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

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Abstract: The inhibition efficiency of lactic acid (LA)-Zn^{2+} system in controlling corrosion of carbon steel in an aqueous environment has been evaluated by mass- loss method. The synergistic effect is noticed between lactic acid and Zn^{2+}. The formulation consisting of 50 ppm of lactic acid and 50 ppm of Zn^{2+}shows 91% inhibition efficiency(IE). At lower pH value IE decreases and in alkaline solution IE increases. Polarisation study reveals that LA-Zn^{2+} system functions as a cathodic inhibitor. 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+}-LA complex and Zn $(OH)_2$.

Keywords: Corrosion inhibition, carbon steel, river water, synergistic effect.

Introduction

Metal corrosion in water conveying systems such as cooling water circuits is of major concern in industrial applications(1). Many inhibitors have been used in cooling water systems in order to solve these problems (2-5).The use of inhibitors is one of the most practical means for protecting metals/alloys against corrosion. They are classified as anodic, cathodic, organic and inorganic etc. In many applications, mixtures of inhibitors are used. Often there are synergistic effects, i.e., the mixtures are more effective than individual components. Many cation-anion mixtures of this type are used as inhibitors in cooling waters and in paints, including those containing zinc cations, e.g.,zinc-phosphate, zinc chromate and zinc molypdate. It is often said that the benefits of these mixtures arise from the presence of both cathodic (Zn^{2+}) and anodic (anions) inhibitors (6-13). Gunasekaran et al (14) have established the synergistic effect of tartrate with organophosphonic acid and zinc metal ions in neutral environment on the corrosion inhibition of steel. Muthumani et al (15) have examined the inhibition efficiency of sodium potassium tartrate in controlling the corrosion of carbon steel immersed in ground water in the absence and presence of Zn^{2+}. Consequently, an objective is to develop low-toxic, heavy metal and phosphorous free corrosion inhibitors with good biodegradability (16).

The present work is undertaken: (i) to evaluate the inhibition efficiency of lactic acid (LA) in controlling corrosion of carbon steel in river(namely, Cauvery 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,(iv) to analyse the film formed on the metal surface by UV absorption spectral studies and (v) to propose a suitable mechanism based on the results from the above studies.

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 × 4.0 × 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 duplicate were suspended by means of glass hooks in 100 ml beakers containing 100 ml of various test solutions. After 72 hours 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 analyzed by the following techniques.

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 cm^2 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.

The UV-visible absorption spectra of solutions:

The possibility of the formation of Zn- inhibitor complex and also iron-inhibitor complex in solution was examined by mixing the respective solutions and recording their UV-visible absorption spectra using Lamda 35 UV-visible spectrophotometer 119 which is a PC controlled single beam scanning spectrophotometer. It covers a wavelength range from 200 nm to 1000 nm with a setting accuracy of ± 1nm.

Results and Discussion

Mass-loss method

The corrosion inhibition efficiencies of lactic acid (LA)-Zn^{2+} system, as determined by mass loss method, are given in **Table-1.** It is found from the table that LA is a poor inhibitor and 50 ppm of LA gives a maximum of 24 % IE. Perusal of the table reveals that a combination of Zn^{2+} and LA shows a better IE. For example, 50 ppm of Zn^{2+} gives an IE of 41 % and 50 ppm of LA gives 24 %, but their combination offers an IE of 89 %, which is found to be the maximum IE offered by the system. This suggests the existence of synergistic effect between Zn^{2+} and LA. The synergism may be due to the formation of complex between Zn^{2+} and LA. Because of the complex formation with Zn^{2+} the inhibitor molecules are readily transported from the bulk to the metal surface.

On the metal surface, Zn^{2+}-LA complex is converted into Fe^{2+}-LA complex on the anodic sites of the metal surface. Zn^{2+} is released. This combines with OH^- to form $Zn(OH)_2$ on the cathodic sites of the metal surface. Thus both the anodic reaction

Fe---------> $Fe^{2+} + 2e^-$ and

Cathodic reaction

$O_2 + 4e^- + 2H_2O$---------> $4OH^-$

are controlled effectively.. This accounts for a synergistic effect between LA and $Zn^{2+.}$

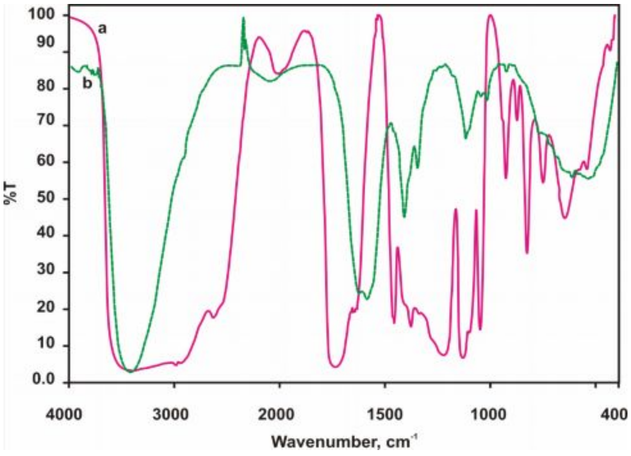
FTIR spectral analysis

The FTIR spectrum of **LA (fig-1a)** shows a very broad peak with centre at 3405 cm^{-1} due to OH stretching of alcoholic OH and carboxylic acid OH. There is a peak at 1731.79 cm^{-1} due to C=O stretching, at 1455.5 cm^{-1} and 1375.10 cm^{-1} due to coupling of in plane OH bending and COO- stretching of dimer and at 922.47 cm^{-1} due to O-H out of plane of bending of dimer. These peaks are characteristic of acids that exist as dimer. The spectrum of thin **film (fig-1b)** exhibits a narrow peak at 3435.68 cm^{-1} due to O-H stretching of the hydroxyl group. The conversion of the broad peak in the LA into a narrow peak in the thin film and increase in the frequency of the OH stretching from 3405cm^{-1} to 3435.68 cm^{-1} clearly shows that COOH group is converted into COO- in the thin film.The spectrum of thin film also exhibits a peak at 1592.77 cm^{-1} and 1415.40cm^{-1} which are characteristics of complexed COO- frequencies. This clearly shows that LA has formed a complex with metal ions through the carboxyl oxygen atom and exists as a complex in the thin film.There is a peak at 3778.48 cm^{-1}, this may be due to the stretching vibration of OH attached to a metal ion. The band at 1352.22 cm^{-1} may be due to the inplane bending vibration of OH group in Zn $(OH)_2$(9). The broad peak around 600cm^{-1} may be due to M-O stretching vibration.(17).

Table-1:Inhibition efficiency of LA-Zn^{2+}system on the corrosion of carbon steel in river (Cauvery) water. Immersion period: 3 days

LA ppm	Zn^{2+},ppm				
	0	5	10	25	50
0	--	20	28	39	41
10	14	36	45	55	70
25	20	37	49	61	79
50	24	46	59	73	89
75	22	45	58	70	87
100	17	41	55	67	84
125	16	39	42	57	82

Fig: 1: FTIR spectra of (a) lactic acid and (b)



Film formed on steel after immersion in river water containing 50 ppm LA & 50ppm Zn^{2+}.

Analysis of the results of potentiodynamic polarization studies:

The potentiodynamic polarization curves of carbon steel immersed in river water in the presence and absence of Zn^{2+} and LA are given **in Figure-2.** The corrosion parameters of carbon steel immersed in river water in the presence and absence of 25 ppm of Zn^{2+} and 50 ppm of Lactic acid 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 x 10^{-5} A/cm^2. When 50 ppm of $Zn^{2+}$and 50 ppm of lactic acid are added to river water the corrosion potential is found to be -554 mV vs SCE. The corrosion current is 0.511 x 10^{-5} A/cm^2. The cathodic slope is found to change from 327 to 542 mV/ decade and the anodic slope from 217 to 177 mV/ decade. The linear polarization resistance has increased from 3.643 x 10^3 to 11.38 x 10^3 Ωcm^2. The increase in the value of b_c is considerably more than that of b_a. This shows that the formulation functions as cathodic inhibitor controlling both anodic and cathodic processes but more predominantly cathodic process. This increase in LPR value and decrease in corrosion current indicate that a protective film is formed on the metal surface.

Analysis of the results of AC impedance studies:

The AC impedance spectra of carbon steel immersed in various test solutions are shown in **Fig.3.**

The AC impedance parameters namely charge transfer resistance (Rt) 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 cm^2. The C_{dl} value is 8.2187 x 10^{-9} F/cm$^{2.}$ When 50 ppm of $Zn^{2+}$and 50 ppm of lactic acid are added the R_t value has increased from 1102 to 1477 Ωcm^2 and the C_{dl} value has decreased from 8.2187 x 10^{-9} to 6.1346 x 10^{-9}. The increase in Rt values and decrease in double layer capacitance values obtained from impedance studies justify the good performance of a compound as an inhibitor in river water. This behaviour means that the film obtained acts as a barrier to the corrosion process that clearly proves the formation of the film.[18]

Fig.2: Polarization curves of carbon steel immersion in river (Cauvery) water and RW containing 50 ppm LA and 50 ppm Zn^{2+}

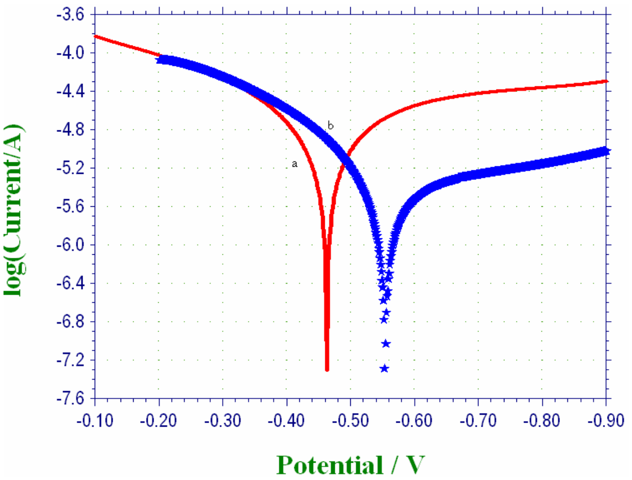


Table-2: Corrosion parameters of carbon steel in river water (Cauvery) in the presence and absence of inhibitor obtained by potentiodynamic polarization

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	$3.643X10^3$	$1.556X10^{-5}$
Riverwater + 50 ppm LA + 50 ppm Zn^{2+}	-554	542	177	$11.38X10^3$	$0.511X10^{-5}$

Fig-3 : AC impedance spectra of carbon steel immersed in various test solutions a) River water b)River water + 50 ppm LA + 50 ppm Zn^{2+}

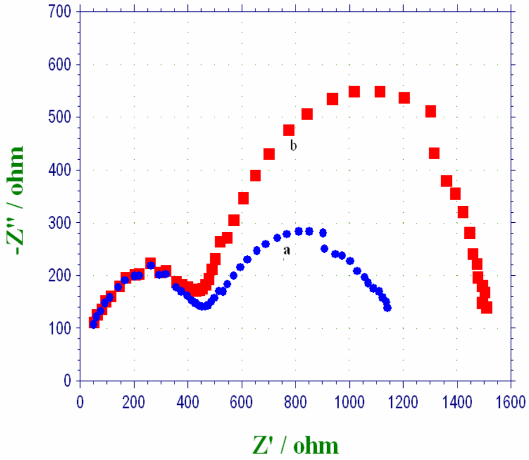


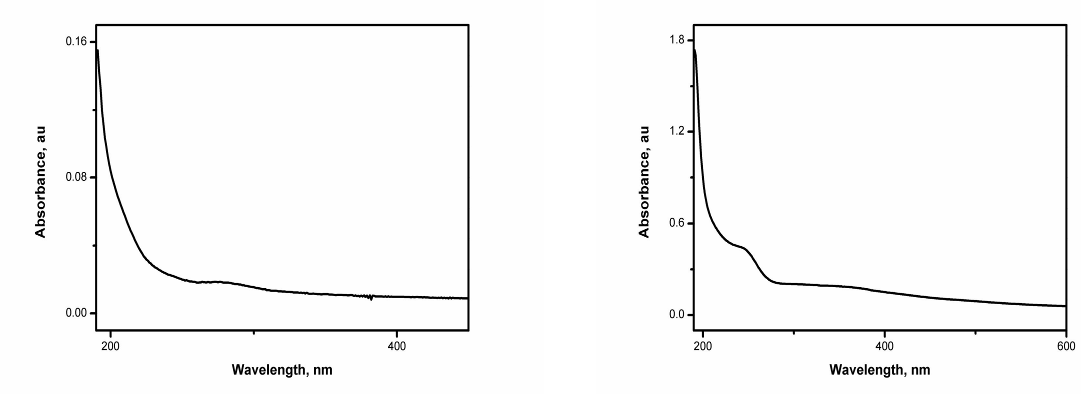
Table-3: Impedance parameters of carbon steel in river water in the absence and presence of inhibitor obtained by AC impedance spectra.

S.N0	Environment	R_t, Ω cm^2	C_{dl}, μ F/cm^2
1	River water	1102	8.2187×10^{-9}
2	River water+ 50ppmLA+ 50ppm Zn^{2+}	1477	6.1346×10^{-9}

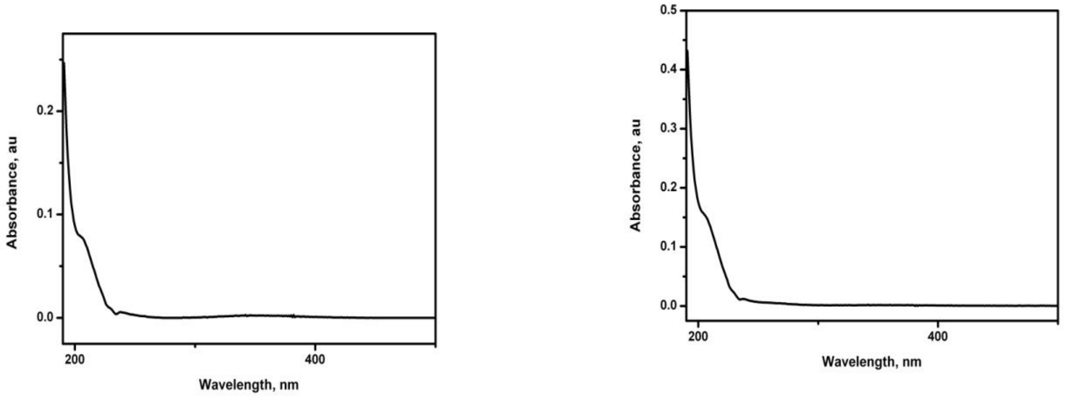
UV-Visible spectral study

The UV -visible spectrum of Zn^{2+}, Fe^{2+} ion, LA, Zn^{2+}- LA and Fe^{2+} - LA in distilled water are given in **figures-4$_{a-e}$.** From the figure-4c it is observed that LA has a maximum absorbance of 0.2957 at 190 nm, and the absorbance falls sharply and reaches 0.0015 at 379 nm and remains almost constant beyond that. The figure-4d reveals that LA-Zn^{2+} gives a maximum absorbance of 0.5059 at 190 nm and decreases sharply with increase in wavelength and reaches 0.0015 at 382 nm. The increase in the absorbance value on the addition of Zn^{2+} clearly indicates the occurrence of interaction between Zn^{2+} and LA. When Fe^{2+} is added to LA (Figure-4e) two small peaks have appeared at 208.02 nm (abs-3.1085) and at 198.28 nm (abs-3.0265). Appearance of the above two peaks is a clear proof for the formation of a complex between Fe^{2+} and LA.

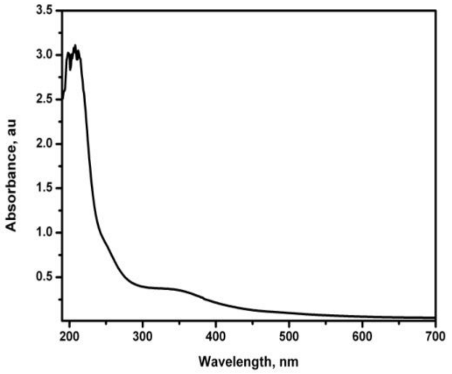
Fig- 4 : UV-Visible absorption spectra of the test solutions in river water



a) **Zn^{2+} ions** **b) Fe^{2+} ions**



c) LA **d) LA and Zn^{2+} ions**



e) LA and Fe^{2+} ions

Mechanism of corrosion inhibition:

- The analysis of the results of the mass-loss method shows that the formulation consisting of 50 ppm of lactic acid and 50 ppm of Zn^{2+} offers maximum IE of 89%.
- The AC impedance spectral studies reveal the formation of a film with higher resistance than that of the river water alone.
- Results of polarization study show that this formulation functions as a mixed inhibitor but more predominantly controlling cathodic process.
- The UV – visible absorption spectra indicate the possibility of formation of iron-LA complex and also Zn^{2+} - LA complex in solution.
- The FTIR spectra confirm the formation of film consisting of iron - LA complex and $Zn(OH)_2$(9).

Based on the above facts the following mechanism is proposed:

- In river (Cauvery) water containing 50 ppm of Zn^{2+} and 50 ppm of lactic acid, a sort of complex is formed between Zn^{2+} and lactic acid.
- When the metal is immersed in this environment, this complex diffuses from the bulk of the solution to the surface of the metal.
- On the surface of the metal, Zn complex is converted into the iron complex at the local anodic sites, as the latter is more stable than the former.

  Zn-Complex + Iron → Iron – Complex + Zn^{2+}.
- The released Zn^{2+} ions will form $Zn\ (OH)_2$ in the local cathodic regions.
- The protective film consists of iron-complex and $Zn\ (OH)_2$(19,20).

Hence the IE of the inhibitor formulation depends on the ability of the inhibitor to form complex with Zn^{2+} and also the ability of Fe^{2+} to react with Zn^{2+}complex to form iron complex.

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References:

1. D.Held,Kuhlwasser, 4th edition, Uulkan verlag Essen(1994).
2. L.L. Sheir, R.A. Jarman, Corrosion, third ed., Butterworth-Heinmann Ltd., Great Britain, 1994.
3. S.N. Banerjee, An Introduction to Science of Corrosion and its Inhibition, Oxonian Press Pvt. Ltd., India, 1985.
4. I.L. Rozenfeld, Corrosion Inhibition, McGraw -Hill Inc., USA, 1981.
5. D.A. Jones, Principles and Prevention of Corrosion, Macmillan Publishing Company, USA, 1991
6. S.Rajendran, B. V.Apparao and N. Palaniswamy,J.Electrochem.Soc., India, 1998, 47, 43.
7. S.Rajendran, B.V.Apparao and N. Palaniswamy, Bulletin of Electrochemistry, 1999, 15, 131.
8. S.Rajendran, B.V.Apparao and N. Palaniswamy, Anti- Corrosion Methods and Materials, 1998, 45, 338.
9. I. Sekine and Y. Hirakawa, Corrosion, 1986, 42, 272.
10. S.Rajendran, B.V.Apparao and N. Palaniswamy,, Electrochimica Acta, 1998, 44, 533.
11. Y. Gonalez, M.C.Lafont and N.Pebere, J. Applied Electrochemistry, 1996, 26, 1259.
12. I. Felhosi, Zs. Keresztes, F.H. Karman, M.Mohai, I.Bertoti and E. Kalman, J.Electrochem.Soc., 1999, 146, 961.
13. J.Mathiarasu, R. Natarajan, N.Palaniswamy and N.S. Rengaswamy, Bulletin of Electrochem, 1997, 13, 161.

14. G.Gunasekaran, R.Natarajan and N. Palaniswamy, Corrosion Science, 2001, 43(9), 1615-1626.
15. N.Muthumani, A. John Amalraj, Susai Rajendran and R.Ramaraj, Eleventh National Convention of Electrochemists, Trichy, Organized by SAEST, CECRI and Bishop Heber College, Trichy, 2003, 26, 27.
16. J.Steber, W. Hater, Henkel,Reterate international Edition 1998, 34, 115.
17. E.S.Prochaska and L.Andrews, J. Chem. Phys. 1980, 72, 6782.
18. A.Jeyasree, F.Rajammal Selvarani, J.Wilson Sahayaraj, A. John Amalraj, S.Rajendran, Portugaliae Electrochimica Acta 2009, 27, 23.
19. G. Ruba Helen Florence, A.Noreen Anthony, J.Wilson Sahayaraj, A.John Amalraj and Susai Rajendran, Indian Journal of Chemical Technology, 2005, 12, 472-476.
20. Felicia Rajammal Selvarani, S. Santhamadharasi, J. Wilson Sahayaraj, A. John Amalraj and Susai Rajendran, Bulletin of Electrochemistry, 2004, 20 (12), 561-565.

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