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Effect of HCl Concentration on Inhibition Efficiency of A New Schiff Base on Aluminum Corrosion

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In this work the corrosion inhibition of aluminum in different concentration of hydrochloric acid by using a synthesized salicylaldiminato Schiff base *bis*-(2-hydroxy-3-methoxy)-1,6-diaminohexane salicylaldimine are studied by weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements. The increase of HCl concentration resulted in increasing of the dissolution rate of aluminum in according to pourbaix diagram. The results of experiments indicated that this inhibitor acted as mixed inhibitor on aluminum corrosion, also increasing the inhibitor concentration up to 100 ppm resulted in reducing the rate of corrosion of aluminum in different concentration of HCl solution. Further increasing of the inhibitor concentration had an adverse effect on the efficiency of this inhibitor. The inhibition process was attributed to the formation of adsorbed film on the metal surface that protecting the metal against corrosive agents. The Langmuir adsorption isotherm fits well with the experimental data. Increasing the HCl concentration did not affect on the percentage of inhibition efficiency of inhibitor, however, the optimum inhibitor concentration remained 100 ppm for various HCl concentration. The microstructure of aluminum in various concentration of HCl without and with optimum concentration of inhibitor after 1h immersion are studied by SEM.

Key Words: Corrosion, Inhibition, Potentiodynamic, Electrochemical.

INTRODUCTION

Aluminum is an important material for use in many applications, such as automobiles, aviation, household appliances, containers and electronic devices, owing to its many favourable characteristics including its good electrical and thermal conductivities, low density, high ductility and good corrosion resistance[1]. It is well known that a compact, strongly adherent and continuous film is developed on aluminum upon exposure to the atmosphere or aqueous solution. This is responsible for the corrosion resistance of aluminum in most environments. Nevertheless, in some cases, aluminum may be exposed to high concentration of acids or bases or may be used in neutral solution containing pitting agents such as chloride ions[2]. For this

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reason the suitable corrosion inhibitors should be used. The corrosion mechanism of aluminum in chloride solutions has been investigated in a number of studies[3-8]. Some organic compound such as Schiff base compounds are used to decrease the aluminum corrosion in acid media[9]. Organic compounds having polar groups, such as oxygen, sulfur and nitrogen[10-19] and heterocyclic compounds containing functional groups and conjugated double bonds[20-23] have been studied by many investigators, for protection of aluminum and its oxide film. Some research works reveal that inhibition efficiency of Schiff base is much greater than corresponding amines and aldehydes. This may be due to the presence of a -C=N- group in the molecule[24]. It has been assumed that inhibitor is adsorbed onto the metal surface. The process of adsorption of inhibitors are influenced by the nature and surface charge of the metal, the chemical structure of organic inhibitors, the distribution of charge in the molecule and the type of aggressive electrolyte. The chemisorptions are the principle type of interaction between organic inhibitors and the metal surface[25,26]. The aim of this work is to investigate the inhibitive action of a synthesized Schiff base *bis*-(2-hydroxy-3-methoxy)-1,6-diaminohexane salicylaldimine toward the corrosion of aluminum in different concentration of HCl, by weight loss and electrochemical measurements.

EXPERIMENTAL

Pure aluminum specimens containing in (wt %) 0.0596 Si, 0.0260 Fe, 0.0001 Cu, 0.0002 Mn, 0.0124 Zn, 0.0017 Ti, 0.0006 Cr, 0.0004 Li and the remainder aluminum were used for experimental measurements. The surfaces of the specimens were mechanically polished before use on wet SiC abrasive paper (grade 120 to 1200), rinsed with distilled water, degreased with acetone and finally dried. All materials were extra pure and solutions were prepared using distilled water. The concentration range of the inhibitor employed was 25-150 ppm.

Gravimetric and electrochemical measurements: The specimens used for gravimetric measurements had a rectangular form (1 cm × 1 cm × 0.1 cm). The weight loss values of specimens were determined in different concentration of HCl (0.5, 1.0, 1.5 and 2.0 M) with and without addition of different concentration of inhibitor after 1 h of immersion at 25 ºC.

In this study, the average values of three samples were used according to the ASTM standard procedure described in the literature[27].

For electrochemical measurements, the cell used was a conventional three electrodes Pyrex glass with a platinum counter electrode and a standard calomel electrode (SCE) as reference. The working electrode was embedded in Teflon so that its cross-sectional area (1 cm^2) was in contact with the solution. The electrochemical impedance experiments were carried out using AC signals of amplitude 5 mV peak to peak at the open circuit potential in the frequency range 100 kHz to 1 Hz after 0.5 h immersion in the electrolyte cell. Polarization curves were recorded with scanning rate of 1 mV/s, after 0.5 h immersion from -1200 to -400 mV *vs.* SCE.

The electrochemical experiments were carried out with a Potentiostat/Galvanostat 263A (EG&G) Princeton Applied Research HF response model 1025.

Scanning electron microscopy was used to characterize the surface of aluminum in various concentration of HCl and various concentration of HCl + 100 ppm inhibitor by using SEM CamScan model MV2300.

RESULTS AND DISCUSSION

Gravimetric measurements: From the experimental data, the addition of inhibitor retards the rate of dissolution and inhibits the acid corrosion of the aluminum samples in different concentration of HCl solution. The inhibition efficiency (η_W %) was determined in different concentration of HCl with and without inhibitor after 1 h immersion as follows[28].

$$\eta_W \% = \frac{w_0 - w}{w_0} \times 100$$

where w_0 and w are the weight loss in the absence and presence of inhibitor, respectively. The obtained data are summarized in Table-1.

TABLE-1
INHIBITION EFFICIENCIES FOR THE CORROSION OF ALUMINUM IN DIFFERENT CONCENTRATION OF HCl OBTAINED FROM WEIGHT LOSS MEASUREMENT WITH DIFFERENT CONCENTRATION OF INHIBITOR

Inhibition conc. (ppm)	η % in HCl conc. (M)			
	0.5	1.0	1.5	2.0
25	55.50	54.93	56.30	54.38
50	66.72	66.82	64.90	65.89
75	81.50	82.30	81.83	80.93
100	84.93	84.79	85.12	85.62
125	70.89	71.70	73.10	72.50
150	61.50	59.88	61.88	61.55

With increasing inhibitor concentration to 100 ppm the inhibition efficiency increased but after it decreased in different concentration of HCl (0.5, 1.0, 1.5 and 2.0 M).

Polarization data: Potentiodynamic polarization tests were done in different acidic media with and without inhibitor and the similar behaviour was observed as the gravimetric measurement. The polarization curves of aluminum are shown in Fig. 1(a,b). The parameters and corrosion inhibition efficiencies (η %) derived from these curves are given in Table-2.

Electrochemical impedance results: Electrochemical impedance spectroscopic (EIS) measurements have been carried out for aluminum in different concentration of HCl in the absence and presence of various concentration of inhibitor. The Nyquist plots are shown in Fig. 2.

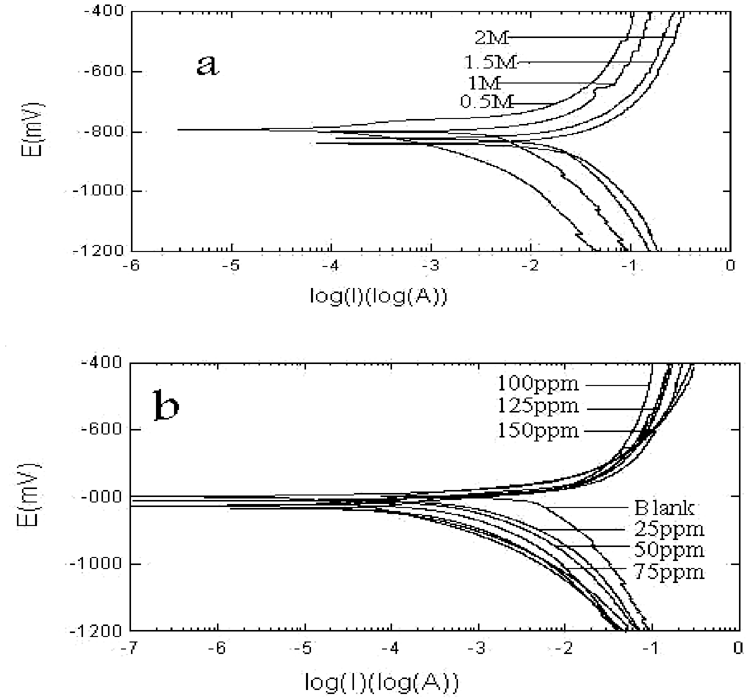


Fig. 1. Polarization curves for aluminum (a) in different concentration of HCl (b) in 1 M HCl + different concentration of inhibitor

TABLE-2
POLARIZATION PARAMETER VALUES FOR 1 M HCl + DIFFERENT CONCENTRATION OF INHIBITOR AND DIFFERENT CONCENTRATION OF HCl + 100 ppm INHIBITOR

HCl conc. (M)	Inhibition conc. (ppm)	I_{corr} (µA/cm^2)	E_{corr} *vs.* SCE (mV)	η (%)
1.0	0	1200	-800	–
1.0	25	516	-814	57.00
1.0	50	504	-827	58.00
1.0	75	420	-780	65.00
1.0	100	175	-760	85.40
1.0	125	228	-772	81.00
1.0	150	356	-827	70.33
0.5	0	600	-794	–
0.5	100	88	-831	85.30
1.0	0	1200	-800	–
1.0	100	175	-760	85.40
1.5	0	6200	-824	–
1.5	100	900	-822	85.45
2.0	0	11660	-840	–
2.0	100	1815	-832	84.44

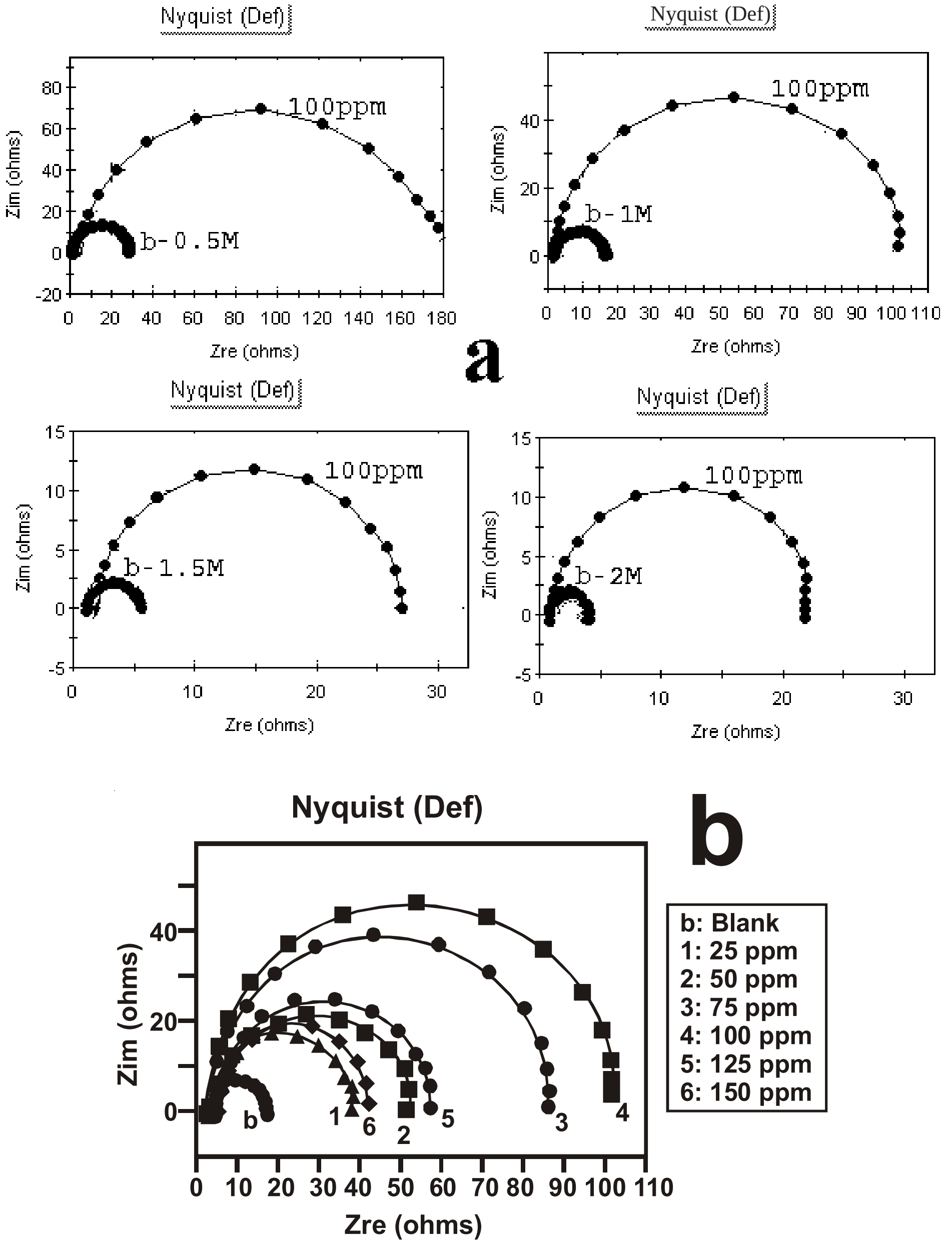


Fig. 2. Nyquist plots for aluminum (a) in different concentration of HCl in absence and presence of 100 ppm inhibitor (b) in 1M HCl + different concentration of inhibitor

The charge transfer resistance, R_{ct} values were calculated from the difference in the resistance measurements obtained at lower and higher frequencies. The double layer capacitance (C_{dl}) was obtained from the follow equation[28]:

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

where, f is the frequency at the apex of the semicircle in the Nyquist plot.

The inhibition efficiency percent (η %) of inhibitor is calculated by the follow equation[29]:

$$\eta\ \% = \frac{R_{ct} - R_{0ct}}{R_{ct}} \times 100$$

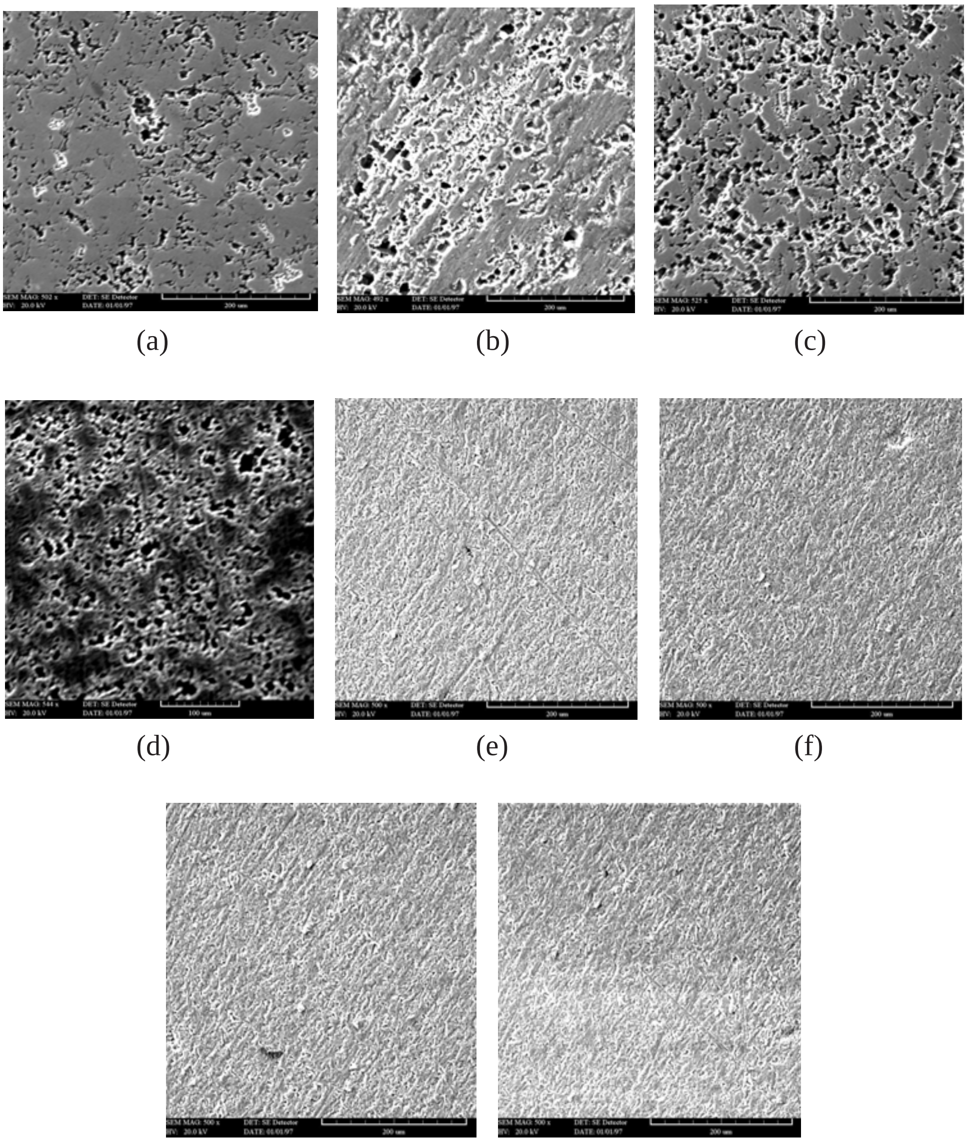
where R_{ct} and R_{0ct} are the charge transfer resistance value with and without inhibitor, respectively. The impedance parameters derived from EIS experiments are listed in Table-3.

TABLE-3
IMPEDANCE PARAMETER VALUES FOR 1 M HCl + DIFFERENT CONCENTRATION OF INHIBITOR AND DIFFERENT CONCENTRATION OF HCl + 100 ppm INHIBITOR

HCl conc. (M)	Inh conc. (ppm)	R_{ct} (Ω cm^2)	C_{dl} (μF/cm^2)	η (%)
1.0	0	14.930	356.4	–
1.0	25	33.875	307.0	55.92
1.0	50	47.284	260.2	68.42
1.0	75	84.028	250.9	82.23
1.0	100	99.737	210.8	85.03
1.0	125	54.682	405.3	72.69
1.0	150	39.848	234.1	62.54
0.5	0	27.297	315.5	–
0.5	100	175.370	228.8	84.43
1.0	0	14.930	356.4	–
1.0	100	99.737	210.8	85.03
1.5	0	4.374	256.1	–
1.5	100	28.112	129.4	84.44
2.0	0	2.807	126.1	–
2.0	100	18.777	123.4	85.05

The scanning electron micrographs (SEM) of aluminum specimens in various concentration of HCl in absence (a-d) and presence of 100 ppm inhibitor (e-h) are shown in Fig. 3, respectively. In Fig. 3(a-d) the corrosion products and pits are appeared but the decrease in corrosion values when exposed to optimum inhibitor concentration was due to coverage of the metal surface with a protective film, as evidence in (e-h) in Fig. 3.

As can be observed from the diameter of the Nyquist plots in presence of inhibitor, as inhibitor concentration increased to 100 ppm, C_{dl} values tend to decrease and R_{ct} values increase, further increase of the inhibitor concentration had an adverse effect on the efficiency of this inhibitor. In absence of inhibitor as HCl concentration increased C_{dl} values tend to increase and R_{ct} values decrease. As evident in Tables 1-3,



(a) (b) (c)

(d) (e) (f)

(g) (h)

Fig. 3. SEM micrographs of aluminum specimens in various concentration of HCl in absence (a-d) and presence of 100 ppm inhibitor (e-h)

derived parameters from weight loss, polarization and impedance experiments, the more corrosion by increasing concentration of HCl solution are appeared.

Although the efficiency of mixture inhibitor to inhibit the corrosion of aluminum in different concentration of HCl are increased with increasing inhibitor concentration to 100 ppm, further increase of the inhibitor concentration had an adverse effect on the efficiency of this inhibitor.

According to the pourbaix diagram, aluminum is passive in the pH range, 4-8.5. Beyond the limits of its passive range, aluminum corrodes in aqueous solutions because its oxides are soluble in many acid and bases, yielding Al^{3+} ions in the former and AlO_2^- (aluminate) ions in the latter. The decrease of the pH, in present case, the increase of HCl concentration leads to an increase of the rate dissolution according to the pourbaix diagram[30]. At high inhibitor concentration, a decrease in efficiency is appeared which correspond to the formation of bimolecular layer at the electrode solution interface by the binding of second layer organic compounds through hydrophobic interaction. The inhibition efficiency decrease considerably, which may be attributed to double layer destabilization by metal dissolution and pit initiation[30]. It can be concluded from Fig. 4 that inhibition efficiency obtained from weight loss, impedance measurements and polarization curves were in good agreement. In order to study the relationship between inhibitor adsorption on the pure aluminum surface and the inhibition concentration (isotherm plot), the degree of surface coverage, by the absorbed inhibitor was obtained from the electrochemical data using the following equation[31]:

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

where I_m is the corrosion current at maximum efficiency. If the plots of inhibitor concentration *versus* the $C_{inh}\ \theta^{-1}$ are linear, this confirms that the adsorption is Langmuir type (Fig. 5).

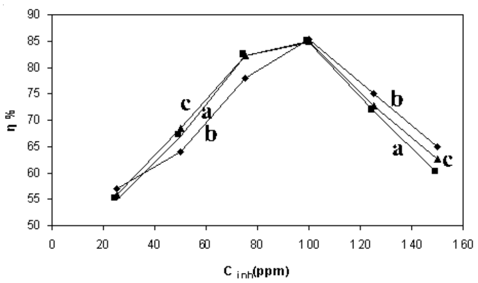


Fig. 4. Inhibition efficiency for aluminum in 1 M HCl containing different concentration of inhibitor (a) weight loss (b) impedance (c) polarization

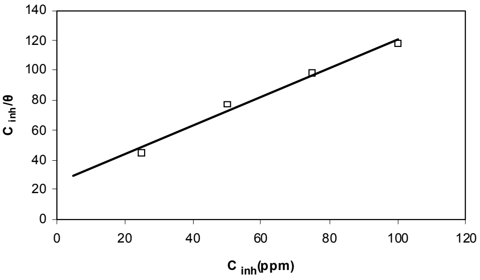


Fig. 5. Langmuir adsorption plots for aluminum in 1 M HCl containing various concentration of inhibitor

Conclusion

(i) The increase of HCl concentration resulted in increasing of the dissolution rate of aluminum in according to pourbaix diagram. (ii) The polarization data indicated that inhibitor compound had a mixed anodic-cathodic inhibitive nature. (iii) The inhibition efficiency of inhibitor increased with concentration and reached a maximum at 100 ppm, further increase of the inhibitor concentration had adverse effect on the efficiency of inhibitor. (iv) Increasing the HCl concentration does not affect the percentage of inhibition efficiency, however, the optimum inhibitor concentration remained 100 ppm for various HCl concentration. (v) The adsorption of inhibitor compound on the aluminum surface was observed to comply with Langmuir adsorption isotherm behaviour. (vi) The estimated inhibitor efficiency, as calculated from various techniques, was in good agreement.

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