Imidazoline-lauric derivative synthesis using MAOS (microwave assisted organic synthesis) method and its activity as corrosion inhibitor towards carbon steel

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Abstract. Imidazoline is a heterocyclic compound containing nitrogen atom, which is well-known in industry, especially in petroleum field as a corrosion inhibitor of oil refineries in sea environment. In searching of potential organic compounds for corrosion inhibitor, imidazoline-lauric derivative had been successfully synthesized by reacting triethylenetetramine (TETA) and lauric acid (LA) with solvent free and variation of reaction time using MAOS (Microwave Assisted Organic Synthesis) method. The optimum yield of TETA-LA imidazoline was 72.6 % at 7 min reaction time in 800 watts. TETA-LA imidazoline was identified using TLC and melting point analyzer while its structure had been confirmed using Fourier Transform Infrared (FTIR), UV-Vis, Proton Nuclear Magnetic Resonance (H-NMR), and Mass Spectrometry (MS) spectral data. The highest percentage of inhibition efficiency (% IE) using Tafel polarization method was 74.5 % at 500 ppm of TETA-LA imidazoline. It can be concluded that imidazoline-lauric derivative is potent to be developed as corrosion inhibitor towards carbon steel.

Keywords: imidazoline, lauric acid, triethylenetetramine, MAOS, corrosion inhibitor.

1. Introduction

In petroleum industry, to fulfil the increasing oil consumption, oil refineries are placed in deep sea to find new resource of oil and gas. Oil refineries are made of carbon steel, which is easily to have corrosion due to salinity of seawater. Therefore, corrosion inhibitor such as imidazoline should be added to the sea since it is the most efficient and economical ways to prevent the corrosion [1–2]. Imidazoline is a heterocyclic compound having three carbons and two nitrogen arranged at 1 and 3 positions on its five-member cyclic and has carbon chain attached to C (2) and N (3). Imidazoline can be synthesized by reacting carboxylic acid derivatives with polyamine having more than two amino groups [3].

In recent years, research on imidazoline derivatives as corrosion inhibitor has been rapidly growing. By varying side chain on carboxyl-derived or amino group, many scholars found how imidazoline structure impacts its activity [1,4–6]. Others also discovered that by modifying imidazoline to its quaternary ammonium salt improves its performance [2–3,7–10]. In this study, lauric acid (LA) was used as a source of carboxylic acid derivative and triethylenetetramine (TETA) as polyamines to produce imidazoline with different pendant group from previous study [1]. Therefore, the aim of this study is to synthesize imidazoline-lauric derivative and evaluate its activity as corrosion inhibitor towards carbon steel. Imidazoline was synthesized using MAOS (Microwave Assisted Organic Synthesis) method since it provides the most effective and efficient method for organic synthesis, as well as to support green chemistry [11].
2. Materials and methods

2.1. General
MAOS method was performed using domestic microwave oven Samsung ME-731K/XSE. Imidazoline-lauric derivative was characterized using Fourier Transform Infrared (FTIR) Shimadzu IR Prestige 21, UV-Vis Shimadzu UV-2450, Proton Nuclear Magnetic Resonance (H-NMR) Agilent 500 MHz, and Mass Spectrometry (MS) Shimadzu Prominance 20-Abesciex. Melting point was measured using Electrothermal Melting Temp. Apparatus. Corrosion inhibition activity was determined using eDAQ 450 potentiostat and Versasatat II with low carbon steel JIS G3123 grade SGD 400D (C 0.08 %, Mn 0.40 %, Si 0.19 %, P 0.033 %, S 0.021 %, and Fe 99.276 %) from PT. Citra Tanamas as working electrode (WE), SCE as reference electrode (RE), and platinum as auxiliary electrode (AE). The chemicals used for synthesis and corrosion activity test were triethylenetetramine (TETA) from Sigma Aldrich, lauric acid (LA) from PT. Eypal, while TLC plates, CHCl3, MeOH, NH4OH 25 %, Ce(SO4), HSO4, 98 %, NaSO4, acetone, and NaCl form Merck.

2.2. MAOS (microwave assisted organic synthesis) method
TETA (5 mmol) and 5 mmol of LA were heated in microwave (800 watts) with variation of time (7, 8, 9, and 11 min) at 200-240 °C. After reaction was completed, the mixture was cooled and dissolved in CHCl3. The organic layer was extracted with water three times to remove unreacted precursors. The organic layer was then dried with NaSO4, and concentrated to obtain imidazoline-lauric derivative. TETA-LA imidazoline. TETA-LA imidazoline was monitored by Thin-Layer Chromatography (TLC) using CHCl3:MeOH 8:2 with one drop NH4OH 25 % as an eluent, visualized under UV lamp (λ = 254 nm), and sprayed with Ce(SO4) in HSO4. TETA-LA imidazoline then was identified using melting point analyzer and characterized using FTIR, UV-Vis, H-NMR, and MS.

TETA-LA imidazoline was obtained as dark-brown oily solid; Rf/0.88 in CHCl3:MeOH (8:2) with one drop NH4OH 25 %; mp. 63–64 °C; FTIR with KBr νv (cm-1): 3304.2, 3071.2, 2913.2, 2851.9, 1648.2, 1554.7, 1467.9; UV-Vis in MeOH λmax (nm): 233; H-NMR (500 MHz, CDCl3) δ (ppm): 3.41 (2H, t, 10 Hz); 3.32 (2H, t, 10 Hz); 2.79–3.14 (4H, m); 2.73 (2H, t, J = 8.0); 2.39–2.55 (2H, m); 2.15 (2H, t, 7.5 Hz); 1.58 (2H, p, 7.5 Hz); 1.22–1.27 (16H, m); 0.84 (3H, t, J = 7.5 Hz); MS (M+:H): 311.3515 m/z.

2.3. Corrosion activity test
The WE was abraded with SiC abrasive paper grade 600 and rinsed with acetone and bidistilled water. NaCl 1 % solution was saturated with CO2 gas for 30 min as corrosive medium and blank solution. Test solution was made by adding various concentration of TETA-LA imidazoline (100, 200, 300, 400, and 500 ppm) to NaCl 1 % solution. WE, RE, and AE were then arranged in NaCl 1 % as an electrochemical cell. Potentiodynamic polarization was performed from -2000 to +500 mV at 50 mV/s scanning rate. The electrochemical parameters, i.e. corrosion potential (Ecorr) and corrosion density (IL), and also percentage of inhibition efficiency (IE) were obtained by using Tafel polarization method and equation (1).

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\%IE = \frac{I_{blank} - I_{sample}}{I_{blank}} \times 100\%
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3. Results and discussion
In this study, imidazoline-lauric derivative synthesis was conducted by reacting TETA with LA using MAOS method yielding TETA-LA imidazoline with the IUPAC name of N-(2-(2-undecyl-4,5-dihydro1H-imidazole-1-yl)ethyl)ethane-1,2-diamine. TETA-LA imidazoline had main structure of imidazoline ring containing N(1)-C(2)-N(3) bonds with long hydrocarbon chain attached to C(2) and pendant group attached to N(3), with a physical form of dark-brown oily solid. Figure 1 shows the reaction scheme of TETA-LA imidazoline synthesis. According to figure 1, TETA-LA imidazoline synthesis consisted of two-stages reaction, i.e. formation of amide followed by cyclization. In both stages, H2O as by product was produced [1]. To our knowledge, although this is not the first reported of the synthesis of TETA-LA imidazoline [6], this is the first reported of H-NMR and MS spectral data of TETA-LA imidazoline as well as its activity as corrosion inhibitor towards carbon steel in NaCl 1 % solution.
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Figure 1. Reaction scheme of imidazoline-lauric derivative (TETA-LA) synthesis.

Figure 2. The percentage yield of TETA-LA imidazoline.

Figure 3. (a) FTIR and (b) UV-Vis spectra of TETA-LA imidazoline

Synthesis of TETA-LA imidazoline was carried out by varying reaction times in 7, 8, 9, and 11 min (figure 2), where the optimum yield was obtained at 7 min (72.6 %). According to figure 2, the shorter reaction time, the higher yield of TETA-LA imidazoline was obtained. However, the minimum time of imidazoline synthesis using MAOS method with domestic microwave oven (800 watts) was 7 min. As reported before, in shorter than 7 min reaction time, there was a possibility that amide product had not completely continued into imidazoline [12].

FTIR spectra of TETA-LA imidazoline are shown in figure 3a. According to figure 3a, the wavenumber of 3050–3300 cm\(^{-1}\) was the absorption peaks of N-H bonds on the ethylene groups while 2800–2950 cm\(^{-1}\) was the shifting vibration of C-H bonds on the alkyl and ethylene groups. The specific absorption of imidazoline ring was appeared at around 1600 and 1400 cm\(^{-1}\) which belong to absorption peaks of C=N and C-N-C bonds on the imidazoline ring, respectively [3, 5–6]. Figure 3b shows UV-Vis spectra of TETA-LA imidazoline, where the maximum absorbance peak appeared at the wavelength of 233 nm. It indicated that imidazoline product had been formed, where the characteristic peak that appeared at around 230 nm indicated C=N bond of imidazoline [3].

H-NMR spectra of imidazoline derived from saturated fatty acid commonly consist of three regions of peak, i.e. peaks from hydrocarbon chain (\(\delta\), 0.80-2.20 ppm), pendant group (\(\delta\), 2.40-3.40 ppm), and imidazoline ring (\(\delta\), 3.30–3.70 ppm) [4, 12-13]. Figure 4a shows H-NMR spectra of TETA-
Figure 4. (a) H-NMR and (b) MS spectra of TETA-LA imidazoline

LA imidazoline (500 MHz, CDCl₃). Based on figure 4a, proton signal at chemical shifts of 3.32 and 3.41 ppm indicated proton signal of imidazoline ring. Proton signal of imidazoline ring usually appears as deshielding peak than others since it is near the electronegative atoms in cyclic. Proton signal at chemical shifts of 2.39–3.14 ppm pointed to proton signal of pendant group with 8 proton integrations belongs to 2 ethyl-amino groups from TETA. The remaining proton signal at chemical shift 0.84–2.15 ppm is specified to proton signal of hydrocarbon chain with 23 proton integrations belongs to -C₃H₆ groups from LA. By elucidating H-NMR spectra, TETA-LA imidazoline had the structure as illustrated in figure 1. Furthermore, MS characterization was also conducted to confirm the imidazoline structure by adding HCOOH and resulting m/z value in [M+H]⁺ (figure 4b). The [M+H]⁺ value for TETA-LA imidazoline was 311.3515 m/z which correspond to C₁₈H₃₈N₄.
Corrosion inhibition by using saturated fatty acid imidazolines was the common method because these compounds are able to be adsorbed on metal surface through π-electron of imidazoline ring and lone pair of electrons of N atoms [1, 14–15]. Table 1 shows the corrosion inhibitor activity of TETA-LA imidazoline on low carbon steel in NaCl 1%. According to table 1, the higher concentration of imidazoline addition, the higher number of inhibition efficiency percentage (% IE). Presumably, this data can be described because the higher imidazoline concentration in test solution, the more imidazoline compound adsorbed and formed an inhibition layer on the metal surface. Therefore, the metal was protected from corrosion medium. This result revealed that the presence of hydrocarbon chain had an important role to inhibit the corrosion since corrosion medium will be difficult to interact with metal surface. The head (imidazoline ring) and pendant group as hydrophilic sites will promote bonding of the molecule to the metal surface while hydrocarbon chain as hydrophobic site will protect the metal surface to keep the corrosion medium away from the metal surface [14–15].

4. Conclusions
Imidazoline-lauric derivative, TETA-LA imidazoline, had been successfully synthesized using MAOS method with the optimum yield of 72.6% at 800 watts at 7 min reaction time. The highest corrosion inhibition activity was achieved at 500 ppm of TETA-LA imidazoline with % IE value of 74.5%. Imidazoline-lauric derivative can be used as an alternative corrosion inhibitor derived from organic compounds, since it gives high activity of anticorrosion in this work.

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References
[1] Quraishi M A, Rafiquee M Z A, Saxena N and Khan S 2008 Prot. Met. 44 91–8
[2] Fei F, Hu J, Wei J, Yu Q and Chen Z 2014 Constr. Build. Mater. 70 43–53
[3] Tyagi R, Tyagi V K and Pandey S K 2007 J. Oleo Sci. 56 211–22
[4] Jawich M W S, Oweimreen A and All S A 2012 Corros. Sci. 65 104–12
[5] Abbasov V M, Gultyiev A A, Jabrailzadeh Sh Z, Mursalov N I, Duzdaban Kh R and Mamedaliev Y 2015 International Journal of Engineering and Innovative Technology (IJEIT) 5 21–3
[6] Kong X, Qian C, Fan W and Liang Z 2018 J. Mol. Struct. 1156 164–71
[7] Fahrurrozie A, Sunarya Y and Mudzakir A 2010 Jurnal Sains and Teknologi Kimia 1 100–11
[8] Karadağ A and Destegül A 2013 J. Mol. Liq. 177 369–75
[9] Zhao M, He H, Dai C, Wu X, Zhang Y, Huang Y and Gu C 2018 J. Mol. Liq. 268 875–81
[10] Bajpai D and Tyagi V K 2008 J. Surfact. Deterg. 11 79–87
[11] Chawla A, Sharma A and Sharma A K 2012 Der Pharma Chem. 4 116–40
[12] Wahyuningrum D, Achmad S, Syah Y M, Buchari and Ariawahjoedi B 2008 Journal of Mathematical and Fundamental Sciences 40 33–48
[13] Yoo S H, Kim Y W, Chung K, Baik S Y and Kim J S 2012 Corros. Sci. 59 42–54
[14] Bajpai D and Tyagi V K 2006 J. Oleo Sci. 55 319–29
[15] Rustandi A, Soedarsono J W, February M C and Barrinaya M A 2017 Proc. Seminar Nasional Teknologi (Senatek) 2015 17 Januari 2015 Malang (Malang: Institut Teknologi Nasional Malang) 851–9