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Corrosion behaviour of carbon steel in river water in the presence of calcium propionate- Zn^{2+} system

The inhibition efficiency of calcium propionate (CP)- Zn^{2+} system in controlling corrosion of carbon steel in an aqueous environment has been evaluated by mass-loss method. A synergistic effect is noticed between calcium propionate and Zn^{2+} . The formulation consisting of 50 ppm of calcium propionate and 50 ppm of Zn^{2+} shows 91% inhibition efficiency (IE). At lower pH value IE decreases and in alkaline solution IE increases. Polarization study reveals that CP- Zn^{2+} system controls cathodic reaction predominantly. AC impedance spectra reveal that a protective film is formed on the metal surface. FTIR spectra reveal that the protective film consists of Fe^{2+} -CP complex $Zn(OH)_2$ and $Ca(OH)_2$.

Key words: Corrosion inhibition, carbon steel, river water, synergistic effect

INTRODUCTION

The major problems in industrial use of the cooling water system are corrosion of the metal equipment, contamination of the circulating water system with microorganisms, and deposit formation that worsens the heat exchange. To solve the above problems complex treatment of the water is required including the use of the corrosion inhibitors and anti-deposit additives. Mixtures of inhibitors frequently provide better inhibition than either of the individual components. This was recognized by Speller [1] in the mid thirties, who reported the finding "compound films", such as formed by phosphates chromate mixtures to be more effective than those of either alone.

Carboxylic acids, their salts and their derivatives have recently emerged as a new and potential class of corrosion inhibitors. Many carboxylates such as Salicylate [2], cinnamate [3], phenyl acetate [4], anthranilates [5], thio divaltrate [6], adipate [7] and their derivatives have been used as inhibitors. Their inhibitive action results from the bonding of the anion to the metal surface through the excess electron on the O^- ion. Inhibitive anions such as benzoate, phthalate and other carboxylates stabilize the oxide film on iron surface [8,9]. Review of carboxylates as corrosion inhibitors have appeared from time to time. Mercer [10] reviewed carboxylates that provide protection to cast iron and non-ferrous metals.

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The present work is undertaken: (i) to evaluate the inhibition efficiency of calcium propionate (CP) in controlling corrosion of carbon steel in a river (namely, Cuavery in Trichy, Tamilnadu, India) water, in the presence and absence of Zn^{2+} (ii) to analyse the protective film by FTIR (iii) to make use of polarization study and AC impedance spectra to know the mechanistic aspects of corrosion inhibition.

EXPERIMENTAL

Preparation of the carbon steel specimens

Carbon steel specimens (0.026 % S, 0.06 % P, 0.40 % Mn, 0.10 % C, and the rest iron) of dimensions 1.0 x 4.0 x 0.2 cm were polished to mirror finish, degreased with trichloroethylene and used for mass-loss and surface examination studies.

Mass-loss method

The weighed specimens in triplicate were suspended by means of glass hooks in 100 ml beakers containing 100 ml of various test solutions. After 3 days of immersion, the specimens were taken out, washed in running water, dried and weighed. From the change in weights of the specimens, corrosion rates and I.E. were calculated.

$$IE = 100 [1 - (W_2 / W_1)] \%$$

Where W_1 =corrosion rate (mdd) in absence of inhibitor, W_2 =corrosion rate (mdd) in presence of inhibitor.

Surface examination studies

The carbon steel specimens were immersed in various test solutions for a period of three days, the specimens were taken out, washed with distilled water and then dried. The nature of the film formed on the surface of metal specimens was analysed by FTIR spectra.

FTIR spectra

The film was carefully removed with sharp edged glass rod, mixed thoroughly with KBr and made into pellets, and the FTIR spectra were recorded on a Perkin- Elmer 1600 spectrophotometer.

Potentiodynamic polarization study

Potentiodynamic polarization studies were carried out using CHI electrochemical impedance analyzer, model 660 A. A three-electrode cell assembly was used. The working electrode was a rectangular specimen of carbon steel with one face of the electrode (1 cm² area) exposed and the rest shielded with red lacquer. A saturated calomel electrode (SCE) was used as the reference electrode and a rectangular platinum foil was used as the counter electrode.

AC impedance measurements

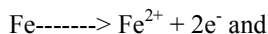
A CHI electrochemical impedance analyzer (model 660 A) was used for AC impedance measurements. A time interval of 5 to 10 minutes was given for the system to attain its open-circuit potential. The real part (Z') and imaginary part (Z'') of the cell impedance were measured in ohms at various frequencies (f). The values of the charge transfer resistance R_t and the double layer capacitance C_{dl} were calculated.

RESULTS AND DISCUSSION

Mass-loss method

The corrosion inhibition efficiencies of calcium propionate(CP)-Zn²⁺ systems in controlling corrosion of carbon steel in Cauvery water, as determined by mass loss method, are given in Table-1 . It is found from the table that CP is a poor inhibitor and 300 ppm of CP gives a maximum of 45% IE. Perusal of the table reveals that a combination of Zn²⁺ and CP shows a better IE. For example, 50 ppm of Zn²⁺ gives an IE of 50 % and 300 ppm of CP gives 45%; but their combination offers an IE of 91 %, which is found to be the maximum IE offered by the system. This suggests the existence of synergistic effect between Zn²⁺ and CP. The synergism may be due to the formation of complex between Zn²⁺ and CP. Because of the complex formation with Zn²⁺ the inhibitor molecules are readily transported from the bulk of the solution to the metal surface

On the metal surface, Zn²⁺-CP complex is converted into Fe²⁺-CP complex on the anodic sites of the metal surface. Zn²⁺ is released. This combines with OH⁻ to form Zn(OH)₂ on the cathodic sites of the metal surface. Thus both the anodic reaction



cathodic reaction



are controlled effectively. This accounts for a synergistic effect between CP and Zn²⁺.

Table 1 - Inhibition efficiency (%) of CP-Zn²⁺ system in controlling corrosion of carbon steel in cauvery river water.

Immersion period: 3 day

Inhibitor system: Calcium Propionate (CP) + Zn²⁺

CP, ppm	Zn ²⁺ , ppm				
	0	5	10	25	50
0	--	28	33	41	50
50	8	49	74	89	91
100	14	42	71	85	87
150	24	39	66	82	84
200	30	45	64	77	79
250	43	46	63	72	78
300	45	43	67	70	71

FTIR spectral analysis

The FTIR spectrum of calcium propionate (CP in KBr) is shown in Fig.1a. The C=O stretching frequency of carboxyl group appears at 1579 cm⁻¹. The FTIR spectrum of the film formed on the metal surface after immersion in Cauvery water containing 50 ppm of CP and 50 ppm of Zn²⁺ is shown in Fig.1b. It can be seen that the C=O stretching frequency of the carboxyl group has shifted from 1579 cm⁻¹ to 1590cm⁻¹. This indicates that the oxygen atom of carboxyl group has coordinated with Fe²⁺ resulting in the formation of Fe²⁺-propionate complex on the anodic sites of the metal surface. The peak at 1352 cm⁻¹ is due to Zn(OH)₂ formed on the cathodic sites [11]. The band at 1505.6cm⁻¹ is due to Ca(OH)₂ formed on the cathodic sites of the metal surface [12].

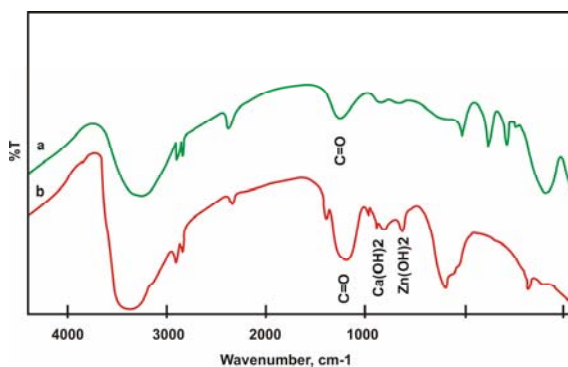


Fig 1: FTIR spectra of (a) calcium propionate and (b) Film formed on steel after immersion in well water containing 50 ppm CP & 50 ppm Zn²⁺

Analysis of the results of potentiodynamic polarization studies

The corrosion parameters of carbon steel immersed in river water in the absence and presence of inhibitor system are given in Table 2.

When carbon steel is immersed in river water, the corrosion potential (E_{corr}) is -463 mV vs SCE and the corrosion current is 1.556×10^{-5} A/cm². When 50 ppm of Zn²⁺ and 50 ppm of calcium propionate are added to river water the corrosion potential shifts to the cathodic side (-536 mV vs SCE). The corrosion

current is 1.174×10^{-5} A/cm². The cathodic slope is found to change from 276 to 492 mV/decade and the anodic slope from 217 to 184 mV/decade. The linear polarization resistance has increased from 3.643×10^3 to 4.963×10^3 Ωcm². The increase in the value of b_c is considerably more than that of b_a . This shows that the cathodic reaction controls the cathodic reaction predominantly. The increase in LPR value and decrease in corrosion current indicate that a protective film is formed on the metal surface [13].

Table 2 - Corrosion parameters of carbon steel in river water (Cauvery) in the presence and absence of inhibitor obtained by potentiodynamic polarization

System	E_{corr} mV vs SCE	b_c mV/decade	b_a mV/decade	LPR Ω cm ²	I_{corr} A/cm ²
River water	-463	327	217	3.643×10^3	1.556×10^{-5}
River water + 50 ppm CP + + 50 ppm Zn ²⁺	-536	492	184	4.963×10^3	1.174×10^{-5}

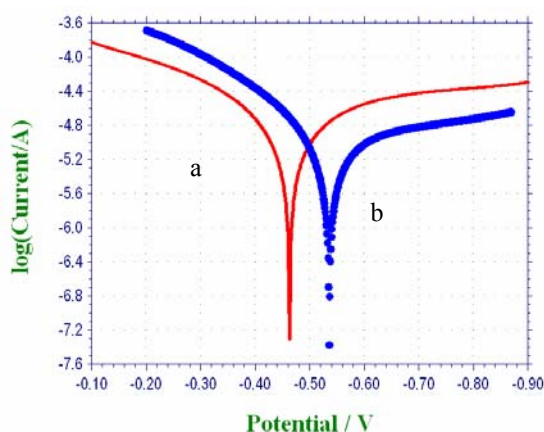


Fig.2: Polarization curves of carbon steel immersion in various test solutions: a) River water (RW), b) RW + 50 ppm CP + 50 ppm Zn²⁺

Analysis of the results of AC impedance spectra

The AC impedance spectra of carbon steel immersed in various test solutions are shown in Fig.2.

The AC impedance parameters, namely, charge transfer resistance (R_t) and the double layer capacitance (C_{dl}) are given in Table 3.

When carbon steel is immersed in river water the R_t value is found to be 1102 Ω cm². The C_{dl} value is 8.2187×10^{-9} F/cm². When 50 ppm of Zn²⁺ and 50 ppm of calcium propionate are added, the R_t value has increased from 1102 to 1697 Ωcm² and the C_{dl} value has decreased from 8.2187×10^{-9} to 5.3391×10^{-9} F/cm². The increase in R_t values and decrease in double layer capacitance values obtained from impedance studies justify the good performance of a com-

pound as an inhibitor in river water. This behavior means that the film obtained acts as a barrier to the corrosion process that clearly proves the formation of the film [14].

Table 3 - Impedance parameters of carbon steel in river water in the absence and presence of inhibitor obtained by AC impedance spectra

System	R_t Ω cm ²	C_{dl} F/cm ²
River water	1102	8.2187×10^{-9}
River water + 50 pm CP + 50 ppm Zn ²⁺	1697	5.3391×10^{-9}

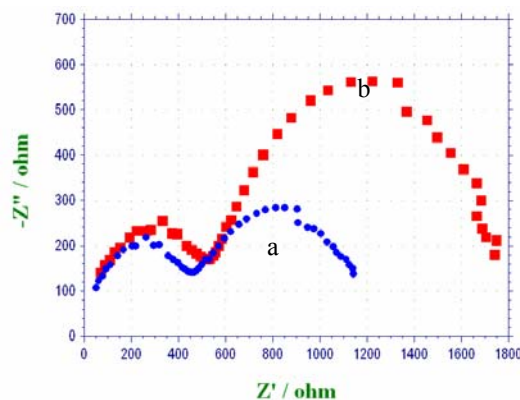


Fig.3: AC impedance spectra of carbon steel immersed in various test solutions: a) River water, b) River water + 50 ppm CP + 50 ppm Zn²⁺

The SEM pictures are shown in Fig.4. In the absence of inhibitors pits are seen. But in the presence of inhibitors, barrier film is visible.

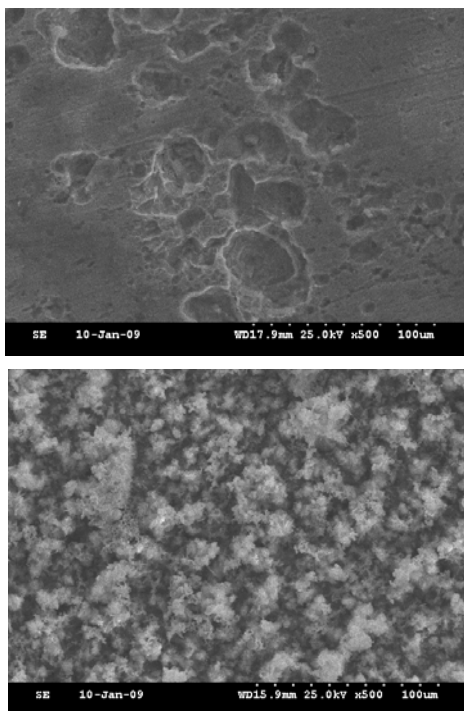


Fig.4: SEM micrographs: a) Film formed on metal surface in presence of river water, b) Film formed on metal surface in presence of river water + 50 ppm CP + 50 ppm Zn²⁺

CONCLUSIONS

Corrosion behaviour of carbon steel in the absence and presence of calcium propionate and Zn²⁺ has been evaluated.

- The analysis of the results of mass-loss method shows that the formulations consisting of 50 ppm of Calcium propionate and 50 ppm of Zn²⁺ offers maximum IE of 91 %.
- The results of polarization studies show that this formulation predominantly controls the cathodic reactions.
- SEM pictures reveal the presence of uniform complex layer on the metal surface.
- The AC impedance spectral studies reveal the formation of a film with higher resistance than that of the Cauvery water.
- FTIR spectra reveal that the protective film consists of Fe²⁺-propionate complex Zn(OH)₂ and Ca(OH)₂.

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REFERENCES

- [1] F. N. Speller, Discussion, Proc. ASTM, (part2), 36 (1936) 695
- [2] E. V. Bogatyreva and S.A. Balezin, Zh Prikl Khim, 32 (1959) 1071.
- [3] E. V. Bogatyreva and V.V. Nagaev, Zh Prikl Khim, 35 (1962)556.
- [4] E.V. Bogatyreva, Khim Khim Tekhnol (1) (1959)
- [5] Yu.I. Kuznetsov, S.V. Oleynik, N.N.Andreev and S. S.Vesely, Sixth European Symposium on Corrosion Inhibitors, Ferrara, Italy, 1(8) (1985) 567.
- [6] E.V. Bogatyreva and M.A.Karepina, Zh Prikl Khim, 36 (1963)147.
- [7] N.G. Klyuchnikov and N.S. Novoshinskaya, Zh Prikl Khim, 36 (1963)2470
- [8] W.Funke and K.Hamann, Werkst Korros, 9 (1958) 202
- [9] I.L. Rosenfeld, Yu.I.Kuznetsov, I.Ya. Kerbeleva, V.P.Persianceva, Prot. Met., 10 (1974) 612.
- [10] A.D.Mercer, Proc. of Fifth Conf. on Corrosion Inhibitors, Ferrara, Italy, (7) (1980) 563
- [11] I. Sekine, Y.Hirakwa, Corrosion 42 (1986) 276.
- [12] S. Rajendran, B.V. Apparao and N. Palaniswamy, British Corrosion Journal, 33 (1998) 315.
- [13] S. Rajendran, M. Kanagamani, M.Sivakalaivani, J. Jeyasundari, B. Narayanasamy and K. Rajam, Zastita Materijala, 49 (2008) 19.
- [14] A. Jeyashree, F. Rajammal Selvarani, J. Wilson Sahayaraj, A. John Amalraj, S. Rajendran, Portugaliae Electrochimica Acta, 27 (2009) 23.

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