

Synthesis of Schiff Base Compounds from Vanillin and *p*-Aminoacetophenone Using Lime Juice as a Natural Acid Catalyst and Their Utilization as Corrosion Inhibitors

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ABSTRACT

Schiff bases can be synthesized by reacting Vanillin and *p*-aminoacetophenone using a natural acid catalyst such as lime juice (*Citrus aurantifolia.*) with the grinding method. The purposes of this study were to determine the characterization. The yield of synthesized compounds calculated and also determined the physical properties such as color and melting point. The product also characterized using NaOH reaction. Further characterization was carried out using FTIR and ¹H-NMR. The synthesized compound is a yellow solid, slightly soluble in water, and has a melting point of 160-162 °C. The Mass obtained is 1,9459 g, with a percentage yield of 94,45%. The compound 1- {4 - [(4-hydroxy-3-methoxy-benzylidene) -amino] -phenyl) -etanone reacts with NaOH to form a bright yellow color. This compound has an imine bond (-C = N-), which showed in the wavenumber 1583 cm⁻¹. ¹H-NMR characterization showed a typical chemical shifting of HC = N- at 8,5 ppm. The inhibition efficiency of these compounds ranged from 23,11-86,16%.

Keywords: Schiff base, Vanillin, *p*-Aminoacetophenone, Grinding methods, Corrosion inhibitor

1. INTRODUCTION

Corrosion of material is worldwide issue that significantly affects natural in industrial environment. In 2017 the United States recorded a loss of \$ 276 annually due to corrosion [1].

Schiff bases in a compounds having an azomethine functional group has being widely accepted due to their cost effective starting materials, facile route of synthesis, low toxicity, high purity and environmental friendly [2]. In previous studies, it has been reported that Schiff bases are effective in inhibiting corrosion of steel, copper and aluminum[3-5]. Inhibitor solubility will increase in the presence of hydrophilic functional groups contained in a molecule[6]. so that the effectiveness of an organic substance as an inhibitor will depend on the structure of the compound[7].

Schiff base compounds can be synthesized conventionally by reflux method, using organic solvents and acid catalysts [8]. The conventional method has several disadvantages, such as low yield took a long time and produced hazardous waste to health and the environment [9]. This method is considered ineffective so that it is modified into an environmentally friendly method, such as using water solvents, grinding, and using natural catalysts known as green synthesis [10].

2. METHODS

2.1 Schiff base synthesis

The synthesis was carried out by grinding Vanillin (7,5 mmol) and *p*-aminoacetophenone (7,5 mmol) for 50 minutes with 0,25 mL lime juice as a natural acid

catalyst. Then, the yield of the synthesized compound is calculated.

2.2 Physical and Chemical Properties Test

The synthesized compound is characterized physically, including its color and melting point. Chemical characterization was carried out by reacting to 0,002 mg of the product in 5 mL of 2 M NaOH.

2.3 Characterization of Schiff Base Compounds

Further characterization was carried out using FTIR (Fourier Transform Infrared) and ¹H-NMR (Nuclear Magnetic Resonance).

2.4 Corrosion Inhibitor Efficiency Test

The test specimen preparation was carried out by cutting 2 cm x 0,05 cm iron plates. Then the surface of the pieces of the iron plate was trimmed by sanding it.

Preparation of a stock solution of 10.000 ppm Schiff base corrosion inhibitor by dissolving 0,25 grams of Schiff's base in 0,5 mL of DMSO (2%), then marking it with 1 M HCl to 25 mL. The stock solution was made with a concentration variation of 2000 ppm; 3000 ppm; 4000 ppm; and 5000 ppm.

Test the Schiff base compound's efficiency as a corrosion inhibitor on metal cutter joyko L-150 in 1M HCl acid medium. then the percent inhibition efficiency is determined [2]:

$$\%EI = \frac{W_0 - W_1}{W_0} \times 100\% \quad (1)$$

EI = Inhibitor Efficiency
 W₀ = Mass of iron without inhibitors
 W₁ = Mass of iron using inhibitors

3. RESULT AND DISCUSSION

3.1 Schiff Base Synthesis

Schiff base compound 1-(4-[(4-hydroxy-3-methoxy-benzylidene)amino]phenyl)ethanone was synthesized using the grinding method with the addition of a natural acid catalyst in the form of lime juice by reacting Vanillin and p-aminoacetophenone. The grinding that is carried out will initiate the collision process between particles, so that energy transfer will occur and products will be formed. Forming the product occurs faster because of the heat caused by the friction that occurs during the grinding process [11][12]. the formation reaction of 1-(4-[(4-hydroxy-3-methoxy-benzylidene)-amino]-phenyl)-ethanone is shown in figure 1.

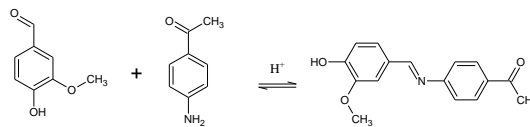


Figure 1. The scheme of Schiff base reaction

Table 1. Physical properties of the product

State	Vanillin	p-Amino- acetophenone	Product
Physical form	Solid	Solid	Solid
Color	White	brownish- yellow	Yellow bright
Mass (g)	1,1411	1,0138	1,9459
% yield	-	-	94,45%
Melting point	80 °C	106 °C	160-162 °C

3.2 Chemical Properties Test with NaOH

Schiff base compound 1-(4-[(4-hydroxy-3-methoxy-benzylidene)-amino]-phenyl)-ethanone is a phenolic group that will react with NaOH to form Na-phenolate. Phenolic compounds have -OH groups that will release H⁺ and NaOH, which will release OH⁻ thus forming Na-phenolate that will soluble in water [13]. The reaction between the Schiff base compound and NaOH is shown in figure 2.

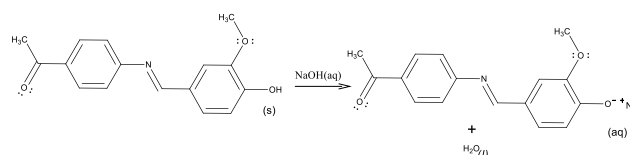


Figure 2. Bronsted-Lowry acid-base reaction

The solubility test results of the Schiff base compound 1-(4-[(4-hydroxy-3-methoxy-benzylidene)-amino]-phenyl)-ethanone are shown in Figure 3. Figure 3. (a) shows that the compound is insoluble in distilled water. This can be seen from the deposits found at the bottom of the test tube. Figure 3. (b) shows the Schiff base compound, which dissolves completely in NaOH and gives a bright yellow color. This color is formed due to the reaction between 1-(4-[(4-hydroxy-3-methoxy-benzylidene)-amino]-phenyl)-ethanone and NaOH.



Figure 3. The solubility test results of Schiff base compound (a) distilled water (b) NaOH.

3.3 Product characterization

3.3.1 Characterization using FTIR

The results of the characterization of synthetic products using FTIR obtained a unique absorption at a wavenumber of 1583 cm^{-1} [14], which is the absorption of the functional group $\text{-C}=\text{N-}$. This indicates that 1- {4- [(4-hydroxy-3-methoxy- benzylidene)- amino]- phenyl)- ethanone is formed. Besides, the typical absorption loss of -NH_2 p-Aminoacetophenone and typical absorption $\text{-C}=\text{O}$ vanillin in the region of wave numbers 3200-3400 cm^{-1} and 1700 cm^{-1} , respectively, indicates that the reactants have reacted and formed new compounds.

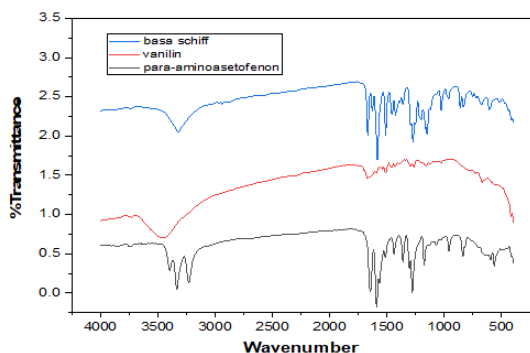


Figure 4. The results of FTIR spectra of products and reactants

3.3.2 Characterization using $^1\text{H-NMR}$

Characterization using $^1\text{H-NMR}$ produced 9 signals from the Schiff base compound 1- {4 - [(4-hydroxy-3-methoxy-benzylidene) -amino] -phenyl)-ethanone. Then in the chemical shift of 8.4722 ppm, there is a signal that shows the protons in the imine group [12]. Besides the signal from 1- {4 - [(4-hydroxy-3-methoxy-benzylidene) -amino]-phenyl)-ethanone compounds on that spectra also found signals from reactants. In (δ) 6,0389 ppm there is the typical signal of p-aminoacetophenone (-NH_2). Then in area (δ) 9,7622 ppm found -COH belonging to vanillin.

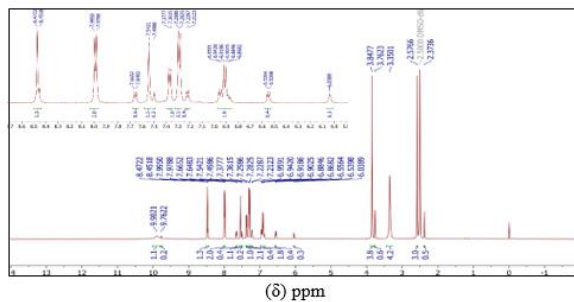


Figure 5. $^1\text{H-NMR}$ spectra of Schiff base compound

Table 2. Interpretation of $^1\text{H-NMR}$ spectra

No	δH (ppm)	ΣH	Splitting	proton
1.	2,3736	0,5H	S	-CH_3
2.	2,5000		S	DMSO-d_6
3.	2,5691	3H	S	-COCH_3
4.	3,3501	4H	S	-dCH_2
5.	3,7623	0,6H	S	R-O-CH_3
6.	3,8475	3H	S	-OCH_3
7.	6,0389	0,3H	S	-NH_2
8.	6,5398	0,4H	D	=CH Aromatic
9.	6,5564			
9.	6,9070	1H	D	=CH Aromatic
	6,9232			
10.	7,2123	0,4H	D	=CH Aromatic
	7,2287			
11.	7,2745	2H	D	=CH Aromatic
	7,2905			
12.	7,3625	1H	D	=CH Aromatic
	7,3787			
13.	7,4986	0,2H	S	=CH Aromatic
14.	7,5434	1H	S	=CH Aromatic
15.	7,6483	0,4H	D	=CH Aromatic
	7,6652			
16.	7,9717	2H	D	=CH Aromatic
	7,9878			

17	8,4631	1H	S	-HC=N
18.	9,7622	1H	S	-COH
19.	9,8714	1H	S	-OH

Explanation : s = singlet
d = doublet

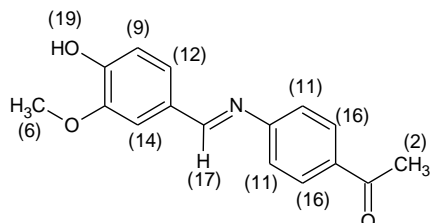


Figure 6. Suspected structure of Schiff base 1-[(4-hydroxy-3-methoxy-benzylidene)-amino]-phenyl)-ethanone.

3.4 Corrosion Inhibitors

Schiff bases have a long conjugation system that gives Schiff bases a more bond (π) than the reactants. During the corrosion process, the iron plate will be positively charged to become Fe^{2+} . The iron ion will interact with the PEB and (π) bonds in the Schiff base compound form ion-dipoles, which will envelop the ferrous metal. So that the corrosion rate will be inhibited by the interaction that occurs [14]. The inhibition efficiency of Schiff 1- [(4 - [(4-hydroxy-3-methoxy-benzylidene) -amino] -phenyl) -ethanone in hydrochloric acid solution is 23,11-86,16%.

4. CONCLUSION

The synthesis of schiff base 1- (4 - [(4-hydroxy-3-methoxy-benzylidene) -amino] -phenyl) -ethanone compound produces a product with the physical characteristics of a yellow solid, slightly soluble in water, and has a melting point of 160- 162 °C. The mass of the synthesis product produced was 1,9459 with yield 96,45%. Characterization using an FTIR spectrophotometer resulted in a typical imine group spectra ($C = N$) at a wavenumber of 1583,909 cm^{-1} . Characterization using 1H -NMR produced 9 signals of Schiff base. Then there is a chemical shift in the imine group at 8,4722 ppm. Inhibition efficiency in hydrochloric acid solution was 23,11-86,16%.

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