

The Inhibition of Mild Steel Corrosion in Sulphuric Acid Media by Acorus Calamus Extract

S. Ananth Kumar

Kandaswami Kandar's College,
P. Velur,
Namakkal-638 182, India

A. Sankar

Kandaswami Kandar's
College, P. Velur,
Namakkal-638 182, India

M. Kumaravel

PSG College of Technology
Peelamedu, Coimbatore
641 004, India

S. Rameshkumar

PSG College of Technology
Peelamedu, Coimbatore
641 004, India

Abstract – The inhibitive action of rhizome extracts of *Acoruscalamus* on mild steel corrosion in 0.5 N H₂SO₄ solution was studied using weight loss method, potentiodynamic polarization and EIS measurements. The results obtained indicate that the extracts functioned as good inhibitors in H₂SO₄ solution. Inhibition efficiency was found to increase with extract concentration. The adsorption of constituents in the plant extract on the surface of the metal is proposed for the inhibition behavior.

Keywords – Corrosion, Green Inhibitors.

I. INTRODUCTION

Since corrosion and abrasion are the effective factors in the degradation of industrial parts, many attempts have been made to find methods for reducing corrosion and wear costs [1–7]. The adsorption of inhibitors containing heteroatoms such as nitrogen, oxygen, phosphorus and sulphur, as well as multiple bonds or aromatic rings, in their molecular structure, on to the metal surface is considered to arrest the corrosion reactions at the active centers [8–13]. As a contribution to the current interest on environmentally friendly corrosion inhibitors, the present study aims at broadening the application of plant extracts for metallic corrosion inhibition by investigating the inhibitive properties of rhizome extracts *Acoruscalamus* on mild steel corrosion in H₂SO₄ using weight loss, potentiodynamic polarization and electrochemical impedance techniques.

II. MATERIALS AND METHODS PREPARATION OF EXTRACT

A methanolic extract of *Acoruscalamus* was prepared from the powdered *Acoruscalamus* by boiling with methanol, then gangues are removed from the suspension by filtration. The extract was used as corrosion inhibitor in the present study.

Preparation of specimens

Carbon steel specimens (0.022% S, 0.038% Mn, 0.027% P, 0.086 C) of dimensions 1.0 cm * 4.0 cm * 0.2 cm were polished to a mirror finished and degreased with trichloroethylene.

Mass loss method

Relevant data for the weight loss study in 0.5 N H₂SO₄ is shown in table 1. Carbon steel specimens in triplicate were immersed in 100 mL of 0.5 N H₂SO₄ solutions containing various concentrations of the inhibitor in the

presence and absence of KI for two hours. The weight of the specimens before and after immersion were determined using shimadzu balance, model Ay 62. The inhibition efficiency (IE) was then calculated using the equation.

$$IE\% = \left(\frac{W_1 - W_2}{W_1} \right) \times 100$$

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

Electrochemical measurements

Impedance measurements

The electrochemical impedance measurements were carried out using a Potentiostat/Galvanostat/FRA (PARSTAT 2273, Princeton Applied Research, USA). Data acquisition was performed utilizing the PowerSuite software and analyzed using Zsimp Win software (version 3.21). A three electrode set up was employed with Pt foil as the auxiliary electrode and a saturated calomel electrode as the reference electrode. The mild steel cylinder coated with teflon, with surface preparation as described in the weight loss experimental method, served as the working electrode. The measurements were carried out in the frequency range 10^6 – 10^{-2} Hz at the open circuit potential by superimposing a sinusoidal AC signal of small amplitude, 10 mV, after immersion for 30 min in the corrosive media. The double layer capacitance (C_{dl}) and charge transfer resistance (R_{ct}) were obtained from the impedance plots as described elsewhere [14]. Because R_{ct} is inversely proportional to corrosion current density, it was used to determine the inhibition efficiency (IE%) using the relationship:

$$IE\% = \frac{R_{ct} - R_{ct}^0}{R_{ct}} \times 100$$

Where R_{ct} and R_{ct}^0 are the charge transfer resistance values in the inhibited and uninhibited solutions respectively.

Polarization measurements

The potentiodynamic polarization curves were recorded using the same cell setup employed for the impedance measurements. The potentials were swept at the rate of 1.66 mVs⁻¹, primarily from a more negative potential than E_{ocp} to a more positive potential than E_{ocp} through E_{corr} . The inhibition efficiencies were calculated using the relationship [15]:

$$IE\% = \frac{I^{ocorr} - I_{corr}}{I^{ocorr}} \times 100$$

Where I_{corr}^0 and I_{corr} are the corrosion current densities in the absence and in the presence of inhibitor, respectively.

III. RESULTS AND DISCUSSION

A. Analysis of results of mass loss method

The weight loss parameters for corrosion of carbon steel immersed in 0.5 N H_2SO_4 in the absence and presence of inhibitor are given table 1. It is seen from this table that the rizhome extract of Acoruscalamus shows 44.87% inhibition efficiency for the corrosion of carbon steel in 0.5 N H_2SO_4 well water and it increases with increase in volume of stock solution added to the corrosive media.

Table1: Mass loss parameters for corrosion of carbon steel in 0.5N H_2SO_4 in the absence and presence of inhibitors.

| Concent ration of AC Extract (ppm) | KI (0)ppm | | KI (50)ppm | |
|--|---|-----|---|---------|
| | CR (mgcm ⁻² h ⁻¹) | IE% | CR (mgcm ⁻² h ⁻¹) | IE % |
| 0 | 112.81 | - | 112.81 | |
| 10 | 62.19 | 44 | 27.81 | 76 |
| 25 | 52.81 | 53 | 25.94 | 77 |
| 50 | 51.56 | 54 | 21.56 | 80 |
| 100 | 41.80 | 62 | 21.56 | 80 |

B. Influence of KI on the inhibition efficiency of AC

The influence of KI on the IE of AC can also be seen from table1. In the presence of KI (50 ppm) the inhibitor shows an excellent inhibition efficiency at all concentrations. This suggests that a synergistic effect exists between AC and KI.

C. Electrochemical impedance spectroscopic measurements (EIS)

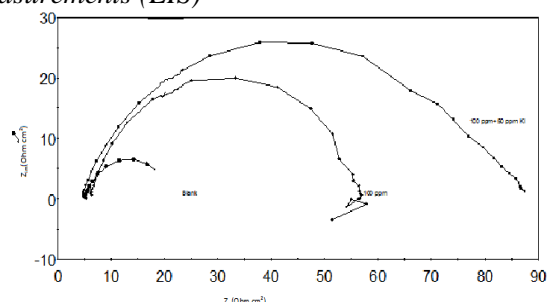


Fig.1. The Impedance measurements of mild steel immersed in sea water in the absence and presence of inhibitors

Table1. Impedance parameters obtained from electrochemical impedance studies

| Inhibitor concentration ppm | R _{ct} Ohm cm ² | C _{dl} μF | IE% |
|-----------------------------------|--|-------------------------|-----|
| 0 | 17.2 | 9.2578×10 ⁻³ | - |
| 100 | 58 | 6.561×10 ⁻⁶ | 70 |
| 100+50ppm(KI) | 88 | 4.324×10 ⁻⁶ | 80 |

Impedance spectra obtained for corrosion of mild steel in 0.5 N H_2SO_4 contains two semicircles in which the second one represents the interaction of metal surface with the corrosive environment. The first semicircle represents the nature of the corrosive media. Since the conductivity of the corrosive medium is very low, this also behaves like a leaky capacitor. The CR-CR model best describes this situation. The second semicircle in the impedance plots contain depressed semicircles with the centre below the real axis. The size of the semicircle increases with the inhibitor concentration, indicating the charge transfer process as the main controlling factor of the corrosion of mild steel. It is apparent from the plots that the impedance of the inhibited solution has increased with the increase in the concentration of the inhibitor. The experimental results of EIS measurements for the corrosion of mild steel in 0.5 N H_2SO_4 in the absence and presence of inhibitor are given in Table 5. Papova et al. said that sum of charge transfer resistance (R_{ct}) and adsorption resistance (R_{ad}) is equivalent to polarization resistance (R_p).

D. Polarization studies

Electrochemical parameters like corrosion potential (E_{corr}), corrosion current density (I_{corr}), cathodic tafel slope (c) Anodic tafel slope a and percentage inhibition efficiency according to polarization studies are listed in table 2. Here I_{corr} decreased with increasing inhibitor concentration. It is clearly observed that the Acorus calamus reduce the corrosion current density.

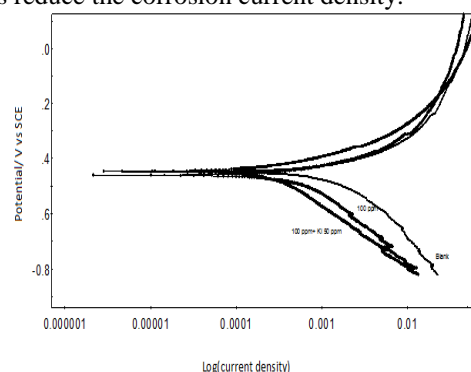


Fig.2. The potentiodynamic polarization curves of mild steel immersed in sea water in the absence and presence of inhibitors

Table 2: Corrosion parameters in the presence and absence of inhibitor obtained from polarization measurements

| Inhibitor Concentratio n (ppm) | E _{corr} (mV) | c (mV/) | a (mV) | I _{corr} μA | IE% |
|--------------------------------------|---------------------------|-------------|-----------|-------------------------|-----------|
| 0 | 448 | 127 | 68 | 1.628 | - |
| 100 | 430 | 168 | 72 | 0.733 | 55.0 |
| 100+50ppmK I | 454 | 179 | 83 | 0.471 | 71.0 5 |

Corrosion current density decreased noticeably with increase in inhibitor concentration, indicating the increased inhibition efficiency with the increase in the concentration of the inhibitor. E_{corr} value shifted towards

more negative potential. It has been reported that a compound can be classified as an anodic and cathodic type inhibitor on the basis of shift E_{corr} value. If displacement of E_{corr} value is greater than 85 mV, towards anode or cathode with reference to the blank, then an inhibitor is categorized as either anodic or cathodic type inhibitor. Otherwise, inhibitor is treated as mixed type. In our study, maximum displacement in E_{corr} value was around 6 mV. Indicating inhibitor is a mixed type inhibitor with more anodic nature. α and β values changed with respect to the inhibitor concentration. Therefore, Acorus calamus extract could be classified as a mixed type inhibitor suggesting that the presence of the inhibitor does not alter the reaction mechanism, and that the inhibition effect has occurred due to simple blocking of the active sites, thereby reducing available surface area of the corroding metal. [16-17]

E. Active compounds

Adsorption of organic molecules may be explained by the presence of an oxygen atom (a heteroatom), π electron of aromatic rings and electron donating groups. The heteroatoms such as oxygen are the major adsorption center in organic compounds for its interaction with the metal surface [19]. The adsorption can also occur via electrostatic interaction between a negatively charged surface, which is provided by a specifically adsorbed anion (Cl^-) on iron, and the positive charge of the inhibitor [20].

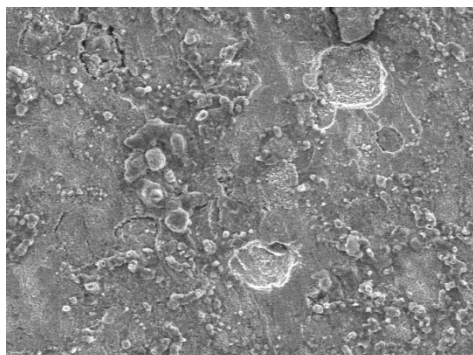


Fig.3. Surface analysis of mild steel 0.5N H_2SO_4 solution

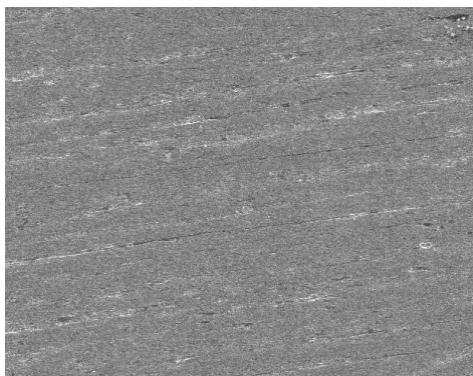


Fig.4. Surface analysis of mild steel in 0.5N H_2SO_4 solution with inhibitor

This observation suggests that inhibitor molecules adsorb on the metal surface by blocking the active sites on the

metal surface [18]. Figures (3,4) show the surface analysis of metal by Scanning Electron Microscopy was carried out on Model- JEOL-JSM-6390. The surface morphological characteristics of the blank and inhibited mild steel were analyzed at magnification of 2.0 KX operated at an accelerating voltage of 15 KV. Scanning electron microscopy reveals that plant extract adsorbed on metal surface that decreases the metal surface for corrosion attack. SEM provides a two-dimensional projection or a two-dimensional image of a samples.

IV. CONCLUSIONS

1. Plant inhibitors inhibited mild steel corrosion in Acid solutions.
2. Corrosion inhibition of mild steel in acid solution is under mixed control.
3. Inhibition efficiency of plant extracts increases with increase in concentration.
4. The mass loss measurements are in good agreement with electrochemical method.

REFERENCES

- [1] CY.Wang, GH.Wu, Q.Zhang, LT.Jiang, "Characterization and corrosion protection properties of cerium conversion coating on $Gr_{(i)}/Al$ composite surface" (2008) *J Mater Sci*43:3327.
- [2] S. M. A. Shibli, R. Manu, "Application of the electrochemical machining technique for the characterization of zinc coatings" (2008) *J Mater Sci* 43:4282.
- [3] D.Batory, T.Blaszczyk, M.Clapa, S.Mitura, "Investigation of anti-corrosion properties of Ti:C gradient layers manufactured in hybrid deposition system" Springer-Verlag (2008) *J Mater Sci* 43:3385. doi:10.1007/s10853-007-2393-0
- [4] SA.Xia, BX.Zhou, WJ.Chen, "Effect of single-step strain and annealing on grain boundary character distribution and intergranular corrosion in Alloy 690" (2008) *J Mater Sci* 43:2990. doi:10.1007/s10853-007-2164-y
- [5] OM.Alyousif, DL.Engelberg, TJ.Marrow, "Surface grain boundary engineering of shot-peened type 304 stainless steel" (2008) *J Mater Sci*43:1270. doi:10.1007/s10853-007-2252-z
- [6] V.Moura, AY.Kina, SSM.Tavares, LD. Lima, FB.Mainier, "Influence of stabilization heat treatments on microstructure, hardness and intergranular corrosion resistance of the AISI 321 stainless steel" *J Mater Sci* (2008) 43:536.
- [7] HM.Geng, XC.Wu, HB.Wang, YG.Min, "Effect of copper addition on mechanical properties of 4Cr16Mo" (2008) *J Mater Sci* 43:83. doi:10.1007/007-2084-x s10853-
- [8] M.A.Quraishi, and J.Rawat, "Corrosion inhibiting action of tetramethyl-dithia-octaaza-cyclotetradeca-hexaene (MTAH) on corrosion of mild steel in hot 20% sulfuric acid" *Mater. Chem. Phys.*, 2002, vol. 73, nos. 2-3, p. 118.
- [9] E.E.Ebenso, U.J. Ekpe, B.I. Ita, O.E. Offiong, and U.J. Ibok, "The Rhodanine inhibition effect on the corrosion of a mild steel in acid along the exposure time" *Mater. Chem. Phys.*, 1999, vol. 60, no. 1, p. 79.
- [10] El.Abd - S.A.Maksoud, "Studies on the effect of pyranocoumarin derivatives on the corrosion of iron in 0.5 M HCl" *Corr. Sci.*, 2002, vol. 44, no. 4, p. 803.
- [11] L.Elkadri, B.Mernari, M.Traissnel, F. Bentiss, M. Lagrenee, "Corrosion inhibition of iron in 1M HCl by 1-phenyl-5-mercapto-1,2,3,4-tetrazole" *Corr. Sci.*, 2000, vol. 42, no. 4, p. 703.
- [12] S.Kertit, and B.Hammouti, "1-Phenyl-5-Mercapto-1,2,3,4-Tetrazole as corrosion inhibitor of iron in 1M HCl" *App. Surf. Sci.*, 1996, vol. 93, no. 1, p. 59-66.

- [13] M.Abdallah,, “Rhodanine azosulpha drugs as corrosion inhibitors for corrosion of 304 stainless steel in hydrochloric acid solution” *Corr. Sci.*, 2002, vol. 44, no. 4, p. 717.
- [14] H. Ashassi-Sorkhabi, B. Shaabani, D. Seifzadeh, “Effectct of some pyrimidinic Shciff bases on the corrosion of mild steel in hydrochloric acid solution” *Electrochim. Acta* 50 (2005)3446.
- [15] M. Shahin, S. Bilgie, H. Yilmaz, “The inhibition effects of some cyclic nitrogen compounds on the corrosion of the steel in NaCl media” *Appl. Surf. Sci.* 195 (2003) 1.
- [16] F.R Selvarani, S.Santhanalakshmi, J.W Sahayaraj,A.John Amalraj, Susai Rajendran, “Influence of succinic acid on the corrosion inhibition of sodium metavanadate in chloride medium, *bull. electrochemistry*, 20, 561-565 (2004).
- [17] S.Susai Rajendran. Mary Reenkala, Noreen Anthonyand R. Ramaraj “Synergistic corrosion inhibition by the sodium dodecylsulphate–Zn²⁺ system” *Corros Sci*, 44 (2002) 2243-2252.
- [18] H. Ashassi-Sorkhabi, B. Shaabani and D. Seifzadeh, “Effect of some pyrimidinic Shciff bases on the corrosion of mild steel in hydrochloric acid solution” *Electrochimica Acta*,50(2005) Issues 16–17, 30 May 2005, Pages 3446-3452
- [19] E. Rocca, C. Rapin and F. Mirambet, “Inhibition treatment of the corrosion of lead artefacts in atmospheric conditions and by acetic acid vapour: use of sodium decanoate ”*Corrosion Science, Volume 46, Issue 3, March 2004, Pages 653-665 Corrosion Science*, 46(2004)653
- [20] K. Tebbji, H. Oudda, B. Hammouti, M. Benkaddour, M. El Kodadi and A. Ramdani, “Inhibition effect of two organic compounds pyridine–pyrazole type in acidic corrosion of steel” *Colloids and Surfaces A: Physicochem. Eng. Aspects* 259(2005)143

AUTHOR’S PROFILE



Mr. S. Ananthkumar

is currently pursuing his Ph.D under the guidance of Dr.A .Sankar. He has presented some research papers in the national and international conferences. His areas research interest include electrochemical corrosion studies, Electrochemical sensors, Schiff’s bases based sensors etc.