Scholars Research Library

Archives of Applied Science Research, 2012, 4 (5):2133-2140
(http://scholarsresearchlibrary.com/archive.html)

ISSN 0975-508X
CODEN (USA) AASRC9

Inhibitive influence of salicylideneaniline on the corrosion of aluminium in 1.0 N NaOH

[1]T. Umasankareswari and [2]T. Jeyaraj

[1]P.G. and Research Department of Chemistry, Bishop Heber College (Autonomous), Trichirappalli – 620017. (INDIA)
[2]P.G and Research Department of Chemistry, Jamal Mohamed College, Tiruchirappalli-620020.

ABSTRACT

The inhibitive influence of salicylideneaniline (a Schiff base) on the corrosion of aluminium in 1.0 N sodium hydroxide was studied by weight loss, potentiodynamic polarisation and electrochemical impedance measurements. The inhibition efficiency of the compound increases with its increasing concentration. The addition of tetrabutylammonium bromide, TBAB (0.0006 M) to varying concentrations of the Schiff base enhanced the inhibition efficiency at each concentration of the Schiff base. The results obtained from mass loss data, polarisation and EIS measurements showed similar trend. The surface coverage, θ, values from mass loss data were fitted to kinetic/thermodynamic modal of El-Awady et al., Langmuir and Temkin adsorption isotherms. The best fit isotherm was the isotherm of El-Awady et al. The values of E_a , Q_{ads} and .$\Delta G°_{ads}$ revealed that the compound inhibits corrosion through physisorption. The polarization studies indicated that the corrosion of aluminium in 1.0 N NaOH was predominantly under anodic control, in the presence as well as in the absence of the inhibitor and the inhibition is of mixed type.

Keywords: salicylideneaniline, tetrabutylammmonium bromide, anodic control, physisorption, lateral interaction parameter.

INTRODUCTION

The high energy density, of 20 MJ/kg and highly negative electrode potential of -2.303 V (vs. SHE) combined with its light mass and high abundance in the earth's crust make aluminium a desirable fuel in metal-air batteries [1-4].

Generally the aluminium/air batteries work with strongly alkaline electrolyte (KOH or NaOH). They permit fairly good performance of air cathode and low level of Al polarisation[5]. The duplex protective oxide layer of aluminium is broken by the action of alkaline solution. As a result aluminium becomes an electrochemically active fuel for electric power generation. Literature survey shows that in alkaline media aluminium readily dissolves and generates a useful voltage at a reasonable current. However it undergoes substantial self-corrosion aluminium and H_2 evolution in alkaline solution. Consequently there is coulombic loss of aluminium on the discharge of alkaline aluminium battery cell and fuel(aluminium) loss during standby[3,6-8]. Therefore the corrosion of aluminium has to be reduced and it can be achieved by adding inhibitor to the electrolyte to make it less corrosive [9,10]. In the present study the usefulness of salicylideneaniline for the inhibition of corrosion of aluminium in 1.0 N NaOH has been investigated.

MATERIALS AND METHODS

Commercially pure aluminium samples, for the weight loss studies, were cut into 2 cm x1 cm x 0.14 cm coupons and polished with emery papers of different grades to mirror shine, degreased with acetone, washed with double distilled water and dried before immersing in the corrosion medium. The aluminium specimens for the electrochemical measurements were machine cut into test electrodes of dimension, 8 cm x 1 cm x 0.14 cm and coated with epoxy resin (araldite) leaving a surface area of 1 cm^2. The corrosion medium, 1.0 N NaOH solution, was prepared from analytical reagent grade NaOH (MERCK) and double distilled water. Tetrabutylammonium bromide (TBAB) was used as received. The inhibitor, salicylideneaniline ,was prepared according to the procedure reported [11].

Weight loss study

The aluminium specimens were suspended with the help of glass hooks in beakers containing 100 ml of 1.0 N sodium hydroxide, without and with the inhibitor for about 1 hour. The specimens were removed after the exposure period, washed with water and rubbed with bristle brush to remove any corrosion product and finally washed with acetone and distilled water. They were dried in an oven and re-weighed to determine the weight loss.

The experiments were carried out in triplicate to ensure reproducibility and the mean values of weight loss were computed. The percentage inhibition (P.I) efficiency was calculated using the following equation:

$$\text{P.I.} = \frac{w_0 - w_i}{w_0} \times 100 \qquad \text{\_\_\_\_\_\_\_\_\_\_\_\_\_\_} \qquad (1)$$

where w_0 and w_i are the weight losses in uninhibited and inhibited corroding solutions, respectively.

Electrochemical measurements

The aluminium coupons, which were prepared as described above, was used as working electrode. Before each experiment, the exposed area of the working electrode was polished with sand paper to a metallic shine. Then it was washed with distilled water, degreased with ethanol, and finally dried with soft paper. The electrochemical measurements were performed in a conventional three electrode glass cell which consists of aluminium as the working electrode (WE), platinum as the counter electrode (CE) and a saturated calomel electrode (SCE) as the reference electrode. The electrode potential was allowed to stabilize in a time period of 60 minutes before starting the measurements.

Measurements were performed using Princeton Applied Research Electrochemical Analyser (model K0264 Micro cell kit). Electrochemical analyser software was used for plotting, graphing and fitting data. Tafel polarisation curves were obtained by changing the electrode potential automatically from +300 to -300 mV around open circuit potential with scan rate of 10 mV/sec. Impedance measurements were carried out in the frequency range from 100 kHz to 1Hz using ac signals with an amplitude of 27 mV peak to peak at open circuit potential.

RESULTS AND DISCUSSION

The values of corrosion rate and percentage inhibition efficiency, obtained by weight loss measurement at different concentrations of salicylideneaniline at 30° C are shown (Table1).

Table 1: Inhibition of corrosion of aluminium in 1.0 N NaOH by salicylideneaniline at 30^0 C (weight loss method)

[salicylideneaniline], M	rate of corrosion x 10^{-4}, g $cm^{-2}min^{-1}$	% inhibition efficiency
0	4.666	--
0.0001	5.000	-07.50
0.0003	4.750	-01.80
0.0005	4.166	10.71
0.0007	3.684	21.03
0.0009	3.450	26.05
0.0020	3.353	28.14
0.0040	3.000	35.71
0.0060	2.850	38.92
0.0090	2.750	41.07

The inhibition efficiency increases with the increasing concentrations of the inhibitor. The maximum inhibition efficiency was found to be 41.07 %.

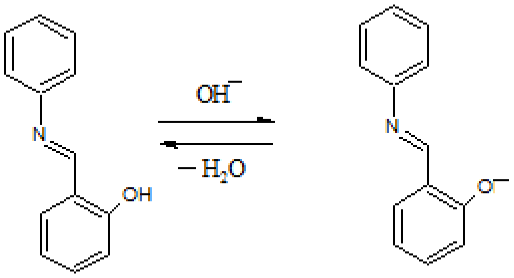
At 50° C, the rate of corrosion is high and the efficiency of inhibition of the Schiff base is not considerable. However in the presence of TBAB , the inhibitive influence of the Schiff base is considerably enhanced both at 30° and 50° C(Table 3).

Generally the organic compounds containing hetero-atoms like O and N, along with aromatic rings are reported to function as very effective corrosion inhibitors [12-14]. The efficiency of these compounds depends upon electron density around the hetero atoms [15].

Schiff's bases with C = N linkage and two aromatic rings have both the above features in their structures and therefore salicylideneaniline is expected to be an effective potential corrosion inhibitor[16].

However at low inhibitor concentrations, salicylideneaniline accelerates corrosion (Table1), probably due to the following reason.

The surface of aluminium is negatively charged at pH > 9 [17].
In 1.0 N NaOH (pH 14), the phenolic - OH group of salicylidene part of the Schiff base, is ionised as follows.



The $-O^{-}$ group in the salicylidene part of the Schiff base, is probably repelled by the negative aluminium oxide surface. Due to this reason, at low concentrations of salicylideneaniline corrosion is accelerated (Table1). As a molecule with great tendency for adsorption[16], at high concentrations, it inhibits corrosion (Table 1)

Table 2: Inhibition of corrosion of aluminium in 1.0 N NaOH by tetrabutylammonium bromide (TBAB) (weight loss method) at 30° C

[TBAB], M	Rate of corrosion x 10^{-4} g cm^{-2} min^{-1}	% inhibition efficiency
Blank	4.449	---
0.0002	4.359	2.0
0.0004	4.270	4.0
0.0006	4.049	9.0

Table3: Inhibition of corrosion of aluminium by 1.0 N NaOH by salicylideneaniline along with TBAB at 30° and 50° *C*
[TBAB] =0.0006 M

[salicylideneaniline] M	Rate of corrosion x 10^{-4}, g cm^{-2} min^{-1}		% inhibition	
	33 ± 0.5^{0}C	50 ± 0.5^{0}C	33 ± 0.5^{0}C	50 ± 0.5^{0}C
0	7.416	---	---	---
0.0001	3.500	---	52.81	---
0.0003	3.416	----	53.93	---
0.0005	3.083	----	58.43	---
0.0007	3.00	----	59.55	---
0.0009	2.719	8.6547	63.33	22.58
0.0020	2.610	7.9337	64.80	29.03
0.0040	2.333	7.2842	68.44	34.84
0.0060	2.250	6.3473	69.66	43.22
0.0090	2.000	5.6252	73.03	49.68

Table 4: Values of apparent activation energy, E_a, and heat of adsorption of inhibitor, Q_{ads}, in the presence of TBAB
[TBAB] = 0.0006 M

[salicylideneaniline], M	Rate of corrosion x10^{-4}, g cm^{-2} min^{-1}		E_a, kJ mol^{-1}	Surface Coverage, θ		Q_{ads}, kJ mol^{-1}
	33±0.5°C	50±0.5°C		33±0.5°C, θ_1	50±0.5°C, θ_2	
0	7.416	-	---	---	---	---
0.0009	2.719	8.6547	47.193	63.33	22.58	-72.370
0.0020	2.610	7.9337	45.310	64.80	29.03	-61.201
0.0040	2.333	7.2842	46.410	68.54	34.84	-57.182
0.0060	2.250	6.3473	42.270	69.66	43.22	-44.927

With the raise of temperature, the rate of corrosion increases and therefore the inhibition efficiency decreases (Table 3) due to the increase of the rate of diffusion of corrosion products[19]. According to Ferreira et al.,[20] a decrease of inhibition efficiency with increase of temperature indicates inhibitor physisorption and reverse behaviour is attributed to chemisorption. Similar observations have also been reported [21,22].

The apparent activation energy, E_a, and the heat of adsorption , Q_{ads}, were calculated using the following equations (2) and (3) :

$$\log\frac{r_1}{r_2} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \text{ ---------------- } (2)$$

$$Q_{ads} = 2.303\,R\left(\log\left[\frac{\theta_2}{1-\theta_2}\right] - \log\left[\frac{\theta_1}{1-\theta_1}\right]\right)\frac{T_1T_2}{(T_1-T_2)} \text{ \_\_\_\_\_\_ } (3)$$

where
r_1 = corrosion rate at the temperature, T_1,
r_2 = corrosion rate at the temperature, T_2,
θ_1 = surface coverage by inhibitor at the temperature , T_1,
and θ_2 = surface coverage by inhibitor at the temperature, T_2.

Increased activation energy , E_a, in inhibited solutions compared to the blank (Table 4) is suggestive of physisorption of inhibitor [21]. The negative Q_{ads} values also supportive of physisorption [24].

Table 5 : Effect of TBAB on the inhibition of corrosion of aluminium in 1.0 N NaOH by salicylideneaniline
[TBAB] = 0.0006 M

[salicylideneaniline], M	% Inhibition	[salicylideneaniline],M + TBAB	% Inhibition	Synergism parameter,S_θ
0.0001	-07.50	0.0001	52.81	2.09
0.0003	-01.80	0.0003	53.93	2.01
0.0005	10.71	0.0005	58.43	1.93
0.0007	21.03	0.0007	59.55	1.73
0.0009	26.05	0.0009	63.33	1.76
0.0020	28.14	0.0020	64.80	1.79
0.0040	35.71	0.0040	68.54	1.76
0.0060	38.92	0.0060	69.66	1.72
0.0090	41.07	0.0090	73.03	1.85

The inhibition efficiency synergistically increases ($S_\theta > 1$) on the addition of 0.0006 M TBAB along with varying concentrations of the salicylideneaniline to 1.0 N NaOH (Table 5) . It can be interpreted, in terms of cooperative adsorption [25] between salicylideneaniline and TBAB.

Aramaki and Hackerman [26] calculated the synergism parameter, S_θ, by the equation :

$$S_\theta = \frac{1-\theta_{1,2}}{1-\theta'_{12}} \text{ ---------------------------- } (4)$$

where $\theta_{1,2} = (\theta_1 + \theta_2)$,

θ_1 = surface coverage by Schiff anion ,
θ_2 = surface coverage by TBA^+ cation , and
θ'_{12} =surface coverage measured for the combination of the Schiff anion and the TBA^+ present together in the solutions.

The S_θ values (Table 5) are greater than unity , suggesting that the enhanced inhibition efficiency caused by the addition of TBAB to the Schiff base is mainly due to the synergistic effect between these substances.

The tetrabutylammonium cation, TBA^+, is initially adsorbed on the negatively charged metal oxide surface and provide a better electrostatic condition for the adsorption of the Schiff base anion.

A similar model was proposed for the adsorption of some organic compounds on the mild steel in acid electrolyte[27,28].

The adsorption of the inhibitors molecules from aqueous solutions can be regarded as a substitution process[29], between the organic compound in the aqueous phase, org $_{(aq)}$, and water molecules at the metal surface , $H_2O_{(s)}$. The following replacement reaction occurs.

$$Org_{(aq)} + xH_2O_{(s)} \longrightarrow Org_{(s)} + xH_2O_{(aq)}$$

where x, the size ratio, is the number of water molecules displaced by one adsorbed organic molecule[30]. The inhibitor molecules could displace water molecule from the surface of the metal, if the energy of interaction between metal surface and inhibitor is strong. In order to determine the adsorption isotherm , the surface coverage,θ, for the inhibitor was calculated according to the equation:

$$\theta = \frac{W_O - W_I}{W_O} \quad \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_(5)$$

where w_O and w_i are the weight losses obtained without and with the inhibitor[13,14,15].

The data were fitted to the adsorption isotherms of El-Awady et al., Langmuir and Temkin. The regression coefficient R^2 was used to determine the best fit isotherm [31]. It was found that

R^2 =0.991 for Langmuir isotherm.

Langmuir adsorption isotherm model has the form,

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_(4)$$

where θ is the surface coverage, C is the concentration of inhibitor and K_{ads} is the equilibrium constant of adsorption process,

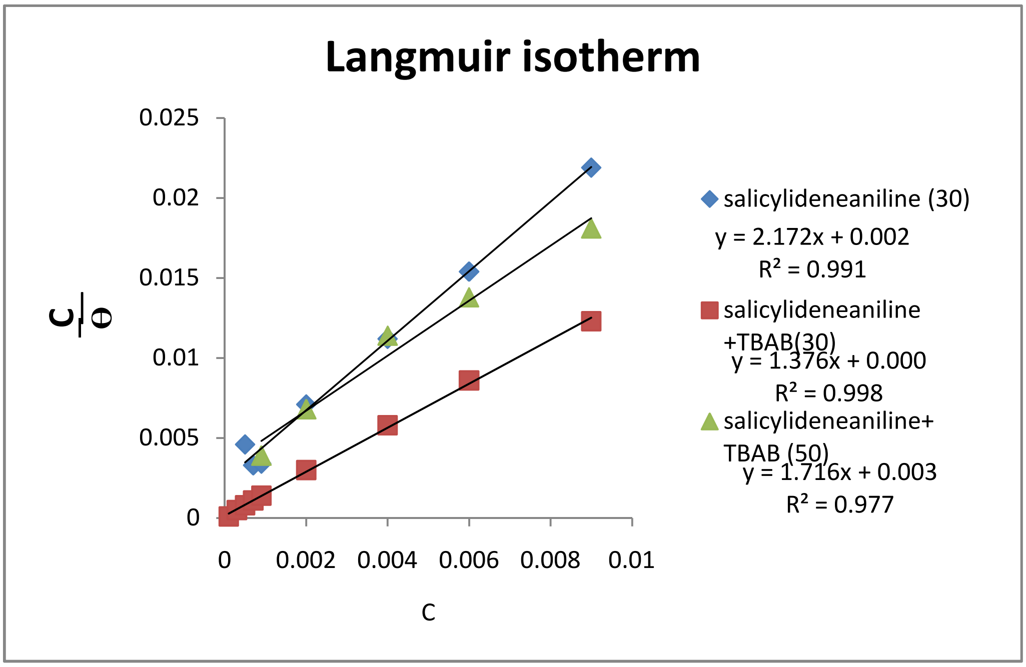
The slope deviates from unity showing that there is attraction or repulsion in the adsorbed layer of inhibitor on the aluminium surface. Since Langmuir isotherm is the best fit isotherm, using Langmuir adsorption isotherm, $K_{ads} = \frac{\theta}{C(1-\theta)}$, K_{ads} values are calculated at different concentrations of the inhibitor. The values of K_{ads} are related to the standard Gibbs free energy of adsorption, $\Delta G°_{ads}$, by the following equation.

$$K_{ads} = \frac{1}{C_{solvent}} \exp\left(\frac{-\Delta G°_{ads}}{RT}\right)$$

$C_{solvent} = C_{H_2O} = 55.55 \text{ mol dm}^{-3}$, R($Jmol^{-1}\ K^{-1}$) is the gas constant and T(K) is the temperature.

The standard Gibbs free energy of adsorption of inhibitor on the aluminium surface at 30° C was calculated (Table 6)

Fig.1 Langmuir adsorption isotherm



Temperature inside paranthesis

Table 6 : Values of $\Delta G°_{ads,}$ for the inhibition of corrosion of aluminium in 1.0 N NaOH by salicylideneaniline

[Salicylideneaniline], M	Θ	$\Delta G°_{ads, kJ\ mol}{}^{1}$
0.0009	0.2605	-25.155
0.0020	0.2814	-23.416
0.0040	0.3571	-22.550
0.0060	0.3892	-21.867
0.0090	0.4107	-21.062

The values of $\Delta G°_{ads}$ are negative and lies between -25.155 and -21.062 k J mol^{-1}. The negative value indicates that the adsorption of the inhibitor molecule on the aluminium surface is spontaneous. The values are less negative with an increase in the inhibitor concentrations, indicating that the adsorption of the inhibitor onto aluminium surface was less favourable with increasing concentrations of the inhibitor. In general , the values of $\Delta G°_{ads}$ around - 20 kJ mol^{-1} are consistent with physisorption while those around - 40 $kJmol^{-1}$ or lower correspond to chemisorption.

Table 7 : Adsorption parameters for the inhibition of corrosion of aluminium in 1.0 N NaOH by salicylideneaniline

Adsorptionisotherm	**Systems**	Regression coefficient (R^2)		$\Delta G°_{,}$ k J mol^{-1}		1/y (or) x		**Lateral Interaction Parameter , a**	
		30 ±0.5°C	50 ±0.5°C	30 ±0.5°C	50 ±0.5°C	30 ±0.5°C	50 ±0.5°C	30 ±0.5°C	30 ±0.5°C
Langmuir isotherm	[Salicylide--neaniline]	0.991		25.3		-	-	-	-
	[Salicylide--neaniline] + TBAB	0.999	0.977	33.3	24.5	-	-	-	-
El- Awady Et al. isotherm	[salicylide--neaniline]	0.835		20.8		1.9106	-	-	-
	[salicylide--neaniline] + TBAB	0.963	0.975	22.11	21.59	2.0157	4.950	-	-
Temkin isotherm	[salicylide--neaniline]	0.919		33.65	-	-	-	-5.45	-
	[salicylide--eaniline] + TBAB	0.965	0.957	60.4	32.30	-	-	- 0.942	-4.311

The lateral interaction parameter, a , has negative values indicating repulsion between inhibitor molecules in the adsorbed layer[32,33].

Table 8. Anodic and cathodic polarization of aluminium in 1.0 N NaOH without and with salicylideneaniline

[salicylideneaniline], M	OCP , V	E_{corr}, V	I_{corr}, mA cm^{-2}	βc, mV/dec	βa, mV/de	Percentage Inhibition
Blank	1.26	-1.499	21.543	274.5	449	-
0.0005	1.225	-1.5824	18.310	284.5	386.8	15.0
0.0020	1.377	-1.5632	13.678	263.9	382.5	36.0
0.0090	1.349	-1.6036	13.377	266.8	380.3	38.0

The anodic and cathodic polarization curves of aluminium in 1.0 N NaOH were recorded in the absence and in the presence of inhibitor under potentiodynamic polarisation condition. It was observed that anodic polarization was greater than cathodic polarization in all solutions. Cathodic and anodic polarization curves are shifted towards lower current density values in the presence of the inhibitor. But only a small shift in E_{corr} is observed.

Thus the nature of inhibition is of mixed type.

This observation indicates that the inhibitor suppresses both anodic as well as cathodic reactions with the increasing addition of the inhibitor.

Impedance measurements

The influence of different concentrations of salicylideneaniline on the impedance response of Al in 1.0 N NaOH solution at OCP (30±0.5° C) is shown (Fig 2).

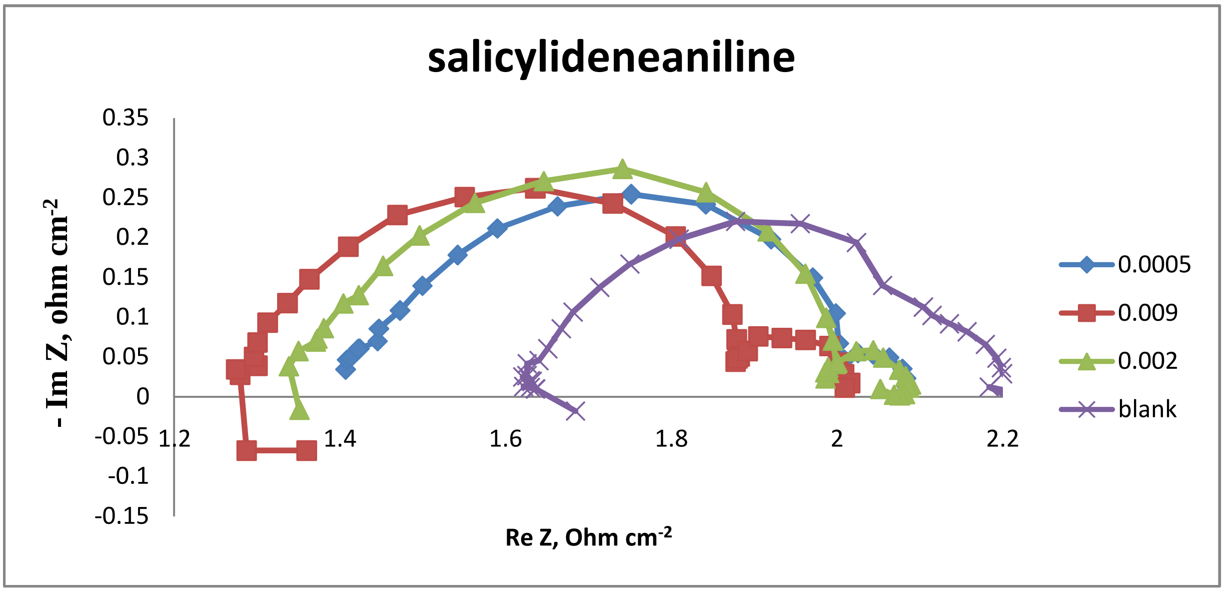


Fig. 2 Nyquist plot for Al in 1.0 N NaOH with different concentrations of salicylideneaniline

The values of the polarisation resistance (Rct) and the double layer capacitance (C_{dl}) were recorded (Table 9). The (R_{ct}) value increases and (C_{dl}) value decreases with increase in inhibitor concentration due to the adsorption of the inhibitor on the electrode surface.

Table 9: Values of C_{dl} and Rct for Al in 1.0 N NaOH solution in the absence and presence of various concentration of the salicylideneaniline at OCP (30±0.5°C)

[salicylideneaniline],M	R_s, ohm cm^{-2}	R_{ct}, ohm cm^{-2}	C_{dl} , F cm^{-2}
Blank	**1.626**	**0.579**	**2.252e^{-3}**
0.0005	**1.409**	**0.6493**	**0.4148 e^{-3}**
0.0020	**1.289**	**0.6903**	**0.3902 e^{-3}**
0.0090	**1.349**	**0.7057**	**0.2573 e^{-3}**

CONCLUSION

The corrosion of aluminium in 1.0 N NaOH was found to decrease with the increasing concentration of the inhibitor, salicylideneaniline. The inhibition efficiency values, obtained from the mass loss studies and polarization measurements, showed, the same trend. The mechanism of corrosion was shown to be physisorption The corrosion inhibition appears to be of mixed type .

Acknowledgement
The authors are thankful to the Principal, Management and the HOD of Chemistry, Bishop Heber College (Autonomous), Trichirappalli for providing facilities.

REFERENCES

[1] MA Zheng-qing, ZUO Lie, PANG Xu, ZENG Su-min, *Trans. Nonferrous. Met. Soc.China*. **2009**, 19, 160-165.
[2] M Paramasivam, S Venkatakrishna Iyer, *J. Appl. Electrochem.*, **2001**, 31, 115-119.
[3] ML Doche, F Novell-Cattin, R Durand, JJ Rameau, *J. Power sources*, **1997,** 65, 197-205.
[4] HZ Wang, DYC Leung, MKH Leung, M Ni, Renewable and Sustainable Energy Reviews, **2009**, 13, 845-853.
[5] DD MaDonald, C English, *J. Appl. Electrochem*.,**1991**, 20, 405.
[6] DM Draziica, JP Popic, *J. Appl. Electrochem*., **1999**, 29, 43-50.
[7] C Vargel, Corrosion of Aluminium. Elsevier Ltd., Oxford. **2004**.
[8] ER Anderson and EJ Anderson, Methods for producing hydrogen. US Patent 6506360, (**2003).**
[9] V Kapil, S Venkatakrishna Iyer, N Subramanyan, *Britt. Corros. J*., **1969**, 4, 305.
[10] LA Nnanna, VU Obasi, OC Nwadiuko, KI Mejeh, ND Ekekwe, SC Udensi, *Arch. Appl. Sci. Res*., **2012**, 4,1, 207-217.
[11] MN Desai, JD Talati, CV Vyas, NK Shah, *Indian J. Chem. Technol*., **2008,** 15, 228 - 237.
[12] Metikos-Hukovic, R Babic, Z Grubac and S Brinic, *J.Appl. Electrochem.*, **1994**, 24, 325.
[13] L Kobotiatis, N Pebere and PG. Koutsookos, *Corr. Sci*., **1999** ,41, 941.
[14] V Guillamuin and G Mankowski, *Corr. Sci*., **1999**, 41, 421.
[15] J M Costa and J M Lluch, *Corros.Sci*., **1984**, 24, 929.
[16] A Akiyama and K Nobe, *J. Electrochem. Soc*., **1970**,117, 9.
[17] AA Mazhar, ST Arab and EA Noor, *Corrosion*, **2002**, 58, 3,1.
[18] H Gilman. Organic Chemistry. Vol.3 ,Wiley, New York, **1953;** 276.
[19] SA Umore, IB Obot, EE Ebenso, PC Okafor, O Ogbobe and EE Oguzie, *Anti-corros. Methods and Material*., **2006,** 535, 277.
[20] ES Ferreia, C Giacomelli, FC Gicomelli and A Spinelli, *Mater. Chem. Phys*., **2004**, 83(1), 129.
[21] A Popova, E Sokolova, S Raicheva and M.z Christov, *Corros Sci*., **2003**, 45,
[22] EE Oguzie, *Corros. Sci*., **2007**, 49, 1529.
[23] LA Nnanna, OC Nwadiuko, ND Ekekwe, EP Eti, KB Okeoma, *Arch. Appl. Sci. Res*. **2011**,3,6, 68-74.
[24] HM Bhajiwala, RT Vashi, *Bull. Electrochem*., **2001**, 17, 441.
[25] IB Obot, No Obi-Egbedi, SA Umoren, *Der Pharma Chemica*, **2009**,1,1, 151-166.
[26] SA Umoren, EE Ebenso, *Mater. Chem. Phys*, **2007**, 106, 387.
[27] NO Eddy, PAP Mamza, *Port. Electrochim. Acta*, **2009,** 27,443-456.
[28] OK Abiola and JOE Otaigbe, *Int. J. Electrchem. Sci*., **2008**, 3,191-198.
[29] BG Atya, BE El-Anadouli, FM El-Nizamy, *Corros. Sci*., **1984**, 24, 497.
[30] M Sivaraju and K Kannan,Int. *J. Chem. Tech. Res*., **2010**, 2, 2, 1243-1253.
[31] D Emregul, KC Emregul and O Atakol, *Corros.Sci*., **2008,** 50, 1460-1468
[32] S A Umoren, I B Obot and EE Ebenso., *E-Journal of Chemistry* **5(2) 2008,** 5(2) 355.
[33] AA El-Shafei, M NH Moussa and A A El-Far., *Master. Chem. Phys.* **2001**, 70, 175.