

A Schiff base compound as effective corrosion inhibitor for Carbon steel AISI 1018 in NaCl, 3.5% media

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Abstract: In this study, the inhibitory effect of a Schiff base compound (Salcn) on carbon steel corrosion in NaCl 3.5% solution was studied. For this aim, electrochemical techniques such as potentiodynamic polarization, weight loss (WL), electrochemical impedance spectroscopy (EIS) and linear polarization resistance (LPR) tests were used. It was shown that, the Salcn Schiff base has a remarkable inhibition efficiency effect on the corrosion of mild steel in in3. 5% NaCl solution.

[M. Abdullahi, M. Farzam, A. Irannejad. **A Schiff base compound as effective corrosion inhibitor for Carbon steel AISI 1018 in NaCl, 3.5% media.** *Researcher* 2014;6(10):71-77]. (ISSN: 1553-9865). <http://www.sciencepub.net/researcher>. 11

Key words: Schiff base compound, Polarization, EIS, Corrosion; Inhibitor; Carbon steel

1. Introduction

Carbon steel is widely used as a constructional material in many industries due to its excellent mechanical properties and low cost, carbon steel has a wide application in various industries as construction material for chemical reactors, heat exchange and boiler systems, storage tanks, and oil and gas transport pipelines. Protection of the equipments and vessels against corrosion is one of chief concern of the maintenance and design engineers. The use of corrosion inhibitors, whenever possible, is one of the most effective methods for this concern [1].

The materials used as corrosion inhibitors are chemicals, organic or inorganic, which when added in small quantities to the corrosive environment, reduce the deterioration of metals. The mechanism of this protection depends on the metal and inhibitor under consideration. In most cases, however, it is due to the absorption of these compounds on the surface of metals which can reduce the extent of corrosion through thermodynamics or kinetics phenomena [2].

The use of inhibitor is one of the best known methods of corrosion protection. The efficiency of inhibitor depends on the nature of the environment, nature of metal surface and electrochemical potential at the interface, and the structural feature of inhibitor, which includes a number of adsorption centers in the molecule, their charge density, the molecular size, and mode of adsorption, formation of metallic complexes and the projected area of inhibitor on the metal surface [3–5]. Organic compounds containing hetero-atoms such as N, O and S have been reported efficient corrosion inhibitors for metals and alloys [6–10].

Nowadays, the study of Schiff's base inhibitors is a hot topic [11, 12].

Due to the presence of the $-C=N$ group in the Schiff base molecules, they are likely to be good corrosion inhibitors [13]. The electron-rich structure serves as potential adsorption sites, due to their capability to share free electrons with the metal substrate surface [14].

The aim of this study is to investigate the corrosion inhibition effect of a salicylic Schiff base compound on carbon steel brine solution using two different electrochemical methods.

2. Experimental details

2.1. Materials

2.1.1 Schiff base

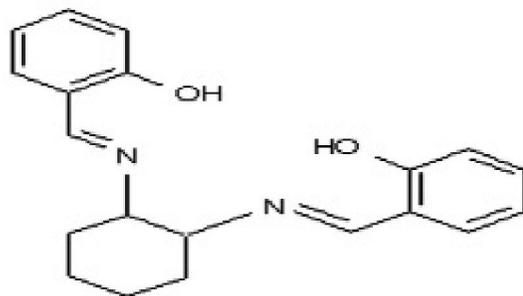


Fig. 1. Chemical structure of the used Schiff base compound

The chemical structure of the used Schiff base compound (Salcn) is shown in Fig.1. Salcn was synthesized by a condensation reaction. First, 50 ml ethanol solution containing 0.004 mole of salicylaldehyde was gradually added to 10 ml ethanol solution containing 0.002 mole of 1, 2 cyclohexandiamin under continuous stirring. Precipitation of Salcn as brilliant yellow flakes in the solution started almost immediately. This mixture

was then stirred for 1 h in order to promote the rate of chemical reaction. Next the solid was filtered and washed with cold ethanol [15]. Finally, the Schiff base ligand was recrystallized in ethanol and dried at room temperature. All chemicals were purchased from Merck.

The observed disappearance of the characteristic

peaks for =C -H and O-H groups at 3009 cm^{-1} and 3398 cm^{-1} , respectively, in the IR spectra of the initial compounds along with the appearance of a new peak at 1614 cm^{-1} , in the FTIR spectrum (Fig. 2), of the Schiff's base, which is the characteristic of the C=N- group, confirmed the formation of the Schiff's base.

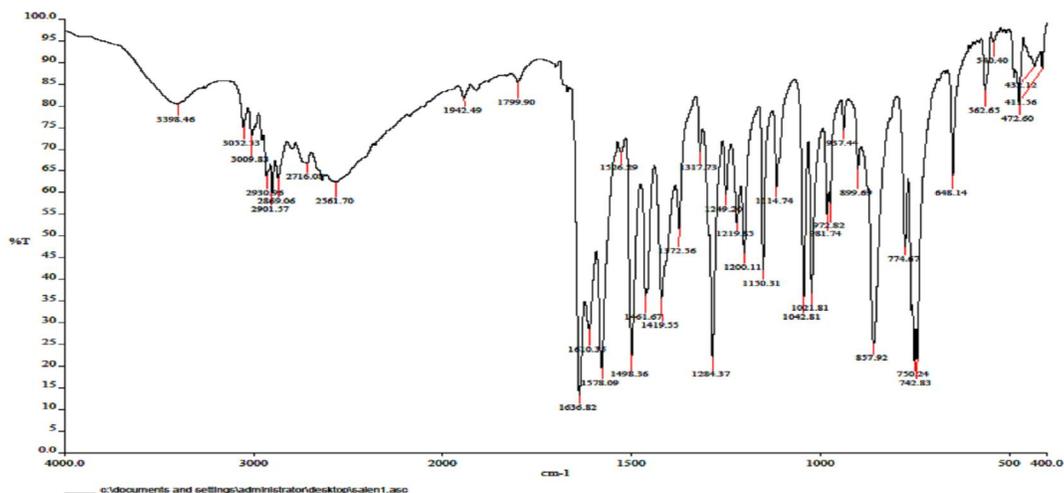


Fig. 2. FTIR spectrum of the unsymmetrical Schiff's base

2.1.2. Preparation of electrodes

Corrosion tests were performed on a mild steel of the following percentage composition: Fe 98.9 %, C 0.16 %, Si 0.11 %, Mn 0.69 %, P 0.009 %, Cr 0.04 %, Ni 0.01 %, Al 0.051 %, and Cu 0.02 %. Prior to all measurements, the mild steel specimens were abraded successively with emery papers from 600 to 2400 grades. The specimens were washed thoroughly with double-distilled water, degreased with acetone, and finally dried in a hot air blower. After drying, the specimens were placed in a desiccator and then used for the experiment. The mild steel embedded in epoxy resin with exposed area of 1 cm^2 was used as working electrode.

2.2. Methods

2.2.1. Weight loss measurements

Weight loss measurements were carried out according to the American Society for Testing and Materials (ASTM) standard procedure [16]. The weight loss measurements were carried out in a glass vessel containing 100 ml of NaCl, 3.5% with and without addition of different concentrations of different inhibitors at temperature 25°C for 72 h immersion time. The specimens were withdrawn, rinsed with doubly distilled water, washed with acetone, dried and weighed. The experiments were done in triplicate and the average value of the weight loss was noted.

2.2.2. Electrochemical methods

A three-electrode cell, consisting of the carbon steel sample as a working electrode, a platinum sheet as counter electrode (CE), and a saturated Ag/AgCl electrode as reference electrode, was used for EIS and polarization measurements. Electrochemical tests were carried out using an autolab3 potentiostat galvanostat. Nova (version 1.8) software was used for data recording.

(%IE), of PMSI was calculated from the following equation [17]:

$$\text{IE (\%)} = (1 - (i'_{\text{cor}}/i_{\text{cor}})) \times 100 \quad (1)$$

Where i_{cor} and i'_{cor} are corrosion current densities measured in the absence and presence of the inhibitor, respectively. Impedance measurements were carried out at open circuit potential. After immersion of the specimen in the test solution, prior to each measurement, a stabilization period of 15 min was observed which proved sufficient to attain a stable value. A sinusoidal potential with an amplitude of 10mV (rms), superimposed on open circuit potential, was applied. The frequency of this AC signal was scanned from 100 kHz to 10 MHz. All EIS measurements were performed at room temperature. The inhibition efficiency of this method was calculated from this equation [17]:

$$IE (\%) = (R_{ct} - R_{ct}^o / R_{ct}) \times 100 \quad (2)$$

Where: R_{ct}^o and R_{ct} are charge transfer resistance in the absence and presence of the inhibitor, respectively. All experiments were performed twice and the mean results were reported.

3. Results and discussion

3.1. Weight loss measurements

The effect of addition of Schiff bases (Salcn) at different concentrations on the corrosion of mild steel in WNaCl, 3.5% solution was studied by weight loss measurements at 25°C. The highest concentration is sometimes limited by the solubility of the compound. If at two consecutive concentrations the inhibitor efficiency showed no further increase, higher concentrations were not tested. The inhibition efficiency (E %) and corrosion rate (C_R , mm year⁻¹) were calculated according to the Eqs. 1 and 2 [18], respectively.

$$(E\%) = \frac{W_0 - W}{W_0} \times 100 \quad (3)$$

Where: W_0 and W are the values of corrosion weight losses of mild steel in uninhibited and inhibited solutions, respectively.

$$(C_R) \left(\frac{mm}{Y} \right) = \frac{57.8W}{ATP} \quad (4)$$

Where W is corrosion weight loss of mild steel (mg), at the area of the mild steel specimen (cm²), T is the exposure time (h) and D the density of mild steel (g cm⁻³). The values of inhibition efficiencies (E %) and corrosion rates (CR) obtained from weight loss measurements for different concentrations of Salcn in NaCl 3.5% are given in Table 1.

Table 1: Corrosion parameters for mild steel in NaCl, 3.5% in the absence and presence of different concentrations of Schiff bases obtained from weight loss measurements.

Inhibitor Concentration (ppm)	ΔW	C_r	θ	%E
Blank	0.0900	13.93	-	-
30	0.0431	6.67	0.521	52.1
50	0.0242	3.74	0.731	73.1
70	0.198	3.06	0.78	78

It is clear that E% increased with increasing inhibitor concentration, reached at a maximum value and further increase in the inhibitor concentration did not cause any significant change in the efficiency. While the corrosion rate decreased with increasing

inhibitor concentration. The corrosion inhibition can be attributed to the adsorption of the Schiff bases at the mild steel/NaCl solution interface [19]. The maximum inhibition efficiency (E %) of 78% was observed for Salcn at 70 ppm concentration (Table 1).

3.2. Potentiodynamic polarization

Fig. 3 represents the potentiodynamic polarization curves of carbon steel in NaCl, 3.5 % in the presence and absence of various concentrations of Salcn Schiff base. As can be seen, both the anodic and cathodic currents decrease after addition of the Schiff base to the corrosive solution. This result suggests that the addition of the Salcn Schiff base reduces anodic dissolution and also retards the hydrogen evolution reaction. The values of corrosion potential (E_{corr}) in the absence and presence of inhibitor of different concentrations are given in Table2.

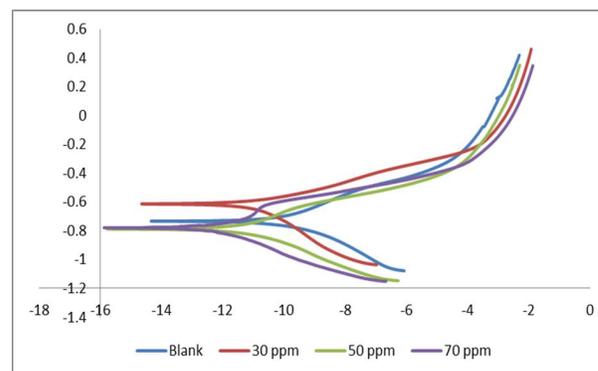


Fig 3. Tafel polarization curves for mild steel in NaCl, 3.5 % in the absence and presence of different concentration of compound salcn

It is clearly seen that the corrosion potential values were shifted to more positive values in the presence of Salcn. Generally, if the displacement in E_{corr} after addition of inhibitor is bigger than 85 mV, the inhibitor can be classified as a cathodic or anodic type; and if the displacement is less than 85 mV, the inhibitor can be considered as a mixed type [20, 21]. In this study the maximum displacement in E_{corr} value was lower than 85 mV towards anodic region, which indicates that the Salcn acts as a mixed type inhibitor. Other electrochemical corrosion parameters such as cathodic and anodic Tafel slopes (B_c and B_a), polarization resistance (R_p) and corrosion current density (j_{corr}) were also obtained from polarization curves (Table 2). The values of anodic and cathodic Tafel slopes were calculated from the linear region of the polarization curves. There were no significant changes in the cathodic and anodic Tafel slopes after the addition of the Schiff base compound. This means that the studied compound cannot change the mechanism of carbon steel dissolution or hydrogen

evolution. It seems that the Salcn acts via adsorption on carbon steel surface and blocking the active corrosion sites [13, 22]. The addition of Schiff base increases the polarization resistance of carbon steel in NaCl, 3.5% and this fact leads to a reduction in corrosion current. These results show that the used compound acts as an effective inhibitor for carbon steel in the studied corrosive media. The inhibition efficiencies (%IE) were calculated from the following equation [23]:

$$\%IE = \left(\frac{R_{inh} - R_{blank}}{R_{inh}} \right) \times 100 \quad (5)$$

Where: R_{blank} and R_{inh} are the polarization resistance of the uninhibited and inhibited solutions, respectively. The values of corrosion inhibition efficiencies of carbon steel in NaCl, 3.5 % are also listed in Table 2. As the inhibitor concentration increases, the inhibition efficiency increases probably because of more inhibitor adsorption on the carbon steel surface. The inhibition efficiencies, increased from 57.85% for the lowest inhibitor concentration to 87.9% for the highest concentration of the inhibitor.

Table 2: Polarization parameters for carbon steel in NaCl, 3.5% in the absence and the presence of the Salcn Schiff base at different concentrations.

Inhibitor Concentration (ppm)	R_p (Ωcm^2)	B_a (mVdec ⁻¹)	B_c (mVdec ⁻¹)	i_{corr} (mAcm ⁻²)	E_{corr} (V vs. sat. Ag/AgCl)	%IE
Blank	668.86	0.28437	0.34393	9.81E-05	-0.68317	-
30	1632.4	0.59701	0.14081	3.03E-05	-0.63987	57.85
50	2639.7	0.23492	0.33101	2.26E-05	-0.77133	73.92
70	5689.1	0.61938	0.731	2.56E-05	-0.82416	87.9

3.3. EIS

Electrochemical impedance spectroscopy (EIS) is an effective instrument for corrosion studies of materials, especially the one that involves corrosion inhibitors. It also provides detailed information for the studied system parameters such as corrosion rates, and electrochemical mechanisms and reaction kinetics [E]. The effect of inhibitor concentration on the impedance behavior of mild steel in NaCl, 3.5 % solutions at 25 °C is shown as in Fig. 4.

Since R_p is inversely proportional to the corrosion current it can be used to calculate the inhibitor efficiency (%IE), from the relation [12]:

$$\%IE = (1 - R_{p,0}/R_{p,i}) \times 100 \quad (6)$$

Where $R_{p,i}$ and $R_{p,0}$ are the polarization resistances in the presence and absence of the organic additives, respectively. It was found that the Nyquist plot for various concentrations of Salcn inhibitor showed a similar trend of curves which depressed semi circle with the center located below the real X-axis. Increasing the inhibitor concentration

will increase the size of the curves, indicating the time constant of the charge transfer and double-layer capacitance [25]. This behavior shows the adsorption of Schiff base on mild steel.

It is clear to observe that the impedance curves is significantly changed with the presence of inhibitors. It was also found that from the Nyquist plot, even with the addition or absence of inhibitor does not alter the style of impedance curves, thus proposing a similar mechanism of inhibition is involved. The impedance parameters derived from these plots are given in Table 3. As noted from Table 3, the polarization resistances values containing inhibitor substantially increased along the concentration compared to without inhibitor

In the studied frequency range, an equivalent structure model (equivalent circuit) was proposed in order to fit and analyze the obtained EIS data (Fig. 5). In this equivalent circuit (Fig. 5), R_s is the solution resistance and R_{ct} is the charge-transfer resistance whose value is a measure of electron transfer across the surface and is inversely proportional to corrosion rate [26] and CPE the constant phase element.

Table 3: Impedance parameter values for the corrosion of mild steel in NaCl 3.5%

Compound	Inhibitor concentration(ppm)	R_s ($\Omega\text{ cm}^2$)	R_p ($\Omega\text{ cm}^2$)	Qdl (μF)	IE%
blank	-	4.77	166.5	502	-
salcn	30	7.888	182.8	305	8.51
	50	4.705	438.6	123	62
	70	5.898	595.9	112	70.6

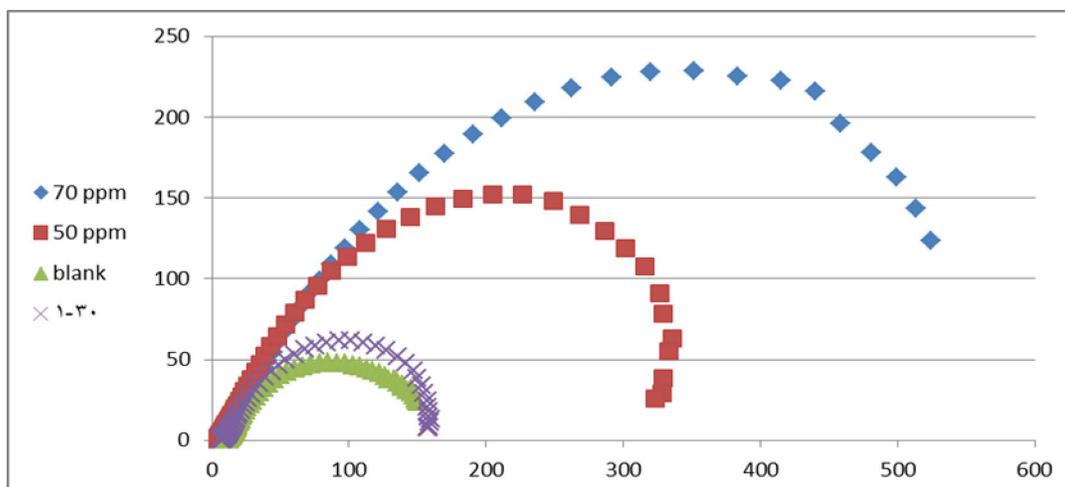


Fig. 4. Nyquist impedance diagram for mild steel in NaCl, 3.5% with inhibitor

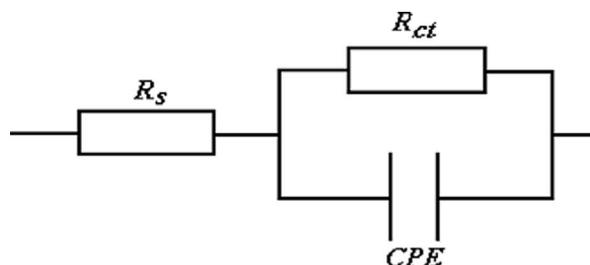


Fig. 5. Equivalent circuit for impedance analysis

The constant phase element, CPE, is introduced in the circuit instead of a pure double layer capacitor (C_{dl}) to give a more accurate fit [27,28]. The CPE element is used to explain the depression of the capacitance semi-circle, which corresponds to surface heterogeneity resulting from surface roughness, impurities, dislocations, grain boundaries, adsorption of inhibitors, formation of porous layers [29–32], etc.

3.4. Adsorption isotherm

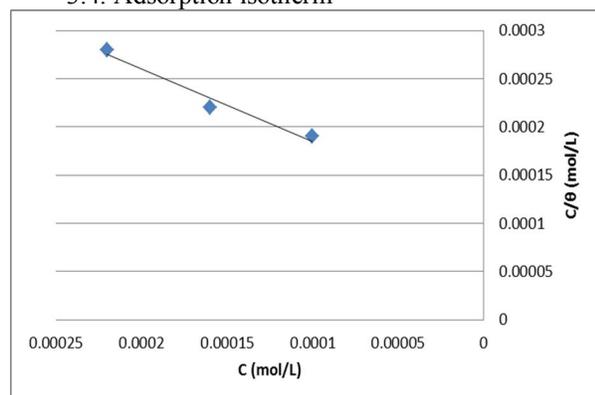


Fig. 6. Experimental results at 298 K according to the Langmuir adsorption isotherm for scaln

The adsorption on the corroding surfaces never reaches the real equilibrium and tends to reach an adsorption steady state. However, when the corrosion

rate is sufficiently small, the adsorbed steady state has a tendency to become a quasi-equilibrium state. In this case, it is reasonable to consider the quasi-equilibrium adsorption in thermodynamic way using the appropriate equilibrium isotherms [33]. The efficiency of Schiff base as a successful corrosion inhibitor mainly depends on its adsorption ability on the metal surface.

So, it is essential to know the mode of adsorption and the adsorption isotherm that can give valuable information on the interaction of inhibitor and metal surface. The surface coverage values, θ ($\theta = IE/100$) for different concentrations of Schiff base were used to explain the best adsorption isotherm. A plot of C/θ versus C (Fig. 6) gives a straight line with an average correlation coefficient of 0.9643 and a slope of nearly unity (1.33) suggests that the adsorption of Scaln Schiff base molecules obeys Langmuir adsorption isotherm, which can be expressed by the following equation:

$$C_{(inh)}/\theta = (1/K_{(ads)}) + C_{(inh)} \tag{7}$$

Where C_{inh} is inhibitor concentration and K_{ads} is the equilibrium constant for the adsorption–desorption process. The value K_{ads} calculated from the reciprocal of the intercept of isotherm line as $1.4662 \times 10^4 M^{-1}$. The high value of the adsorption equilibrium constant reflects the high adsorption ability of this inhibitor on mild steel surface. The standard free energy of adsorption of the inhibitor (ΔG°_{ads}) on mild steel surface can be evaluated with the following equation;

$$\Delta G^{\circ}_{ads} = -RT \ln (55.5K_{ads}) \tag{8}$$

From Eq. (8), the ΔG°_{ads} was calculated as $-33.70 \text{ kJ mol}^{-1}$. The negative value of standard free energy of adsorption indicates spontaneous adsorption of Schiff base molecules on mild steel surface and also the strong interaction between inhibitor molecules and the metal surface [34, 36].

Generally, the standard free energy values of -20 KJ mol^{-1} or less negative are associated with an electrostatic interaction between charged molecules and charged metal surface (physical adsorption); those of -40 KJ mol^{-1} or more negative involves charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate covalent bond (chemical adsorption) [37,38]. The calculated standard free energy of adsorption value is closer to -40 KJ mol^{-1} . Therefore, it can be concluded that the adsorption is more chemical than physical adsorption [35,39].

5. Conclusion

The corrosion inhibition of mild steel in NaCl, 3.5% solution by Salcn was studied using common electrochemical techniques. According to experimental findings, it could be concluded that:

1- Salcn is a good corrosion inhibitor for the mild steel protection in NaCl 3.5% solution. The inhibitory efficiency of this compound depends on its concentration.

2- Salcn acts by reducing the rates of both anodic and cathodic reactions.

3- The high inhibition efficiency of the inhibitor was explained by adsorption of the Salcn molecules on the steel surface and a protective film formation.

4- The surface film was found to be very stable at low anodic and cathodic overpotentials.

5- The adsorption of Salcn on the steel surface from NaCl, 3.5% solution follows Langmuir adsorption isotherm. The thermodynamic parameters suggest that this inhibitor is strongly

Adsorbed on the mild steel surface.

6- The adsorption of the inhibitor on the mild steel surface takes place through electrostatic interactions as well as charge sharing or transfer from the inhibitor molecules to the metal surface in order to form chemical bonds.

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10/15/2014