



Mutual Influence of HEDP and SDS - Zn²⁺ System on Corrosion Inhibition of Carbon Steel

Susai Rajendran^{1*}, A. John Amalraj¹, J. Wilson Sahayaraj¹, R. Joseph Rathish², Noreen Anthony³ and N. Palaniswamy⁴

^{1*} Corrosion Research Centre, GTN Arts College, Dindigul 624 005, India.

² Sathyabama Institute of Science & Technology (Deemed University), Chennai 600 119, India

³ Department of Chemistry, Holy Cross College, Trichy 620 002, India.

⁴ Corrosion Science and Engineering Division, Central Electro Chemical Research Institute, Karaikudi 630 006, India

Received: 29 October 2004 Accepted: 1 February 2005

Abstract

Rain water running down from the terrace was stored in concrete tanks and used for the study. The inhibition efficiency (IE) of sodium dodecyl sulphate (SDS) in controlling corrosion of carbon steel immersed in rain water in the presence of Zn²⁺ and 1-hydroxyethane-1,1-diphosphonic acid (HEDP) has been evaluated by weight loss method. SDS accelerates the corrosion rate. SDS-Zn²⁺ system also accelerates the corrosion rate. Interestingly the SDS-Zn²⁺-HEDP system shows excellent IE. The SDS (150 ppm) - Zn²⁺ (50 ppm) system is corrosive. When 50 ppm HEDP is added the IE becomes 80%. The HEDP (100 ppm) - Zn²⁺ (50 ppm) system has only 65% IE. When 100 ppm of SDS is added, IE increases to 93%. The protective film consists of Fe²⁺-SDS complex, Fe²⁺-HEDP complex and Zn(OH)₂ as revealed by FTIR spectra. The HEDP-Zn²⁺ system shows good IE. The protective film consists of Fe²⁺-HEDP complex and Zn(OH)₂. Rain water along with these formulations may be used in cooling water systems in various industries.

Keywords : Corrosion inhibition, carbon steel, phosphonic acid, surfactant, sodium dodecyl sulphate.

Introduction

Now a days water is considered as a rare commodity. There is scarcity for water to be used in houses and industries. There is a drive to harvest the rain water and store it in concrete tanks. This harvested-rain water along with inhibitors may be used in cooling water system in various industries. Phosphonic acids have been widely used as corrosion inhibitors in cooling water systems due to their hydrolytic stability, scale inhibiting property, ability to form complexes with metal ions and low toxicity. Among the phosphonic acids, 1-hydroxyethane-1,1-diphosphonic acid (HEDP) has attracted the attention of several researchers [1-4]. The use of sodium dodecyl sulphate (SDS), an anionic surfactant, as corrosion

inhibitor has been reported [5-7]. Effect of metallic cations on corrosion inhibition of SDS for carbon steel in hydrochloric acid has been reported [5]. Corrosion inhibition of carbon steel by non-ionic polyoxyethylene (80) monopalmitate, cationic N-cetyl-N,N,N-trimethylammonium bromide (CTAB) and anionic SDS in sea water has been evaluated by weight - loss method, correlated with adsorption measurements and X-ray analysis. At very low surfactant (SDS) concentration, the corrosion is inhibited to a certain extent due to the adsorption of the surfactant molecules on the steel surface. An increase in the inhibitory action was observed when the concentration of the surfactant in the corrosive solution approaches to the critical micelles concentration values [6]. The synergistic corrosion inhibition by the SDS-Zn²⁺ system in controlling corrosion of carbon steel immersed in the environment containing 60 ppm of Cl⁻

* Corresponding author: Susai Rajendran

E-mail address: srmjoany@satyam.net.in

has been evaluated by weight loss method. The influence of pH, Na_2SO_3 and immersion period on the inhibition efficiency of the SDS- Zn^{2+} system has been investigated. The protective film has been analysed by FTIR and fluorescence spectroscopy [7]. The present work is undertaken (i) to evaluate the utility of harvested-rain water in cooling water systems in the presence of inhibitors such as HEDP, Zn^{2+} and SDS and (ii) to analyse the protective film using FTIR spectroscopy and (iii) to study the mechanistic aspects by polarization study and AC impedance spectra.

Experimental

Rain water, running down from terrace was collected and stored in concrete tanks. This water used in the present study. The various parameters of this water are given in Table 1.

Table 1. Physico chemical parameters of harvested rainwater

Parameter	Value
pH	8.87
Conductivity	122 μ mhos/cm
TDS	55 ppm
Chloride	0 ppm
Sulphate	0 ppm
Total hardness	20 ppm

Preparation of the specimens

Mild steel specimens [iron containing 0.02% S, 0.06% P, 0.4% Mn and 0.1% C] of dimensions 1.0 x 4.0 x 0.2 cm were polished to a mirror finish and degreased with trichloroethylene and used for the weight-loss method and surface examination studies.

Weight – loss method

Mild steel specimens, in triplicate, were immersed in 100 ml of the solutions containing various concentrations of the inhibitor in the absence and presence of Zn^{2+} , for three days. The weight of the specimens before and after immersion was determined using a Mettler balance, AE-240. The corrosion inhibition efficiency (IE) was then calculated using the equation.

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

Where W_1 = corrosion rate in the absence of inhibitor

W_2 = corrosion rate in the presence of inhibitor

Surface examination study

The mild steel specimens were immersed in various test solutions for a period of three days. After three days, the

specimens were taken out and dried. The nature of the film formed on the surface of the metal specimens was analysed by various surface analysis techniques.

FTIR spectra

These spectra (KBr) were recorded in Perkin Elmer – 1600 spectrophotometer.

Results and Discussion

The efficiencies of sodium dodecyl sulphate (SDS), Zn^{2+} and 1-hydroxyethane-1,1-diphosphonic acid (HEDP) in controlling corrosion of carbon steel immersed in harvested – rain water are given in Tables 2 to 5. It is observed that various concentrations of SDS (50 ppm to 300 ppm) accelerate corrosion. Similarly in the presence of 50 ppm of Zn^{2+} also, SDS accelerates corrosion.

Table 2. Corrosion Inhibition efficiency (IE) offered by SDS and Zn^{2+} to carbon steel immersed in rain water Immersion period : 3 days

SDS ppm	IE %	
	Zn^{2+} , ppm	
	0	50
50	-ve	-ve
100	-ve	-ve
150	-ve	-ve
200	-ve	-ve
250	-ve	-ve
300	-ve	-ve

Table 3. Corrosion inhibition efficiency offered by HEDP to carbon steel immersed in rain water Immersion period : 3 days

HEDP ppm	IE %
50	6
100	50
150	72
200	88
250	92

Table 4. Corrosion inhibition efficiency offered by HEDP system to carbon steel immersed in rain water Immersion period : 3 days

Zn^{2+} ppm	SDS ppm	HEDP ppm	IE %
50	150	50	80
50	150	100	95
50	150	150	96
50	150	200	96
50	150	250	98

Table 5. Corrosion inhibition efficiency offered by the Zn^{2+} -HEDP system to carbon steel immersed in rain water
Immersion period : 3 days

Zn^{2+} ppm	HEDP ppm	IE %
50	50	31
50	100	65
50	150	70
50	200	95
50	250	98

Interestingly when various concentrations of HEDP are added to the Zn^{2+} (50 ppm) – SDS (150 ppm) system very excellent corrosion inhibition efficiencies are noted. As the concentration of HEDP increases, the IE also increases. The Zn^{2+} (50 ppm) – SDS (150 ppm) – HEDP (250 ppm) has 98% IE. Comparison of the results found in Tables 4 and 5 reveals that the IE of the Zn^{2+} -HEDP system is improved by the addition of 150 ppm of SDS.

Influence of SDS on the inhibition efficiency of the Zn^{2+} (50 ppm) – HEDP (100 ppm) system

The influence of SDS on the IE of the Zn^{2+} (50 PPM) – HEDP (100 ppm) system is shown in Fig.1. It reveals that when 50 ppm of SDS is added, the IE decreases from 65% to 60%. When 100 ppm of SSD is added IE is very high, ie 98% further addition of SDS slightly lowers the IE. It is suggested that up to 100 ppm of SDS, an anionic surfactant exists as monomer. After this concentration, several molecules of SDS aggregate to form micelles. Hence the amount of SDS present on the metal surface decreases, leading to a decrease in IE. Further, after the formation of micelles, the surface tension of the solution increases. The amount of Zn^{2+} , HEDP and SDS transported from the bulk of the solution towards the metal

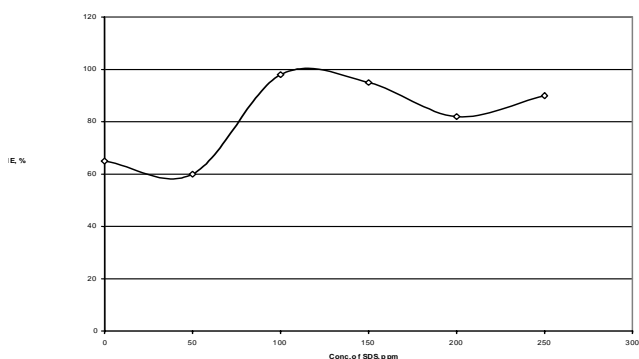
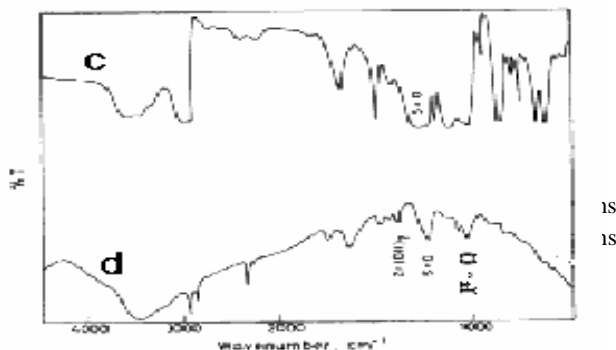
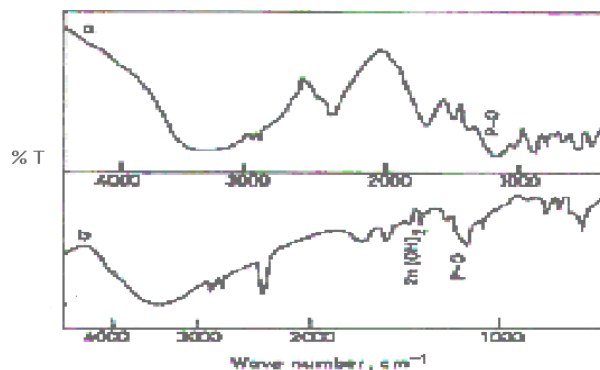


Fig.1. Influence of SDS on the inhibition efficiency of the Zn^{2+} (50 ppm) – HEDP (100 ppm) system

surface decreases and hence a decrease in IE. It is interesting to note at higher concentration of SDS, namely, at 250 ppm, there is increase in IE. It is suggested that at this concentration, reverse micelle formation may take place. Further investigation will lead to interesting facts.



The FTIR spectrum of pure HEDP is shown in Fig.2a. The P-O stretching frequency of the phosphonic acid appears at 1119 cm^{-1} . The formulation consisting of 50 ppm of Zn^{2+} and 100 ppm HEDP has 65% IE (Table 5). FTIR spectral analysis (Fig.2b) of the film (KBr) formed on the metal surface reveals that the P-O stretching frequency has decreased from 1119 cm^{-1} to 1095 cm^{-1} . This shift is caused by the decreased of the electron cloud density of the P-O bond. Due to the shift of the electron cloud density from the oxygen atom to Fe^{2+} , it is suggested that oxygen atom of the phosphonic acid is coordinated to Fe^{2+} , resulting in the formation of Fe^{2+} -HEDP

complex on the anodic sites of the metal surface. The peak at 1380 cm^{-1} is due to $\text{Zn}(\text{OH})_2$ formed on the cathodic sites of the metal surface [3, 8-10].

The FTIR spectrum of pure SDS is shown in Fig.2c. The aliphatic C-H stretching frequency appears at 2846 cm^{-1} . The peaks due to S-O-C stretching appear at 762.4 , 830.3 , 918.5 and 995.9 cm^{-1} . The S=O stretching frequency absorbs at 1227 cm^{-1} .

The formulation consisting of 50 ppm of Zn^{2+} , 100 ppm of HEDP and 100 ppm of SDS shows 98% IE (Fig.1). FTIR spectral analysis (Fig.2d) of the film (KBr) reveals that the P-O stretching frequency of HEDP has decreased from 1119 cm^{-1} to 1042 cm^{-1} . This suggests the formation of Fe^{2+} -HEDP complex on the anodic sites of the metal surface. The S=O stretching frequency has decreased from 1226 cm^{-1} to 1222 cm^{-1} . This suggests that the electron cloud has shifted from S=O towards Fe^{2+} , resulting in the formation of Fe^{2+} -SDS complex on the anodic sites of the metal surface. The band at 1360 cm^{-1} is due to $\text{Zn}(\text{OH})_2$ formed on the cathodic sites of the metal surface.[3, 8-10].

Analysis of potentiostatic polarization curves

The polarization curves of carbon steel immersed in rain water in the absence and presence of inhibitors are shown in Fig.3. The corrosion parameters are given in Table 6. When carbon steel is immersed in rain water the corrosion potential is -710 mV vs SCE . In the presence of the inhibitor system (50 ppm of Zn^{2+} 100 ppm of HEDP + 100 ppm of SDS) the corrosion potential is shifted to the anodic side (-535 mV vs SCE). This suggests that in the presence of Zn^{2+} More of the inhibitors, namely, SDS and HEDP are transported towards the metal surface and deposited on the anodic sites as Fe^{2+} -SDS complex and Fe^{2+} -HEDP complex. The anodic and cathodic Tafel slopes are almost equal (60 mV and 62 mV). This suggests that this formulation function as a mixed inhibitor controlling the anodic reaction and cathodic reaction almost equally.

Table 6. Corrosion parameters of carbon steel in rain water in the presence of inhibitors

System	E_{corr} mV vs SCE	b_a mV	b_c mV
Rain water	-710	270	215
Rain water + Zn^{2+} 50 ppm+ HDEP 100 ppm +SDS 100 ppm	-535	60	62

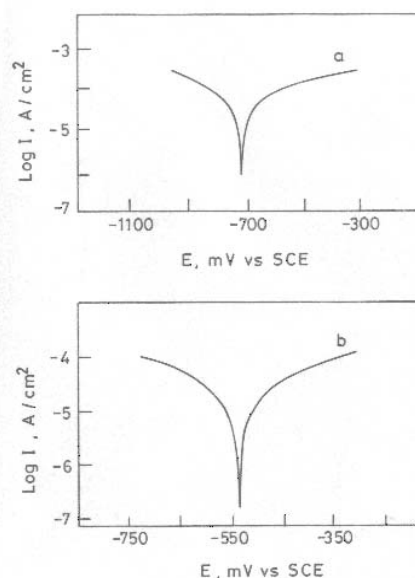


Fig. 3. Potentiostatic polarization curves of carbon steel immersed in various test solutions

- rain water
- rain water + Zn^{2+} 50 ppm + HEDP 100 ppm + SDS 100 ppm

Analysis of AC Impedance spectra

The AC impedance spectra of carbon steel immersed in various test solution are shown in Fig.4. The charge transfer resistance (R_t) and double layer capacitance (C_{dl}) are given in Table 7. When carbon steel is immersed in rain water, the R_t value is $930\ \Omega\text{ cm}^2$ and C_{dl} value is $0.345 \times 10^{-3}\text{ m F cm}^{-2}$. In the presence of inhibitor system (50 ppm of Zn^{2+} +100 ppm of HEDP+100 ppm of SDS), the R_t value increases ($1680\ \Omega\text{ cm}^2$) and the C_{dl} value decreases (0.153×10^{-3}). This confirms the formation of a protective film on the metal surface.

Table 7. AC impedance parameter of carbon steel.

System	$R_t\ \Omega\text{ cm}^2$	$C_{dl}\ \mu\text{ F cm}^{-2}$
Rain water	930	0.345×10^{-3}
Rain water + Zn^{2+} 50 ppm+ HDEP 100 ppm + SDS 100 ppm	1680	0.152×10^{-3}

HEDP complex, Fe^{2+} -SDS complex and $\text{Zn}(\text{OH})_2$. The HEDP- Zn^{2+} has excellent IE. The protective film consists of Fe^{2+} -HEDP complex and $\text{Zn}(\text{OH})_2$. Rain water along with this formulation may be used in cooling water systems in various industries.

Acknowledgement

The authors are thankful to their respective managements. S. Rajendran is thankful to UGC, New Delhi, India for financial assistance.

References

1. E. Kalman, B. Varheghi, I. Bako, I. Felhosi, F.H. Karman and A. Shaban, *J. Electrochem. Soc.*, 141 (1994) 3357
2. A. Veres, G. Reinhard and E. Kalman, *Bri. Corrosion J.*, 27 (1992) 147
3. I. Sekine and Y. Hirakawa, *Corrosion* 42 (1986) 272
4. S. Rajendran, B.V. Apparao and N. Palaniswamy, *Bull. of Electrochem.*, 13 (1997) 441
5. G.N. Mu, T.P. Zhao, M. Liu, T. Gu, *Corrosion*, 52 (1996) 853
6. M.N. Shalaby, M.M. Osman and A.A.El Feky, *Anti-Corrosion Methods and Materials*, 46 (1999) 254
7. S. Rajendran, S. Mary Reenkala, N. Anthony and R. Ramaraj, *Corr. Sci.*, 44 (2002) 2243
8. R.M. Silverstein, G.C. Bassler and T.C. Morrill, *Spectrometric Identification of Organic Compounds*, John Wiley Sons, New York, (1981) 95.
9. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley Intersciency, New York, (1986) 168.
10. A.D. Cross, *Introduction to Practical Infrared Spectroscopy*, Butterworths Scientific Publication, London, (1990) 73.

Fig. 4. AC Impedance spectra of carbon steel immersed in various test solutions

- a) rain water
- b) rain water + Zn^{2+} 50 ppm + HEDP 100 ppm + SDS 100 ppm

Conclusions

Sodium dodecyl sulphate (SDS) accelerates the corrosion rate of carbon steel immersed in the rain water. The SDS- Zn^{2+} system also accelerates the corrosion rate. Interestingly when HEDP is added to the SDS- Zn^{2+} system excellent inhibition efficiency is observed. The protective film consists of Fe^{2+} -

