

Corrosion Inhibitory Effects of A New Synthetic Schiff Base On Aluminium in Sulphuric Acid

Echem, O.G , James A.O.

Abstract - In this investigation, the inhibitory effect of a new synthesized (E)-N-(4-methylphenyl)-1-(4-nitrobenzyl) methanimine Schiff base (SBMNM) on the corrosion of aluminium in 2M H₂SO₄ solution was studied using weight loss and gasometric techniques. The Schiff base was prepared using reflux method; the characterization was carried out by electronic absorption spectra, infrared spectra, solubility and melting point tests. The results showed that the inhibition efficiency decreased as the temperature increased, a physical reaction mechanism is proposed. The plot of log (wi-Δw) against time gave linear graph which suggests a first order reaction mechanism. The percentage efficiency was 75.43% at 1.0x10⁻²M concentration of the Schiff base. The negative free energy of adsorption obtained confirms a spontaneous adsorption. The Langmuir adsorption isotherm result showed a deviation from an ideal Langmuir adsorption isotherm equation.

Index Terms: Aluminium, corrosion inhibitors, weight loss, Schiff base, gasometer, adsorption, efficiency

1 INTRODUCTION

Corrosion resistance of aluminium is dependent upon a protective oxide film. This film is stable in aqueous media when the pH is between about 4.0 and 8.5. The oxide film is naturally self-renewing and accidental abrasion or other mechanical damage of the surface film is rapidly repaired. The conditions that promote corrosion of aluminium and its alloys, therefore, must be those that continuously abrade the film mechanically or promote conditions that locally degrade the protective oxide film and minimize the availability of oxygen to rebuild it.

The acidity of the environment significantly affects the corrosion behavior of aluminium alloys. At lower pH aluminium is more likely to corrode, the oxide is more rapidly attacked than aluminium, thereby exposing the aluminium to further attack. In acidic medium, hydrogen evolution reaction predominates and corrosion inhibitors reduce or prevent these reactions [1].

Schiff bases have been reported as an effective corrosion inhibitor due to their ability to spontaneously form a monolayer on the surface of the metal to be protected. The aim of this paper is to investigate the corrosion inhibitory effects of synthesized (E)-N-(4-methylphenyl)-1-(4-nitrobenzyl) methanimine Schiff base on the acid corrosion of aluminium in 2M sulphuric acid (H₂SO₄) solutions at 303K, 313K and 323K using weight loss and gasometric methods.

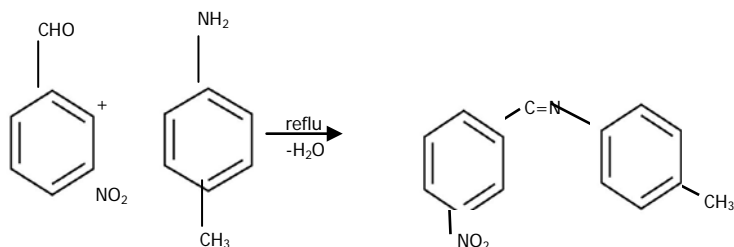
2 MATERIALS AND METHODS

Preparation of (E)-N-(4-methylphenyl)-1-(4-nitrophenyl) methanimine, SBMNM.

Reflux technique 4.5336g (0.030mol) of 3-nitrobenzaldehyde was added to 60ml benzene, the resultant solution was added drop wise into benzene (30ml) solution containing p-toluidine 3.21g (0.030 mol). The mixture was heated at a temperature of 60°C in a reflux apparatus until no water appeared. The residue was recrystallized

from ethyl acetate (25ml) to obtain the title grey coloured crystalline solid compound.

Scheme 1: Synthesis of (E)-N-(4-methylphenyl)-1-(4-nitrobenzyl) methanimine (SBMNM)



Measurement of corrosion rate: The rate of corrosion of aluminium in 2.0 M H₂SO₄ solution with and without the inhibitor was measured by gasometric and weight loss techniques [2].

3 Experimental Procedure

3.1 Gasometric Measurement: Six pieces of 3SR aluminium (98.5076% purity) coupons (2cm x 5cm x 0.052cm) were used in the experiments for test solutions containing 8.0M H₂SO₄ (blank) only and with the five different concentrations of the Schiff base additive in 8.0M H₂SO₄ solution. The two faces of each of the metal coupons had 20.0cm² total surface area and the weight ranges from 4.8148g - 5.9084g.

The volume of the test solutions used in each experiment was 50ml. A 50ml of each test solution was introduced into the reaction vessel connected to a burette through a delivery tube. The initial volume of air in the burette was recorded. One metal coupon was dropped into the test solution and the reaction vessel quickly

closed. The various possible outlets where the expected hydrogen gas from the reaction cell would likely escape were properly sealed with a masking tape. Each experiment was conducted on a fresh specimen of metal coupon with different concentrations of 1.0 x 10⁻² M to 1.0 x 10⁻⁶ M of the studied Schiff base. The hydrogen gas evolved in the gasometric set - up displaced the dilute solution of sodium chloride coloured with methyl orange; the solution was coloured for easy reading of the burette. The volume of the hydrogen gas evolved was read directly and recorded every 1 minute for 30 minutes. The evolved hydrogen gas is not readily soluble in sodium chloride solution. The volume of the gas is always measured at atmospheric pressure using a pressure leveler reservoir bulb.

3.2 Weight loss Determination: Eighteen pieces of 3SR aluminium alloy sheets of 0.052cm thickness, 4cm breadth and 5cm length; 98.5076% purity were used for weight loss measurements. The total surface area of the coupons exposed to the corrodent was 40cm² (since both faces of the coupons were immersed in the corrodent).

The coupons were dried in the desiccator and carefully weighed; three aluminium coupons were placed into three different 250ml beakers containing 2.0M sulphuric acid solution(blank) maintained at 303K, 313K, and 323K, they were retrieved at 30 minutes intervals progressively for 240

minutes (4hours) because of the increased rate of reaction.

The aluminium coupons retrieved were immediately brushed with iron brush, washed in water, rinsed in ethanol and acetone, then dried inside a 1000ml beaker place in a thermostat heating mantle to constant weight before final weighing. The weight loss was calculated in grams as the difference between the initial weight prior to immersion, and weight after removal of the corrosion product. Each reading reported was an average of two readings recorded to the 0.01mg, [3].

Experiments were repeated with the introduction of five different concentrations ($1.0 \times 10^{-2}M$, $1.0 \times 10^{-3}M$, $1.0 \times 10^{-4}M$, $1.0 \times 10^{-5}M$, and $1.0 \times 10^{-6}M$) of SBMNM, in 2.0M H_2SO_4 solutions at 303k, 313k and 323k. Fifteen 250ml beakers which separately contained $1.0 \times 10^{-2}M$ to $1.0 \times 10^{-6}M$ concentrations of SBMNM were maintained at 303k, 313k and 323k. The difference in weight of the coupons was taken as the weight loss.

The procedure adopted for this experiment was in accordance with ASTM standard procedure described in the literature [4].

Glass beakers were used for the corrosion studies and in each set of experiments. 250ml beakers were used and one metal coupon per beaker was used. The coupon was placed inside the test solution with the aid of rubber thread, [5].

4. RESULTS AND DISCUSSION

Table 1 : Kinetic data for aluminium corrosion in 2.0M H₂SO₄ containing SBMNM from weight loss measurement.

Inhibitor Conc. (M)	Inhibition Efficiency (%)			Rate constant (K) (min ⁻¹)			Half life (t _{1/2}) (min ⁻¹) X 10 ⁴			Activation Energy (KJmol ⁻²)		Average Activation Energy (KJmol ⁻¹)	
	303k	313K	323k	303K	313K x 10 ⁻⁵	323K x 10 ⁻⁵	303K	313 x 10 ⁴	323K x 10 ⁴	303-313K	313-323K	303-313K	313-323K
1.0x10 ⁻⁶	58.20	17.15	11.61	1.11 x10 ⁻⁵	2.90	3.66	6.24 x 10 ⁴	2.39	1.89	72.60	19.57	80.29	27.52
1.0 x 10 ⁻⁵	60.49	20.47	13.38	9.90 x10 ⁻⁶	2.76	3.65	7.00 x 10 ⁴	2.51	1.90	77.51	23.50		
1.0 x 10 ⁻⁴	66.28	21.73	17.72	9.08 x10 ⁻⁶	2.73	3.62	7.67 x 10 ⁴	2.54	1.91	83.63	23.72		
1.0 x10 ⁻³	68.50	25.32	18.48	8.31 x10 ⁻⁶	2.56	3.57	8.34 x 10 ⁴	2.71	1.94	85.05	27.96		
1.0 x 10 ⁻²	75.43	45.89	28.57	6.30 x10 ⁻⁶	1.88	3.13	1.10 x 10 ⁵	3.69	2.21	82.64	42.86		

Table 2: Comparison of percentage inhibition efficiency by weight loss and hydrogen gas evolution technique for aluminium corrosion in 2M H₂SO₄ containing SBMNM at 303K

Inhibition Concentration(M)	Percentage inhibition efficiency %	
	Weight loss	Hydrogen evolution method
0.000001	58.20	58.14
0.00001	60.49	60.47
0.0001	66.28	66.67
0.001	68.50	68.99
0.01	75.43	75.19

Table 3: Surface coverage (θ) and corrosion rate for the inhibition of aluminium corrosion by SBMNM in 2.0M H₂SO₄ solution at different temperatures

Conc.(θ)	Surface coverage θ			Corrosion 10 ³ rate (mdd)/mgdm ⁻² day			Corrosion rate(mm/year) or mmpyr year		
	303K	313K	323K	303K	313K	323K	303K	313K	323K
0.000001	0.59	0.18	0.12	2.16	5.44	7.76	1.64	4.20	5.68
0.00001	0.62	0.21	0.14	2.01	5.25	7.59	1.43	4.02	5.66
0.0001	0.68	0.23	0.18	1.69	5.13	7.23	1.30	3.95	5.62
0.001	0.70	0.26	0.19	1.59	4.89	7.14	1.19	3.69	5.52
0.01	0.76	0.47	0.29	1.26	3.52	6.26	0.93	2.69	4.84

Table 4: Free energy of adsorption for the inhibition of aluminium corrosion in 2.0M H₂SO₄ solution by SBMNM as a function of surface coverage at 303K

Concentration (M)	Free energy of adsorption ΔGads (JKmol ⁻¹)		
	303K	313K	323K
0.000001	-43.30	-37.24	-36.96
0.00001	-38.18	-31.85	-31.31
0.0001	-33.96	-26.24	-26.06
0.001	-28.77	-20.78	-20.09
0.01	-25.16	-18.36	-15.80
Average	-33.87	-26.89	-26.04

Table 5: Heat of adsorption ΔHads and Entropy of adsorption ΔSads for the inhibition of corrosion of aluminium by SBMNM at different concentrations in 2.0M H₂SO₄ solutions at 303K

Conc (M)	Heat of adsorption (KJ/mol)	Entropy of adsorption (J/mol/k)
0.000001	70.08	374.19
0.00001	74.99	373.50
0.0001	81.11	379.77
0.001	82.53	367.33
0.01	80.12	347.46
Average	77.77	368.45

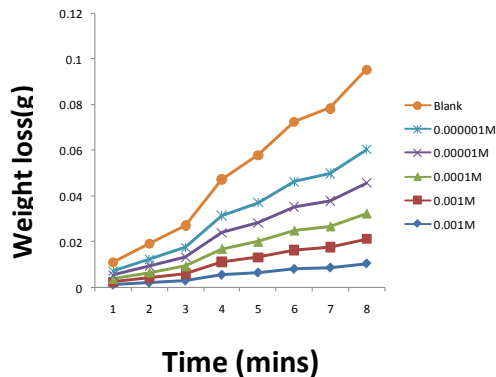


Fig. 1. Variation of weight loss(g) with time (mins) for the corrosion of aluminium coupons in 2.0M H₂SO₄ solution containing different concentrations of SBMNM at 303K

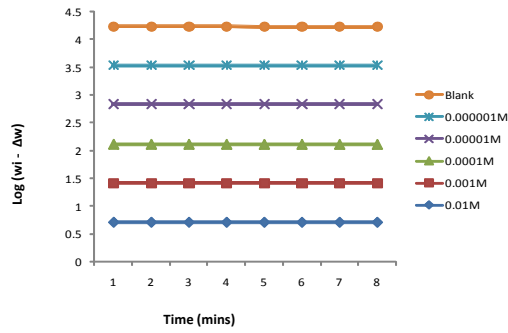


Fig. 2. Variation of $\text{Log}(w_i - \Delta w)$ with time (mins) for the dissolution of aluminium coupons in 2.0M H_2SO_4 solution containing different concentrations of SBMNM at 303K

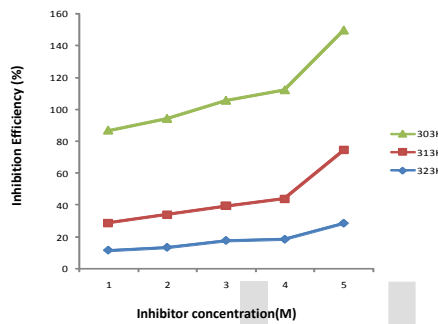


Fig. 3. Variation of inhibitor efficiency with inhibitor concentration (M) for the corrosion of aluminium coupons in 2.0M H_2SO_4 solution containing SBMNM at different temperatures.

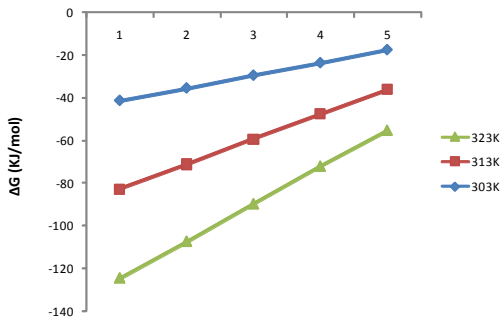
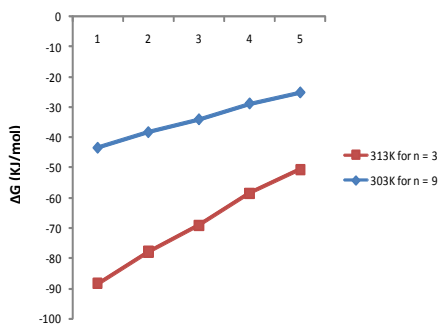
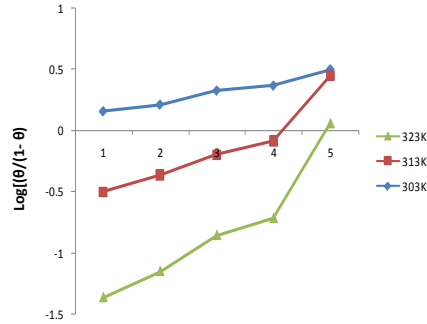


Fig. 4. Variation of Free energy of adsorption ΔG_{ads} with temperature at different concentrations for SBMNM the inhibition of aluminium corrosion in 2.0M H_2SO_4 solution.



Surface coverage (θ)

Fig.5. Variation of Free energy of adsorption for the inhibition of aluminium corrosion in 2.0M H_2SO_4 solution by SBMNM as a function of surface coverage at 303K



Log C

Fig. 6. Langmuir adsorption isotherm (plotted as $\text{Log}[\theta/(1-\theta)]$) versus $\text{Log} C$ for the inhibition of aluminium corrosion in 2.0M H_2SO_4 solution by SBMNM

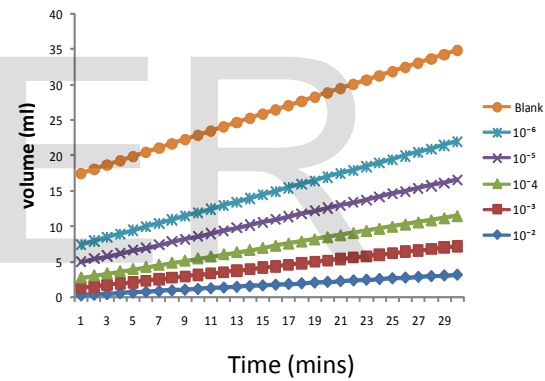


Fig. 7. Variation of Volume of hydrogen gas evolved with time (minutes) for the inhibition of aluminium corrosion in 8M H_2SO_4 solution by SBMNM at 303.

The effect of temperature on the corrosion of aluminium was carried out and the result presented in Fig 3. As the temperature increased from 303k to 323k the weight loss also increased; similar observation was made in [6].

This observation is due to the fact that chemical reaction rates generally increase with rising temperature. Increase in temperature leads to increase in the kinetic energy possessed by the reacting molecules thereby making the molecules to overcome the energy barrier faster. Other factors that may be responsible for the increase in weight loss at increasing temperature were increase in solubility of the protective films on the metal, increase in the rate of diffusion and ionization of the reacting species in the corrosion process [7].

In Fig 1, SBMNM inhibits aluminium corrosion in H_2SO_4 acid solution, this is demonstrated by a general decrease in weight of aluminium. The weight loss of aluminium was observed to decrease with increase in the concentrations of the inhibitors. The highest weight loss of 0.0144g was obtained in H_2SO_4 solution containing $1.0 \times 10^{-6}M$ SBMNM, while the weight loss of 0.0106g was recorded for H_2SO_4 solutions containing $1.0 \times 10^{-2}M$ SBMNM. The results presented in Table 2 confirmed that the percentage inhibition efficiency obtained from the weight loss method and hydrogen gas evolution technique is similar, this is in agreement with the findings in [8], [9],[10].

The highest percentage inhibition efficiency of 75.43%, was obtained at a concentration of $1.0 \times 10^{-2}M$ while the least percentage inhibition efficiency of 58.14% was obtained at a concentration of $1.0 \times 10^{-6}M$; from the results it can be deduced that the higher

the concentration of the inhibitor, the higher the inhibition efficiency at all the temperatures studied (Fig 3).

similar result was gotten in the study of sulpha Schiff bases as corrosion inhibitors [11].

Table 1 displayed the effect of different temperature on inhibition efficiency, which decreased as the temperature of the system increased from 303K to 323K. The inhibition efficiencies of 75.43% was obtained with inhibitor concentration of $1.0 \times 10^{-2}M$, at 303K; 45.89% at 313K and 28.57% at 323K. Inhibition efficiency was highest at 303K and lowest at 323K. This may be attributed to physical adsorption mechanism.

Physisorption predominates if inhibition efficiency decreases with increase in temperature [12].

Fig 2 revealed that the plot of $\log(w_i - \Delta w)$ with time (minutes) is linear, confirming a first order reactions kinetics for aluminium in 2M H_2SO_4 solutions in the presence for the inhibitor. There was a general decrease in the rate constant values at all the studied temperatures with increasing concentrations of the inhibitor Tables 1. The

increase in half-life $\left(t_{1/2} \right)$ with increase in

the concentrations of the inhibitor is an additional confirmation of the inhibition of aluminium in 2M H_2SO_4 acid solution by the inhibitor. Research findings in [13] suggest that the increase in half-life means more

protection of the aluminium coupons by the inhibitors. The observed average activation energies of 27.52 KJmol^{-1} was obtained for the inhibition of the corrosion of aluminium in $2\text{M H}_2\text{SO}_4$ solution. This value tends to suggest a physically adsorption reaction mechanism.

Table 4 gave negative values for ΔG_{ads} , suggesting spontaneous adsorption of the inhibitors molecules on the aluminium surface. Negative values of ΔG_{ads} was obtained using Eco-friendly corrosion inhibitors of delonix regia extract for corrosion of aluminium in acidic media. The mean values of ΔG_{ads} obtained was below -40 KJmol^{-1} , thus suggesting electrostatic interactions between the charged metal surface which assume physical adsorption reaction mechanism [14].

The positive values of ΔH_{ads} and ΔS_{ads} in Table 5 may be due to the replacement of water molecules by the inhibitors molecules on the aluminium surface and the evidence of reaction randomness. Figures 5 revealed that an increase in the concentration of the inhibitors increases the negative value of ΔG_{ads} and surface coverage θ , which indicate a better adsorption of the inhibitors on the aluminium surface.

It was further observed that the plot of $\log [\theta / (1 - \theta)]$ against $\log C$ was linear but the gradients was not equal to unity as shown in Fig 6. This suggests physisorption adsorption reaction mechanism [15].

Fig 7 showed the variation of the volume (ml) of hydrogen gas evolved with time (minutes) in the presence and absence of different concentrations of SBMNM. The graph was linear because the volume of hydrogen gas which was collected over a dilute solution of sodium chloride (hydrogen gas has negligible solubility in sodium chloride solution) coloured by methyl red in a gas collector was enough to displace the water molecules steadily for a duration of 30 minutes. This agrees with some earlier studies using similar method [11]. The addition of the Schiff base under investigation caused an observable decrease in the amount of hydrogen gas evolved at 303k when compared with the volume of hydrogen gas released without the inhibitor. This confirms that the studied Schiff base inhibit the dissolution of aluminium in the acid solution.

The concentration of the H_2SO_4 , solution used was $8\text{M H}_2\text{SO}_4$, this is because concentrations less than 8M did not produce appreciable volume of hydrogen gas due to slow reaction rate.

This is supported by an earlier study carried out in [16]. It was observed that the volume of hydrogen gas evolved decreased with increase in the concentration of the inhibitors. This confirms the assertion that increase in concentration of inhibitors increases inhibition efficiency.

CONCLUSION

The results obtained from this study reveal that the investigated Schiff base inhibits the

corrosion of aluminium in H_2SO_4 acid solutions. The size, shape and orientation of the molecules and the electronic charge on the molecules determine the degree of adsorption as well as the adsorption bond strength and hence the effectiveness of this inhibitor.

This may be due to its high molecular weight which most likely leads to a formation of wide spread film on the metal surface thereby preventing corrosion. [11]. obtained similar findings with sulphur Schiff bases as corrosion inhibitors for mild steel in sulphuric acid. The presence of additional nitrogen, oxygen atoms and methyl group ($-CH_3$) may also have contributed to the high inhibition efficiency, this is supported by the publication of [17]. The Langmuir adsorption isotherm from this study suggests multi-layer adsorption of the inhibitor molecules on the metal.

The positive values of heat of adsorption indicates endothermic reaction and the values obtained for the investigated Schiff base was less than $-80KJmol^{-1}$ expected for physical adsorption, this further supports physisorption reaction mechanism.

The observed inhibition of the corrosion of aluminium is assumed to be due to the adsorption of the studied Schiff bases molecules on the metal surface and the subsequent blocking of the metal's active sites. The compounds generally adsorbed through the $HC = N$ functional group, the π

– electrons of the aromatic rings and other hetero atoms present in the compound.

The calculated negative values of the average free energy of adsorption, (ΔG_{ads}) suggest a spontaneous adsorption of the Schiff base under study on the surface of aluminium.

REFERENCES

- [1] Q.M. Mohamed "Synthesis and characterization of new Schiff bases and evaluation as corrosion inhibitors", *Journal of Basrah Researches (science)* 37(4): 116-130, 2011.
- [2] O.G. Echem, N.C Oforika, and A. O.James, "Synthesis and characterization of 4-[(E)-(-2,dimethoxybenzylidene)amino]benzoic acid Schiff base and evaluation as corrosion inhibitor of steel in 2.0 M H_2SO_4 ", *J. Appl. Sci. Environ. Manage.* 18(1): 63-69, 2014.
- [3] S .D Toliwal, J. Kalpesh, and I. Pavagahh, "Inhibition of corrosion of mild steel in HCl solutions by Schiff base derived from non traditional oils", *Journal of Applied chemical Research*12:24 -36, 2010.
- [4] ASTM "Standard practice for laboratory immersion corrosion testing of metals", volG 31 – 72, P.401, 1990.
- [5] S. Sethi, A. Chaturvedi, R.K. Upadhyay and S.P. Mathur, "Corrosion inhibitory effect of some Schiff's bases on mild steel in acid media", *Journal of*

- Chilean chemical society* 52 (3) :1206-1213, 2007.
- [6] K.O. Orubite, and N.C.. Oforika, "Inhibition of the corrosion of mild steel in hydrochloric acid solutions by the extracts of the leaves of *Nypa fruticans* Wurmb", *Materials letters*. Vol. 58, 1768-1772, 2004.
- [7] I.P.C. Okafor, E.E Ebenso, & U.J. Ekpe, "Inhibition of the acid corrosion of aluminium by some derivatives of thiosemicarbazone", *Bulletin of Chemical Society of Ethiopia*. Vol. 18, No. 12, 181-192, 2004.
- [8] A.O. James, "Inhibition of the corrosion of aluminium and mild steel in hydrochloric and sulphuric acid solutions by pyridoxal hydrochloride, pyridoxol hydrochloride and 2-Benzoyl pyridine". A Ph.D Thesis, Dept. of Pure and Industrial Chemistry, University of Port Harcourt, 2006.
- [9] A. Bansiwala, P. Anthony, and S.P. Mathur, "Inhibitive effects of some Schiff bases on corrosion of aluminium in hydrochloric acid solutions", *British Corrosion Journal*, vol. 35, No. 4, 301, 2000.
- [10] E.E. Ebenso "Inhibition of aluminium (AA3105) corrosion in hydrochloric acid by acetamide and thiourea", *Nigerian Corrosion Journal*, vol. 1, No. 1, 29 - 43, 1998.
- [11] S. Chitra, K. Parameswari, C Sivakani, and A Selvaraj, Sulpha Schiff base as corrosion inhibitors for mild steel in sulphuric acid", *Chemical Engineering Research Bulletin* 14:1-6, 2010.
- [12] S. Chitra, K. Parameswari, and A. Selvaraj, "Dianiline Schiff bases as inhibitors of mild steel corrosion in acid media". *Int. J. Electrochem. Sci.*, 5: 1675 – 1697, 2010.
- [13] B.I. Ita, "A study of corrosion inhibition of mild steel in 0.1 M hydrochloric acid by O-Vanillin and O-vanillin hydrazone", *Bulletin of Electrochemistry*, vol.20, No. 8, 363-370, 2004.
- [14] O.K. Abiola, N.C. Oforika, E.E Ebenso and N.M Nwinuka, "Eco-friendly Corrosion inhibitors: the inhibitive action of Delonix Regia extract for the corrosion of aluminium in acidic media", *Anti corrosion methods and materials*. Vol 54 No.4 Pp219-224, 2007.
- [15] M. Abdel-Aal, and M.Morad, "Inhibiting effects of some quinolines and organic phosphonium compound on corrosion of mild steel in 3MHCl solution and their absorption characteristics", *British corrosion Journal* , 36(4):253-260, 2001.
- [16] U.J. Ekpe U.J. Ibok, B.I., Ita, O.E. Offiong, and E.E. Ebenso, "Inhibitory action of methyl and phenyl thiosemicarbazone derivatives on the corrosion of mild steel in hydrochloric acid", *Material chemistry and physics*, vol.40, 87-93, 1995.

- [17] K. M. Devender, K.U. Rajesh, and C. Alok, "Study of corrosion inhibition, efficiency of some Schiff's base on aluminum in trichloroacetic acid solution", *Rev.Roun.Chem.559(4):227-232*, 2010.

IJSER