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1 Synthesis of A Novel Carrier Compound Thiazoethyl Methyl Eugenoxyacetate from Eugenol and Its Use in the Bulk Liquid Membrane Technique

1 Muhammad Cholid Djunaidi*, Pratama Jujur Wibawa, and Ratna Hari Murti

Department of Chemistry, Faculty of Science and Mathematics, Diponegoro University,
Jl. Prof. H. Soedarto, S.H., Tembalang, Semarang 50275, Indonesia

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ABSTRACT

Research into the synthesis and use of a novel carrier compound, thiazoethyl methyl eugenoxycetic acid (TMEAA) for selective transport of Cu(II), Cd(II) and Cr(III) metal ions in the bulk liquid membrane (BLM) technique was conducted. TMEAA was synthesized from eugenol by acidification into eugenoxycetic acid and subsequently esterified using 4-methyl-5-thiazoethanol. Analysis of the result was performed using GC-MS and FTIR. The TMEAA obtained was liquid, viscous, blackish-brown and fragrant, with a yield of 88%. This compound was soluble in benzene and chloroform but insoluble in methanol. The GC-MS analysis showed the presence of a single peak, with a retention time of 26.5 min, while the disappearance of vibration mode at 1727 cm^{-1} was attributed to acid absorption and the FTIR spectrum indicated that formation of an ester group had occurred. TMEAA was used as a carrier compound in the BLM technique to transport Cu(II), Cd(II) and Cr(III), using chloroform as a solvent. The results showed that TMEAA was more selective for Cu(II) and Cd(II) than Cr(III). Moreover, the research proved that N and S groups of TMEAA were selective for Cu (II) and Cd (II).

Keywords: Bulk Liquid Membrane (BLM); selective transport; thiazoethyl methyl eugenoxycetic acid; eugenol

ABSTRAK

Telah dilakukan penelitian tentang sintesis dan penggunaan senyawa carrier tiazoetil metil eugenoksi asetat untuk transpor selektif logam-logam Cu(II), Cd(II) dan Cr(III) menggunakan Teknik Membran Cair Ruah (BLM). TMEAA disintesis dari eugenol menjadi asam eugenoksi asetat dilanjutkan dengan esterifikasi menggunakan senyawa 4-metil-5 tiazoetanol. Analisis hasil dilakukan dengan GC-MS dan FTIR. TMEAA yang diperoleh berbentuk cair, kental, berwarna coklat kehitaman, berbau harum dengan rendemen 88%. Senyawa ini larut dalam benzene dan kloroform, namun sukar larut dalam metanol. Hasil analisa GC-MS menunjukkan satu puncak dengan waktu retensi 26,5 menit, sementara hilangnya serapan asam pada 1727 cm^{-1} pada spektra FTIR menunjukkan terbentuknya gugus ester. TMEAA hasil sintesis digunakan sebagai carrier teknik BLM dalam pelarut kloroform untuk transpor Cu(II), Cd(II) dan Cr(III). Hasil yang diperoleh TMEAA lebih selektif terhadap Cu(II) dan Cd(II) daripada Cr(III). Hasil penelitian membuktikan bahwa gugus N dan S dari TMEAA selektif terhadap Cu(II) dan Cd(II).

Kata Kunci: membran cair ruah; transpor selektif; tiazoetil metil eugenoksi asetat; eugenol

INTRODUCTION

Separation of heavy metals using liquid membranes is a solvent extraction method developed for use in the recovery of heavy metals from wastewater and for the extraction of valuable metals in the mining of materials. It can also be used for analysis purposes. The advantages of liquid membrane systems are that they are selective and efficient, involve low solvent consumption, are simple and inexpensive, and can be carried out continuously in a single unit operation [1]. In addition, molecular diffusion in liquids is faster than in solids, and so solid membranes with micron thicknesses cannot compete with liquid membranes in terms of transfer intensity [2].

The stability of the complex between the metal and the carrier compound determines the selectivity of separation in liquid membrane techniques. The stability of the complex is determined by several factors, including the type of donor atoms (active group) contained in the carrier compound (ligand structure), suitability for a metal electron configuration [3-7], and the pH of solutions [4-5]. The use of a carrier compound in liquid membrane techniques improves the efficiency and selectivity of transport [8].

Eugenol contained in clove oil has three active groups: allyl, methoxy and hydroxy. The hydroxyl group, which can be substituted by a more selective group, leads to eugenol being a potential selective carrier compound. Eugenol has been widely used for

* Corresponding author.
Email address : choliddjunaidi@live.undip.ac.id

the separation of heavy metals, including eugenol polymer (polyeugenol) used to adsorb Fe(III) ions [9-10], as a functional polymer in in-situ formations of membranes [11] and in membrane particles [12].

Eugenol derivatives with N-donor atoms from pyridyl carbinols are selective for borderline metals (Cu^{2+}) [13]. The working principle of the compound carrier is based on HSAB theory (grouping acids and bases based on their hardness and softness) which states that, in general, hard metal ions (such as alkali metals, alkaline earths, and Cr^{3+}) form a stronger complex with hard donor atoms (such as O) [14], soft metal ions (such as Cd^{2+}) with soft donor atoms (such as S) [15] and borderline metal ions (such as Cu^{2+}) with borderline donor atoms (such as N) [13,16-18]. A carrier compound that has nitrogen (N) and sulfur (S) active groups is expected to be selective for Cu^{2+} and Cd^{2+} .

In this research, Cr^{3+} , Cd^{2+} and Cu^{2+} metal ions will be recovered from a waste model using thiazoethyl methyl eugenoxycetic acid (TMEAA) synthesized from eugenol, using the BLM technique. A BLM is a simple liquid membrane used for the study of liquid membrane transport processes.

EXPERIMENTAL SECTION

Materials

The materials used in this research were eugenol p.a (SIGMA-Aldrich), BF_3 -diethylether p.a. (SIGMA-Aldrich), SOCl_2 p.a (Merck), 4-methyl-5-thiazoleethanol p.a (Merck), NaOH p.a. (Merck), chloroacetic acid p.a (Merck), $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ p.a (Merck), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ p.a (Merck), $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ p.a (Merck), HCl p.a (Merck), sodium bicarbonate p.a. (Merck), sodium sulfate anhydrate p.a. (Merck). Other reagents, including chloroform, methanol, diethyl ether and demineralized water, were purchased from Bratachem.

Instrumentation

The instruments used to characterize TMEAA in this study were FTIR Spectrophotometer (Shimadzu 8201PC), GC-MS (Shimadzu QP2010S), analytical balance (Mettler Toledo AB54-S), AAS (Perkin Elmer), pH meter (HACH E C20). A set of BLM tools (U-tube) was used for transport study.

Procedure

Synthesis of compound carrier TMEAA

Synthesis of eugenoxycetic acid (EOA). Eugenol (5 g) was placed in a round-bottomed 100 mL boiling flask. 17.5 mL NaOH 33% was added and the mixture was then stirred for approximately 30 min. Then 12.5 mL of

50% chloroacetic acid was slowly added with a pipette and the mixture was stirred constantly. The mixture was heated in a water bath with a temperature of 80–90 °C for 2 h, and was then cooled and acidified using 6 M HCl until the pH reached 1. The next step was the extraction of the mixture three times using 50 mL of diethyl ether, resulting in ether extracts. The ether extracts were then combined and re-extracted three times using 30 mL sodium bicarbonate 5% w/v. This extraction process produced water and ether layers. The water layer was then acidified using concentrated HCl 6 M to achieve pH 1. The final steps respectively were filtering, drying and weighing. The results were analyzed by FTIR.

Synthesis of TMEAA. Eugenoxycetic acid (3 g) was placed in a reflux apparatus and 3 mL of thionyl chloride was added dropwise. The mixture was refluxed for 15 min in a water bath with a temperature of 40 °C and then allowed to cool at room temperature. In the next step 2.5 mL of thiazolethanol was added dropwise and refluxed again in the water bath at 40 °C for 6 h. After cooling, the result obtained was extracted using chloroform and then washed with water. The extract was dried over anhydrous sodium sulfate, filtered, and then evaporated to remove remaining solvent. The result obtained was analyzed using FTIR and GC-MS.

Separation experiment

Transport of metals using the BLM technique. TMEAA (0.7 g) was dissolved in 30 mL chloroform and was then used as a carrier compound to transport metal ions using the BLM technique. Metal ion transport using the BLM technique was carried out by filling a u-tube with a feed phase containing 13 mL of a mixture consisting of 30 ppm Cu^{2+} , Cd^{2+} and Cr^{3+} with pH of 3.2. The TMEAA carrier compound in weights 0.7, 0.5, and 0.3 g was then poured into 30 mL chloroform for each weight. In the meantime, the stripping phase contained 13 mL HCl at a variety of pHs (pH 1, 1.48–1.5, and 1.9). These systems were then stirred at a constant speed for 24 h. After stirring for 24 h, pH of both feed and receiver phases was measured using a pH meter. Analysis of the metal ion content in the feed and receiver phases after the separation process was carried out using an atomic absorption spectrometer.

RESULT AND DISCUSSION

This section describes the synthesis of TMEAA and its use as a carrier in the recovery of Cu^{2+} , Cd^{2+} , and Cr^{3+} metal ions using the BLM technique. TMEAA compound was synthesized from eugenol. Eugenol was converted into EOA, which was then converted into

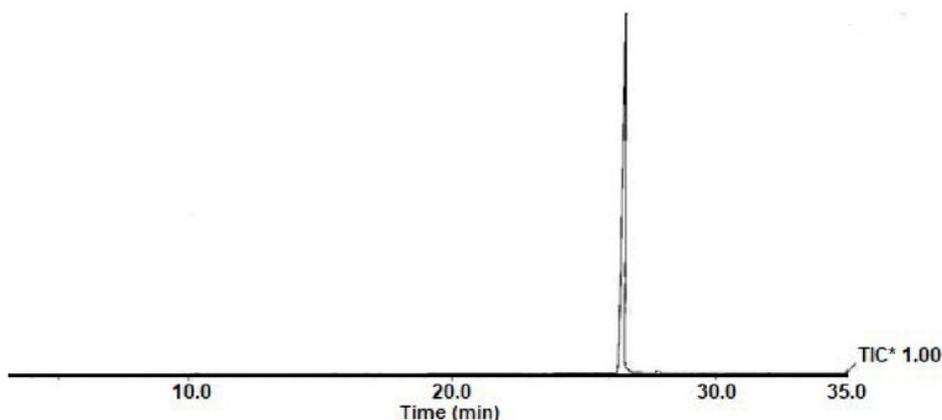


Fig 1. Gas chromatograph of TMEAA

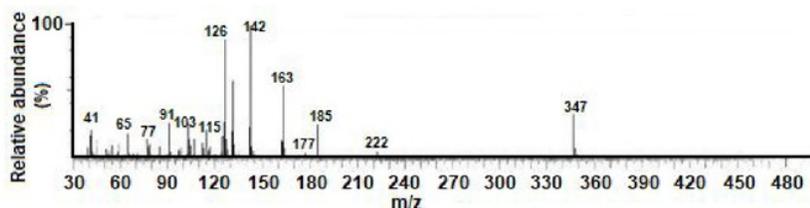


Fig 2. Spectrum mass of TMEAA

TMEAA by an esterification reaction with 4-methyl-5-thiazooetanol.

Synthesis of Eugenoxycetic Acid

The eugenoxycetic acid synthesis was carried out by the addition of NaOH and chloroacetic acid. The hydroxy group in eugenol can react with NaOH to form a eugenolate salt. This eugenolate salt reacts easily with chloroacetic acid to form eugenoxycetic acid.

The eugenoxycetic acid formed was purified using diethyl ether in order to remove non-polar impurities and NaHCO_3 to remove polar impurities. The eugenoxycetic acid produced was a pure white substance, insoluble in ether, methanol, and chloroform. The yield was 77.4%.

Synthesis of TMEAA

TMEAA was synthesized from the eugenoxycetic acid by the addition of thionyl chloride. Synthesis of TMEAA is an esterification reaction which is reversible, so TMEAA should be conducted in hydrochloric acid formed by the addition of thionyl chloride so that results yield above 80% [19].

The TMEAA produced was a liquid, viscous, blackish-brown, fragrant substance, and gave a yield of 88%. This compound was soluble in benzene and

chloroform but insoluble in methanol. The analysis of TMEAA using GC-MS can be seen in Fig. 1, which shows a single peak with a retention time of 26.5 min. Peak in relative abundance (m/z) of 347 and the spectrum mass of fragmentation (Fig. 2) were suitable. The FTIR spectrum of TMEAA compound is presented in Fig. 3. The absorption band in the area of 3077 cm^{-1} is attributed to $=\text{C}-\text{H sp}^2$. The absorption band at 1511 cm^{-1} indicates the presence of vibrations of the $\text{C}=\text{C}$ aromatic core, and this is supported by the absorption at 916 cm^{-1} region showing the aromatic substituents. The $\text{sp}^3\text{ C}-\text{H}$ bond absorption band appears at the 1416 cm^{-1} region. The vibration mode emerges at 1761 cm^{-1} indicating the existence of an ester carbonyl group. Based on the FTIR spectrum of the TMEAA compound, the wide band at wavenumber of 3888 and 3388 cm^{-1} is attributed to a hydroxyl group (OH) which belongs to EOA [10] disappearing, proving that an ester has been formed.

Based on the analysis by GC-MS and FTIR, it can be concluded that the TMEAA was formed with high purity and molecular weight of 347 g/mol .

In the process of recovery of heavy metals using this BLM technique, changes of pH both in the feed and the stripping phases occurred. These pH changes indicated the exchange mechanism of metal and H^+ ions between the two phases. The mechanism of metal

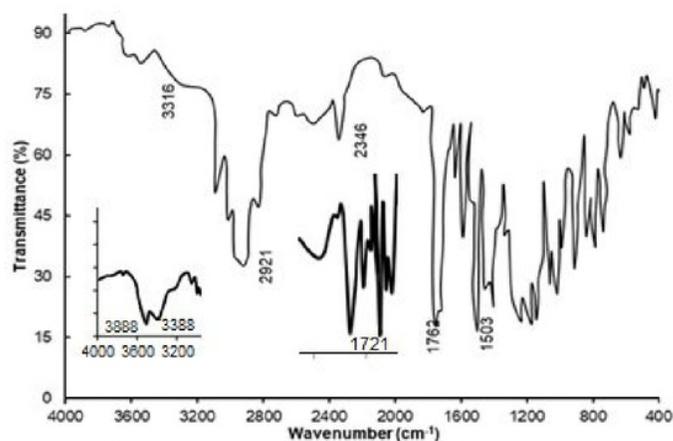
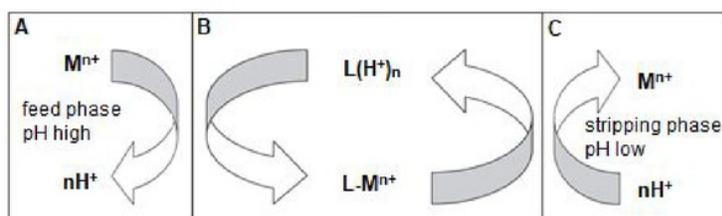


Fig 3. FTIR spectrum of TMEAA, insert FTIR spectrum of EOA



Legend: A: feed phase, B: organic phase, C: stripping phase, M: metal, L: carrier

Fig 4. Cation exchange mechanism

Table 1. Measurement of changes in pH

pH	Membrane	pH feed		pH stripping	
		Initial	After 24 h	Initial	After 24 h
1	TMEAA-2	3.2	2.9	1	1.7
	TMEAA-1	3.2	2.9	1.5	2.7
1.5	TMEAA-2	3.2	2.2	1.5	1.6
	TMEAA-3	3.2	2.4	1.5	1.7
1.9	TMEAA-2	3.2	2.1	1.9	2.4

Legend:

TMEAA-1: TMEAA with a mass of 0.7 g

TMEAA-2: TMEAA with a mass of 0.5 g

TMEAA-3: TMEAA with a mass of 0.3 g

ion transport from the feed phase to the stripping phase through the membrane is shown in Fig. 4 and the pH changes are presented in Table 1.

In Table 1 the changes in pH after stirring for 24 h can be seen. In the feed phase pH decreased, in contrast, the pH increased in the stripping phase. This resulted from the feed and the membrane phase contact, in which carrier compounds bound to metal ions to form complexes and these complexes were then brought to the interface of the membrane-stripping phase. At this interface, the carrier compounds released metal ions and replaced them with H⁺. An H⁺ ion in the feed phase was released and replaced with a metal ion. This

process occurred repeatedly until no further metal ions were exchanged.

Metals Transport Using TMEAA

Recovery of heavy metals by TMEAA in this study was conducted by performing transport with different concentration of liquid membranes to determine the selectivity and effectiveness of TMEAA used in the BLM technique. The result of metal transport at pH 1.5 is shown in Fig. 5, which shows that the sequence of selectivity of TMEAA was Cu²⁺, Cd²⁺, and Cr³⁺, or borderline, soft, and hard metals, respectively. This

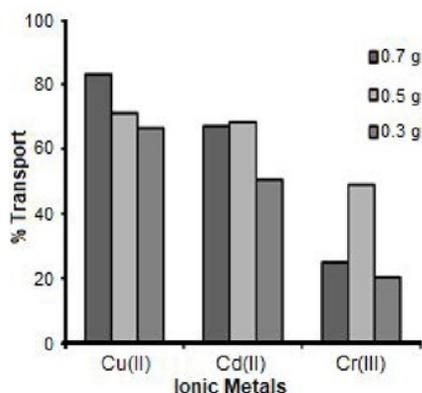


Fig 5. Heavy metal ion transport in stripping phase

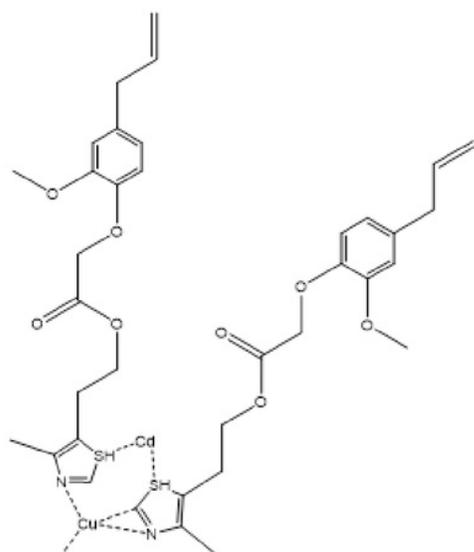


Fig 6. Interaction proposed between metal ions and TMEAA

phenomenon occurred because TMEAA contains N and S groups. N belongs to the borderline bases and will form strong complexes with borderline acids (Cu^{2+}), while the S group belongs to the soft category and so will form strong complexes with soft acids (Cd^{2+}). This was consistent with HSAB theory [3]. Based on the transport results obtained, as shown in Fig. 6, it can be seen that the transport of Cu^{2+} metal ions showed the greatest percentage. This was due to the unsaturated nitrogen contained in TMEAA. The nitrogen atom bonds with a metal atom closing it in a double bond. This double bond participated in π bonds with metal ions (Cu^{2+}) improving the stability of the complex [20] and so the

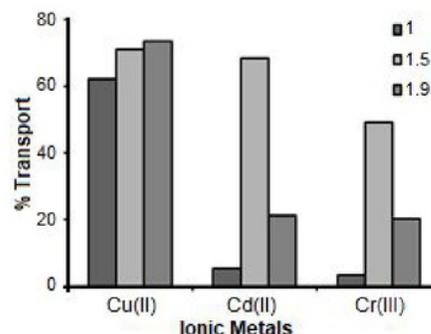


Fig 7. Ionic Metal transport at variations of pH in stripping phase

amount of Cu^{2+} transported is higher than for Cd^{2+} and Cr^{3+} (Fig. 6). The polymer of TMEAA was used by Djunaidi et al. [21] with the same objective and a similar sequence of $\text{Cd}^{2+} > \text{Cu}^{2+} > \text{Cr}^{3+}$ was found. Cahyono and Djunaidi [13] synthesized pyridin-2-ylmethyl 2-(eugenoxo)acetate (PMEOA) as a carrier with an N active atom giving transport sequence $\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Cr}^{3+}$.

The mass of the carrier compounds used can also affect the amount of metal transport [4]. The result of this research shows that the greater the mass of the carrier compound used, the more metal can be transported. The transport of heavy metals with pH variations is shown in Fig. 7.

Determination of the effect of pH in the stripping phase for metal ion transport using the BLM technique was conducted by varying the pH of HCl in the stripping phase. It can be seen in Fig. 7 that at pH 1.5, Cu^{2+} , Cd^{2+} , and Cr^{3+} were transported in large enough quantities for this pH condition to be used for exploration. In investigating separation among the metal ions pH 1 was used, because at pH 1, Cu^{2+} was transported to a greater extent than Cd^{2+} and Cr^{3+} . Selectivity coefficients of Cu(II)/Cd(II) and Cu(II)/Cr(III) for BLMs decreased with increasing HCl concentration in the stripping phase. The same tendency was reported in the literature [6,22]. The changes of pH in both feed and stripping phases can be seen in Table 1.

CONCLUSION

In the present study, TMEAA can be synthesized from eugenol and can be used as a carrier compound in the BLM technique. The N and S active groups in TMEAA act selectively with Cu^{2+} (borderline) and Cd^{2+} (soft) metal ions.

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