

Synthesis of Dipeptide Benzoylalanine Methyl Ester and Corrosion Inhibitor Evaluation by Tafel Equation

(Sintesis Ester Metil Dipeptida Benzoilalanilglisin dan Penilaian Penghalang Pengaratan Menggunakan Persamaan Tafel)

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ABSTRACT

Corrosion is one of the major problems in petroleum mining and processing industry. The pipelines used to transport crude oil from reservoir to the processing installation were made from carbon steel that is susceptible towards corrosion. One of the best methods to prevent corrosion that occurred at the inner parts of carbon steel pipelines is to use organic corrosion inhibitor. One of the potent organic corrosion inhibitors is amino acids derivatives. In this study, dipeptide compound namely benzoylalanine methyl ester and benzoylalanine have been synthesized. The structure elucidation of the products was performed by IR, MS and NMR spectroscopy. The determination of corrosion inhibition activity utilized the Tafel method. The corrosion inhibition efficiency of glycine methyl ester, benzoylalanine, dipeptide benzoylalanine methyl ester and dipeptide benzoylalanine were 63.34%, 35.86%, 68.40% and 27.72%, respectively. These results showed that the formation of dipeptide benzoylalanine methyl ester, derived from carboxylic protected glycine and amine protected alanine, increased the corrosion inhibition activity due to the loss of acidity center in the structure of glycine and L-alanine that would induce the corrosive environment towards carbon steel.

Keywords: Benzoylalanine methyl ester; carbon steel; corrosion inhibitor; dipeptide synthesis; Tafel method

ABSTRAK

Kakisan merupakan salah satu masalah utama dalam industri perlombongan dan pemrosesan petroleum. Paip yang digunakan untuk menyalurkan minyak mentah dari sumber ke bahagian pemrosesan yang dibuat daripada bahan aloi karbon mudah terdedah kepada kakisan. Salah satu cara terbaik dalam mencegah kakisan yang terjadi pada bahagian dalam paip aloi karbon adalah dengan menggunakan penebat kakisan organik. Salah satu penghalang kakisan organik yang berpotensi adalah terbitan asid amino. Dalam kajian ini, sebatian dipeptida iaitu ester metil benzoilalanilglisin dan benzoilalanilglisin telah disintesis. Penentuan struktur produk dilakukan dengan pengukuran spektroskopi IR, MS dan NMR. Penentuan keaktifan penghalang pengaratan dilakukan dengan kaedah Tafel. Kecekapan penebat kakisan glisin metil ester, benzoilalanin, dipeptida benzoilalanilglisin metil ester dan dipeptida benzoilalanilglisin, secara berturut-turut adalah 63.34%, 35.86%, 68.40% dan 27.72%. Hasil menunjukkan bahawa pembentukan dipeptida benzoilalanilglisin metil ester, yang berasal daripada glisin dengan kumpulan karboksilik dan alanin dengan kumpulan amina, meningkatkan keaktifan penebat kakisannya akibat kehilangan pusat keasidan dalam struktur glisin dan alanin yang boleh mendorong keadaan pengaratan terhadap aloi karbon.

Kata kunci: Aloi karbon; benzoilalanilglisin metil ester; kaedah Tafel; penebat pengaratan; sintesis dipeptida

INTRODUCTION

Corrosion is one of major problems in petroleum mining and processing industry. Many catastrophic cases were initiated by corrosion, for example the damage of oil reservoirs, underground pipelines and other equipments (Jones 1992; Kelly et al. 2003). The pipelines used to transport crude oil from reservoir to the processing installation were made by carbon steel that is susceptible towards corrosion.

One of the best methods to prevent corrosion that occurred at the inner parts of carbon steel pipelines is the use of inhibitor. Organic corrosion inhibitor have more advantages than inorganic corrosion inhibitor because

it is easily degraded by the environment (Bundjali 2005; Burstein 2005). One of potent organic corrosion inhibitors is amino acids. However, the presence of the acidic carboxylic acid groups could also induce the corrosion process. Therefore it is necessary to perform the protection of carboxylic functional group. The protection of carboxylic functional group could increase the corrosion inhibition activity of amino acid.

Previous studies (Brahma 2005; Rahmansyah 2007) on corrosion inhibition activity of amino acid glycine and alanine found the acids have low inhibition efficiency. Therefore, in this study the carboxylic group of a single amino acid was protected by making a peptide bond

between glycine and alanine by esterification of the free carboxylic group to form dipeptide.

MATERIALS AND METHODS

GENERAL EXPERIMENTAL PROCEDURES

To determine of melting point of the products we utilized the *Fisher-Jhon*® Melt-Temp Apparatus. The TLC analysis was performed on precoated Silica Gel plates (Merck Kieselgel 60 G F₂₅₄, 0.25 mm, 20 × 20 cm²). The Column Chromatography was carried out by using silica gel Merk 60 mesh. The characterization of the products was done by using BUCK-IR M-500 for the determination of infrared spectrum, and the structure elucidation was carried using DELTA NMR 500 MHz (¹H-NMR) and 125 MHz (¹³C-NMR) at LIPI Serpong, and GCMS at UPI Bandung. The determination of corrosion inhibition activity of the synthesized products employing Potentiostat/Galvanostat Model PGZ 301 VoltaLab® 30 and VoltaMaster® software program at Chemistry Study Program of ITB, with carbon steel as working electrode, calomel as reference electrode, and platinumium as auxilliary electrode.

SYNTHESIS OF DIPEPTIDE BENZOYLALANILGLYCINE METHYL ESTER

Synthesis of glycine methyl ester (Blatchly et al. 1989; Bodanszky 1993): Anhydrous methanol (60 mL) was cooled to 0°C and 2.90 mL of thionyl chloride was added with vigorous stirring and 3 g of L-glycine was added dropwisely. Upon completion, the mixture was heated under reflux at 60°C for 4 h. The excess of methanol was then removed using rotary epevaporator, the solid residue was dissolved in the minimum volume of boiling methanol, and the solution was cooled to 0°C. The hydrochloride form of the product precipitated after slow addition of diethylether with stiring. The salt was collected by suction filtration, washed with diethylether and dried in vacuo. The product is white crystalline; 82.92 % of chemical yield; m.p 176.2°C ; IR ν_{maks} (KBr): 3424 cm⁻¹ (-N-H stretching of primary amine), 3166 and 2972 cm⁻¹ (correspond to the aliphatic alkyl groups), 1705 cm⁻¹ (C=O carbonyl group of ester), 1592 and 1413 cm⁻¹ (-N-H stretching of amine), 1259 cm⁻¹ (C-O-C of ester group), 1034 cm⁻¹ (C-N stretching of amine), 912 cm⁻¹ (-N-H bending of primary amine). ¹H-NMR (500 MHz, DMSO): δ (ppm) 8.60 (s, 3H), 3.74 (s, 2H), 3.70 (s, 2H). ¹³C-NMR (125 MHz, DMSO): δ (ppm) 168.7; 52.53; 24.64.

Synthesis of benzoyl alanine (Blatchly et al. 1989; Bodanszky 1993): L- alanine (2 g) was added into 30 mL of 1N NaOH solution and then cooled to 0°C. After 15 min 2.5 mL benzoyl chloride was added simultaneously into the well-stirred solution, in such a proportion that the reaction mixture maintains a pH of 8-9 (control with indicator paper). After the addition was completed (4) the stirring was continued for further 1 h. The reaction mixture

was then acidified with concentrated HCl until pH 2 was reached. The precipitated product was extrated from 2 × 50 mL ethyl acetate, and the combined extracts were dried using anhydrous Na₂SO₄ (sodium sulphate), filtered, and concentrated in vacuum (rotary evaporator). The resulting oily residue was dissolved in 20 mL ethyl acetate. Then the solution was cooled to 0°C, and n-hexane was slowly added with stirring. The stirring was continued for 15 min and further 20 mL n-hexane was added. The precipitated product crystallized completely on stirring, it was collected by suction filtration, washed with pre-cooled n-hexane, and dried in vacuo. The product was white crystalline; 69.23% of chemical yield; m.p 148,9°C ; IR ν_{maks} (KBr): 3373 cm⁻¹ (-N-H stretching of secondary amine), 3070 cm⁻¹ (C-H aromatic stretching vibration), 2954 cm⁻¹ (C-H aliphatic stretching vibration), 1751 cm⁻¹ (C=O carbonyl group of ester), 1563 cm⁻¹ (C=C stretching of aromatic), 1548 cm⁻¹ (-N-H stretching of secondary amine), 1176-1209 cm⁻¹ (C-N stretching of amine and C-O-C stretching of ester, 873 cm⁻¹ (-N-H bending of amine), 713 cm⁻¹ (C-H bending out of plane).

Synthesis of dipeptide benzoylalanilglycine methyl ester (Blatchly et al. 1989; Bodanszky 1993): Glycine methyl ester (0.25 g) and 0.5 g of benzoyl alanine were suspended in anhydrous 40 mL CH₂Cl₂ and the suspension was cooled to 0°C. 0.5 mL anhydrous triethylamine was added with stirring, followed, after 10 min, by 0.65 g dicyclohexylcarbodiimide (DCC). The reaction mixture was stirred for 1 hour at 0°C and for 16 h at room temperature. The precipitated dicyclohexylurea was then filtered off and washed with CH₂Cl₂. The combined filtrate and washing were washed successively with 20 mL 2 N HCl, 20 mL aqua dm (demineralized). The organic phase was then dried using anhydrous Na₂SO₄ and the solvent was remevod in rotary evaporator. The residue was recrystallized from ethyl acetate/n-hexane mixtures. The product was white crystalline; 38.92 % of chemical yield; m.p 112-113°C ; Rf. 0,61; IR ν_{maks} (KBr): 3261 cm⁻¹ (-N-H stretching of secondary amine), 3093 cm⁻¹ (C-H aromatic stretching vibration), 2850-2945 cm⁻¹ (C-H aliphatic stretching vibration), 1751 cm⁻¹ (C=O carbonyl group of ester), 1674 cm⁻¹ (C=O carbonyl group of first amide), 1635 cm⁻¹ (C=O carbonyl group of second amide), 1544-1573 cm⁻¹ (C=C stretching or aromatic), 1207 cm⁻¹ (C-O-C stretching of ester), 1184 cm⁻¹ (C-O stretching of methyl ester), 696 cm⁻¹ (C-C bending out of plane of benzene ring). ¹H-NMR (500 MHz, CDCl₃): δ (ppm) 7.75-7.77 (dd), 7.49-7.51 (dd), 7.40-7.43 (t), 4.84-4.86 (s, 1H), 1.70-1.85 (q, 1H), 1.29-1.35 (d, 3H), 4.11-4.15 (s, 1H), 2.03 (s,2H), 3.70-3.71 (s, 3H). ¹³C-NMR (125 MHz, CDCl₃): δ (ppm) 168.27; 163.01; 160.64; 133.58; 132.11; 128.7; 127.34; 50.62; 31.66-32.06; 24.95-25.56. m/e = 264 [M], 233 [M-OCH₃], 176 [M-NH-CH₂-CO-OCH₃], 148 [M-CO-NH-CH₂-CO-OCH₃], 105 [M-NH-CH(CH₃)-CO-NH-CH₂-CO-OCH₃], 77 [M-CO-NH-CH(CH₃)-CO-NH-CH₂-CO-OCH₃].

ELECTROCHEMICAL MEASUREMENTS OF THE PRODUCTS

An amount of 0.8 mg of the products was dissolved in 100 mL 1% NaCl solution, to give 8 ppm concentration of sample solutions. NaCl solution (1%) was also used as blank solution in each measurement. The 1% (w/v) NaCl solution was also used as blank solution in each measurement. Into 110 mL specialized chamber equipped with magnetic stirrer was introduced 100 mL of blank solution or sample 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, approximately 20 min. 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). The measurement was carried out using a potentiostat/galvanostat Model PGZ 301 VoltaLab@ 30 and VoltaMaster@ software program until the curve of potential measurement versus time was completely formed. The measurements of each sample solution should be initiated by the measurement of blank solution. The inhibition activity can be calculated using following equation:

$$\text{Inhibition Efficiency (IE\%)} = \frac{I_{\text{corr}} - I_{\text{corr(inh)}}}{I_{\text{corr}}} \times 100\% \quad (1)$$

where I_{corr} and $I_{\text{corr(inh)}}$ (in mA/cm²) are the corrosion current density in the absence and presence of inhibitors.

RESULTS AND DISCUSSION

The dipeptide compound of benzoylalanilglycine methyl ester has been synthesized in three steps. The first step is the esterification reaction of glycine with methanol utilizing thionyl chloride (SOCl₂) as activator, producing white crystalline of glycine methyl ester with melting point of 176.2°C. The characterization of glycine methyl ester was performed by IR and NMR techniques which showed the characteristic peaks and chemical shifts of ester C=O, ester C-O-C and primer -NH- functional groups. The second step is the benzoylation reaction of L-alanine using benzoyl chloride as reagent in basic condition producing transparent white crystalline of benzoyl alanine with melting point of 148.9°C. The IR spectrum of benzoyl alanine showed the characteristic peaks of secondary -NH- and carboxylic -OH functional groups. The third step was the condensation reaction of glycine methyl ester and benzoyl alanine utilizing DCC (*N,N'*-dicyclohexylcarbodiimide) to form white crystalline of dipeptide benzoylalanilglycine methyl ester with melting point of 112-113°C along with transparent white crystalline of dipeptide benzoylalanilglycine with melting point of 186-187°C. The by product was formed because of hydrolysis reaction towards dipeptide benzoylalanilglycine

methyl ester when extracted by aqua dm (demineralized). The IR Spectrum of dipeptide benzoylalanilglycine methyl ester showed the characteristic peaks of ester C=O (1751 cm⁻¹), ester C-O-C (1184-1207 cm⁻¹), whilst dipeptide benzoylalanilglycine showed characteristic peaks of carboxylic -OH (3068-2600 cm⁻¹). The ¹H-NMR spectrum of benzoylalanilglycine methyl ester showed the chemical shift of ester C-O-C at 3.70 ppm and secondary -NH- at 4.10 dan 4.80 ppm. The ¹³C-NMR spectrum of benzoylalanilglycine methyl ester showed the chemical shift of carbonyl ester at 168.20 ppm and carbonyl amide at 163.01 ppm and 160.64 ppm. Mass spectrophotometry (MS) data of benzoylalanilglycine methyl ester and benzoylalanilglycine showed the peaks of molecular mass ratio (m/e) of 264 and 250, respectively. Based on the results it can be suggested that the structure of the dipeptide (benzoylalanilglycine methyl ester) is as shown in Figure 1.

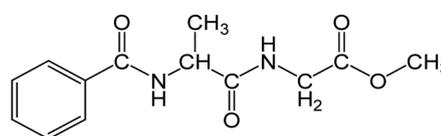


FIGURE 1. The structure of dipeptide benzoylalanilglycine methyl ester

The corrosion inhibition activities of the synthesized products were determined utilizing Tafel method (Burstein 2005) and performed by using potentiostat/galvanostat Model PGZ 301 instrument at the concentration of 8 ppm in 1% NaCl solution induced by CO₂ gas. The data is presented in Table 1. The principal consideration of Tafel method is that this method involves the determination of the Tafel slopes β_a and β_b as well as E_{corr} and I_{corr} from a single polarization curve (Perez 2004), where β_a and β_b are taken as positive kinetic parameters for determining of a corroding or oxidizing metallic material. The polarization curve predicts the corrosion rate through the current density, I_{corr} , for metal oxidation and the passivation rate through the passive current density for metallic cation reduction to form an oxide protective film on the electrode surface (Jones 1992; Perez 2004).

Based on the results, the corrosion inhibition efficiency of glycine methyl ester, benzoyl alanine, and dipeptide benzoylalanilglycine methyl are 63.34%, 35.86%, 68.40% and 27.72%, respectively. It can be seen that the corrosion inhibition efficiency of benzoyl alanine is low compared to glycine methyl ester because of the protected carboxylic functional group in glycine methyl ester structure; therefore its acidity property was decreased compared to the unprotected carboxylic group in benzoyl alanine. The dipeptide benzoylalanilglycine methyl ester showed the highest corrosion inhibition activity compared to its precursors, which are benzoyl alanine and glycine methyl ester. It is well understood that the dipeptide have

TABEL 1. The corrosion inhibition efficiency of synthesized compounds utilizing Tafel methods towards carbon steel in 1% NaCl solution

Synthesized Compounds	I_{corr} ($\mu\text{A}/\text{cm}^2$)		% Inhibition efficiency
	Blank solution (1 % NaCl solution)	Sample solution	
Glycine methyl ester	95.6199	34.9681	63.34
Benzoyl alanine	103.7786	66.5566	35.86
Benzoylalanilglycine methyl ester	112.4753	35.5372	68.40

more functional groups that have lone pair's electrons than the single amino acid. Moreover, the peptide bond of dipeptide has the potent to interact with the carbon steel (iron) surface as addition to the other interactions formed by other functional groups. The more lone pair electrons found in the compound the more potent to have the good interaction between those electron clouds and the metal's orbital, especially the *d* orbital. The clouds of phi electrons of benzene ring of benzoyl chloride in the structure of the products also have the additional effect to strengthen the interaction between the dipeptide and carbon steel surface. These results showed that the formation of dipeptide benzoylalanilglycine methyl ester, which derived from carboxylic protected glycine and amine protected alanine, increase the corrosion inhibition activity due to the loss of acidity center in the structure of glycine and L-alanine that would induce the corrosive environment towards carbon steel. Therefore the synthesized peptide is a potent corrosion inhibitor towards carbon steel in mild electrolyte condition (1% NaCl).

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