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# Recent Advances in the Investigation of Corrosion Inhibitors

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## INTRODUCTION

The use of inhibitors is one of the most practical and widely used methods to protect metal against corrosion, especially in acid media like HCl, $H_2SO_4$, etc. [1-6]. Literature survey reveals that organic compounds with functional groups containing heteroatoms like nitrogen, oxygen, sulfur atoms, triple or conjugated double bonds, or aromatic rings in their structure act as efficient corrosion inhibitors for metals in acid solution [7-8]. The major industries using corrosion inhibitors are the chemical industry, the oil and gas exploration industry, the petroleum refining industry, the water treatment industry, the heavy industrial manufacturing industry etc. Earlier, the weight loss method was employed to investigate corrosion inhibitors for metal corrosion in the aggressive environments like HCl, $H_2SO_4$ solution etc. Earlier weight loss method was employed to investigate the corrosion inhibition properties of the inhibitors but over time so many experimental and theoretical techniques have been revealed, which are easier, quicker, and simpler with high accuracy. In recent advances in the investigation of corrosion inhibitors, Field emission scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM) have been proven to an important tool to explore the effect of the addition of inhibitors on the surface morphology of the metal.

The main aim of this paper is to review recent advances in the investigation of corrosion inhibition properties of corrosion inhibitors especially for metals in corrosive environments like HCl. $H_2SO_4$ solution.

## 2. Recent advances in Experimental and Theoretical Techniques to investigate corrosion inhibitors:

A literature survey reveals that various experimental and theoretical techniques are in use today to investigate corrosion inhibitors. These are as follows:

### Experimental Techniques:

- Weight loss method
- Electrochemical method: Polarisation measurements, Electrochemical Impedance Spectroscopy
- Surface morphology study: Field emission scanning electron microscopy (FE-SEM), Atomic force microscopy (AFM) etc.

### Theoretical Techniques:

It includes the following:

- Quantum Chemical calculations,
- Molecular Dynamic Simulation etc.

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## 3. Determination of corrosion parameters:

### 3.1 Determination of corrosion rate by weight loss measurements:

After surface preparation mild specimens in triplicate are immersed in the given experimental acidic solution for the given period at the required experimental temperature in the absence and presence of various concentrations of inhibitors. The specimens are taken out from the corrosive solution after the specified time of immersion, washed in running water, and then in cleaning solution to remove the adhered corrosion products. The mass of each mild steel specimen is determined before and after immersion and the average of the triplicate measurements was used. The corrosion rate ($C_R$) and the percentage inhibition efficiency ($\eta\%$) are determined by the following equations [9-10]:

$$C_{\mathrm{R}} = \frac{\Delta w}{s \times t} \tag{1}$$

where $\Delta w$ is the weight loss after corrosion, $S$ is the total exposed surface area of the specimen, $t$ is time of exposure.

$$\eta\% = \frac{(C_{\mathrm{R}})_{\mathrm{o}} - (C_{\mathrm{R}})_{\mathrm{i}}}{(C_{\mathrm{R}})_{\mathrm{o}}} \times 100 \tag{2}$$

Where $(C_R)_0$ and $(C_R)_i$ are the corrosion rates in the absence (Blank) and presence of inhibitor.

### 3.2 Electrochemical methods:

Usually, metallic corrosion occurs via electrochemical reactions at the interface of metal/electrolyte solution. Therefore, electrochemical techniques provide very convenient way to study corrosion process of metal in corrosive environment. Electrochemical methods have various advantages such as quantitative measurements, quick measurements and results, insignificant disturbance on corroding surface and the results obtained can easily be transmitted, amplified, digitized or displayed. Therefore, these techniques are used consistently for the evaluation of corrosion inhibition potential of inhibitors.

All the electrochemical measurements are performed in a three-electrodes assembly in stagnant condition using an Electrochemical Workstation (Model: CHI 660C etc.). Platinum rod is used as a counter electrode, saturated calomel electrode (SCE) as the reference electrode, and the working electrode. Before each electrochemical test, the working electrode is immersed in the test solution and left till it attains steady-state open circuit potential (OCP).

### 3.3 Determination of corrosion parameters by potentiodynamic polarization method

In electrochemical kinetics, the Butler-Volmer equation is one of the most fundamental equations that describe the relationship between electrical current and electrode potential by considering both cathodic and anodic reactions take place at the same electrode. Butler Volmer equation can be shown as:

$$i = i_{corr}\left[\exp\left(\frac{\alpha nF}{RT}\eta\right) - \exp\left(\frac{-\beta n'F}{RT}\eta\right)\right] \tag{3}$$

Where, $\eta$ = over potential as the difference between applied potential ($E$) and corrosion potential ($E_{corr}$).

$i$ = current density

$i_0$ = corrosion current density

$F$ = Faraday's constant

$R$ = Universal gas constant

T = Absolute Temperature

$n$ and $n'$ = No. of electron transferred in anodic and cathodic reactions

$\alpha$ and $\beta$ = coefficients related to potential drop through electrical double layer.

However, this equation is valid over the full potential range, it can be simplified for more restricted range of potential to calculate electrochemical corrosion current. Tafel equation and the Stern-Geary equation are the two most simplified form of Butler-Volmer equation.

**The Tafel equation and Tafel Plots**

This can be deduced from Butler-Volmer equation for sufficiently high value of applied potential. As over potential becomes larger than $5\times10^{-2}$ V (either positive or negative) second or first term of the Butler-Volmer equation becomes negligible.

For anodic polarisation, when $\eta >> RT/\beta n'F$, then the equation (3) can be reduced as:

$$i = i_{corr}\left[\exp\left(\frac{\alpha nF}{RT}\eta\right)\right] \tag{4}$$

$$\text{or, } \eta = -\frac{2.303RT}{\alpha F}\log i_{corr} + \frac{2.303RT}{\alpha F}\log i \tag{5}$$

Again, for cathodic polarisation, when $-\eta >> RT/\alpha nF$

$$i = i_{corr}\left[\exp\left(\frac{-\beta n'F}{RT}\eta\right)\right] \tag{6}$$

$$\text{or} -\eta = -\frac{2.303RT}{\beta F}\log i_{corr} + \frac{2.303RT}{\beta F}\log i \tag{7}$$

The equations (2.5) and (2.7) are the forms of Tafel equation, these two equations can be combined as in equation (2.8)

$$|\eta| = a + b\log i \tag{8}$$

Where a and b are constants.

$a == -\frac{2.303RT}{\alpha F}\log i_{corr}$, and $b == \frac{2.303RT}{\alpha F}$ for anodic polarisation

$a == -\frac{2.303RT}{\beta F}\log i_{corr}$, and $b == -\frac{2.303RT}{\beta F}$ for cathodic polarisation.

A plot of electrode potential vs. logarithm of current density is called a 'Tafel plot' and the resulting straight line is the 'Tafel line'. The slope of a Tafel plot, "b" gives information about the mechanism of the reaction, and slope "a" at $\eta = 0$ gives the exchange current density $i_0$ and provides information about the rate constant of the reaction.

The potentiodynamic polarization measurements were carried out in the given potential range like -250 to +250 mV, -300 to +300 mV, etc. relative to the OCP at a given scan rate in the absence (Blank) and presence of inhibitors. The electrochemical parameters like corrosion current density ($i_{corr}$), corrosion potential ($E_{corr}$), and cathodic and anodic Tafel slopes ($\beta_c$ and $\beta_a$) are derived from polarisation curves by extrapolation method (as explained in Fig. 1) using software implemented in electrochemical workstation. The percentage inhibition efficiency of the inhibitor ($\eta\%$) can be determined by using the following equation [11-13].

$$\eta\% = \frac{i^{\circ}_{\mathrm{corr}} - i_{\mathrm{corr}}}{i^{\circ}_{\mathrm{corr}}} \times 100 \tag{9}$$

Where $i^{\circ}_{\mathrm{corr}}$ and $i_{\mathrm{corr}}$ are corrosion current density values in the absence (Blank) and presence of inhibitors, respectively.

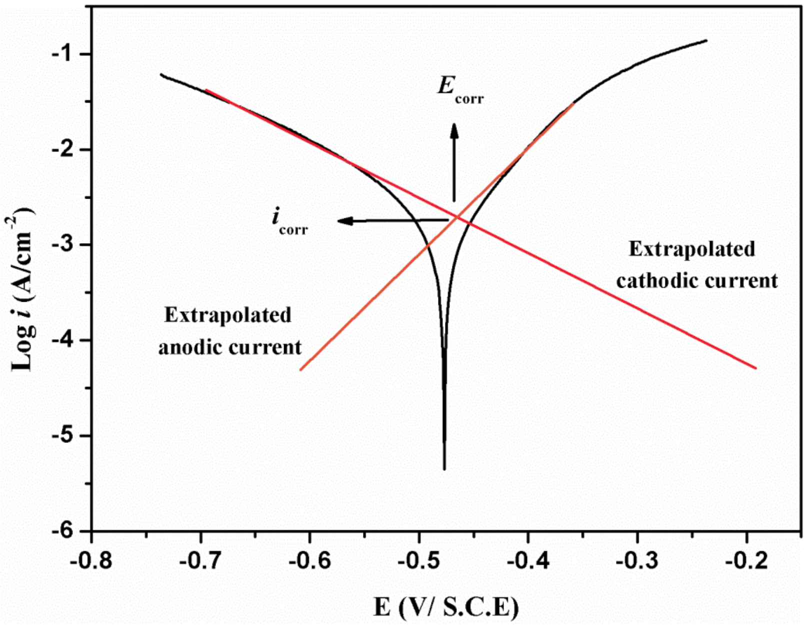

Fig. 1 Classic Tafel analysis

### 3.4 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical Impedance Spectroscopy is a powerful technique to analyse a wide variety of electrochemical system including metal corrosion in acidic environment.

The electrochemical impedance measurements is carried out at the steady state over a frequency range using the AC signal. Using impedance data, Nyquist plots can be drawn and the different impedance parameters can be calculated by fitting EIS data to the different equivalent circuit models containing elements like solution resistance ($R_s$), charge transfer resistance ($R_{ct}$), film resistance ($R_f$), constant phase element (CPE) etc. The some of the equivalent circuit diagrams are represented in Fig. 2

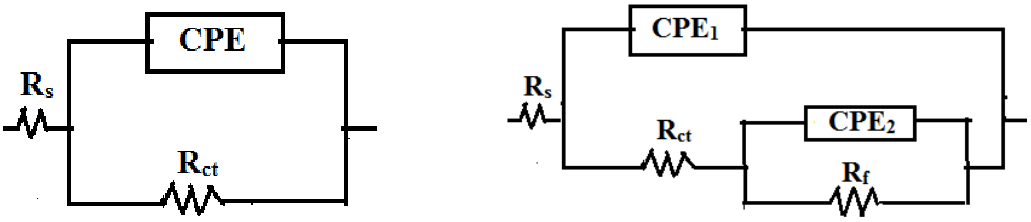

Fig. 2 Equivalent circuit diagrams

The percentage inhibition efficiency of the studied inhibitors can be calculated using the following equation [14-15]:

$$\eta\% = \frac{R_p - R_p^{\circ}}{R_p} \times 100 \quad (10)$$

Where $R_p^{\circ}$ ($R^{\circ}_{ct}$ + $R^{\circ}_{f}$) and $R_p$ ($R_{ct}$ + $R_f$) are the polarisation resistance in the absence (Blank solution) and presence of inhibitor, respectively.

Resit Yıldız studied inhibiting effect of 4,6-diamino-2-pyrimidinethiol (4D2P) on mild steel corrosion (MS) in 0.1 M HCl solution by linear polarization resistance, electrochemical impedance spectroscopy and potentiodynamic measurements in the presence of different concentrations of 4D2P ranging from 10.0 mM to 0.5 mM. [16]

Ali Doner et al studied corrosion behaviour of mild steel (MS) in 0.5 M $H_2SO_4$ using 3-[(2-hydroxy-benzylidene)-amino]-2-thioxo-thiazolidin-4-one (HBTT) as inhibitor using the conventional potentiodynamic polarization studies, linear polarization studies (LPR), electrochemical impedance spectroscopy studies (EIS). [17]

I. Ahmad et al investigated the effect of a Schiff base namely 2-[2-(2-(3 phenylallylidene) hydrazine carbonothioyl) hydrazinecarbonyl]benzoic acid (SB), on corrosion inhibition of mild steel in 1 M HCl. Electrochemical impedance measurement, potentiodynamic polarization and weight loss methods were applied to study adsorption of SB at metal/solution interface.[18]

### 3.5 Morphology study:

#### 3.5.1 Field Emission Scanning Electron Microscope (FE-SEM)

To explore the effect of addition of inhibitor, the surface morphology of the abraded mild steel immersed in acidic solution in the presence and absence of inhibitors is studied using Field Emission scanning electron microscope (FE-SEM). It can performed by FE-SEM machine like Supra 55 (Carl Zeiss, Germany).The metal samples for FE- SEM analysis is prepared as per standard described process then immersed in acidic solution in the presence and absence of certain concentration of the inhibitor for the given period of time and then taken out from the test solution, cleaned with doubly-distilled water and dried with cool air.

Bin Xu et al[15] investigated two pyridinecarboxaldehyde thiosemicarbazone compounds as corrosion inhibitors for mild steel in hydrochloric acid solution by electrochemical techniques, SEM and theoretical calculation methods.[19]

Gökmen Sı gırcık et al [16] investigated the inhibition efficiency of benzonitriles with functional amine groups in different positions, for mild steel corrosion in 0.5 M HCl solution. For this purpose, electro-chemical impedance spectroscopy and potentiodynamic measurements were realized. The surface analysis was also carried out by scanning electron microscopy technique. The SEM results were found in good agreements with that of electrochemical results. [20]

#### 3.5.2 Atomic Force microscope (AFM)

To get quantification of surface roughness of mild steel in the presence and absence of inhibitors owing to attack of acid solution or in other words, to enhance surface morphology investigation, the mild steel surface can also be investigated using atomic force microscopy (AFM). In this study, three-dimensional topography and the average surface roughness of the metal can be calculated. In the presence of inhibitor, if the surface roughness decreases as compared to blank acid solution without inhibitor, then we consider that the studied inhibitor has protecting ability of the metal in acid solution.

Ashish et al employed AFM to investigate the effect of three mannich bases corrosion inhibitors inhibitor on mild steel surface morphology. They found that the results of AFM were in good agreements with that of electrochemical measurements. [21]

Vedapriya Pandarinathan et al investigated the Adsorption of Corrosion Inhibitor 1-Dodecylpyridinium Chloride on Carbon Steel Studied by *in Situ* AFM and Electrochemical Methods. [22]

### 3.6 Computational Theoretical studies:

The computational theoretical studies techniques are very useful in predicting corrosion inhibition properties of the inhibitors. As molecular parameters are closely related to inhibition efficiency of the inhibitors and these parameters can theoretically be calculated using different software. So that before going with experiment, it is possible to predict the inhibition properties of the inhibitors by using theoretical calculations. In recent advances these theoretical methods like quantum chemical calculation by Gaussian software, molecular dynamic simulation etc. have been proved as an important tool in the study of the corrosion inhibitors.

### 3.6.1 Quantum Chemical calculation

Quantum chemical calculations can be performed with complete geometry optimisation using semi empirical method, density functional theory (DFT) method implemented in Gaussian 09W (interfaced with GaussView 5.0 as molecular modeller) software. The important molecular parameters like $E_{HOMO}$, $E_{LUMO}$, energy gap ($\Delta E$) and dipole moment ($\mu$) for the inhibitor molecules can be calculated. The study of these molecular parameters can be useful in investigating corrosion inhibitors. There is close relationship between molecular parameters and corrosion inhibition efficiency of the inhibitors.

Some amides and their derivatives, e.g. urea, thiourea, thioacetamide, and thiosemicarbazide are good inhibitors for mild steel in acid solutions. Several quantum chemical studies [23-24] have been carried out on these compounds by using semiempirical methods.

A. Kosari et al [25], I.B. Obot et al [26] investigated various compound as corrosion inhibitor and calculated various molecular parameters by DFT method to correlate with experimental results.

### *3.6.2 Molecular dynamics simulation*

Molecular dynamics simulation technique has attracted attention of researchers, scientist, academician associated with the field of corrosion inhibitor technology. In this technique. adsorption of single inhibitor molecule on the metal plane is simulated with the aid of Materials studio (MS) 6.0 from Accelrys.

D.K et al studied Non-toxic Schiff bases as efficient corrosion inhibitors for mild steel in 1 M HCl using Electrochemical, AFM, FE-SEM and theoretical methods. They calculated interaction energies derived from molecular dynamics simulation which are in agreement with experimental results.[27]

2-Acetyl pyridine nicotinic hydrazone and acetophenone nicotinic hydrazone have prepared and their corrosion inhibition properties for mild steel in 1 M HCl were studied by D.K. Singh et al [28] using weight loss, electrochemical, and density functional theory (DFT) methods.

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