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The Correlation between Structure and Corrosion Inhibition Activity of 4,5-Diphenyl-1-vinylimidazole Derivative Compounds towards Mild Steel in 1% NaCl Solution

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Three derivatives of 4,5-diphenyl-1-vinylimidazole: compound **1** (2-hexyl-4,5-diphenyl-1-vinyl-1*H*-imidazole), **2** (2,4,5-triphenyl-1-vinyl-1*H*-imidazole), and **3** (2-(4-methoxyphenyl)-4,5-diphenyl-1-vinyl-1*H*-imidazole) have been synthesized utilizing microwave assisted organic synthesis (MAOS) method, in order to investigate the correlation between structure and corrosion inhibition activity towards mild steel. The analysis of degree of surface coverage of each compound showed the linearity of Langmuir isotherm adsorptions, which represent the monolayer formation of each compound on mild steel surface. The free Gibbs adsorption energy values, ΔG^0_{ads}, of each synthesized compound is negative, which indicated the spontaneity of adsorption process of each compound on mild steel surface and also have the potential to interact with mild steel through semi-physiosorption and/or semi-chemisorption.

Keywords: 4,5-diphenyl-1-vinylimidazole; adsorption; corrosion inhibition; mild steel

1. INTRODUCTION

The corrosion process of mild steel pipelines in gas and oilfield mining induced by the presence of carbon dioxide, acid and water has been a serious problem, economically and environmentally, in the oil and gas industries for decades [1]. In Indonesia, the gas and oilfield mining are vital industries that give valuable commodity and income to the nation. Meanwhile, the loss caused by corrosion in Indonesia was estimated 1 - 1,5 % of GDP (Gross Domestic Production) or approximately trillion of rupiahs has been spent to overcome the corrosion problems [2]. One of the most effective ways to protect the corrosion, especially the internal parts of mild steel pipelines, is the use of organic corrosion inhibitors [1, 3-5]. Therefore, the development of improved organic corrosion inhibitors could be quite crucial in the cost-effectiveness of oil and gas industries in Indonesia. In recent times, many researchers all over the worlds have been studied the correlation between the structure of organic corrosion inhibitors and their corrosion inhibition activities. There are several studies involving the effect of oxygen, nitrogen and sulphur containing compounds, acyclic and heterocyclic, towards the corrosion inhibition activity, including imidazole derivative compounds [3, 6-13]. The aims of this work mainly are to synthesize some imidazole derivative compounds utilizing the novel method in organic synthesis, microwave assisted organic synthesis (MAOS) [14-18] and to study the correlation between the structure of synthesized products and their corrosion inhibition activities towards mild steel in 1% NaCl solution utilizing Tafel plot method.

2. EXPERIMENTAL PART

2.1. General Procedure

All of reagents used in this research are GR grade. All of solvents were distilled prior to use. The microwave assisted organic synthesis (MAOS) method was utilizing a GE domestic microwave oven type JEI642WC. The characterization of synthesized products was analyzed using BUCK-IR® M-500 at Department of Chemistry ITB for the determination of infrared spectrums, and the determination of the melting point of products utilizing the ***Fisher-Johns***® Melt-Temp Apparatus. The structure elucidation was determined utilizing JEOL DELTA NMR 400 and 500 MHz (^{1}H-NMR); 100 and 125 MHz (^{13}C-NMR), at Universiti Kebangsaan Malaysia, Malaysia, and FU Berlin, Germany, using $CDCl_3$ solvent. The mass spectroscopy measurements were carried out in Department of Chemistry of Universitas Gajah Mada, Yogyakarta, Indonesia. The determination of inhibition activity of synthesized products employing ***VoltaLab***® apparatus at Department of Chemistry Institut Teknologi Bandung, Indonesia, with carbon steel electrode as working electrode, SCE (Saturated Calomel Electrode) as reference electrode, and platinum electrode as auxiliary electrode. The carbon steel type used is API 5L X65 with compositions (in percentage, %): Fe (97,9327); C (0,0737); Si (0,2882); S (0,0068); P (0,0153); Mn (1,5353); Ni (0,0129); Cr (0,0224); V (0,0276); Cu (0,0051); W (0,0029); Ti (0,0169); Sn (0,0005); Al (0,0282); Nb (0,0396); Zr (0,0009); Zn (0,0014) [19].

2.2. The Synthesis of 4,5-Diphenyl-1-vinylimidazole Derivative Compounds

All of the synthesis procedures of imidazole derivative compounds were summarized as follows (also presented in Table 1). This method was the modification of the method used previously by Wolkenberg and partners [17] and Usyatinsky [18]: 2 mmols of diketones (benzil), 2 mmols of aldehydes, 2 mmols of ethylenediamine, 20 mmols of ammonium acetate and 10 mL acetic acid glacial were placed in 100 mL PYREX® Erlenmeyer flask. The reaction mixtures were stirred well, and then the flask was placed in the GE domestic microwave oven type JEI642WC. The reaction mixtures were irradiated at 700 W of power for several times until the reaction temperature was no longer raised or achieving the stable temperature. The flask was taken out from the oven and was cooled to 40 ^{o}C.

Then the flask was placed in the ice bath. Into the reaction mixtures were added drop wises of saturated ammonium hydroxide solution until the cloudiness appeared. The crude products were filtered out and the residue was washed with aquadest. The crude products were purified utilizing preparative TLC with n-hexane:ethyl acetate = 7:3 (*v/v*) as eluents. The product were recrystallized in n-hexane:ethyl acetate = 1:1 (*v/v*).

Compound 1 (2-hexyl-4,5-diphenyl-1-vinyl-1*H*-imidazole): white crystalline; 83.09% of chemical yields; m.p. 243 – 245 ^{o}C; IR ν_{maks} (KBR): 3429, 3064, 2965, 2857, 2727, 1600, 1492, 1461, 1410, 1319, 1255 1127, 1073 – 779, 697 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 7.66 – 7.63 (*dd*, 8 and 2 Hz, 2H); 7.46 – 7.44 (*dd*, 8 and 2 Hz,); 7.35 – 7.30 (*m*, 7.33 and 7.56 Hz, 4H); 7.26 (*d*, 2.19 Hz, 1H); 7.19 (*d*, 2.19 Hz, 1H); 3.77 (*s*, 2H); 2.01 – 1.98 (*t*, 4H), 1.26 – 1.33 (*m*, 7.05 Hz, 6H); 0.90 (*t*, 6.51 Hz, 3H). ^{13}C-RMI 100 MHz JEOL DELTA ($CDCl_3$): δ (ppm) 148.4; 138.4; 130.9; 129.9; 129.4; 128.6; 128.2; 128.0; 126.7; 103.0; 31.7; 29.2; 28.0; 26.4; 22.6; 14.1. **m/z**: **330** (48%); 317; 287; 273; 259; 233; 218; 193; 178; 165; 152; 128; 115; 103 (*base peak*); 89;77; 55; 43

Compound 2 (2,4,5-triphenyl-1-vinyl-1*H*-imidazole): white crystalline; 78.16% of chemical yields; m.p. 227 – 229 ^{o}C; IR ν_{maks} (KBR): 3423, 3064, 2965, 2857, 2727, 1600, 1492, 1461, 1410, 1322, 1202, 1129, 1073 – 779, 697 cm^{-1}. ^{1}H-NMR JEOL DELTA NMR 400 MHz (Acetone-*d*6): δ (ppm) 7.39 – 7.28 (*m*, 7.33; 7.56; 2.19 Hz, 10 H); 5.10 (*s*, 1H), 4.23; 4,27 (*d*, 16.01 Hz, 2H). **m/z: 322** (100%); 295; 243; 218; 203; 176; 160; 146; 122; 115 (*base peak*); 89; 77; 65; 39

Compound 3 (2-(4-methoxyphenyl)-4,5-diphenyl-1-vinyl-1*H*-imidazole): white crystalline; 78.25% of chemical yields; m.p. 230 – 232 ^{o}C; IR ν_{maks} (KBR): 3423, 3064, 2965, 2857, 2727, 1600, 1492, 1461, 1410, 1384, 1237, 1129, 1073 – 779, 697 cm^{-1}. ^{1}H-NMR 400 MHz JEOL DELTA (Acetone-*d*6): δ (ppm) ^{1}H-RMI 400 MHz JEOL DELTA ($CDCl_3$): 7,39 – 7,28 (*m*, 7,52, 7,63, 7,65, 7,97 dsan 7,99 Hz, 10 H); 5,10 (*s*, 1H), 4,21; 4,25 (*d*, 15,89 Hz, 2H), 3,83 (*s*, 1H). **m/z: 352** (*base peak*) (100%); 337; 309; 243; 229; 204; 176; 159; 131; 121; 103; 91; 77; 63; 51; 39.

2.3. Electrochemical Measurements

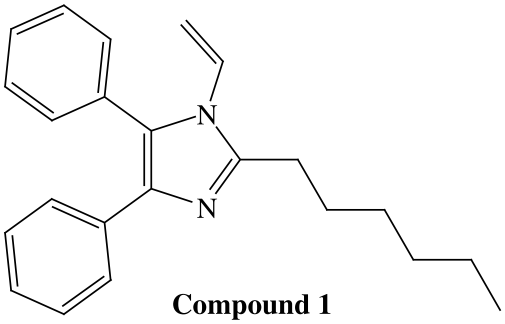
An amount of 2 mgs of products was dissolved in 250 mL 1% (*w/v*) NaCl solution, to give 8 ppm concentration of sample solutions. The 1% (*w/v*) NaCl solution was also used as blank solution in each measurement. Into the 400 mL beaker glass equip with magnetic stirrer was introduced 250 mL of blank solution. The working electrode (carbon steel), the reference electrode (SCE), and auxiliary electrode (platinum electrode) were immersed into the electrolyte solution. Carbon dioxide gas was introduced into the electrolyte solution until saturation reached. The measurements utilizing *Voltalab*® and Tafel Method software program until the curve of potential measurement towards time was completely formed well. The measurements of each sample solution must be initiated by the measurement of blank solution. The inhibition activity can be calculated using following equation [8, 9, 20]:

$$\%\,\mathrm{EI} = \frac{I_{\mathrm{Blank}}\ (\mathrm{mA/cm^2}) - I_{\mathrm{Sample}}\ (\mathrm{mA/cm^2})}{I_{\mathrm{Blank}}\ (\mathrm{mA/cm^2})} \mathrm{x}100\% \qquad (1)$$

where I_{Blank} is the current density (in mA/cm^2) of blank solution (1% NaCl solution) and I_{Sample} is the current density of solution containing 4,5-diphenyl-1-vinylimidazole derivative compound, and %EI is the percentage of efficiency inhibition activity.

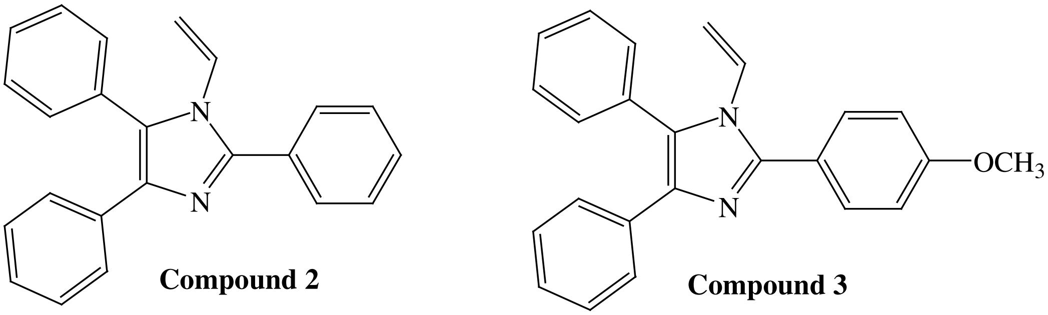
3. RESULTS AND DISCUSSION

The synthesis of 4,5-diphenyl-1-vinylimidazole derivative compounds was carried out utilizing the MAOS (*Microwave Assisted Organic Synthesis*) method, which was the modification of the methods represented by Wolkenberg [17] and Usyatinsky [18]. The results of the synthesis of imidazole derivative compounds were summarized in Table 1. The structures of each product were presented on Figure 1.



Compound 1

2-hexyl-4,5-diphenyl-1-vinyl-1*H*-imidazole



Compound 2

2,4,5-triphenyl-1-vinyl-1*H*-imidazole

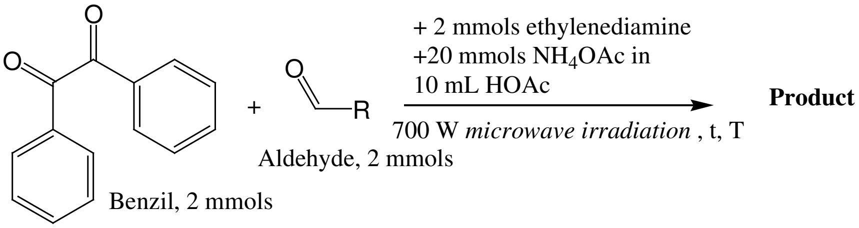
Compound 3

2-(4-methoxyphenyl)-4,5-diphenyl
-1-vinyl-1*H*-imidazole

Figure 1. The structures of 4,5-diphenyl-1-vinyl-imidazole derivative compounds based on spectroscopy data analysis

The investigation of the corrosion inhibition activities of imidazole, compound **1** (2-hexyl-4,5-diphenyl-1-vinyl-1*H*-imidazole), **2** (2,4,5-triphenyl-1-vinyl-1*H*-imidazole), and **3** (2-(4-methoxyphenyl)-4,5-diphenyl-1-vinyl-1*H*-imidazole) toward carbon steel in 1% NaCl solution were determined utilizing the Tafel plot method. The results of electrochemical measurements at concentration of 8 ppm were summarized in Table 2. The efficiency inhibition activities of each compound were calculated based on equation (1).

Table 1. The synthesis of 4,5-diphenyl-1-vinylimidazole derivative compounds utilizing the MAOS method at 700 W irradiation powers



Entry	-R	Reaction Times (seconds)	Reaction Temperature (°C)	Melting Point (°C)	Yield (%)
1	$-C_6H_{13}$	110	132	243-245	91.21
2	$-C_6H_5$	180	112	227-229	88.24
3	$-((C_6H_4)OMe)$	150	122	230-232	87.25

Table 2. The efficiency inhibition activities (%EI) of synthesized 4,5-diphenyl-1-vinylimidazole derivative compounds towards carbon steel in 1% NaCl solution at concentration of 8 ppm utilizing Tafel method (27 °C)

Sample	I_{cor} of 1% NaCl solution (mA/cm^2)	I_{cor} of sample in 1% NaCl solution (mA/cm^2)	% EI (Efficiency Inhibition)
Compound **1**	0.1298	0.0867	33.20
Compound **2**	0.1298	0.1058	18.49
Compound **3**	0.1262	0.0969	23.22

In order to investigate the corrosion inhibition mechanism, the relationship between the various concentrations of corrosion inhibitors and their corrosion inhibition efficiency percentages was analyzed. The analysis of the adsorption mechanism of 4,5-diphenyl-1-vinylimidazole derivative compounds toward carbon steel can be performed by the determination of the degree of surface coverage (θ) according to the following equation [6-8, 13, 20],

$$\theta = 1 - \left(\frac{I_{inh}}{I_{uninh}} \right) \qquad (2)$$

with I_{inh} and I_{uninh} is the corrosion current density (in mA/cm^2) of sample solution with and without inhibitor, respectively. The data of the degree of surface coverage, θ, at various concentrations of compound **1**, **2**, and **3** at 27 °C was also presented on Table 3.

Table 3. The correlation between %EI of 4,5-diphenyl-1-vinylimidazole derivative compounds and the degree of surface coverage, *θ*, on mild steel at 27°C

Sample	C (M)	%EI	θ
Compound 1	2.4×10^{-5}	33.20	0.33
	4.8×10^{-5}	21.00	0.21
	9.7×10^{-5}	28.92	0.29
Compound 2	2.5×10^{-5}	18.49	0.18
	5.0×10^{-5}	58.68	0.59
	9.9×10^{-5}	71.09	0.71
Compound 3	2.3×10^{-5}	23.22	0.23
	4.5×10^{-5}	45.37	0.45
	9.1×10^{-5}	48.71	0.49

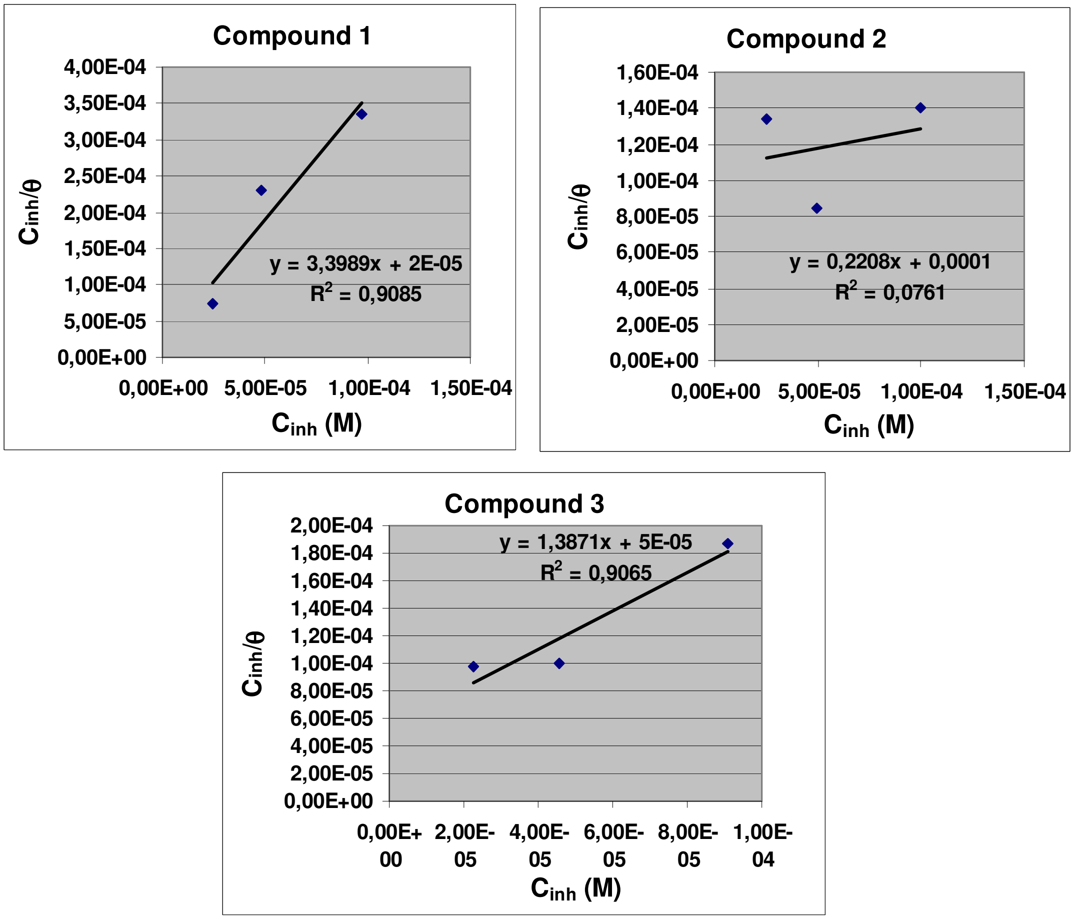


Figure 2. The linear relationship between concentration of corrosion inhibitor compounds, C_{inh}, and C_{inh}/θ, according to the simplest form of Langmuir adsorption isotherm (equation (3)) of compound **1**, **2**, and **3**

Based on Table 3, the most suitable relationship between concentration of corrosion inhibitor compounds, C_{inh}, and the degree of surface coverage, θ, is the Langmuir isotherm adsorption in the simplest form, which is the linear relationship between C_{inh} and C_{inh}/θ, according to the following equation [8, 20]

$$\theta = \frac{bC_{inh}}{1 + bC_{inh}} \tag{3}$$

with b is the adsorption coefficient**;** C_{inh} is the concentration of corrosion inhibitor compounds and θ is the degree of surface coverage. Table 3 represents the data of each compound at concentration of 8, 16 and 32 ppm of sample in 1% (*w/v*) NaCl solution. Figure 2 represents the linear relationship according to the simplest form of Langmuir adsorption isotherm of the synthesized products.

The linearity of each Langmuir adsorption isotherm of each compound, as shown on Figure 2, represents the monolayer formation of each compound on the mild steel surface. However, compound **2** have low linear regression coefficient ($R^2 < 0.900$) for the simplest form of Langmuir adsorption isotherm (equation (3)). Therefore, compound **2** was well suited when plotted as $\log(\theta/(1-\theta))$ to the logarithm of concentration ($\log C_{inh}$), which is also the linear relationship of modified Langmuir adsorption isotherm, according to the following equation [21]:

$$\log\left[\frac{\theta}{(1-\theta)}\right] = \log K_{ads} + \log C_{inh} \tag{4}$$

with θ is the degree of surface coverage, K_{ads} is the adsorption coefficient or the adsorption equilibrium constant, and C_{inh} is the concentration of compounds. Compound **2** are also well suited to the modified form of Langmuir adsorption isotherm (equation 4 and 6) and Temkin adsorption isotherm (equation 5) [20, 22], as presented on Figure 3. The equation of Temkin adsorption isotherm is presented as follows.

$$\theta = \frac{1}{f}\ln\left(K_{ads}C\right) \tag{5}$$

with θ is the degree of surface coverage, K_{ads} is the adsorption coefficient or the adsorption equilibrium constant, f is parameter of molecular interaction, and C_{inh} is the concentration of compounds.

Langmuir adsorption isotherm related to the monolayer formation on metal surface and is also a characteristic of physical adsorption or electrostatic adsorption [20, 21, 23]. According to the linear relationship of modified Langmuir adsorption isotherm of compound **2**, as shown on Figure 3, it is possible to determine the slope that indicated the adsorption phenomenon according to kinetic-thermodynamic El-Awady, which is followed the corrected Langmuir adsorption isotherm [21]:

$$\log\left[\frac{\theta}{(1-\theta)}\right] = \log K_{ads} + y\log C_{inh} \tag{6}$$

with *y* is the graphic slope between log(*θ*/(1-*θ*)) and the logarithm of corrosion inhibitor concentration. The (1/*y*) value represents the number of active sites on metal surface covered by corrosion inhibitor molecules [21]. The (1/*y*) value of compound **2** is equivalent to 1, which showed that compound **2** was adsorbed on mild steel surface by replacing or eliminating one water (H_2O) molecule from metal surface [6, 12, 13, 21].

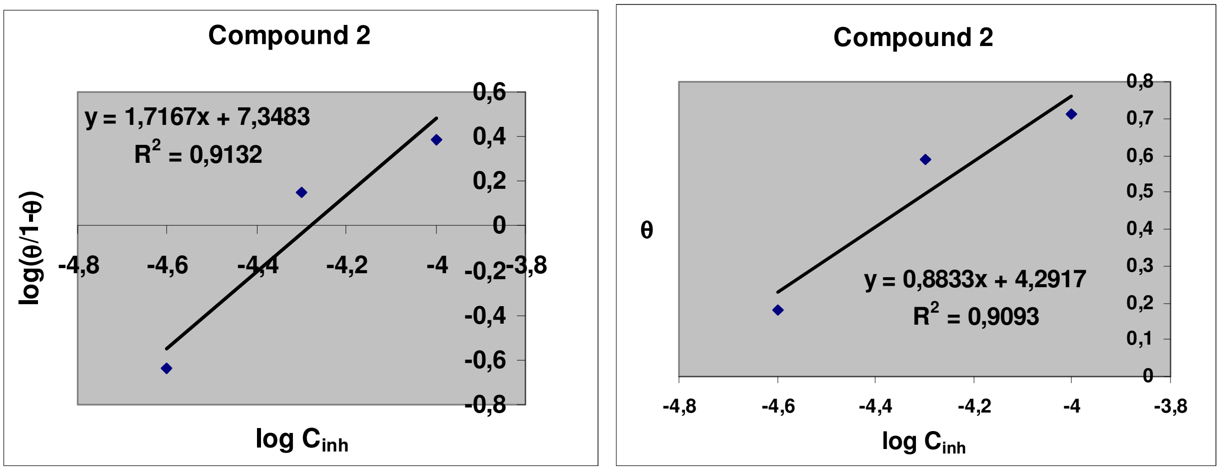


Figure 3. The linear relationship between log(*θ*/(1-*θ*)) and the logarithm of concentration (log C_{inh}), according to modified Langmuir adsorption isotherm (left) and Temkin adsorption isotherm (right) of compound **2**

The value of *b*, the adsorption coefficient, which is equal to the adsorption equilibrium constant (K_{ads}), of each compound was presented on Table 4. The value of free Gibbs adsorption energy (ΔG^0_{ads}, in kJ/mol) of each compound, which is also presented on Table 4, can be determined using the following equation [8, 20]

$$K_{ads} = \frac{1}{55,55} \exp\left(-\frac{\Delta G^0_{ads}}{RT} \right) \qquad (7)$$

with *R* = ideal gas constant = 8.314 J/mol.K, the value of 55.5 is the concentration of water in the solution in moles and T is temperature in K.

Table 4. The coefficient adsorption values (K_{ads}) and free Gibbs adsorption energy (ΔG^0_{ads}, in kJ/mol) of the synthesized 4,5-diphenyl-1-vinylimidazole derivative compounds at 27°C (300K), according to the simplest form of Langmuir adsorption isotherm

Compound	K_{ads} (M^{-1})	ΔG^0_{ads}, (kJ/mol)
1	10061.33	- 33.01
2	20820.79	- 34.82
3	14008.67	- 33.83

Based on Table 4, it was shown that all of free Gibbs adsorption energy values, ΔG^0_{ads}, for each compound is negative, which indicated the spontaneity of adsorption process of each compound on mild steel surface. The value of ΔG^0_{ads} of compound **2** according to Langmuir and Temkin adsorption isotherm is -34.82 kJ/mol and -36.64 kJ/mol, respectively. The more negative of ΔG^0_{ads} value the more spontaneous its adsorption process on metal surface, therefore the corrosion inhibition activity would increase. The value of ΔG^0_{ads} up to – 20 kJ/mol is consistent with the physical adsorption (physiosorption), whether the value of ΔG^0_{ads}, which is above – 40 kJ/mol, is consistent with the chemical adsorption (chemisorptions) [9, 21]. Therefore, compound **1**, **2**, and **3** have the potent to interact with carbon steel through semi-physiosorption and/or semi-chemisorptions because of their ΔG^0_{ads} values are in between – 20 kJ/mol and – 40 kJ/mol.

Table 5. The data of corrosion current density of 4,5-diphenyl-1-vinylimidazole at various temperatures (32, 42, 52 and 62^{o}C) at concentration of 8 ppm (in 1% (*w/v*) NaCl solution) utilizing Tafel plot method

		Temperature (^{o}C)			
I_{cor} (mA/cm^2)	Sample	32	42	52	62
	Blank (NaCl 1% (*w/v*))	0.081	0.118	0.119	0.125
	Solution of compound 1	0.050	0.088	0.097	0.108
	Solution of Compound 2	0.063	0.080	0.112	0.115
	Solution of Compound 3	0.061	0.094	0.099	0.111

The determination of activation energy (E_a) of inhibition process of each 4,5-diphenyl-1-vinylimidazole compound towards mild steel in 1% (*w/v*) NaCl solution utilized the data of corrosion current density (I_{cor}, in mA/cm^2) of sample solutions at various temperatures within range of 32 – 62 ^{o}C. The data was plotted as linear graphic between logarithms of corrosion current density (log I_{cor}) and temperature (in K, as 1000/T). The slope is equivalent to the value of activation energy, E_a, divided by the ideal gas constant, R (8.314 kJ/mol.K). Based on the data, the activation energy can be determined utilizing the following equation[13, 20].

$$I_{cor} = A\exp-\frac{E_a}{RT} \tag{8}$$

with I_{cor} is the corrosion current density (in mA/cm^2), A is pre-exponential factor (Arrhenius constant), E_a is the activation energy of corrosion process (in kJ/mol), R is ideal gas constant (8.314 kJ/mol.K), and T is temperature (in K). In addition, the other parameters, as the change in enthalpy and entropy of activated state can be determined according to the following equation [6, 13, 20]

$$I_{cor} = \frac{RT}{Nh}\exp\left(\frac{\Delta S^*}{R}\right)\exp\left(-\frac{\Delta H^*}{RT}\right) \tag{9}$$

with N is Avogadro number (6.023 x 10^{23} particles/mol), h is Planck constant (6.626 x 10^{-34} J.s), ΔS^* is the change in activated state entropy (in kJ/mol) and ΔH^* is the change in activated state enthalpy (in kJ/mol). The data of corrosion current density at various temperatures was presented on Table 5. The linear plot between logarithms of corrosion current density and 1000/T, and the plot between ln(I_{cor}/T) and 1000/T were presented on Figure 4 and 5, respectively.

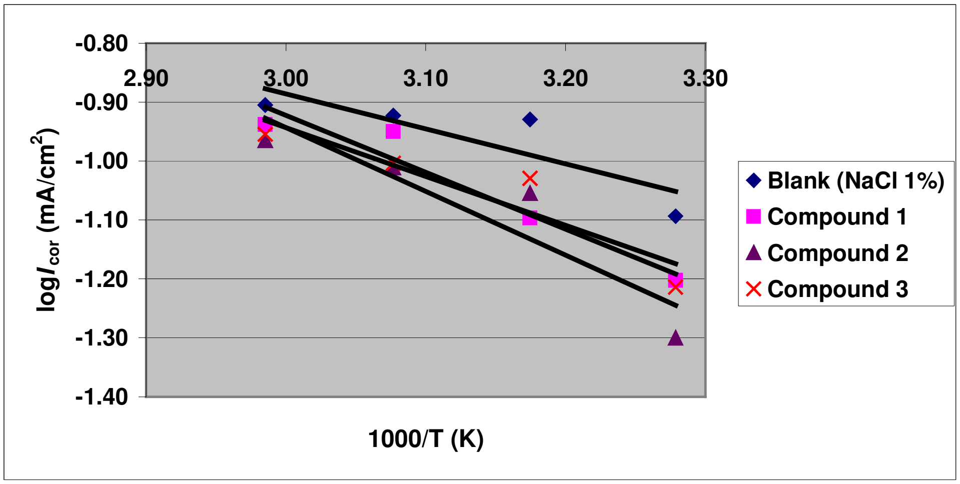


Figure 4. The linear plot between logarithms of corrosion current density (logI_{cor}, in mA/cm^2) of 4,5-diphenyl-1-vinylimidazole derivative compounds and 1% NaCl solution, and 1000/T (T in K)

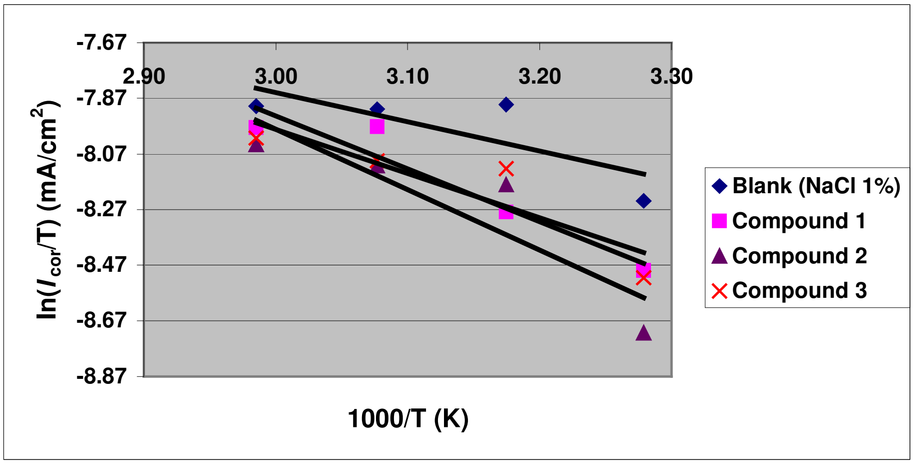


Figure 5. The linear plot between normal logarithms of corrosion current density per temperature unit (ln(I_{cor}/T)) of 4,5-diphenyl-1-vinylimidazole derivative compounds and 1% NaCl solution, and 1000/T (T in K)

Based on the graphics on Figure 4 and 5, the activation energy, E_a, the change in activated state enthalpy, ΔH^*, and entropy, ΔS^*, and the free Gibbs energy of activated state, ΔG^* can be determined according to equation (8) and (9), and the results were summarized on Table 6.

Table 6. The activation energy, E_a, the change in activated state enthalpy, ΔH^*, entropy, ΔS^*, and free Gibbs energy, ΔG^* of 4,5-diphenyl-1-vinylimidazole derivative compounds in 1% (*w/v*) NaCl solution

Sample	E_a (kJ/mol)	ΔH^* (kJ/mol)	ΔS^* (kJ/mol.K)	ΔG^* (kJ/mol)
Blank (NaCl 1% (*w/v*))	11.38	8.72	-0.24	84.44
Solution of compound 1	18.50	15.84	-0.22	84.95
Solution of Compound 2	20.73	18.07	-0.21	85.17
Solution of Compound 3	15.88	13.22	-0.22	84.98

Based on Table 4 and 6, it was observed that the corrosion inhibition activities of 4,5-diphenyl-1-vinylimidazole derivative compounds depend on the structure and substituents attached to the imidazole ring framework. Compound **2** (2,4,5-triphenyl-1-vinyl-1*H*-imidazole) has the more negative value of free Gibbs adsorption energy, ΔG^0_{ads}, and higher activation energy, E_a, than compound **1** (2-hexyl-4,5-diphenyl-1-vinyl-1*H*-imidazole) and **3** (2-(4-methoxyphenyl)-4,5-diphenyl-1-vinyl-1*H*-imidazole). This phenomenon indicated the spontaneity of compound **2** to adsorb on mild steel surface, therefore compound **2** exhibits the inhibition of corrosion rate of mild steel through its high-energy barrier of corrosion reaction. The corrosion inhibition activity of compound **2** should be related to the planarity and the rich phi's (π) aromatic electrons of phenyl groups within the structure of compound **2**. The presence of the long alkyl group attached to imidazole ring framework within structure of compound **1** have the potent to act as hydrophobic tail that would prevent the interaction of corrosive media towards metal. However, this hexyl group would also retard the adsorption process of compound **1** on metal surface, comparing to compound **2**. This retardation process came into account from the steric hindrance of hexyl group within structure of compound **1**, therefore its adsorption process would be less spontaneous than compound **2**. The planarity and the rich phi's (π) aromatic electrons of phenyl groups within the structure of compound **1** should be an additional account to the interaction process as Lewis base with mild steel surface, therefore the ΔG^0_{ads} of compound **1** is more negative than compound **3**. The additional electron-donating group of methoxy group at *para* position of phenyl substituent at C-2 position within structure of compound **3** should give significant more basic properties of compound **3** compare to compound **2**. However, this methoxy group also disturbs the planarity of 4,5-diphenyl-1-vinylimidazole structures, therefore the adsorption process of compound **3** towards metal surface would be less spontaneous than compound **2**.

According to the results presented on Table 6, the activation energy of blank solution (1% (*w/v*) NaCl solution) is lower than the solutions containing 4,5-diphenyl-1-vinylimidazole derivative compounds. This fact showed the presence of physical adsorption (physiosorption) of 4,5-dihenyl-1-vinylimidazole derivatives on to mild steel surface [6, 13, 20]. In addition, the higher the activation energy, the lower the corrosion current density, that indicates the inhibition of corrosion process. According to equation (8), the corrosion current density (I_{cor}) in electrochemical system corresponds to the corrosion reaction rate. The lower the corrosion current density, the less dense the electron transfer in oxidation-reduction process (corrosion), therefore the corrosion reaction rate became slower. As a conclusion, all of 4,5-diphenyl-1-vinylimidazole derivative compounds that have been synthesized showed the potent to inhibit the corrosion process toward carbon steel in 1% NaCl (*w/v*) solution.

The values of the change in activated state enthalpy and entropy of solution containing 4,5-diphenyl-1-vinylimidazole derivatives were higher than the blank solution (1% (*w/v*) solution). This phenomenon showed the replacement process of water (H_2O) molecules from mild steel surface during the adsorption process of 4,5-diphenyl-1-vinyl-imidazole derivatives on mild steel surface [20]. The change in activated state enthalpy values, $\Delta H*$, of 4,5-diphenyl-1-vinyl-imidazole solutions are more positives than blank solution, indicating that the corrosion process in the solution containing 4,5-diphenyl-1-vinyl-imidazole derivatives needs more energy to achieve the activated state or equilibrium state. The activated state entropy, $\Delta S*$, of solutions containing 4,5-diphenyl-1-vinylimidazole group are higher than $\Delta S*$ of blank solution, indicating that in the presence of inhibitor, the system passes from less orderly to a more random arrangement and hence an increase in the values of $\Delta S*$ is observed [13, 20] . The activated state free Gibbs energy, $\Delta G*$, of blank solution is lower than the solution containing 4,5-dipenyl-1-vinyl-imidazole derivatives, indicating that the equilibrium state towards the products (corrode state or oxidative state) is more preferable than returning to the initial state (reductive state). In other words, the blank solution (without 4,5-diphenyl-1-vinylimidazole derivative compounds) gave more possibility to perform corrosion process towards mild steel than the sample solutions containing 4,5-diphenyl-1-vinylimidazole derivative compounds [20].

4. CONCLUSIONS

The synthesis of imidazole derivative compounds utilizing the MAOS method produced three derivatives of 4,5-diphenyl-1-vinylimidazole compounds: compound **1** (2-hexyl-4,5-diphenyl-1-vinyl-1*H*-imidazole), **2** (2,4,5-triphenyl-1-vinyl-1*H*-imidazole), and **3** (2-(4-methoxyphenyl)-4,5-diphenyl-1-vinyl-1*H*-imidazole). The analysis of degree of surface coverage of each compound showed the linearity of Langmuir isotherm adsorptions, which represent the monolayer formation of each compound on mild steel surface. The free Gibbs adsorption energy values, ΔG^0_{ads}, of synthesized compound is negative, which indicated the spontaneity of adsorption process of each compound on carbon steel surface and also have the potential to interact with mild steel through semi-physiosorption and/or semi-chemisorptions. There is close correlation between the structure of 4,5-diphenyl-1-vinylimidazole derivative compounds, their adsorption capacity towards mild steel surface and the activation energy of corrosion process. The planarity of structure, the presence of donating electron groups, the hydrophobic effect of structure, the steric hindrance and the electron density of molecular structure are some crucial factors that would affect the corrosion inhibition activity of 4,5-diphenyl-1-vinylimidazole derivative compounds towards mild steel.

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