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Corrosion Inhibition of Carbon Steel by a Multi-component Blend Containing Zinc Diethyldithiocarbamate Complex in Combination with Trisodium Orthophosphate

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The inhibiting action of a multi-component blend of inhibitors containing sodium salt of diethyldithiocarbamate (NaDEDTC), 1-hydroxy ethyledene-1, 1-diphosphonic acid (HEDP) and $ZnSO_4.7H_2O$ (in 1:1.4:1 ratio) towards scaling ,fouling, underdeposit and microbiological corrosion has been studied in combination with various concentrations (30ppm to 150ppm) of trisodium orthophosphate (TOP) by weight loss and potentiodynamic polarization methods. The influence of temperature in the range of 25 ^oC to 55 ^oC has also been investigated. The corrosion inhibition efficiency at a specific temperature of a particular blend increases on increasing the TOP concentration from 30 ppm to 150 ppm.The efficiency of the same blend with temperature increases on increasing the temperature from 25^{o}C to 35^{o}C but after that it gradually decreases as the temperature goes to 55^{o}C, indicating the instability of the protective film beyond 40^{o}C. SEM and EDS study confirm the formation of an adsorbed protective film on the carbon steel surface. Potentiodynamic polarization curves indicate the mixed nature of the inhibitors of the blend. Adsorption of the new blend of inhibitors on the carbon steel surface was found to obey Langmuir adsorption isotherm.

Keywords: Corrosion inhibition, trisodium orthophosphate,weight loss method, potentiodynamic polarization method, SEM and EDS

1. INTRODUCTION

The treatment philosophy of open recirculating cooling system (ORCS) of petroleum refinery takes an important role on its productivity and profitability. It is necessary to control scaling, fouling, underdeposit and microbiological problem simultaneously. Although a large number of investigations have been performed with various chemicals individually, their synergic study in a blend is an interesting problem to inhibit scaling, fouling, underdeposit and microbiological problem at the same time. In this study, we report the role of Zn^{2+} as cathodic inhibitor, HEDP as an antiscalent agent and NaDEDTC as both an anodic inhibitor and a reducing biocide as well. Further, presence of HEDP makes Zn^{2+} complex of DEDTC highly soluble. These compounds in 1:1.4:1 ratio work as a good blend to solve these problems of scaling, fouling, underdeposit and microbiological growth [1]. To increase the solubility further as well as its inhibition efficiency, this blend is studied in presence of various amount of TOP (30 to 150ppm), since the solubility of ZnDEDTC complex increases in presence of orthophosphate group [2]. On the other hand the use of chlorine as biocide in cooling water system is not giving encouraging returns as it increases metal corrosion, wood delignification and total dissolve solids (TDS). Moreover, in presence of light hydrocarbon, chlorine can form trihalomethane (THM), which are carcinogenic even in ppb level [3]. To overcome these problems simultaneously, an effective multi-component blend of inhibitors containing the minimal amount (ppm) of sodium salt of diethyldithiocarbamate, zinc sulphate, HEDP and trisodium orthophosphate was formulated instead of a single component system. Dithiocomplexes of Cu (II) and Zn (II) were already reported to be good antioxidant and biocides [4, 5].

2. EXPERIMENTAL PROCEDURES

Experiments were carried out by weight loss and potentiodynamic polarization methods. For performing these experiments, blends of NaDEDTC(AR, Merck,40 ppm), HEDP(Commercial grade,55 ppm), $ZnSO_4.7H_2O$(AR,CDH,40 ppm) and TOP (AR, Merck,30 ppm to 150 ppm) of different concentrations were prepared separately. Table 1 gives the details of these blends.

2.1. Weight loss method

The carbon steel corrosion coupons of known composition(S, 0.05; P, 0.04; Mn, 0.306, C; 0.08-0.13; Al, 0.03; Si, 0.21and Fe remainder) and size (1.0×1.0×0.15 cm) were used for the measurement of corrosion rate in weight loss method. The coupons were cleaned properly, degreased using acetone and finally dried in an oven at 105^0C before and after each experiment. After that coupons were stored in a moisture free desiccator for conditioning.

The weights of the test coupons were recorded and tests were carried out in a constant temperature bath of cooling water used in ORCS of Numaligarh Refinery Limited (NRL), Golaghat, Assam, in absence and presence of various blends of inhibitors separately for 15 days at 25^o, 35^o, 45^o and 55^oC.

The cooling water was analyzed for various parameters by using standard method [6] (Table 2). These treated coupons were then removed and again stored in a moisture free desiccator for conditioning. After conditioning, coupons were reweighed. From the weight difference the corrosion rate (CR) and percentage of inhibition efficiency (%IE) were calculated by using the equations 1[7] and 2[8] respectively (Table 3).

Table 1. Composition of various O-blends inhibitors.

Blends	Zn^{2+}(ppm)	HEDP(ppm)	NaDEDTC(ppm)	TOP(ppm)
Blend O-30	40	55	40	30
Blend O-50	40	55	40	50
Blend O-100	40	55	40	100
Blend O-150	40	55	40	150

$$CR = \frac{143{,}700 \times \text{Weightloss(grams)}}{\text{Metal density (g/cm}^3) \times \text{Coupon area} \times \text{time (T)}} \quad (1)$$

Where CR is expressed in mpy, weight loss in grams,corrosion period (T) in days and coupon area in cm^2.

$$IE\% = R_0 – R \times 100/R_0 \quad (2)$$

Here R_0 and R are the corrosion rates in absence and in presence of inhibitors respectively.

Table 2. Parameters of cooling water used.

P^H	Turbidity(NTU)	Conductivity (µs /cm^2)	TDS (ppm)	Total hardness(ppm)	Ca Hardness(ppm)
7.5	<0.10	171.0	153.9	28.0	22.0

2.2. Electrochemical studies

All potentiodynamic polarization studies were carried out with the help of a potentiostate of model 600C of CH instrument. A carbon steel rode of the same composition as those of the coupons used in weight loss experiments of exposed area $0.05cm^2$ was used as a working electrode. A platinum foil was used as a counter electrode and a silver-silver chloride electrode was used as reference electrode. Before each experiment, the specimen was polished with silicon carbide paper, degreased with acetone, and washed with distilled water. Before starting the polarization scan a minimum of thirty minutes was given to stabilize the open- circuit potential (OCP) within ±10 mv. All tests were carried out at a scan rate of 0.05v/s. The plot of E (potential) versus log I was drawn and from this the corrosion kinetic parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}) were evaluated [9] (Fig. 1, Table 4). The percentage of inhibition efficiency (%IE) can be calculated from the equation

3[10]. All these experiments were carried out at ambient temperature (~30^{o}C) in the absence (blank) and presence of various O-blends of inhibitors as in the case of weight loss studies.

Table 3. Corrosion parameters obtained from weight loss measurements for carbon steel at various inhibitors concentrations and temperatures.

Blends/ blank	**Corrosion rate,R (mpy), IE% and weight loss values(g)**	**Temperature**				**P^H**
		25 ^{o}C	35 ^{o}C	45 ^{o}C	55 ^{o}C	
Blank	weight loss values(g)	0.01173	0.01493	0.01898	0.02256	7.5
	R_O	5.50	7.00	8.90	10.58	
Blend-O-30	weight loss values(g)	0.00270	0.00310	0.00571	0.00790	6.0
	R	1.27	1.45	2.68	3.7	
	IE%	76.90	79.28	69.89	65.03	
Blend-O-50	weight loss values(g)	0.00200	0.00230	0.00430	0.00590	6.3
	R	0.94	1.08	2.01	2.77	
	IE%	82.90	84.57	77.42	73.82	
Blend-O-100	weight loss values(g)	0.00130	0.00150	0.00280	0.00400	7.0
	R	0.61	0.72	1.33	1.88	
	IE%	88.91	89.71	85.06	82.23	
Blend-O-150	weight loss values(g)	0.00100	0.00120	0.00220	0.00320	7.5
	R	0.47	0.56	1.06	1.50	
	IE%	91.45	92.00	88.09	85.82	

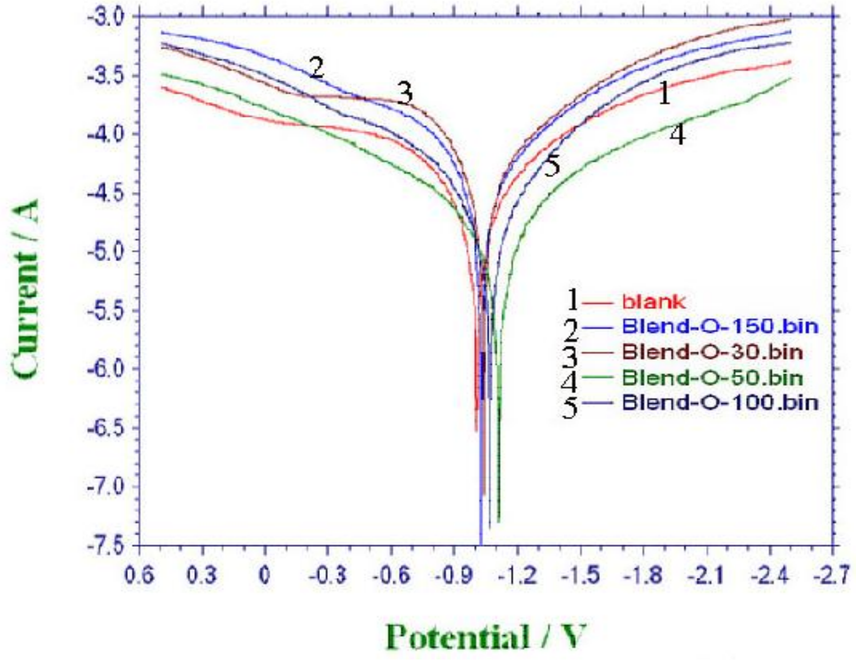

Figure 1. Potentiodynamic polarization curves for blend -o

Table 4. Corrosion parameters of various O-blends by potentiodynamic polarization method

Blends	**$-E_{corr}$ (mv)**	**I_{corr} (µA/cm^2)**	**IE(%)**
Blank	1011.0	4.518	---
Blend-O-30	1038.0	0.826	81.72
Blend-O-50	1108.0	0.537	88.11
Blend-O-100	1070.0	0.426	90.57
Blend-O-150	1027.0	0.319	92.94

2.3. Adsorption Isotherm

Adsorption isotherm gives the basic information on the interaction between the inhibitor and the metal surface. This can be obtained from degree of surface coverage (Θ) and fraction of unoccupied surface (1- Θ), which is a function of exposed area. The value of Θ is given by the equation (3) [11].

$$\Theta=1-R/R_o \tag{3}$$

Where R and R_o are the corrosion rates in presence and in absence of inhibitors respectively.

From the equation (3), Θ values can be evaluated by using the corrosion rate values obtained from weight loss method. The plot of log (Θ/ 1- Θ) against log C shows a straight line (Fig 2.), indicates that adsorption of inhibitors follows Langmuir's isotherm [12]. This suggests that the inhibitor molecules are adsorbed on the metal surface forming a monolayer which prevents further contact of the metal with electrolyte.

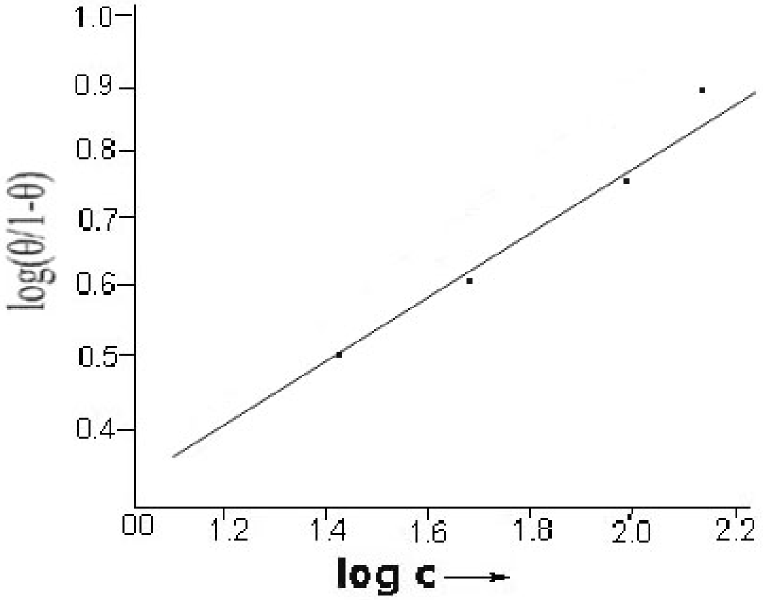

Figure 2. Langmuir adsorption isotherm plots for the adsorption of different concentration of inhibitors on the metal surface. (Taking average value of θ at four different temperatures)

2.4 Temperature Effects

Effect of temperature on inhibition efficiency was observed in presence and in absence of different O-blends inhibitors at four different temperatures 25°, 35°, 45° and 55°C by weight loss method. The various thermodynamic and activation parameters such as activation energy (E_a), degree of surface coverage (ϴ) and free energy of adsorption (ΔG_{ads}) were determined for the new blends of inhibitors (Table 5).

The equilibrium constant (K) for adsorption and desorption process was calculated from the equation

$$K=\Theta/C\,(1-\Theta) \qquad (4)$$

Where ϴ is degree of coverage on the metal surface, C is the concentration of inhibitor in mol L^{-1}.

The values of E_a were calculated by using the Arrhenious equation (5)[13].

$$\mathrm{Log}\,k_1/k_2 =- E/2.303R\,[\Delta T /T_2\, T_1] \qquad (5)$$

Where k_1 and k_2 are the corrosion rates at temperature T_1 and T_2 respectively, $\Delta T= T_2- T_1$ and R is the gas constant.

Table 5. Thermodynamic parameters of different blend of inhibitors for carbon steel.

Blend/ blank	Thermodynamic and activation parameters	Temperature				Average
		25 °C	35 °C	45 °C	55 °C	
Blank	E_a (kj mol^{-1})	17.72	17.35	14.99	-	16.68
Blend O-30	E_a (kj mol^{-1})	28.97	35.47	27.97	-	30.80
	ϴ	0.77	0.79	0.70	0.65	0.76
	K	42920.85	48229.55	29914.53	23809.52	37084.6
	ΔG(kj mol^{-1})	-36.68	-37.90	-37.87	-38.43	-38.44
Blend O-50	E_a (kj mol^{-1})	29.27	39.56	27.81	-	32.21
	ϴ	0.82	0.85	0.77	0.74	0.80
	K	35042.74	43589.74	25752.51	21893.49	37411.27
	ΔG(kj mol^{-1})	-35.88	-37.64	-37.47	-38.20	-37.30
Blend O-100	E_a (kj mol^{-1})	30.49	40.31	30.01	-	33.60
	ϴ	0.88	0.89	0.85	0.82	0.86
	K	28205.13	31118.88	21794.87	17521.37	36768.48
	ΔG (kj mol^{-1})	-35.34	-36.78	-37.03	-37.60	-36.68
Blend O-150	E_a (kj mol^{-1})	31.44	41.38	30.11	-	34.31
	ϴ	0.91	0.92	0.88	0.86	0.89
	K	25925.93	29487.18	18803.41	15750.91	36528.99
	ΔG (kj mol^{-1})	-35.13	-36.64	-36.64	-37.31	-36.36

The free energy of adsorption (ΔG_{ads}) at different temperatures was evaluated by using the equation (6) [14].

$$(\Delta G_{ads} = -RT \ln(55.5K) \tag{6}$$

Where K is the equilibrium constant of the adsorption and desorption process. 55.5 is the concentration of water in the solution in mole.

3. SCANNING ELECTRON MICROGRAPH

Carbon steel samples of $1 cm^2$ surface area were treated in cooling water in absence and in presence of inhibitors (O-100 blend was taken) for a period of five days separately for SEM and EDS analysis, which were recorded at CIF, IIT, Guwahati. Assam, India (model, JEOL, JSM-35M-35CF electron microscope)(Fig 3. Fig 4. , Fig 5.).

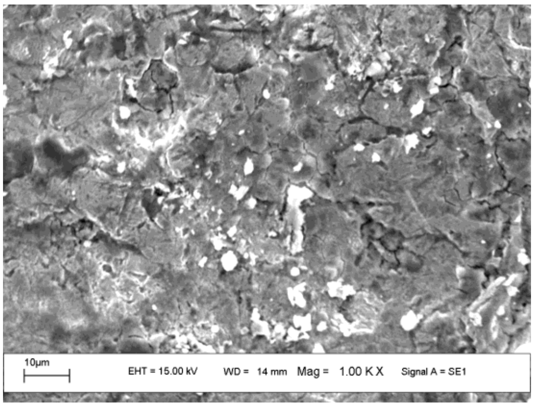

Figure 3. SEM micrograph of carbon steel after 5 days in absence of inhibitors

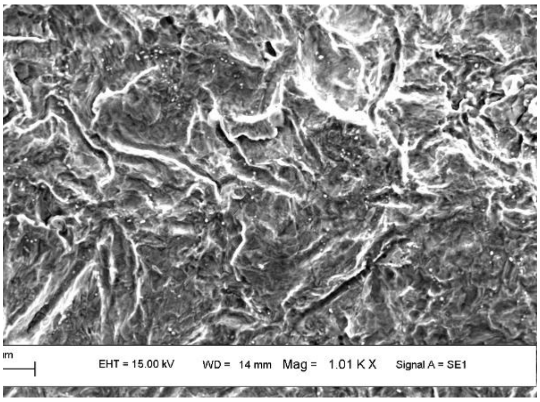

Figure 4. SEM micrograph of carbon steel after 5 days in presence of inhibitors

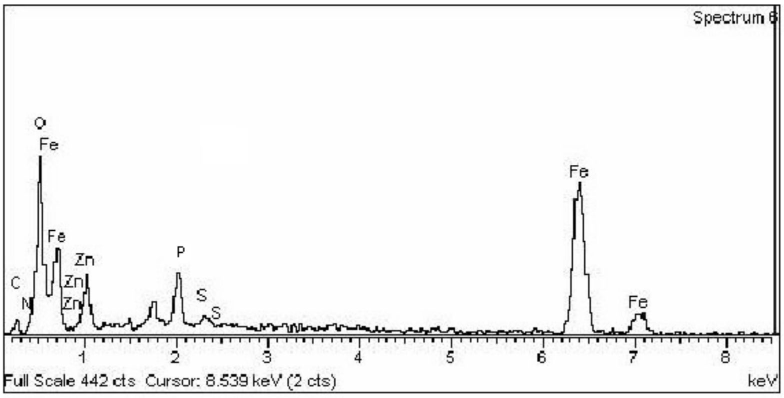

Figure 5. EDS analysis of carbon steel after testing for five days in presence of inhibitors.

4. RESULTS AND DISCUSSION

The inhibition efficiency of a molecule towards corrosion depends upon its aromaticity, conjugation as well as the bonding strength of the inhibitor molecule to the metal surface [15]. It also depends to the type and number of bonding atoms or groups present in the inhibited molecule. The ability of inhibition increases with the increase of solubility. In the present study the performance of Zn complexes of DEDTC, HEDP as corrosion inhibitors may be attributed due to the presence of sulphur, nitrogen and oxygen atoms containing lone pair electrons in the molecular structure, which favours the greater adsorption of it on the carbon steel surface. Like thiourea molecule, where sulphur is having negative charge and nitrogen have a slight positive charge, Zn-diethyldithiocarbamate complex may also have a similar charge separation[16,17] (Fig 6.). As the molecule approaches to the positively charge metal surface, the molecules polarize and induce additional charges on sulphur and nitrogen atoms, which enhances the adsorption of the molecules on the metal surface [15].

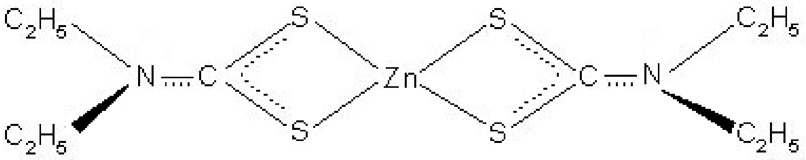

Figure 6. Structure of Zn-diethyldithiocarbamate complex

The results obtained from weight loss method indicated that the inhibition efficiency at a specific temperature within the temperature range of experiment (i.e. 25^o to 55 ^oC), increases on increasing the TOP concentration from 30ppm to 150ppm (inhibition efficiency increases from 76.90% to 91.45% at 25 ^oC), which is also corroborated by potentiodynamic polarization method. In potentiodynamic polarization method the corrosion current density value (I_{corr}) decreases (i.e. inhibition efficiency increases) [18] considerably from the blank value of 4.518 $\mu A/cm^2$ to 0.319

μA/cm^2 on increasing the TOP concentration from 30 to 150 ppm (inhibition efficiency increases from 81.72% to 92.94%). The decrease in I_{corr} value with increasing TOP concentration was associated with no significant change of corrosion potential (E_{corr}) values (Fig 1.), suggesting that all these blends of inhibitors are cathodic as well as anodic in nature i.e. they retard the corrosion reaction by blocking both anodic and cathodic sites of the metal[19].

In the absence of inhibitors on increasing the temperature from 25^{o}C to55^{o}C, the corrosion rate enhances from 5.50 mpy to 10.58 mpy, which is sharply reduced in presence of inhibitors (Table-3). The average value of activation energy (E_a) at four different temperatures (25^o,35^o,45^o and55 ^{o}C) in the absence of inhibitor is 16.68 kj mol^{-1}, while in presence of various TOP concentration the average value of activation energies at 25^o,35^o,45^o and55 ^{o}C are 30.80, 32.21 , 33.60 and 34.31 kj mol^{-1} respectively. The higher E_a values in presence of inhibitors than in the absence of inhibitors reveals the reduction of dissolution reaction of carbon steel as well as the adsorption of inhibitors on the metal surface[15]. All these activation energy values are less than 80 kj mol^{-1}, which signify the physical adsorption of inhibitors on the metal surface [20]. However, with an increase in temperature from 25 ^{o}C to35 ^{o}C ,the rate of adsorption of a particular blend of inhibitors increases on the metal surface but after that it gradually decreases as the temperature goes to 55^{o}C, which is also explainable with the help of activation energy as well as degree of surface coverage (Θ) values at various temperatures (Table-5).The decrease in corrosion inhibition efficiency at higher temperature could be due to the decomposition of the Zn-diethyldithiocarbamate complex ,which was adsorbed in the metal surface[21,22]. All the values of free energy are negative as well as less than - 40 KJmol^{-1}, indicates the spontaneous physical adsorption of the inhibitors on the metal surface [8, 23, 24].

The SEM and EDS patterns of the test coupons after treatment for 5 days in test cooling water solutions at 40^o C temperature without and with inhibitor additives are shown in Figs 3 to 4. The SEM pattern of the test coupon without inhibitor (Fig. 3) shows a distinct uneven surface morphology indicating severe corrosion while the SEM of test coupon immersed in presence of O-100 blend inhibitors showed a comparatively smooth surface, indicating the formation of an adsorbed layer of the inhibitors on the metal surface[25] (Fig. 4). EDS analysis of the specimen surface (Fig. 5) showed presence of carbon, oxygen, sulphur, phosphorus, zinc and iron after immersion in the solution containing the blended mixture, which indicates the formation of an adsorbed layer containing of Fe^{2+}-HEDP,Zn^{2+}-HEDP,Zn^{2+}-DEDTC complexes on the metal surface.

5. CONCLUSION

The present study shows that NaDEDTC, $ZnSO_4.7H_2O$ and HEDP in 1:1.4:1 ratio of each component in presence of trisodium orthophosphate gives an effective blend of inhibitors for corrosion, scale as well as microbiological problem. Blend is effective slightly in alkaline condition. The corrosion inhibition efficiency of a particular blend at a specific temperature increases on increasing the TOP concentration from 30 ppm to 150 ppm. The efficiency of the same blend with temperature increases on increasing the temperature from 25^{o}C to35^{o}C but beyond that it gradually decreases as the temperature goes to 55^{o}C. The Polarization study indicates that this blends inhibit anodic as well as cathodic corrosion current equally, indicating mixed nature of inhibitors. The inhibition of corrosion is due to formation of an adsorbed passive film on the metal surface as observed from SEM and EDS results. Adsorption of the new blend of inhibitors on the carbon steel surface obey Langmuir adsorption isotherm.

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