

Corrosion Inhibition Of Mild Steel In 0.5 M H₂SO₄ By 1-(2-Methyl-4-(2-Methylphenyldiazenyl) Phenyl) Azonaphthalen-2-Ol

S.ANANTH KUMAR^a Dr.A.SANKAR^{*a},S.RAMESHKUMAR^b,

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

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

Abstract: - The effect of addition of 1-(2-methyl-4-(2-methylphenyldiazenyl) phenyl) azonaphthalen-2-ol on the corrosion of steel in 0.5M H₂SO₄ acid has been studied by weight loss measurements, potentiodynamic polarization and Electrochemical Impedance Spectroscopy (EIS) measurements. The inhibition efficiency was found to increase with inhibitors content to attain 61.00% and 79.66% 1-(2-methyl-4-(2-methylphenyldiazenyl) phenyl) azonaphthalen-2-ol and 25ppm(Tetra butyl ammonium bromide)TBAB respectively. Data obtained from EIS studies were analyzed to determinate the model inhibition process through appropriate equivalent circuit models. Inhibition efficiency E (%) obtained from the various methods is in good agreement.

Key words: - Inhibitor, 1-(2-methyl-4-(2-methylphenyldiazenyl) phenyl) azonaphthalen-2-ol

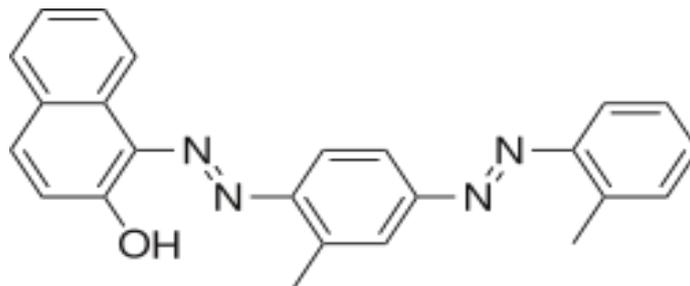
I. INTRODUCTION

Acid solutions are often used in industry for cleaning, decaling and pickling of steel structures, processes which are normally accompanied by considerable dissolution of the metal. A useful method to protect metals deployed in service in such aggressive environments against corrosion is the addition of species to the solution in contact with the surface in order to inhibit the corrosion reaction and reduce the corrosion rate. A number of organic compounds [1-8] are known to be applicable as corrosion inhibitors for steel in acidic environments. Such compounds typically contain nitrogen, oxygen or sulphur in a conjugated system and function via adsorption of the molecules on the metal surface, creating a barrier to corrodent attack. To further upgrade the performance of such organic inhibitors, extensive studies have been undertaken to identify synergistic effects of other additives. Interestingly, addition of halide ions to sulphuric acid solutions containing some organic compounds has been reported to yield the required enhancement [1-13]. The inhibitive effects for the halides have been Observed to increase in the order Cl- < Br- < I-, with the iodide ion being the most Effective. It is thought that the initial specific adsorption of the halide ions on the metal surface facilitates the adsorption of organic cations by forming Intermediate bridges between the positively charged metal surface and the positive end of the inhibitor. A few reports from our laboratory highlighted the synergistic effect of halide ions on the corrosion of mild steel in acidic solution [15-17], while the synergistic inhibition between organic compounds and iodide ions has been reported by some research groups [18-22]. However, reports on synergistic influence of halide ions and polymers are very scanty [23, 24]. As part of our contribution to the growing interest of exploring polymeric materials as corrosion inhibitors, the present study investigates the inhibitive effect of 1-(2-methyl-4-(2-methylphenyldiazenyl) phenyl) azonaphthalen-2-ol (Sudan-IV) on mild steel corrosion in sulphuric acid, including the synergistic effect of iodide ions using weight loss and potentiodynamic polarization methods.

II. MATERIAL AND METHODS

2.1 Preparation of Stock solution :

1-(2-methyl-4-(2-methylphenyldiazenyl) phenyl) azonaphthalen-2-ol (Sudan-IV) was purchased from NICE chemicals.0.1g of sample was dissolved in ethanol, and made up to 100 ml. This solution was used as corrosion inhibitor in the present study.



1-(2-methyl-4-(2-methylphenyldiazenyl) phenyl) azonaphthalen-2-ol (Sudan-IV)

2.2 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.

2.3 Weight loss method.

Carbon steel specimens in triplicate were immersed in 100 mL of the inhibited and uninhibited 0.5 M H₂SO₄ solutions 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 W_1 and W_2 are the corrosion rates in the absence and presence of the inhibitor, respectively.

2.4 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 10^6 – 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 [25]. 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.

2.5. 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 [26];

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

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

III. RESULTS AND DISCUSSION

3.1 Analysis of results of mass loss method

The corrosion rates and inhibition efficiency values, calculated using weight loss data, for various concentrations of Sudan-IV solution in 0.5M H₂SO₄ solutions are presented in Table.1. It is apparent that the

inhibition efficiency increased with the increase in inhibitor concentration. 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 100 ppm. 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 the lone pair of electrons present on the O and π electrons in benzene ring. It is also seen from table.1 that the Sudan-III at 10 ppm and 100ppm concentrations shows 64.02 % and 81.31 % inhibition efficiencies respectively.

Table1. Corrosion rate (CR) of mild steel in 0.5M H₂SO₄ solutions the absence and presence of inhibitor and the inhibition efficiency (IE) obtained by weight loss method.

Inhibitor concentration (ppm)	CR (mg cm ⁻² h ⁻¹)	IE %
0	128.54	-
10	46.24	64.02
25	43.70	66.00
50	27.90	78.29
75	25.42	80.22
100	24.02	81.31

3.2 Electrochemical impedance spectroscopic measurements (EIS)

Impedance spectra obtained for corrosion of mild steel in 0.5 M H₂SO₄ 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 H₂SO₄ in the absence and presence of inhibitor are given in Table 3. Said that sum of charge transfer resistance (R_{ct}) and adsorption resistance (Rad) is equivalent to polarization resistance (Rp).

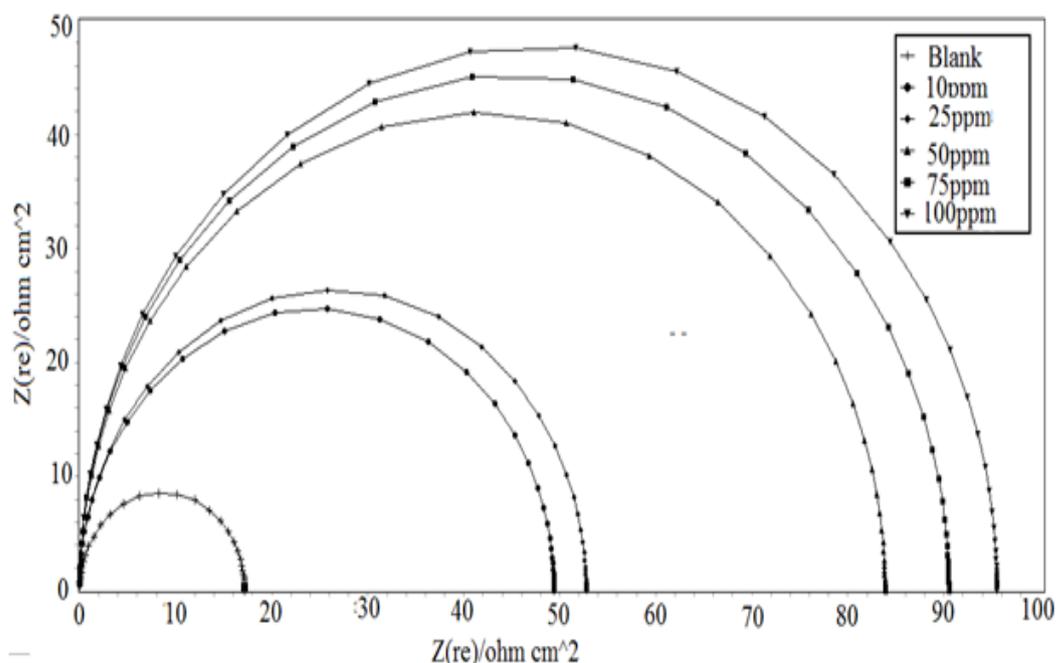


Table 2. Impedance parameters obtained from electrochemical impedance studies.

Inhibitor concentration ppm	Rct Ohm cm ²	C _{dl} μF	IE%
0	17.2	9.2578×10 ⁻³	-
10	65.2	2.442×10 ⁻⁶	49.42
25	67.4	2.362×10 ⁻⁶	52.76
50	79.5	2.002×10 ⁻⁶	83.90
75	81.0	1.965×10 ⁻⁶	90.53
100	82.0	1.941×10 ⁻⁶	95.55

3.3. polarization measurements

Fig 2. Potentiodynamic polarization curves of mild steel immersed in 0.5M H₂SO₄ solution in the absence and presence of inhibitors

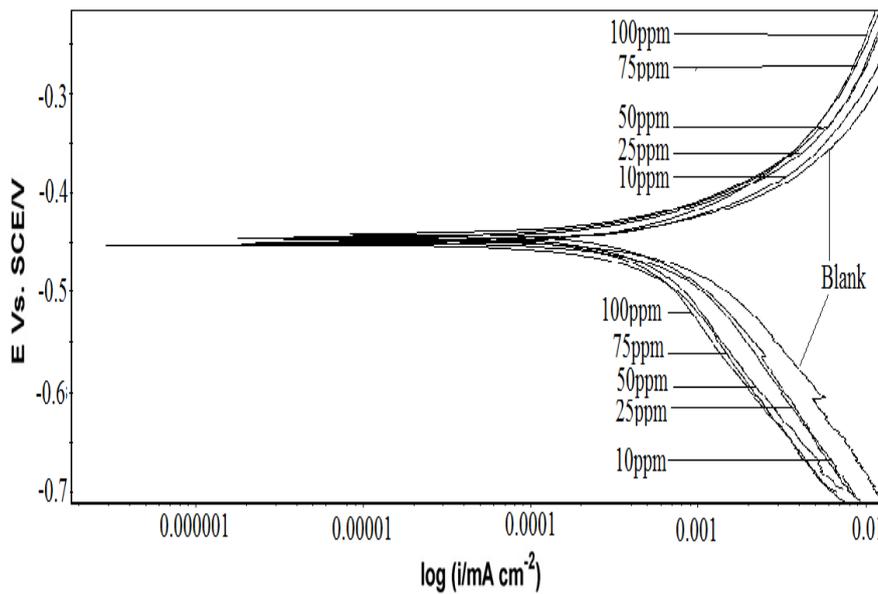


Table 3. Corrosion parameters in the presence and absence of inhibitor obtained from polarization measurements.

Inhibitor concentration ppm	-E _{corr} (mV)	β _c (mV/)	β _a (mV)	I _{corr} ×10*6 μA	IE%
0	457	127	68	1.35	-
10	450	160	70	0.473	65.0
25	451	163	72	0.446	67.0
50	452	167	75	0.284	79.0
75	453	170	76	0.257	81.0
100	455	172	78	0.246	81.8

The polarization curves obtained for the corrosion of mild steel in the inhibited (100 ppm) and uninhibited 0.5 M H₂SO₄ solutions 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 3. 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 reaction[27].

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[28]. 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[29,30]. In our study, maximum displacement in E_{corr} value was around 6 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 [31-34].

IV. CONCLUSION

The effect of acid concentration and the effect of addition the 1-(2-methyl-4-(2-methylphenyldiazenyl) phenyl) azonaphthalen-2-ol 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 10 ppm to 100 ppm
- 2) The polarization measurements also showed that, the increase of 0.5 M H_2SO_4 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 ethanolic solution of 1-(2-methyl-4-(2-methylphenyldiazenyl) phenyl) azonaphthalen-2-ol acts as good inhibitor for the corrosion of mild steel in 0.5 M H_2SO_4 solution.
- 5) Electrochemical polarization results indicates that the 1-(2-methyl-4-(2-methylphenyldiazenyl) phenyl) azonaphthalen-2-ol 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 1-(2-methyl-4-(2-methylphenyldiazenyl) phenyl) azonaphthalen-2-ol in acid solution does not alter the mechanism of mild dissolution.

V. AKNOWELEDGEMENTS

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] J. Mathiyamsu, I.C. Nebru, P. Subramania, N. Palaniswamy, N.S.Rengaswamy, *Anticorros. Methods & Mater.* 48 (5) ,2001, 342.
- [2] N. Ochoa, F. Moran, N. Pebre, *J. Appl. Electrochem.* 34 ,2004, 487.
- [3] E.E. Oguzie, C. Unaegbu, C.N. Ogukwe, B.N. Okolue, A.I. Onuchukwu,*Mater. Chem. Phys.* 84 ,2004, 363.
- [4] E.E. Oguzie, *Mater. Chem. Phys.* 87 ,2004, 212.
- [5] S. Rajendran, R. Maria Joany, B.V. Apparao, N. Palaniswamy, *Trans.SAEST* 35 (3/4) ,2000, 113.
- [6] S. Rajendran, B.V. Apparao, N. Palaniswamy, *Anticorros. Methods & Mater.* 44(5) ,1998, 338.
- [7] M.N. Shalaby, M.M. Osman, *Anti-corros. Methods Mater.* 48(5) ,2001,309.
- [8] E.E. Ebenso, *Mater. Chem. Phys.* 79 ,2003, 58.
- [9] E.E. Ebenso, *Bull. Electrochem.* 19 (5) ,2003, 209.
- [10] E.E. Ebenso, *Bull Electrochem.* 20 (12) ,2004, 551.
- [11] G.K. Gomma, *Asian J. Chem.* 5 (3) ,1993, 761.
- [12] G.K. Gomma, *Mater. Chem. Phys.* 54 ,1998, 241.
- [13] D. Gopi, N. Bhauvanerwaran, S. Rajewari, *Bull. Electrochem.* 18 (1) ,2002,120.
- [14] E. Kalman, I. Lukovits, G. Palinkas, *ACH Models Chem.* 132 (4) ,1995,527.
- [15] E.E. Ebenso, U.J. Ekpe, S.A. Umoren, E. Jackson, O.K. Abiola, N.C.Oforika, *J. Appl. Polym . Sci.* 100(4) ,2006, 2889.
- [16] S.A. Umoren, O. Ogbobe, E.E. Ebenso, U.J. Ekpe, *Pigment & Resin Tech.*35(5) ,2006, 284.
- [17] S.A. Umoren, O. Ogbobe, E.E. Ebenso , *Bull. Electrochem.* 22(4) ,2006,155.
- [18] M. Bouklah, B. Hammouti, A. Aounti, M. Benkaddour, A. Bouyanzer,*Appl. Surf. Sci.* 252 ,2006, 6236.
- [19] Y. Feng, K.S. Siow, W.K. Teo, A.K. Hsieh, *Corros. Sci.* 41 ,1999, 829.
- [20] M. Abdallah, E.A. Helal, A.S. Fouda, *Corros. Sci.* 48 ,2006, 1639.
- [21] M.A. Quraishi, J. Rawat, *Mater. Chem. Phys.* 70 ,2001, 95.
- [22] D.Q. Zhang, L.X. Gao, G.D. Zhou, *J. Appl. Electrochem.* 33 ,2003, 361.

- [23] L. Larabi, Y. Harek, *Portugaliae Electrochim. Acta* 22 ,2004, 227.
- [24] L. Larabi, Y. Harek, M. Traisnel, A. Mansri, *J. Appl. Electrochem.* 34,2004, 833
- [25] Ashassi-Sorkhabi.H.,Shaabani.B,Seifzadeh.D, *Electrochim.Acta*,50, 2005,3446.Shahin.M, Bilgie.S, Yilmaz.H, *Appl. Surf. Sci.* 195, 2003,1.
- [26] 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.
- [27] Prabhu., T.V. Venkatesha, A.V. Shanbhag. Praveen. B.M, Kulkarni. G.M.,Kalkhambkar R.G, *Mater. Chem. Phys.* 108 , 2008,283
- [28] Sanghvi. R.A, M.J., et al., *Bull. Electrochem.* 13, 1999, 358.
- [29] Felicia Rajammal Selvarani, S.Santhanalakshmi, J. Wilson sahayaraja, A. John Amalraj,and Susai Rajendran , *Bull. Electrochemistry.* 20 , 2004, 561-565.
- [30] Susai RajendranS. Mary Reenkala, Noreen Anthony and Ramaraj,R. *Corros Sci*, 44, 2002, 2243-2252.
- [31] Scully. J. R., "*Polarization Resistance Method for Determination of Instantaneous Corrosion Rates*", *Corrosion, Vol.*,56, 2000 p. 199.
- [32] Kumaravel Mallaiyaa, Rameshkumar Subramaniama, Subramanian Sathyamangalam Srikandana,S. Gowria, N. Rajasekaranb, A. Selvaraj,*Electrochimica Acta* 56 , 2011,3857–3863
- [33] Ananth Kumar.S, Sankar.A, and Ramesh Kumar.S.,. *International Journal of Chemistry and Chemical Engineering.* Volume 3, Number 1(2013), pp. 7-14