



Received: 09-06-2014
Accepted: 05-07-2014

ISSN: 2321-4902
Volume 2 Issue 2



Online Available at www.chemijournal.com

International Journal of Chemical Studies

Schiff bases as corrosion inhibitor for mild steel in H₂SO₄ and characterization of Schiff bases by spectral studies

P. Karuppasamy¹, R. Arumugam¹, G. Veeramanikandan¹, M. Ragu¹, J. Thiruppathy¹, M. Ganesan¹, T. Rajendran¹, V. K. Sivasubramanian¹

1. Post Graduate and Research Department of Chemistry, Vivekananda College, Tiruvedakam West, Madurai -625 234, Tamil Nadu, India.

Corresponding Author: K. Sivasubramanian & P. Karuppasamy; Email: vk_siva1957@yahoo.com, pkaruppasamy23@gmail.com

The effect of Schiff base compounds was investigated by weight loss method, potentiodynamic polarization, UV-Vis, IR and Electrochemical impedance spectroscopy (EIS). The inhibition efficiency of the Schiff bases on mild steel was depend the effect of molecular planarity, vacant d-orbitals of the metal and conjugation of π electrons present in the schiff bases. The potentiodynamic polarization study revealed that the Schiff bases acted as mixed type inhibitors. The EIS parameter is indicative of adsorption of Schiff bases on mild steel surface leading to formation of a protective layer. The weight loss study showed that the inhibition efficiency of these compounds increases with increase in concentration and vary with immersion time. Adsorption of schiff bases obeyed the Langmuir adsorption isotherm. In the UV-visible spectral studies the wavelength of absorption (λ_{max}) of all the Schiff bases are reported and the values are in accordance with the structure and polarity of the solvents and absorption maximum is sensitive to the nature of the substituent present in the Schiff bases. IR spectral data gave the exact matching frequencies of the groups which are in accordance with the literature values. These values support the exact structure of the Schiff bases.

Keyword: Schiff Bases, UV-vis Spectra, Weight Loss Method, Potentiodynamic Polarization, EIS.

1. Introduction

Schiff bases are condensation products of primary amines with carbonyl compounds and they were first reported by Schiff^[1] in 1864. The common structural feature of these compounds is the azomethine group with a general formula $RHC=N-R^1$, where R and R¹ are alkyl, aryl, cyclo alkyl or heterocyclic groups which may be variously substituted. These compounds are also known as anils, imines or azomethines. Several studies^[2-8] showed that the presence of a lone pair of electrons in a sp² hybridized orbital of nitrogen atom of the azomethine group is of considerable chemical and biological importance. Because of the relative easiness of preparation, synthetic flexibility, and the special property of C=N group, Schiff bases are generally excellent chelating agents^[6-12] especially when a functional group like –OH or –SH is present close to the azomethine group so as to form a five or six membered ring with the metal ion. The importance of Schiff base complexes for bioinorganic chemistry, biomedical applications, supramolecular chemistry, catalysis and material

science, separation and encapsulation processes, and formation of compounds with unusual properties and structures has been well recognized and reviewed^[13-22]. Schiff bases of salicylaldehydes have also been reported as plant growth regulators^[23] and antimicrobial^[24] or Antimycotic^[25] activity. Schiff bases also show some analytical applications^[26]. Schiff bases are characterized by the –N=CH– (imine) group which is important in elucidating the mechanism of transamination and rasemination reaction in biological system^[27, 28]. An interesting application of Schiff bases is their use as an effective corrosion inhibitor, which is based on their ability to spontaneously form a monolayer on the surface to be protected^[29-31]. Many commercial inhibitors include aldehydes or amines, but presumably due to the C=N bond the Schiff bases function more efficiently in many cases^[32]. The principal interaction between the inhibitor and the metal surface is chemisorption^[33]. The inhibitor molecule should have centers capable of forming bonds with the metal surface by electron transfer. In such cases the metal acts as an

electrophile and the inhibitor acts as a Lewis base. Schiff bases have been reported in their biological properties, such as, antibacterial, antifungal activities [34-38]. O-phenylenediamine Schiff bases show clinical properties [39]. Isatin Schiff bases were reported to possess antiviral, anti-HIV, antiprotozoal and anthelmintic activities [40]. Schiff bases show remarkable activities on plant hormone such as the auxins on root growth [41] and the Schiff base of ester and carboxylic acid show remarkable activity as plant growth hormone [42]. Macrocyclic Schiff bases of Dithiocarbazic acid have many fundamental biological functions, such as photosynthesis and the transport of oxygen in mammalian and other respiratory system [43]. Schiff bases are condensation products of amines and a ketones or aldehydes. The greatest advantage of Schiff bases is that they can be easily synthesized from relatively inexpensive materials. Schiff bases containing the hetero atoms like oxygen, nitrogen, sulfur are of much importance in the corrosion of mild steel has been studied in acid medium [41-46]. In this present work we studied the corrosion rate of mild steel by using the symmetrical Schiff base inhibitors (H₂-salen (**SB1**), 5,5'-p-NO₂salen(**SB2**), -5,5'-p-Cl₂salen(**SB3**), 5,5'-p-Br₂salen(**SB4**)) in sulphuric acid medium. Weight loss method is used to study corrosion rate values, with and without the addition of various concentrations of Schiff base inhibitors and also at different time durations. The inhibition efficiency is calculated from both weight loss method and electrochemical methods (Tafel potentiodynamic polarization and electrochemical impedance

spectroscopy). The present investigation is to synthesize various Schiff bases (**SB1-SB4**) with utmost purity spectral studies. The surface coverage (θ) of the adsorbed inhibitor is calculated and the suitable plot of surface coverage (θ) with the concentration of the inhibitor(C) is made to understand the nature of mechanism involved in the corrosion inhibition.

2. Experimental Part

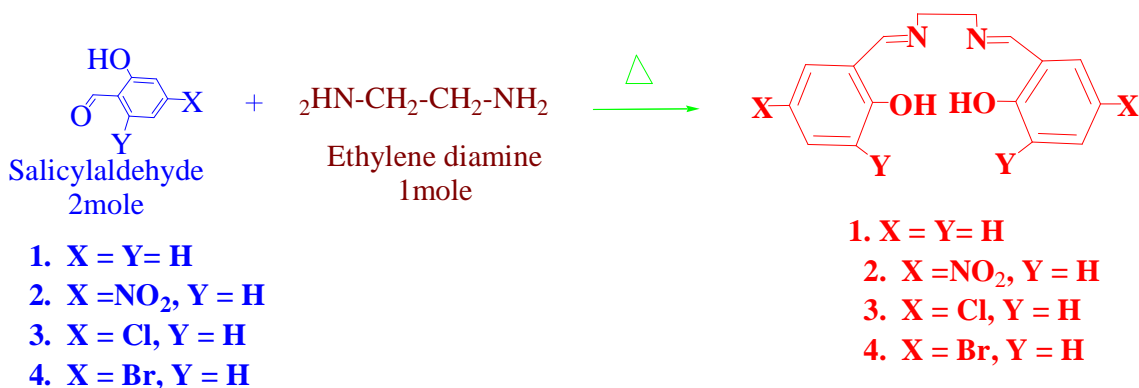
2.1 Materials

Salicylaldehyde, and the substituted salicylaldehydes (5, 5'-chloro, 5-bromo, 5-nitro) were purchased from sigma Aldrich and ethylene diamine were purchased from Merck (AnalaR grade). Ethanol, acetonitrile, hexane, ethyl acetate and Deionized water have been used as solvents for purification, recrystallization and solution makings.

2.2 Preparation of Schiff Bases

The general procedure for the synthesis of Schiff base ligands involves the condensation of substituted aldehyde with amines in an alcoholic medium (2:1 ratio). All the Schiff bases were purified by washing with n-hexane and ethyl acetate until the unreacted starting materials were removed. The yield of all the Schiff bases is very good and the values are given in Table 1. The purification was monitored by TLC technique. All the Schiff bases were characterized by UV-vis, FT-IR spectral studies.

Structures of symmetrical schiff bases are given in **Scheme 1**.



Scheme 1: Synthesis of symmetrical Schiff Bases (1-4)

2.3 Selection of sample and Preparation of specimen, medium

Here we choose an alloy (Mild steel). Mild Steel is an alloy of iron, consisting of 0.2% to 2.1% of carbon. The corrosion rate of the above specimens studied in acid condition (1M, 1.5M, 2M, 2.5M, 3M H₂SO₄) using a weight loss method. Rectangular samples were cut from different metal plates. The samples are mechanically polished and numbered by punching before using. The specimens were polished by using emery papers with 80 grades and then the samples are degreased by acetone. Then a line is drawn with known area to have the same amount of corrosion possibilities. The area of the sample which we have taken is 1x1 cm².

Sulfuric acid medium (1M, 1.5M, 2M, 2.5M, and 3M) is used as the medium for immersion studies. The four Schiff Bases have been used in this study all are dissolved in Acetonitrile. These solutions are prepared using AnalaR grade chemicals with deionized water.

2.4 Methods

The UV-visible absorption spectral measurements have been carried out using spectrophotometer JASCO V-530 with constant time (in secs) over a range of 200-800 nm. The infrared spectra have been recorded in a JASCO FT-IR-410 spectrophotometer, in a solid phase using KBr pellets. These weight loss values are used to calculate the corrosion rate and inhibition efficiency. The corrosion rate was calculated from the weight loss using the relationship

$$\text{Corrosion rate (mppy)} = \frac{87.6 \times W \text{ (mg)}}{A \text{ (cm}^2\text{)} \times T \text{ (hrs)} \times D \text{ (g/cc)}}$$

Where,

W is the weight loss in mg,

D is the density in g/cc,

A is the area of exposure in cm²,

T is the exposure time in hour,

mppy is millimeter per year.

Inhibitor efficiency has been determined by using the following relationship.

$$\text{Inhibitor efficiency (\%)} = \frac{W_{\text{free}} - W_{\text{add}}}{W_{\text{free}}} \times 100$$

$$\text{Inhibitor efficiency (\%)} = \frac{CR_{\text{free}} - CR_{\text{add}}}{CR_{\text{free}}} \times 100$$

The potentiodynamic polarization and Electrochemical Impedance (EIS) were measured by using electrochemical Workstation (CH-Instrument), at 0.1M TBAP (tetrabutylammoniumperchlorate) as the supporting electrolyte and Ag/AgCl as the reference electrode.

3. Results and Discussion

3.1 UV-visible spectral study

All the UV-visible absorption spectral measurements have been carried out using spectrophotometer JASCO V-530 with constant time (in secs) over a range of 200-800 nm. The Schiff base (**1**) absorbs at $\lambda_{\text{max}} = 313$ nm (**Figure 1**) in 100% CH₃CN medium and change of solvent from acetonitrile to ethanol the absorption of Schiff base (**SB1**) shifts from $\lambda_{\text{max}} = 313$ nm to $\lambda_{\text{max}} = 322$ nm (red shift). The Schiff base (**SB2**) shows the absorption at $\lambda_{\text{max}} = 301$ nm in 100% CH₃CN medium and change of solvent to ethanol the absorption of Schiff base (**3**) shift from $\lambda_{\text{max}} = 301$ nm to $\lambda_{\text{max}} = 319$ nm (red shift). Introduction of bromo group in the 5, 5'-position of Schiff base (**SB3**) the λ_{max} value is 351 nm in CH₃CN and 385 nm in ethanol. The same trend has been observed for the introduction of nitro group in the 5,5'-position of Schiff base (**SB4**). We tested the spectral changes of all Schiff bases (**SB 1- SB 4**) when water is added to CH₃CN and Ethanol medium. Interestingly, every addition of water in 90:10, 80:20, 70:30, 60:40, 50:50 v/v ratio leads to marginal red shift in the absorption maximum for all Schiff bases (**SB 1- SB 4**) and also the intensity decreased (hypochromic shift) (Figures 2). For example in Schiff base (**SB1**) increase in the water content in acetonitrile the λ_{max} value shifts in the following pattern (256,257, 258, 259, 260nm) and in ethanol 234, 235, 237, 238, 239 nm (Figure 3).

Similar spectral changes are observed with all Schiff bases (**SB 1- SB 4**) when the solvent medium is changed from acetonitrile to aqueous acetonitrile and Ethanol to aqueous Ethanol the λ_{max} and the values are shown in Tables 1. This absorption maximum is sensitive to the nature of the substituent in the Schiff bases. From the data provided in **Table 1**, it is obvious that the same trend of shifting of λ_{max} to higher wavelengths is observed for all Schiff bases (**SB 1- SB 4**). It is interesting to note that there is a marginal decrease in the absorption maxima when the electron withdrawing groups are introduced in the

5,5'- position. In the presence of a polar solvent the energy required for π - π^* electronic transition is affected by solvent polarity. In the presence of a polar solvent, the more polar π^* orbital of the LUMO will

be better stabilized than the π orbital of the HOMO leading to a net decrease in the transition energy. This resulted in an increase in the transition wavelength called a bathochromic shift (red shift).

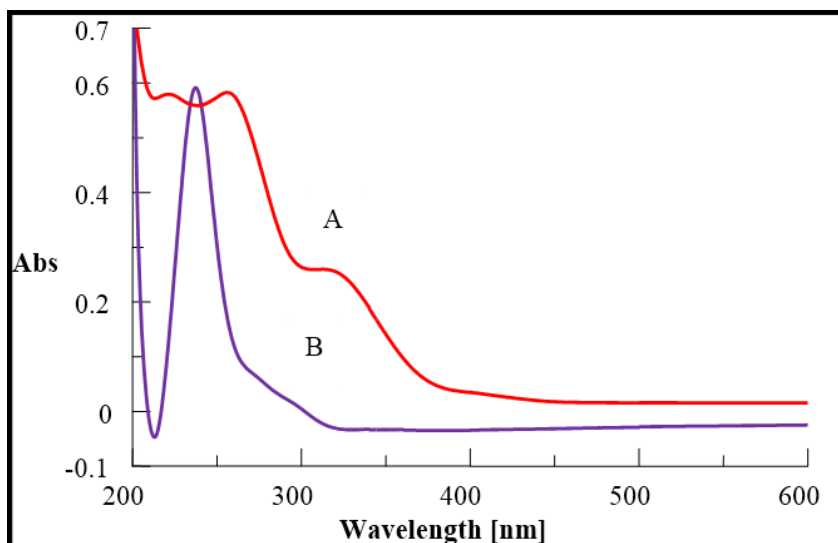


Fig 1: Absorption Spectral changes of SB (1) with the change of medium from (A). aqueous acetonitrile to (B). aqueous Ethanol.

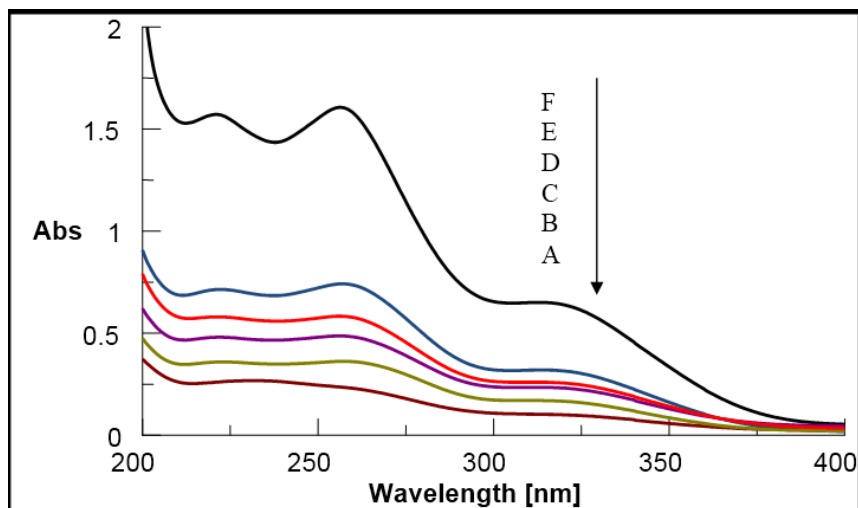


Fig 2: Absorption Spectral changes of SB (1) with the change of medium from acetonitrile to aqueous acetonitrile. [SB 1]= 2×10^{-4} M. CH₃CN/ H₂O (v/v) Solvent ratio A). 50:50 B).60:40 C). 70:30 D). 80:20 E). 90:10. F).100% CH₃CN.

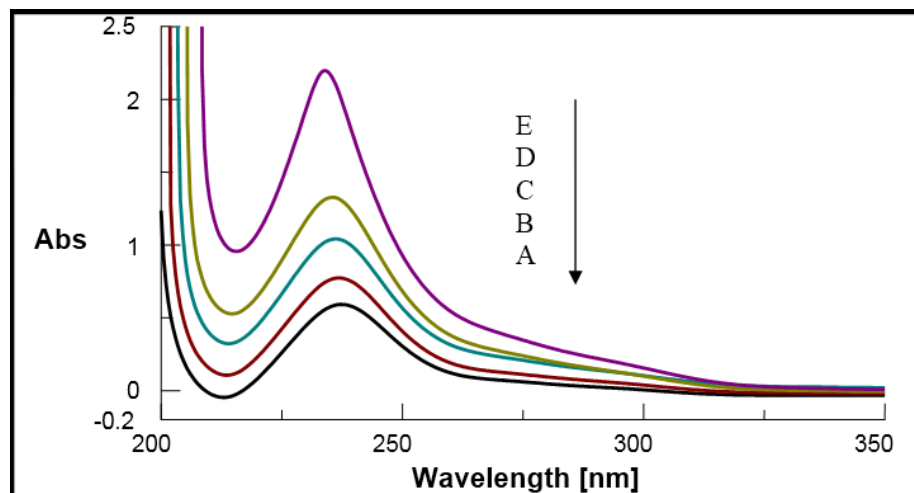


Fig 3: Absorption Spectral changes of SB (1) with the change of medium from Ethanol to aqueous Ethanol. [SB]= 2×10^{-4} M. Ethanol/ H₂O (v/v) Solvent ratio A). 50:50 B).60:40 C). 70:30 D). 80:20 E). 90:10.

Table 1: Yield (in %) and Spectral data [UV-vis] for Schiff bases (1-5) in acetonitrile, ethanol and ethyl acetate at constant temperature T=298K.

Schiff Bases	Yield (in %)	UV-vis Spectral data	
		$\lambda_{\max}(\text{nm})$ in CH ₃ CN	$\lambda_{\max}(\text{nm})$ in C ₂ H ₅ OH
1	96.2	313, 400.5	321.5, 400.5
2	92.7	242	253.4
3	92.1	301,405.5,	318.5, 398.5
4	95.4	340, 350.5	260, 384.5

Table 2: Spectral data [UV-vis] for Schiff bases (SB: 1) in acetonitrile+water and ethanol+water at constant temperature T=298K.

Solvent ratio	UV-vis Spectral data	
	$\lambda_{\max}(\text{nm})$ in CH ₃ CN+ H ₂ O	λ_{\max} in C ₂ H ₅ OH +H ₂ O
90:10	221, 256	234
80:20	222, 257	235
70:30	222.5, 257.5	236.5
60:40	223, 258	237
50:50	231, 260	237.5

3.2 Infra-Red spectral study

The infrared spectra of all Schiff bases (**SB 1- SB 4**) have been recorded in a JASCO FT-IR-410 spectrophotometer, in a solid phase using KBr pellets. The IR spectra shows the stretching frequency (ν) of Schiff base (**SB 1**) for $\nu_{\text{C=N}}$ is 1635 cm^{-1} and $\nu_{\text{O-H}}$ is 3461 cm^{-1} . In the case of Schiff base (**SB 2**) the

stretching frequency (ν) $\nu_{\text{C=N}}$ is 1610 cm^{-1} and $\nu_{\text{O-H}}$ is 3438 cm^{-1} . Introduction of the chloro group in the 5, 5'-position of Schiff base (**SB 3**) the stretching frequency (ν) $\nu_{\text{C=N}}$ is 1635 cm^{-1} and $\nu_{\text{O-H}}$ is 3440 cm^{-1} .

Whereas, introduction of bromo group in the 5, 5' position of Schiff base (**SB 4**) the stretching

frequency (ν) $\nu_{\text{C=N}}$ is 1637cm^{-1} and $\nu_{\text{O-H}}$ is 3473cm^{-1} . The IR spectra show the stretching frequency (ν) of Schiff bases are shown in Table 3.

Table 3: IR stretching frequencies of Schiff Bases (1-4)

Schiff Bases	IR stretching frequencies, cm^{-1}		
	C=N	O-H	C-X
SB:1	1635	3461	775
SB:2	1610	3438	747
SB :3	1628	3459	557
SB: 4	1637	3473	730

3.3 Weight loss method

Corrosion of mild steel in sulfuric acid (3M) medium was studied. Initially the variation of corrosion rate, for change in time (1-5 hrs) was studied in 3M sulfuric acid medium. The corrosion rate was calculated by weight loss method and the data is given in Table 4. It is found with increasing in time the corrosion rate increases. However, in longer duration there is a slight increase in corrosion rate. Similarly the corrosion of mild steel is studied by weight loss method by keeping time as constant and there is a change in concentration of sulfuric acid from 1M to 3M. It is observed that with an increase in concentration of sulfuric acid there is a substantial increase in corrosion rate. Because of the aggressive properties of acid solutions towards metals, inhibitors are commonly used to reduce the corrosive attack of acids. The selection of appropriate inhibitors depends on the type of acid, its concentration; temperature and type of metallic components used of various acids, sulfuric acid and hydrochloric acid frequently use in industrial environments. The most proven compounds are nitrogen containing organic compounds which are having the higher inhibition efficiency is obtained by the presence of heteroatoms in molecular structure such as sulfur, nitrogen and oxygen that promotes coordination bond with metal ^[1-7]. Corrosion of mild steel in the presence of all the inhibitors (**SB1**, **SB2**, **SB3** and **SB4**) was studied with the weight loss method exposure time as constant and varying the

concentration of the inhibitor and by keeping the concentration of the inhibitor constant and varying the exposure time. Generally it is observed that by using the inhibitor the corrosion rate is decreased. As a case study for the inhibitor **SB1** with exposure time of three hours the corrosion rate without inhibitor is 2.317×10^{-3} mmpy whereas with inhibitor **SB1** the corrosion rate is 1.785×10^{-3} mmpy. The same trend is observed for all the remaining three inhibitors (**SB2**, **SB3** & **SB4**). It is observed by keeping the concentration of Inhibitors as constant and by varying the time (**Figure 4**), with an increase in the exposure time the corrosion rate decreases. Correspondingly the inhibition efficiency is also increasing (**Table 5**) (**Figure 5**). It is interesting to observe that the inhibition efficiency starts with the value of 88.58% for 0.1 M [**SB1**] for one hour exposure time and goes upto 94.04% for the same concentration at 5 hours of exposure time. Almost the same trend is observed for all the three remaining inhibitors **SB2**, **SB3** and **SB4** (**Table 4**). Similarly the graph showing the corrosion rate with change in concentration of H_2SO_4 is given in the **Figure 6**. The graph shows that with an increase in concentration of Schiff bases the corrosion rate decreases and the inhibition efficiency (IE %) increases (**Figure 7**) (**Table 5**). The similar graphs are drawn in the presence of all the four inhibitors. It is pertinent to see that in all the four cases there is a remarkable decrease in the corrosion rate and the inhibition efficiency (IE %) increases.

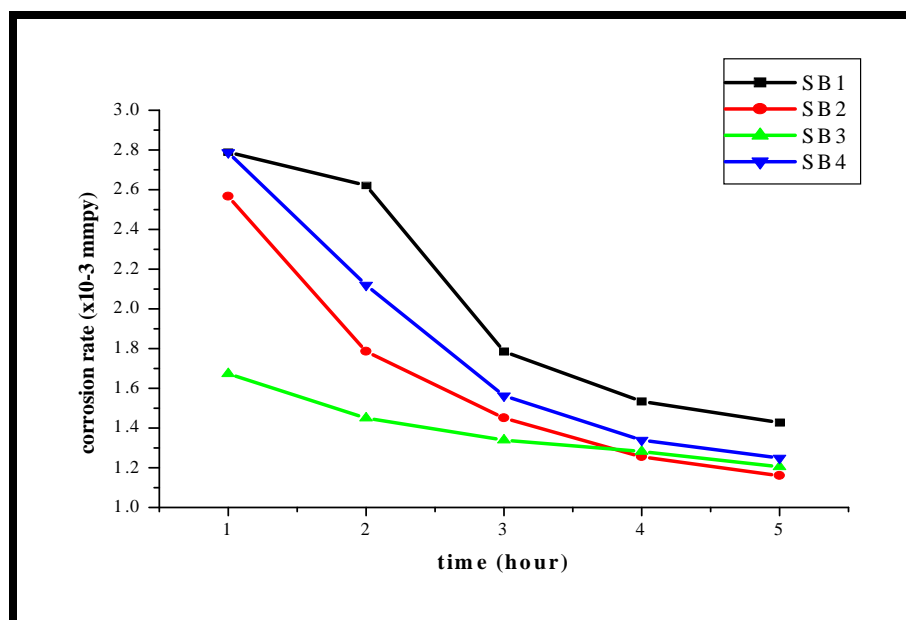


Fig 4: Corrosion rate (mppy) of mild steel in H_2SO_4 (3M) with **SB1**, **SB2**, **SB3** and **SB4** for the variation of time in hours.

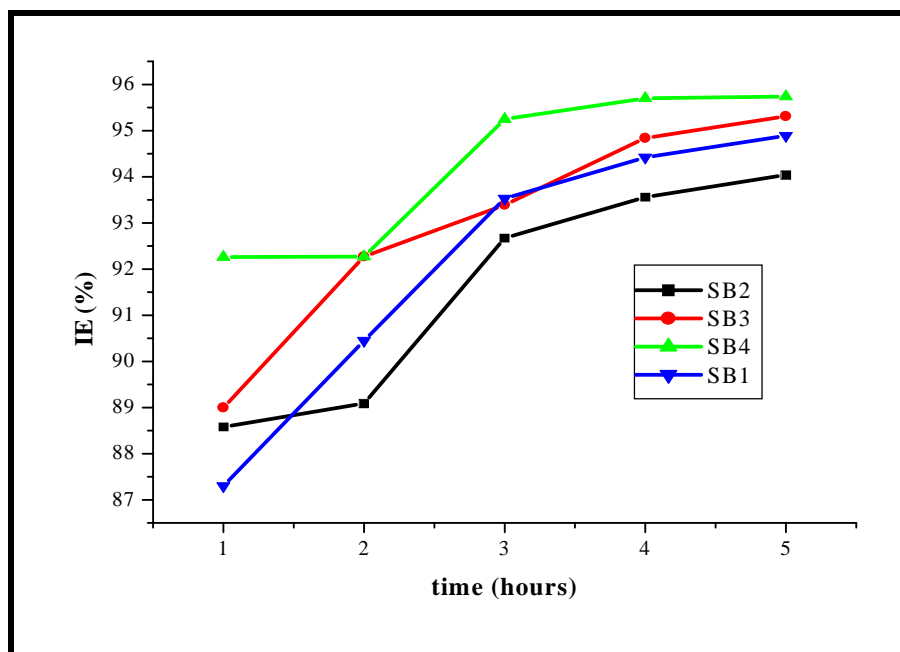


Fig 5: Inhibition efficiency (IE %) of **SB4** in H_2SO_4 (3M) with mild steel for the variation of time in hours.

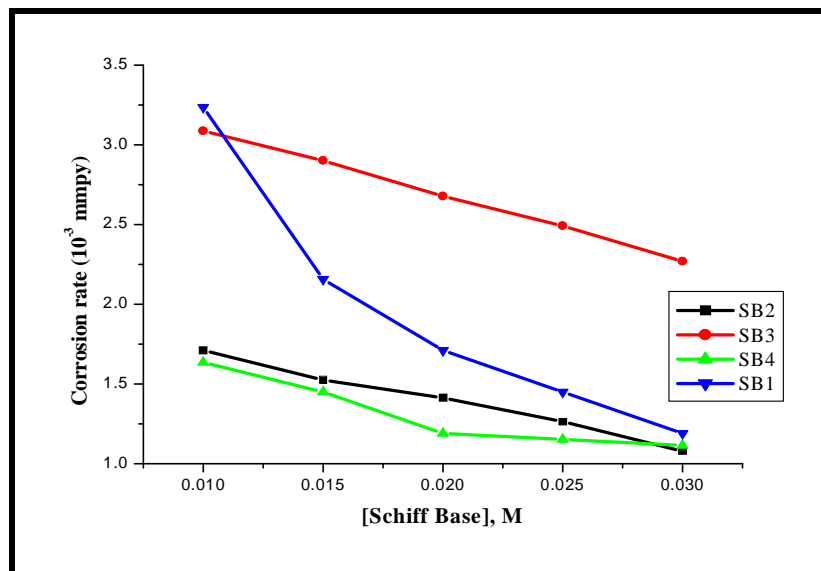


Fig 6: Corrosion rate of mild steel in H₂SO₄ (3M) with SB1, SB2, SB3 and SB4 for the variation of Inhibitor concentration.

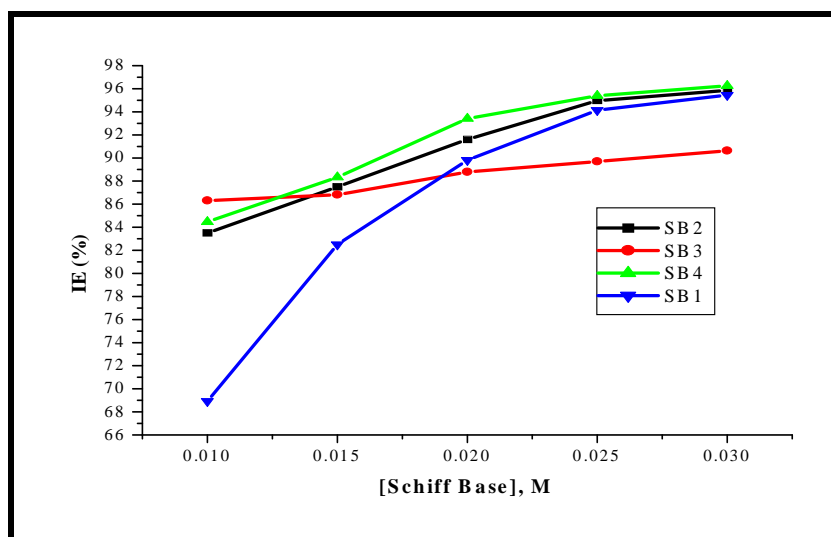


Fig 7: Inhibition efficiency (IE %) of SB 4 in H₂SO₄ (3M) with mild steel for the variation of concentration of SB4.

Table 4: Corrosion rate of Mild Steel in H₂SO₄ (3M) with SB1, SB2, SB3 and SB4 as a function of variation of exposure time.

Time in (hours)	[SB 1] M	W ₁ gm	W ₂ gm	W gm	Corrosion rate x10 ⁻³ mmpy	IE%	θ
1	0.1	1.6908	1.6883	0.0025	2.789	88.58	0.8858
2	0.1	1.7969	1.7925	0.0044	2.622	89.09	0.8909
3	0.1	1.7832	1.7784	0.0048	1.785	92.67	0.9267
4	0.1	1.8042	1.7987	0.0055	1.534	93.56	0.9356
5	0.1	1.6237	1.6237	0.0064	1.428	94.04	0.9404

Time duration (hours)	[SB 2] M	W ₁ gm	W ₂ gm	W gm	Corrosion rate x10 ⁻³ mmpy	IE%	ϑ
1	0.01	1.7788	1.7765	0.0023	2.566	89.00	0.8858
2	0.01	1.7598	1.7566	0.0032	1.785	92.27	0.9227
3	0.01	2.0229	2.0190	0.0039	1.450	93.39	0.9339
4	0.01	1.6535	1.6490	0.0045	1.255	94.84	0.9484
5	0.01	1.5881	1.5829	0.0052	1.160	95.31	0.9531

Time duration (hours)	[SB 3] M	W ₁ gm	W ₂ gm	W gm	Corrosion rate x10 ⁻³ mmpy	IE%	ϑ
1	0.01	2.0016	2.0001	0.0018	1.673	92.26	0.9226
2	0.01	1.7633	1.7621	0.0021	1.450	92.27	0.9227
3	0.01	1.7647	1.7615	0.0032	1.339	95.25	0.9525
4	0.01	1.6984	1.6948	0.0037	1.282	95.70	0.9570
5	0.01	1.7142	1.7096	0.0046	1.205	95.74	0.9574

Time duration (hours)	[SB 4] M	W ₁ gm	W ₂ gm	W gm	Corrosion rate x10 ⁻³ mmpy	IE%	ϑ
1	0.01	1.8155	1.8130	0.0025	2.787	87.30	0.8730
2	0.01	1.8592	1.8554	0.0038	2.120	90.45	0.9045
3	0.01	1.7942	1.7900	0.0042	1.562	93.53	0.9353
4	0.01	1.6398	1.6350	0.0048	1.339	94.42	0.9442
5	0.01	1.7448	1.7392	0.0056	1.249	94.89	0.9489

Table 5: Corrosion rate of Mild Steel in H₂SO₄ (3M) with SB1, SB2, SB3 and SB4 as a function of variation of inhibitor concentration

Time duration (hours)	[SB1], M	W ₁ gm	W ₂ gm	W gm	Corrosion rate x10 ⁻³ mmpy	IE%	ϑ
3	0.01	1.8013	1.7967	0.0046	1.711	83.49	0.8349
3	0.015	1.4609	1.4568	0.0041	1.525	87.50	0.8750
3	0.02	1.6795	1.6757	0.0038	1.413	91.61	0.9161
3	0.025	1.8514	1.8480	0.0034	1.264	94.97	0.9497
3	0.03	1.9592	1.9563	0.0029	1.078	95.86	0.9586

Time duration (hours)	[SB 2] M	W ₁ gm	W ₂ gm	W gm	Corrosion rate x10 ⁻³ mmpy	IE%	ϑ
3	0.01	1.7150	1.7067	0.0083	3.087	86.30	0.8630
3	0.015	1.6664	1.6586	0.0078	2.901	86.81	0.8681
3	0.02	2.1005	2.0933	0.0072	2.678	88.79	0.8879
3	0.025	1.4446	1.4379	0.0067	2.492	89.69	0.8969
3	0.03	1.9190	1.9129	0.0061	2.269	90.63	0.9063

Time duration (hours)	[SB 3] M	W ₁ gm	W ₂ gm	W gm	Corrosion rate $\times 10^{-3}$ mmpy	IE%	θ
3	0.01	1.9000	1.8956	0.0044	1.636	84.46	0.8446
3	0.015	1.9307	1.9260	0.0039	1.450	88.33	0.8833
3	0.02	1.6613	1.6581	0.0032	1.190	93.41	0.9341
3	0.025	1.5646	1.5695	0.0031	1.153	95.39	0.9539
3	0.03	1.4319	1.4289	0.0030	1.115	96.25	0.9625

Time duration (hours)	[SB 4] M	W ₁ gm	W ₂ gm	W gm	Corrosion rate $\times 10^{-3}$ mmpy	IE%	θ
3	0.01	1.7047	1.6960	0.0087	3.236	68.93	0.6893
3	0.015	1.7003	1.6945	0.0058	2.157	82.5	0.825
3	0.02	1.7780	1.7734	0.0046	1.711	89.82	0.8982
3	0.025	1.8190	1.8151	0.0039	1.450	94.14	0.9414
3	0.03	1.7065	1.7033	0.0032	1.190	95.45	0.9545

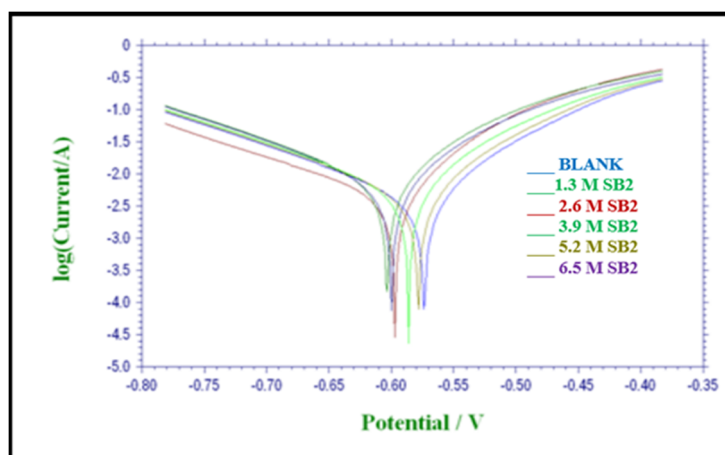


Fig 8: Potentiodynamic polarization behavior of mild steel in (1M) H₂SO₄ with SB-2

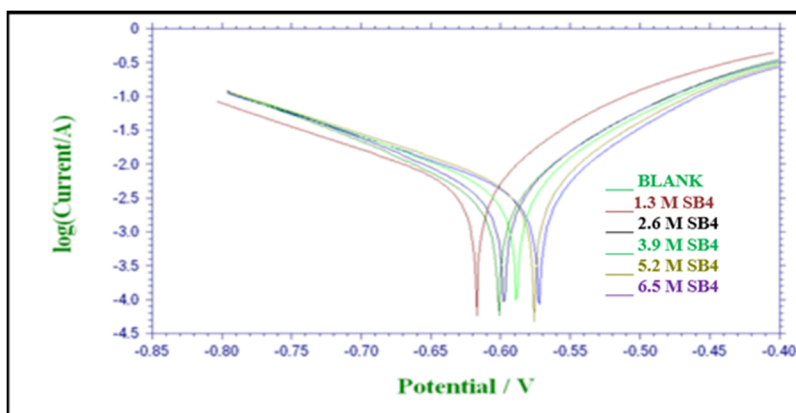


Fig 9: Potentiodynamic polarization behavior of mild steel in (1M) H₂SO₄ with SB-4

3.4 Tafel Polarisation Studies

The potentiodynamic polarization studies of the corrosion of mild steel in sulfuric acid medium in the absence and in the presence of inhibitors were carried out. The **Figure 8 & 9** Shows the anodic and cathodic polarization behavior in the absence of and in the presence of inhibitors (**SB2 & SB4**) of various concentrations Electrochemical parameters such as corrosion potential (E_{corr}), anodic Tafel slope (β_a), cathodic Tafel slope (β_c), corrosion current density (I_{corr}) and percentage inhibition efficiency (IE%) are given in **Table 6**. It is observed that the corrosion rate is decreased and inhibition efficiency IE (%) increases with increase in inhibitor Concentration. The same trend is observed in all the remaining

inhibitors. This result suggests that the addition of the preparation of the prepared inhibitors reduces anodic dissolution and also cathodic reaction, i.e. Retards the hydrogen evolution reaction^[8].

These inhibitors cause change in the anodic and cathodic Tafel slopes and no definite trend was observed in the shift of E_{corr} values in the presence of different concentrations of the added inhibitors, suggesting that these substrates. Behave as mixed type (anodic/cathodic) inhibitors^[9-11] Increase in inhibition efficiencies with the increase of concentrations of Schiff bases shows that the inhibition actions are due to its adsorption on mild steel surface^[12].

Table 6: The polarization parameters for mild steel in H_2SO_4 (1M) in the presence of **SB1, SB2, SB3** and **SB4**.

[SB 1] X10 ⁻⁴ , M	Corrosion potential E_{corr} mV/sec	Corrosion current density I_{corr} $\mu\text{A}/\text{cm}^2$	Anodic Tafel slope β_a mV/dec	Cathodic Tafel slope β_c mV /dec	IE (%)
Blank	-0.596	1.905	12.657	9.493	—
1.3	-0.615	1.019	8.929	7.121	98.59
2.6	-0.609	7.332	9.130	7.542	89.88
3.9	-0.604	5.556	9.499	7.961	92.33
5.2	-0.588	5.535	9.740	7.245	92.36
6.5	-0.582	2.986	11.038	7.971	95.88

[SB 2] X10 ⁻⁴ , M	Corrosion potential E_{corr} mV/sec	Corrosion current density I_{corr} $\mu\text{A}/\text{cm}^2$	Anodic Tafel slope β_a mV/dec	Cathodic Tafel slope β_c mV /dec	IE (%)
Blank	-0.597	6.366	10.085	6.326	—
1.3	-0.603	9.877	8.771	7.134	86.38
2.6	-0.600	8.553	8.905	7.250	88.20
3.9	-0.568	7.361	9.095	7.007	89.84
5.2	-0.578	5.913	9.699	7.155	91.84
6.5	-0.574	4.998	10.054	7.235	93.10

[SB 3] X10 ⁻⁴ , M	Corrosion potential E_{corr} mV/sec	Corrosion current density I_{corr} $\mu\text{A}/\text{cm}^2$	Anodic Tafel slope β_a mV/dec	Cathodic Tafel slope β_c mV /dec	IE (%)
Blank	-0.560	5.337	12.904	7.392	---
1.3	-0.576	9.426	9.536	7.524	86.99
2.6	-0.573	8.061	9.801	7.812	88.88

3.9	-0.559	8.022	9.798	7.024	88.93
5.2	-0.557	5.201	10.891	7.648	92.82
6.5	-0.556	3.590	11.541	8.253	95.04

[SB 4] X10 ⁻⁴ , M	Corrosion potential E _{corr} mV/sec	Corrosion current density I _{corr} μA/cm ²	Anodic Tafel slope β _a mV/dec	Cathodic Tafel slope β _c mV/dec	IE (%)
Blank	-0.597	7.25	10.783	5.802	-
1.3	-0.606	2.75	8.929	6.913	93.02
2.6	-0.601	2.86	9.311	7.097	93.03
3.9	-0.596	8.779	9.556	7.303	93.12
5.2	-0.592	7.116	10.244	7.549	93.46
6.5	-0.590	5.563	10.635	7.842	93.50

3.5 Electrochemical Impedance Spectroscopy Studies (EIS)

The corrosion of mild steel in H₂SO₄ medium was investigated by electrochemical impedance spectroscopy method. The Nyquist plots in uninhibited and inhibited acidic solutions containing different concentrations of Schiff bases are shown in Figure 11 & 12. The analysis of the impedance spectra containing a single capacitive semicircle, the standard Randles circuit is used.¹⁴ where the circuit is composed of a solution resistance component (R_s), a polarization resistance component (R_p) and a capacitance component (C_{dl}). These values are given in **Table 7**. The results show that the R_p values are increasing with increasing concentrations of

inhibitors. Since R_p is inversely proportional to the corrosion current it can be used to calculate the corrosion efficiency (IE %) from the relation.

$$IE (\%) = \frac{R_p - R_p^0}{R_p} \times 100$$

Where,

R_p and R_p⁰ are the polarization resistance in the presence and absence of inhibitors respectively. The trend in the values of C_{dl} in the adsorption of the inhibitor on the metal surface which leads to the formation of surface film in the acidic medium.¹⁵ the impedance study also gave the same efficiency trend as given in Tafel polarization study

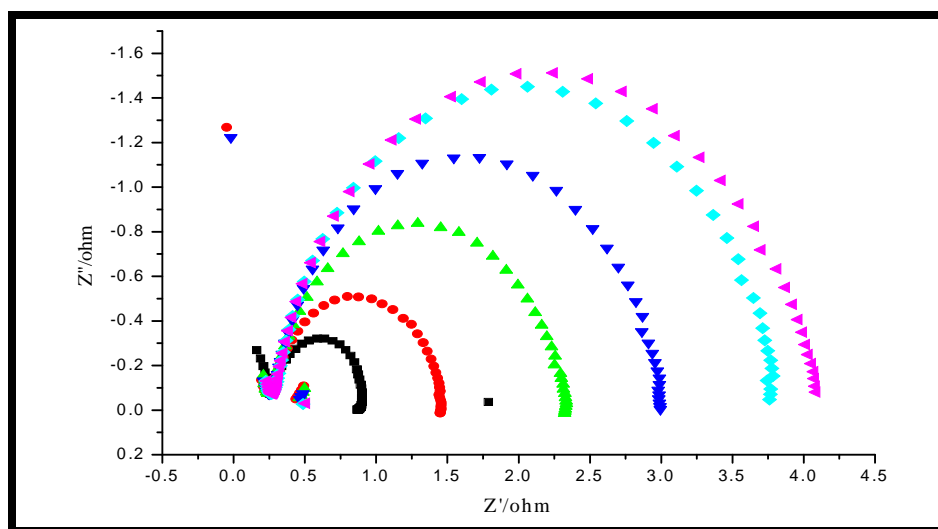


Fig 10: Nyquist plot for the behavior of mild steel in (1M) H₂SO₄ with concentration of SB1. a) Blank b) 1.3x 10⁻⁴ M c) 2.6x10⁻⁴ M. d) 3.9x10⁻⁴ M e) 5.2x10⁻⁴ M. f) 6.6x10⁻⁴ M.

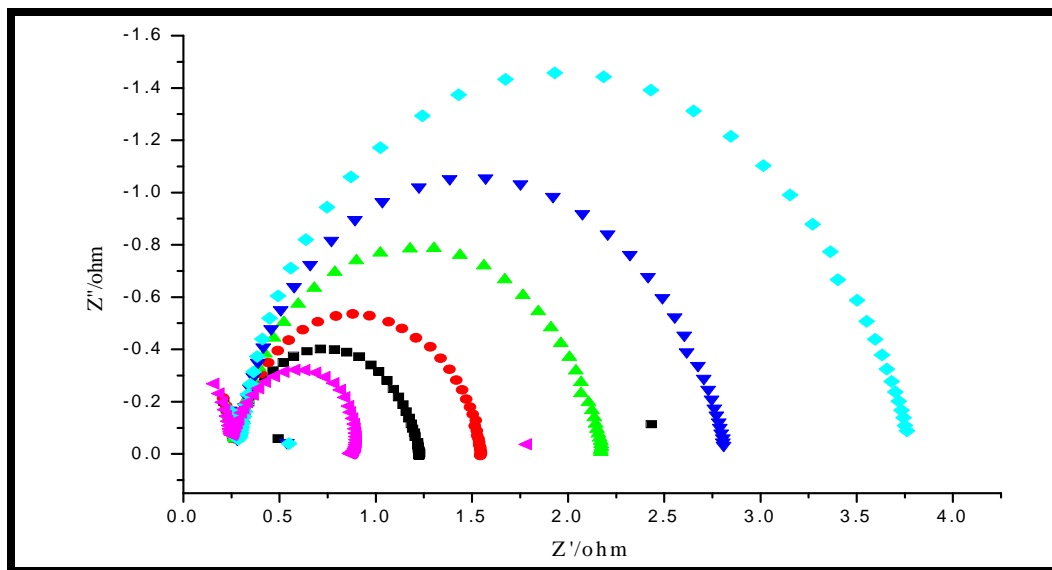


Fig 11: Nyquist plot for the behavior of mild steel in (1M) H_2SO_4 with concentration of SB 3. a) Blank b) $1.3 \times 10^{-4} M$ c) $2.6 \times 10^{-4} M$. d) $3.9 \times 10^{-4} M$ e) $5.2 \times 10^{-4} M$. f) $6.6 \times 10^{-4} M$.

Table 7: ESI parameter of mild steel in H_2SO_4 (1M) with SB1, SB2, SB3 and SB4

[SB 1] $\times 10^{-4}$, M	R_{ct} (Ωcm^2)	C_{dl} ($\mu F cm^2$)	IE(%)
Blank	0.8932	1.1973	---
1.3	1.214	0.2725	26.42
2.6	1.544	0.2666	42.52
3.9	2.180	0.3080	59.02
5.2	2.810	0.3696	68.21
6.5	3.578	1.0856	76.23

[SB 2] $\times 10^{-4}$, M	R_{ct} (Ωcm^2)	C_{dl} ($\mu F cm^2$)	IE(%)
Blank	0.8932	1.1973	---
1.3	1.214	0.2725	20.71
2.6	1.544	0.2666	50.45
3.9	2.180	0.3080	61.41
5.2	2.810	0.3696	69.57
6.5	3.578	1.0856	71.78

[SB 3] $\times 10^{-4}$, M	R_{ct} (Ωcm^2)	C_{dl} ($\mu F cm^2$)	IE(%)
Blank	0.8932	1.1973	---
1.3	1.214	0.2725	23.65
2.6	1.544	0.2666	45.9
3.9	2.180	0.3080	57.49
5.2	2.810	0.3696	67.52
6.5	3.578	1.0856	75.03

[SB 4] X10 ⁻⁴ , M	Rct (Ωcm^2)	Cdl (μFcm^2)	IE(%)
Blank	0.8932	1.1973	---
1.3	1.214	0.2725	22.67
2.6	1.544	0.2666	19.69
3.9	2.180	0.3080	12.29
5.2	2.810	0.3696	7.12
6.5	3.578	1.0856	17.89

3.6 Langmuir adsorption isotherm:

Study of adsorption isotherm

The interaction of the inhibitor with the mild steel surface can be examined by the adsorption isotherm. The degree of surface coverage (θ) values for various concentrations of the inhibitors in the solution has been evaluated from the polarization measurements

(Table 5). The linear relationships of $\text{Log } \theta/1-\theta$ versus $\text{Log } C$ and of $\text{Log } \theta/1-\theta$ versus $\text{Log } t$ for **SB2** as given in **Figure 12 & 13**. For all the inhibitors suggest that adsorption on the mild steel obeyed the Langmuir adsorption isotherm [16]. Langmuir adsorption isotherms infer that the adsorption of organic molecules on the adsorbent is a monolayer.

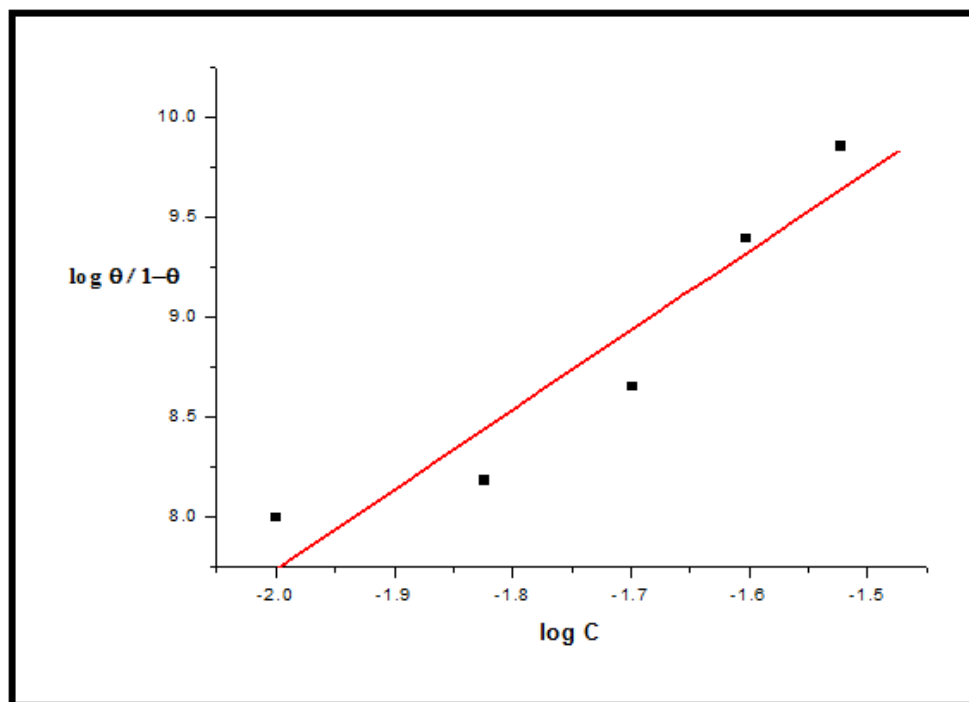


Fig 12: Langmuir adsorption isotherm of mild steel in H_2SO_4 (3M) with **SB 2**

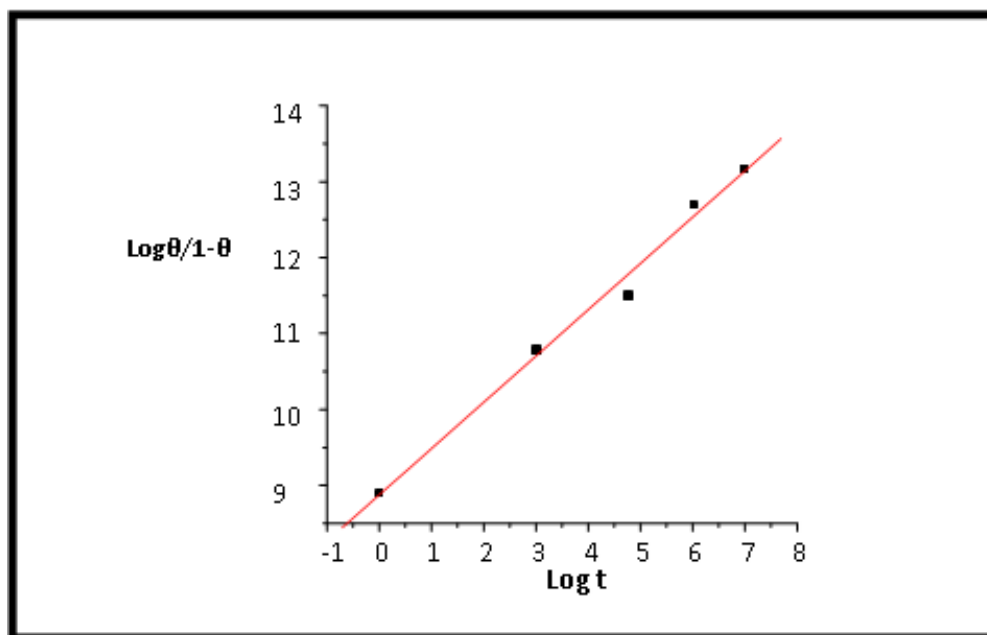


Fig 13: Langmuir adsorption isotherm of mild steel in H_2SO_4 (3M) with SB 2

4. Conclusion

All the Schiff Bases are used as the inhibitors in the corrosion of mild steel in H_2SO_4 medium. In the UV-visible spectral studies the wavelength of absorption of all the Schiff bases are reported and the values are in accordance with the structure and polarity of the solvents. When there is more conjugation, there is red shift in λ_{max} values. Likewise with an increase in the polarity of the medium there is red shift in the wavelength absorption values. IR spectral data gave the exact matching frequencies of the groups which are in accordance with the literature values. These values support the exact structures of the Schiff bases. Weight loss measurements show that the inhibitors reduce the corrosion rate and with increasing of concentration of inhibitors the inhibition efficiency increases. The Tafel polarization studies conclude that the inhibitors behave as mixed type (anodic/cathodic) inhibitors and inhibition efficiency (IE %) increases with increase in concentration of inhibitors. Electrochemical impedance spectroscopy (EIS) studies also prove the same mechanisms. The adsorption of Schiff bases on mild steel in H_2SO_4 medium obeys Langmuir adsorption isotherm.

5. Acknowledgement

The author thanks to the Management, Principal and Head of the Department of Chemistry, Tiruvedakam West for research facilities.

6. References

1. Cimerman Z, Miljanic S, Galic N. Schiff bases derived from aminopyridines as spectrofluorimetric analytical reagents. *Croatica Chemica Acta* 2000; 73: 81-95
2. Singh P, Goel RL, Singh BP. Synthesis characterization and biological activity of Schiff bases. *J. Indian Chem. Soc* 1975; 52:958-959
3. Perry BF, Beezer AE, Miles RJ, Smith BW, Miller J, Nascimento MG. Evaluation of microcalorimetry as a drug bioactivity screening procedure: application to a series of novel Schiff base compounds. *Microbois* 1988; 45:181-191
4. Elmali A, Kabak M, Elerman Y. Keto-enol tautomerism, conformations and structure of N-(2-hydroxy-5-methylphenyl), 2-hydroxybenzaldehydeimine. *J Mol Struct* 2000; 477:151-158.
5. Patel PR, Thaker BT, Zele S. Preparation and characterization of some lanthanide complexes involving a hetero β -diketone. *Indian J Chem* 1999; 38A:563-567.
6. Valcarcel M, Laque de Castro MD. *Flow-Through Biochemical Sensors*, Elsevier 1994; Amsterdam.

7. Spichiger-Keller U. *Chemical Sensors and Biosensors for Medical and Biological Applications*, Wiley-VCH 1998; Weinheim
8. Lawrence JF, Frei RW. *Chemical Derivatization in Chromatography*, Elsevier, 1976; Amsterdam.
9. Patai S. *The Chemistry of the Carbon-Nitrogen Double Bond*. J Wiley & Sons, London, 1970.
10. Jungreis E, Thabet S. *Analytical Applications of Schiff bases*. Marcell Dekker, New York, 1969.
11. Metzler CM, Cahill A, Metzler DE. Equilibria and absorption spectra of Schiff bases. *J Am Chem Soc* 1980; 102:6075-6082.
12. Dudek GO, Dudek EP. Spectroscopic study of keto-enol tautomerization in phenol derivatives. *Chem Commun* 1965; 464-466.
13. Dudek GO, Dudek, EP. Spectroscopic Studies of Keto-Enol Equilibria. IX. N¹⁵-Substituted Anilides. *J Am Chem Soc* 1966; 88:2407-2412.
14. Cimerman Z, Stefanac Z. Cyclic and open-chain tautomerism and complex formation behaviour of the condensation product of 2-amino-3-aminomethyl-4-methoxymethyl-6-methylpyridine with salicylaldehyde. *Polyhedron* 1985; 4:1755-1760.
15. Galic N, Cimerman Z, Tomisic V. Tautomeric and protonation equilibria of Schiff bases of salicylaldehyde with aminopyridines. *Anal. Chim. Acta* 1997; 343:135-143.
16. Pfeiffer P, Breith E, Lübke E, Tsumaki T. Tricyclische orthokondensierte Nebenvaleenzringe. *Justus Liebigs Ann. Chem* 1933; 503:84-130.
17. Sacconi L, Ciampolini M, Maggio F, Cavasini FP. *Studies in Coordination Chemistry IX. Investigation of the Stereochemistry of Some Complex Compounds of Cobalt(II) with N-Substituted Salicylaldimines*. *J Am Chem Soc* 1962; 84:3246-3248.
18. Holm RH, Swaminathan K. *Studies on Nickel(II) Complexes III. Bis-(N-arylsalicylaldimine) Complexes*. *Inorg Chem* 1962; 1:599-607.
19. Hodnett EM, Dunn WJ. Structure-antitumor activity correlation of some Schiff bases. *J Med Chem* 1970; 13:768-770.
20. Hodnett EM, Mooney PD. Antitumor activities of some Schiff bases. *J Med Chem* 1970; 13:786.
21. Palet PR, Thaker BT, Zele S. Preparation and characterization of some lanthanide complexes involving a heterocyclic β -diketone. *Indian J Chem A* 1999; 38:563-567.
22. Lau KY, Mayr A, Cheung KK. Synthesis of transition metal isocyanide complexes containing hydrogen bonding sites in peripheral locations. *Inorg Chim Acta* 1999; 285:223-232.
23. Shawali AS, Harb NMS, Badahdah KO. A study of tautomerism in diazonium coupling products of 4-hydroxycoumarin. *J Heterocyclic Chem* 1985; 22:1397-1403.
24. Abbaspour A, Esmaeilbeig AR, Jarrahpour AA, Khajeh B, Kia R. Aluminium(III)-selective electrode based on a newly synthesized tetradentate Schiff base. *Talanta* 2002; 58:397.
25. Mahajan RK, Kaur I, Kumar M. Silver ion-selective electrodes employing Schiff base p-tertbutylcalix[4]arene derivatives as neutral carrier. *Sensors and Actuators B: Chemical* 2003; 91:26.
26. Ganjali MR, Norouzi P, Alizadeh T, Salavati-Niasari M. Synthesis of a New Hexadentate Schiff's Base and Its Application in the Fabrication of a Highly Selective Mercury(II) Sensor. *Bull. Korean Chem. Soc* 2007; 28:68-72.
27. Jain AK, Gupta VK, Ganeshpure PA, Raisonni JR. Ni (II)-selective ion sensors of salen type schiff base chelates. *Anal Chim Acta* 2005; 553:177-184.
28. Jeong T, Lee HK, Jeong DC, Jeon S. A lead (II)-selective PVC membrane based on a schiff base complex of N,N'-bis(salicylidene)-2,6-pyridinediamine. *Talanta* 2005; 65:543-548.
29. Gupta VK, Singh AK, Mehtab S, Gupta B. A cobalt (II)-selective PVC membrane based on a Schiff base complex of N, N'-bis(salicylidene)-3, 4-diaminotoluene. *Anal Chem Acta* 2006; 566:5-10.
30. Hernandez MM, McKee ML, Keizer TS, Yeaswood BC, Atwood DA. Six-coordinate aluminum cations: characterization, catalysis,

- and theory. *J Chem Soc Dalton Trans* 2002; 410-414.
31. Olie GH, Olive S. *The Chemistry of the Catalyzes hydrogenation of Carbon Monoxide*. Berlin, Springer 1984, 152.
32. Li S, Chen S, Ma H, Yu R, Liu D. Investigation on some Schiff bases as HCl corrosion inhibitors for copper. *Corros Sci* 1999; 41:1273–1287.
33. Ashassi-Sorkhabi H, Shaabani B, Seifzadeh D. Corrosion inhibition of mild steel by some Schiff base compounds in hydrochloric acid. *Appl Surf Sci* 2005; 239:154-164.
34. Da-Quan Z, Cai He XM, Gao LX, Kim GS. The corrosion inhibition of copper in hydrochloric acid solutions by a tripeptide compound. *Corros Sci* 2009; 51:2349–2354.
35. Williams DR. Metals, ligands and cancer. *Chem. Rev* 1972; 72:203.
36. Campos A, Anacona JR, Campos-Vallette MM. Mian group Metal chem 1999; 22:283.
37. Sari N, Arslan S, Logoglu E, Sakiyan I. Antibacterial activities of some aminoacid Schiff bases. *G U J Sci* 2003; 16:283.
38. Verma M, Pandeya SN, Singh KN, Stables JP. Anticonvulsant activity of Schiff bases of Isatin derivatives. *Acta Pharmaceutica* 2004; 54:49–56.
39. Cozzi PG. Metal–Salen Schiff base complexes in catalysis: practical aspects. *Chem Soc Rev* 2004; 33:410-42.
40. Chandra S, Sangeetika J. EPR electronic spectral studies on copper (II) complexes of some N-O donor ligands. *J Indian Chem Soc* 2004; 81:203-206.
41. Mahindra AM, Fisher JM, Rabinovitz. *Textbook of practical organic chemistry*. Nature 1983; 303:64.
42. Pandeya SN, Yogeewari P, Sriram D, De-Clercq E, Pannecouque C, Witvrouw M. Synthesis and screening for anti-HIV activity of some *N*-Mannich bases of isatin derivatives. *Chemotherapy* 1999; 45:192–6.
43. Sawodny WJ, Riederer M. Addition Compounds with Polymeric Chromium (II)-Schiff Base Complexes. *Angew Chem Int Edn Engi* 1977; 16:859–860.
44. Singh AK, Quraishi MA. Study of Some Bidentate Schiff Bases of Isatin as Corrosion Inhibitors for Mild Steel in Hydrochloric Acid Solution. *Int J Electrochem Sci* 2012; 7:3222 – 3241.
45. Ghasemi O, Ghanbariadiivi H, Ghasemi V. Inhibition Effect of Benzaldehyde Schiff Bases on Mild Steel Corrosion in Hydrochloric Acid: Electrochemical and Surface Analyses *Journal of Dispersion Science and Technology*, 2014.
46. Al-Amiery AA, Kadhum HAA, Alobaidy AHM, Mohamed AB, Hoon PS. Novel Corrosion Inhibitor for Mild Steel in HCl. *Material* 2014; 7:662-672.