Corrosion Inhibition of Mild Steel in Sulphuric Acid Medium by Kovac's Reagent

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Abstract – **The corrosion inhibition nature of Kovac' reagent for the corrosion of mild steel in 0.5 N H$_2$SO$_4$ was investigated using weight loss, electrochemical impedance and potentiodynamic polarization methods The results revealed that of Kovac'reagent acts as a corrosion inhibitor in 0.5 N H$_2$SO$_4$ medium. The inhibition efficiency increased with an increase in inhibitor concentration. The inhibition is attributed to adsorption of the inhibitor on the steel surface.**

Keywords – **Inhibitor, Mass loss, Impedance, Polarization, Kovac's reagent, SEM.**

I. INTRODUCTION

Aqueous solutions of acids are among the most corrosive media. So, the rate of corrosion at which metals are destroyed in acidic media is very high, especially when soluble corrosion products are formed. Acid solutions are generally used in several processes; industrial cleaning, acid descaling and in the petrochemical processes. Hydrochloric acid and sulphuric acid is widely used in the pickling processes of metals. The use of inhibitors is one of the most practical methods for protection against corrosion; especially in acidic media [1] is well-known that the presence of an organic molecule in the medium inhibits corrosion of metals by adsorbing at the metal-solution interface [2]. The modes of adsorption are dependent on (i) the chemical structure of the molecule, (ii) the chemical composition of the solution, (iii) the nature of the metal surface and (iv) the electrochemical potential of the metal-solution interface [3]. The most important aspect of inhibition, normally considered by corrosion scientists is the relation between the molecular structure and corrosion inhibition efficiency; such effects were studied by many authors [4–8]. Most of the well-known acid inhibitors are organic compounds containing nitrogen, sulphur or oxygen atoms. Nitrogen-containing compounds function more effectively in HCl [9, 10], whereas sulphur-containing compounds are sometimes preferred for H$_2$SO$_4$. The influence of organic compounds containing both nitrogen and sulphur atoms have been investigated by several authors [11–14]. The corrosion inhibition property of these compounds is attributed to their molecular structure. The planarity and the lone pair electrons in the hetero atoms are important features that determine the adsorption of these molecules on the metallic surface. The effect of inhibitors adsorbed on metallic surfaces in acid solutions, is slow down the cathodic and anodic process of dissolution of the metal. This is due to the formation of a barrier of diffusion or by means of the blockage of the reaction sites and thereby reducing the corrosion rate [15]. The main objective of this work is to investigate the corrosion inhibiting capability of Kovac'reagent against the corrosion of mild steel in 0.5 M H$_2$SO$_4$ solutions by various methods.

II. MATERIALS AND METHODS

2.1 Inhibitor

The kovac's reagent was bought from Sigma-Aldrich chemicals. This reagent was used as such. This is 4-Dimethylamino) benzaldehyde solution.
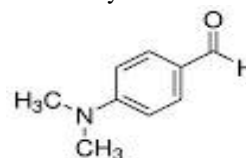
4-(Dimethylamino) benzaldehyde

2.2 Preparation of Specimens

Carbon steel specimens (0.022% S, 0.038% Mn, 0.027%P, 0.086 C) of dimensions 1.0 cm *4.0cm*0.2cm were polished to a mirror finished with emery sheets of various grades. Then washed with distilled water and degreased using trichloroethylene.

2.3 Mass Loss Method

Carbon steel specimens in triplicate were immersed in 100 mL of the 0.5 N H$_2$SO$_4$ solution containing various concentrations of the inhibitor for two hours. The weight of the specimens before and after immersion was determined. 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.

2.4. Electrochemical 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 Power Suite software and analyzed using ZsimpWin 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. A Teflon coated mild steel cylinder with 0.1768 cm^2 area of cross section with surface preparation as described in the weight loss 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 immersing 30 minutes 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 [16]. Because R_{ct} is inversely proportional to corrosion current density, it was used to determine the inhibition efficiency (IE %) using the relationship:

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

Where R_{ct} and R^0_{ct} 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 1.66mVs−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 [17]:

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

Where I^0_{corr} 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 Kovac's Reagent in 0.5N H_2SO_4 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.

Table 1: Corrosion rate (CR) of mild steel in 0.5N H_2SO_4 in the absence and presence of inhibitors, and the inhibition efficiency (IE) obtained by mass loss method.

Kovac's Solution (mL)	CR (mg cm^{-2} h^{-1})	IE %
0	69.1	-
1	15.6	77.42
2	9.0	86.98
3	7.4	89.29
4	6.6	90.44

Immersion period: 2 hours; Inhibitor :Kovac's Reagent.

The maximum inhibition efficiency was observed at an inhibitor concentration at 4mL. 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 Kovac's Reagent at 1mL and 4mL concentrations shows 77.42 % and 90.44 % inhibition efficiencies respectively.

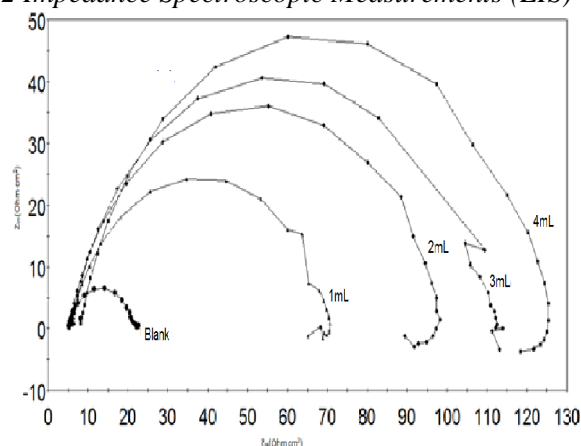### 3.2 Impedance Spectroscopic Measurements (EIS)

Fig.1. The Impedance measurements of mild steel immersed in 0.5 N H_2SO_4 in the absence and presence of inhibitors.

Table 2: Impedance parameters obtained from electrochemical impedance studies.

Inhibitor Concentration (mL)	Rct Ohm cm^2	C_{dl} µF	IE%
0	17.2	9.2578×10^{-3}	-
1	63	7.649×10^{-6}	73
2	94	5.127×10^{-6}	82
3	109	4.421×10^{-6}	84
4	124	3.886×10^{-6}	86

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 (Rct) and adsorption resistance (Rad) is equivalent to polarization resistance (Rp).

3.3 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 3. Here I_{corr} decreased with increasing inhibitor concentration. It is clearly observed that the Kovac's reagent reduce the corrosion current density.
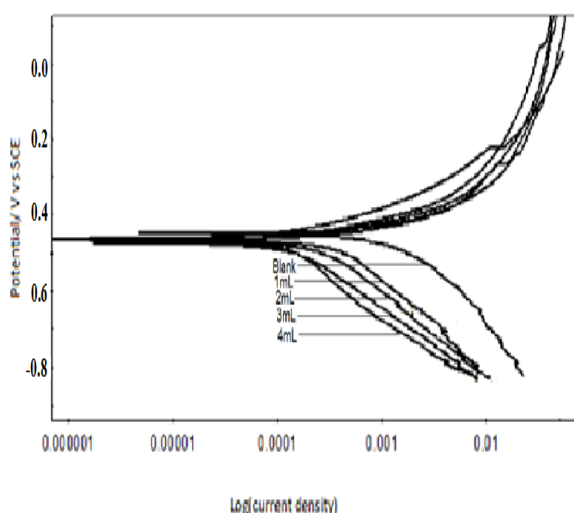

Fig.2. The potentiodynamic polarization curves of mild steel immersed in 0.5 N H_2SO_4 in the absence and presence of inhibitors.

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

Inhibitor concentration (ppm)	-Ecorr (mV)	c (mV)	a (mV)	Icorr×10*6 μA	IE%
0	448	127	68	1.628	
1	-465	143	69	-0.358	78
2	-468	147	73	-0.212	87
3	-445	151	78	-0.163	90
4	-469	185	79	-0.147	91

Corrosion current density decreased noticeably with 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 21 mV. Indicating inhibitor is a mixed type inhibitor with more anodic nature. c and a values changed with respect to the inhibitor concentration. Therefore, Kovac's reagent 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. [18-19]

3.4 SEM

Figures (3-4) shows 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 sample.
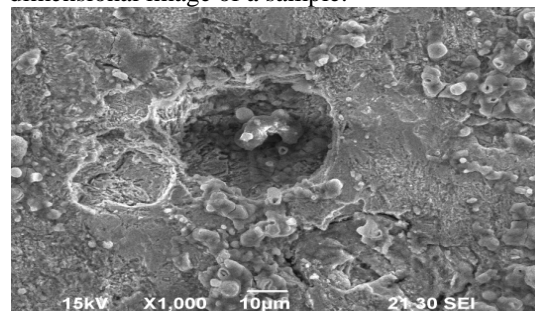

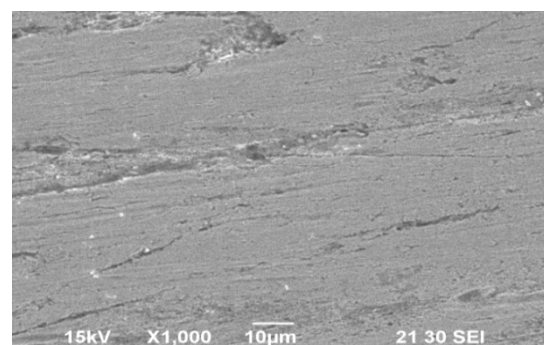Fig.3. Surface analysis of mild steel blank.

Fig.4. Surface analysis of mild steel in 0.5N H2SO4 solution with Kovac's reagent .

IV. CONCLUSIONS

1. Kovac's reagent is one of the best inhibitor for the corrosion of mild steel in 0.5 N H_2SO_4.
2. The inhibition efficiency increase with increasing of the reagent concentrations.
3. The mass loss measurements are in good agreement with electrochemical methods.

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