



Synthesis and characterization of 4-[(E)-(-2,5- dimethoxybenzylidene)amino] benzoic acid Schiff base and evaluation as corrosion inhibitor of steel in 2.0 M H₂SO₄.

*¹ECEM OGBONDA G; OFORKA, NC; JAMES ABOSEDE

¹Department of Science Laboratory Technology, Rivers State Polytechnic, Bori.

^{2&3}Department of pure and industrial chemistry university of Port Harcourt
PMB 5023; Port Harcourt River State

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ABSTRACT: The synthesis of 4-[(E)-(-2,5- dimethoxybenzylidene)amino] benzoic acid Schiff base, SBDAB was carried out in order to determine its inhibitory efficiency at higher temperature using weight loss and gasometric techniques. The results showed that the inhibition efficiency of the studied Schiff base increased with increase in temperature for the corrosion of mild steel which suggests chemisorption reaction mechanism. The negative free energy of adsorption obtained confirms a spontaneous adsorption of the Schiff base on the metal surface. The positive values of the heat of adsorption suggest an endothermic reaction. The positive values of the entropy of adsorption suggest a disordered system. The Langmuir adsorption Isotherm result showed a deviation from an ideal Langmuir adsorption isotherm equation, this is due to the interaction of the inhibitor molecules with one another. The inhibition efficiency of 35.20% and 35.31% was obtained for the weight loss and gasometric techniques respectively. The plots of $\log(w_i - \Delta w)$ against time gave linear graph which confirms a first order reaction mechanism. ©JASEM

Introduction: Compounds containing an azomethine group ($-C=N-$) are known as Schiff bases; (Jones, 2000, Mohammed, 2011). They are usually formed by condensation of a primary amine with a carbonyl compounds according to the following reaction:

$R-NH_2 + R-COH \rightarrow R-N=CH-R + H_2O$ where R may be an aromatic or aliphatic group.

Schiff bases of aliphatic aldehyde are relatively unstable and are readily polymerizable while those of aromatic aldehydes, having an effective conjugation system, and are more stable. The chain on the nitrogen makes the Schiff base a stable imine, Jezowska, et al., (1988).

According to Zumdahl (1986), metals corrode because they oxidize easily. With the exception of gold, those metals commonly used for structural and decorative purposes all have standard reduction potentials less positive than that of oxygen gas. The UV- Vis spectra of Schiff base depend on the transition of unpaired electrons from the ground state to the excited state. Some of acceptable absorption band suggesting the presence of $n \rightarrow \pi^*$ transition are 242nm (El-hassy, 2004); 237nm, 270nm, and 335nm (Mounika et al., 2010).

Pavia et al., (2001) gave the range of $\nu(C=N)$ absorption band of free azomethine to be between 1650 - 1550 cm^{-1} . The investigation of the IR absorption band for substituent groups such as $\nu(C=N)$ and aromatic carbons were reported as 1430 cm^{-1} - 1514 cm^{-1} and 3068 cm^{-1} - 3218 cm^{-1}

respectively by Singh et al., (1994) and Bukhari (2002).

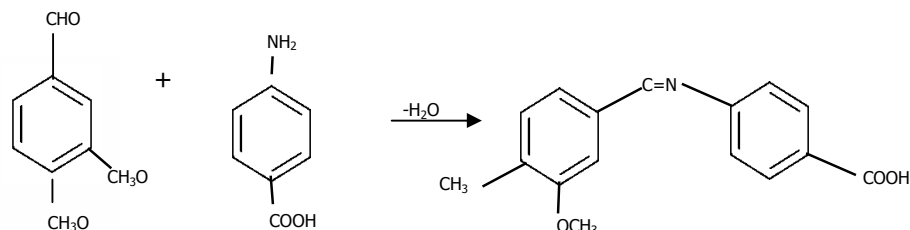
Mild steel and their alloys are extensively used in construction, automobile, food industries; unwanted scale such as rust formed in mild steel are removed by immersing the metal in hydrochloric or sulphuric acid solution, this process is known as an acid pickling bath. After the scale is removed, the metal may be subject to attack by the acid, hence in order to reduce the degree of the metal attack, and the rate of consumption of the acid, corrosion inhibitors that are soluble in the acid used for pickling are added to the pickling solution.

Cotton et al., (1987) have reported that nitrogen ligands such as Schiff bases are important in coordination chemistry because of the particular affinity they show toward transition metals.

Ahamad et al., (2009) as cited in Erma (2010) research study stated that the efficiency of Schiff base inhibitor may depend on the nature of the environment, nature of metal surface, electrochemical potential at the interface, and the structural feature of the inhibitor, which includes number of adsorption centers in the molecule, their charge density, the molecular size, and mode of adsorption, formation of metallic complexes and the projected area of inhibitor on the metal surface. The aim of this study is to synthesize 4-[(E)-(-2,5 imethoxybenzylidene)amino] benzoic acid Schiff base, study its efficiency in inhibiting steel corrosion at higher temperature in acidic media (2M H₂SO₄) by weight loss and gasometric methods.

MATERIALS METHODS

Preparation of 4-[(E)-(-2,5-dimethoxybenzylidene)amino] benzoic acid Schiff base. 4.2127 g (0.025 mol) of 3,4-dimethoxybenzaldehyde was weighed and dissolved in 80ml of benzene; into the solution was added 3.4730 g (0.025 mol) of 4-aminobenzoic acid. 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 (40ml), an orange solid crystal was obtained and allowed to dry



Weight loss method: Preparation of Metal Coupon: Mild steel of 0.1cm thickness used for the study was cut into 4cm by 5cm coupon size for weight loss measurement. The coupons were polished using sandpaper and a hole of 2mm was opened at one edge of each coupon. A rubber thread of 25cm was passed through the opened hole of each coupon. The coupons were soaked in ethanol solution for 10 minutes for de-greasing, rinsed with distill water, dried in acetone, then heated to constant weight and finally kept in a desicator containing calcium chloride. This is necessary to prevent contamination before usage for corrosion studies. The procedure adopted for this experiment was in accordance with ASTM standard procedure described in the literature (ASTM, 1990, Sethi et al., 2007).

The coupons were added to 0.01M, 0.001M, 0.0001M, 0.00001 M and 0.000001M concentrations of the inhibitor in acid media. The corrosion rate is calculated using the following equations:

$$\text{Corrosion rate mmp/year} = \frac{87.6\Delta w}{\text{Density} \times \text{Area} \times \text{Time}} \dots\dots\dots(1)$$

$$(\text{g/cm}^3) (\text{cm}^2) (\text{hr})$$

Where Δw = weight loss, 87.6 is constant.

$$\text{Corrosion rate (mg/dm}^2\text{/day)} = \frac{\Delta w(\text{mg}) \times 1000}{\text{Area} \times 100 \times \text{day}} \dots\dots\dots(2)$$

Gasometric method: The corrosion inhibition experiment involving six mild steel coupons (4cm x 5cm x 0.1cm) in 2.0M H₂SO₄ acid solutions with the inhibition additives were carried out. The two faces of each of the mild steel metal coupons

under room temperature. The compound was found to be soluble in DMSO and H₂SO₄.

Scheme 1: Synthesis of 4-[(E)-(-2,5-dimethoxybenzylidene)amino] benzoic acid Schiff base (SBDAB)

Measurement of corrosion rate: The corrosion rate of steel in 2.0 M H₂SO₄ was measured by weight loss and gasometric methods (Mohammed, 2011; Chitra et al., 2010).

had 40.0cm² total surface area and the weight ranges from 10.1186g - 14.3905g.

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. The volume of hydrogen gas evolved was recorded every 1 minute for 30 minutes for Al in 2.0M H₂SO₄ test solutions. Each experiment was conducted on a fresh specimen of metal coupon. The hydrogen gas evolved displaced the fluid in the gasometric set - up, which was read directly.

The experiment was repeated in the presence of the five different concentrations of 1.0 x 10⁻² M to 1.0 x 10⁻⁶ M of the studied Schiff base; as used in the weight loss experiment with the same corrodent concentrations of 2.0M H₂SO₄ solutions.

RESULTS AND DISCUSSIONS

Identification of the prepared Schiff base: The IR result showed a signal at 1603 (C = N) and 1697 (COOH) functional groups, Pavia et al., (2001). The UV-Vis electronic spectral data for the compound gave λ_{max} 235 ($\pi \rightarrow \pi^*$), Mounika et al., (2010). The melting point was 63-64°C. This agrees with the result of Echem, et al; (2013).

Corrosion study: The inhibition efficiency is calculated using the equations below:

% Inhibition Efficiency =

$$\frac{\Delta W_B - \Delta W_i}{\Delta W_B} \times \frac{100}{1} \dots\dots\dots (3)$$

Where ΔW_B and ΔW_i are weight losses without and with inhibitor respectively.

Table 1: Inhibitor Efficiency with inhibitor concentration (M) for the corrosion of mild steel coupons in 2.0M H₂SO₄ solution containing SBDAB at different temperatures.

Concentration (M)	Inhibition Efficiency (%)		
	303K	313K	323K
0.000001	8.63	18.65	24.94
0.00001	19.30	25.47	27.67
0.0001	20.73	30.30	31.71
0.001	32.92	35.64	38.62
0.01	35.20	37.81	39.67

The inhibition efficiency of this Schiff base increases with increase in concentration (Table 1 and Figure 3). This can be attributed to the blocking of active sites of the metal surface, Toliwal et al; (2010). With increase temperature (303K-313K) a significant increase in inhibition efficiency was observed, this might be due to the presence of reactive functional groups, high electron density of the donor atom which do not decompose easily at higher temperature; but appears to reduce at a higher temperature of 323K probably as a result of decomposition of hydrophobic long chain (Sastri, 1998).

Table 2: Free energy of adsorption ΔG_{ads} with temperature at different concentrations for SBDAB the inhibition of mild steel corrosion in 2.0M H₂SO₄ solution.

Concentration (M)	Free energy of adsorption ΔG_{ads}		
	303K	313K	323K
0.000001	-38.62	-41.54	-43.40
0.00001	-34.48	-36.13	-37.41
0.0001	-28.80	-30.41	-31.47
0.001	-23.76	-24.61	-25.48
0.01	-18.02	-18.68	-19.32
Average	-28.74	-30.27	-31.42
0.01	35.20	35.31	

The negative values of ΔG_{ads} listed in Table 2 indicate the spontaneous adsorption of the additives molecules on the steel surface. The values of free energy ΔG less than -40 KJ/mol indicates that such inhibitors are physically adsorbed on the metal surface (Toliwal et al., 2010). However, in this present case the ΔG values increased with increase in temperature reaching a maximum of -43.40KJ/mol at 323K; this tends to suggest a combination of physical and chemical adsorption. However, which predominates over the other is detected from the temperature studies, which in this case favours chemical adsorption. This means that a covalent type of bonding involving electron transfer from the inhibitor to the metal surface is assumed to have occurred (Athareh, et al., 2004).

$\Delta G = -2.303RT \log (55.5 K)$ (4) $K = \theta/C [1 - \theta]$ Where C = concentration of the inhibitor. The percentage inhibition efficiency of the inhibitor from hydrogen gas evolution experiment can be calculated using

$$\% \text{ inhibitor efficiency} = \frac{V_b - V_i}{V_b} \times 100\% \quad (5)$$

Where V_b and V_i are the volumes of hydrogen evolved from gasometric method without and with inhibitor respectively at 30 minutes. The per cent inhibition efficiency results obtained from the gasometric method agrees with that of the weight loss as shown in Table 3.

Table 3: Comparison of percentage inhibition efficiency by weight loss and hydrogen gas evolution technique for mild steel corrosion in 2.0M H₂SO₄ containing SBDAB at 303K

Inhibition Concentration (M)	Percentage inhibition efficiency %	
	Weight loss	Hydrogen evolution method
0.000001	8.63	9.09
0.00001	19.30	18.53
0.0001	20.73	20.63
0.001	32.92	32.52

Table 4: Kinetic data for mild steel corrosion in 2M H₂SO₄ containing SBDAB from weight loss measurement.

inhibitor Conc. (M)	Rate constant (K)		Half life (t _{1/2}) (min) x			Activation energy		Average (min ⁻¹) x 10 ⁻³		
	10 ²		(KJmol ⁻¹)			activation		energy		
								(KJmol ⁻¹)		
	303K	313K	323K	303K	313K	323K	303-313K	313-323K	303-313K	313-323K
1.0x10 ⁻⁶	4.25	5.09	5.18	1.63	1.36	1.34	13.63	1.47	8.79	2.92
1.0 x 10 ⁻⁵	4.17	4.75	5.02	1.66	1.46	1.38	9.84	4.65		
1.0 x 10 ⁻⁴	4.09	4.42	4.51	1.69	1.57	1.54	5.87	1.69		
1.0 x 10 ⁻³	3.62	4.24	4.36	1.91	1.63	1.59	11.95	2.35		
1.0 x 10 ⁻²	3.38	3.50	3.69	2.05	1.98	1.88	2.64	4.44		

The rate constants and the half life ($t_{1/2}$) for the corrosion of steel at the various studied temperatures decreased from 303K to 323K and increased with increase in concentrations (Table 4); these confirm the inhibition of steel

corrosion in 2.0M H₂SO₄ by the inhibitor. The average activation energy is 8.79 KJmol⁻¹ and 2.92 KJmol⁻¹ for 303-313 K and 313-323 K respectively.

Rate constant (k) at 303K, 313K and 323K for first order reaction $k = \frac{2.303}{\text{Time}} \log \frac{w_i}{w_f} \dots\dots\dots 6)$

Half- life (t_{1/2}) at 30°C, 40°C and 50°C For first order reaction $t_{1/2} = \frac{0.693}{k} \dots\dots\dots 7)...$

Activation energy (K Jmol⁻¹) $E_a = \frac{2.303RT_2(\log K_2/K_1)}{T_2-T_1} = \frac{Jmol}{1000} = KJmol^{-1} \dots\dots\dots 8)$

Where R= is the gas constant in Joule (J) T= Absolute temperature in Kelvin
R= 8.314 Jmol⁻¹ K⁻¹ or 8.314 x 10⁻³ KJmol⁻¹ K⁻¹ K₁ and K₂ are rate constants at T₁ (303K) and T₂ (313K) respectively or T₁ (313K) and T₂ (323K).

Table 5: Surface coverage (θ) and corrosion rate for the inhibition of mild steel corrosion by SBDAB in 2.0M H₂SO₄ solution at different temperatures.

Conc (M)	Surface Coverage θ			Corrosion rate (mdd) mgdm ⁻² day ⁻¹ x 10 ³			Corrosion rate (mm/year) or mm per year		
	303K	313k	323k	303K	313k	323k	303K	313k	323k
0.000001	0.09	0.19	0.25	3.23	3.38	3.58	22.01	25.89	26.67
0.00001	0.20	0.26	0.28	2.83	3.10	3.44	21.40	23.94	25.59
0.0001	0.21	0.31	0.33	2.81	2.90	3.20	21.38	22.02	22.14
0.001	0.34	0.36	0.39	2.36	2.67	2.91	18.22	20.92	21.66
0.01	0.36	0.38	0.40	2.28	2.58	2.87	16.80	16.81	17.86

The surface coverage θ increased with concentrations of the additives at the various temperatures which means that more of the inhibitors adsorbed on the steel surface (Table 5). Also the rate of corrosion decreased with increase in concentration of the additives at the studied temperatures which supports a chemisorption reaction mechanism.

Table 6: Heat of adsorption ΔH_{ads} and Entropy of adsorption ΔS_{ads} for the inhibition of corrosion of mild steel by SBDAB at different concentrations in 2.0M H₂SO₄ solutions at 303K

Concentration (M)	Heat of adsorption (KJ/mol)	Entropy of adsorption (J/mol/K)
0.000001	11.11	148.15
0.00001	7.32	125.31
0.0001	3.35	93.66
0.001	9.43	101.85
0.01	10.12	53.04

The positive values of ΔH_{ads} and ΔS_{ads} (Table 6) may likely be as a result of possible replacement of water molecules by the inhibitor during adsorption of the additives on steel surface.

$$\Delta G_{\text{ads}} = \Delta H_{\text{ads}} - T \Delta S_{\text{ads}} \quad (9)$$

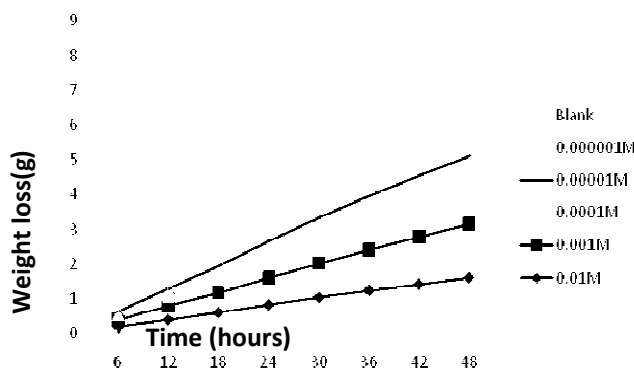


Fig 1 : Variation of Weight loss(g) with time(hours) for the corrosion of mild steel coupons in 2.0M H₂SO₄ solution containing different concentrations of SBDAB at 303K

Weight loss decreased with increase in concentration of the inhibitor (Figure 1), this shows that the inhibitor molecules formed more monolayer on the surface of the steel thereby reducing the corrosion.

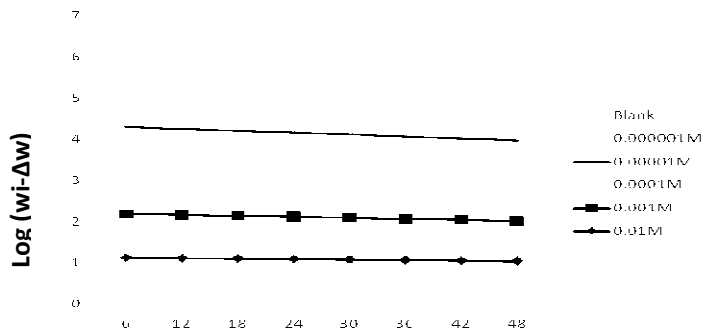


Fig 2: Variation of Log (wi-Δw) with time (hours) for mild steel coupon dissolution in 2.0M H₂SO₄ at different concentrations of SBDAB at 303K. The plots of Log (wi-Δw) against time (Figure 2) are linear, these confirm a first order rate reaction kinetics for mild steel corrosion in H₂SO₄ solutions at the studied temperatures.

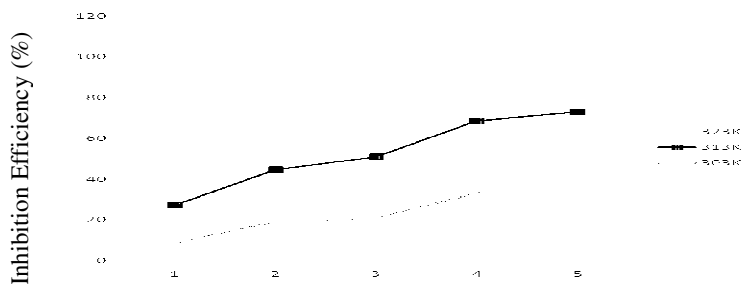


Fig 3: Variation of Inhibitor Efficiency with inhibitor concentration (M) for the corrosion of mild steel coupons in 2.0M H₂SO₄ solution containing SBDAB at different temperatures.

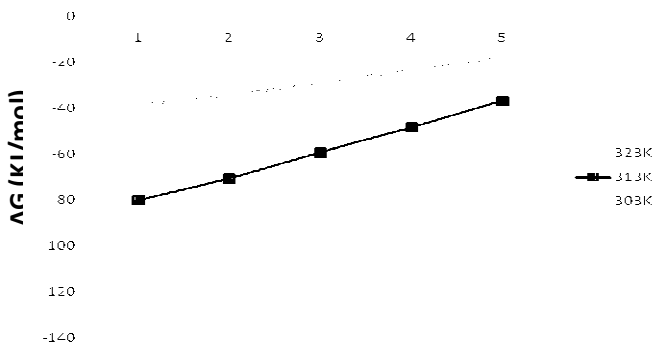


Fig 4: Variation of Free energy of adsorption ΔGads with temperature at different concentrations for SBDAB the inhibition of mild steel corrosion in 2.0M H₂SO₄ solution.

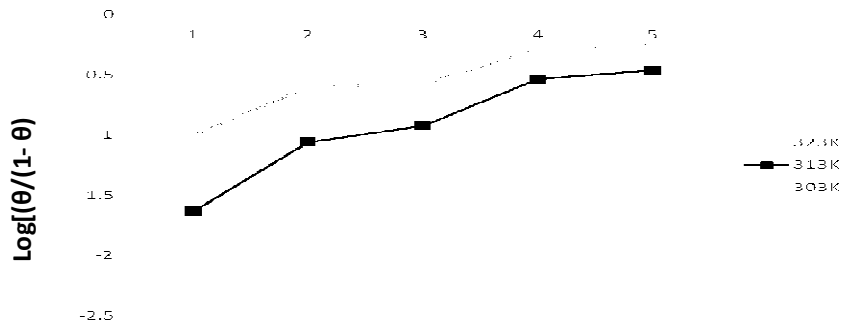


Fig 5 : Langmuir adsorption isotherm (plotted as Log [θ/(1-θ)]) versus Log C for the inhibition of mild steel corrosion in 2.0M H₂SO₄ solution by SBDAB.

Figure 5 plot is linear but the gradient is not equal to unity. The deviation may be due to the fact that adsorbed species interact with each other on the metallic surface, Upadhyay and Mathur, (2007).

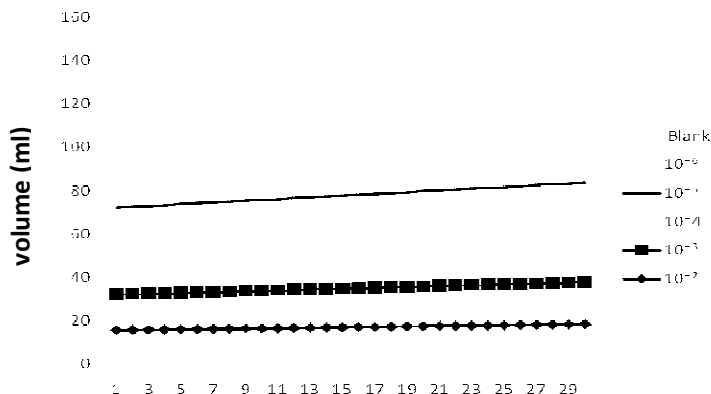


Fig 6 : Variation of Volume of hydrogen gas evolved with time (minutes) for the inhibition of mild steel corrosion in 8M H₂SO₄ solution by SBDAB at 303K

Conclusion: The 4-[(E)-(-2,5 dimethoxybenzylidene)amino] benzoic acid Schiff base inhibited corrosion of steel in 2.0M H₂SO₄. The inhibition efficiency increased with increase in temperature which suggests a chemisorption reaction mechanism. The inhibition efficiency increased with increase in concentration.

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