Corrosion Inhibitor 5- Sulpho Salicylic Acid Controlling the Corrosion of Carbon Steel in Well Water

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Abstract: The corrosion inhibition efficiency (IE) of the 5-sulpho salicylic $acid(SSA) - Zn^{2+}$ system control the corrosion of carbon steel well water environment has been investigated by weight loss method. It is observed that the formulation consisting of 400 ppm of SSA and 100 ppm of Zn^{2+} offers 78% inhibition efficiency. The sodium gluconate(SG) are added to enhance the IE of the above mentioned system. The formulation consisting of 400 ppm of SSA, 100 ppm of Zn^{2+} and 100 ppm of SG offers 92% inhibition efficiency. The synergistic effect exists between SSA - Zn^{2+} - SG system. Polarization study reveals that this formulation controls the anodic reaction predominantly. The FTIR spectra reveals that the protective film consisting of Fe²⁺ - SSA complex on anodic sites of the metal surface and Zn(OH)₂ on cathodic sites of the metal surface. The 5-sulpho salicylic acid (SSA) – Zn²⁺ system may find in cooling water system.

Keywords: Corrosion, Inhibition efficiency, 5-sulpho salicylic acid, synergistic effect, carbon steel

1. Introduction

Corrosion is the deterioration of a metal by chemical or electrochemical reaction with its environment. The Cooling systems are exposed to many types of corrosion from general electrochemical corrosion, to pitting caused by deposits, electrolysis, or microorganisms. Corrosion can reduce the life-span of equipment by years, requiring expensive replacement. It can lead to costly equipment repairs and production downtime. Corrosion related deposits lead to reduced capacity and wasted energy because of heat transfer efficiency losses. In order to prevent or minimize corrosion, the corrosion inhibitors are usually used in flow cooling water systems. A corrosion inhibitor is a substance which when added in small concentration to an environment, effectively reduces the corrosion rate of a metal exposed to it. The organic compounds and several carboxylates such as sodium salicylate, sodium cinnamate and adipate have been used as inhibitors[1-5]. Reviews of carboxylates as corrosion inhibitors have appeared from time to time. More detailed studies of particular carboxylates have also been published. Corrosion of tin in citric acid solution and effect of some inorganic anion have been studied[6]. Synergistic effect of succinic acid and Zn²⁺ in controlling corrosion of carbon steel in well water has been reported[7]. The corrosion inhibition of carbon steel by sodium potassium tartrate has been studied by Arockia selvi et al.[8] Florence et al. have investigated the corrosion inhibition of carbon steel by adipic acid[9]. The inhibition efficiency of sodium potassium tartarate in controlling corrosion of stainless steel in sea water has been studied by Wilson et al[10].

The present work is undertaken:

1. To evaluate the inhibition efficiency (IE) of 5-sulpho salicylic acid(SSA) in controlling the corrosion of

carbon steel in well water in the absence and presence of $\text{Zn}^{2\scriptscriptstyle+}$

- 2. The influence of sodium gluconate (SG) on SSA-Zn²⁺ system analysis by weight loss method.
- 3. To understand the mechanistic aspects of corrosion inhibition by polarization studies
- 4. To analysis the protective film formed on the carbon steel by FTIR spectra and proposes a suitable mechanism for corrosion inhibition.

2. Methods and Materials

2.1. Preparation of specimens

Carbon steel specimens (0.0267% sulphur, 0.06% phosphorous, 0.4% manganese, 0.1% carbon and the rest iron) of dimensions 1.0 cm x 4.0 cm x 0.2 cm were polished to a mirror finish and degreased with trichloroethylene.

2.2. Weight-loss method

Carbon steel specimens in triplicate were immersed in 100 ml well water (Table 1) containing various concentrations of the inhibitor in the presence and absence of Zn^{2+} for one day. The weight of the specimens before and after immersion was determined using Shimadzu balance, AY62 model. The corrosion products were cleansed with Clarke's solution [11]. From the change in weight of the specimens, corrosion rates were calculated with the help of the following relationship:

$$CR = \frac{\Delta m}{A^* t} \tag{1}$$

Where

CR - corrosion rate

 Δm - loss in weight (mg)

A - Surface area of the specimen (dm^2)

t - Period of immersion (days)]

The inhibition efficiency (IE, %) was then calculated using the equation

$$IE = 100 \left(1 - \frac{W_2}{W_1} \right) \tag{2}$$

Where, W_1 and W_2 are the corrosion rates in the absence and presence of the inhibitor, respectively.

Table 1: Parameters of well water

Parameters	Value
pН	8.5
Conductivity	3100 µmhos/cm
TDS	2010 ppm
Chloride	590 ppm
Sulphate	14 ppm
Total Hardness	1100 ppm

2.3. Potentiodynamic polarization study

Polarization studies were carried out in an H & CH electrochemical work station impedance analyzer model CHI660A. A three electrode cell assembly was used. The working electrode was carbon steel. A saturated calomel electrode (SCE) was used as the reference electrode and a rectangular platinum foil was used as the counter electrode.

2.4. Surface Examination

The carbon steel specimens were immersed in various test solutions for a period of one day, after one day the carbon steel specimen were taken out and dried.

The nature of the film formed on the surface of metal specimen was analysed by FTIR spectroscopic study.

2.4.1. FTIR Spectra

FTIR spectra were recorded in a Perkin-Elmer 1600 spectrophotometer. The film was carefully removed, mixed thoroughly with KBr made in to pellets and FTIR spectra were recorded.

3. Results and Discussion

3.1. Analysis of results of weight loss method

The corrosion inhibition efficiency (IE) of carbon steel in the absence and presence of various concentrations of inhibitor obtained by the weight - loss method in one day system are given in the Table 2 and 4.

The weight - loss method reveals that 5-sulpho salicylic acid(SSA) alone shows some inhibition efficiency at higher concentration. But the presence of Zn^{2+} offers good IE. For example 400 ppm of SSA alone is 18% inhibition efficiency; 100 ppm of Zn^{2+} alone is 5% IE. But it is interestingly noted that the formulation consisting of 400 ppm of SSA and 100 ppm of Zn^{2+} system shows 78% inhibition efficiency.

This is due to the fact that there is synergistic effect existing between SSA and Zn^{2+} system [12]. This means that the mixed inhibitor shows good inhibition efficiency than individuals.

Table 2: Corrosion inhibition efficiency (IE) of Carbon in the presence and absence of inhibitor and obtained by weight loss method.

Inhibitor system: SSA alone; Immersion Period: one day

S Ma	SSA	IE
<i>S.NO</i> .	ррт	%
1	0	
2	50	8
3	100	10
4	200	14
5	300	15
6	400	18
7	500	19

Table 3:	Cor	rosion	inhit	oition	effic	eiency	y (IE))) of	f Ca	arbon i	in th	ıe
presence	and	absenc	ce of	inhib	itor	and	obtai	ned	by	weigh	t los	ss
method.												
		- '	2+ -			-		-				

Inhibitor system : Zn ²⁺ alone;		⁺ alone;	Immersion Period: one of		
	S No	Zn^{2+}	IE		
	<i>5.W0</i> .	ppm	%		
	1	0			
	2	50	-7		
	3	100	5		
	4	200	12		
	5	300	15		
	6	400	18		
	7	500	19		

 Table 4:
 Corrosion inhibition efficiency(IE)) of Carbon in the presence and absence of inhibitor and obtained by weight loss method.

Inhibitor system: SSA - Zn²⁺ system; Immersion Period: one day

$CCA = 7.2^{+}$	IF
SNo SSA Zh	112
5.1vo. ppm ppm	%
1 0 0	
2 50 100	49
3 100 100	55
4 200 100	64
5 300 100	68
6 400 100	78
7 500 100	78

3.2. The influence of SG on SSA-Zn²⁺ system

The influence of sodium gloconate (SG) on SSA-Zn²⁺ system has been studied by weight – loss method. When the various concentration of SG are added to the best formulation, the IE increases. It is evident from the Table 5 that 400 ppm of SSA, 100 ppm of Zn²⁺ and 100 ppm of SG shows 92% inhibition efficiency. This is due to the inhibitor systems are much transported to the metal surface and form protective film. So the system observes very high inhibition efficiency [13].

Table 5: Corrosion inhibition efficiency (IE)) of Carbon in the presence and absence of inhibitor and obtained by weight loss method.

Inhibitor system: SSA - Zn²⁺-SG system; Immersion Period: one day

S.No.	SSA	Zn^{2+}	SG	IE
	ррт	ррт	ррт	%
1	0	0		78
2	400	100	100	92
3	400	100	200	94
4	400	100	300	98
5	400	100	400	98
6	400	100	500	98
7	400	100	600	98

3.3. Analysis of potentiodynamic polarization study

The polarization curves of carbon steel immersed in well water in the presence and absence of inhibitors are shown in Figure 1. The corrosion parameters are given in Table 6.

Table 6 : Corrosion parameters of carbon steel immersed in various test solution obtained by polarization method.

System	E _{corr, m} V vs SCE	b _{c,} mV	$b_{a,}$ $decade^{-1}$	$I_{corr,}$ A cm ⁻²
Well water	-620	432	611	5.333x10 ⁻⁶
400 ppm of SSA + 100 ppm of Zn ²⁺	-572	415	596	4.730x10 ⁻⁶

When carbon steels immersed in well water, the corrosion potential (E_{corr}) -620 mV Vs SCE. The formulation consisting of 400 ppm of SSA and 100ppm of Zn²⁺ shifts the corrosion potential to -572 mV Vs SCE, ie., corrosion potential shifts to anodic direction (from -620 mV to -572 mV). This suggests that the anodic reaction is controlled predominantly indicating the reduction of metal as more SSA are

transported to the anodic sides in the presence Zn^{2+} ions[14,15]. Now the shifts in the anodic and cathodic slopes can be compared. Tafel values for the well water are different. The tafel values for the formulation are not equal($b_a = 596 \text{ mV/decade } b_c = 415 \text{ mV/decade})$

The corrosion current (I_{corr}) of well water is 5.333×10^{-6} A/cm². It is decreased to 4.730×10^{-6} A/cm² for the best formulation. The current of the iron dissolution is decreased significantly indicating that the metal surface was passivated by the formed inhibitor layer. The passivity ion is probably due to the formation of SSA – Fe²⁺ surface layer. The significant reduction in corrosion current for inhibitor formulation may indicate more adsorption of the inhibitors and better inhibitions performance. This result suggests that a protective film (SSA – Fe²⁺-complex) is formed on the metal surface. This protects the metal from corrosion.



Figure 1: Polarization curves of carbon steel immersed in various test solution

a. Well water

b. Well water contains 400 ppm of SSA and 100 ppm Zn²⁺

3.4. Analysis of FTIR spectra

The structure of 5-sulpho salicylic acid(SSA) is shown in scheme -1. It contains S=O group, C=O group and OH group Stretching vibrations.



The FTIR spectrum (KBr) of pure 5-sulpho salicylic acid(SSA) is shown in figure 2a. S=O stretching frequency appears at 1035 cm⁻¹. The C=O stretching frequency appears at 1673 cm⁻¹. The OH stretching frequency appears at 3372 cm⁻¹. The FTIR spectrum (KBr) of the film formed on the surface of the metal after immersion of the solution containing 400 ppm of SSA and 100 ppm Zn²⁺ is shown in figure 2b. It is found that S=O stretching frequency of SSA decreased from 1035 cm⁻¹ to 1002 cm⁻¹. The C=O stretching frequency of SSA has decreased from 1673 cm⁻¹ to 1598 cm⁻¹. The OH stretching frequency of SSA has increased from 3372 cm⁻¹ to 3422 cm⁻¹. The FTIR spectrum (KBr) of the film formed on the surface of the metal after immersion of

the solution containing 400 ppm of SSA and 100 ppm Zn^{2+} is shown in figure 2b. It is found that S=O stretching frequency of SSA decreased from 1035 cm⁻¹ to 1002 cm⁻¹. The C=O stretching frequency of SSA has decreased from 1673 cm⁻¹ to 1598 cm⁻¹. The OH stretching frequency of SSA has increased from 3372 cm⁻¹ to 3422 cm⁻¹.



Figure 2. FTIR spectra; a) Pure solid 5-sulpho salicylic acid(SSA); b) Film formed on the metal surface after the immersion of the solution of 400 ppm of SSA and 100 ppm Zn^{2+}

It is suggested that the groups in 5-sulpho salicylic acid(SSA) are coordinated to Fe^{2+} resulting in the formation of Fe^{2+} -SSA complex on the anodic sites of the metal surface. The peak at 1398 cm⁻¹ is due to $Zn(OH)_2$ formed on the cathodic sites of the metal surface[16-17].

4. Corrosion Inhibition Mechanism

The weight - loss study reveals that the formulation consisting of 100 ppm of Zn^{2+} and 400 ppm of 5-sulpho salicylic acid(SSA) has 78% inhibition efficiency. The FTIR spectrum reveals that the protective film consist of Fe^{2+} -SSA complex and Zn(OH)₂. In order to explain the above observations, the following mechanism of corrosion inhibition[18] is proposed as shown in figure 3.



When the environment consisting of 100 ppm of Zn^{2+} and 400 ppm of SSA are prepared, there is a formation of Zn^{2+} -SSA complex.

When Carbon steel is introduced in this solution there is diffusion of Zinc complex towards the metal surface.

On the metal surface Zinc complex is converted into iron complex on the anodic site.

 Zn^{2+} - SSA+ Fe^{2+} \rightarrow Fe^{2+} - SSA+ Zn^{2+} The released Zn^{2+} combined with OH⁻ to form $Zn(OH)_2$ on the cathodic sites.

 $\operatorname{Zn}^{2+} + 2\operatorname{OH}^{-} \rightarrow \operatorname{Zn}(\operatorname{OH})_{2} \Psi$

Thus, the protective film consists of Fe²⁺ - SSA and Zn(OH)₂.

5. Conclusion

- \checkmark The weight loss study reveals that the formulation consisting of 100 ppm of Zn²⁺ and 400 ppm of SSA has 78% inhibition efficiency. Synergistic effect exists between SSA and Zn^{2+} system.
- \checkmark The results of polarization study suggest that the formulation of 400 ppm of SSA and 100 ppm of Zn²⁺ system controls the anodic reaction predominantly.
- ✓ The protective film consists of Fe^{2+} SSA and Zn(OH)₂ by FTIR spectroscopy.

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