CORROSION INHIBITION OF AA6061 AND AA6063 ALLOY IN HYDROCHLORIC ACID MEDIA BY SCHIFF BASE COMPOUNDS

SANAULLA PATHAPALYA FAKRUDEEN^{a*}, ANANDA MURTHY H. C^b, BHEEMA RAJU V^c.

^{a*}Department of Engineering Chemistry, HKBK College of Engineering, Nagawara, Bangalore -560045, Karnataka, India. Tel: 080-25441722

^bDepartment of Chemistry, R N Shetty Institute of Technology, Channasandra, Bangalore-560061, Karnataka, India. Tel: 080-28603880.

^cDepartment of Chemistry, Dr. Ambedkar Institute of Technology, Mallathahalli, Bangalore – 560056, Karnataka, India. Tel: 080-23211505

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ABSTRACT

N, N'-bis (Salicylidene)-1, 4-Diaminophenelyne (SDP) and N, N'-bis (3-Methoxy Salicylidene)-1, 4 Diaminophenelyne (MSDP) were synthesized, and their molecular structure were determined by FT-IR and ¹H NMR. The corrosion inhibitions of these compounds on AA6061 in 1M Hydrochloric acid were evaluated by weight loss method and scanning electron microscopic technique. The weight loss study showed that the inhibition efficiency of these compounds increases with increase in concentration and vary with solution temperature and immersion time. The various thermodynamic parameters were also calculated to investigate the mechanism of corrosion inhibition. The effectiveness of these inhibitors were in the order of MSDP> MDP. The adsorption of Schiff bases on AA6061 and AA6063 alloy surface in acid obeyed Freundlich adsorption isotherm. The surface characteristics of inhibited and uninhibited alloy samples were investigated by scanning electron microscopy (SEM).

Keywords Corrosion inhibitors, AA6061 alloy, AA6063 alloy, Hydrochloric acid, Schiff-bases

INTRODUCTION

Corrosion of aluminum and its alloys has been a subject of numerous studies due to their high technological value and wide range of industrial applications especially in aerospace and house-hold industries. Aluminum and its alloys, however, are reactive materials and are prone to corrosion. A strong adherent and continuous passive oxide film is developed on Al upon exposure to aqueous solutions. This surface film is amphoteric and dissolves when the metal is exposed to high concentrations of acids or bases [1]. Hydrochloric acid solutions are used for acid cleaning, acid de-scaling, chemical and electrochemical etching in many chemical process industries where in aluminium alloys are used. It is very important to add corrosion inhibitors to prevent metal dissolution and minimize acid consumption [2]. Most of the efficient acid inhibitors are organic compounds that contain mainly nitrogen, sulfur or oxygen atoms in their structure. The choice of inhibitor is based on two considerations: first it could be synthesized conveniently from relatively cheap raw materials; second, it contains the electron cloud on the aromatic ring or electronegative atoms such as nitrogen, oxygen in relatively long-chain compounds. Numerous organic substances containing polar functions with nitrogen, oxygen, and sulphur atoms and aromatic rings in a conjugated system have been reported as effective corrosion inhibitors for aluminium alloys [3-5]. Some Schiff bases have been reported earlier as corrosion inhibitors for aluminium alloys [6-8], iron [9-10] and copper [11-12]. Compounds with π -bonds also generally exhibit good inhibitive properties due to interaction of π orbital with metal surface. Schiff bases with RC = NR' as general formula have both the features combined with their structure which may then give rise to particularly potential inhibitors.

The present work is aimed at investigating the inhibitive ability of Schiff bases on corrosion of AA6061 and AA6063 in 1M Hydrochloric acid medium in the temperature range 303–333K using weight loss method and scanning electron microscopic technique.

EXPERIMENTAL

Materials and methods

Synthesis of Schiff bases

The corrosive medium selected for this study was 1M hydrochloric acid, which was prepared from analytical grade 37 per cent acid concentrated (Merck) in double distilled water. The preparation of the Schiff Bases employed in this study was done according to the method used by Zolezzi *et. al* [13]. The Schiff Bases were prepared by the condensation of respective aromatic aldehydes with each of diamines. All reagents used were of analytical grade procured from Sigma Aldrich. N,N'-bis(Salicylidene)-1,4-Diaminophenelyne(SDP) was

prepared by slow addition of Salicylaldehyde (2 mmol) in 30 mL methanol over a solution of 1,4-Phenylenediamine (1 mmol) in 30 mL methanol and N,N'-bis(3-MethoxySalicylidene)-1,4-Diaminophenelyne(MSDP) by slow addition of Methoxysalicylaldehyde (2 mmol) in 30 mL methanol over a solution of 1,4 - Phenylenediamine (1 mmol) in 30 mL methanol taken in a 250 mL condensation flask. In each case, 2-3drops of acetic acid was added to the mixture of aldehyde and diamine with stirring at constant temperature 25°C for 1 hour. Further the mixture was refluxed for 4-5 hours on a water bath, heating occasionally to improve the yield of the product. The reaction mixture was cooled to room temperature overnight and the colored compound was filtered off and dried. The compounds were recrystallised with ethanol. The product identity was confirmed *via* melting points, Fourier transform infrared spectroscopy (FT-IR) and Proton Nuclear Magnetic Resonance (¹H NMR). The structure, molecular formula and molecular mass are shown in Table 1.

FT-IR spectroscopy and NMR spectroscopy

FT-IR spectra of Schiff bases were obtained in KBr with Fourier transform spectrometer (Interspec 2020, UK), for the detection of various functional groups present in these inhibitors. ¹H-NMR spectra run in CDCl₃ on a Bruker spectropin 300 MHz spectrometer with TMS (Me₄Si) as the internal standard and its values are given in ppm (δ). The chemical shift was recorded relative to TMS assigned at zero. NMR helps in analyzing the type of protons attached to different groups of the inhibitors used

N, N'-bis (Salicylidene)-1, 4-Diaminophenelyne

Mp: 228°C, IR (KBr cm⁻¹): 3450(OH), 3047(=C-H), 1606(C=N).

¹HNMR (CDCl₃): δ 6.93–7.42 (m, 12H, ArH). 8.66(s, 2H, N=CH), 13.16 (s, 1H, OH),

Mp: 242°C, N, N'-bis (3-Methoxy Salicylidene)-1, 4 Diaminophenelyne

IR (KBr cm⁻¹): 3443(OH), 2996(=C-H), 1606(C=N). 1246(-OCH₃).

¹HNMR (CDCl₃): 3.95(s, 6H, -OCH₃), 6.88–7.36 (m, 10H, ArH). 8.67(s, 2H, N=CH), 13.57 (s, 1H, OH),

Aluminium Alloy Specimen preparation

The cylindrical alloy rods were cut into 18mm dia and 3mm length circular cylindrical disc specimens using an abrasive cutting wheel. The cylindrical alloy specimens were moulded in cold setting Acrylic resin exposing a surface area of 5.0 cm² (2.5 cm² each side) as shown in Fig-4 and 5. Before each experiment, the electrodes were abraded with a sequence of emery papers of different grades (600, 800, and 1200), washed with double distilled water, degreased with acetone and dried at 353 K for 30 min in a thermostated electric oven and stored in a moisture-free desiccator prior to use. The typical chemical composition of AA6061 and AA6063 alloys in weight percentage is shown in Table 2 and 3.

Table 1

Structure and Name	Molecular Formula	Molecular Mass
N,N'-bis(Salicylidene)-1,4-Diaminophenylene (SDP)	$C_{20}H_{16}N_2O_2$	316.36
N,N'-bis(3-Methoxy Salicylidene)-1,4-Diaminophenylene (MSDP)	$C_{22}H_{20}N_2O_4$	376.41

Table-2. Typical Chemical Composition of AA 6061.

Element	Cu	Mg	Si	Fe	Mn	Ti	Cr	Zn	Others	Al
Wt. %	0.15 -0.40	0.8 -1.2	0.4 -0.8	0.7 Max	0.15 Max	0.15 Max	0.04- 0.35	0.25 Max	0.15 Max	Reminder

Table-3. Typical Chemical Composition of AA 6063

Element	Cu	Mg	Si	Fe	Mn	Ti	Cr	Zn	Others	Al
Wt. %	0.10	0.45 -0.90	0.2 -0.6	0.35 Max	0.10 Max	0.10 Max	0.10 Max	0.10 Max	0.15 Max	Reminder

Weight loss measurements

The test pieces of Aluminium Alloy 6061 and 6063 samples were weighed up to fourth decimal place using digital electronic balance and the exact specimen weights were noted down. The test samples were immersed in 100 mL of 1M HCl in absence and presence of varying concentration of SDP and MSDP Schiff base inhibitor taken in beaker at different temperature ranges (303, 313, 323 and 333 K) in thermostated water bath. Initial weight of samples were measured before immersion and after specified period of exposed time, each piece was taken out of the test solution, rinsed with double distilled water, dried between two filter papers and weighed again using a digital electronic balance. The difference in weight for an exposed period of 2, 4, 6, 8, and 24 hours was taken as the total weight loss. The experiments were carried out at various concentrations (100, 200, 300, 400, 500 and 600 ppm) of all Schiff base inhibitors. Triplicate samples were used to check reproducibility of results. From the average weight loss results (average of three replicate analyses), the corrosion rate, the percentage of inhibition efficiency (% IE) and the degree of surface coverage (θ) were calculated using equations (1), (2) and (3)^[14]:

$$\text{Corrosion rate} = \Delta W / AT \quad \text{mg/cm}^2/\text{h} \quad (1)$$

Where ' ΔW ' is the weight loss in mg, ' A ' is the area of the specimen in sq-cm and ' T ' is the exposure time in hours.

$$\text{Inhibition efficiency (\%IE)} = \frac{CR_o - CR_i}{CR_o} \times 100 \quad (2)$$

Where, CR_o = Corrosion rate in blank Hydrochloric acid
 CR_i = Corrosion rate after adding inhibitors

$$\text{Degree of Surface Coverage } (\theta) = \frac{W_1 - W_2}{W_1} \quad (3)$$

Where W_2 and W_1 are the weight losses (mg) for aluminium alloys sample in the presence and absence of the inhibitor and θ is the degree of surface coverage of the inhibitor.

The percentage of inhibition efficiency (% IE) and the degree of surface coverage (θ) were tabulated.

Scanning electron microscopy

A scanning electron microscope (SEM) [Model No JSM-840A-JEOL] was used to study the morphology of the corroded surface in the presence and

absence of inhibitors. The specimens were thoroughly washed with double distilled water before examination. To understand the morphology of the aluminium surface in the absence and presence of inhibitors, the following cases were examined.

- Polished aluminium specimen.
- Aluminium specimen dipped in 1M HCl.
- Aluminium alloy specimen dipped in 1M HCl containing 500 ppm of Schiff base inhibitor.

RESULTS AND DISCUSSION

The Schiff base compounds inhibited corrosion rate of aluminium alloys AA6061 and AA6063 in 1M HCl at all concentrations under study. Inhibition efficiency increases with increase in inhibitor concentration from 100 to 500 ppm, as shown in Figs. 1(a) and 1(b). The maximum inhibition efficiency was achieved at 500 ppm and a further increase in inhibitor concentration caused no appreciable change in performance. The effect of immersion time on inhibition efficiency is shown in Figs. 2(a) and (b). All the tested Schiff bases show a decrease in inhibition efficiency with increase in immersion time from 2 to 24 hours. This indicates desorption of the Schiff Base over a longer test period and may be attributed to various other factors such as increase in cathodic reaction or increase in ferrous ion concentration^[15]. The influence of solution temperature on inhibition efficiency is shown in Figs. 3(a) and (b). The inhibition efficiency for all the Schiff base compounds decreases with increase in temperature from 303 to 333K. The decrease in inhibition efficiency with rise in temperature may be attributed to desorption of the inhibitor molecules at higher temperatures. The degree of surface coverage (θ) for different inhibitor concentrations in 1M HCl at 303K after 2 hours immersion time was evaluated from weight loss values.

The experimental data of weight loss (Δw), Percentage of Inhibition Efficiency (% IE), Corrosion Rate (C.R.) and degree of Surface Coverage (θ) for AA6061 and AA6063 in 1M HCl and presence of various concentration of SDP and MSDP Schiff bases at different exposure time and different temperature are shown in Table. 4.

Fig 1(a)

Fig 1(b)

Fig-1. Showing Variation of Inhibition efficiency with inhibitor concentration a) AA6061-SDP and MSDP, b) AA6063-SDP and MSDP**Table-4:** Weight loss data of AA6061 and AA6063 in 1M HCl (Blank) and in presence of various concentrations of SDP and MSDP inhibitors at different temperatures-2hours exposure time.

Inhibitor	Concentration / ppm	Weight Loss in mg (Δw), Percentage of Inhibition (% I E), Corrosion Rate in mg/cm ² /h, Surface Coverage (θ)															
		303 K				313 K				323 K				333 K			
		Δw	% IE	CR	θ	w Δ	% IE	CR	θ	w Δ	% IE	CR	θ	w Δ	% IE	CR	θ
AA6061	Blank	154		15.43		339		33.91		662		66.19		904		90.43	
SDP	100	40	74	4.01	0.74	149	56	14.92	0.56	338	49	33.76	0.49	497	45	49.74	0.45
	200	37	76	3.70	0.76	132	61	13.22	0.61	298	55	29.79	0.55	443	51	44.31	0.51
	300	29	81	2.93	0.81	119	65	11.87	0.65	265	60	26.48	0.6	380	58	37.98	0.58
	400	26	83	2.62	0.83	95	72	9.49	0.72	218	67	21.84	0.67	335	63	33.46	0.63
	500	20	87	2.01	0.87	75	78	7.46	0.78	179	73	17.87	0.73	280	69	28.03	0.69
MSDP	100	39	75	3.86	0.75	129	62	12.89	0.62	285	57	28.46	0.57	434	52	43.41	0.52
	200	32	79	3.24	0.79	85	75	8.48	0.75	205	69	20.52	0.69	344	62	34.36	0.62
	300	26	83	2.62	0.83	61	82	6.10	0.82	179	73	17.87	0.73	289	68	28.94	0.68
	400	22	86	2.16	0.86	54	84	5.43	0.84	159	76	15.89	0.76	262	71	26.22	0.71
	500	9	94	0.93	0.94	41	88	4.07	0.88	126	81	12.58	0.81	226	75	22.61	0.75
AA6063	Blank	109		10.90		296		29.56		557		55.65		854		85.38	
SDP	100	32	71	3.16	0.71	124	58	12.42	0.58	250	55	25.04	0.55	470	45	46.96	0.45
	200	26	76	2.62	0.76	109	63	10.94	0.63	228	59	22.82	0.59	384	55	38.42	0.55
	300	24	78	2.40	0.78	95	68	9.46	0.68	211	62	21.15	0.62	342	60	34.15	0.6
	400	20	82	1.96	0.82	74	75	7.39	0.75	173	69	17.25	0.69	316	63	31.59	0.63
	500	15	84	1.53	0.84	62	79	6.21	0.79	145	74	14.47	0.74	265	69	26.47	0.69
MSDP	100	31	72	3.05	0.72	127	57	12.71	0.57	262	53	26.16	0.53	470	45	46.96	0.45
	200	25	77	2.51	0.77	92	69	9.16	0.69	217	61	21.70	0.61	453	47	45.25	0.47
	300	21	81	2.07	0.81	77	74	7.69	0.74	167	70	16.70	0.7	324	62	32.44	0.62
	400	19	83	1.85	0.83	65	78	6.50	0.78	150	73	15.03	0.73	299	65	29.88	0.65
	500	15	86	1.53	0.86	56	81	5.62	0.81	122	78	12.24	0.78	265	69	26.47	0.69

Fig 2(a)

Fig 2(b)

Fig-2. Showing Variation of Inhibition efficiency with immersion time at a concentration of 500ppm and at 303K. a) AA6061-SDP and MSDP b) AA6063-SDP and MSDP

Fig 3(a)

Fig 3(b)

Fig-3. Showing Variation of Inhibition efficiency with temperature at a concentration of 500ppm.. a) AA6061-SDP and MSDP b) AA6063-SDP and MSDP

Thermodynamic activation parameters

The degree of surface coverage (θ) for different inhibitor concentrations in 1 M HCl at 303K after 2 hours immersion time was evaluated from weight loss values. The data were tested graphically by fitting to various isotherms. A plot of $\log(\theta/1-\theta)$ versus $1/T$ is shown in Figs. 4(a) and 4(b). The heat of adsorption (Q) was calculated from the slope ($-Q/2.303R$) of the plot and are given in Tables 5 and 6. The values of heat of adsorption ($< 40 \text{ kJ mol}^{-1}$) suggest physical adsorption [16]. A number of authors [17, 18, 19] have reported that, in acid solution, the logarithm of the corrosion rate is a linear function of $1/T$ (Arrhenius equation):

$$\log(\text{CR}) = -E_a / 2.303RT + A \quad (4)$$

Where, E_a is the apparent effective activation energy, R is the universal gas constant and A is the Arrhenius pre exponential factor. Plots of logarithm of corrosion rate obtained by weight loss measurement versus $1/T$ gave straight lines as shown in Figs. 5(a) and 5(b).

Fig 4(a)

Fig 4(b)

Fig-4. Plots of $\log(\theta/1-\theta)$ vs. $1/T$ in Presence of SDP and MSDP at a concentration of 500ppm for, (a) AA6061 and (b) AA6063

Fig 5(a)

Fig 5(b)

Fig-5. Plots of log (CR) vs. $1/T$ in Presence of SDP and MSDP at a concentration of 500ppm for. (a) AA6061 and (b) AA6063

The thermodynamic parameters (Table 5 and 6) show that the values of the activation energy E_a are higher for inhibited system as compared to the uninhibited system (Blank) suggesting that dissolution of aluminium alloys is slow in the presence of inhibitors. It is known from the Equation (4) that the higher E_a values lead to the lower corrosion rate. This is due to the formation of a film on the surface of aluminium alloys, which serves as a protective barrier. The inhibition efficiency follows the order: MSDP > SDP for AA6061 and AA6063. From the values of thermodynamic parameters, it is observed that the inhibitors are effective at lower temperatures.

An alternative formula for the Arrhenius equation is the transition state equation ^[20,21] (5):

$$C.R = \frac{RT}{Nh} e^{(\Delta S / R)} e^{(-\Delta H / RT)} \quad (5)$$

Where, h is the Plank constant, N is the Avogadro number, ΔS is entropy of activation and ΔH is the enthalpy of activation.

A plot of $\log (CR/T)$ versus $1/T$ gave a straight line, (Figs. 6(a) and 6(b)) with a slope of $(-\Delta H/2.303 R)$ and an intercept of $[(\log (R/Nh) + (\Delta S/2.303 R))]$, from which the values of ΔS and ΔH were calculated.

Fig 6(a)

Fig 6(b)

Fig-6. Plots of log (CR/T) vs. $1/T$ in Presence of SDP and MSDP at a concentration of 500ppm at 2 hours immersion time for (a) AA6061 and (b) AA6063

The values of enthalpy of activation, ΔH (Table 5 and 6.) follow the order MSDP > SDP for AA6061 and AA6063. The values of ΔH are positive; this indicates that the corrosion process is an endothermic. The entropy of activation, ΔS in the absence and presence of inhibitors is large and negative indicating that the activated complex in the rate-determining step represents an association rather than a dissociation step. Thus, a greater degree of orderliness appears during its transformation from reactant to activated complex.

Table-5. Thermodynamic activation parameters for dissolution of AA6061 in 1M HCl and in presence of 500 ppm of SDP and MSDP inhibitor.

System	E_a (kJmole ⁻¹)	ΔH (kJmole ⁻¹)	$-\Delta S$ (Jmole ⁻¹ K ⁻¹)	$-Q$ (kJmole ⁻¹)
1M HCl	48.85	46.40	147.72	-----
SDP	74.55	56.87	77.73	35.81
MSDP	87.27	60.87	99.42	42.17

Table-6. Thermodynamic activation parameters for dissolution of AA6063 in 1M HCl and in presence of 500 ppm of SDP and MSDP inhibitor.

System	Ea (kJmole ⁻¹)	ΔH (kJmole ⁻¹)	–ΔS (Jmole ⁻¹ K ⁻¹)	–Q (kJmole ⁻¹)
1M HCl	57.06	54.44	113.95	-----
SDP	75.22	61.80	53.31	29.35
MSDP	79.13	65.13	67.23	30.63

Adsorption Isotherms

Adsorption plays an important role in the inhibition of metallic corrosion by organic inhibitors. Adsorption isotherms are very important in understanding the mechanism of inhibition of corrosion reaction of metals and alloys. Generally, the adsorption of organic molecules on a metallic surface involves oxygen, nitrogen and sulphur atoms and in some cases, selenium and phosphorus. In Schiff bases, oxygen and nitrogen atoms are responsible for the adsorption. This process may block active sites on metallic surface and hence, decrease the corrosion of the metal. Assuming that the inhibitors adsorbed on the alloy surface decrease the surface available for cathodic and anodic reactions to take place. The nitrogen atoms of the Schiff bases act as the reaction centers (polar function) because of its higher electron density resulting in the formation of a monolayer on the metal surface^[22, 23]. It is generally assumed that the adsorption of the inhibitors on the metal surface is an essential step in the inhibition mechanism^[24]. To determine the adsorption mode, various isotherms were tested and curve fitting of corrosion data in 1M HCl in presence of different concentration of Schiff bases at 303K evaluated. A plot of log C vs. log θ gave a straight line as shown in the Fig 7(a) and Fig 7(b) and the Freundlich model is the best fitted.

Fig 7(a) **Fig 7(b)****Fig-7.** Plots of log C vs log θ in Presence of SDP and MSDP inhibitors at 303K for (a) AA6061 and, (b) AA6063

The Freundlich isotherm is given by ^[25] equation. (6):

$$\theta = K_a C^n \quad (6)$$

Where n is a constant, C is the inhibitor concentration and K_a is the equilibrium constant of adsorption process and is related to the standard free energy of adsorption ΔG_{ads} by the equation (7):

$$K_a = 1/55.5 \exp (-\Delta G_{ads}/RT) \quad (7)$$

The value of 55.5 is the concentration of water in solution expressed in mole per liter, R is the universal gas constant and T is the absolute temperature. To calculate the surface coverage θ it was assumed that the inhibitor efficiency is due mainly to the blocking effect of the adsorbed species and hence % IE = 100 × θ ^[26]. The weight loss results were used to calculate the adsorption isotherm parameters. The surface coverage (θ) data are very useful while discussing the adsorption characteristics. The plot of log θ vs. log C for all investigated Schiff Base compounds gave a straight line and is characteristic of the Freundlich adsorption isotherm.

Table-7. Adsorption equilibrium constant and adsorption free energy of the Schiff bases adsorbed on AA6061 and AA6063 at 303K.

Alloy	Inhibitor	Freundlich Isotherm		
		N	K_a	$-\Delta G_{ads}$ kJmol ⁻¹
AA6061	SDP	0.10	1.66	11.40
	MSDP	0.13	2.20	12.11
AA6063	SDP	0.10	1.71	11.47
	MSDP	0.13	2.04	11.92

The free energy of adsorption (ΔG_{ads}), was calculated, using Equation. (6 and 7), are also given in Table 7. ΔG_{ads} is expressed in kJ mol⁻¹ of Org_{ads}. The negative values of ΔG_{ads} ensure the spontaneity of the adsorption process and the stability of the adsorbed layer on the Al surface. It is well known that values of ΔG_{ads} of the order of 40 kJ mol⁻¹ or higher involve charge sharing or transfer from the inhibitor molecules to metal surface to form coordinate type of bond (chemisorption); those of order of 20 kJ mol⁻¹ or lower indicate a physisorption^[27-28]. The calculated ΔG_{ads} values are less negative than -20 kJmol⁻¹ indicate, therefore, that the adsorption mechanism of the investigated Schiff bases on aluminium alloy in 1M HCl solution is typical of physisorption. The lower negative values of ΔG_{ads} indicate that these inhibitors are not strongly adsorbed on the Al surface. Moreover, | ΔG_{ads} | of investigated Schiff bases decreases in the order MSDP > SDP for AA6061 and AA6063. This is in good agreement with the ranking of inhibitors efficiency obtained from the different investigated techniques.

Scanning electron microscopy

Scanning electron microscopy of the AA6061 sample of inhibited and uninhibited metal samples is presented in Fig. 8. The SEM study shows that the inhibited alloy surface is found smoother than the uninhibited surface.

Fig. 8. Scanning electron micrographs of (a) Polished AA6061 alloy, (b) After immersion in 1M HCl for 4h, (c) After immersion in 1M HCl for 4h in presence of 500 ppm SDP.

Mechanism of corrosion inhibition

The observation drawn from the different methods, one can conclude that the Schiff base inhibitors are adsorbed on aluminium alloy surface forming a barrier film and protect the alloys in 1M HCl. The inhibitive action can be explained on the basis of N and O atoms in addition to π electron interaction of the benzene nucleus with unshared p electrons of aluminium atoms. The simple concept of coordination chemistry applies in the imine ($C=N$) containing ligands where the lone pair of electrons attaches to the central metal ion. The lone pair of electrons on nitrogen is readily available for sharing with metal atoms to form a native covalent bond. Hence, the adsorbed Schiff bases will cover and protect the metal surface from the corrosive environment in 1M HCl solution.

There is a general consensus by several authors that the more negatively charged the heteroatom is, more is its ability to adsorb on the metal surface through a donor-acceptor type reaction [29-31].

As far as the inhibition process is concerned, it is generally assumed that adsorption of the inhibitor at the metal/solution interface is the first step in the action mechanism of the inhibitors in aggressive acid media. The adsorption may be the result of one or more of three types of interactions^[32, 33], namely; electrostatic attraction between charged molecules and charged metal, coordination of the unshared pairs of electron on the molecule to the metal atom, and involvement of π electrons of the inhibitor molecule in coordination process.

In general, the investigated Schiff bases may be adsorbed on aluminium alloy surface in their neutral or protonated forms (cationic form). Since it is well known that the aluminum surface is negatively charged in acid solution^[34], it is easier for the protonated molecules to approach the negatively charged aluminium alloy surface due to the electrostatic attraction. In case of adsorption, this involves the displacement of water molecules from the aluminium alloy surface and sharing of electrons between the hetero-atoms and aluminium alloy. Also, the inhibitor molecules can adsorb on aluminium alloy surface on the basis of donor-acceptor interactions between π -electrons of aromatic rings and vacant p-orbitals of surface aluminium atoms. Thus we can conclude that inhibition of aluminium alloy corrosion in HCl is mainly due to electrostatic interaction. The decrease in inhibition efficiency with rise in temperature supports electrostatic interaction. The adsorption of Schiff base on the aluminium alloy surface can be attributed to adsorption of the organic compounds via phenolic and iminic groups in both cases. Among these two Schiff bases, the chelate effect of MSDP is greater than that of SDP. This is due to the presence of two electron donating groups of $-OCH_3$ in MSDP structure than SDP. The more efficient adsorption of MSDP is the result of electronegative oxygen atoms present in the MSDP compared to SDP Structure. The adsorption of inhibitor SDP and MSDP on aluminum surface is presented by the diagram in Fig 10 a) and 10 b) .

Fig 10: Diagram showing adsorption of inhibitor a) SDP and b) MSDP on aluminium alloy surface.

CONCLUSIONS

1. The investigated Schiff bases are good inhibitors for aluminium alloys in 1M HCl solution.
2. In weight loss studies, the inhibition efficiency (IE) of all Schiff bases increase with increase in inhibitor concentration, whereas decreases with increase in immersion time and temperature.
3. The percentage inhibition (% IE) in accordance to the order: MSDP > SDP for AA6061 and AA6063.
4. The adsorption of Schiff bases on alloy surface in 1M HCl solution follows Freundlich adsorption isotherm.
5. The negative values of ΔG_{ads} shows the spontaneity of the adsorption, suggesting that corrosion inhibition takes place by desorption.
6. Scanning Electron Microscopy (SEM) shows a smoother surface for inhibited alloy samples than uninhibited samples due to formation of protective barrier film.

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