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Investigation on Two Salen Type Schiff base Compounds as Corrosion Inhibition of Copper in 0.5 M H_2SO_4

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ABSTRACT

The inhibition of copper corrosion by two new Schiff bases under 0.5 M H2SO4 at 250C was studied by electrochemical tests (potentiodynamic polarization and AC impedance technique).These studies have shown that two Schiff bases are good inhibitors for copper in 0.5 M H2SO4. Results obtained reveal that, as the concentration of two Schiff bases increases, the polarization resistance values (Rt) increases, the double layer capacitance values (Cdl) decrease and inhibition efficiency increases. The inhibition process was attributed to the formation of an adsorbed film on the metal surface that protects the metal against corrosive agents. It was found that these two Schiff bases were chemically adsorbed on the copper surface and follow Langmuir isotherm. The Tafel polarization have shown that two Schiff bases act as anodic inhibitors.

Key Words: *Corrosion inhibition, Schiff base, AC impedance, Inhibition efficiency*.

1. INTRODUCTION

Copper and its alloys are good corrosion resistance in water and have excellent heat conductivity, but these corrode easily in acid solutions. Copper and its alloys are broadly used in heating systems and condensers. However these systems should be regularly cleaned due to inlays of carbonates and oxides diminish their heating transmission. Diluted acids are normally used to clean these surfaces. For preventing of copper corrosion, additives such as inhibitors are generally added to acid. Among the protection mechanism were attributed to the formation an absorbed film on the metal surface; the inhibitor provokes a small corrosion on the surface of metal and also it is absorbed forming a compact protective thin layer; the inhibitor forms a precipitate on the surface of metal; acting on the aggressive medium in such a way to form protective precipitate or to remove aggressive agents. Various organic inhibitors have been studied as corrosion inhibitors. The heteroatoms containing organic compounds, such as P, S, N, and O, having lone pair of electrons, may interact with the metal substrate through an electron donation mechanism, reducing metal dissolution at the metal-electrolyte interface [1-5]. Recent studies presented that Schiff bases were effective inhibitors for generalized corrosion of mild steel [6-10] and copper and its alloys [11-15]. The processes of Schiff bases synthesis are simple and can easily introduce groups according expected properties.

The aim of this work is to study the effect of two salen Schiff bases of bis -(2-hydroxy-3-methoxy)-1,6-diaminohexane salicyladimine (A1) and bis-(2-hydroxy)-1,6-diaminohexane salicyladimine (A2) on the copper corrosion in 0.5M H2SO4 by the use of electrochemical tests at 250C.

2. EXPERIMENTAL

2.1. Materials

The working electrode employed in this work was made of spec pure copper (99.9%). For electrochemical measurements, the working electrode (WE) were cut as cylindrical rods, welded with Cu-wire sealed with epoxy resin, leaving an exposed area of 1 cm^2. Before each experimental the area of WE was first briefly ground with No.800 emery paper, subsequently polished with No. 2000 emery paper, washed with double distilled water, degreased absolute ethanol and dried. Two Schiff bases were synthesized in the laboratory and evaluated as corrosion inhibitors on copper. In Figure 1, the structure of two Schiff bases A1 and A2 are show. The concentration of the inhibitors employed were 25, 50, 75 and 100 ppm. The aggressive solution (0.5M H_2SO_4) is prepared by dilution of analytical grade 98% H_2SO_4 with double distilled water. The experiments were performed in 100cm^3 volumecell.

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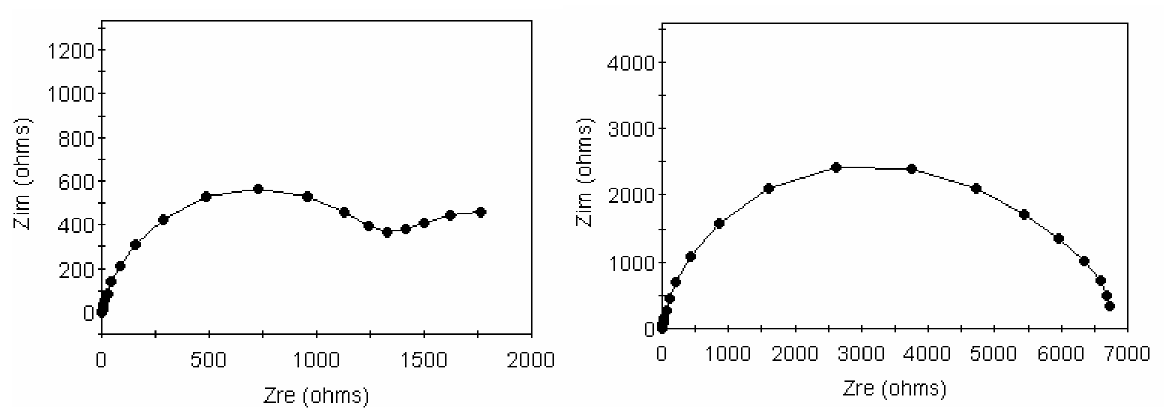
A1 A2

Figure 1. Structure of Schiff bases, A1 and A2.

Tafel polarization measurement were carried out at open circuit potential (E_{ocp}), using a computer–controlled potentiostat/Galvanostate (PAR EG&G Model 263 A), using counter electrode (Pt) and a Saturated Calomle Eletrode (SCE) as reference electrode. All potentials are referred to this reference electrode. The Tafel current-potential curves were carried out at a scan rate 1mV/s. For impedance measurement, the same equipment was used for the Tafel polarization measurements, and frequency response analyzer (Princton Model 1020). The impedance measurement were carried out using AC signals of amplitude 10 mV peak to peak at the open circuit potential in the frequency range 100 KHz to 10 mHz.

3. RESULTS AND DISCUSSION

Figure 2 shows the Nyquist plots recorded for copper in $0.5MH_2SO_4$ solution without and with of 50 ppm of A1. For the bare copper electrode without A1 (Figure 2a), a High Frequency (HF) semicircle was observed followed by a straight line portion in the Low Frequency (LF) region. The HF semicircle is attributed to the time constant of charge transfer and double layer capacitance [16-18].



(a) (b)

Figure 2.(a)The Nyquist plot of copper in 0.5 M H_2SO_4 (b) The Nyquist plot of copper in 0.5 M $H_2SO_4$with 50ppmA1.

The intercept of the HF charge-transfer semicircle with the real axis gives the charge transfer resistance (Rt) value. The Warburg type impedance, at the LF linear portion is related to diffusion of soluble copper from electrode surface to bulk solution, indicating that the corrosion process was controlled by mixed charge-transfer and diffusion in solution. Figure 2b, the larger semicircle observed from HF to LF in the presence inhibitors indicates that charge-transfer resistance became dominant in the corrosion process due to the formation of film on the copper electrode by A1 inhibitor, indicating that the corrosion process was controlled by charge-transfer in solution.

Figure 3 shows, the impedance data were interpreted according to two suitable equivalent circuits. Figure 3a the equivalent circuit was used to stimulate the EIS data displaying a Warburg impedance and Figure 3b the equivalent circuit was used to fit the EIS data displaying a capacitive loop. In these two circuits, R_S is the solution resistance, R_t is the charge transfer resistance, C_{dl} is the double-layer capacitance, and Z_d represents the diffusion impedance appearing in the LF region. One Constant Phase Element (CPE) is substituted for a capacitive element to give a more accurate fit [19].

(a) (b)

Figure 3.The equivalent circuit used to fit EIS data for copper displaying a Warburg impedance (a). The equivalent circuit used to fit EIS data for copper displaying a capacitive loop (b).

In practical electrode system, the impedance spectra obtained often were depressed semi-circles with their center below the real axis. This kind of phenomenon is known as the dispersing effect. Considering that the impedance of a double-layer did not behavior as an ideal capacitor in the presence of dispersing effect, the CPE was used as a substitute for capacitor in the equivalent circuit, to fit more accurately the impedance behavior of electric double-layer. The CPE is a special element, whose admittance value is a function of the angular frequency (ω), and whose phase is independent of the frequency. Its admittance and impedance are respectively, expressed as: [20].

$$Y_{CPE}=Y_0(j\omega)^n \quad (3.1)$$

And

$$Z_{CPE}=(1/Y_0)\ [(j\omega)^n]^{-1} \quad (3.2)$$

Where Y_0 is the magnitude of the CPE, j is the imaginary number ($j^2=-1$), α is the phase angle of CPE and n= α/(π/2).The factor n is an adjustable parameter that usually lies between 0.5 and 1.0. The CPE describes an ideal capacitor when n=1. Values of α are usually related to the roughness of the electrode surface. The smaller value of α, the higher the surface roughness [19].

Figure 4 and 5 shows the Nyquist plots recorded for copper in 0.5MH_2SO_4 solution with different concentration of A1 and A2.The Nyquist plots were regarded one part of semicircle.

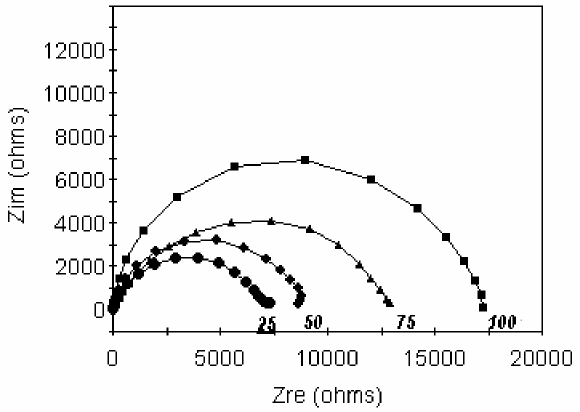


Figure 4. Nyquist plots for copper in 0.5 M H_2SO_4 containing different concentration of A1.

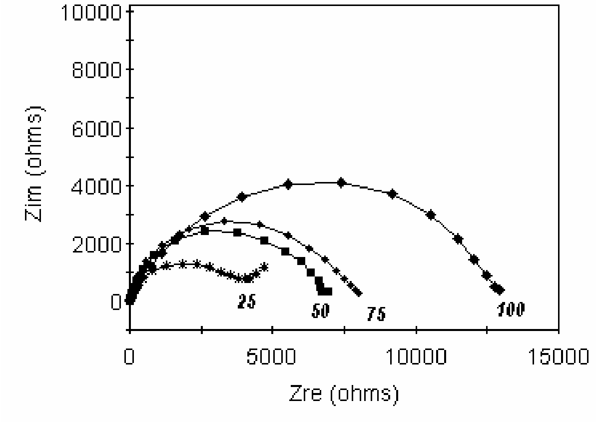


Figure 5. Nyquist plots for copper in 0.5 M H_2SO_4 containing different concentration of A2.

The charge transfer resistance, R_t, values are calculated from the difference of impedance at lower and higher frequencies [19,21]. To obtain the double layer capacitance (C_{dl}), the frequency at which the imaginary component of the impedance is maximum (-Z''max) is found and C_{dl} values are obtained from the equation [18].

$$f(-Z''_{max})=1/(2\pi C_{dl}R_t) \quad (3.3)$$

The charge transfer resistance value was used to calculate the inhibition efficiency (η(%)) of A1 and A2 for copper at different concentrations, using equation:

$$\eta(\%)=[(R_{ti}-R_{t0}/R_{ti})]x100 \quad (3.4)$$

Where R_{t0} and R_{ti} are the charge transfer resistance values without and with inhibitor, respectively. The impedance parameters derived from these investigation is given in Table 1. It is found (Table 1) that, as the A1 and A2 concentrations increase, the R_t values increase, but the C_{dl} values tend to decrease. The decrease in the C_{dl} value is due to the adsorption of A1 and A2 on the metal surface. This decrease can be caused by a decrease in the local dielectric constant and /or the increase in the thickness of the double layer. It shows that the molecules of inhibitor act by adsorption at the solution-metal interface [22]. The capacity of an organic coating is given by the formula:

$$C_{dl}=\epsilon\epsilon_0/d \quad (3.5)$$

Where d is the thickness of the organic coating, ε is the relative permittivity, and ε_0 is the permittivity of vacuum. Therefore, the decrease in the values of C_{dl} shows that, the adsorption layer formed by A1and A2 on the metal surface is stable and thick [23].

Table 1.Impedanc parameter for copper in $0.5MH_2SO_4$ containing different concentration of A1and A2.

	C(ppm)	R_t (KΩCm^2)	C_{dl} (μFCm^{-2})	η(%)
Blank	-	1.821	109.2	-
A1	25	7.683	79.1	75.1
	50	8.809	58.4	79.3
	75	12.950	46.1	85.9
	100	17.209	37.3	89.5
A2	25	4.820	82.7	62.5
	50	6.930	78.1	73.7
	75	8.030	76.8	77.3
	100	12.930	63.2	85.1

The anodic and cathodic Tafel polarization curves for copper in $0.5MH_2SO_4$ at various concentrations of A1 and A2 in Figure 6 and 7 are shown. The results showed that increase in inhibitor concentration slightly shifts E_{corr} in the positive direction and enhances corrosion current densities (I_{corr}).

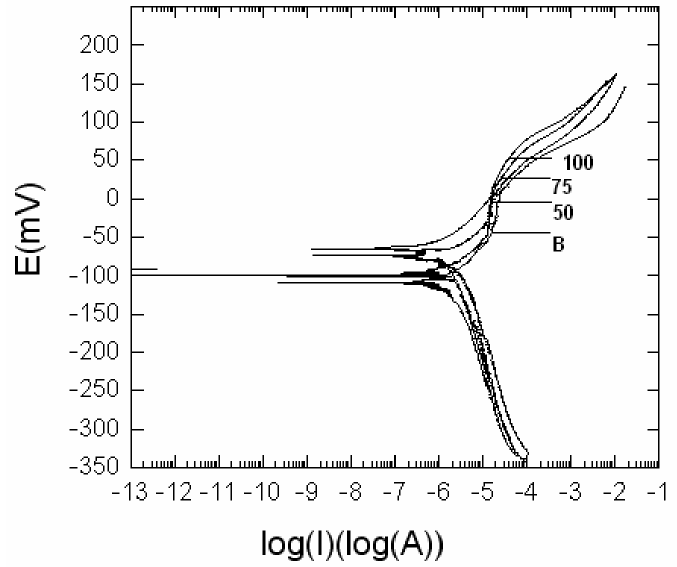


Figure 6.Tafel curves for copper in 0.5 M H_2SO_4(B) and containing different concentration A1.

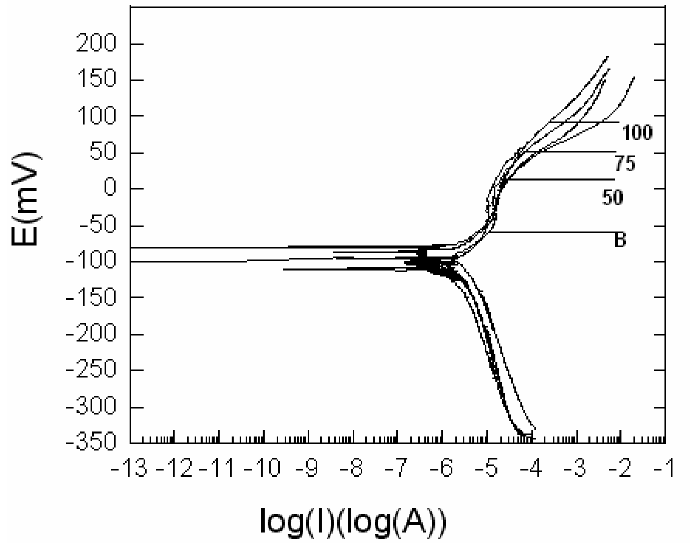


Figure 7. Tafel curves for copper in 0.5 M H_2SO_4(B) and containing different concentration A2.

The corrosion current densities were obtained from the polarization curves by linear extrapolation of theTafel curves at point 50mV more positive, respectively, more negative than E_{ocp}, the open circuit potential value. The inhibition efficiency is defined as:

$$(\%)=(I_0- I_i)/ I_0\eta \qquad (3.6)$$

Where I_0 and I_i are corrosion current densities values without and with inhibitor, respectively. The values of corrosion current density (I_{corr}), corrosion potential (E_{corr}) and corrosion inhibition efficiency η(%) of copper for different concentration of A1 and A2 in 0.5 M H_2SO_4 are given in Table 2.

Table 2. Tafel polarization parameter for copper in 0.5MH_2SO_4 containing different concentration of A1and A2.

	C(ppm)	E_{corr} mV vs(SCE)	I_{corr} $(\mu A cm^{-2})$	$\eta(\%)$
Blank	-	-101	3.6	-
A1	25	-92	1.3	63.8
	50	-73	1.1	69.4
	75	-93	0.9	75.0
	100	-100	0.6	83.3
A2	25	-66	1.5	58.3
	50	-101	1.4	61.1
	75	-100	1.2	66.6
	100	-99	0.8	77.7

The adsorptive behavior of a corrosion inhibitor is an important part of its study. The adsorption of inhibitors is governed by the residual charge on the surface of the metal and by the nature and chemical structure of inhibitor. Two main type of adsorption of organic inhibitor on a metal surface are physical or electrostatic and chemisorptions. The chemisorption involves the share or transfer of charge from the molecules to the surface to form a coordinate type bound. Electron transfer is typical for transition metals having vacant low-energy electron orbital. As for inhibitors, the electron transfer can be expected with compounds having relatively loosely bound electrons. The most frequently used isotherms are the Langmuir isotherm, the Freundlich isotherm and the Temkin isotherm [24,25]. All these isotherms are of the general form:

$$f(\theta,x)\ \exp(-2\alpha\theta)= KC \qquad (3.7)$$

Where $f(\theta,x)$ is the configurational factor which depends upon the physical model and the assumptions underlying the derivation of the isotherm, θ the surface coverage, C the inhibitor concentration in the bulk solution, α the molecular interaction and K is adsorption constant. In this study the Langmuir adsorption isotherm (Eqn. 3.8) was found. This isotherm is:

$$\frac{\theta}{1-\theta} = ACexp(-2\alpha\theta) = KC \qquad (3.8)$$

The above equation can be simplified as:

$$\frac{C}{\theta} = C + \frac{1}{K} \qquad (3.9)$$

The degree of surface coverage (θ) can readily be calculated from any Eqs. (3.5) or (3.6) , as in that case its is numerically identical to the value of percentage inhibition efficiency divided by 100: ($\theta=\eta/100$). Where C is the concentration of the inhibitor and K_{ads} represent the adsorption equilibrium constant. The plots of C/θ versus C yields a straight line (correlation coefficients R^2 equal 0.997 for both A1 and A2) proving that: experimental results are in good agreement with Langmuir adsorption isotherm as it is shown in Figure 8 and 9. The value of K_{ads} is found as, for A1, value of $K_{ads}=43.48\text{X}10^3$ dm^3mol^{-1} for A2, $K_{ads}=20.41\times10^3$ dm^3mol^{-1}. The increasing value of K_{ads} reflects the increasing adsorption capability , due to structural formation , on the metal surface[26].

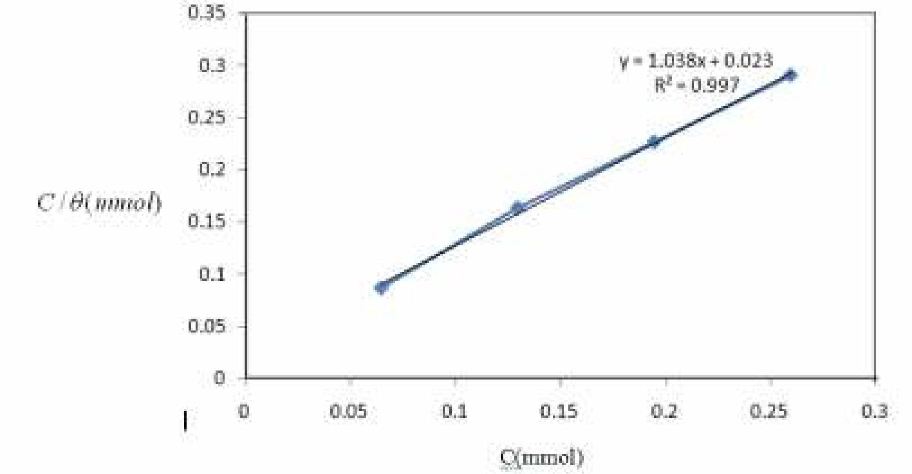


Figure 8. Langmuir adsorption plots for copper in 0.5 M H_2SO_4 containing different concentration of A1.

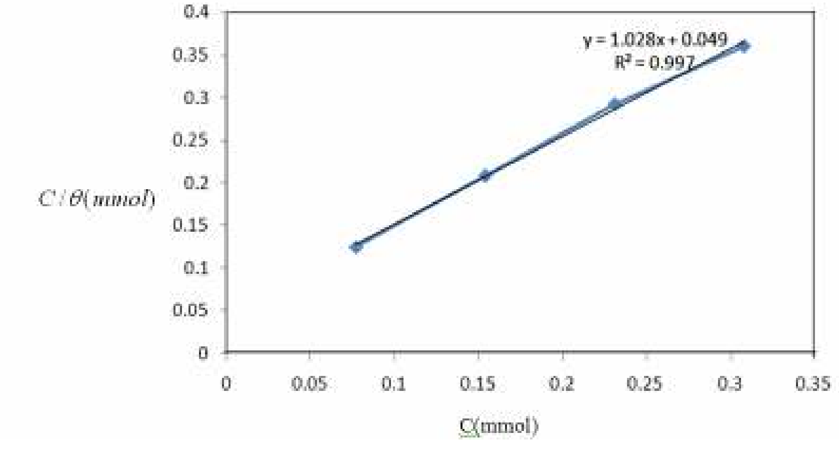


Figure 9. Langmuir adsorption plots for copper in 0.5 M H_2SO_4 containing different concentration of A2.

The Langmuir isotherm is in many case too simple model. It can be inferred that the process under study is spontaneous and the inhibitor is chemically adsorbed on metal surface. This isotherm assumes that adsorbed molecule, occupy only site and there are not interaction with other molecule adsorbed. The relation between the adsorption constant (K_{ads}) and adsorption free energy (ΔG^0_{ads}) is known as:

$$K_{ads}=e^{-\Delta G0\ /RT} \qquad (3.10)$$

Where R is the universal gas constant and T is the absolute temperature. The value for the Gibbs energy of adsorption ΔG^0_{ads} Can be calculated and for A1, ΔG^0_{ads}= -26.46 $KJmol^{-1}$ and for A2, ΔG^0_{ads}= -24.57 $KJmol^{-1}$ are found. The negative value of ΔG^0_{ads} indicate spontaneous adsorption of inhibitor molecule on the metal surface and more negative value of ΔG^0_{ads} reflects the increasing adsorption capability [27].

5. CONCLUSION

1-The results prove that Schiff bases of A1 and A2 display inhibitor properties, the effect of A1 as inhibitor is better than A2.

2-The percentage of inhibition efficiency is seen to increase with the increase of concentration due to adsorption of the A1 and A2 on the copper surface.

3-The η(%) obtained from the polarization measurements show good agreement with those obtained from AC impedance measurements.

4-The polarization measurements indicate that both A1 and A2 acted as anodic type inhibitors.

5-The adsorption process of A1 and A2 obey the Langmuir adsorption isotherm.

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