

The inhibitive effect of Schiff base compound on corrosion behaviour of mild steel in hydrochloric acid solution

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Abstract

The inhibiting effect Schiff base on the corrosion of the mild steel in 1M HCl has been studied by electrochemical impedance spectroscopy (EIS) and Tafel polarisation measurements. The Schiff base 4,4 - bis(salicylideneimino) diphenylether (S) is synthesized from salicylaldehyde and the corresponding amine. Polarization curves indicated that the studied Schiff base act as mixed type (cathodic/anodic) inhibitor and the inhibition efficiency have increased when the concentration of the Schiff base have increased. Thermodynamic adsorption parameters (K_{ads} , ΔG_{ads}) of studied Schiff base were calculated using the Langmuir adsorption isotherm. Activation parameters of the corrosion process such as activation energies, E_a , activation enthalpies, ΔH^* , and activation entropies, ΔS^* , were calculated by the obtained corrosion currents at different temperatures.

Keywords: Corrosion; Inhibitor; Schiff base; mild steel; Hydrochloric acid.

Introduction

Chemical cleaning and pickling processes are widely used in industrial processes. The most important fields of application are acid pickling and industrial acid cleaning bathes. Because of their aggressiveness, the use of corrosion inhibitors reduces the rate of dissolution of metals and it is considered as the most effective method for the protection of many metals and alloys against such acid attack [1-4]. The adsorption of these compounds is influenced by the electronic structure of inhibiting molecules, steric factor, aromaticity, and electron density at donor site, presence of functional group such as -CHO, -C=N-, R-OH etc., molecular area and molecular weight of the inhibitor molecule [5-8].

Schiff bases can be synthesized easily from relatively cheap initial materials. They have been investigated for their corrosion inhibition effect on various metals and alloys in acid media. Schiff bases are the condensation product of an amine and a ketone or aldehyde. The inhibition efficiency of Schiff bases is much more than that of the corresponding amines and aldehyde due to the presence of the RC=NR group which enriches the electron cloud. In the structure of the Schiff base, the atoms of the aromatic ring and -C=N group can form a π bond. Then, π electrons in the Schiff base molecule not only can locate the unoccupied orbital of the transition metal, but also can accept the electrons of the d orbital of the transition metal to form feedback metal-inhibitor bond, which is not possible with an amine. Based on the presence of nitrogen atoms and the imine functional group in its structure, Schiff base molecule may reasonably justify its use as an effective corrosion inhibitor [9,10].

The aim of this work is to investigate inhibitive effect of Schiff base compound (S) for the corrosion of mild steel in 1M HCl solution in the absence and presence of inhibitor were studied via electrochemical impedance and polarisation methods.

Compound (S) is synthesized according to published methods [11, 12]. To 1 mmol of diamine (hot EtOH, 20 mL) was added dropwise 2 mmol of salicylaldehyde (Fluka Chemical Company). m.p. = 209 °C; IR (KBr): $\nu(\text{C}=\text{N}) = 1620 \text{ cm}^{-1}$. The ^1H NMR spectrum exhibits a singlet at 13.3 ppm, corresponding to phenolic group, the aromatic protons give a multiplet centred at 6.5 ppm. A singlet at 8.5 ppm is due to the imino part. The molecule structure of compound (S) is shown in Fig. 1. The ^1H NMR spectra were recorded with using a Bruker AM-250 (France). The electrolyte solution was 1 M HCl, prepared from analytical grade 37% HCl (Merck) and double distilled water. All tests have been performed in deaerated solutions and at ambient temperature. The working electrode was prepared from a cylindrical mild steel (MS) rods having following chemical composition: C 0.7%, Mn 0.4%, Cu 0.12%, Si 0.05%, P 0.025%, S 0.025%, Sn 0.01%, Ni 0.009% and remainder iron. The electrode was inserted in Teflon tube and isolated with polyester was allowed to contact the aggressive solutions. The electrode was polished using different grades of emery paper (800 and 1200) before each experiment, rinsed with double distilled water and finally degreased with acetone. The concentration range of inhibitor employed was 1×10^{-4} to 5×10^{-3} M in 1 M HCl. Electrochemical measurements were conducted in a conventional three-electrode thermostated cell. A platinum disk as counter electrode and standard calomel electrode (SCE) as the reference electrode have been used in the electrochemical studies. The potentiodynamic curves were recorded using a PGZ 301 voltalab 4 system connected to a personal computer. The working electrode was first immersed into the test solution for 120 min to establish a steady state open circuit potential. After measuring the open circuit potential dynamic polarisation curves were obtained with a scan rate of 1 mV/s in the potential range from -150 to +150 mV relative to the E_{ocp} . Corrosion current density values were obtained by Tafel extrapolation method. Electrochemical impedance (EIS) measurements were performed at

open circuit potential in the frequency range from 80 kHz to 80 mhz. The cyclic voltammetry was carried out for bare electrode and inhibitor covered electrode in the test solution. The working electrode was scanned from negative to positive in the potential range of -0.6V to 0.0V at a scan rate of 50 mVs⁻¹.

3. Results and discussion

3.1. Tafel polarisation measurements

Polarization profiles for mild steel in 1 M HCl in the absence and presence of (S) of various concentrations is shown in Fig. 2. Corrosion parameters, such as corrosion potential (E_{corr}), corrosion current density (I_{corr}) obtained by extrapolation of the Tafel lines and the inhibition efficiency values η (%) are listed in table 1. The maximum inhibition efficiency (80 %) was obtained at 5×10^{-3} M. The presence of Schiff base in HCl solution resulted in shift of corrosion potential towards more negative direction in comparison with that obtained in the absence of inhibitor. These results indicate that all Schiff base act as mixed type inhibitor with predominant control of cathodic reaction and variation in both of Tafel slopes [13]. Increase in inhibition efficiencies with the increase of concentrations of studied Schiff base shows that inhibition actions are due to adsorption on mild steel surface.

The inhibition efficiencies; η , were calculated using the following formula :

$$\eta (\%) = \frac{i^0_{\text{corr}} - i_{\text{corr}}}{i^0_{\text{corr}}} \times 100 \quad (1)$$

Where i and i^0 are values of the current densities with and without inhibitor, respectively.

Fig.3 shows the change of η with the inhibitor concentration. The increase in the inhibition efficiencies of mild steel, in 1M acid chlorid solution, with increasing additive concentration can be explained on the basis of additive adsorption.

Corrosion inhibition behaviour of mild steel in 1M HCl solution with different concentrations of the studied Schiff base was investigated by EIS. Fig. 4 , shows the impedance diagrams for mild steel in 1M HCl solution without and with addition of compound (S) a at various concentrations. The corresponding Bode plots are shown in Fig. 5. Generally the Nyquist plots are regarded as semicircles. These types of Nyquist plots can be modeled by a simple Randel s circuit including the charge transfer resistance (R_t) parallel with double layer capacitance (C_{dl}) in series with solution resistance (R_s) [14].The equivalent circuit model for this system shown in Fig. 6, was identical to those reported previously [15,16]. Solution resistance, R_s , and charge transfer resistance, R_t , values were obtained from nyquist plots. Inhibition efficiencies, η_z , were calculated using the following formula (Eq.)

$$\eta_z(\%) = \frac{R_t - R_{t0}}{R_t} \times 100 \quad (2)$$

Where R_t and R_{t0} are the values of the charge transfer resistance with and without inhibitor, respectively. The impedance parameters for the corrosion of mild steel in 1 HCl are given in table 2. R_t values obtained from Nyquist diagrams given in table 2, are parallel to the order of inhibition efficiencies obtained from Tafel polarisation methods. The obtained results show that the inhibition efficiency increases with inhibitor concentration . It is clear, that inhibition efficiencies of the studied Schiff base obtained from the two methods are not the same but their trends are the same. The inhibition action of (S) towards the corrosion of mild steel in 1M HCl can be explained in termes of interaction between the adsorbed species [17] which is known to depend on the chemical structure of the inhibitor [18]. Iron is well known for its coordination affinity towards nitrogen and oxygen bearing ligand.

Cyclic voltammograms for mild steel in 1M HCl in the absence and presence of inhibitor (S) is shown in Fig. 7. It can be seen that the presence of inhibitor (S) causes significant decrease in the current density of the anodic peaks. The results show that (S) is an effective inhibitor for mild steel.

3.4. Adsorption isotherm and thermodynamics calculations

The interactions between the inhibitor and the mild steel surface can be examined by the adsorption isotherm. The degree of surface coverage values (θ) for various concentrations of the inhibitor in acidic media have been evaluated from the polarisation measurements Table 2. Suitable adsorption isotherm was obtained, using these calculated values. The linear relationships of C/θ versus C , depicted in Fig. 8, suggest that the adsorption of compound (S) on the mild steel obeyed the Langmuir adsorption isotherm [19]. This isotherm can be represented as

$$\frac{C}{\theta} = \frac{1}{k} + C \quad (3)$$

The degree of surface coverage of each inhibitor at a given concentration can be calculated using the equation:

$$\theta = \frac{i^0 - i}{i^0} \quad (4)$$

The strong correlation ($R^2 = 0.997$) of the Langmuir adsorption isotherm for (S) was observed. Langmuir adsorption isotherm assumes that the adsorption of organic molecule on the adsorbent is monolayer. Values of adsorption equilibrium constant (K_{ads}) calculated from the Langmuir adsorption isotherm is 1.1×10^4 . The relatively high values of the adsorption equilibrium constant reflect the high adsorption ability of these molecules on mild steel

surface. The free energy of adsorption ΔG_{ads} of the inhibitors on mild steel surface can be determined using the following relation:

$$\Delta G_{\text{ads}} = -RT \ln K_{\text{ads}} \quad (5)$$

The negative values of ΔG_{ads} indicating the spontaneous adsorption of these molecules on the metal surface is found to be $-22.76 \text{ kJ mol}^{-1}$. Values of ΔG_{ads} around -20 kJ mol^{-1} or lower are consistent with the electrostatic interaction between charged organic molecules and the charged metal surface (physisorption); those around -40 kJ mol^{-1} or higher involve charge sharing or transfer from the organic molecule to the metal surface to form a co-ordinate type of bond (chemisorption). The values of ΔG_{ads} for both compounds being less than -40 kJ mol^{-1} indicates physical adsorption. In addition to electrostatic interaction, there may be some other interactions.

The effect of temperature on the corrosion parameters of mild steel in free and inhibited solutions of 1 M HCl was studied using polarization technique in temperature range of 20-40 °C. The acid solutions were inhibited by addition of $5 \cdot 10^{-3} \text{ M}$ of inhibitor (S). The obtained corrosion parameters are given in Table 3 and show when temperature increases, in the absence and presence of inhibitor, the I_{corr} increases. From Table 3 can find that the investigated Schiff base has inhibiting properties at all the studied temperatures and when temperature increases the values of inhibition efficiencies decrease. A decrease in inhibition efficiencies with the increase in temperature might be due to weakening of physical adsorption.

The activation energy of corrosion process with and without the inhibitor could be calculated using the equation

$$k = A \exp \left(\frac{-E_a}{RT} \right) \quad (6)$$

where E_a is the activation energy, A the frequency factor, T the absolute temperature, R the gas constant and k is the rate of corrosion reaction, that is directly proportional to the corrosion current density. The apparent activation energies (E_a) and pre-exponential factors (A) at 5.10^{-3} M of inhibitors are calculated by linear regression between $\ln(I_{corr})$ and $1/T$ Fig 9, and also the results shown in Table 4. All the linear regression coefficients are close to 1, indicating that the mild steel corrosion in hydrochloric acid can be elucidated using the kinetic model. Enthalpy and entropy of activation (ΔH^* , ΔS^*) were calculated from the equation:

$$K = \frac{RT}{Nh} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(-\frac{\Delta H^*}{RT}\right) \quad (7)$$

where h is the Plank constant, N is the Avogadros number. A plot of $\ln(I_{corr}/T)$ versus $1/T$ equa 7, gave straight lines as shown in Fig 10, for mild steel dissolution in 1 HCl in the absence and presence of 5.10^{-3} M of inhibitor (S). Straight lines are obtained with a slope of $-\Delta H^*/R$ and an intercept of $\ln R/Nh + \Delta S^*/R$ from which the values of ΔH^* and ΔS^* are calculated and listed in table 4.

Inspection of these data reveals the positive sign for both E_a and ΔH^* , reflecting the endothermic nature of corrosion process. It is obviously seen that the activation energy strongly increases in the presence of inhibitor, this result due to that the inhibitor species are physically adsorbed on the metal surface [20]. The negative values of ΔS^* pointed to a greater order produced during the process of activation. This can be achieved by the formation of activated complex represents association or fixation with consequent loss in the degrees of freedom of the system during the process [21].

4. Conclusion

The corrosion behaviour of mild steel was investigated in 1 M HCl with and without addition of various concentrations of Schiff base at different concentrations, using potentiodynamic and electrochemical impedance techniques.

-Polarization curves indicated that all studied Schiff base act as mixed type (cathodic/anodic) inhibitor.

-The Schiff bases adsorbed on mild steel surface followed Langmuir adsorption isotherm. The calculated values of free energy adsorption of the studied Schiff base indicated that their adsorption on mild steel in 1M HCl is physical in nature.

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Table 1

Polarisation parameters and corresponding inhibition efficiency for the mild steel in 1 M HCl with and without addition of various concentrations of Schiff base S.

Inhibitor	Cncentration (M)	$-E_{\text{corr}}$ (mV)	I_{corr} (μAcm^{-2})	ba (mV/dec)	-bc (mV/dec)	η_p (%)	θ
HCl	1	467	521	166	68	-	
S	1×10^{-4}	451	215	69	177	58.7	58
	5×10^{-4}	474	172	111	131	66.9	66
	1×10^{-3}	480	124	125	175	76.9	76
	5×10^{-3}	478	100	76	71.7	80.8	80

Table 2

Electrochemical impedance parameters for mild steel in 1 M HCl without and with addition of various concentrations of studied Schiff base S.

Inhibitor	C (M)	R_s ($\Omega \text{ cm}^2$)	R_t ($\Omega \text{ cm}^2$)	C_{dl} ($\mu\text{F cm}^{-2}$)	η_z (%)
HCl	1	0.7	44	215	-
S	1×10^{-4}	0.9	129	101	65.8
	5×10^{-4}	0.97	140	98	68.5
	1×10^{-3}	1.02	155	83	71.6
	5×10^{-3}	1.44	191	81	76.9

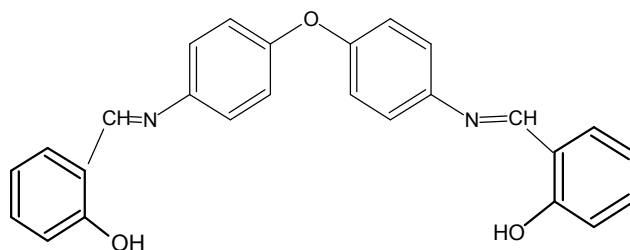
Polarization parameters for the corrosion of the mild steel in 1 HCl without and with addition of 5.10^{-3} M of schiff base at different temperatures.

Inhibitor	Temperature ($^{\circ}\text{C}$)	$-E_{\text{corr}}$ (mV)	$I_{\text{corr}}(\mu\text{Acm}^{-2})$	ba(mV)	-bc(mV)	η_t (%)
HCl	20	467	521	68.8	156	-
	30	500	591	128	103	-
	40	507	626	115	126	-
S	20	478	100	76	71.7	80.8
	30	512	165	107	116	72.0
	40	507	233	98	129	62.7

Table 4

Activation parameters of dissolution reaction of mild steel in 1 HCl solution containing 5.10^{-3} M concentrations of studied Schiff base

Inhibitor	E_a (kJ mol $^{-1}$)	ΔH^* (kJ mol $^{-1}$)	ΔS^* (J mol $^{-1}$ K $^{-1}$)
HCl	6.73	6.4	- 171
S	32.11	29.45	-104.49



4,4 - bis(salicylideneimino) diphenylether

Fig. 1. Structure of studied Schiff base (S)

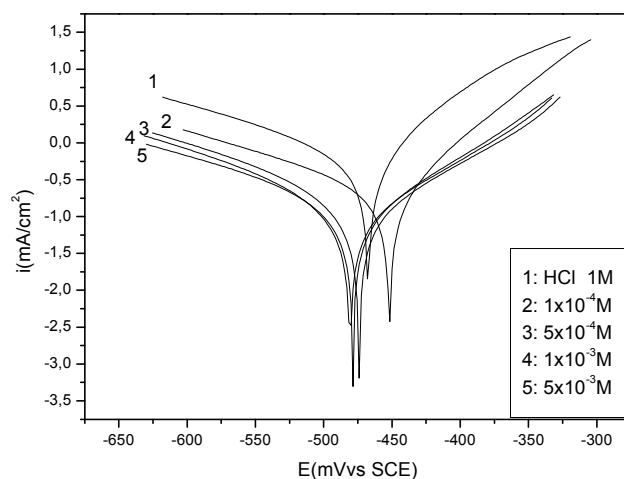


Fig. 2. Tafel polarisation curves for mild steel in 1M HCl in the presence and absence of different concentrations of compound S

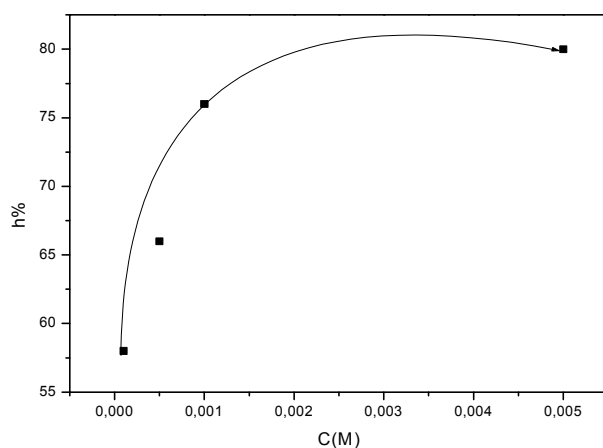


Fig. 3 . Effect of inhibitor concentration on the efficiencies of mild steel in 1M HCl for compound S.

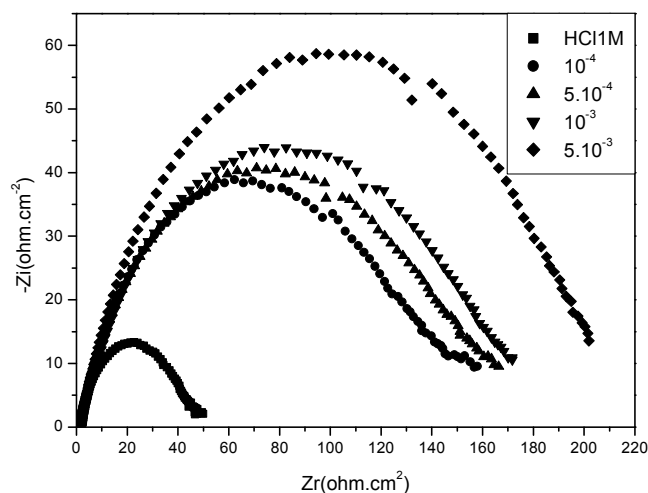


Fig. 4. Nyquist impedance diagrams for mild steel in 1M HCl solution in the presence and absence of different concentrations of compound S

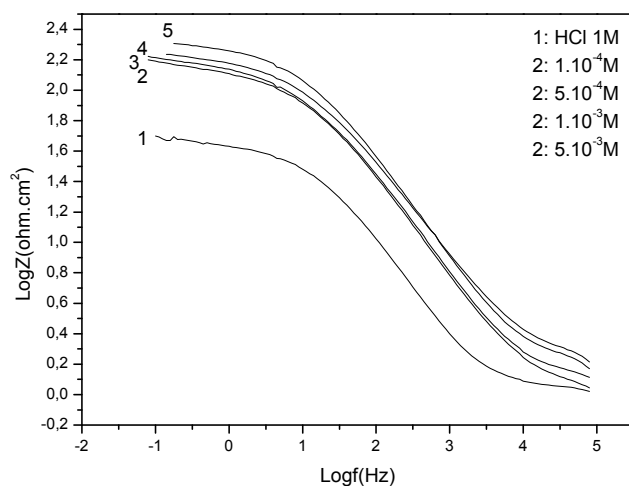


Fig. 5. Bode plots for mild steel in 1 M HCl in the absence and presence of S at different concentrations.

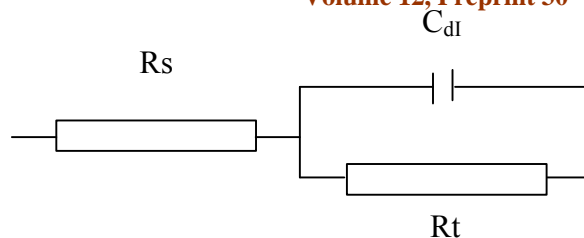


Fig.6. Electrochemical equivalent circuit diagram for metal- electrolyte interface obtained for compound S.

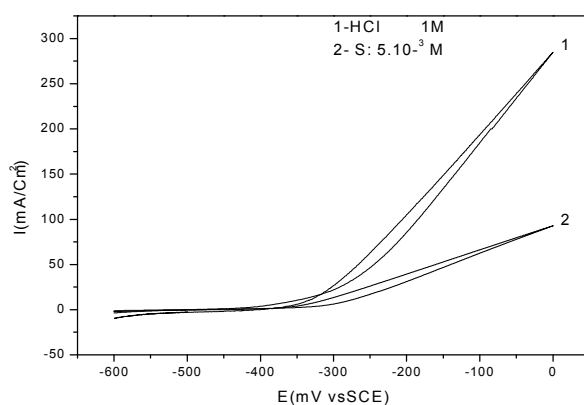


Fig. 7. Cyclic voltammograms for mild steel in 1M HCl in the absence and presence of inhibitors S1 and S2 at 5.10^{-3} M

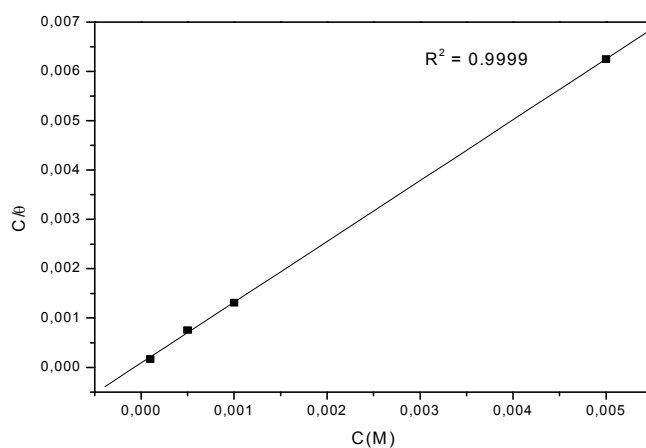


Fig.8. Langmuir adsorption isotherm for compound S.

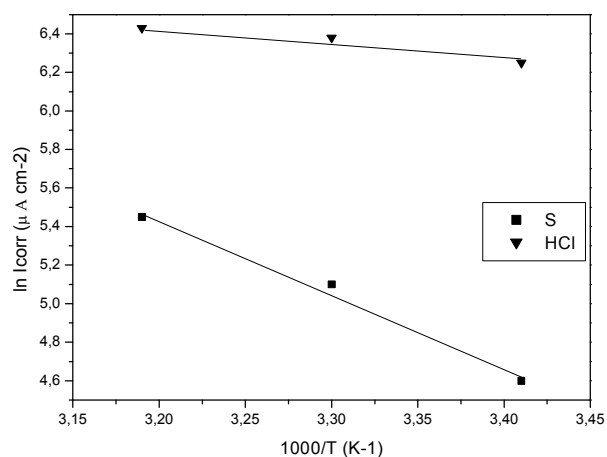


Fig. 9. Plotting $\ln(I_{corr})$ vs. $1/T$ to calculate the activation energy of corrosion process in the presence of inhibitor S

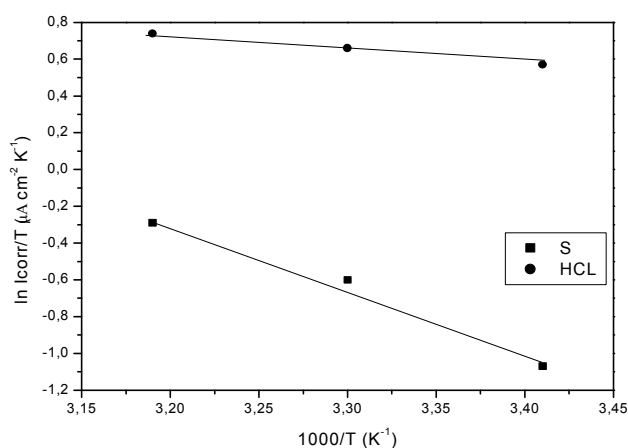


Fig. 10. Arrhenius plots of $\ln(I_{corr}/T)$ versus $1/T$ in the absence and presence of 5.10^{-3} M Schiff base S.