

Part III

Corrosion inhibition studies

Chapter 2

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CHAPTER 2

MATERIALS AND METHODS

This chapter deals with the study of the corrosion inhibition behaviour of the newly synthesized Schiff bases on mild steel. Conventional methods like weight loss measurements and electrochemical measurements such as Tafel polarization studies and electrochemical impedance spectroscopy (EIS) are employed for the analysis of corrosion inhibition nature of the Schiff bases. The preparation of metal specimens, aggressive solutions and different methods adopted for the evaluation of corrosion inhibition properties are described in detail here.

Metal specimens

For weight loss studies, mild steel specimens of composition: C, 0.56 %; Mn, 0.025%; S, 0.09 %; P, 0.01 %; Si, 0.02 % and the remaining Fe, were cut in the dimension 1.0x 1.0x 0.098cm and abraded with various grades of silicon carbide papers (120, 400, 600, 800, 1000 and 1200) to obtain well polished surfaces as per ASTM standards. The exact surface area of the metal specimens was accurately determined using vernier calipers and screw gage. Then the metal pieces were degreased with acetone, washed with detergent and distilled water, dried and finally weighed. Specimens were immersed in aggressive solutions in the absence and presence of the inhibitor in different concentrations.

Aggressive solutions

0.1M HCl and 0.5M H₂SO₄ solutions were prepared using distilled water. Stock solutions of each Schiff base inhibitor were prepared with respective acids and diluted to

different concentrations in the range 0.2mM –1.0mM. For weight loss studies, 50ml acid solutions were used, but 100ml was appropriate for the electrochemical investigations.

Weight loss measurements

In weight loss studies, the metal surfaces were directly subjected to acidic environments for a particular period of time in the absence and presence of inhibitors and then weight loss was measured from which the inhibition efficiencies were calculated.

Aggressive solutions which contain different concentrations of the inhibitor were prepared and well polished mild steel (MS) specimens were immersed in these solutions for 24 hour. A blank experiment was also conducted without adding the inhibitor. The weight loss of metal specimens was measured after 24 h. The reproducibility of the experiments was ensured by carrying out duplicate and the average values were reported. The corrosion rates and percentage of inhibition efficiencies of each inhibitor were calculated by the following equations. The corrosion rates were expressed in mm/y and the inhibition efficiencies were obtained from corrosion rates.

$$\text{Rate of corrosion } W = \frac{K \times \text{wt.loss in grams}}{\text{Area in sq.cm} \times \text{time in Hrs} \times \text{Density}} \quad (1)$$

where 'K' =87600 (This factor is used for the conversion of cm/hour into mm/year)

Density of MS specimen= 7.88g/cc

Percentage of inhibition or the inhibition efficiency (η) of the inhibitor was calculated by

$$\eta = \frac{W-W'}{W} \times 100 \quad (2)$$

where W & W' are the corrosion rates of the MS specimens in the absence and presence of the inhibitor respectively⁴².

The corrosion inhibition efficiency of Schiff bases was compared with their parent amine, in aggressive solutions for a period of 24 h. This evaluation explores the role of azomethine linkage in Schiff base in the corrosion inhibition activity.

Adsorption isotherms

The inhibitory action of Schiff bases is due to the adsorption of these molecules on the surface of the metal. The adsorption on the metal surface may be physical, chemical or both. The extend of corrosion inhibition can be explained by considering the adsorption isotherms. These isotherms can represent the molecular interactions of the inhibitor molecules with the active sites on the metal surfaces. The most commonly used adsorption isotherms are Langmiur, Freundlich, Temkin and Frumkin. All the isotherms are represented as equations below and the best fit isotherm is accepted with the aid of correlation coefficient.

$$\text{Langmiur adsorption isotherm } \frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (3)$$

$$\text{Freundlich adsorption isotherm } \theta = K_{ads}C \quad (4)$$

$$\text{Temkin adsorption isotherm } e^{f\theta} = K_{ads} C \quad (5)$$

$$\text{Frumkin adsorption isotherm } \frac{\theta}{1-\theta} \exp(f\theta) = K_{ads} C \quad (6)$$

where C is the concentration of the inhibitor, θ is the fractional surface coverage, f is the molecular interaction parameter and K_{ads} is the adsorption equilibrium constant. Among the different isotherms considered, the one which has the highest the correlation coefficient (R^2) value was accepted for interpreting the mechanism of adsorption⁴³⁻⁴⁶.

The following is the relation between fractional surface coverage and percentage inhibition efficiency, $\theta = \frac{\text{Percentage inhibition efficiency}}{100}$ (7)

The adsorption equilibrium constant K_{ads} is related to the standard free energy of adsorption ΔG_{ads}^0 , by

$$\Delta G_{\text{ads}}^0 = -RT \ln (55.5 K_{\text{ads}}) \quad (8)$$

where 55.5 is the molar concentration of water, R is the universal gas constant and T is the temperature in Kelvin⁴⁷.

Effect of temperature

The variation of corrosion inhibition with temperature was studied in the range 30-60°C. The specimens for weight loss measurements were kept at different temperatures i.e., 30°C, 40°C, 50°C and 60°C on a thermostat for 24 hours in the presence and absence of Schiff bases in acidic solution and the data obtained was utilized to calculate the thermodynamic parameters of corrosion such as activation energy (E_a), Arrhenius parameter (A), enthalpy of corrosion (ΔH^*) and entropy of corrosion (ΔS^*). The energy of activation can be calculated using Arrhenius equation,

$$K = A \exp \left(-\frac{E_a}{RT} \right) \quad (9)$$

where K is the rate constant, A is the pre exponential or Arrhenius factor, E_a is the activation energy, R is the universal gas constant and T is the temperature in Kelvin scale. A plot of $\log K$ Vs $1000/T$ will be a straight line with a slope $-E_a/2.303R$ and intercept $\log A$.

From the transition state theory⁴⁸ the enthalpy and entropy of activation (ΔH^* , ΔS^*) can be calculated as,

$$K = \left(\frac{RT}{Nh} \right) \exp \left(\frac{\Delta S^*}{R} \right) \exp \left(\frac{-\Delta H^*}{RT} \right) \quad (10)$$

where, N is the Avogadro number and h is the Planck's constant. The plot of logarithmic form of this equation gives a straight line with a slope $-\Delta H^*/2.303R$ and intercept

$\log \frac{R}{Nh} + \frac{\Delta S}{2.303 R}$, from which enthalpy of activation and entropy of activation can be calculated.

Electrochemical measurements

Electrochemical techniques are extensively used in the study of corrosion of metals. These advanced techniques are helpful in determining the corrosion rate and exploring the mechanism of corrosion. One of the prominent advantage of electrochemical method is that it requires short measurement time and provides a fast and accurate mechanistic information about the corrosion.

The electrochemical behaviour of the metal in the presence and absence of the inhibitor can be determined by electrochemical systems and thus provide a mechanistic way to predict the inhibitive efficiency of the various organic compounds in acidic media⁴⁹⁻⁵⁴. Most popular electrochemical corrosion measurement techniques are electrochemical impedance spectroscopy (EIS) and polarization studies. Polarization techniques are further classified into Tafel polarization analysis and linear polarization resistance analysis.

Metallic corrosion involves the anodic oxidation of the metal and the cathodic reaction which may be either the reduction of dissolved oxygen or the evolution of hydrogen. Analysis of charge transfer processes during electrode reactions give parameters such as corrosion potential, corrosion current density, charge transfer resistance, cathodic and anodic slope values etc which will lead to the determination of rate of corrosion, the mechanism of corrosion and inhibition efficiency of molecules.

Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) or AC impedance methods are widely utilized in recent years as an advanced and accurate method in corrosion experiments⁵⁵⁻⁶¹. Kinetic and mechanistic information on corrosion inhibition can be obtained by impedance measurements. The system response provides information about the reactions taking place at the interface. The identification of dielectric and electric properties of components under investigation is made possible by the system. Electrochemical analysis can be performed with the help of suitable equivalent electrical circuits⁶².

The electrochemical system employed for the corrosion evaluation is an Ivium compactstat-e system which is associated with an advanced version of 'IviumSoft' software which makes it possible that analytical procedures like selection of proper equivalent circuit, simulation of curves, calculation of resistance and current densities easier. Three electrode assembly was used as the electrochemical cell in which a saturated calomel electrode (SCE) is the reference electrode, platinum electrode of 1cm² area is the counter or auxiliary electrode and well polished metal surface of 1cm² exposed area towards the corroding medium is the working electrode.

The measurement of capacitance (C_{dl}) around the electrical double layer formed between the charged metal surface and the oppositely charged ions of acid solution can be considered as equivalent to an electrical capacitor. The presence of a corrosion inhibitor in the solution will result in decreasing of electrical capacity which is due to the formation of an adsorption layer of the inhibitor molecules on the electrode surface. As the concentration of the inhibitor increases the capacitance also decreases.

While impedance measurement, a small and steady sinusoidal current is applied and the resulting current is measured along with the phase angle, from which the real and imaginary parts of impedances are derived. The real component of impedance $Z'(\omega)$ corresponds to the resistance and the imaginary part $Z''(\omega)$ corresponds to capacitance and they are related as

$$Z(\omega) = Z'(\omega) + jZ''(\omega)$$

where $Z(\omega)$ is the impedance, $Z'(\omega)$ is given by $Z_0 \cos\Phi$ and $Z''(\omega)$ is given by $Z_0 \sin\Phi$, Z_0 is the magnitude of the impedance and j is the imaginary number $\sqrt{-1}$.

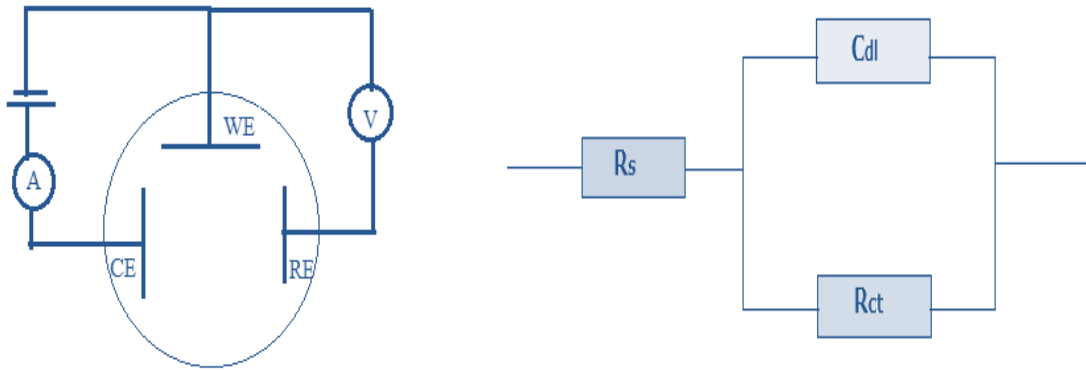


Fig. 3.1 Equivalent circuit model

Impedance measurement plots

Impedance measurements can be plotted using the Nyquist (Cole-Cole) plot, Bode plot and impedance plot. In Nyquist plots, which are commonly used, the square of the real part of impedance is plotted against the square of imaginary part. The solution resistance R_s (ohmic resistance), which is the resistance between the working electrode and reference electrode, is given by the impedance at high frequencies in the semicircular Nyquist plot. The frequency reaches its high limit at the leftmost end of the semicircle, where the semicircle touches the x-axis. The frequency reaches its low limit at the

rightmost end of the semicircle where the impedance of the system will be the sum of R_s and R_{ct} (Figure 3.2). R_{ct} is the charge transfer resistance at the electrode-solution interface. From the values of the charge transfer resistances, the inhibition efficiency of the compounds can be calculated using the following equation

$$\eta_{EIS} \% = \frac{R_{ct} - R'_{ct}}{R_{ct}} \times 100 \quad (11)$$

where R_{ct} and R'_{ct} are the charge transfer resistances of working electrode with and without the inhibitor respectively⁶³.

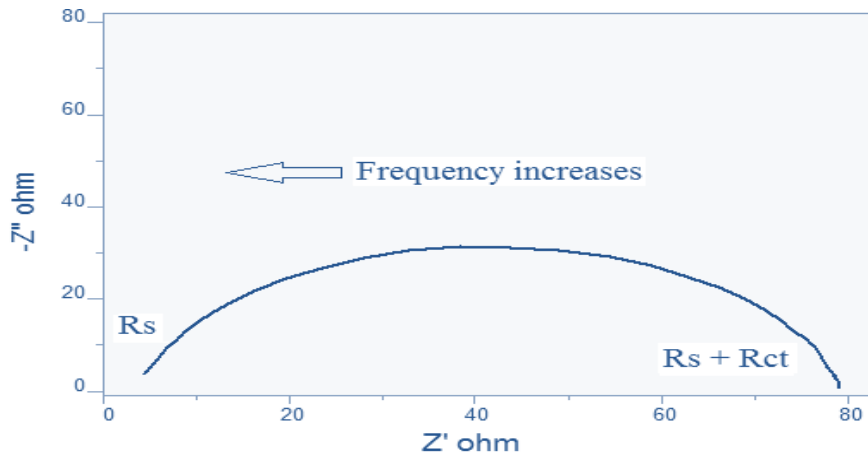


Fig. 3.2 A Nyquist plot

In Bode plots, the impedance magnitude $|Z|$ and phase angle θ , are plotted against frequency. $|Z|$ is obtained from the equation $|Z| = \sqrt{Z'^2 + Z''^2}$. The curve representing $\log|Z|$ versus \log frequency will give the value of R_s and R_{ct} . This curve is called the impedance plot. The break point of this curve should lie on a straight line with a slope -1. On extrapolation to y-axis, at $f=1$ or $\log f = 0$, the value of C_{dl} is obtained.

$$|Z| = \frac{1}{C_{dl}} \quad (12)$$

In the plot of θ against $\log f$, appearance of a peak which corresponds to $f(\theta^{\max})$ shows the maximum phase shift and from which C_{dl} can be evaluated. Frequency break points associated with each step are the characteristic of Bode and impedance plots. The Bode plot is an alternative to the Nyquist plot since the problem of longer measurement period associated with low frequency can be avoided.

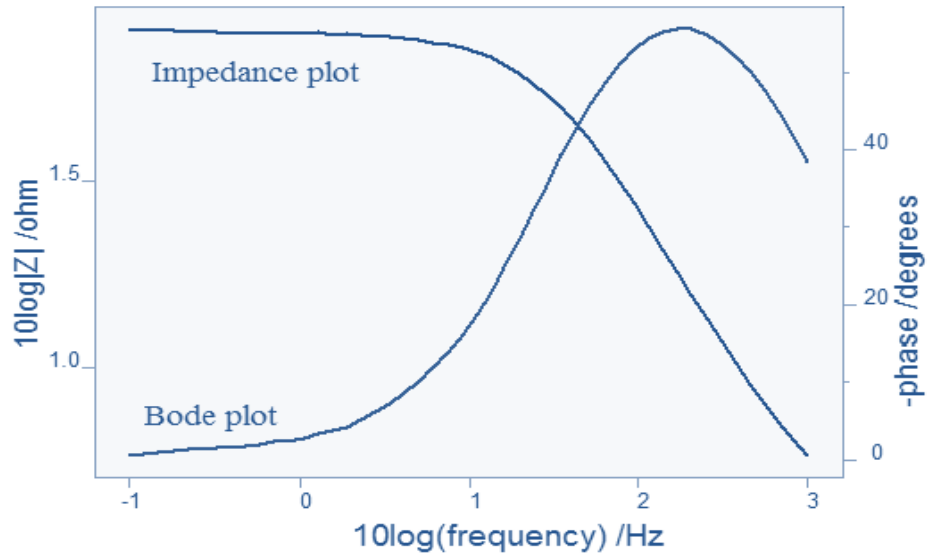


Fig. 3.3 Bode and impedance plots

Potentiodynamic polarization studies

Polarization method is evolved when the potential of the working electrode is changed ie, polarized and measuring the current produced as a function of time or potential. Polarization may be activation polarization and concentration polarization, the former generated by the resistance developed when electrical charges transfer through double layer and the latter from the concentration gradient between the interface of bulk solution and the electrode. When the polarization potential comes in the range of activation polarization, there are two types of polarization measurements i) Tafel extrapolation and ii) linear polarization measurements.

Tafel extrapolation method

Polarization can be either anodic or cathodic; the anodic reaction being oxidation of the metal and cathodic being the reduction of H⁺ ions to H₂. When the rates of anodic and cathodic processes become equal, there is no charge accumulation. The mixed potential at this moment is called the open circuit potential (OCP) and designated as corrosion potential or E_{corr}. To get the applied current density, i_{app} as a function of the applied potential E, the potential between the reference electrode and the working electrode is controlled and scanned at constant rate.

The famous Butler-Volmer equation⁶⁴ describes the polarization of reversible electrodes which are controlled by activation process

$$i_{app} = i_{corr} \left\{ \exp \left[\frac{\alpha_a}{RT} zF(E - E_{corr}) \right] - \exp \left[-\frac{\alpha_c}{RT} zF(E - E_{corr}) \right] \right\} \quad (13)$$

where i_{app} is applied or measured current density; i_{corr} is corrosion current density; α_a and α_c are the charge transfer coefficients for anodic and cathodic reactions respectively. E - E_{corr} is the polarization ie, the difference between applied and corrosion potential; z is metal valence; F is Faraday constant; R, the gas constant and T is the absolute temperature. A plot of electrode potential versus the logarithm of current density was found to be in a straight line. For anodic and cathodic polarizations, the corresponding equations can be deduced and from which the Tafel slope for the anodic and cathodic processes can be represented as

$$b_a = \frac{2.303 RT}{\alpha_a zF} \text{ and} \quad (14)$$

$$b_c = \frac{2.303 RT}{\alpha_c zF} \quad (15)$$

The slope of a Tafel plot provides information about the mechanism of the electrode process and the extrapolations of the linear segment of cathodic and anodic curves gives E_{corr} . The $\log i_{corr}$ values at the point of intersection of coordinates will give corrosion current density from which the percentage of inhibition can be calculated by the following equation

$$\eta_{pol} \% = \frac{i_{corr} - i'_{corr}}{i_{corr}} \times 100 \quad (16)$$

where i_{corr} and i'_{corr} are uninhibited and inhibited corrosion current densities respectively⁶⁵.

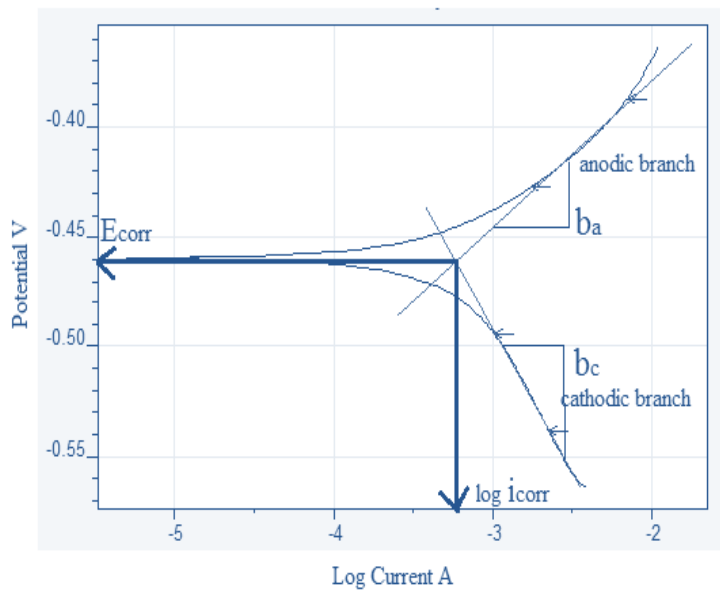


Fig. 3.4 Tafel extrapolation method

Linear polarization method

The rate of corrosion is mainly controlled by the charge transfer process at the metal-solution interface. So when the inhibitor molecules are adsorbed on the metal surfaces the rate of charge transfer process is decreased. As a result, the rate of corrosion is decreased and thereby the polarization resistance is increased. Linear polarization

technique is based on the fact that for a potential displacement in the range of +/- 10mV, the applied current density is a linear function of the electrode potential.

Stern and Geary equation⁶⁶ which relates i_{corr} to the inverse of polarisation resistance is

$$i_{corr} = \left(\frac{1}{2.303 R_p} \right) \left(\frac{b_a b_c}{b_a + b_c} \right) = \frac{B}{R_p} \quad (17)$$

where R_p is $\frac{\Delta E}{\Delta i}$, which is the polarization resistance and B is a constant. The variation of i_{app} is linear with the potential. The slope of the linear polarisation curve dE/di gives the polarisation resistance, which can be obtained by drawing a tangential line to the curve at E_{corr} and at zero current. The corrosion inhibition efficiency can be calculated using the equation

$$\eta_{R_p} \% = \frac{R'_p - R_p}{R'_p} \times 100 \quad (18)$$

where R'_p and R_p are the polarization resistance in the presence and absence of inhibitor respectively.

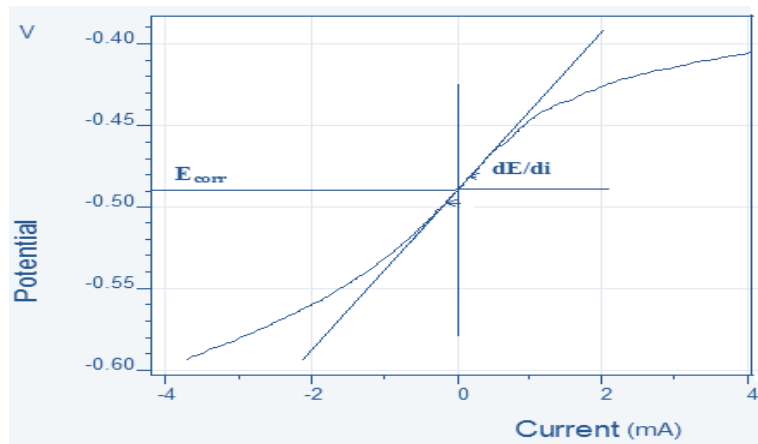


Fig. 3.5 Linear polarization method