CORROSION INHIBITORY EFFECTS OF 4-[(3-NITROBENZYLIDENE) AMINO] BENZOIC ACID SCHIFF BASE (SBNAB) ON MILD STEEL IN ACID MEDIA.

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Abstract

The purpose of this study was to synthesize, characterize and investigate the corrosion inhibitory effects of a Schiff base that can inhibit mild steel more efficiently at higher temperature. Weight loss and gasometric methods were used to study the corrosion inhibition of mild steel in sulphuric acidic solution by 4-[(3-nitrobenzylidene) amino] benzoic acid Schiff base (SBNAB). The results of inhibition efficiencies of 44.89%, 48.50% and 50.85% at 303K, 313K and 323K temperatures respectively were obtained. The inhibition efficiency increased with increase in temperature which suggests a chemisorption reaction mechanism. The plots of log (wi-Δw) against time gave a linear graph which confirms a first order reaction mechanism. The positive values of the entropy of adsorption suggest a disordered system, while a negative free energy of adsorption indicates a spontaneous reaction.

Keywords: mild steel, corrosion inhibition, Schiff base, chemisorption, gasometric, adsorption, weight loss
Introduction

Mild steel is one of the most common of all metals and one of the least expensive steels used in almost all metal products. It is weldable, relatively hard and is easily annealed. However, it has poor resistance to corrosion, hence the need to protect it.

Corrosion is the gradual deterioration of metals due to their reaction with oxygen and water; the metal's surface provides both the anodic and cathode sites needed for the oxidation and reduction reactions. For mild steel, the oxidation half reaction produces electrons which reduce oxygen to water at the cathode (Erma, 2010). The corrosion product is called ‘rust’.

Corrosion inhibitors are chemical substances which, when added in small concentrations to an environment, minimizes or prevents corrosion, Papavinasam, (2000). According to Papavinasam, (2000), an efficient inhibitor is compatible with the environment, is economical for application, and produces the desired effect when present in small concentrations.

The active ingredients of organic inhibitors invariably contain one or more functional groups containing one or more heteroatoms, N, O, S, P or Se, through which the inhibitors anchor onto the metal surface. Substituted benzoic acids are widely used as corrosion inhibitors; their adsorption and inhibition efficiencies depend on the nature of the substituent. Electron-donating substituents increase inhibition by increasing the electron density of the anchoring group; on the other hand, electron-withdrawing substituents decrease inhibition by decreasing the electron density.

Organic molecules decompose at higher temperatures, this implies that film forming inhibitors that depend on physical adsorption mechanism become less effective at higher temperature whereas those that depend on chemisorptions increases with increase in temperature up to the temperature at which decomposition of the inhibitor occurs; this is due to the strengthening of chemical bonds.

Schiff bases are found to inhibit corrosion effectively based on their ability to spontaneously form a monolayer on the surface to be protected.

Toliwal et al; (2010), attributes the good inhibitive properties of Schiff bases to the presence of $\pi$-bonds and the interaction of $\pi$ orbital with metal surface.
**Experimental Methods**

**Preparation of 4-[(3-nitrobenzylidene) amino] benzoic acid, SBNAB.**

Microwave technique

4.5336g (0.030mol) of 3-nitrobenzaldehyde was weighed and mixed with 4.11g (0.030mol) of 4-aminobenzoic acid in a conical flask. The mixture was stirred thoroughly and allowed to heat in a microwave oven. After 2mins of heating, the color of the mixture changed to brown and later to dark brown. After 30mins of heating the mixture was brought out and allowed to cool. Ethanol was added to the mixture and heated on a heating mantle, it was brought down and allowed to cool and filtered. The filtrate was recrystallized with water and the precipitate formed was filtered and dried which has a brown color.

**Scheme 1: Synthesis of 4-[(3-nitrobenzylidene)amino] benzoic acid Schiff base (SBNAB)**

![Chemical Scheme](image)

(a) = 3-nitrobenzaldehyde  (b) = 4-aminobenzoic acid  (c) = SBNAB

**Measurement of Corrosion Rate**

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

The mild steel of 0.1cm thickness used for the study were cut into 4cm by 5cm coupon size for weight loss and 2cm by 5cm for hydrogen gas evolution measurements. The coupons were polished using sand-paper 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.

Experimental set - up of weight loss measurements

The procedure adopted for this experiment was in accordance with ASTM standard procedure described in the literature (ASTM, 1990). 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, Sethi et al., (2007).

Gasometric Technique

The Gasometer

The term gasometer was originally coined by William Murdoch in the early 19th century. This instrument is not a meter but a container used in measuring volumes of gas evolved in a reaction; Chitra et al., (2010).

According to Umoren et al., (2011), the gasometric assembly is essentially an apparatus that measures the volume of gas evolved from a corrosion reaction system. It consists of essentially a conical or round bottom flask that serves as the reaction medium containing the corrodent and the metal coupons. Others include a reservoir bulb, a burette fitted with taps, and an outer glass jacket that serves as a water condenser.

Results and Discussion

Identification of the prepared Schiff Base

The time duration for the microwave method of synthesizing 4-[(3-Nitrobenzylidene)amino]benzoic acid (SBNAB) was about 30 minutes, this result agrees with other studies (Hassan et al., 2009) which showed that microwave irradiation takes shorter reaction time in Schiff base synthesis when compared with the reflux method. The microwave reaction
method is fast, clean, cheap and convenient, however, its yield depend on the nature of the reactants and the amount of the starting materials.

Furthermore, the IR spectra measurements result for 4-[(3-Nitrobenzylidene)amino]benzoic acid (SBNAB) showed the following absorption bands: 1607 [\(\nu(C=N)\)], 1693 [\(\nu(C=O)\) for carboxylic acid], 3092 [\(\nu(-OH)\)], 1337 [\(\nu(N=O)\)].

1H NMR (200MHz, DMSO, ppm) \(\delta\): 8.65 (-C=N), 6.5-8.5 (Ar-H), 10.12 (-COOH). 13C NMR (50MHz, DMSO, ppm) \(\delta\c\): 167.3 (C-7, C=N), 161.0 (C-3, aromatic ring). UV-Vis (Hexane, \(\lambda_{\text{max}}\) nm): 235. The proposed structure was in agreement with other published works, (Azogu, 2010; Echem, et al., 2013).

**Corrosion Study**

The inhibition efficiency is calculated using the equations below:

\[
\% \text{ Inhibition Efficiency} = \frac{\Delta W_B - \Delta W_i}{\Delta W_B} \times 100
\]

Where \(\Delta W_B\) and \(\Delta W_i\) are the weight loss of metal coupons without and with inhibitor respectively.

Table 1: Comparison of percentage inhibition efficiency by weight loss and hydrogen gas evolution technique for mild steel corrosion in 2M H\(_2\)SO\(_4\) containing SBNAB at 303K

<table>
<thead>
<tr>
<th>Inhibition Concentration(M)</th>
<th>Percentage inhibition efficiency % at 303K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weight loss</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>-------------</td>
</tr>
<tr>
<td>0.000001</td>
<td>25.40</td>
</tr>
<tr>
<td>0.00001</td>
<td>29.98</td>
</tr>
<tr>
<td>0.0001</td>
<td>33.90</td>
</tr>
<tr>
<td>0.001</td>
<td>39.90</td>
</tr>
<tr>
<td>0.01</td>
<td>44.89</td>
</tr>
</tbody>
</table>

Table 1 and Figure 3 showed that the inhibition efficiency of the Schiff base increased with increase in concentration, this is most likely due to the formation of monolayers of the inhibitor on the surface of the metal. It was also observed that the inhibition efficiency increased with increase in temperature; this might be as a result of chemical bonds between the metal and the inhibitor, which suggests that the inhibitor is capable of withstanding higher temperature within a given limit. This is in agreement with the results of Upadhyay and Mathur (2007).
The kinetic data obtained from this study showed that the rate constants and the half life for the corrosion of the metal under study decreased as the temperature is varied from 303 K to 323 K and increased with increase in concentrations as shown in Table 2. This demonstrates that the inhibitor inhibited the corrosion of the mild steel in 2.0 M H2SO4. The average activation energy is 11.40 KJmol\(^{-1}\) and 10.06 KJmol\(^{-1}\) for 303-313 K and 313-323 K respectively.

The equations for rate constant, half life and activation energy are given below:

Rate constant (k) at 303k, 313k and 323k for first order reaction

\[
k = \frac{2.303}{Time} \log \frac{w_i}{w_f} \quad \text{..................................................(2)}
\]

Half- life (\(\frac{t}{2}\)) at 303k, 313k and 323k for first order reaction

\[
\frac{t}{2} = \frac{0.693}{k} \quad \text{..................................................(3)}
\]

The activation energies, Ea of the metal in acid solutions containing SBNAB, was calculated by making use of the integrated form of the Arrhenius equation as
Activation energy (K Jmol−1)

\[ Ea = \frac{2.303RT_2 \left(\log \frac{K_2}{K_1}\right)}{T_2 - T_1} = \frac{Jmol^{-1}}{1000} = KJmol^{-1} \quad \text{...............(4)} \]

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-1K-1

\( K_1 \) and \( K_2 \) are rate constants at \( T_1 \) (303K) and \( T_2 \) (313K) respectively or \( T_1 \) (313K) and \( T_2 \) (323K)

\( K_1 \) and \( K_2 \) are rate constants at \( T_1 \) (303K) and \( T_2 \) (313K) respectively or \( T_1 \) (313K) and \( T_2 \) (323K).

Table 3: Surface coverage (\( \theta \)) and corrosion rate for the inhibition of mild steel corrosion by SBNAB in 2.0M H₂SO₄ solution at different temperatures.

<table>
<thead>
<tr>
<th>Conc(M)</th>
<th>Surface Coverage ( \theta )</th>
<th>Corrosion rate (mgdm⁻²day⁻¹)</th>
<th>Corrosion rate (mm/year) or mm per year</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>303K</td>
<td>313K</td>
<td>323K</td>
</tr>
<tr>
<td>0.000001</td>
<td>0.26</td>
<td>0.28</td>
<td>0.30</td>
</tr>
<tr>
<td>0.00001</td>
<td>0.30</td>
<td>0.33</td>
<td>0.36</td>
</tr>
<tr>
<td>0.0001</td>
<td>0.34</td>
<td>0.37</td>
<td>0.40</td>
</tr>
<tr>
<td>0.001</td>
<td>0.39</td>
<td>0.41</td>
<td>0.44</td>
</tr>
<tr>
<td>0.01</td>
<td>0.45</td>
<td>0.48</td>
<td>0.51</td>
</tr>
</tbody>
</table>

Table 3 revealed that the surface coverage \( \theta \) of the inhibitor on the metal increased as the concentration of the inhibitor increases; also the corrosion rate decreased with increase in concentration of the inhibitor at the three different temperatures under investigation. This result indicates that the inhibitor adsorbed on the metal surface.
Table 4: Free energy of adsorption $\Delta G_{ads}$ for the inhibition of mild steel corrosion in 2.0M H2SO4 solution by SBNAB as a function of surface coverage at different temperatures.

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>Free energy of adsorption $\Delta G_{ads}$ (JKmol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>303k</td>
</tr>
<tr>
<td>0.000001</td>
<td>-37.53</td>
</tr>
<tr>
<td>0.00001</td>
<td>-32.39</td>
</tr>
<tr>
<td>0.0001</td>
<td>-27.24</td>
</tr>
<tr>
<td>0.001</td>
<td>-21.24</td>
</tr>
<tr>
<td>0.01</td>
<td>-17.43</td>
</tr>
<tr>
<td>Average</td>
<td>-27.17</td>
</tr>
</tbody>
</table>

Table 4 above showed that the free energy of adsorptions at the various concentrations were negative values and the average values for each of studied temperatures were less than -40KJ/mol. These imply that the inhibitor adsorbed spontaneously on the metal surface through electrostatic attraction.

$$\Delta G_{ads} = -2.303RT\log(55.5K)...................................................(5)$$

$$K = \theta / C \left[ 1 - \theta \right]$$ where C is the concentration of the inhibitor.

Table 5: Heat of adsorption $\Delta H_{ads}$ and Entropy of adsorption $\Delta S_{ads}$ for the inhibition of corrosion of mild steel by SBNAB at different concentrations in 2M H2SO4 solutions at 303K.

<table>
<thead>
<tr>
<th>Conc (M)</th>
<th>Heat of adsorption (KJ/mol)</th>
<th>Entropy of adsorption(J/mol/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000001</td>
<td>7.69</td>
<td>149.24</td>
</tr>
<tr>
<td>0.00001</td>
<td>6.71</td>
<td>129.04</td>
</tr>
<tr>
<td>0.0001</td>
<td>9.24</td>
<td>120.40</td>
</tr>
<tr>
<td>0.001</td>
<td>11.40</td>
<td>111.02</td>
</tr>
<tr>
<td>0.01</td>
<td>9.36</td>
<td>88.42</td>
</tr>
<tr>
<td>Average</td>
<td>8.88</td>
<td>119.62</td>
</tr>
</tbody>
</table>
The positive values of $\Delta H_{ads}$ and $\Delta S_{ads}$ may be attributed to the likely replacement of water molecules by the inhibitor during adsorption of the additives on the mild steel surface.

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads}$$

Fig 1: Weight loss(g) with time(hours) for the corrosion of mild steel coupons in 2.0M $\text{H}_2\text{SO}_4$ solution containing different concentrations of SBNAB at 303K.

As the concentration of the inhibitor increased from $1.0 \times 10^{-6}$ M to $1.0 \times 10^{-2}$ M, the value of the weight loss decreased as shown in Figure 1. This means that the inhibitor molecules formed more protective layers on the metal surface which effectively reduced the corrosion of the test metal coupons.
Fig 2: Variation of Log (\(wi-\Delta w\)) with time (hours) for Mild steel in 2.0M H\(_2\)SO\(_4\) solution containing different concentrations of SBNAB at 303K

Figure 2 is a linear graph which confirms a first order reaction rate kinetics of the corrosion inhibitory effect of the studied Schiff base on the mild steel surface.
Fig 3: Variation of Inhibitor Efficiency with inhibitor concentration (M) for the corrosion of mild steel coupons in 2.0M H₂SO₄ solution containing SBNAB at different temperatures.

Fig 4: Variation of Free energy of adsorption ΔGads with temperature at different concentrations for SBNAB the inhibition of mild steel corrosion in 2.0M H₂SO₄ solution.
Fig 5: Langmuir adsorption isotherm (plotted as log Log $\theta/(1-\theta)$) versus Log C for the inhibition of mild steel corrosion in 2.0M H$_2$SO$_4$ solution by SBDNAP.

At 303K the Langmuir adsorption isotherm plot had a unity gradient, suggesting that the molecules of the inhibitor were not interacting with each other, but as the temperature increased to 313K and 323K, the plots gradually shift away from linearity, indicating that the inhibitor molecules began to interact with one another, Upadhay and Mathur (2007).

Fig 6: Variation of Volume of hydrogen gas evolved with time (minutes) for the inhibition of mild steel corrosion in 8M H$_2$SO$_4$ solution by SBNAB at 303K.

CONCLUSION

The inhibitory behavior of this Schiff base as the temperature of the medium increased from 303K to 323K showed a chemisorption reaction mechanism while the average value of the activation energy and free energy supports physisorption, however, this is a clear demonstration of mixed reaction mechanism. Athareh, et al.,(2004) postulated that when a mixed reaction mechanism occurs, that the reaction mechanism based on temperature variation predominates, consequently, the proposed reaction mechanism for the adsorption of this Schiff base on mild steel is chemisorption.
REFERENCES


Erma, S.B.M.I (2010). Non–symmetrical Schiff Bases as corrosion inhibitors of mild steel in acidic solution. An unpublished Bachelor of Science degree project report, Universiti Teknologi MARA

Hassan, K., Majid, R., Yagamare, F & Ahmad, A.D (2009). Solvent-free synthesis of some N4O2, N4S2 and N6 schiff base ligands assisted by microwave irradiation. ARKIVOC (X) : 292 – 301.


