

Examination a New Synthesized Schiff Base (sn) as Corrsion Inhibitor for Carbone Steel x52 in Hydrochloric Acid

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Abstract: The aim of this work is to investigate the corrosion inhibition of steel X₅₂ in 1MHCl by new synthesized Schiff base containing Sulphur nitrogen as heteroatom namely 4,4'bis [thiophène -3, carboxaldehyde] diphenyle methane d'imine (SN). This examination have been determined in atmospheric condition by potentiodynamic polarization and electrochemical impedance spectroscopy(EIS) techniques. Results obtained of these methods consistently identify this compound as excellent mixed type (cathodic/anodic) inhibitor. That corrosion parameters and adsorption isotherms were determined from current-potential curves, it was found that corrosion rates decrease and percentage inhibition efficiency (η_p %), surface coverage degree (θ_p) and polarisation resistance (R_p) increase with increasing additive concentration. Impedance measurements confirm these results where it was observed, that the effect of inhibitor addition appears by an increase in the charge transfer resistance (R_t) and by a decrease in the capacity of interface (C_{id}). Values of inhibitor with increase in the concentration of schiff base show that inhibitive abilities of inhibitor depend on the adsorption of molecule on metal surface. The adsorption of used compound is correlated with his chemical structure, so it obeys Langmuir's isotherm.

1. Introduction.

Evaluation of corrosion inhibitors for steel in acidic media is important for some industrial facilities as well as very interesting from theoretical aspects [1]. Specific chemical compounds are often used as inhibitors in these processes mainly to control the metal dissolution reaction and thereby increased the service life of steel materials [2]. Most of the effective inhibitors are organic compounds containing nitrogen, phosphorus and sulphur in their structures [1]. Due to the presence of the $-C=N$ group in the Schiff base molecules, they should be good corrosion inhibitors. Some Schiff base compounds have recently been reported as effective corrosion inhibitors for mild steel, aluminum, copper, and zinc in acid media [3].

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The objective of our work is to investigate the inhibition effect of newly prepared Schiff's base molecule (SN) on the corrosion of steel X₅₂ in 1MHCl solution using polarisation and impedance (EIS) measurements.

2. Experimental

The studied Schiff base was synthesized by reacting the mixture of 4,4'-Diaminodiphenylmethane (0.002mol) and thiophene-3carboxaldehyde (0.004mol) in 15ml of ethanol at 60 °C for 5 hours, after that, the separated solid was filtered, washed with heated alcohol, dried, and crystallized from ethanol. Properties of our inhibitor are shown in Table. 1.

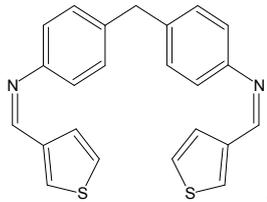
The aggressive solution (1MHCl) was prepared by HCl 37% (E. Merck) and bi-distilled water. The concentration range of used inhibitor was 10^{-4} to 10^{-2} M in 1M of HCl.

The working electrode was prepared from a cylindrical steel (X₅₂), it was mounted in polyester, and so only its cross section (0.5cm^2) was allowed contact the aggressive solution. The contact section of this metal must be mechanically polished using different grades of emery paper, and then washed with double distilled water and at the end degreased

with ethanol [4]. The chemical compositions of steel

X₅₂ are given in Table. 2.

Table. 1 The physical and chemical proprieties of a newly prepared Schiff base SN.

Name and Chemical structure	Formula	Molecular mass (g/mol)	Melting point(°C)	Solvent	Abbreviation
	C ₂₃ H ₁₈ N ₂ S ₂	386.24	129	Ethanol	SN
4,4'bis [thiophène -3, carboxaldehyde] diphenyle méthane d'imine .					

A three-electrode cell, consisting of steel X₅₂ working electrode (WE), a platinum counter electrode (CE), and a saturated calomel electrode (SCE) as a reference electrode, was used for measurements. All experiments were performed in room temperature without stirring.

EIS experiments were performed in the frequency range 80 kHz to 0.08 Hz, at the rest potential, with the signal amplitude perturbation of 5mV.

In the case of polarisation measurements, the potential sweep rate was 2mVs⁻¹, in the potential range from -700 to -250 mV (between -250 and 250 from open circuit potential (E_{OCP})), it was scanned primarily in the cathodic direction from the corrosion potential and subsequently in the anodic direction. For both these methods, the working electrode was first immersed into the test solution for 20 min to establish a steady state E_{OCP}.

All EIS and polarization techniques were conducted on a Voltalab PGZ 301 model potentiostat/galvanostat. Measurements data were analysed using a Pentium IV computer with Volta Master IV and origin 6.0 software's [5].

3. Results and discussion.

3.1 Electrochemical impedance spectroscopy (EIS).

Table. 2.

Chemical composition (Wt %) of steel X₅₂ specimens obtained from quantometric method

C	0.1038	Co	0.5000
Si	0.1261	Cu	0.0100
Mn	0.9710	No	0.0419
P	0.0020	Ti	0.0025
S	0.0021	V	0.0050
Cr	0.0100	W	0.0500
Mo	0.0050	Sn	0.0050
Ni	0.0050	Fe	98.670
Al	0.0320		

In general, the efficiency of an organic substance as an inhibitor for metallic corrosion depend on the structure of the inhibitor, nature of the metal and the other experimental conditions, such as concentration of inhibitor, etc [4]. In order study the effect of these parameters on steel X₅₂ corrosion Electrochemical impedance spectroscopy experiment was carried out.

The double layer capacitance (C_{dl}) and charge transfer resistance (R_t) were calculated from Nyquist plots as described in Figure. 1. The inhibition efficiency (η_Z, %) is calculated using charge transfer resistance as follows [6] :

$$\eta_Z(\%) = \frac{R_{t(inh)} - R_t}{R_{t(inh)}} \times 100 \quad (1).$$

Where R_{t(inh)} and R_t are the charge transfer resistance in inhibited and uninhibited solution, respectively.

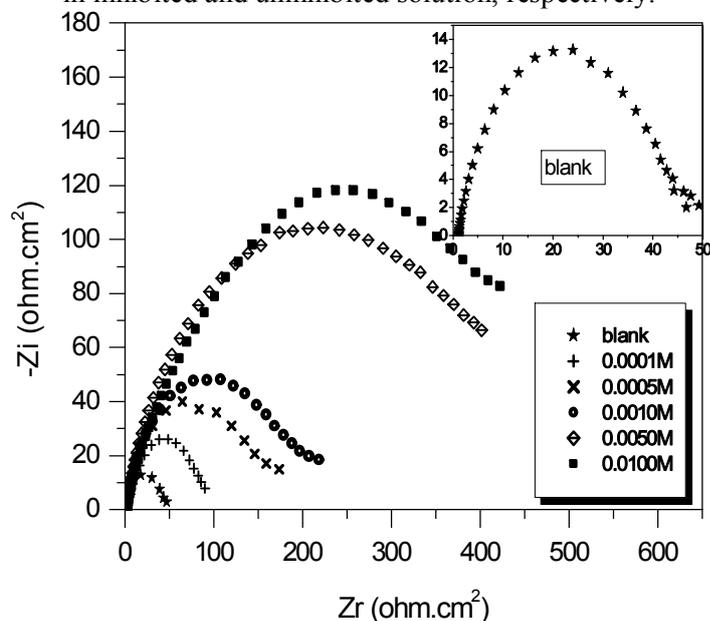


Fig. 1 Impedance plots the steel X₅₂ in 1MHCl with and without of different concentration of inhibitor

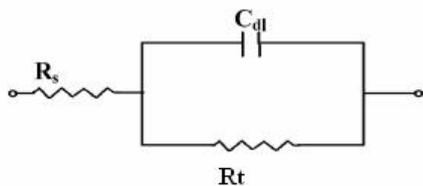


Fig. 2 The equivalent circuit of the impedance spectroscopy.

All the impedance spectra are analyzed in terms of the equivalent Circuits shown in Fig. 2. The Nyquist plots obtained in the real system represent a general behaviour where the double layer on the interface of metal/solution does not behave as a real capacitor. On the metal side electrons control the charge distribution where as on the solution side it is controlled by ions. As ions are much larger than the electrons, the equivalent ions to the charge on the metal will occupy quite a large volume on the solution side of the double layer [7]. From Table 3, it was clear that transfer charge resistance values were increased and the capacitance values decreased with increasing inhibitors' concentration. Decrease in the capacitance, which can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that the inhibitor molecules act by adsorption at the metal/solution interface. This indicated the formation of a surface film on the mild steel [1, 4]

3.2 polarisation behaviour

In order to better define the effect of our compound and concentration on the corrosion process, anodic and cathodic polarisation curves for steel X₅₂ in 1MHCl with and without of various concentrations of SN are shown in figure. 3.

Electrochemical corrosion parameters, Such as corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (β_a and β_c), corrosion current (i_{corr}) were obtained from the polarisation curves by linear extrapolation of the Tafel curves at points 50 mV more positive and more negative than E_{corr} , surface coverage degree (θ_p), polarisation resistance (R_p) and inhibition efficiency η_p (%) are given in Table. 4.

Table. 3. Impedance parameters for steel in 1MHCl containing different concentrations of Schiff base SN

C (mol dm ³)	R _t (Ωcm ²)	C _{dl} (μF)	η _Z %
Non	41.21	516.0	-
1×10 ⁻⁴	89.00	300.6	53.96
5×10 ⁻⁴	130.0	153.5	68.30
1×10 ⁻³	173.8	162.9	76.14
5×10 ⁻³	371.6	135.5	88.91
1×10 ⁻²	506.1	114.4	91.85

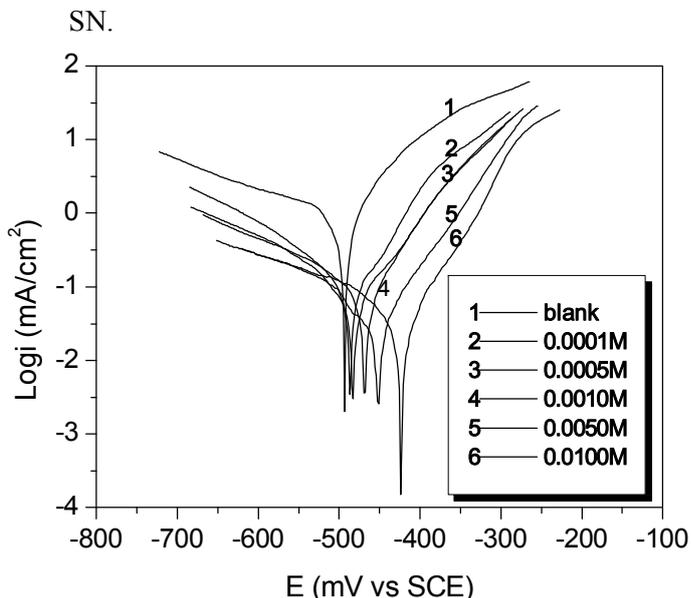


Fig. 3 Anodic and cathodic polarisation curves for steel X₅₂ in 1MHCl in the absence and presence of different concentrations of Schiff base SN.

The percentage inhibition efficiency η_p (%), and the Surface coverage (θ_p), were calculated from the following equations [8]:

$$\eta_p (\%) = \frac{I_0 - I_{corr}}{I_0} \times 100 \quad (2)$$

$$\theta_p = \frac{I_0 - I_{inh}}{I_0} \quad (3)$$

Where I_0 and I_{inh} are the corrosion current densities without and with inhibitor.

As it can be observed from Table.4, the percentage inhibition efficiency and surface coverage degree increase, when the concentration of our additive increase and in addition to this corrosion current density decreases and shift the corrosion potential in the positive direction. The results obtained from the polarization technique are similar to those obtained from the EIS method. It is clear, inhibition efficiency of the examined organic molecule that was obtained from the both methods is not parallel but their trends are the same.

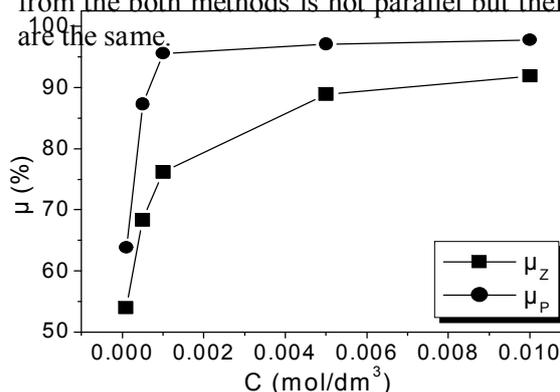


Fig. 4 Variation of inhibition efficiencies with different concentrations of Schiff base SN.

Table. 2 Electrochemical polarization parameters for steel in 1MHCl containing different concentrations of Schiff base SN.

C (mol dm ³)	-E _{cor} (mV)	-B _c (mV)	B _a (mV)	R _p (Ωcm ²)	I _{inh,corr} (mA/cm ²)	η _p %	θ _p
Non	493.0	91.70	53.7	23.81	0.4985	-	-
1×10 ⁻⁴	469.6	153.7	50.8	87.02	0.1802	63.85	0.6385
5×10 ⁻⁴	468.1	113.0	66.8	201.3	0.0634	87.28	0.8728
1×10 ⁻³	457.3	49.50	21.7	303.2	0.0219	95.60	0.9560
5×10 ⁻³	453.6	64.00	35.1	482.4	0.0151	97.11	0.9711
1×10 ⁻²	423.3	39.40	34.5	517.2	0.0116	97.78	0.9778

It must be also mentioned by Figure. 4 that similar experimental data in which inhibition efficiency from the polarization measurements is higher than those results obtained from the EIS method are reported before. [4]. It is clear from table.4 that β_a and β_c parameters in the presence and absence of the inhibitor are different from each other.

The inhibitor molecules can be adsorbed onto the metal surface through the electron transfer from the adsorbed species to the vacant electron orbital of low energy in the metal to form a coordinate type link. As stated before, the adsorption process is often a displacement reaction between water and inhibitor molecules. The inhibition efficiency lies mostly in the size and structure of the organic compound. Efficient adsorption is the result of π electrons of the aromatic system, double bonds and electronegative nitrogen and sulphur atoms present in the structure. During chemisorptions of the compound, electron transfer can be expected with compounds having relatively loose band electrons. The π electrons in the system are then likely to be the determining factor in the adsorption process [9].

4. Conclusion

This studied Schiff base acts as an excellent mixed type (cathodic/anodic) inhibitor for steel X₅₂ in Hydrochloric acid medium. Inhibition efficiency and polarisation resistance increase by an increase in additive concentration. EIS technique gives similar results obtained by polarisation measurements, so increasing the charge transfer resistance. Due to double bonds, nitrogen and sulphur electronegative atoms, and aromatic rings which are found in his chemical structure, the inhibiting efficiency of used compound is apparently based on the adsorption of our organic molecule on the metal surface.

6. References

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