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Adsorption Mechanism of 4-(4,5-diphenyl-1*H*-imidazole)-*N*,*N*-dimethylbenzenamine as a Corrosion Inhibitor Towards Carbon Steel in 1% NaCl Solution

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Abstract

Corrosion inhibitor is one of the materials widely known to effectively minimize damages caused by corrosion. Design and development of corrosion inhibitor have been intensively studied. Understanding the mechanisms responsible in corrosion inhibition is demanded in developing techniques to prevent corrosion. This study employed an imidazole derivate compound, 4-(4,5-diphenyl-1*H*-imidazole)-*N*,*N*-dimethylbenzenamine, as a corrosion inhibitor on carbon steel in a corrosive environment of 1% NaCl at 25 ^{o}C. Analysis of the mechanisms underlying the adsorption of the organic inhibitor on metal surface was performed by electrochemical impedance spectroscopy method. The adsorption mechanisms were analyzed by Langmuir and Temkin adsorption isotherm models. The fitting results showed that the linear regression obtained from Langmuir and Temkin adsorption isotherm were 0.9738 and 0.8694, respectively. The adsorption free energy was -34.04 kJ/mol, indicated that Langmuir adsorption isotherm was applied in the adsorption mechanism and that the inhibitor was adsorbed semi-physically or semi-chemically on the metal surface.

Keywords: adsorption; corrosion inhibitor; Langmuir.

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1. Introduction

Corrosion has been a serious problem in industry since it strongly correlates with the safety and environment. Thus far, materials that are able to prevent corrosion are highly demanded. Technologies were developed to minimize corrosion, one of them is corrosion inhibitor. Corrosion inhibitors are chemicals able to effectively slow down or reduce the rate of rusting when added in very small amounts into a corrosive environment. Commonly, the inhibitors were added continuously or periodically according to a certain time interval. There are several mechanisms of inhibition, however in general the inhibitors inhibit corrosion through adsorption mechanisms [1,2]. Based on the materials constitution, there are two types of compounds used as corrosion inhibitors, i.e. inorganic and organic compounds. Inorganic inhibitors usually contain chromates, nitrites, silicates, phosphates. Organic inhibitors are mostly derived from aliphatic fatty acids, monoamines, diamines, amides, oleates, and amphoteric compounds such as imidazole and its derivatives [3,4]. Organic inhibitors are considered more environmentally friendly. It is because of inorganic inhibitors triggering many problems to the environment when accumulated, while organic inhibitors are degradable by the environment [5]. Organic compounds that pose inhibitory abilities are compounds that contain N, O, P, S atoms, and also that contain lone pairs and π electrons. These features are responsible for the adsorption on metal surfaces [6]. Heterocyclic organic compounds that contain nitrogen atoms are widely employed as corrosion inhibitors for carbon steels in acidic environments [7,8]. In this study, we employed a heterocyclic organic compound, 4-(4,5-diphenyl-1*H*-imidazole)-*N,N*-dimethylbenzenamine (from now on will be denoted as inhibitor) as a corrosion inhibitor in a corrosive environment of 1% NaCl at room temperature. This compound was chosen because it poses heterocyclic functional group which is the imidazole, π electrons, and nitrogen atoms (Figure 1). Performance of inhibitor used in this study was evaluated by electrochemical impedance spectroscopy (EIS) method. Employing electrochemical method, the corrosion rate can be determined in the range of minutes and the changes in the performance of inhibitor can be observed over time [4].

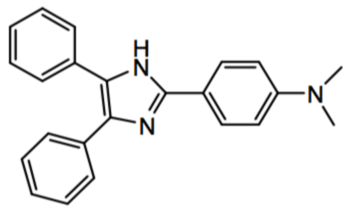

Figure 1: 4-(4,5-diphenyl-1*H*-imidazole)-*N,N*-dimethylbenzenamine

Performance of a compound as an effective corrosion inhibitor strongly correlated to the adsorption mechanism of the compound on metal surfaces. Generally, adsorption mechanism on metal surfaces may follow the Langmuir or Temkin adsorption isotherm models. Langmuir adsorption isotherm describes monolayer forms of adsorption, wherein the adsorbed molecules are homogeneous and the changes in the enthalpy of adsorption (ΔH_{ads}) do not depend on the degree of surface coverage (θ). Equation 1 applies to the Langmuir adsorption isotherm, where θ is the degree of surface closure, b is the adsorption coefficient, C_{inh} is the concentration of the inhibitor [9].

$$\theta = \frac{b\ C_{inh}}{1+b\ C_{inh}} \quad (1)$$

Temkin adsorption isotherm describes monolayer adsorption where adsorbates are adsorbed heterogeneously on metal surface. In this case, interactions between adsorbate molecules occur. Equation 2 applies to the Temkin adsorption isotherm, where θ is the degree of surface closure, f is the parameter between adsorbed molecules, K_{ads} is the adsorption coefficient, and C_{inh} is the inhibitor concentration [9].

$$\theta = \frac{1}{f}\ln(\ K_{ads}.C_{inh}) \quad (2)$$

Understanding the mechanism involved in the adsorption of organic corrosion inhibitor on metal surfaces helps the development of materials that may suppress the problems caused by corrosion. In this study, we employed an imidazole derivate compound as a corrosion inhibitor toward carbon steel in a corrosive environment of 1% NaCl at 25 ^{o}C. The adsorption mechanisms, i.e. whether based on Langmuir or Temkin adsorption isotherm models and also whether the inhibitor is adsorbed physically, semi-physically or semi-chemically, or chemically on the metal surfaces, were investigated. This study contributes to the development of environmentally friendly materials promising to be applied as corrosion inhibitors.

2. Materials and methods

2.1. Preparation of corrosive solution 1% NaCl

An amount of 10 grams of NaCl (Merck) was dissolved with demineralized water in a beaker glass and transferred to 1000 mL measuring flask. Demineralized water was added up to the mark.

2.2. Preparation of corrosion inhibitor solution

The inhibitor solution with concentration of 500 ppm was prepared by dissolving 50 mg 4-(4,5-diphenyl-1*H*-imidazole-2-il)-*N,N*-dimethylbenzenamine (details of the preparation methods of the compound is described elsewhere [13]) to small amount of acetone (p.a., Merck) and 1% NaCl solution in a beaker glass, then transferred to 100 mL measuring flask. 1% NaCl solution was added up to the mark. The series concentrations of 10, 30, 50 and 70 ppm inhibitor solutions were prepared by diluting 500 ppm inhibitor solution with 1% NaCl solution.

2.3. Electrochemical Impedance Spectroscopy (EIS) measurements

An amount 100 mL of 1% NaCl solution was employed as a corrosive environment and placed in electrochemical cells. The electrodes used are carbon steel as working electrodes, saturated calomel electrodes, and platinum electrodes as auxiliary electrodes. CO_2 gas was set in 15 minutes. The impedance measurement was carried out at the initial frequency of 50 KHz and the final frequency of 10 MHz. The EIS measurements were performed in a corrosive environment of 1% NaCl at 25 ^{o}C with variations in inhibitor concentrations of 0, 10, 30, 50 and 70 ppm.

3. Results and discussion

Performance of inhibitor used in this study was evaluated by electrochemical method, in particular the EIS method. In this study, the EIS measurements were conducted in a corrosive environment of 1% NaCl at 25 ^{o}C with variations in inhibitor concentrations. The electrodes used were carbon steel as the working electrodes, platinum electrodes as the auxiliary electrodes, and saturated calomel electrodes. The important factors affecting the measurement are the surface area of the working electrode and also the distance between the assisting electrodes and the working electrodes. In this method, the values of R_p, which is the internal resistance between the metal surface and the corrosive environment, were determined. R_p was obtained as the regression of the Nyquist curve plotting the real impedance (Z_r) and the imaginary impedance (Z_i) in the form of semicircular curves. Figure 2 showed the Nyquist curve obtained in the measurements. R_p increases with the increasing radius of the Nyquist curve (Table 1). R_p was converted to inhibition efficiency (IE) by equation 3. The IE describes the decrease in the corrosion rate. In general, increasing the concentration of the inhibitor will increase the efficiency of inhibition (Table 1).

$$\%IE = \left[1 - \frac{Rp\ (blank)}{Rp\ (inhibited)}\right] x\ 100\% \tag{3}$$

The results of EIS measurements showed that increase in amount of inhibitor added to the system was able to decrease the corrosion occurred on the metal surfaces. This indicated that surface of the metal that was covered by the inhibitor has been protected from the corrosive environment. Interactions between the inhibitor and metal surface were attributed to the presence of electron donors from inhibitor. This is due to the imidazole, amine, and phenyl functional groups poses by the inhibitor used in this study. Interactions between inhibitor and metal surface might occur physically, chemically, semi-physically, or semi-chemically [10]. These interactions led to adsorption of inhibitor on metal surface. Organic inhibitors undergo adsorption on metal surfaces based on the Langmuir or Temkin adsorption isotherm models.

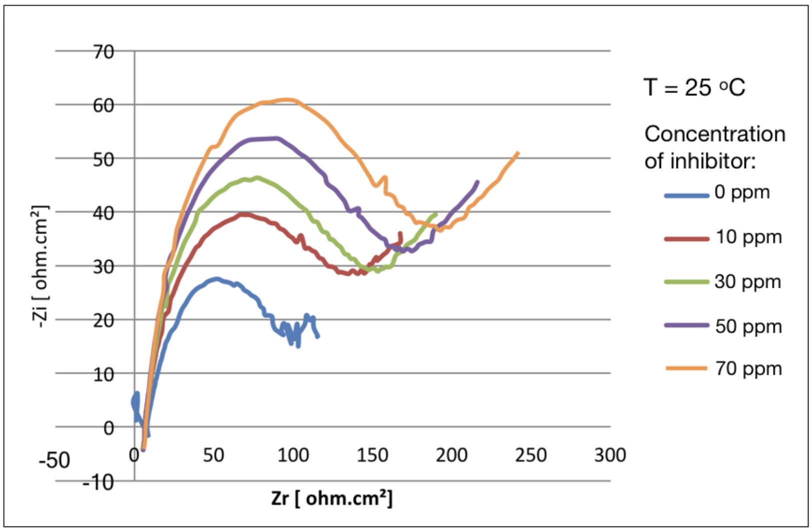

Figure 2: Nyquist curve obtained from EIS measurements in the corrosive environtment of 1% NaCl at 25 ^{o}C

Table 1: The internal resistance (R_p) and Inhibition efficiency (IE) of the inhibitor measured by EIS in the corrosive environment of 1% NaCl at 25 ^oC

Concentration of inhibitor (ppm)	R_p (ohm.cm^2)	IE (%)
0	118,1	0
10	173,7	32,01
30	184,4	35,95
50	208,3	43,30
70	233,2	49,36

Assumptions that apply to the Langmuir adsorption isotherm model are that the surface of the adsorbent is homogeneous and the adsorbed molecules experience delocalization. Parameters determining Langmuir are shown in Equation 4, where θ is the degree of surface closure, b is the adsorption coefficient, and C is the molar concentration of the inhibitor [11]. Herein, θ corresponds to the IE.

$$\frac{C}{\theta} = C + \frac{1}{b} \tag{4}$$

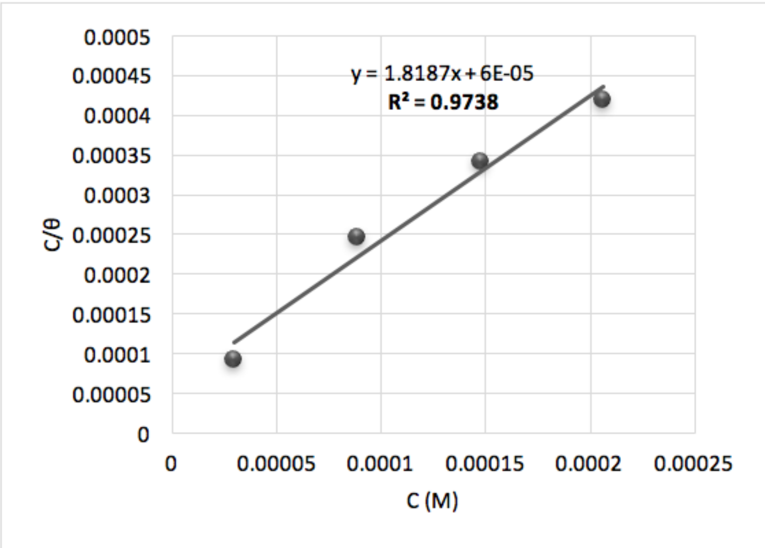

Figure 3: Langmuir adsorption isotherm fitting curve

Based on the linear equation for the Langmuir adsorption isotherm fitting, the intercept is taken to obtain the value of *b*. The value of *b* equals to the constant of adsorption process, K_{ads}, as expressed in Equation 5.

$$b = K_{ads} = \frac{\theta}{C\,(1-\theta)} \tag{5}$$

K_{ads} was used to determine adsorption free energy, ΔG_{ads}, as shown in Equation 6. The ΔG_{ads} indicated whether the inhibitor is adsorbed physically, semi-physically or semi-chemically, or chemically. The physical absorption occurs when the ΔG_{ads} is in the range of 0 – 20 kJ/mol, whereas the chemical adsorption occurs when the ΔG_{ads} is more negative than -40 kJ/mol [9]. ΔG_{ads} obtained in this study was -34.04 kJ/mol, indicated that the inhibitor adsorbed semi-physically or semi-chemically on the metal surface.

$$\Delta G_{ads} = -RT \ln (55{,}55\ K_{ads}) \quad (6)$$

The determination of the adsorption isotherm model must be done by comparing the linear regression of the linear equations of both Langmuir and Temkin adsorption isotherm fittings. The assumptions that apply to the Temkin adsorption mechanism are that the adsorption is heterogeneous on the surface of the adsorbent and intermolecular interactions between the adsorbate molecules might occur. Temkin adsorption isotherms are expressed by Equation 7, where θ is the degree of surface closure, f is the intermolecular parameter adsorbed, K_{ads} is the adsorption coefficient, and C is the concentration of the inhibitor [12].

$$\theta = \frac{1}{f} \ln K_{ads} + \frac{1}{f} \ln C \quad (7)$$

Linear regression obtained from Langmuir adsorption isotherm fitting was 0.9738 (Figure 3), whereas that of from Temkin was 0.8694 (Figure 4). This showed that adsorption of inhibitor used in this study on metal surface was based Langmuir adsorption isotherm. Hence, it is revealed that monolayer coverage occurred on the metal surface while the inhibitor protected the metal from corrosive environment. The monolayer coverage was originated from interactions between imidazole group and π electrons with the metal surface. These findings, for the first time, demonstrated that 4-(4,5-diphenyl-1*H*-imidazole)-*N*,*N*-dimethylbenzenamine is promising to be applied as a corrosion inhibitor towards carbon steel in 1% NaCl solution at 25 °C.

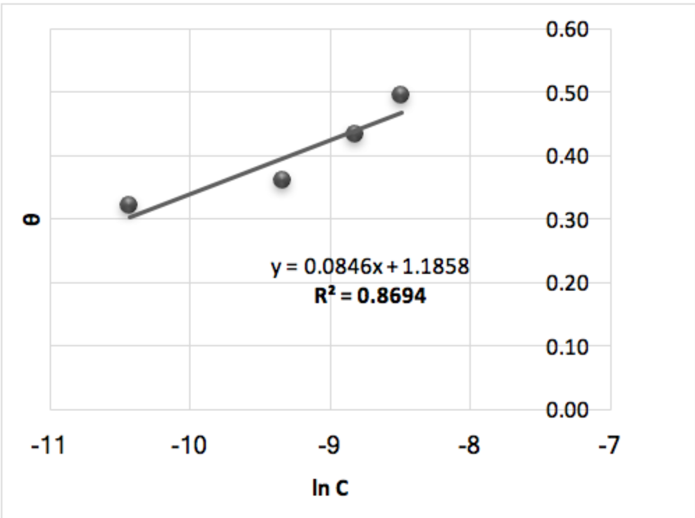

Figure 4: Temkin adsorption isotherm fitting curve

4. Conclusions

Adsorption mechanism of an organic corrosion inhibitor from imidazole group on the surface of carbon steel was studied employing EIS method. The measurements were carried out in a corrosive environment of 1% NaCl at 25 ^{o}C with variations in inhibitor concentrations. The internal resistance between the metal surface and the corrosive environment was obtained, and the inhibition efficiency was determined. The results showed that increase in inhibitor concentration leads to increase in inhibition efficiency, attributed to increase in surface coverage of the inhibitor on metal surface. Thus, the adsorption mechanisms as well as the interactions between inhibitor and metal surface were investigated. Linear regressions obtained from fitting of Langmuir and Temkin adsorption isotherm models were 0.9738 and 0.8694, respectively. This suggest that the adsorption occurred based on Langmuir adsorption isotherm, indicating that the monolayer coverage of inhibitor on metal surface plays important role in the mechanism of corrosion inhibition. The adsorption free energy was -34.04 kJ/mol, showing that interactions between inhibitor and metal made the inhibitor adsorbed semi-physically or semi-chemically on the metal surface.

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