



THE SYNTHESIS OF DIPEPTIDE BENZOYLALANYLGLYCINE METHYL ESTER AS CORROSION INHIBITOR TOWARDS CARBON STEEL

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ABSTRACT

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

Keywords: *carbon steel, benzoylalanylglycine methyl ester, dipeptide synthesis, corrosion inhibitor, Tafel method*

INTRODUCTION

Corrosion is one of major problems in petroleum mining and processing industry. A lot of catastrophic cases was generated by corrosion, for example the damage of oil

reservoirs, underground pipelines and other equipments (Jones, 1992; Kelly et.al, 2003). The pipelines used to trasport crude oil from reservoir to the processing installation were made by carbon steel that is irrisistance towards corrosion. The best method 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 easier to perform the degradation process by the environment (Bundjali, 2005; Burstein, 2005). There are still small amount of studies in performing the synthesis of organic corrosion inhibitor. 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. The previous study (Brahma, 2005; Rahmansyah, 2007) has carried out the determination of corrosion inhibition activity of amino acid glycine and alanine that found to 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 and the esterification of the free carboxylic group of the formed dipeptide.

MATERIALS AND METHODS

General experimental procedures

The determination of melting point of products utlizing the *Fisher-Jhon*® Melt-Temp Apparatus. The TLC analysis was performed on precoated Silica Gel plates (Merck Kieselgel 60 G F₂₅₄, 0.25 mm, 20x20 cm). The Column Chromatography using silica gel Merk 60 mesh. The characterization of synthesized products was analyzed using BUCK-IR M-500 at Chemistry Study Program of ITB for the determination of infrared spectrum, and the structure elucidation was determined utilizing 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 Potentiostate/Galvanostate PGZ 301 VoltaLab® 30 model and VoltaMaster® software program at Chemistry Study Program of ITB, with carbon steel electrode as working electrode, calomel electrode as reference electrode, and platinumium electrode as auxilliary electrode.

The synthesis of dipeptide benzoylalanilglycine methyl ester

The synthesis of glycine methyl ester (Blatchly et.al, 1989; Bodanszky, 1993): An amount of 60 mL of anhydrous methanol was cooled to 0°C and 2.90 mL of thionyl

chloride was added with vigorous stirring. The stirring was continued and 3 g of L-glycine was added portionwisely. When the addition completed, the mixture was heated under reflux at 60°C for 4 hours. The excess of methanol was then removed using rotary evaporator, 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, 3166, 2972, 1705, 1592, 1413, 1034, 912 cm^{-1} . $^1\text{H-NMR}$ (500 MHz, DMSO): δ (ppm) 8.60 (s, 3H), 3.74 (s, 2H), 3.70 (s, 2H). $^{13}\text{C-NMR}$ (125 MHz, DMSO): δ (ppm) 168.7; 52.53; 24.64.

The Synthesis of benzoyl alanine (Blatchly et.al, 1989; Bodanszky, 1993): An amount of 2 g of L- alanine was added into 30 mL of 1N NaOH solution and then cooled to 0°C. After 15 minutes 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 completed after 4 hours the stirring was continued for further 1 hour. The reaction mixture was then acidified with the concentrated HCl until pH 2 was reached. The precipitated product was extrated from 2 x 50 mL ethyl acetate, and the combined extracts were dried using anhydrous Na_2SO_4 (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 minutes 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 is white crystalline ; 69.23 % of chemical yield; m.p 148,9°C ; IR ν_{maks} (KBr): 3373, 3070, 2954, 1751, 1563, 1548, 1176-1209, 873, 713 cm^{-1} .

The Synthesis of dipeptide benzoylalanilglycine methyl ester (Blatchly et.al, 1989; Bodanszky, 1993): An amount of 0.25 g of glycine methyl ester and 0.5 g of benzoyl alanine were suspended in anhydrous 40 mL CH_2Cl_2 and the suspension was cooled to 0°C. 0.5 mL anhydrous triethylamine was added with stirring, followed, after 10 minutes, by 0.65 g dicyclohexylcarbodiimide (DCC). The reaction mixture was stirred for 1 hour at 0°C and for 16 hours at room temperature. The precipitated dicyclohexylurea was then filtered off and washed with CH_2Cl_2 . The combined filtrate and washing were washed successively with 20 mL 2 N HCl, 20 mL aqua dm. The organic phase was then dried

using anhydrous Na_2SO_4 and the solvent was removed in rotary evaporator. The residue was recrystallized from ethyl acetate/n-hexane. The product is white crystalline ; 38.92 % of chemical yield; m.p 112-113°C ; Rf. 0,61; IR ν_{maks} (KBr): 3261, 3093, 2850-2945, 1751, 1674, 1635, 1544-1573, 1207, 1184, 696 cm^{-1} . $^1\text{H-NMR}$ (500 MHz, CDCl_3): 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). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): 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].

The electrochemical measurements

An amount of 0.8 mg products was dissolved in 100 mL 1 % NaCl solution, to give 8 ppm concentration of sample solutions. The 1 % NaCl solution 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 minutes. 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 utilizing Potentiostat/Galvanostat PGZ 301 VoltaLab® 30 model and VoltaMaster® software program until the curve of potential measurement towards time was completely formed well. The measurements of each sample solution should be initiated by the measurement of blank solution. The inhibition activity can be calculated using following equation:

$$\text{Efficiency Inhibition (EI \%)} = \frac{I_{\text{cor}}^{\text{blank}} - I_{\text{cor}}^{\text{sample}}}{I_{\text{cor}}^{\text{blank}}} \times 100 \% \quad (1)$$

where i_{corr} and $i_{\text{corr(inh)}}$ (in mA/cm^2) are the corrosion current density in the absence and presence of inhibitors.

RESULTS AND DISCUSSION

In this study, the dipeptide compound of benzoylalanine glycine methyl ester has been synthesized. The synthesis takes place in three steps. The first step is the esterification reaction of glycine with methanol utilizing thionyl chloride (SOCl_2) 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 showed characteristic peaks and chemical shifts of ester $\text{C}=\text{O}$, ester $\text{C}-\text{O}-\text{C}$ and primer $-\text{NH}-$ 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 characteristic peaks of secondary $-\text{NH}-$ and carboxylic $-\text{OH}$ functional groups. The third step is the condensation reaction of glycine methyl ester and benzoyl alanine utilizing DCC (*N,N'*-Dicyclohexylcarbodiimide) to form white crystalline of dipeptide benzoylalanine glycine methyl ester with melting point of $112-113^\circ\text{C}$ along with transparent white crystalline of dipeptide benzoylalanine glycine with melting point of $186-187^\circ\text{C}$. The by product was formed because of hydrolysis reaction towards dipeptide benzoylalanine glycine methyl ester when extracted by aqua dm. The characterization of dipeptide benzoylalanine glycine methyl ester utilized IR and MS spectroscopy showed characteristic peaks of ester $\text{C}=\text{O}$ (1751 cm^{-1}), ester $\text{C}-\text{O}-\text{C}$ ($1184-1207\text{ cm}^{-1}$), whilst dipeptide benzoylalanine glycine showed characteristic peaks of carboxylic $-\text{OH}$ ($3068-2600\text{ cm}^{-1}$). The $^1\text{H-NMR}$ spectrum of benzoylalanine glycine methyl ester showed the chemical shift of ester $\text{C}-\text{O}-\text{C}$ at 3.70 ppm and secondary $-\text{NH}-$ at 4.10 dan 4.80 ppm. The $^{13}\text{C-NMR}$ spectrum of benzoylalanine glycine 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 benzoylalanine glycine methyl ester and benzoylalanine glycine showed fragmentation 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 is as shown in Figure 1.

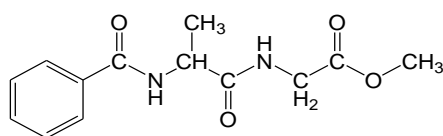


Figure 1 The structure of dipeptide benzoylalanine glycine methyl ester

The corrosion inhibition activities of the synthesized products were determined utilizing Tafel method (Burstein, 2005) and performed using potentiostat/Galvanostat PGZ 301

instrument at the concentration of 8 ppm in 1% NaCl solution induced by CO₂ gas. The data is presented in Table 1.

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

Based on the results, the corrosion inhibition efficiency of glycine methyl ester, benzoyl alanine, and dipeptide benzoylalanilglycine methyl presents as follows, respectively: 63.34 %, 35.86 %, 68.40 % and 27.72 %. 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 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's electrons found in structure of 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 synthesized 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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