# The Study of Corrosion Inhibition of Al-pure in HCl by Some New Organic Schiff Bases Using Chemical and Electrochemical Methods

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## Abstract

The inhibiting effects of some newly synthesized Schiff bases on the corrosion of Al-Pure in 1.0 M HCl have been studied by means of the chemical and electrochemical methods. The Schiff bases m-Chloroaniline-N-benzylidene (*m*-CANB), *p*-Chloroaniline–N-benzylidene (p-CANB), Benzylamine-N-(p-methoxy benzylidene) (BANPMB) and 2-Phenylethylamine-N-(p-methoxy benzylidene) (2PANPMB) were synthesized from benzyldehyde or substituted benzyldehyde with the corresponding amines and characterized by IR studies. The corrosion inhibition properties of these compounds on Al-Pure in 1.0 M HCl were investigated by weight loss, galvanostatic polarization and electrochemical impedance techniques. The weight loss study showed that the inhibition efficiency increases with increase in the concentration of the inhibitor and was found to be inversely related to temperature. The values of activation energy ($E_a$), free energy of adsorption ($\Delta G_{ads}$) and heat of adsorption ($Q_{ads}$) were calculated from the temperature data. The adsorption of these compounds on aluminium surface follows the Langmuir adsorption isotherm. The galvanostatic polarization data show that these compounds studied are mixed type inhibitors with predominant effect on the cathode. The mechanism of corrosion inhibition is also proposed.

***Keywords :*** *Al-Pure, Schiff bases, Inhibition efficiency, EIS, Adsorption isotherm.*

## Introduction

Aluminium plays an important role in several industrial applications such as reaction vessels, pipes, automobiles, food-handling containers, machinery, aviation, buliding and chemical batteries because of its excellent physical and mechanical properties and its outstanding corrosion resistance. For these reasons, this metal is commonly used in electrolytic capacitors and as current collectors in Li-ion batteries, exactly where ILs could be employed as electrolytes. Aluminium is corrosion resistant in neutral aqueous solutions when aggressive ions, such as halides, are not present [1]. This resistance is attributed to the presence of a thin, adherent and protective passive film,

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which is either naturally or electrochemically formed. This film consists mainly of oxides, oxyhydroxides and hydroxides [2-4], with a twin-layer structure formed by an inner thin protective barrier oxide layer and an outer non-protective porous hydrous oxide. In acidic and alkaline environments, the solubility of this passive oxide increases, and aluminium exhibits uniform corrosion [5]. Acid solutions are used for the removal of undesirable scale and rust in many industrial processes. Corrosion inhibitors are needed to reduce the corrosion rates of metallic materials in these media. [6-8].

The use of inhibitors is one of the most practical methods for protection of metal against corrosion, especially in acidic media [9]. As acidic media, hydrochloric acid (HCl) and sulfuric acid ($H_2SO_4$) are cleaners and pickling acids. Among various acid organic inhibitors, N-containing compounds are considered to be the most effective corrosion inhibitors [10].

These inhibitors block the active sites and enhance the adsorption process, thus decreasing the corrosion rate and extending the life of the equipment [11, 12]. More recent studies have shown that the inhibitive effect for aluminium and its alloys in acid solutions can be enhanced by several nitrogen containing organic compounds. The nitrogen containing compounds are known to be efficient inhibitors forming covalent bond with metal surface; their adsorption depends on physicochemical properties such as functional group, steric factor and the electronic structure of the molecule [13].

Schiff bases have been investigated for their corrosion inhibition effect of various metals and alloys in acid media. In literature, some Schiff bases have recently reported as effective corrosion inhibitors for aluminium and zinc in acid media [14, 15, 16, 17, 18]. 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 aldehydes because Schiff bases ($R_2C=NR$) have both the features (heteroatom and $\pi$-electrons) combined with their structure. $\pi$-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 p-orbital or 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 group in its structure. Schiff base molecule may reasonably justify its use as an effective corrosion inhibitor [19].

In this present paper, we investigate the action of (m-CANB), (p-CANB), (BANPMB) and (2PANPMB) as corrosion inhibitors for Al-Pure in 1.0 M HCl solution by galvanostatic polarization, electrochemical impedance spectroscopy (EIS) and weight loss method. The thermodynamic parameters and activation energy have been estimated from

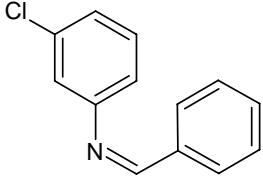the data concerned the study of the effect of temperature on the corrosion process.
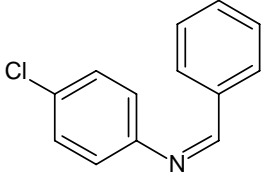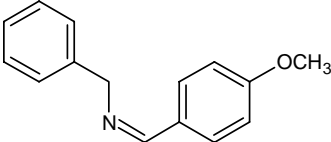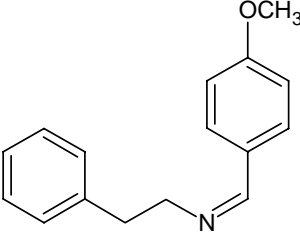
**Experimental**

*Synthesis of Schiff bases*

The Schiff bases were synthesized from equimolar amount of benzyldehyde or p-methoxy benzaldehyde with corresponding amines such as m-aniline, p-aniline, benzylamine and 2-phenylethylamine through a condensation reaction in ethanol media as per described by Desai et al. [20].

**Scheme 1.** Name, structure and registry number of the used compounds.

| Sr. No. | Structure | Name and abbreviation | Registry number | IR Spectroscopy |
|---|---|---|---|---|
| 1. |  | m-Chloroaniline-N-benzylidene (m-CANB) *Physical properties* : Brownish liquid, insoluble in water, soluble in ethanol. b.p. : 334.3°C, 0.9452 W/mg | 7519-65-5 | aromatic ring :- 3128 cm$^{-1}$, >C=N– :- 1635 cm$^{-1}$, –C–Cl :- 741 cm$^{-1}$ |
| 2. |  | p-Chloroaniline-N-benzylidene (p-CANB) *Physical properties* : Off white crystalline substance, insoluble in water, soluble in ethanol. m.p. : 307.5°C, 1.412 mW/mg | 780-21-2 | aromatic ring :- 3122 cm$^{-1}$, >C=N– :- 1640 cm$^{-1}$, –C–Cl :- 750 cm$^{-1}$ |
| 3. |  | Benzylamine-N-(p-methoxy benzylidene) (BANPMB) *Physical properties* : Dark yellowish liquid, insoluble in water, soluble in ethanol. b.p. : 225.1°C, 0.5268 W/mg | 622-72-0 | aromatic ring :- 3080 cm$^{-1}$, >C=N– :- 1647 cm$^{-1}$, –C–OCH$_3$ :- 1258 cm$^{-1}$ |
| 4. |  | 2-Phenylethylamine-N-(p-methoxy benzylidene) (2PANPMB) *Physical properties* : Yellowish liquid, insoluble in water, soluble in ethanol. | 3240-96-8 | aromatic ring :- 3072 cm$^{-1}$, >C=N– :- 1645 cm$^{-1}$, –C–OCH$_3$ :- 1232 cm$^{-1}$ |

*Electrodes and electrolytes*

The 99.9% pure aluminium was used in this study. Rectangular specimens of Al-Pure of size 6 cm × 3 cm and thickness 0.050 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 0.050 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 cm$^2$ exposed to the solution.

The corrosive solution (1.0 M HCl) was prepared by dilution of analytical grade 37% HCl (NICE) with double distilled water. The concentration range of employed inhibitors was 0.001 to 0.5% in 1.0 M HCl. All chemicals for preparation of Schiff bases were used A. R. grade (MERCK).

*Measurement*

Three methods namely polarization study, electrochemical impedance spectroscopy and weight loss method were used to determine the corrosion inhibition efficiencies of Schiff bases.

*Electrochemical measurements*

Electrochemical experiments (polarization study and electrochemical impedance study) were carried out using a standard electrochemical three-electrode cell. Al-Pure 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 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 $2 \times 10^{-4}$ to $3.25 \times 10^{-2}$ 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 60 minutes of immersion, by applying amplitude of 5 mV sine wave ac signal (AUTOLAB). Double layer capacitance ($C_{dl}$) and charge transfer resistance ($R_{ct}$) values were calculated from Nyquist plots as described by Hosseini [21]. EIS data were analyzed using frequency response analyzer (FRA)

electrochemical setup.

*Weight loss (chemical) method*

In weight loss method, the specimens were exposed to 1.0 M HCl solution containing controlled addition of inhibitors 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 60 minutes.

**Results and discussion**

*Galavanostatic polarization study*

The galvanostatic polarization curves of Al-Pure in 1.0 M HCl at 35°C in the presence and absence of two concentrations of all the inhibitors are shown in Figure 1. (a to e),

and it was observed that in the presence of inhibitors (m-CANB, p-CANB, BANPMB and 2PANPMB), both of the cathodic and anodic curves show lower current density than those observed in the uninhibited solution. This behavior indicated that all the Schiff bases have effect on both cathodic and anodic reactions of corrosion process. Therefore, these compounds could be classified as mixed type inhibitors at lower inhibitor concentration. The inhibitors shift the potential in the negative direction; this effect is more evident at higher concentration, which means that the inhibitor affect cathodic reaction more than anodic reaction at higher concentration. The values of cathodic Tafel slope ($b_c$) and anodic Tafel slope ($b_a$) were calculated from the linear region of the polarization curves are given in Table 1. The corrosion current density ($I_{corr}$) was determined from the intersection of the linear parts of the cathodic curves with stationary corrosion potential ($E_{corr}$).



(a)



(b)

(c)                                                    (d)



(e)
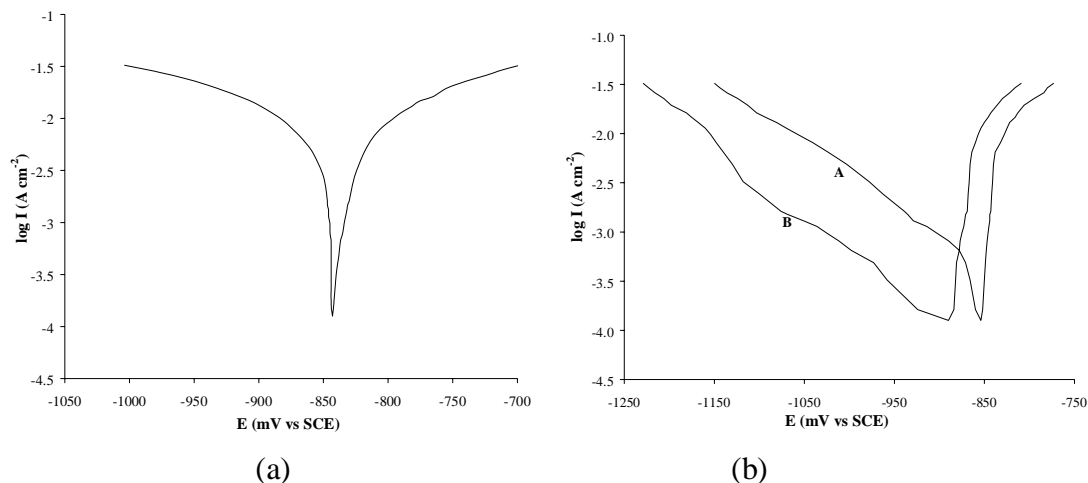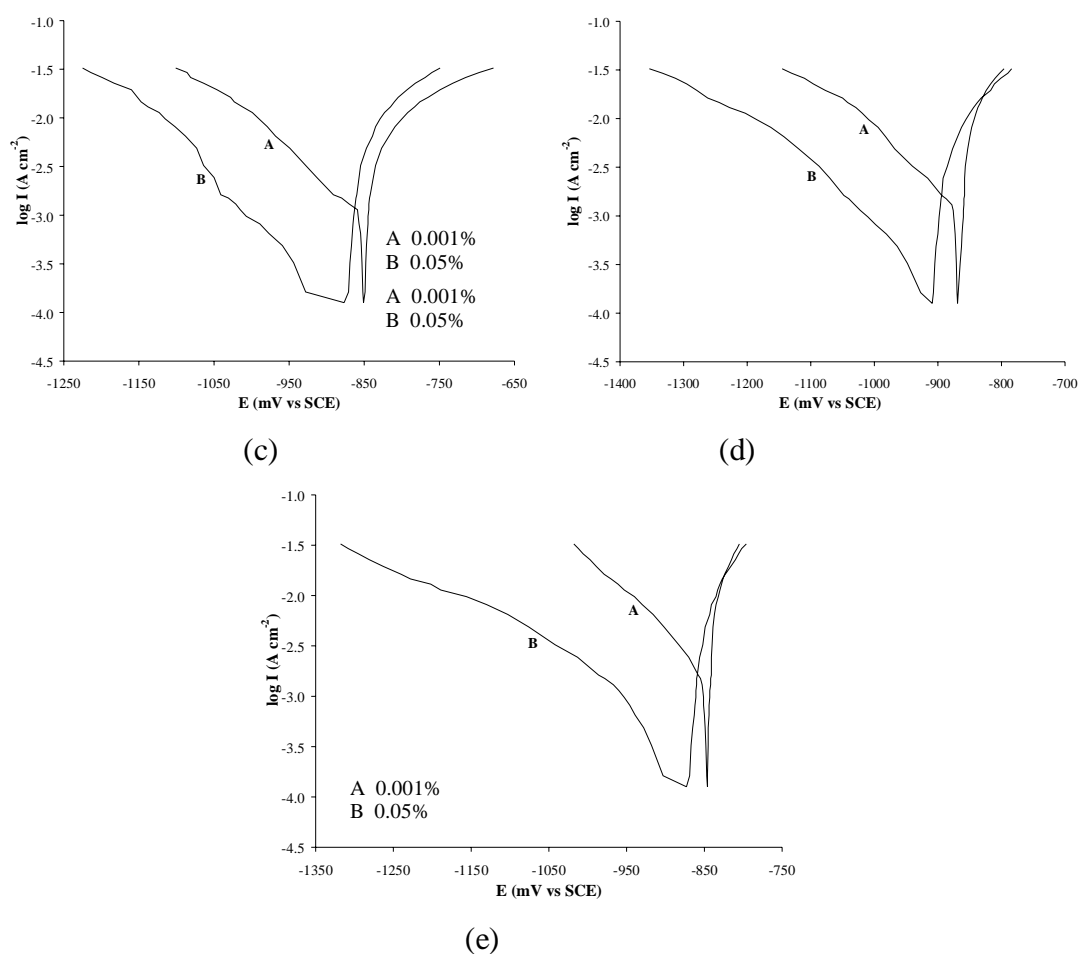
**Figure 1.** Anodic and cathodic polarization curves obtained for Al-Pure metal at 35°C ± 0.5°C in 1.0 M HCl in various concentrations of studied Schiff bases (a) Blank, (b) m-CANB, (c) p-CANB, (d) BANPMB and (e) 2PANPMB.

The percentage inhibition efficiency (%IE) was calculated using the following equation:

$$Inhibition\ efficiency\ (\%IE) = \frac{I^{\circ}corr - Icorr}{I^{\circ}corr}\ X\ 100 \qquad (1)$$

Where $I^{\circ}_{corr}$ and $I_{corr}$ are the corrosion current densities in the absence and presence of the inhibitor.

**Table 1.** Electrochemical parameters of corrosion of Al-Pure in the presence of two different concentration of inhibitors at 35°C ± 0.5°C and corresponding inhibition efficiencies obtained from polarization method.

| Inhibitor | Concentration (%) | $E_{corr}$ (mV) | $b_a$ (mV/dec) | $b_c$ (mV/dec) | $I_{corr}$ for cathodic (A cm⁻²) | (%IE) |
|---|---|---|---|---|---|---|
| Blank | - | -843 | 113 | 120 | $4.467 \times 10^{-3}$ | - |
| *m*-CANB | 0.001 | -854 | 50 | 182 | $0.812 \times 10^{-3}$ | 81.8 |
| | 0.05 | -890 | 63 | 166 | $3.235 \times 10^{-4}$ | 92.8 |
| *p*-CANB | 0.001 | -851 | 98 | 132 | $0.977 \times 10^{-3}$ | 78.1 |
| | 0.05 | -877 | 100 | 165 | $3.890 \times 10^{-4}$ | 91.3 |
| BANPMB | 0.001 | -869 | 56 | 139 | $1.023 \times 10^{-3}$ | 77.1 |
| | 0.05 | -909 | 89 | 160 | $2.691 \times 10^{-4}$ | 94.0 |
| 2PANPMB | 0.001 | -846 | 34 | 130 | $1.479 \times 10^{-3}$ | 66.9 |
| | 0.05 | -873 | 71 | 178 | $3.981 \times 10^{-4}$ | 91.1 |

From the results, it is observed that in presence of inhibitors, there is a marginal shift in $E_{corr}$ and a decrease in $I_{corr}$. The inhibitor present on the surface of metal hinders the attack of corrosive medium, and thereby reduces the $I_{corr}$. The values of inhibition efficiency (%IE) increased with increase in inhibitor concentration, which indicates higher surface coverage of the metal. Corrosion potential values indicated that inhibitors act as mixed type of inhibitors with predominant effect on cathode.

At 0.05% inhibitor concentration the order of inhibition efficiencies from extrapolation of cathodic Tafel line to $E_{corr}$ is given below:

*BANPMB > m-CANB > p-CANB ≥ 2PANPMB*
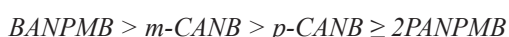
*Electrochemical impedance spectroscopy (EIS)*

The corrosion of Al-Pure in 1.0 M HCl solution in the absence and presence of *m*-CANB, *p*-CANB, BANPMB and 2PANPMB were investigated by EIS at the open circuit potential condition. Nyquist plots for Al-Pure obtained at the influence in the absence and presence of inhibitors at 0.1% concentration is given in Figure 2. The Nyquist diagram obtained with 1.0 M HCl shows only one capacitive loop and the diameter of the semicircle increases on increasing the inhibitor concentration suggesting that the formed inhibitive film was strengthened by the addition of inhibitors. All the obtained plots show only one semicircle and they were fitted using one time constant equivalent model (Randle's model) with capacitance (C) and charge transfer resistance ($R_{ct}$).
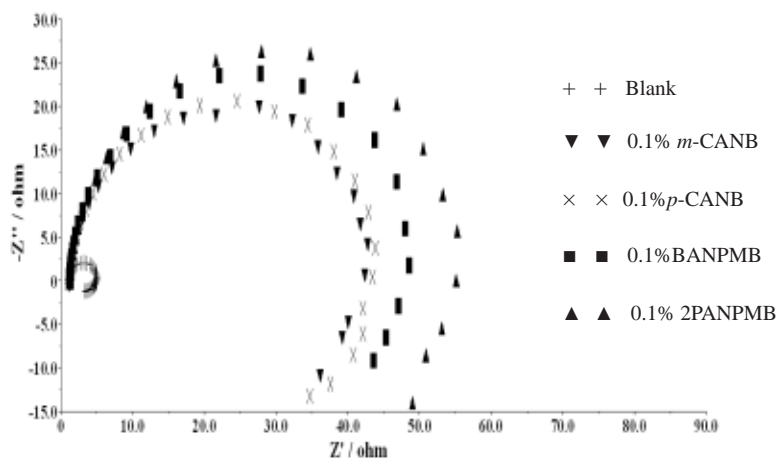


**Figure 2.** Impedance plot obtained at 35ºC in 1.0 M HCl at 0.1% of concentration.

The FRA (frequency response analyzer) is used for impedance data analysis and the fit parameters are listed in Table 2. Where, $R_{ct}$, $R_s$ and $C_{dl}$ are the charge transfer resistance, solution resistance and double layer capacitance, respectively. From the impedance measurements, inhibition efficiency was calculated using the following expression:

*Inhibition efficiency (%IE)* $= \dfrac{Rct - R^\circ ct}{Rct} \times 100$ (2)

Where, $R_{ct}$ and $R^\circ_{ct}$ are the charge transfer resistance of the electrode with and without the inhibitor, respectively. The lower capacitance ($C_{dl}$) values for 1.0 M HCl medium indicates the inhomogeneity of surface of the metal roughened due to corrosion. The $C_{dl}$ values decreases on increasing the inhibitor concentration and reaches very low value for the optimum concentrations of all the studied systems indicating that the reduction of charges accumulated in the double layer due to formation of adsorbed inhibitor layer [22]. In

these cases, $R_s$ values can be neglected because the value is too small as compact to that of the value of $R_{ct}$. The charge transfer resistance ($R_{ct}$) of double layer increases on increasing the concentration of the inhibitors upto the optimum level indicating the decreased corrosion rate (i.e., increased corrosion inhibition). The inhibition efficiencies calculated according to the impedance results are in the order :

*BANPMB ≥ m-CANB > p-CANB > 2PANPMB*

and these results follow the same trend as the polarization results.

**Table 2.** Impedance parameters and corresponding inhibition efficiencies for the corrosion of Al-Pure in 1.0 M HCl.

| Inhibitor | Concentration (%) | $R_s$ (ohm) | $R_{ct}$ (ohm) | $C_{dl}$ (µF) | (%IE) |
|---|---|---|---|---|---|
| **Blank** | - | 1.079 | 3.99 | 85.7 | - |
| *m*-**CANB** | 0.1 | 1.086 | 53.39 | 70.2 | 92.5 |
| *p*-**CANB** | 0.1 | 1.140 | 43.24 | 69.9 | 90.8 |
| **BANPMB** | 0.1 | 1.366 | 53.11 | 68.5 | 92.5 |
| **2PANPMB** | 0.1 | 1.148 | 41.10 | 70.2 | 90.3 |

The increase in inhibiting efficiencies with the increase in the concentrations of the studied Schiff bases show that the inhibitory actions are may be due to the adsorption of the inhibitors on Al-Pure surface. It is generally assumed that the adsorption of inhibitor at the metal/solution interface is the mechanism of inhibition through electrostatic attraction between the charged molecules and charged metal. Among the compounds investigated in the present study, *m*-CANB and BANPMB

have been found to give an excellent inhibition due to the presence of the electron donating group (such as $-OCH_3$ in BANPMB) and electronegative group (such as $-Cl$ in m-CANB) on the Schiff base structure, which increase the electron density on the nitrogen of the >C=N− group. These lead to the strong adsorption of *m*-CANB and BANPMB on the metal surface thereby resulting in high inhibition efficiency.

*Weight loss method*

The corrosion of Al-Pure in 1.0 M HCl medium containing various concentrations of *m*-CANB, *p*-CANB, BANPMB and 2PANPMB (0.001%, 0.01%, 0.05%, 0.1% and 0.5%) were studied by weight loss method. The calculated values of inhibition efficiency (%IE) and the degree of surface coverage (θ) are shown in Table 3. The percentage inhibition efficiency (%IE) and the degree of surface coverage (θ) were calculated using following equations:

$$\text{Inhibition efficiency (\%IE)} = \frac{W_u - W_i}{W_u} \times 100 \quad (3)$$

$$\text{Surface coverage } \theta = \frac{W_u - W_i}{W_u} \quad (4)$$

where, $W_u$ = weight loss of Al-Pure in uninhibited acid and $W_i$ = weight loss of Al-Pure in inhibited acid.

From the results, it is observed that all Schiff bases inhibit the corrosion of Al-Pure in 1.0 M HCl solution at all concentrations used in this study and the inhibition efficiency was seen to increase with increasing additive concentration upto the optimum level after which there is no significant change in the inhibition efficiency. The studied inhibitors attain maximum (%IE) at 0.5% inhibitor concentration. Thus, we deduce that these Schiff bases are good inhibitors for Al-Pure corrosion and (%IE) are found to be in the following order:

*BANPMB > m-CANB > 2PANPMB ≥ p-CANB*

at their optimum concentration.

**Table 3.** Corrosion parameters for Al-Pure in the presence and absence of different concentrations of Schiff bases obtained from weight loss measurement at 35°C ± 0.5°C for exposure period of 60 minutes.

| Inhibitor | Concentration (%) | Weight loss (mg dm⁻²) | Surface coverage (θ) | (%IE) |
|---|---|---|---|---|
| **Blank** | - | 2300 | - | - |
| **m-CANB** | 0.001 | 813 | 0.647 | 64.7 |
| | 0.01 | 537 | 0.767 | 76.7 |
| | 0.05 | 293 | 0.873 | 87.3 |
| | 0.10 | 182 | 0.921 | 92.1 |
| | 0.50 | 24 | 0.990 | 99.0 |
| **p-CANB** | 0.001 | 927 | 0.597 | 59.7 |
| | 0.01 | 637 | 0.723 | 72.3 |
| | 0.05 | 341 | 0.852 | 85.2 |
| | 0.10 | 206 | 0.910 | 91.0 |
| | 0.50 | 38 | 0.983 | 98.3 |
| **BANPMB** | 0.001 | 683 | 0.703 | 70.3 |
| | 0.01 | 455 | 0.802 | 80.2 |
| | 0.05 | 276 | 0.880 | 88.0 |
| | 0.10 | 179 | 0.922 | 92.2 |
| | 0.50 | 16 | 0.993 | 99.3 |

| | 0.001 | 892 | 0.612 | 61.2 |
|---|---|---|---|---|
| **2PANPMB** | 0.01 | 610 | 0.735 | 73.5 |
| | 0.05 | 358 | 0.844 | 84.4 |
| | 0.10 | 236 | 0.897 | 89.7 |
| | 0.50 | 27 | 0.988 | 98.8 |

The difference in their inhibitive action can be explained on the basis of the type of functional group present in the benzene ring which contributes to the adsorption strength through the donor acceptor bond between the non-bonding electron pairs and the vacant orbitals of the metal surface. In order to have better understanding of the inhibition mechanism of Schiff bases, we already mentioned a detailed study on corrosion inhibition of these compounds using galvanostatic polarization and electrochemical impedance spectroscopy.

*Effect of temperature and thermodynamic parameters*

To study the effect of temperature on the inhibition efficiency, weight losses were determined at 35°C, 45°C, 55°C and 65°C in 1.0 M HCl, plain as well as inhibited. The results given in Table 5 show that the inhibition efficiency increases with inhibitor concentration but decreased with temperature. Increasing of inhibition efficiency with the increase of inhibitor concentration indicates that, these compounds are acting as adsorption inhibitors. But decrease in inhibition efficiency with increase in temperature can be explained by desorption of inhibitor molecules on the metal surface (Table 4).

**Table 4.** Effect of temperature on weight loss and inhibition efficiency for Al-Pure in 1.0 M hydrochloric acid.

| Inhibitor | Concentration (%) | Weight loss (mg dm$^{-2}$) at temperature | | | |
|---|---|---|---|---|---|
| | | 35°C | 45°C | 55°C | 65°C |
| **Blank** | - | 2300 | 4436 | 5303 | 5808 |
| *m*-CANB | 0.5 | 24 (99.0%) | 54 (98.8%) | 122 (97.7%) | 249 (95.7%) |
| *p*-CANB | 0.5 | 38 (98.3%) | 92 (97.9%) | 168 (96.8%) | 314 (94.6%) |
| BANPMB | 0.5 | 16 (99.3%) | 43 (99.0%) | 95 (98.2%) | 211 (96.4%) |
| 2PANPMB | 0.5 | 27 (98.8%) | 60 (98.6%) | 119 (97.8%) | 276 (95.2%) |

Activation energies for Al-Pure dissolution process can be evaluated from the following relationship [23]:

$$\rho = k \, exp \left( - \frac{E_a}{RT} \right) \qquad (5)$$

Where, $\rho$ is the corrosion rate, $E_a$ is the activation energy, T is the temperature and k is constant. Plotting log $\rho$ versus $T^{-1} \times 10^4$ gave straight lines with slope of $-E_a / R$ (Figure 3). Calculated activation energies are given in Table 5. As we see from these data, activation energies strongly increase in the presence of inhibitors. This fact indicates that the adsorption of these inhibitors occurs through physical mechanism [24].
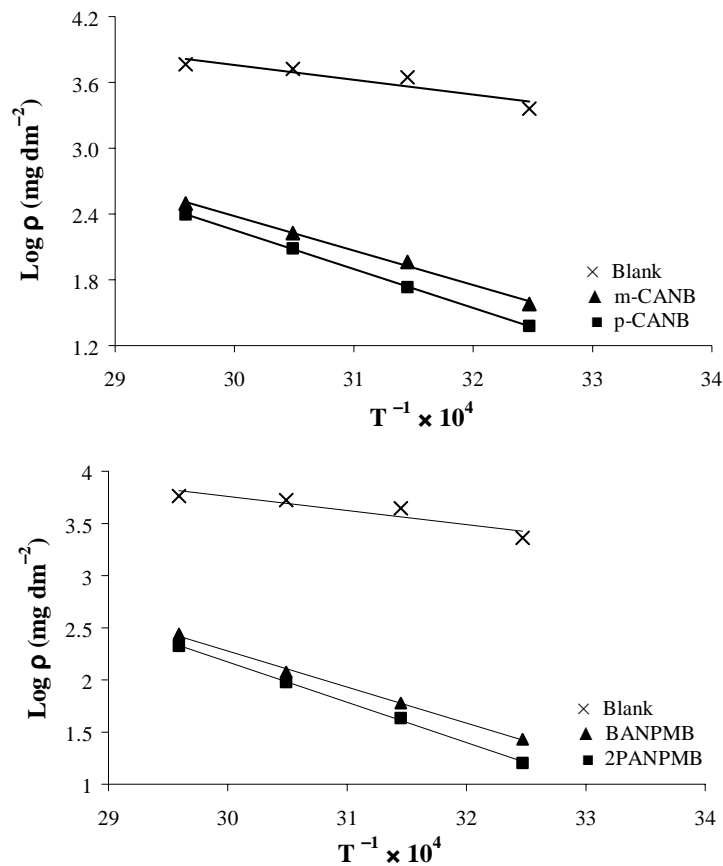


**Figure 3.** Plotting log $\rho$ vs. $T^{-1} \times 10^4$ to calculate the activation energy of corrosion process in the presence and absence of inhibitors.

**Table 5.** Thermodynamic parameters and activation energy for inhibitor adsorption for corrosion of Al-Pure in 1.0 M HCl.

| Inhibitor | $E_a$ (kJ mole$^{-1}$) | $Q_{ads}$ (kJ mole$^{-1}$) | $\Delta G_{ads}$ (kJ mole$^{-1}$) |
|---|---|---|---|
| **Blank** | 25.9 | - | - |
| ***m*-CANB** | 67.8 | -43.5 | -31.4 |
| ***p*-CANB** | 57.7 | -36.0 | -30.3 |
| **BANPMB** | 74.1 | -49.4 | -32.3 |
| **2PANPMB** | 65.7 | -42.3 | -31.5 |

*Adsorption isotherm*

Adsorption plays a very important role in the inhibition of metallic corrosion by organic molecules. Many investigators have used Langmuir adsorption isotherm to study inhibitor characteristics assuming that the inhibitors adsorbed on the metal surface decrease the surface area available for electrode reactions to take place [25]. The values of surface coverage (θ) (θ values are given in Table 4) related to different concentrations of the inhibitors (*m*-CANB, *p*-CANB, BANPMB and 2PANPMB) in 1.0 M HCl at 35°C and for 60 min. have been used to explain the best isotherm to determine the adsorption process.

The adsorption of organic corrosion inhibitor onto metal-solution interface is a substitutional adsorption process between organic molecules and the metallic surface. The Langmuir isotherm for monolayer adsorption [26] is given by the equation :

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

Where, θ is the surface coverage degree, $C_{inh}$ is the inhibitor concentration in the electrolyte and K is the equilibrium constant of the adsorption process. The plots of versus log $C_{inh}$ of $\frac{\theta}{(1-\theta)}$ m-CANB, p-CANB, BANPMB and 2PANPMB in 1.0 M HCl give straight lines as shown in Figure 4.
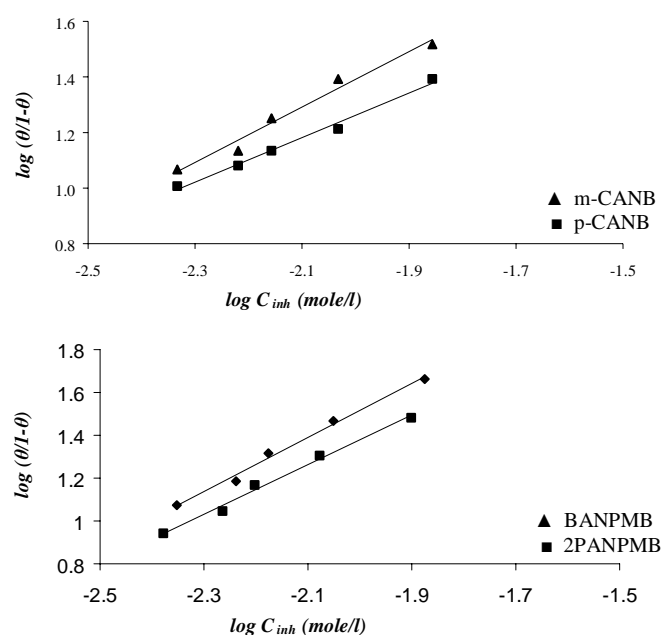


**Figure 4.** Langmuir isotherm for adsorption of Schiff bases on the Al-Pure metal surface.

If it is assumed that the inhibitors are 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 :

$$(Q_{ads}) = 2.303R$$

$$\left\{ \log \frac{\theta_2}{1-\theta_2} - \log \frac{\theta_1}{1-\theta_1} \right\} \left( \frac{T_1 T_2}{T_2 - T_1} \right) \quad (7)$$

The values of the free energy of adsorption ($\Delta G_{ads}$) were calculated from the following equation [27] :

$$log\ C_{inh} = log\ \frac{\theta}{1-\theta} - \log B \quad (8)$$

*where, $log\ B = -\ 1.74 - \left( \Delta Gads \middle/ 2.303 RT \right) \quad (9)$*

The values of $\Delta G_{ads}$ and $Q_{ads}$ are listed in Table 5. The negative values of $\Delta G_{ads}$ indicate that the adsorption of inhibitor molecule on Al-Pure surface is a spontaneous process. Generally the free energy of adsorption values of –20 kJmol$^{-1}$ or less negative are associated with an electrostatic interaction between charged molecules and charged metal surface (physical adsorption); those of −40 kJmol$^{-1}$ or more negative involves charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate covalent bond (chemical adsorption) [28]. In the present study, the values of $\Delta G_{ads}$ is found to be within the range –40 to –20 kJmol$^{-1}$, probably mean that the adsorption of inhibitors (*m*-CANB, *p*-CANB, BANPMB and 2PANPMB) on Al-Pure surface involves both physical adsorption and chemical adsorption. The negative values of $Q_{ads}$ indicated that the adsorption of used inhibitor on Al-Pure surface is exothermic.

*Mechanism of inhibition*

Various theories have been put forward to explain the mechanism of corrosion by different types of inhibitors. Organic substances capable of forming onium ions give cations in acid solutions which would be adsorbed on the cathodic part of the metal surface [29]. This could act as a mechanical barrier for H$^+$ ions to reach the metal surface. If the inhibitor molecule is in an ionic form, it may also get attached to the metal surface by electrostatic attraction to the anodic or cathodic sites, depending upon the charge on inhibitor molecule.

Most organic inhibitors are compounds with at least one polar functional group, having hetero atoms like nitrogen, sulphur, oxygen or in some cases, selenium and phosphorous. The polar unit is usually regarded as the reaction centre for the adsorption process. In such cases, the adsorption bond strength is determined by the electron density on the functional atom and by the polarisability of the unit. Amine-type inhibitors have electron-donating ability and their action is attributed to the adsorption of the molecule on the metal surface through an unshared pair of electrons belonging to the nitrogen atom [30]. The inhibitor molecules are adsorbed chemically on the surface of the bulk metal, M, forming a charge transfer complex between the polar atom/atoms and the metal;

$$M + RnX \leftrightarrow M : XRn \quad (9)$$

Where:

M = metal

X = ligand or polar atom

Rn = subsisted group on polar atom or ligand. Further, this inhibitor, which is in a distinct ionic form, also may get attached to the metal surface of opposite polarity through electrostatic attraction. The adsorbed layer then will block the dissolution of the metal. The size, orientation and shape of the molecule, and the electronic charge on it, will determine the degree of adsorption and hence the effectiveness of the inhibitor.

Molecular structure of inhibitor is the main factor determining its characteristics. Presence of heteroatoms (S, N, O) with free electron pairs, aromatic rings with delocalized $\pi-$electrons, high molecular weight alkyl chains, substituted groups, in general improves inhibition efficiency. The effect of electron-donor groups in particularly favorable. Group position is also important [31].

It is noticed that higher inhibition efficiency is achieved by application of organic compounds to the metal surface. Benzylidenes and p-methoxy benzylidenes give good protection in strongly acidic media. But the inhibition efficiency of four Schiff bases can change only by the different position of substituent groups on inhibitors. Order of inhibition efficiency of four inhibitors is:

*BANPMB ≥ m-CANB > p-CANB ≥*
*2PANPMB*

BANPMB and 2PANPMB have same substituent group (i.e., −OCH$_3$ group). But BANPMB has –CH$_2$– (methylene group)

group on anilinic part, where 2PANPMB has –CH$_2$–CH$_2$– (ethylene group) group on anilinic part. In *m*-CANB and *p*-CANB, there is one difference that is the position of −Cl (chloro) group. *m*-CANB, *p*-CANB, BANPMB and 2PANPMB contain seven conjugated double bonds (six in the aromatic ring + one iminic). The adsorption takes place due to the iminic group. 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 $\pi$-electrons of the benzene moiety.

**Conclusion**

1. Results obtained from the experimental data show all four Schiff bases are effective inhibitors for the corrosion of Al-Pure in 1.0 M HCl. Inhibition efficiencies increase with increase in the concentration of the studied inhibitor but decrease with rise in temperature.

2. The adsorption of m-CANB, p-CANB, BANPMB and 2PANPMB on Al-Pure surface from 1.0 M HCl obeys the Langmuir adsorption isotherm.

3. Phenomenon of physical adsorption is proposed from the values of thermodynamic parameters ($E_a$, $\Delta G_{ads}$) obtained for the inhibitors.

4. All Schiff bases act as mixed type inhibitors with predominant action on cathode and their inhibition efficiencies tend to increase with

increasing inhibitor concentration.

5. The EIS measurement clarified that the values of $R_{ct}$ increased with the addition of the inhibitors, while the $C_{dl}$ value decreased, indicating the formation of a surface film.

6. Obtained results about inhibition efficiencies (within range of ±5%) from weight loss, polarization study and EIS are in good agreement with each other.

7. Among the four inhibitors, BANPMB gives good inhibition because of the presence of the electron donating group such as $-OCH_3$ on Schiff base structure, which increases the electron density on the nitrogen of the >C=N− group. This leads to the strong adsorption of BANPMB on the metal surface thereby resulting in high inhibition efficiency.

**Acknowledgments**

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