*Gazi University Journal of Science*
*GU J Sci*
*25(3):593-600 (2012)*

**ORIGINAL ARTICLE**

# Electrochemical Investigation of the Inhibitive Effect of a New Synthetic Schiff-base on the Corrosion of Mild Steel in Acidic Media

Athareh DADGARINEZHAD[1,♠] , Fatemeh.BAGHAEI[1]

[1] *Material Science and Engineering Department, Shahid-Bahonar University of Kerman, Kerman , IRAN*

*Received: 11.05.2011 Revised: 17.04.2012 Accepted: 04.05.2012*

**ABSTRACT**

In this work the inhibition effect of a new synthetic Schiff base on mild steel corrosion in 1M HCl and 0.5 M H2SO4 was investigated using various electrochemical techniques (potentiodynamic polarization , AC impedance) and weight loss measurements. These measurements revealed that this Schiff base inhibited the corrosion of mild steel in both media and was a mixed-type inhibitor. This inhibitor was adsorbed on the mild steel surface according to a Langmuir isotherm adsorption model. In both media, inhibition efficiency increased with increasing Schiff base concentration. The values of free energy of adsorption were calculated to investigate the mechanism of corrosion inhibition. Scanning electron microscopy (SEM) observation confirmed the existence of an absorbed protective film on the metal surface.

**Key Words**: *Schiff-base, mild steel, AC impedance, corrosion inhibition, Langmuir isotherm.*

## 1. INTRODUCTION

The investigation of the inhibition of iron corrosion is a matter of high theoretical as well as practical interest [1]. Acid solutions are widely used for pickling of mild steel, cleaning, descaling, etc. The dissolution rate of the metal is very high and therefore, it is desirable to inhibit these solutions by adding organic compound while may retard the unnecessary dissolution of the base metal. The choice of the inhibitor is based on two consideration: first it could be synthesized conveniently from relatively cheap raw materials, secondly ,it contain the electron cloud on the aromatic ring or , the electronegative atoms such as nitrogen and oxygen in the relatively long chain compounds[2]. Due to the presence of the –C=N group in the Schiff base molecules, they should be good corrosion inhibitors. Some Schiff base inhibitors have been previously reported as effective corrosion inhibitors for

---

[♠] Corresponding author, e-mail: a.dadgar@mail.uk.ac.ir

steel, copper, zinc and aluminum [3-9].These substances generally become effective by adsorption on the metal surface. The adsorbed species protect the metal from the aggressive medium, which causes decomposition of the metal. Adsorption depends on not only the nature and charge of the metal but on the chemical structure of the inhibitor. The aim of the present study is to examine the inhibitive effect of a new synthetic Schiff base (A), namely,N,N-O-phenylen-bis(salicylidenimine) towards the corrosion of iron in 1M HCl and 0.5M $H_2SO_4$ .

## 2. EXPERIMENTAL

### 2.1. Materials Preparation

The used Schiff base compound was generally synthesized and recrystallized from ethanol. The structure of Schiff base is shown in Figure.1:

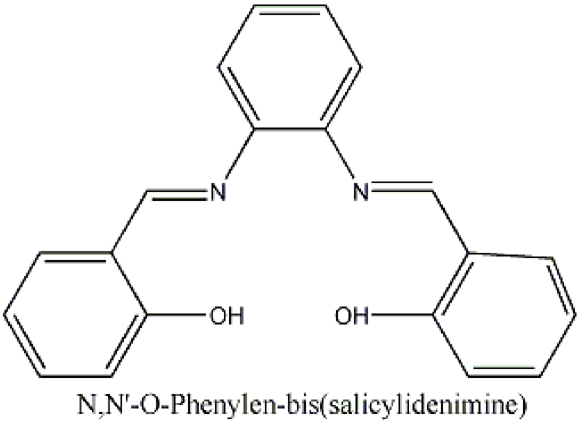

Figure 1. Structure of Schiff base (A).

The aggressive solutions used were made of analytical grade 37% HCl and 96% H2SO4. Appropriate used concentrations of acids were prepared using bidistilled water. All experiments were performed at room temperature.

Mild steel strips of percentage composition P 0.02,C 0.31, Ni 0.07, Mn 0.65, S 0.02 and Fe rest were used for electrochemical and gravimetric studies. specimens were mechanically polished on wet sic paper (120-2400) washed with double distilled water, degreased in ethanol, and finally dried at room temperature, before being immerse in the acid solution. Inhibitor compound with structure shown in Figure.1 was dissolved in absolute ethanol to obtain 1000ppm concentration, then from this concentration by adding to corrosive electrolyte were prepared designated concentration of inhibitor. The concentration range of inhibitor employed was (30, 60, 90,120 and 150 ppm).

### 2.2. Gravimetric and Electrochemical Measurements

The specimens used for gravimetric measurements had a rectangular form (1 cm × 1 cm × 0.1 cm). The weight loss values of specimens were determined in 1M HCl and 0.5M $H_2SO_4$ with and without addition of different concentration of inhibitor after 1h of immersion at 25° C. In this study, the average values of three samples were used according to the ASTM standard procedure described in the literature[10].

For electrochemical measurements, the cell used was a conventional three electrodes Pyrex glass with a platinum counter electrode and a standard calomel electrode (SCE) as reference. The working electrode was embedded in Teflon so that its cross-sectional area ($1Cm^2$) was in contact with the solution. The electrochemical impedance experiments were carried out using AC signals of amplitude 5Mv peak to peak at the open circuit potential (OCP) in the frequency range 100 kHz to 10 mHz after 30 min immersion in the electrolyte cell. Polarization curves were recorded with scanning rate of 1 mV/s, after 30 min immersion from -350 to +350 mV with respect to the corrosion potential vs. SCE. The linear TAFEL segments of the anodic and cathodic curves were extrapolated to corrosion potential to obtain the corrosion current densities. The electrochemical experiments were carried out with a Potentiostat/Galvanostat 263A (EG&G) Princeton Applied Research HF response model 1025.

## 3. RESULT AND DISCUSSION

### 3.1. Polarization Curves

Anodic and cathodic polarization curves for mild steel in 1M HCl and 0.5 M $H_2SO_4$ without and with various concentrations of Schiff base (A) are shown in Figure 2, respectively .A decrease in both cathodic and anodic currents is noted. The cathodic current potential curves give rise to parallel TAFEL lines, which indicate that hydrogen evolution reaction is activation controlled and that the addition of the studied Schiff base does not modify the mechanism of this process[11].

The corrosion kinetic parameters such as corrosion potential($E_{corrr}$),corrosion current density ($I_{corr}$),and inhibition efficiency of inhibitor deduced from the curves are given in table.1 by the intersection of extrapolated cathodic and anodic TAFEL lines at 150 mV more positive and negative than $E_{corr}$ in inhibited and uninhibited solution, respectively . The inhibition efficiency (η%)was calculated according to the following equation[12].

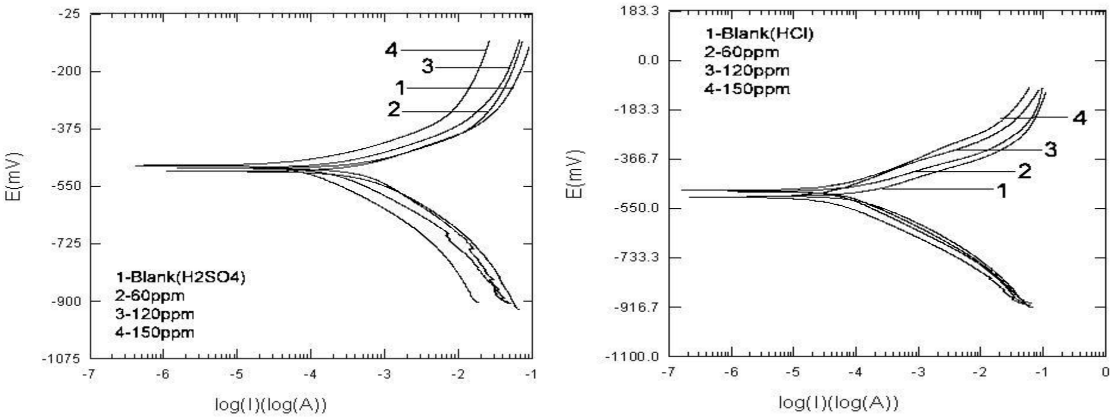

Figure 2. Polarization curves for mild steel in 1M HCl and 0.5M $H_2SO_4$ +different concentration of inhibitor.

$$\%\eta = \frac{I_0 - I}{I_0} \times 100 \qquad (1)$$

Where $I_0$ and I are the uninhibited and inhibited corrosion current densities determined by extrapolation of cathodic and anodic Tafel lines.

According to results of table 1 the inhibition efficiency increases with inhibitor concentration. By the increase in concentration of the inhibitor the $i_{corr}$ values decreases, but $E_{corr}$ values do not change appreciably with the addition of the inhibitor indicating that the inhibitor acts as mixed type of inhibitor, in both acids .

Table 3. Polarization parameter values for mild steel in 1M HCl and 0.5M $H_2SO_4$+ different conc. of inhibitor..

| Solution | Inh.conc. (ppm) | $E_{corr}$ vs SCE/mv | $I_{corr}$ $\mu A/cm^2$ | %η |
|---|---|---|---|---|
| HCl | 0 | -505.1 | 133.3 | - |
| | 30 | -501.9 | 66.0 | 50.5 |
| | 60 | -508.3 | 35.6 | 73.3 |
| | 90 | -493.6 | 24.9 | 81.3 |
| | 120 | -495.1 | 18.8 | 85.9 |
| | 150 | -490.2 | 14.0 | 89.5 |
| H2SO4 | 0 | -505.0 | 616.6 | - |
| | 30 | -494.0 | 469.8 | 23.8 |
| | 60 | -495.3 | 353.9 | 42.6 |
| | 90 | -493.2 | 241.4 | 60.8 |
| | 120 | -494.7 | 193.0 | 68.7 |
| | 150 | -492.1 | 131.9 | 78.6 |

### 3.2. EIS Measurements

Figure 3. is presented Nyquist plots of mild steel without and with various concentration of inhibitor in both acidic solutions. It is clear from the plots that the impedance response of mild steel in both media was significantly changed after the addition of the inhibitor compound. EIS spectra of the Schiff base (A) in both acid solutions were analyzed using the equivalent circuit in Figure 4, which represents a single charge transfer reaction and fits well with our experimental results. The intersection of the capacitive loop with the real axis represents the ohmic resistances of the corrosion product films and the solution enclosed between the working electrode and the reference electrode, $R_s$ .$R_{ct}$ represents the charge transfer resistance whose value is a measure of electron transfer across the surface and is inversely proportional to corrosion rate. The constant phase element, CPE, is introduced in the circuit instead of a pure double layer capacitor to give a more accurate fit[13].These plots having the shape of semi circle indicated the activation controlled nature of the reactions with single charge transfer process. The existence of depressed nature of the semi circle with its center of the semi circle below the X axis is the characteristics of solid electrodes and it attributed to the increased micro-roughness of surface and other inhomogeneous of solid electrode during corrosion [14-15].

The charge transfer resistance, $R_{ct}$ values were calculated from the difference in the resistance measurements obtained at lower and higher frequencies [16]. The double layer capacitance ($C_{dl}$) was obtained from the follow equation [17].

$$f(-Z''_{max}) = \frac{1}{2\pi C_{dl} R_t} \qquad (2)$$

Where f is the frequency at the apex of the semicircle in the Nyquist plot. The inhibition efficiency percent (η percent) of inhibitor was calculated by the follow equation [18].

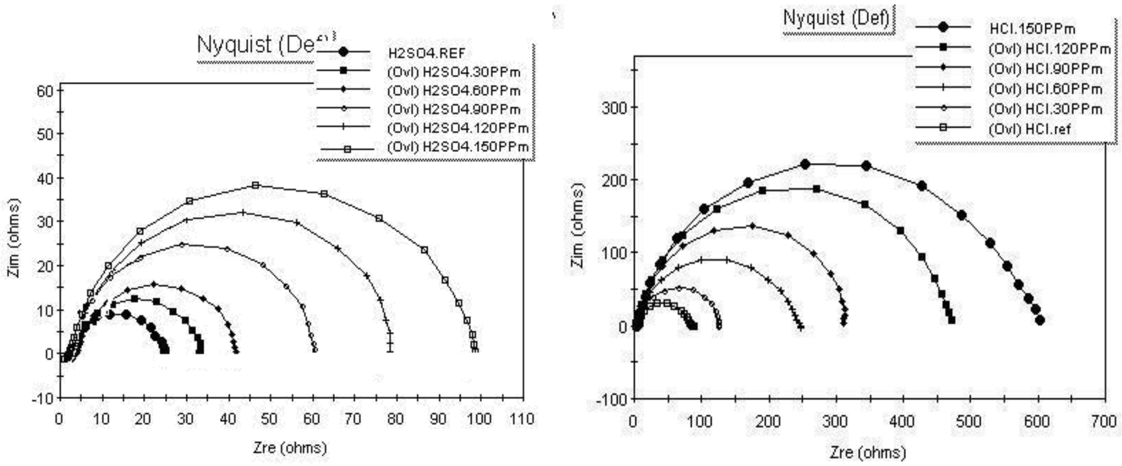

Figure 3. Nyquist plot for mild steel in 0.5M $H_2SO_4$ and 1M HCl in absence and presence of various concentration of Schiff base (A).

$$\eta\% = \frac{R_{ct} - R_{0ct}}{R_{ct}} \times 100 \qquad (3)$$

Where $R_{ct}$ and $R_{0ct}$ are the charge transfer resistance value with and without inhibitor, respectively .The impedance parameters derived from EIS experiments were listed in Table 2. As can be observed from the diameter of the Nyquist plots in presence of inhibitor, as inhibitor concentration increased, $C_{dl}$ values tend to decrease and $R_{ct}$ Values increase, that was in good agreement with polarization results. The decrease in $C_{dl}$ value is due to the adsorption of inhibitor on the metal surface and leads to protective film formation[19]. Similar behavior is observed in both acid media.

Table 2. Nyquist parameter values for mild steel in 1M HCl and 0.5M $H_2SO_4$+ different conc. of inhibitor.

| Solution | Inh.conc/ppm | $R_{ct}/\Omega cm^2$ | $C_{dl}/\mu Fcm^{-2}$ | %η | $\Delta G°_{ads}$ KJ/mol |
|---|---|---|---|---|---|
| HCl | 0 | 59.00 | 176.70 | - | -34.18 |
| | 30 | 122.70 | 163.20 | 51.75 | |
| | 60 | 245.90 | 155.00 | 75.92 | |
| | 90 | 309.20 | 138.20 | 80.85 | |
| | 120 | 468.70 | 134.30 | 78.36 | |
| | 150 | 598.20 | 101.70 | 90.1 | |
| H2SO4 | 0 | 22.20 | 223.60 | - | -31.68 |
| | 30 | 29.50 | 187.30 | 24.74 | |
| | 60 | 36.50 | 161.40 | 39.17 | |
| | 90 | 56.30 | 134.50 | 60.56 | |
| | 120 | 73.20 | 133.70 | 69.67 | |
| | 150 | 95.90 | 122.50 | 76.85 | |

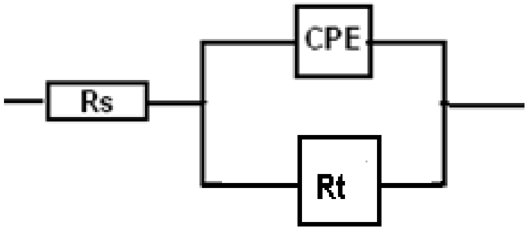

Figure 4.The equivalent circuit used to fit the obtained impedance spectra in both acids.

Table 3 is shown the data of the weight loss determination for different concentration of Schiff base in both acidic media at room temperature. The inhibition efficiency ($\eta_{\%}$) was determined in 1M HCl and 0.5M H2SO4 in absence and presence of inhibitor after 1 hour immersion as follows[17].

$$\eta_w\% = \frac{w_0 - w}{w_0} \times 100 \tag{4}$$

where $w_0$ and w are the weight loss in the absence and presence of inhibitor respectively .The obtained results from EIS, polarization curves and weight loss are in reasonably good agreement.

### 3.3. Gravimetric Measurements

Table 3. inhibition efficiencies values for mild steel in 1M HCl and 0.5M $H_2SO_4$+ different conc. of inhibitor obtained from weight loss measurement.

| Inh.conc. (ppm) | %η(HCl) | %η(H2SO4) |
|---|---|---|
| 30 | 52.3 | 25.3 |
| 60 | 76.4 | 42.7 |
| 90 | 84.5 | 62.6 |
| 120 | 88.0 | 69.3 |
| 150 | 92.3 | 77.8 |

## 4. ADSORPTION ISOTHERM

Basic information on the interaction between the inhibitor and mild steel surface can be provided by the adsorption isotherm. The degrees of surface coverage (θ) of different concentrations of inhibitor in acidic media have been evaluated from electrochemical measurements according to the follow equation[20].

$$\theta = \frac{I_0 - I}{I_0 - I_m} \tag{5}$$

Where $I_m$ and $I_0$ are the corrosion currents at maximum efficiency, and inhibitor free respectively .The surface coverage values (θ) were tested graphically to allow fitting of a suitable adsorption. Plots of θ/(1-θ) versus $C_{inh}$ yield a straight line, clearly proving that the adsorption of the Schiff base (A) in 1M HCl and 0.5 M H2SO4 solutions on the mild steel obeys the Langmuir Adsorption isotherm (Figure 5- 6). According to this isotherm, θ is related to the inhibitor concentration $C_{inh}$ via

$$\theta = \frac{bC_{inh}}{1 + bC_{inh}} \tag{6}$$

Where b designates the adsorption coefficient [21].

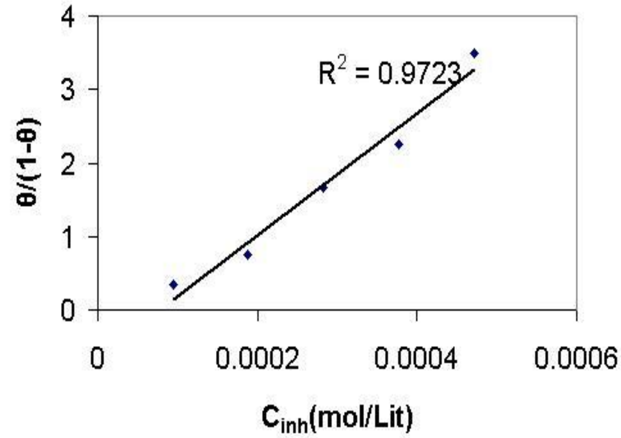

Figure 5 Langmuir adsorption plots for inhibited mild steel in1M HCl.

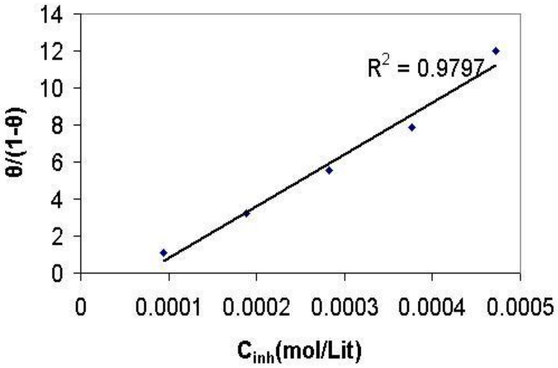

Figure 6 Langmuir adsorption plots for inhibited mild steel in0.5M $H_2SO_4$..

The values of the adsorption coefficient (b) for mild steel in presence of Schiff base (A) was calculated to be 0.06 $lmg^{-1}$ and 0.02 $lmg^{-1}$ in 1M HCL and 0.5 M $H_2SO_4$respectively .The results show that Schiff base is more strongly adsorbed on the steel surface in 1M HCl than 0.5 M $H_2SO_4$.This is in good agreement with the values of inhibitor efficiency obtained from the EIS, polarization curves and weight loss measurements. Thus inhibition efficiency increases with increasing adsorption coefficient [17].

The adsorption of Schiff base (A) can occur through Π-electron interaction between the Schiff base molecule and the metal surface or via interaction of Schiff base with already adsorbed chloride or sulfate ions [22].

The Schiff base may be adsorbed on the metal surface in the form of neutral molecule via the chemisorption mechanism, involving the displacement of water molecules from the metal surface and sharing electron between the nitrogen and oxygen atoms and iron. Adsorption of Schiff base can also occur with the positively charged part of the molecule oriented toward the negatively charged metal surface. Since chloride or sulfate ions are adsorbed on steel surface then the cationic form of the Schiff base can jointly adsorb through electrostatic interactions. It has been observed that the adsorption of the inhibitor can be influenced by the nature of anions in acidic solutions [23-24]. The specific adsorption of anions having a smaller degree of hydration, such as chloride ions, is expected to be more pronounced. Being specifically adsorbed, they create an excess negative charge towards the solution and favor more adsorption of the cations. The adsorption of the inhibitor can also be influenced by the shape of the adsorbed anions as well as by those of the molecular orbitals of the organic molecules due to the great bulk of the sulfate anions compared to that of the chloride anions, the sulfate anions leave less space for the direct interaction between the organic species and the metal surface.

The free energy of adsorption ($\Delta G_{ads}$) at room temperature was calculated by using the follow equation[25].

$$\Delta G^{\circ}_{ads} = -RTln(55.5K) \qquad (7)$$

And K is given by the follow equation

$$K = \frac{\theta}{C_{inh}(1-\theta)} \qquad (8)$$

Where θ is degree of coverage on the metal surface, C is the inhibitor concentration in mol $l^{-1}$ and K is equilibrium constant.

The values of $\Delta G_{ads}$ are given in table 2 .The negative values of $\Delta G_{ads}$ means that the adsorption of the Schiff base (A) on carbon steel surface is a spontaneous process and also show a strong interaction of the inhibitor molecule onto the carbon steel surface[26].

Generally, values of $\Delta G_{ads}$ around -20 $KJmole^{-1}$ or lower are consistend without the electrostatic interaction between the charged molecules and the charged metal (physisorption).While those more negative than -40 $KJmole^{-1}$ involve charge sharing or transfer from the inhibitor molecules to the metal surface to from a coordinate type of bond (chemisorption) .The calculated $\Delta G_{ads}$ values (-34.174 and -31.680 $KJmole^{-1}$ in HCl and $H_2SO_4$) indicated that the adsorption mechanism of the prepared Schiff base on carbon steel in 1M HCl and 0.5M $H_2SO_4$ solutions is a mixed form physical and chemical adsorption [27].

## 5. SEM ANALYSES

The surface morphology of the sample before immersion in acidic media showed a freshly polished steel surface Figure.7a. SEM surface morphology obtained from mild steel surface after specimens immersion in 0.5 M $H_2SO_4$ and in 1M HCl for 2 h in the absence and presence of 150ppm of Schiff base (A) were shown in Figure.7 (b-e), respectively. It could be observed from Figure. 7(b and d) that the specimen's surfaces were strongly damaged in the absence of the inhibitor in both acidic media, from Figure 7(c and e) it could be seen that in presence of the inhibitor, the rate of corrosion was suppressed, it revealed that there was a good protective film absorbed on specimens surface, which was responsible for the inhibition of corrosion

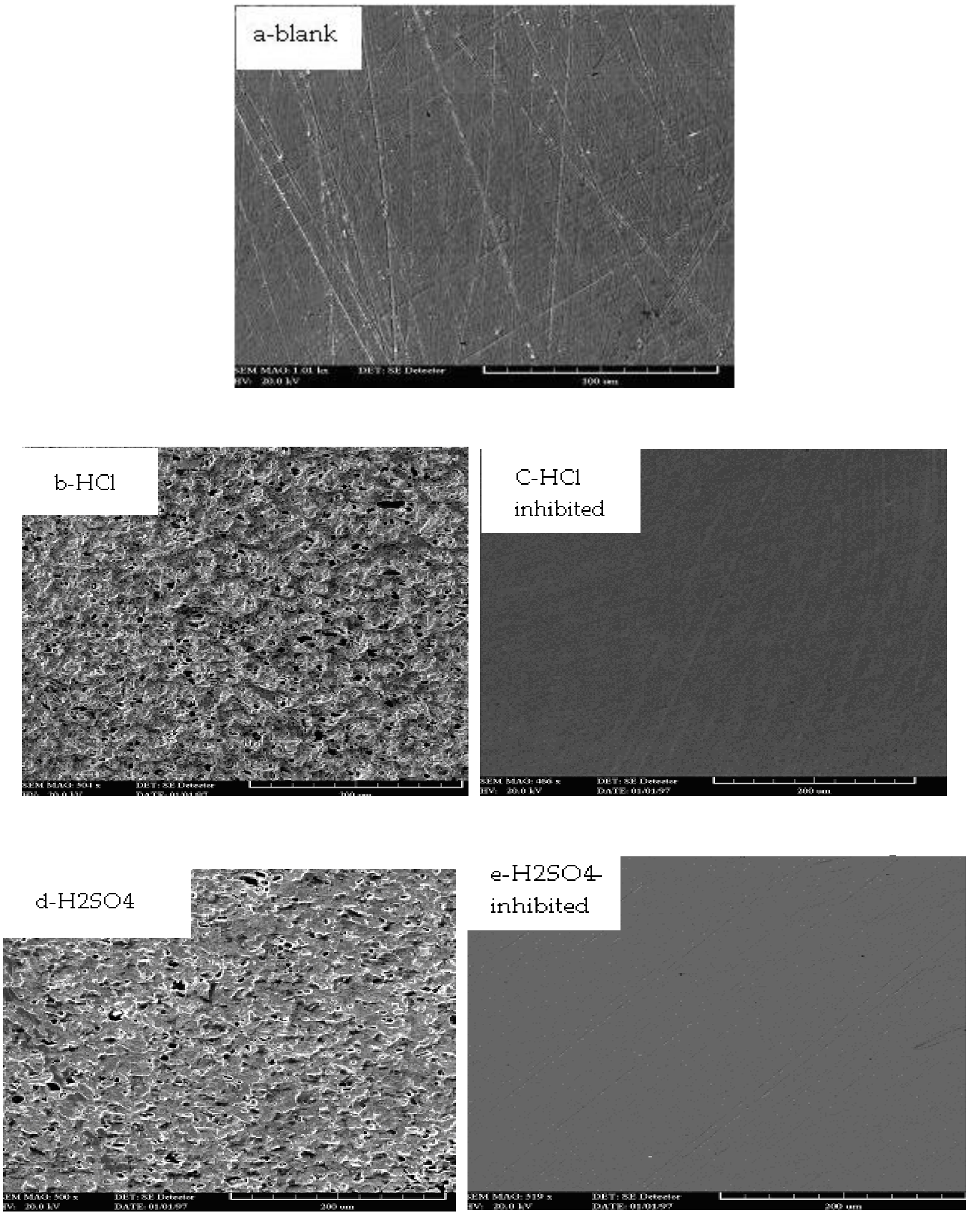

Figure 7. SEM micrographs of mild steel samples (a) only polishing, (b and d) after immersion in1M HCl and 0.5M $H_2SO_4$ solution without inhibitor, (c and e) with 150 ppm Schiff base(A).

## CONCLUSIONS

1. Polarization curves showed that Schiff base (A)was a mixed-type inhibitor for mid steel in 1M HCl and 0.5 M $H_2SO_4$ media.

2. The studied inhibitor was suggested to be mixed from physical and chemical adsorption on the steel surface.

3. The negative values of $\Delta G_{ads}$ showed the spontaneity of the adsorption.

4. Adsorption of the Schiff base on the surface obeyed the Longmuir's isotherm in both media.

5. The Schiff base (A) is a good inhibitor for mild steel corrosion in both acidic media.

## REFERENCES

[1] Ali, S.A., Al-Muallem, H.A., Rahman, S.U., Saeed, M.T., "Bis-isoxazolidines: A new class of corrosion inhibitors of mild steel in acidic media", ***Corros. Sci.***, 50: 3070 (2008 ).

[2] Shokry, H., Yuasa, M., Sekine,. I., Issa, R.M., El-Baradie, H.Y., Gomma,G.K., "Corrosion inhibition of mild steel by schiff base compounds in various aqueous solutions: part 1 ", ***Corros. Sci.***, 40: 2173 (1998).

[3] Hong Ju, Zhen-Peng Kai, Yan Li.," Aminic nitrogen-bearing polydentate Schiff base compounds as corrosion inhibitors for iron in acidic media: A quantum chemical calculation ", ***Corrosion Science***, *50: 865* (2008).

[4] Samiento-Bustos,E., González Rodriguez,. J.G., Uruchurtu, G., "Effect of inorganic inhibitors on the corrosion behavior of 1018 carbon steel in the LiBr + ethylene glycol + $H_2O$ mixture", ***Corrosion Science,*** *50: 2296 (2008).*

[5] Guannan , Mu., Xianghong, Li., Qing, Qu., Zhou, Jun., "Molybdate and tungstate as corrosion inhibitors for cold rolling steel in hydrochloric acid solution ", ***Corrosion Science****,* 48: 445 (2006).

[6] Moretti,G., Quartarone, G., Tassan, A., Zlngales,A., "5-Amino- and 5-chloro-indole as mild steel corrosion inhibitors in 1 N sulphuric acid", ***Electrochimica Acta.****,* 41: *1971*, (1996).

[7] K.C.Emregul.,O.Atakol.,"Corrosion inhibition of iron in 1M HCl solution with schiff base compounds and derivatives", **Mater. Chem.Phys**., 83: 373, (2004).

[8] Desimone, M.P., Grundmeier,G., Gordillo,G., Simison,S.N., " Amphiphilic amido-amine as an effective corrosion inhibitor for mild steel exposed to $CO_2$ saturated solution: Polarization, EIS and PM-IRRAS studies ", ***Electrochimica Acta****, 56: 2990 ( 2011).*

[9] Jafari, A.H., Hosseini, S.M.A., Jamalizadeh Emregul, E., Kurtaran, K.C., Atacol, o., "Investigation of Smart Nanocapsules Containing Inhibitors for Corrosion Protection of Copper", ***4 Electrochimica Acta***, 55: 9004 (2010).

[10] ASTM, "Standard practice for laboratory immersion corrosion testing of metals", G31-72, ASTM, 401 (1990).

[11] Kertit, S., Hammouti, B., "Corrosion inhibition of iron in 1M HCl by 1-phenyl-5-mercapto-1,2,3,4-tetrazole " , ***Metallurgie-Cit****, 251,* (1998).

[12] Hosseini, M.G,, Mertens, S.F.L., Ghorbani, M,, Arshadi, M.R., "Effect of carbon steel microstructures and molecular structure of two new Schiff base compounds on inhibition performance in 1 M HCl solution by EIS " , ***Mater. Chem.Phys***, 2647 (2002).

[13] Behour, M.; Ghoreishi, S.M., Soltani, N., Salavati-Niasari, M., Hamadanian, M., Gandomi, A., "Electrochemical and theoretical investigation on the corrosion inhibition of mild steel by thiosalicylaldehyde derivatives in hydrochloric acid solution", ***Corros.Sci***., 50: 2172 (2008).

[14] Juttner, K., "Electrochemical impedance spectroscopy (EIS) of corrosion processes on inhomogeneous surfaces", ***Electrochim.Acta****,* 35: 1501 (1990).

[15] Growcock, F.B., Jasinski, R.J., "Time-resolved impedance spectroscopy of mild steel in concentrated hydrochloric acid", ***J. Electrolchem. Soc.,*** 136, 2310 (1989).

[16] Quan, Z., Chen, S., Li, S., "Protection of copper corrosion by modification of self-assembled films of Schiff bases with alkanethiol", ***Corros. Sci***., 43: 1071 (2001 ).

[17] Bentiss, F., Traisnel, M., Lagrence, M., "The substituted 1,3,4-oxadiazoles: a new class of corrosion inhibitors of mild steel in acidic media " , ***Corros. Sci***., 42: *127* (2000).

[18] Quan, Z., Chen, S., Li, Y., and Cui, X., "Adsorption behaviour of Schiff base and corrosion protection of resulting films to copper substrate", ***Corros.Sci***., 44: *703* (2002).

[19] El Mehdi,B., Mernari, B., Traisnel, M., Bentiss, F., Lagrenee,M., "Synthesis and comparative study of the inhibitive effect of some new triazole derivatives towards corrosion of mild steel in hydrochloric acid solution", ***Mater. Chem.Phys***.,77: 489 (2002).

[20] Arshadi, M. R., Hosseni, M. G., Ghorbani, M., "Inhibition effect of 3,5 bis(2-pyridil)1,2,4 triazole and 1-10 phenantrolin on corrosion of mild steel in acid solutions" , ***J. British***, 37(1): 76 (2002).

[21] D. Landot, Corrosion and Metals Surface Chemistry, Alden Press, Oxford, 495 (1993).

[22] Hosseini,m., Mertens,S.F.L., Ghorbani, M., "Assimetrical Schiff base as inhibitors of mild steel corrosion in sulphuric acid media", ***Mater. Chem.Phys***.,78: 800 (2003).

[23] Foroulis, Z.A., Proceedings of the sixth European Symposium on Corrosion Inhibitors, 8: 130 (1985).

[24] Rengamani, S., Muralidharam, S., Anbu, M,. Kulandainathan, S., Venkatakrishna, I., "Inhibiting and accelerating effect of aminophenols on the corrosion and permeation of hydrogen through mild steel in acidic solutions", ***J.Appl. Electrochem***, 24: 355 (1994).

[25] Quraishi, M.A., Jamal, D., "Dianils as new and effective corrosion inhibitors for mild steel in acidic solutions", ***Mater. Chem. Phys***., 78: 608 (2003).

[26] Hegazy, M.A., "A novel Schiff base-based cationic gemini surfactants: Synthesis and effect on corrosion inhibition of carbon steel in hydrochloric acid solution", ***Corros. Sci***., 51: 2610 (2009 ).

[27] Dadgarinezhad. A.B.," A new synthesized corrosion inhibitor for mild steel in 0.5 M H2SO4" , ***G.U.Journal of Science***, 24: 219 (2011).