756.65 cm-1, 1388.50 cm-1 and 952.66 cm-1 may be due to the –O–H stretching, in-plane bending and out-of-plane bending respectively of the hydroxyl ions present in Zn(OH)2 [15,17]. The band at 769.46 cm-1 may be due to Zn–O stretching frequency [19]. The band at 495.62 cm-1 may be due to Fe–O stretching frequency [20]. This clearly shows that the SMS is absorbed on the surface of the metal. However the spectrum does not show any characteristic peak of BTAC. So it is obvious that BTAC reacts only with the electrolyte and responsible for the change in the environment there by changing the mechanism of electrode reaction.

CONCLUSIONS

Analysis of the results by mass-loss method clearly indicate that BTAC can act as a second synergist for the following inhibitor formulations. Caffeine-Zn2+ system, sodium meta silicate–Zn2+ system, poly vinyl–Zn2+ system, carboxy methyl cellulose–Zn2+ system. Analysis of the FTIR spectra reveals that BTAC is not absorbed in the surface of the carbon steel.

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