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Inhibition of Al-Mg alloy in hydrochloric acid using schiff bases as corrosion inhibitors

The effect of some new synthesized Schiff bases namely o-Chloroaniline-N-(p-methoxy benzylidene) and p-Chloroaniline-N-(p-methoxy benzylidene) on the corrosion of Al-Mg alloy in 2 M HCl was investigated. The investigation involved weight loss, galvanostatic polarization and EIS measurements. The inhibition efficiency increased with increase in inhibitor concentration but decreased with increase in temperature. Schiff bases are found to adsorb on the metal surface according to the Langmuir isotherm. Thermodynamic parameters and activation energy were calculated to elaborate the mechanism of inhibition. The results of polarization method show that these Schiff bases act as mixed type, but the cathode is more preferentially polarized.

Key words : Aluminium, EIS, Polarization, Weight loss, Acid inhibition

1. INTRODUCTION

The reaction and subsequent deterioration of metals when exposed to the environment encompasses a fundamental principle of electrochemistry and metallurgy, known as corrosion. Corrosion is defined as the deterioration of the material, usually a metal, because of reaction with its environment and which requires the presence of an anode, a cathode, an electrolyte and an electrical circuit.

The aluminum and its alloys are important materials due to their high technological value and wide range of industrial applications, especially in aerospace, household industries, and commonly used in marine applications as well. In addition, they are justified by low price, high electrical capacity and high energy density [1]. Many researchers were devoted to study the corrosion of aluminum in different aqueous solutions [2–7], and research into their electrochemical behavior and corrosion inhibition in wide variety of media [8–13].

Hydrochloric acid and sulphuric acid solutions are used for pickling of aluminium or for its chemical or electrochemical etching. It is very important to add corrosion inhibitors to decrease the rate of metal dissolution in such solutions. An important method of protecting materials against deterioration from corrosion is by using inhibitors [14–16]. Acid inhibitors have many important roles in the industrial field as a component in pre-treatment composition, in cleaning

solution for industrial equipment and in acidization of oil wells. The inhibition of aluminium and its alloys in acidic solutions were extensively studied using organic compounds [17–24]. It was found that the organic compounds are effective corrosion inhibitors due to their ability to form an adsorbed protective film at the metal surface. The adsorption of the surfactant on the metal surface can markedly change the corrosion resisting properties of the metal [25, 26]. So the study of the relations between the adsorption and corrosion inhibition is of great importance.

Some Schiff bases have recently reported as effective corrosion inhibitors for steel [27, 28], aluminium [29], aluminium alloys [30, 31], and copper [32] in acidic media. Due to the presence of the $>C=N$ group, electronegative nitrogen, sulfur and/or oxygen atoms in the molecules, Schiff bases should be good corrosion inhibitors. The action of such inhibitors depends on the specific interaction between the functional groups and the metal surface. So it is very important to clarify the interactions between inhibitor molecules and metal surfaces in order to search new and efficient corrosion inhibitors [33–36].

In earlier work the inhibition of corrosion of zinc in sulphuric acid by Schiff bases of ethylenediamine [37], ortho-substituted aniline-N-salicylidenes [38], ortho-, meta-, and para-aminophenol-N-salicylidenes [39], meta-substituted aniline-N-salicylidenes [40] and Salicylidene-N-N²-morpholine [41] has been reported.

In the present work, the inhibitive effectiveness of o-Chloroaniline-N-(p-methoxy benzylidene) [o-CANPMB] and p-Chloroaniline-N-(p-methoxy benzylidene) [p-CANPMB] have been studied in retarding corrosion of Al-Mg alloy in 2.0 M HCl.

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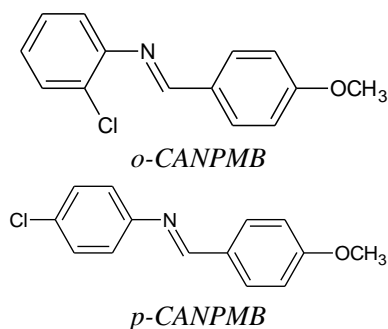
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Weight loss method, galvanostatic polarization, electrochemical impedance spectroscopy (EIS) and quantum chemical calculation techniques were used to investigate the inhibiting influence of inhibitors.

2. EXPERIMENTAL

2.1. Synthesis of Schiff bases

The Schiff bases used in the present work were synthesized from equimolar amount of p-methoxy benzaldehyde and corresponding aniline (o- and p-chloro aniline) through a condensation reaction in ethanol media as per described by Shah et al. [42]. o-CANPMB and p-CANPMB are insoluble in water but soluble in ethanol. The compounds were characterized through its structure data [IR data (Figure 1)] and its purity was confirmed by thin-layer chromatography (TLC). The chemical structure of the investigated compounds are given below:



2.2. Electrodes and electrolytes

Corrosion test were performed using coupons prepared from Al-Mg alloy. The chemical composition (wt%) of the Al-Mg alloy sample is Mg(2.6%), Cu(0.1%), Si(0.6%), Fe(0.5%), Mn(0.5%), Cr(0.4%) and balance Al. Rectangular specimens of Al-Mg alloy of size 6 cm × 3 cm and thickness 0.087 cm with a small hole of about 2 mm diameter just near the upper end of the specimen were used for the determination of weight losses. The specimens were polished with '0', '00', '000' and '0000' grade Oakey emery paper. The specimens degreased by A. R. carbon tetrachloride (sulphur free).

For polarization and impedance measurements, metal coupons of circular design, diameter 2.802 cm with a handle 3 cm long and 0.5 cm wide and thickness 0.087 cm with a small hole of about 2 mm diameter just near the upper end of the specimen were used. The handle and the back of the coupon and of the auxiliary platinum electrode were coated with Perspex leaving only the circular portion of the specimen of apparent surface area 6.156 cm² exposed to the solution.

The corrosive solution (2.0 M HCl) was prepared by dilution of analytical grade 37% HCl (NICE) with

double distilled water. The concentration range of employed inhibitor was 0.001% to 0.5% in 2.0 M HCl. The used all chemicals for preparation of Schiff bases were AR grade (MERCK).

2.3. Measurements

Three methods namely weight loss method, impedance spectroscopy, polarization study and quantum chemical calculation were used to determine the corrosion inhibition efficiencies of o-CANPMB and p-CANPMB.

2.3.1. Weight loss method

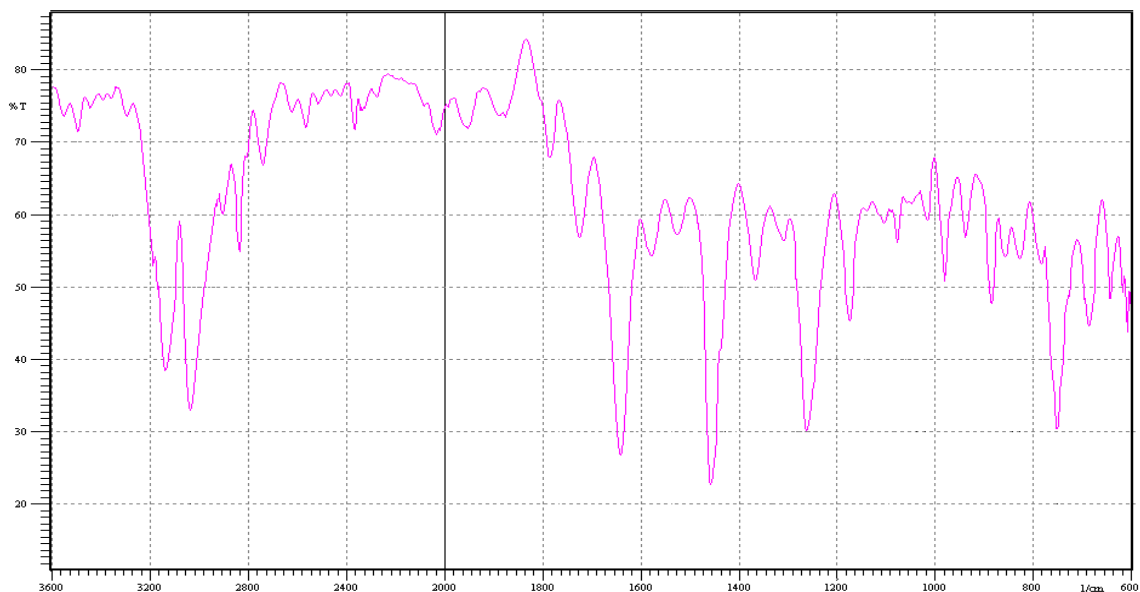
In weight loss method, the specimens were exposed to 2.0 M HCl solution containing controlled addition of o-CANPMB and p-CANPMB in the range of 0.001% to 0.5% inhibitor concentration. One specimen only was suspended by a glass hook in each beaker containing 230 ml of the test solution which was open to the air at 35° ± 0.5°C, to the same depth of about 1.5cm below the surface of the test solution. The experiments were repeated at different temperatures, ranging from 35° ± 0.5°C to 65° ± 0.5°C in the absence and presence of 0.5% inhibitor's concentration after 30 minutes.

2.3.2. Electrochemical measurements

Electrochemical experiments were carried out using a standard electrochemical three-electrode cell. Al-Mg alloy was used as working electrode, platinum as counter electrode and saturated calomel electrode (SCE) as reference electrode. The test solution was contained in a H-type (80 ml in each limb) Pyrex glass cell with Luggin capillary as near to the electrode surface as possible and a porous partition to separate the two compartments. The potential was measured against a saturated calomel electrode (SCE), in polarization study. The specimens were exposed to 2.0 M HCl solution containing controlled addition of 0.001%, 0.05% and 0.5% inhibitor concentration in polarization study.

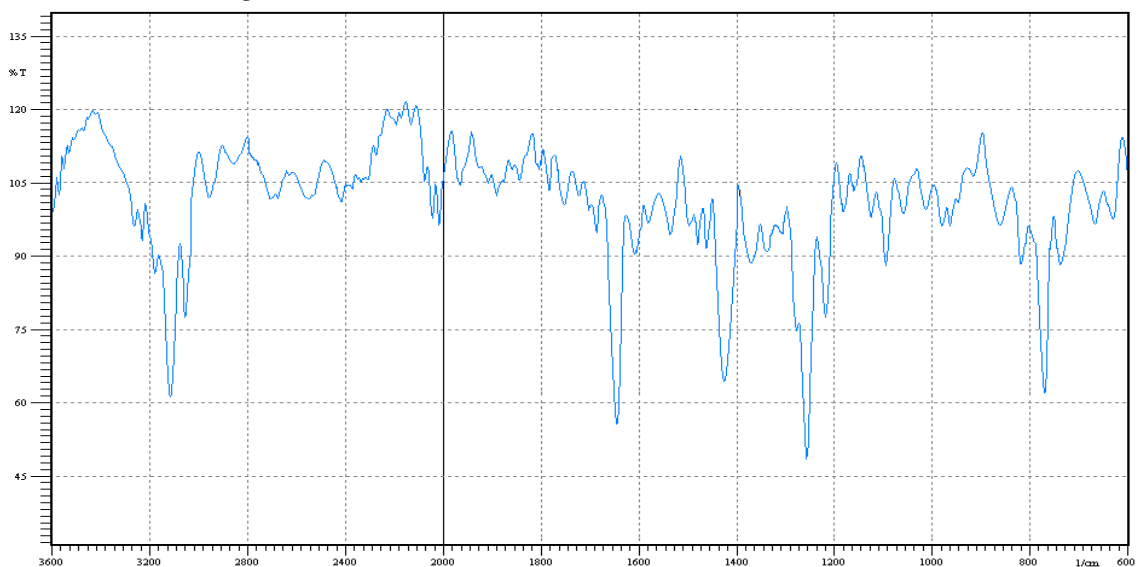
The corrosion parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}) and Tafel plots were measured in polarization method. In this study, the current density was varied in the range of 2×10^{-4} to 3.25×10^{-2} A cm⁻².

Electrochemical impedance measurements were carried out in the frequency range of 20 kHz – 0.1 Hz at the open circuit potential, after 30 minutes of immersion, by applying amplitude of 5 mV sine wave ac signal (AUTOLAB) in the range of 0.001% to 0.1% of inhibitor concentration. Double layer capacitance (C_{dl}) and charge transfer resistance (R_{ct}) values were calculated from Nyquist plots as described by Hosseini [43]. EIS data were analyzed using frequency response analyzer (FRA) electrochemical setup.



o-chloroaniline-*N*-(*p*-methoxy benzylidene) [*o*-CANPMB]

aromatic ring :- 3130 nm, >C=N- :- 1642 nm, -C-OCH₃ :- 1263 nm, -C-Cl :- 754 nm



m-chloroaniline-*N*-(*p*-methoxy benzylidene) [*p*-CANPMB]

aromatic ring :- 3165 nm, >C=N- :- 1634 nm, -C-OCH₃ :- 1242 nm, -C-Cl :- 737 nm

Figure 1 - IR Spectra of *o*-CANPMB and *p*-CANPMB

2.3.3 Quantum chemical calculations

The quantum chemical calculation was performed using Discovery studio 2.1 (Accelrys Inc.USA) program. MNDO semi-empirical method was employed to obtain the optimized geometry.

3. RESULTS AND DISCUSSION

3.1. Weight loss method

3.1.1. Effect of inhibitor concentration

The weight loss method of monitoring corrosion rate is useful because of its simple application and

reliability [44]. Weight loss of Al-Mg alloy was determined after 30 minute of immersion in 2.0 M HCl in the absence and presence of various concentrations of *o*-CANPMB and *p*-CANPMB at 35°C. Table-1 shows that the calculated values of inhibition efficiency (%IE) and surface coverage (θ) for Al-Mg alloy dissolution in 2.0 M HCl in the absence and presence of inhibitors.

The inhibition efficiency (%IE) and surface coverage (θ) were calculated using following equations [45],

$$\text{Inhibition efficiency (\%IE)} = \frac{W_u - W_i}{W_u} \times 100 \quad (1)$$

$$\text{Surface coverage } (\theta) = \frac{W_u - W_i}{W_u} \quad (2)$$

where W_u and W_i are the weight loss of Al-Mg alloy in 2.0 M HCl in the absence and presence of o-CANPMB and p-CANPMB.

Table 1 - Corrosion parameters for Al-Mg alloy in the presence and absence of different concentrations of o-CANPMB and p-CANPMB obtained from weight loss measurement at $35^\circ\text{C} \pm 0.5^\circ\text{C}$ for exposure period of 30 minutes

Inhibitor	Concentration (% V/V)	Weight loss (mg dm^{-2})	Surface coverage (θ)	(%IE)
Blank	-	1120	-	-
o-CANPMB	0.001	617	0.4491	44.9
	0.01	364	0.6750	67.5
	0.05	221	0.8026	80.3
	0.10	141	0.8741	87.4
	0.50	19	0.9830	98.3
p-CANPMB	0.001	388	0.6535	65.4
	0.01	263	0.7651	76.5
	0.05	165	0.8526	85.3
	0.10	96	0.9142	91.4
	0.50	5	0.9955	99.6

It is clearly seen from the Table 1 that corrosion rates were reduced in the presence of o-CANPMB and p-CANPMB compared to their absence for Al-Mg alloy in 2.0 M HCl. Inhibition efficiency as given in Table-1 is found to increase with increase in concentration of inhibitors. Inhibition efficiency increases with inhibitor concentration to reach 99.6% for o-CANPMB and 98.3% for p-CANPMB at 0.5%, respectively. Increased inhibition efficiency with concentration indicates that more o-CANPMB and p-CANPMB components are adsorbed on the metal surface at higher concentration leading to greater surface coverage.

This actually shows that the addition of inhibitors to the acid solution retards the corrosion rate of metal and that the extent of retardation is concentration depended. Both o-CANPMB and p-CANPMB inhibit the corrosion of Al-Mg alloy in 2.0M HCl in the range of concentrations studied but p-CANPMB is found to be more effective than o-CANPMB.

3.1.2. Adsorption behavior

As known that organic inhibitors establish their inhibition via the adsorption of the inhibitors molecules onto the metal surface. For organic inhibitors that have the ability to adsorb strongly on metal surface, thus impeding the dissolution reaction, the surface coverage (θ) can be evaluated as the inhibition efficiency. The relationship between the inhibition efficiency and bulk concentration of the inhibitor at constant temperature, which is known as isotherm, gives an insight into the adsorption process.

It is generally assumed that the adsorption of the inhibitor at the metal/solution interface is the first step in the mechanism of inhibition in aggressive media. Two main types of interaction can describe the adsorption of inhibition namely: 1) Physical adsorption, 2) Chemical adsorption. The proceeding of physical adsorption requires the presence of electrically charged metal surface and charged species in the bulk of the solution [46]. While chemical adsorption process involved charge sharing or charge transfer from the inhibitor molecules to the vacant p-orbital in Al surface [46].

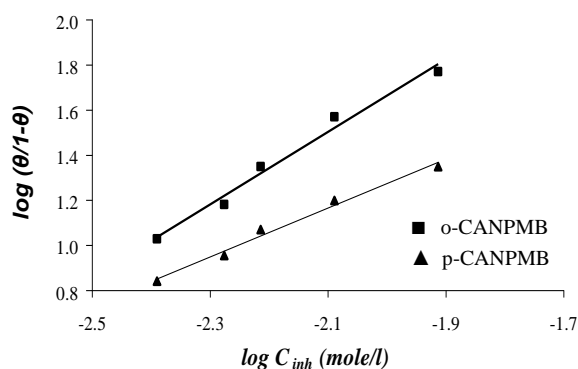


Figure 2 - Langmuir isotherm for adsorption of Schiff bases on the Al-Mg alloy metal surface

The extent of corrosion inhibition depends on the surface conditions and the mode of adsorption of the inhibitors [47], under the assumptions that the corrosion of the covered parts of the surface is equal to zero and that corrosion takes place only on the uncovered parts of the surface. The interaction between the inhibitor and the metal surface can be examined by the adsorption isotherm. The values of surface coverage, θ , for the different concentrations of the studied inhibitors have been used to explain the best adsorption isotherm to determine the adsorption process. The surface coverage (θ) values were calculated from Eq.(2) and shows in Table 1. The data obtained from weight loss method has been tested with several adsorption isotherms [Langmuir, Freundlich, Temkin]. Langmuir adsorption isotherm was found to fit well with our experimental data. A straight line was obtained on plotting $\log(\theta/(1-\theta))$ vs

$\log C_{inh}$ (concentration of inhibitors) as shown in Figure 2, which suggested that the adsorption of the inhibitors used for 2.0 M HCl solution on metal follows Langmuir adsorption isotherm given by Eq.3.

$$C_{inh} = \frac{\theta}{K(1-\theta)} \quad (3)$$

where C_{inh} is the inhibitor concentration, θ is the surface coverage values and K is the equilibrium constants of adsorption process. Thus, these results suggest that there are no interaction or repulsion forces between the adsorbed molecules. Langmuir isotherm assumed that the solid surface contains a fixed number of adsorption sites and each site holds

one adsorbed species [48] and the adsorption of organic molecule on the adsorbent is monolayer.

3.1.3. Effect of temperature

The temperature could affect the interaction between the metal surface and acidic media in the absence and presence of inhibitors. The effect of temperature on the inhibition efficiency in 2.0 M HCl containing 0.5% of o-CANPMB and p-CANPMB at temperature ranging 35°C to 65°C was obtained to calculate the thermodynamic parameters. The results are given in Table-2.

Table 2 - Effect of temperature on weight loss and inhibition efficiency for Al-Mg alloy in 2.0 M hydrochloric acid

Inhibitor	Concentration (% V/V)	Weight loss (mg dm ⁻²) at temperature			
		35° C	45° C	55° C	65° C
Blank	-	1120	2399	4910	7608
o-CANPMB	0.5	19 (98.3%)	56 (97.7%)	133 (97.3%)	375 (95.1%)
p-CANPMB	0.5	5 (99.6%)	19 (99.2%)	80 (98.4%)	160 (97.9%)

At constant inhibitor concentration the inhibition efficiency decreases with increasing temperature. This is due to increased effect of temperature on the dissolution process of metal and partial desorption of the inhibitor from the metal surface. The decrease in inhibition efficiency shows that the film formed on the metal surface is less protective at higher temperature.

3.1.4 Thermodynamic parameters

In acidic solution the corrosion rate is related to temperature by Arrhenius equation [49],

$$\rho = A \exp\left(-\frac{E_a}{RT}\right) \quad (4)$$

where ρ is corrosion rate determined from the weight loss measurement, E_a is the apparent activation energy, A is the Arrhenius constant, R is the molar gas constant and T is the absolute temperature. The apparent activation energy was determined from the slopes of $\log \rho$ versus $1/T \times 10^4$ graph depicted in Figure 3.

The values of activation energies were calculated and given in Table-3. These values indicate that the presence of inhibitors increase the activation energy of the metal dissolution reaction. Inspection of Table-3 shows that the values of E_a determined in solutions containing o-CANPMB and p-CANPMB are higher

then that of in the absence of inhibitors (blank). The increase in E_a in the presence of inhibitor may be interpreted as physical adsorption that occurs in the first stage [50]. Szaues and Brandt [51], explained that the increase in activation energy can be attributed to an appreciable decrease in the adsorption of the inhibitor on the metal surface with increase in temperature. A corresponding increase in the corrosion rate occurs because of the greater area of metal that is consequently exposed to the acid environment [52].

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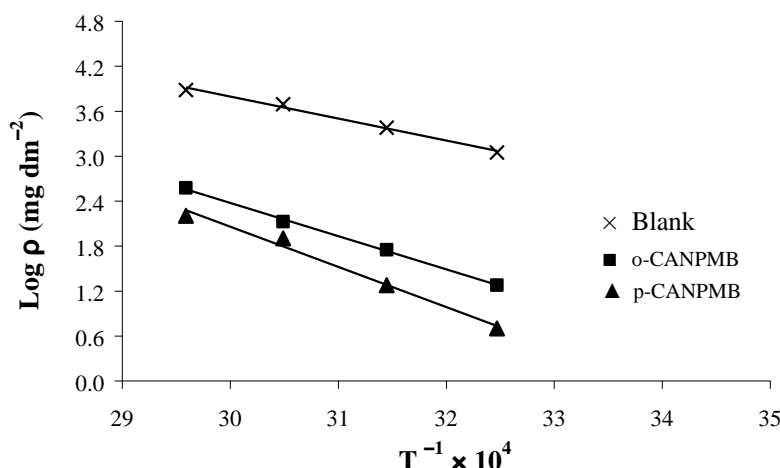


Figure 3 - Plotting $\log \rho$ vs. $T^{-1} \times 10^4$ to calculate the activation energy of corrosion process in the presence and absence of o-CANPMB and p-CANPMB

Table 3 - Thermodynamic parameters and activation energy for inhibitor adsorption in 2.0 M HCl for temperature range of 35°- 65°C at 0.5% Inhibitor Concentration.

Inhibitor	Temperature	E_a (kJ mol ⁻¹)	Q_{ads} (kJ mol ⁻¹)	ΔG_{ads} (kJ mol ⁻¹)
Blank	-	59.8	-	-
o-CANPMB		85.8	-30.5	-30.9
p-CANPMB		102.1	-46.4	-33.3

The higher values of E_a in the presence of o-CANPMB and p-CANPMB compared to that in their absence and the decrease in the inhibition efficiency (%IE) with rise in temperature is interpreted as an indication of physisorption [53, 54].

If it is assumed that the inhibitor is adsorbed on the metal surface in the form of a monolayer film, covering at any instant a fraction, θ , of the metal surface in a uniform random manner, then the heat of adsorption (Q_{ads}) of the inhibitor can be calculated from the equation [55]:

$$(Q_{ads}) = 2.303R \left\{ \log \frac{\theta_2}{1-\theta_2} - \log \frac{\theta_1}{1-\theta_1} \right\} \left(\frac{T_1 T_2}{T_2 - T_1} \right) \quad (5)$$

where θ_1 and θ_2 are the values of surface coverage at temperature T_1 and T_2 , respectively.

The values of the free energy of adsorption (ΔG_{ads}) were calculated from the following equation [55]:

$$\log C_{inh} = \log \frac{\theta}{1-\theta} - \log B \quad (6)$$

where

$$\log B = -1.74 - \left[\frac{\Delta G_{ads}}{2.303RT} \right] \quad (7)$$

The values of ΔG_{ads} and Q_{ads} are shown in Table-3. The negative values of free energy of adsorption ΔG_{ads} , as recorded in Table-3, indicate the spontaneous adsorption of inhibitor molecules on metal surface. The large negative values of ΔG_{ads} indicate the spontaneous adsorption of inhibitor molecules and are usually characteristics of strong interaction with the metal surface [56, 57].

Generally values of ΔG_{ads} up to -20 kJ mol⁻¹ are consistent with the electrostatic interaction between the charged molecule and the charged metal (physical adsorption), while those more negative than -40 kJ mol⁻¹ involve charge sharing or transfer from inhibitor molecules to the metal surface to form a coordinate type of bond (chemical adsorption) [56]. In the present work, the calculated ΔG_{ads} values are almost slightly less negative than -40 kJ mol⁻¹ indicating that the adsorption of inhibitor molecule is merely physisorption or chemisorption but obeying a comprehensive adsorption (physical and chemical adsorption). It was observed, limited decrease in the absolute value of ΔG_{ads} with an increase in the temperatures, indicating that the adsorption was somewhat unfavorable with increasing experimental temperature, indicating that physisorption has the major contribution while chemisorption has the minor contribution in the adsorption mechanism.

The negative values of the heat of adsorption (Q_{ads}) indicates that the adsorption process is exothermic in nature. It also indicates that the degree of surface coverage decreased with rise in temperature, supporting the earlier proposed physisorption mechanism [58].

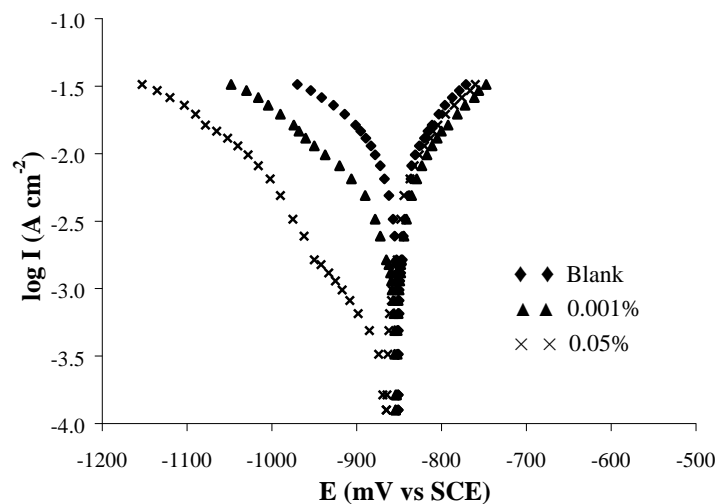
3.2. Galvanostatic polarization

Figure 4 shows that the cathodic and anodic polarization plots of Al-Mg alloy in 2.0 M HCl at 35°C in the absence and presence of different concentrations of o-CANPMB and p-CANPMB. Electrochemical parameters such as corrosion potential (E_{corr}), cathodic and anodic slopes (b_c and b_a) and corrosion current density (I_{corr}) were extracted by Tafel extrapolating the anodic and cathodic lines

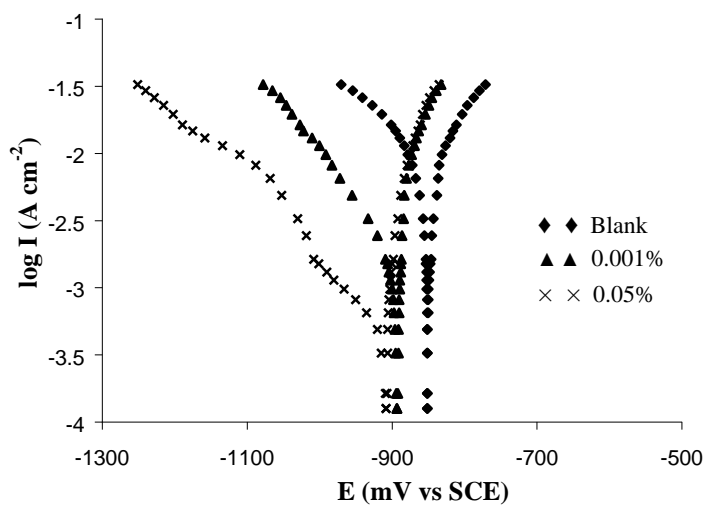
and are listed in Table 4. The inhibition efficiency (%IE) was calculated using the following equation [59, 60].

$$\text{Inhibition Efficiency (\%IE)} = \frac{I_{\text{corr}}^{\circ} - I_{\text{corr}}}{I_{\text{corr}}^{\circ}} \times 100 \quad (8)$$

where I_{corr}° and I_{corr} are uninhibited and inhibited corrosion current density, respectively.



(a)



(b)

Figure 4 - Anodic and cathodic polarization curves obtained for Al-Mg alloy metal at 35°C ± 0.5°C in 2.0 M HCl in various concentrations of studied Schiff bases (a) o-CANPMB, (b) p-CANPMB

From the results in Table-4 it can be observed that the values of corrosion current density of Al-Mg alloy in the inhibitor containing solutions were lower than those for the inhibitor free solution. The corrosion current densities at all inhibitor concentrations are decreased in the order o-CANPMB > p-CANPMB. This indicates on the more beneficial effect of inhibitors on corrosion inhibition of metal in

2.0 M HCl solution. From Figure 4, it is clear that both the cathodic and anodic reactions are inhibited and inhibition efficiency increased as the inhibitor concentration increased in acid media, but the cathode is more polarized. It is clear that the current density decreases with increasing of the concentration, this indicates that these compounds are adsorbed on the metal surface and hence inhibition occurs. The

polarization curves (Figure 4) show that these inhibitors have an effect on both, the cathodic and anodic slopes but the effect of inhibition is too small on anodic part so it can be ignored and inhibitor suppress only cathodic process at higher concentration, and indicate that the inhibitors act as adsorptive inhibitors (mainly cathodic), i.e., they retards the hydrogen evolution reaction via blocking the active reaction sites on the metal surface or even can screen the covered part of the electrode and therefore protect it from the action of the corrosion medium [61], which suggest that inhibitors are

powerfully inhibit the corrosion process of metal, and its ability as corrosion inhibitors are enhanced as its concentration is increased. The suppressed of cathodic process can be due to the covering of the surface with monolayer due to the adsorbed inhibitor molecules. Further inspection of Table-4 reveals also that E_{corr} values do not show any significantly change in the presence of various concentrations of the inhibitors suggesting that inhibitors can be classified as mixed type of inhibitors predominantly cathodic in 2 M HCl solution.

Table 4 - Electrochemical parameters of corrosion of Al-Mg alloy in the presence of different concentration of o-CANPMB and p-CANPMB at $35^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$ and corresponding inhibition efficiencies obtained from polarization method.

Inhibitor	Concentration (% W/V)	E_{corr} (mV)	b_a (mV/dec)	b_c (mV/dec)	I_{corr} for cathodic (A cm^{-2})	(%IE)
Blank	-	-851	113	121	6.309×10^{-3}	-
o-CANPMB	0.001	-854	134	146	2.454×10^{-3}	61.1
	0.05	-865	136	128	7.413×10^{-4}	88.3
p-CANPMB	0.001	-893	75	108	1.202×10^{-3}	80.9
	0.05	-908	98	126	3.467×10^{-4}	94.5

3.3 Electrochemical impedance spectroscopy (EIS)

The corrosion behavior of Al-Mg alloy in acidic solution in the absence and presence of inhibitors was investigated by the electrochemical impedance spectroscopy (EIS) at 35°C after 30 minute of immersion. The technique is based on the measurement of the impedance of the double layer at the metal/solution interface. Impedance diagrams are obtained for frequency range 20 kHz – 0.1 Hz at the open circuit potential for Al-Mg alloy in 2.0 M HCl in the presence and absence of inhibitors.

Table 5 - Impedance parameters and corresponding inhibition efficiency for the corrosion of Al-Mg alloy in the 2.0 M HCl.

Inhibitor	Concentration (% W/V)	R_s (ohm)	R_{ct} (ohm)	C_{dl} (μF)	(%IE)
Blank	-	1.036	2.89	109.7	-
o-CANPMB	0.001	1.015	5.29	103.0	45.2
	0.01	0.861	8.98	96.97	67.7
	0.05	0.838	15.20	88.61	80.9
	0.10	0.940	24.42	78.35	88.1
p-CANPMB	0.001	0.880	8.70	106.6	66.7
	0.01	0.923	12.67	98.21	77.1
	0.05	0.854	21.39	92.54	86.4
	0.10	0.813	37.35	84.71	92.2

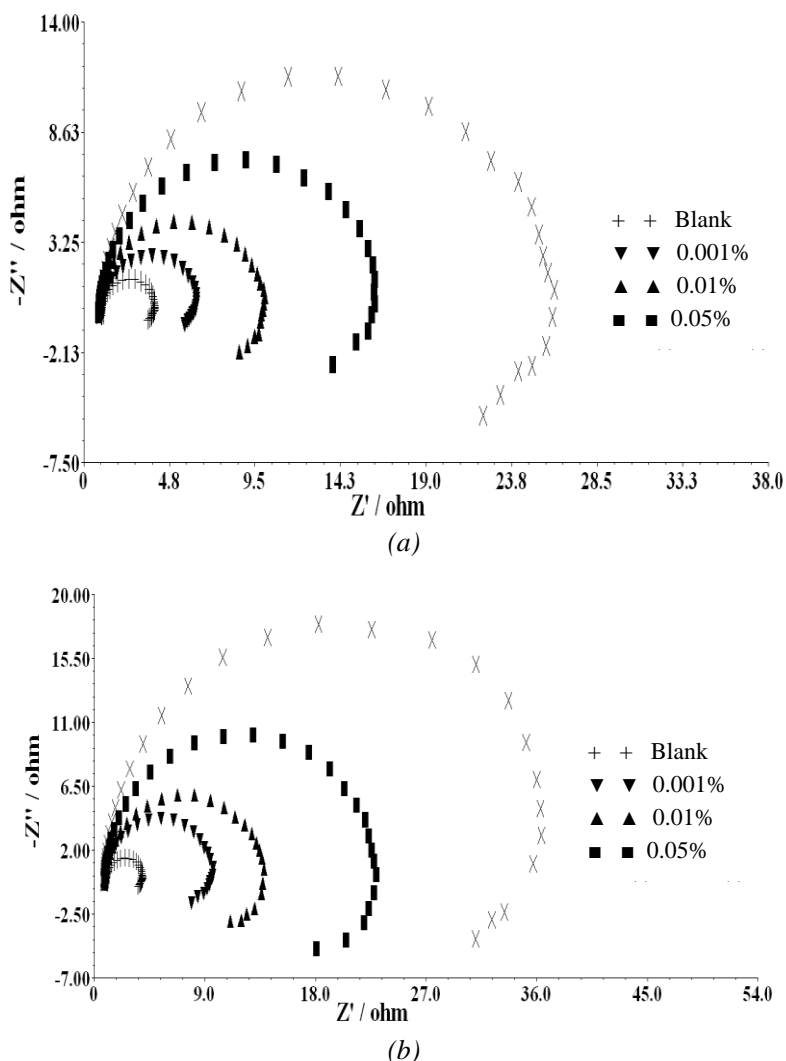


Figure 5 - Impedance plot obtained at 35°C in 2.0 M HCl in various concentrations of (a) o-CANPMB (b) p-CANPMB

The charge transfer resistance (R_{ct}) values were calculated from the difference in impedance at lower and higher frequencies as suggested by Tsuru et. al. [62]. To obtain the double layer capacitance (C_{dl}) the frequency at which the imaginary component of the impedance is maximal ($-Z''_{max}$) was found as represented as following equation,

$$C_{dl} = \frac{1}{\omega R_{ct}} \tag{9}$$

Table-5 gives values of charge transfer resistance (R_{ct}), double layer capacitance (C_{dl}) and solution

resistance (R_s) derived from Nyquist plots and inhibition efficiency (%IE) calculated by the following equation

$$\text{Inhibition Efficiency (\%IE)} = \frac{R_{ct} - R^{\circ}_{ct}}{R_{ct}} \times 100 \tag{10}$$

where R_{ct} and R°_{ct} are the charge transfer resistance in the HCl solution in the presence and absence of inhibitors, respectively. The corresponding Bode plots are show in Figure 6.

Table 6 - Quantum chemical parameters for used Schiff bases obtained from MNDO method.

Inhibitor	E_{Homo} (eV)	E_{Lumo} (eV)	ΔE (eV)	μ (Debye)	Surface area (\AA^2)	Inhibition efficiency (%IE)
o-CANPMB	-8.612	-0.868	7.744	1.309	268.7	83.2
p-CANPMB	-8.614	-0.951	7.663	3.355	270.0	88.7

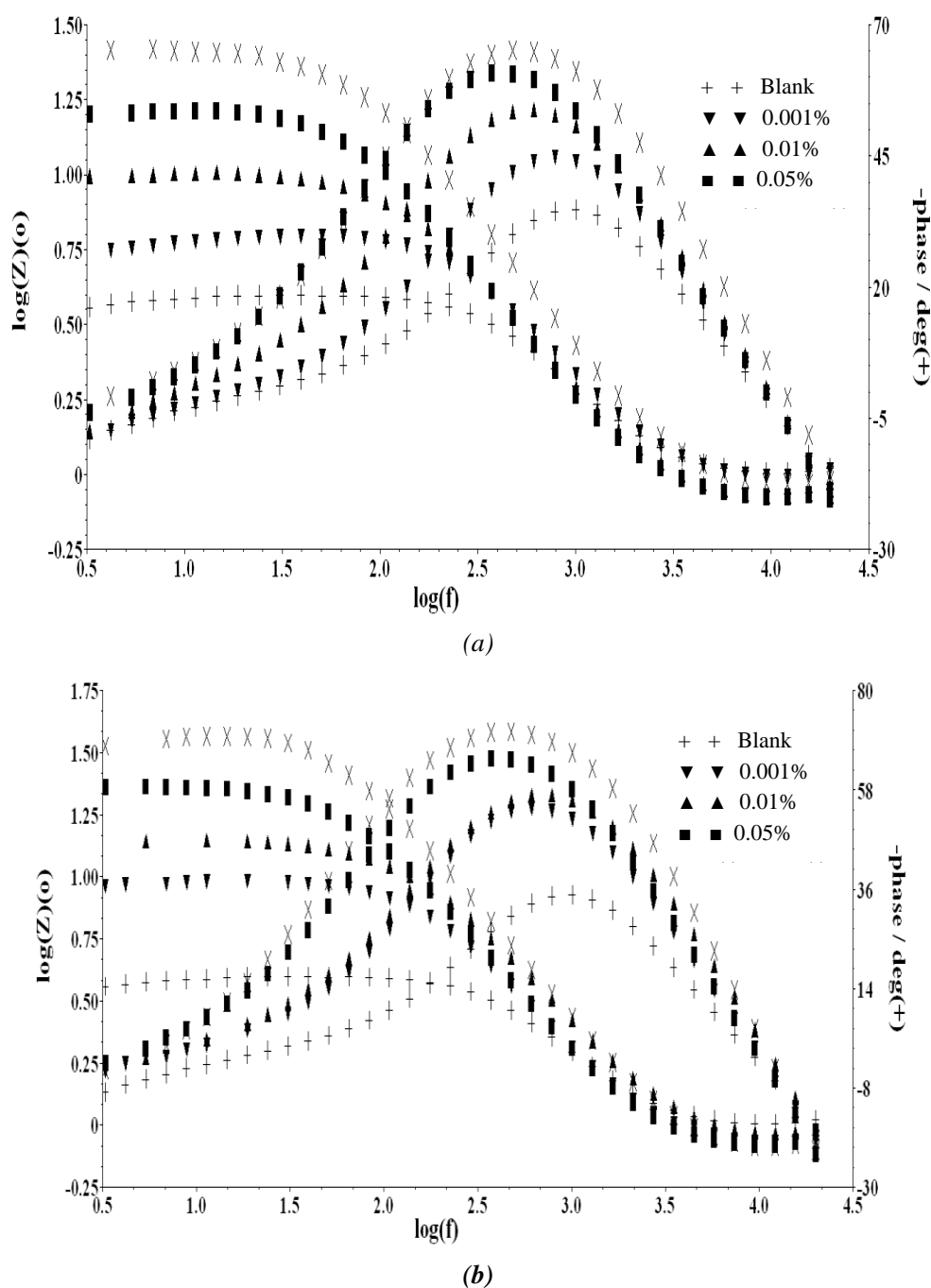


Figure 6 - Bode plots obtained at 35°C in 2.0 M HCl in various concentrations of (a) *o*-CANPMB (b) *p*-CANPMB

The impedance spectra for the Nyquist plots were analyzed by fitting to the equivalent circuit model shown in Figure 7, which has been used previously to model the aluminium/acid interface. The circuit comprises a solution resistance R_s , in series with the parallel combination of the charge transfer resistance R_t and a constant phase element (CPE), replaced with a double layer C_{dl} [63, 64].

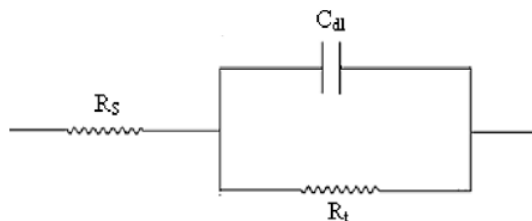


Figure 7 - The equivalent circuit model (Randle's model) used to fit the experimental result

Nyquist plots for Al-Mg alloy in 2.0 M HCl at various concentrations of inhibitors are presented in Figure 5. It is clear from these plots that impedance response of Al-Mg alloy in acid has significantly changed after the addition of inhibitor. As can be seen in Figure 5, Nyquist plots are depressed into the real axis and not perfect semicircles as expected from theory of EIS of assumed equivalent circuit and this is generally attributed to the inhomogeneity of the metal surface arising from surface roughness or interfacial phenomena [65, 66].

From Table-5. it is seen that R_{ct} values increase and C_{dl} values decrease with increasing inhibitor concentration. The decrease in C_{dl} values can be attributed to a decrease in local dielectric constant and/or an increase in the thickness of electrical double layer. This suggests that inhibitor molecules inhibit the corrosion rate by adsorption at metal /solution interface [67].

3.4. Quantum chemical study

To investigate the effect of molecular structure on the inhibition mechanism and inhibition efficiency, some quantum chemical calculations were performed.

Quantum structure-activity relationship (QSAR) has been used to study the effect of molecular structure on inhibition efficiency of used Schiff base compounds. However, satisfactory correlation has been recorded between the inhibition efficiency of other inhibitors and some quantum chemical parameters by other investigators [68-72].

The computation of some of the quantum chemical parameters such as the energies of the molecular orbitals, E_{Homo} (highest occupied molecular energy) and E_{Lumo} (lowest unoccupied molecular energy), $\Delta E = E_{Lumo} - E_{Homo}$ (energy of the gap), μ (dipole moment) as well as some other structural parameters have been obtained from MNDO semi empirical method and are given in Table 6.

Average values of inhibition efficiency were obtained using three experimental methods (weight loss, polarization and EIS) used for QSAR modeling. The optimized MNDO geometry of inhibitors is shown in Figure 8. It could easily be found that the molecules are planer which results in the good interaction between inhibitors and coating surface.

A linear regression analysis was made of relation between %IE and E_{Homo} , E_{Lumo} and μ values of the Schiff bases (o-CANPMB and p-CANPMB) following equations were obtained,

$$\%IE = -23599.8 - 2750 E_{Homo} \quad (r^2 = 1) \quad (11)$$

$$\%IE = 25.681 - 66.265 E_{Lumo} \quad (r^2 = 1) \quad (12)$$

$$\%IE = 79.681 + 2.688 \mu \quad (r^2 = 1) \quad (13)$$

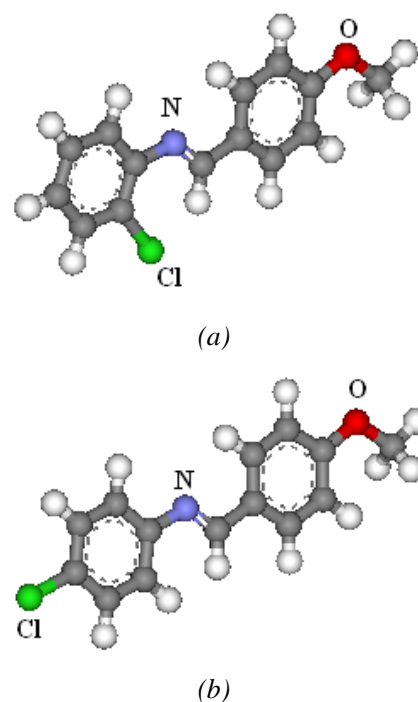


Figure 8 - Optimized molecular structure of (a) o-CANPMB (b) p-CANPMB

E_{Homo} is often associated with the electron donating ability of a molecule. High values of E_{Homo} are likely to indicate a tendency of the molecule to donate electrons to appropriate acceptors with low energy and empty molecular orbital. Therefore, the energy of the lowest unoccupied molecular orbital (E_{Lumo}) indicates the ability of the molecules to accept electrons. The lower values of E_{Lumo} , the more probable, it is the molecule would accept electrons.

The coefficient of E_{Lumo} in the Eq.12 is negative. This fact proves that the metal accept electrons from Schiff base compounds and feed back bonds form between metal and inhibitor molecules. Forming of feed back bond increases adsorption of Schiff base molecules on the metal surface and so increases the inhibition efficiencies of these in compounds. In the case of p-CANPMB E_{Lumo} is the lowest (-0.951) and the strong feed back bond form with respect to o-CANPMB. The forming of feed back bonds is the ability of the inhibitors to offer electrons, so the inhibition efficiency increases.

The negative sign of the coefficient of E_{Homo} can be concluded that the adsorption of these Schiff bases on the metal surface has not chemical mechanism and it may be physical [52]. Physical adsorption results from electrostatic interaction between the charged centers of molecules and charged metal surface which results in a dipole interaction of molecule and metal surface, so the positive sign of the coefficient of μ

suggest that these Schiff bases can be adsorbed on metal surface by physical mechanism.

The separation energy (energy gap) ΔE is an important parameter as a function of reactivity of the inhibitor molecules towards the adsorption on metallic surface. As ΔE values decrease, the reactivity of the molecule increasing leading to increase the inhibition of the molecules [73]. For, p-CANPMB, the ΔE has the value 7.663 eV, which can facilitate its adsorption on the metal surface and according has higher inhibition efficiency.

3.5. Mechanism of Inhibition

Organic compounds containing one or more polar units, which may be regarded as the reaction centre/centres for the adsorption process function as corrosion inhibitors. The adsorption bond strength is determined by the electron density on the atom (e.g., N, S, O, etc.) acting as the reaction centre and by the polarizability of the unit. Thus, organic corrosion inhibitors are adsorbed on the bulk metal, M, forming a charge transfer complex between their polar atoms and the metal:



The size, shape and orientation of the molecule, and the electron charge on the molecule determine the degree of adsorption and that way the effectiveness of the inhibitor. The inhibitors confer high degree of protection of Al-Mg alloy in hydrochloric acid when present in sufficient amount (0.5%) and function through adsorption on the metal surface following Langmuir adsorption isotherm. Galvanostatic polarization data have shown that the actions of the inhibitors are of mixed type with predominance on the cathodic regions.

The inhibitors contain three parts through which they can get adsorbed on the metal : a benzaldehydic part having an aromatic ring containing methoxy group ($-\text{OCH}_3$) in para-position, an iminic nitrogen ($>\text{C}=\text{N}-$) and aromatic ring with a chloro group ($-\text{Cl}$) in the ortho- and para- position. The first two are common to both the inhibitors studied and the compounds differ only by the position of the chloro group on the anilinic aromatic ring.

It is generally assumed that the adsorption of inhibitor at the metal/solution interface is the mechanism of inhibitor through electrostatic attraction between the charged molecules and charged metal. Inhibitors have been found to give an excellent inhibition due to the presence of the electron donating groups (such as $-\text{Cl}$, $-\text{OCH}_3$) on the Schiff bases structure, which increases the electron density on the

nitrogen of the $>\text{C}=\text{N}-$ group. Thus leads to be the strong adsorption of inhibitors on the metal surface thereby resulting in high inhibition efficiency.

The free energy of adsorption (ΔG_{ads}) and heat of adsorption (Q_{ads}) are negative, which suggest that the adsorption process is spontaneous and exothermic, and values of ΔG_{ads} ($<-40 \text{ kJ mol}^{-1}$) and E_a suggest that the adsorption is a physisorption type.

It is also possible that the compounds may form onium ions in acidic medium and move to the cathodic regions and then the adsorption will take place through the iminic nitrogen and also through the delocalized π -electrons of the benzene moiety. Then molecule will lie flat on the metal surface and further cover the adjoining positions of the surface. In p-CANPMB, the presence of $-\text{Cl}$ group with +R (resonance), $-\text{I}$ (inductive) effects will easily affect the electron density and activate of the aromatic ring.

4. CONCLUSION

The present study leads to the following the corrosion of Al-Mg alloy by o-CANPMB and p-CANPMB in 2.0 M HCl.

1. o-CANPMB and p-CANPMB have been found to be good candidates of corrosion inhibitors for Al-Mg alloy in 2.0 M HCl medium. The inhibition efficiency of the studied inhibitors, increase with increasing inhibitor concentration and decreases with increasing temperature.
2. The inhibitor molecules adsorbed on the metal surface and tend to retard the rate of corrosion by reducing the number of available surface sites for corrosion.
3. The adsorption of both inhibitors investigated follows the Langmuir adsorption isotherm.
4. Thermodynamic parameters (ΔG_{ads} , Q_{ads} and E_a) show that the studied compounds are adsorbed on Al-Mg alloy surface by an exothermic, spontaneous process and physical adsorption.
5. o-CANPMB and p-CANPMB inhibit both cathodic and anodic reactions by adsorption but tremendous polarization effect on cathode and hence behave like mixed type inhibitors.
6. Obtained results about inhibition efficiencies from weight loss method, polarization study and EIS are in good agreement with each other.

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ИЗВОД

ИНХИБИЦИЈА Al-Mg ЛЕГУРЕ У ХЛОРОВОДОНИЧНОЈ КИСЕЛИНИ УПОТРЕБОМ ШИФОВЕ БАЗЕ КАО КОРОЗИОНИХ ИНХИБИТОРА

Утицај неких ново синтетизованих Шифових база типа *o*-хлороанилин-*N*-(*p*-метокси бензилиден) и *p*-хлороанилин-*N*-(*p*-метокси бензилиден) на корозију Al-Mg легуре у 2 M HCl је био истражен. Истраживање је обухватило одређивање губитка тежине, галваностатска поларизациона мерења и мерење методом електрохемијске импедансне спектроскопије. Ефикасност инхибиције се повећавала са повећањем концентрације инхибитора али се смањивала са повећањем температуре. Нађено је да су се Шифове базе адсорбовале на металној површини према Ленгмировој изотерми. Термодинамички параметри и активациона енергија су били срачунати да елаборирају механизам инхибиције. Резултати поларизационих мерења показују да ове Шифове базе делују као мешовити тип, али катода је првенствено поларизована.

Кључне речи: алуминијум, електрохемијска импедансна спектроскопија, поларизација, губитак тежине, инхибиција

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