



Santalum paniculatum leaves extract as corrosion inhibitor for mild steel in acid medium

S.Ananth Kumar^{1,*}, A.Sankar¹, M.Kumaravel² and S.Rameshkumar²

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

^bPSG College of Technology, Peelamedu, Coimbatore 641 004, India.

ARTICLE INFO

Article history:

Received: 22 September 2013;

Received in revised form:

1 November 2013;

Accepted: 9 November 2013;

Keywords

Inhibitor,
Mass loss,
Impedance,
Polarization,
Santalum paniculatum.

ABSTRACT

The effect of addition of Santalum paniculatum leaves extract on the corrosion of steel in 0.5M H₂SO₄ acid has been studied by weight loss measurements, potentiodynamic polarisation and Electrochemical Impedance Spectroscopy (EIS) measurements. The inhibition efficiency was found to increase with inhibitors content to attain 59.38% and 91.66% Santalum paniculatum leaves extract on and 25ppmTBAB respectively. Data obtained from EIS studies were analyzed to determinate the model inhibition process through appropriate equivalent circuit models. Inhibition efficiency IE (%) obtained from the various methods is in good agreement.

© 2013 Elixir All rights reserved

Introduction

Acids are widely used in the industrial operations of pickling, descaling, oil well acidizing and cleaning of steel and ferrous alloys [2-9]. These operations ensure that machine components come in contact with these hostile species leading to metal loss or depletion in form of reduction in effective size of the component which may inevitably lead to catastrophic failure [9]. Several tested methods for preventing and controlling corrosion are influenced by the specific material to be protected; environmental concerns such as soil resistivity, humidity, and exposure to marine or industrial environments; the type of product to be processed or transported; and many other factors. The most commonly used methods include organic and metallic protective coatings; corrosion resistant alloys,

plastics, and polymers; corrosion inhibitors; and cathodic protection technique which is used on pipings, underground storage cisterns, and offshore facilities that creates an electrochemical cell in which the surface to be protected is the cathode and corrosion reactions are abated [1]. It is well known that in developed countries corrosion mitigation management has improved over the past several decades, but more and better ways to encourage, support, and implement optimal corrosion control practices should be sought out. In a bid to inspire and sustain these efforts, practical attempts have been made by several researchers to investigate the effect of using green inhibitors to combat corrosion of metals in acid media [10-21]. These investigations have shown that green inhibitors represent a veritable source of environmentally friendly, cheaply available and easily applicable resource [5, 7] The aim of this study was to investigate the inhibition effect of Santalum paniculatum leaves extract as a cheap, raw and non-toxic corrosion inhibitor on mild steel corrosion in 0.5M H₂SO₄. The electrochemical measurements were used to evaluate the inhibition efficiencies.

Material and methods:

Preparation of Santalum paniculatum extract:

An aqueous extract of Santalum paniculatum leaves extract was prepared by grinding 5g of plant leaves, with distilled water, filtering the suspending impurities, and making up to 100 ml. 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 dimension 1.0 cm *4.0cm*0.2cm were polished to a mirror finished with the emery sheets of various grades and degreased with trichloroethylene.

Weight loss method

Carbon steel specimens in triplicate were immersed in 100 mL of the inhibited and uninhibited 0.5M H₂SO₄ solutions in the presence and absence of KI for two hours. The weight of each specimen before and after immersion was determined using shimadzu balance, model Ay 62. The inhibition efficiency (IE) was then calculated using the expression;

$$IE\% = \left[\frac{W_1 - W_2}{W_1} \right] \times 100$$

Where W₁ and W₂ are the corrosion rates in the absence and presence of the inhibitor, respectively.

Electrochemical impedance measurements

The impedance measurements were performed using a computer –controlled potentiostat (model Solartron SI-1260) and the data were analysed using gain phase analyser electrochemical interface (Solartron SI-1287). A three electrode set up was employed with Pt foil as the auxiliary electrode and a saturated calomel electrode as the reference electrode. The Teflon coated mild steel rod, with the surface prepared as described in the weight loss experimental method, served as the working electrode. The measurements were carried out in the frequency range 10⁶–10⁻² Hz at the open circuit potential by

superimposing sinusoidal AC signal of small amplitude, 10 mV, after an immersion period of 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 [22]. 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 1.66mV/s, 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 [23];

$$IE\% = \frac{I_{corr}^0 - I_{corr}}{I_{corr}^0} \times 100$$

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

Results and discussion

Analysis of results of mass loss method

The corrosion rates and inhibition efficiency values, calculated using weight loss data, for various concentrations of Santalum paniculatum leaves extract in the presence and absence of TBAB the corrosion of carbon steel in 0.5M H_2SO_4 solution are presented in Table.1. It is apparent that the inhibition efficiency increased with the increase in inhibitor concentration in the presence and absence of TBAB. This behavior can be explained based on the strong interaction of the inhibitor molecule with the metal surface resulting in adsorption. The extent of adsorption increases with the increase in concentration of the inhibitor leading to increased inhibition efficiency. The maximum inhibition efficiency was observed at an inhibitor concentration of 5mL. Generally, inhibitor molecules suppress the metal dissolution by forming a protective film adsorbed to the metal surface and separating it from the corrosion medium. The corrosion suppressing ability of the inhibitor molecule originates from the tendency to form either strong or weak chemical bonds with Fe atoms using the lone pair of electrons present on the O and π electrons in benzene ring. It is also seen from table.1 that the leaf extract of Sandal wood at 1mL and 5mL concentrations shows 78.14% and 84.30 % inhibition efficiencies respectively, Then the values increased to 94.82 % after adding 25 ppm of TBAB solution in 0.5M H_2SO_4 solutions containing 5mL of plant extract respectively. This showed a good synergistic effect between Santalum paniculatum extract and TBAB.

Table 1. Corrosion rate (CR) of mild steel in 0.5M H_2SO_4 solutions the absence and presence of inhibitor and the inhibition efficiency (IE) obtained by weight loss method.

Inhibitor concentration (mL)	TBAB (0) ppm	
	CR (mg cm ⁻² h ⁻¹)	IE %
0	294.00	-
1	64.24	78.14
2	81.57	54.16
3	50.20	82.93
4	48.26	83.58
5	46.15	84.30

Influence of TBAB on the inhibition efficiency of Santalum paniculatum leaves extracts

Table 2. Corrosion rate (CR) of mild steel in 0.5M H_2SO_4 solutions the presence of inhibitor with TBAB and the inhibition efficiency (IE) obtained by mass loss method

Inhibitor concentration (mL)	TBAB (25) ppm	
	CR (mdd)	IE %
5	15.22	94.82

Electrochemical impedance spectroscopic measurements (EIS)

Impedance spectra obtained for corrosion of mild steel in 0.5 M H_2SO_4 contains a semicircle, representing the interaction of metal surface with the corrosive environment.. The -R(CR) model best describes this situation. The 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 M H_2SO_4 in the absence and presence of inhibitor are given in Table 3. Said that sum of charge transfer resistance (R_{ct}) and adsorption resistance (R_{ad}) is equivalent to polarization resistance (R_p).

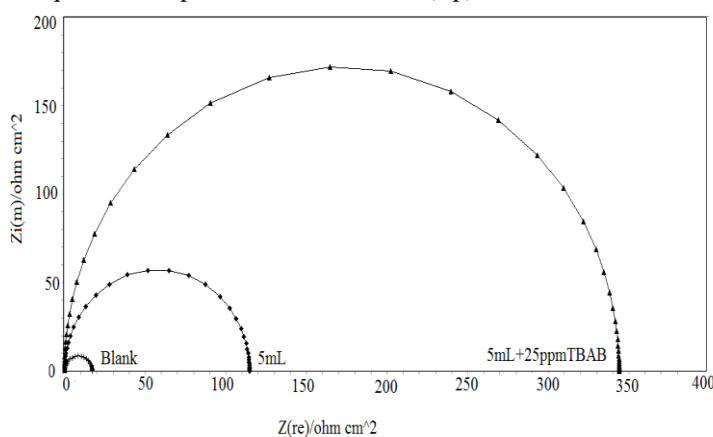


Table 3. Impedance parameters obtained from electrochemical impedance studies.

Inhibitor concentration (mL)	R_{ct} Ohm cm ²	C_{dl} μF	IE%
0	17.2	9.2578×10^{-3}	-
5	114.66	1.388×10^{-6}	85.0
5+ 25ppmTBAB	344.00	0.562×10^{-6}	95.10

Potentiodynamic Polarization studies :

Fig 2. Potentiodynamic polarization curves of mild steel immersed in 0.5M H_2SO_4 solution in the absence and presence of inhibitors

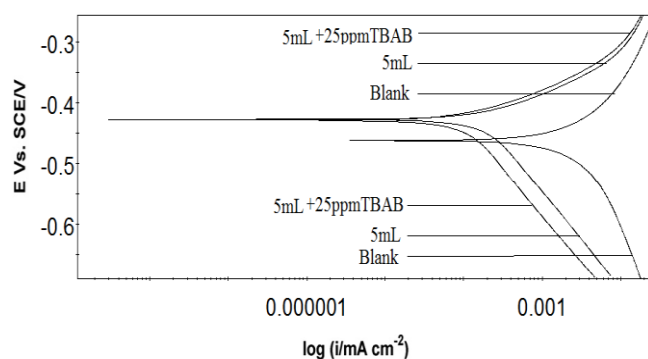


Table 4. Corrosion parameters in the presence and absence of inhibitor obtained from polarization measurements.

Inhibitor concentration (mL)	-E _{corr} (mV)	β _c (mV/)	β _a (mV)	I _{corr} ×10 ⁶ μA	IE%
0	461	127	68	1.35	-
5	427	206	126	0.205	84.8
5ml+25ppmTBAB	425	215	99	0.0666	95.1

The polarization curves obtained for the corrosion of mild steel in the inhibited (5mL) and uninhibited 0.5 M H₂SO₄ solutions in the absence and presence of TBAB are shown in Fig.2. Electrochemical parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), cathodic and anodic tafel slopes (β_c and β_a) and percentage inhibition efficiency according to polarization studies are listed in table 4. Here I_{corr} decreased with increasing inhibitor concentration. From the figures, it can be interpreted that the addition of this inhibitor to corrosive media changes the anodic and cathodic tafel slopes. The changes in slopes showed the influence of the inhibitor both in the cathodic and anodic reactions. However, the influence is more pronounced in the cathodic polarization plots compared to that in the anodic polarization plots. Even though β_c and β_a values (table.3) change with an increase in inhibitor concentrations, a high β_c value indicates that the cathodic reaction is retarded to a higher extent than the anodic reaction²⁴.

From Fig.2 it is also clear that the addition of the inhibitor shifts the cathodic curves to a greater extent toward the lower current density when compared to the anodic curves. The E_{corr} value is also shifted to the more negative side with an increase in the inhibitor concentration. These shifts can be attributed to the decrease in the rate of the hydrogen evolution reaction on the mild steel surface caused by the adsorption of the inhibitor molecule to the metal surface[25]. It has been reported that a compound can be classified as an anodic and cathodic type inhibitor on the basis of shift of 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[26,27]. In our study, maximum displacement in E_{corr} value was around 36 mV, indicating the inhibitor is a mixed type and more anodic nature and does not alter the reaction mechanism. The inhibition effect has occurred due to simple blocking of the active sites, thereby reducing available surface area of the corroding metal[28-31]. The increase in inhibitor efficiency of inhibited (5mL) 0.5M H₂SO₄ solution for the corrosion of mild steel after adding 25 ppm TBAB shows synergism between inhibitor molecules and TBAB.

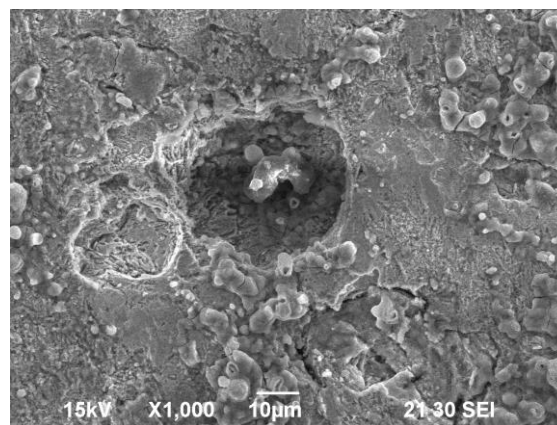
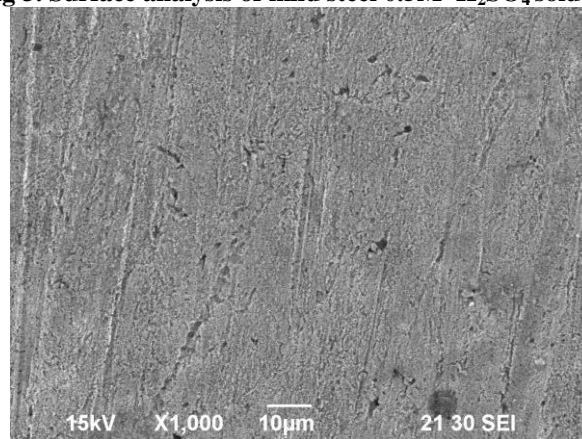
SEM

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

Conclusion:

The effect of acid concentration and the effect of addition of the aqueous extract of Santalum paniculatum leaves on the corrosion of Mild steel has been studied. The following conclusions may be drawn:

1) The chemical results showed that the corrosion rate of mild steel sample is increase with increasing acid concentrations 1mL to 5mL.

**Fig 3. Surface analysis of mild steel 0.5M H₂SO₄ solution****Fig 4. Surface analysis of mild steel in 0.5N H₂SO₄ solution with inhibitor**

2) The polarization measurements also showed that, the increase of 0.5M H₂SO₄ concentration leads to displacement of the anodic and cathodic curves to high current densities (I_{corr}), also increase the corrosion rate will be found.

3) The electrochemical impedance measurements showed that the corrosion of mild steel sample is mainly controlled by charge transfer process.

4) The aqueous extract of Santalum paniculatum leaves extract acts as good inhibitor for the corrosion of mild steel in 0.5M H₂SO₄ solution.

5) Electrochemical polarization results indicates that the Santalum paniculatum leaves act as mixed type inhibitor and impedance results showed that the corrosion of mild steel is mainly controlled by a charge transfer process and the presence of Santalum paniculatum leaves leaves extract in acid solution does not alter the mechanism of mild dissolution.

Acknowledgements

The authors generously acknowledge the support by Dr.R.Somasundaram M.D., Dr.R.Arul M.Sc.,Ph.D., Dr.S.Vedanayaki M.Sc.,Ph.D., President ,Principal and head of the department chemistry respectively of Kandaswami Kandar's College,P.Velur for providing necessary chemical and lab facilities to carry out chemical studies..

References

1. Koch, G. H., Brongers, M. P. H., Thompson, N. G., Virmani, P., Payer, J.H. F.HWA-RD-01-156 (2001)
2. Faltermeier, R., AMT: A new corrosion inhibitor. B.Sc report, University College London, London (1992).
3. Iannuzzi, M., Young, T., Frankel, G.S. *Journal of the electrochemical society*, (2006) 153 ,533.
4. Ralston, K.D. Chromate free corrosion inhibitors of aluminium alloys: Vanadates and anionic exchange clay

- pigments. Ph. D dissertation, Ohio State University, Ohio. (2008).
5. Ahamad, I., Quraishi, M.A. *Corros. Sci.* (2009) 51 ,2006.
 6. Ralston, K.D., Young, T.L. Buchheit, R.G. *Journal of the electrochemical society*, (2009) 156 ,135.
 7. Khaled K.F, El-mghraby, A., Ibrahim, O.B., Elhabib, O.A., Ibrahim, M.A.M. *J. Mater. Environ. Sci.* (2010) 1,139.
 8. Omotosho, O.A., Okeniyi, J.O. Ajayi, O.O. *J Fail. Anal. And Preven.*, (2010) 10 ,408.
 9. Ajayi, O.O., Omotosho, O.A., Ajanaku, K.O., Olawore, B.O. *J. Eng. Applied Sci.*, (2011) 6 ,10.
 10. Oguzie, E.E. *Corros. Sci.* (2008) 50 ,2993.
 11. Okafor, P.C., Ikpi, M.E., Uwaha, I.E., Ebenso, E.E., Ekpe, U.J., Umoren, S.A. *Corros. Sci.* (2008) 50 ,2310.
 12. Valek, L., Martinez, S. *Mater. Lett.* (2007) 61 ,148.
 13. Singh, Ambrish, Ahamad, I., Singh, Vinod Kumar, Quraishi, M.A. (2010) *J.S.E.L.* 2010 JSEL-D-10-00143R2.
 14. Raja, P.B., Sethuraman, M.G. *Mater. Lett.* (2008) 62 ,1602.
 15. Singh, A., Singh, V. K., Quraishi, M. A. *J. Mater. Environ. Sci.* (2010) 1 ,162.
 16. Noor, E.A. *J. Engg. Appl. Sci.* (2008) 3 ,23.
 17. Buchweishaija, J., Mhinzi, G.S. *Port. Electrochim. Acta* (2008) 26,257.
 18. El-Etre, A.Y. *Corros. Sci.* (2003) 45 ,2485.
 19. Badiea, A.M., Mohana, K.N. *J. Mater. Eng. Perform.* (2009) 18 ,1264.
 20. Noor, E.A. *J. Appl. Electrochem.* (2009) 39 ,1465.
 21. De Souza, F.S., Spinelli, A. *Corros. Sci.*, (2009) 51 ,642.
 22. Ashassi-Sorkhabi.H., Shaabani.B, Seifzadeh.D, *Electrochim. Acta*, (2005) 50 ,3446.
 23. Shahin.M, Bilgie.S, Yilmaz.H, *Appl. Surf. Sci.* (2003) 195,1.
 24. Silverman D. C., "Practical Corrosion Prediction Using Electrochemical Techniques", ch. 68 in Uhlig's *Corrosion Handbook*, 2nd edition (Revie,R.W, ed.), *The Electrochemical Society*, 2000
 25. Prabhu., T.V. Venkatesha, A.V. Shanbhag. Praveen. B.M, Kulkarni. G.M.,Kalkhambkar R.G, *Mater. Chem. Phys.* (2008) 108 , 283
 26. Sanghvi. R.A, M.J., et al., *Bull. Electrochem.*, (1999) 13,358.
 27. Felicia Rajammal Selvarani, S.Santhanalakshmi, J. Wilson sahayaraja, A. John Amalraj, and Susai Rajendran , *Bull. Electrochemistry.* (2004) 20 , 561-565.
 28. Susai Rajendran S. Mary Reenkala, Noreen Anthony and Ramaraj,R. *Corros Sci*, (2002) 44, 2243-2252.
 29. Scully. J. R., "Polarization Resistance Method for Determination of Instantaneous Corrosion Rates", *Corrosion*, (2000) Vol.,56, p. 199.
 - [30]. Kumaravel Mallaiyaa, Rameshkumar Subramaniaman, Subramanian Sathyamangalam Srikandana,S. Gowria, N. Rajasekaranb, A. Selvaraj, *Electrochimica Acta*(2011) 56, 3857–3863
 - [31]. S. Ananth Kumar., A.Sankar, and S. Ramesh Kumar, *International Journal of Chemistry and Chemical Engineering*. Volume 3, Number (2013)1 , pp. 7-14