Synthesis of polyeugenoxy acetyl thiophene methanolate as a new selective carrier

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Synthesis of polyeugenoxy acetyl thiophene methanolate as a new selective carrier

Muhammad Cholid Djunaidi[1,*], Retno Ariadi Lusiana[1], Pardoyo[1], Didik Setiyo Widodo[1], Titi Wulan Utami[1]

[1] Chemistry Department, Faculty of Sciences and Mathematics, Diponegoro University, Semarang, Indonesia

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

Abstract. Research on the *Synthesis* of Polyeugenoxy Acetyl Thiophene Methanolate (PEATM) as a new selective *Carrier* using the Bulk Liquid Membrane (BLM) Method has been done. PEATM was synthesized from eugenol that was polymerized to form polyeugenol, acidified to make polieugenoxy acetate and then etherized with thiophenemethanol. The product obtained was characterized using FTIR and ^{1}H-NMR. PEATM produced in the form of thick brownish-black liquid. The solubility test incorporating organic compounds showed that this compound dissolved in chloroform and benzene but was difficult to dissolve in n-hexane. Molecular weight value of 700 was obtained using Ubbollohde viscometer with about 22 times monomer repetition. PEATM was used as a BLM carrier to separate mixture of Cd^{2+}, Cr^{3+} and Cu^{2+}. The results showed that PEATM was selective towards Cd^{2+}.
Keywords: Polyeugenoxy Acetyl Thiophene Methanolate, selective carrier

1. Introduction

One method of separating metal ions is by using a liquid membrane [1-3]. In liquid membranes, carrier compounds play a very important role. Carrier compounds must have the ability to extract through the formation of stable complexes in membranes, have high separation selectivity in certain species, have high solubility in organic solvents and can be used in relatively small amounts [4]. Another important thing that must be owned by a carrier is the selectivity of the carrier compound to certain metal ions determined by the active group possessed by the carrier compound. The carrier will complex metal ions through chemical bonds between active groups and metal ions based on the HSAB theory (*Hard and Soft Acids Base*).

Now the liquid membrane process appears as an efficient and economical technique for the separation of cationic and anionic dyes from industrial waste. Liquid membranes have been studied by inorganic, organic and analytical chemistry, chemical engineering, biotechnology and biomedicine researchers as well as wastewater treatments. Liquid membranes have the potential to separate organic and inorganic pollutants, especially low concentration pollutants, where other techniques cannot be efficiently applied [5].

Eugenol, contained in clove oil, has three functional groups, namely allyl, hydroxy and methoxy [6]. Through the three functional groups the structure of eugenol can be changed to form into a selective carrier compound against certain metal ions. The eugenol derivatives, resulted from the synthesis, both monomers and polymers with the active group N and donor atoms S from 4-methyl-5-thiazoethanol, were proven to be selective against borderline metal ions such as Cu^{2+} and soft metal ions such as Cd^{2+} [7, 8]. The working principle of these carrier compounds is based on the theory of HSAB (acid-base

grouping based on hardness and softness) which states that, in general, hard metal ions such as alkali metal, alkaline earth, and chromium (III) ions are going to form stronger complexes with hard donor atoms (such as O), soft metal ions (such as Cd^{2+}) will form stronger complexes with soft donor atoms (such as S derived from 2-thiophenemethanol), and *borderline* metal ions (like Cu^{2+}) will form stronger complexes with the *borderline* donor atoms such as N [9]. Taking into account the above successes, in this research, PEATM was synthesized from eugenol to change to polyeugenoxy acetate. Polyeugenoxy acetic acid is a carboxylic acid which can react with alcohol (with active group S derived from 2-thiophenemethanol) to form PEATM ester. PEATM formed was expected to be used as a *carrier* in heavy metal ion recovery of Cr^{3+}, Cd^{2+}, and Cu^{2+}. PEATM is expected to extract Cd^{2+} ions more than others according to HSAB theory. This study aims to synthesize carriers with active S groups that are selective for certain ions (Cd^{2+}) based on the HSAB theory. Cd^{2+} is one of the dangerous heavy metal ions if it exceeds the environmental threshold.

2. Research Method

Polyeugenoxy Acetyl Thiophene Methanolate (PEATM) was synthesized from polyeugenol obtained from the polymerization of eugenol. Subsequently, polyeugenol was converted into polyeugenoxy acetic acid and esterified by using 2-thiophenemethanol compound to form PEATM. To detect that polyeugenol and PEATM had become polymers, the molecular masses of polycarboxylic acid and PEATM molecules were measured by using the Ubbehlohde viscometer. PEATM was used as a carrier in the recovery of heavy metal ions of Cr^{3+}, Cu^{2+} and Cd^{2+} using the Bulk Liquid Membrane (BLM) technique.

In this research, Cr^{3+}, Cu^{2+} and Cd^{2+} metal ion mixtures were used, each with concentration of 30 ppm as feed phase and HCl as the receiving phase. The pH of the feed phase was constantly made at pH 5.01 and the pH of the receiving phase was also made constant at pH value of 1.07. Meanwhile, the PEATM mass used as a carrier was made into variations of 0.7 g, 0.5 g and 0.3 g in 30 ml of chloroform. Quantitatively, the remaining heavy metals as well as those taken up were determined using AAS.

3. Equipments and Materials

3.1. Equipment

Laboratory glass equipment, analytical balance (Mettler-200), pH meter (HACH E C20), Ubbelohde viscometer, atomic absorption spectrophotometer (Perkin Elmer), FT-IR (Nicolete Avatar 360), ^{1}H-NMR (JEOL-MY60) 60 MHz, and a set of reflux apparatus.

3.2. Materials

Eugenol p.a, $SOCl_2$ p.a, BF_3-diethyl ether p.a, 2-thiophenemethanol p.a, anhydrous Na_2SO_4 p.a, concentrated HCl, $NaHCO_3$ p.a, NaOH p.a, chloroacetic acid p.a, technical grade chloroform, technical grade diethylether, distilled water, technical grade methanol, $CrCl_3.6H_2O$ p.a, $CuCl_2.2H_2O$ p.a, $CdCl_2.H_2O$ p.a.

3.3. Methodology

3.3.1. Polyeugenol Synthesis. Polyeugenol was synthesised from eugenol by catalyst BF_3 diethyl ether [10]. Molecular weight measurements of synthesized polyeugenol was done by Ubbehlohde viscometer to detect whether it has become polymer.

3.3.2. Polyeugenoxy Acetic Acid Synthesis. Converting polyeugenol to acid using chloro acetic acid [7]. Molecular weight measurements of synthesized polyeugenoxy acetic acid was done by Ubbehlohde viscometer to detect whether it has become other polymer. The results obtained were tested for melting points and identified with FTIR and ^{1}H NMR.

3.3.3. Polyeugenoxy Acetyl Thiophene Methanolate Synthesis (PEATM). A total of 3 g (0.0135 mol) of polyeugenoxy acetic acid was introduced into a 100 mL three-neck flask with auxiliary equipment

(funnel, reflux). The polyeugenoxy acetate was then added with 1.6 mL (2,624 g, 0.022 mol) of thionyl chloride, dropwise. Then the mixture was refluxed for 150 minutes in a warm water bath (40°C) and later allowed to cool. The mixture was then added with 2 mL (2.262 g, 0.0207 mol) of 2-thiophenemethanol dropwise and refluxed again in warm water bath (40°C) for 6 hours. After cooling, the product obtained was dissolved in chloroform and was washed with water. The product of extraction was dried with anhydrous sodium sulphate, filtered, and then evaporated to remove any remaining solvent. It was then analysed using FTIR and ^{1}H-NMR. Molecular weight measurements of synthesized PEATM were done by Ubbehlohde viscometer.

3.3.4. Feed Solution Preparation. Preparation of Parent-solution

a. Cr^{3+} 500 ppm solution was prepared by dissolving $CrCl_3.6H_2O$ 0.6403 g into distilled water in a 250 mL volumetric flask.
b. Cu^{2+} 500 ppm solution was prepared by dissolving $CuCl_2.2H_2O$ 0.3352 g into distilled water in a 250 mL volumetric flask.
c. Cd^{2+} 500 ppm solution was prepared by dissolving $CdCl_2.H_2O$ 0.2238 g into distilled water in a 250 mL volumetric flask.

3.3.5. Preparation of Feed Solution. The metal ion mixture solution was prepared by taking the solutions of Cr^{3+}, Cu^{2+}, and Cd^{2+} from the parent-solutions, each 6 mL, diluted in a 100 mL volumetric flask with buffer with pH value of 5. The pH value of metal ion mixture was measured using a pH meter.

3.3.6. Receiving Solution Preparation. A total of 0.8 mL of a concentrated HCl 12 M was diluted into distilled water in a 250 mL flask. The diluted solution pH value was measured using a pH meter.

3.3.7. Liquid Membrane Preparation. Throughout this study, BLM testing was conducted three times. The testing used polyeugenoxy acetyl thiophene methanolate (PEATM) with variations of 0.7 gram, 0.5 gram and 0.3 gram in 30 mL chloroform.

3.3.8. Recovery Process. Solution containing 30 mL of polyeugenoxy acetyl thiophene methanolate (PEATM) was added into a U-tube placed between the feeding phase and the receiver phase of 13 mL each. The solutions in both ends of the tubes were then stirred for 24 hours.

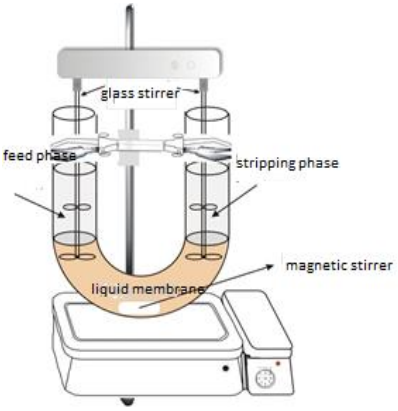

Figure 1. Bulk Liquid Membrane Testing Apparatus [7]

3.3.9. pH Value Measurement. After the feed phase and the receiving phase went through the stirring process, the pH value was measured using a pH meter.

3.3.10. AAS Analysis. Analysis of the metal ion content in the feed phase and the receiving phase after the separation process was carried out using an atomic absorption spectrometer (AAS).

4. Results and Discussions

Polyeugenoxy Acetyl Thiophene Methanolate (PEATM) was synthesized from eugenol, a natural ingredient. Subsequently, eugenol was polymerized to form polyeugenol. Polyeugenol was later

converted into polyeugenoxy acetic acid which was then esterified using 2-thiophenemethanol to form PEATM. To detect whether polyeugenol and PEATM had become polymers or not, the molecular masses of polycarboxylic acid and PEATM molecules were measured by using the Ubbehlohde viscometer. PEATM was used as a carrier in the recovery of heavy metal ions of Cr^{3+}, Cu^{2+} and Cd^{2+} using the Bulk Liquid Membrane (BLM) technique.

Complex stability between metal ions and carrier compounds is determined by several factors, including the type of donor atom (active group) contained in the carrier compound (ligand structure) [9, 11-13], compatibility with the metal electron configuration and pH of the solution [11, 12].

4.1. Synthesis of Polyeugenol and Polyeugenoxy Acetic Acid

The synthesis has already been published [7, 8, 14]. After that, molecular weight measurement was done by Ubbollohde viscometer. The intercept obtained from the chart were 8.6102 which is the intrinsic viscosity value [η] so that the relative molecular weight can be determined [15]. From the calculation, it was achieved that the relative molecular weight of polyeugenol are 9799 $gmol^{-1}$ with a repetition degree of n = 60. This proved that the synthesized polyeugenol were polymer.

4.2. Synthesis of Polyeugenoxy Acetyl Thiophene Methanolate(PEATM)

The Polyeugenoxy Acetyl Thiophene Methanolate (PEATM) compound was synthesized from polyeugenoxy acetic acid. PEATM is a carboxylic acid which can react with alcohol to form ester. However, the resulting yield is less than satisfactory because the esterification reaction is reversible [16]. Hence, in this study, instead of direct ester synthesis, the conversion of acetic acid into acyl chloride was done first using thionyl chloride. Subsequently, the formed acyl chloride was then reacted with alcohol. This method produced ester with a better yield. The theoretical esterification mechanism is shown in Fig. 2 below.

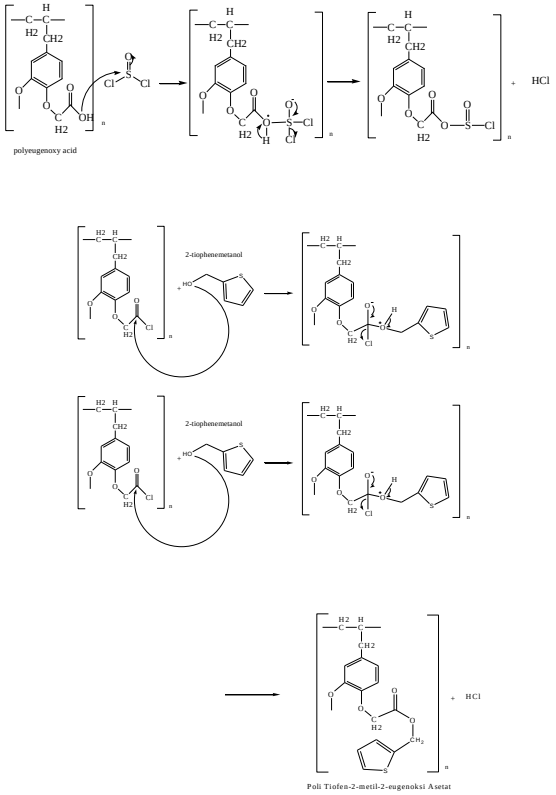

Figure 2. Reaction in the Synthesis of Polyeugenoxy Acetyl Thiophene Methanolate (PEATM).

PEATM produced in this study has a yield of 93.2%, in the form of brownish-black thick liquid. The solubility test which incorporates organic compounds showed that this compound dissolved in chloroform and benzene but was found difficult to be dissolve in n-hexane. From the graph, the obtained intercept was 6.7605 which is the intrinsic viscosity value [η]. From that, the relative molecular mass can be determined. By using the calculation method, the achieved relative molecular mass was 7019,8 $gmol^{-1}$ with repetition degree n = 22. The reduced degree of repetition (n) compared with polyethylene was caused by the termination of the polymer chain due to the formation of unstable polymer chains.

4.3. Polyeugenoxi Acetyl Thiophene Methanolate (PEATM) Analysis using FTIR

FTIR analysis result of Polyeugenoxy Acetyl Thiophene Methanolate (PEATM) and Polyeugenoxy Acetate compounds can be seen in Fig. 3 and Fig. 4.

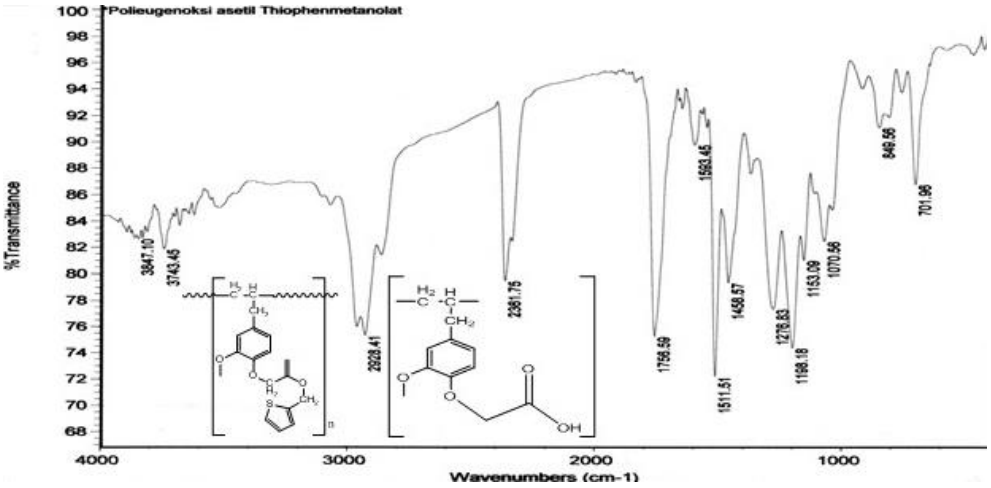

Figure 3. FTIR Spectra of Acetyl Thiophene Methanolate (PEATM) Compound.

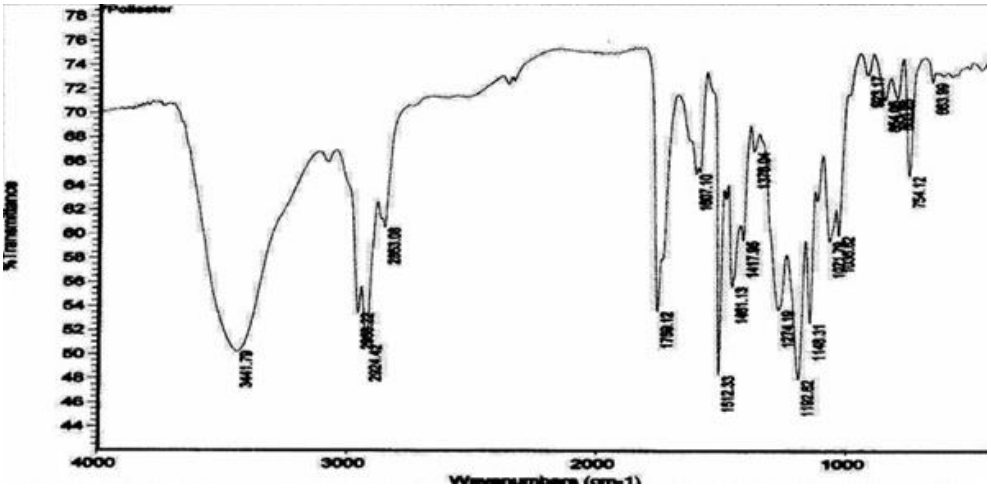

Figure 4. FTIR Spectra of Polyeugenoxy Acetic Acid.

The formation of ester can be known from the infrared spectrophotometry wavenumber of 1756 cm^{-1} which is the spectra of the carbonyl ester group (Fig. 3). The difference between carbonyl ester and carbonyl acid is that carbonyl esters appear at larger wavenumbers [17]. Due to the esterification reaction, characteristic spectra of the OH group hydrogen bonds which form a wider band at a wavenumber of about 3400-3500 cm^{-1} were loss, this is also an evidence of ester formation.

The FTIR results of Polyeugenoxyacetate analysis can be seen in Fig. 4. In FTIR spectra there is an absorption band of 3441 cm^{-1} which shows the presence of hydroxyl (O-H) groups. The absorption band in the range 3000-2800 cm^{-1} is a saturated carbon group (Csp^3-H), absorption bands of 1607 cm^{-1} and 1512 cm^{-1} are aromatic groups (C = C), absorption bands 1431 cm^{-1} shows methylene (-CH_2-) groups and absorption bands in the absorption band 814 cm^{-1} and 823 cm^{-1} indicating that the aromatics are substituted. The acid carbonyl group is shown by absorption at 1739 cm^{-1}.

4.4. Polyeugenoxy Acetyl Thiophene Methanolate (PEATM) Analysis using ^1H NMR

^{1}H-NMR spectroscopy provides information on the amount of each type of hydrogen atom. ^{1}H-NMR spectroscopy also provide information on the environmental properties of each type of hydrogen atom [18]. The analysis results of Polyeugenoxy Acetyl Thiophene Methanolate (PEATM) using ^{1}H-NMR can be seen in Fig. 5.

The apparent difference between the PEATM and polyeugenol acetic acid ^{1}H-NMR spectra is the appearance of new peak at δ 6.83 - 7.40 ppm (A) which indicates the presence of thiophene compounds (Appendix E), peak at δ 4.46 ppm (D) and δ 4.89 ppm indicates the presence of methylene (-CH_2-) group. Thus, it can be concluded that the esterification reaction occurred.

In the spectra of polyeugenoxy acetate a chemical shift δ = 6,7-7 ppm (A) indicates the presence of a -C_6H_3 group (*singlet*), the peak at δ = 4,6 ppm (B) indicates the presence of a -OCH_2- group (*singlet*), the presence uptake at δ = 3,8 ppm (C) shows the presence of -OCH_3- group (*singlet*) and peak at δ = 0,5 – 1,5 ppm (D) shows the group strength -CH_2-CH_2- (*multiplet*). This is shown in Fig. 6 below.

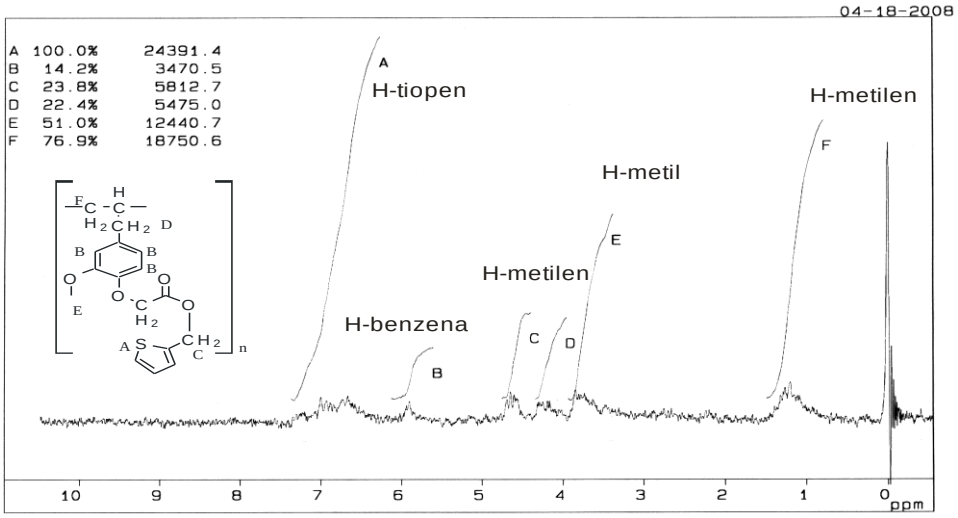

Figure 5. ^{1}H NMR Spectra of Polyeugenoxy Acetyl Thiophene Methanolate (PEATM).

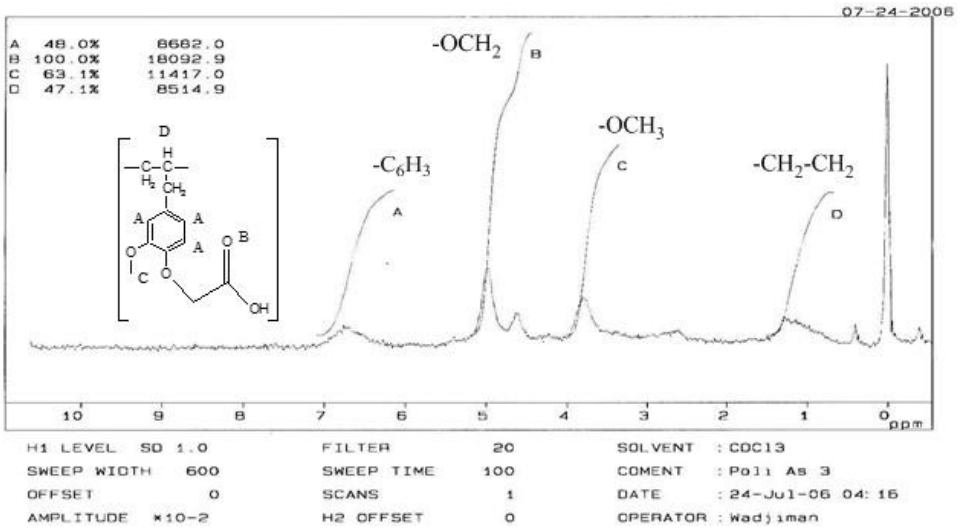

Figure 6. [1]H NMR Spectra of Polyeugenoxy Acetic Acid [14].

4.5. Transport of Metals with Polyeugenoxy Acetyl Thiophene Methanolate (PEATM) as a Carrier with BLM (Bulk Liquid Membrane) Technique

PEATM ability as a carrier in metal separation was observed using the BLM technique. This method used U pipe that contained the feed phase, the organic phase (liquid membrane) and the receiving phase. The feed phase, with a total volume of 13 mL, contained a mixture of heavy metal ions. The metal ions were tested and was found to be Cu (II), Cd (II) and Cr (III) with concentration of 30 ppm each (pH 5.01). Phosphate buffer solution with pH 5.01 was used in this study because all metals were extracted at a pH close to neutral [19]. The Liquid membrane used was PEATM with a variation of 0.7, 0.5 and 0.3 gram in 30 ml of chloroform solvent. The receiving phase was 0.1 M HCl solution with volume of 13 mL (pH 1.07). In this study, the membrane system was chosen along with 0.1 M HCl receiving solution (pH 1.07) as the optimum condition for the separation of Cu^{2+}, Cd^{2+} and Cr^{3+} ions [19]. The receiving solution pH need to be more acidic than the feed solution because the receiving solution should have stronger acidic property to break the complex formed at interface between the receiving phase and the membrane phase. The selection of the feed phase with pH value of 5 and the receiving phase with pH value of 1 in the chloroform solution was also based on previous study conducted by Cleij *et al.* [1] where N, N'-dioctylglycylglycine was used as a liquid membrane using the BLM technique. The solution was continuously stirred at constant speed during the transport process for 24 hours.

BLM process was undertaken three times with varying PEATM mass. In BLM I, PEATM used was 0.7 gram, BLM 2 used 0.5 gram of PEATM and BLM 3 used 0.3 gram of PEATM. In the recovery process of heavy metal ions by BLM technique there were changes of pH value in the feed and receiving phase from its initial state. The exchange mechanism of metal ions and H^+ ions between the two phases were indicated by these pH changes. In Fig. 7, the mechanism of transporting metal ions from the feed phase to the receiving phase through the chloroform membrane [19], can be seen.

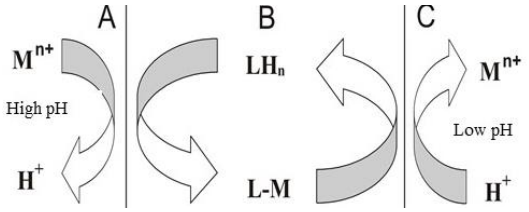

Figure 7. Mechanism of Cation Exchange. A: feed phase, B: organic phase, C: receiving phase, L: carrier, M: metal ion.

After 24 hours of stirring process, the pH at the feed phase decreased and the pH at the receiving phase increased (Table 1). This was because of the exchange of H^+ ions released by the ligand *(carrier)* with the metal ions present in the feed phase, then the metal ion formed a metal-ligand ion complex and was carried to the receiving phase to release the metal ion that later would be exchanged with H^+ in the receiving phase. The process was done repeatedly until there were no interchangeable metal ions. This indicated that there was a process of metal ions transport from the feed phase to the receiving phase.

Table 1. Changes of pH values between the initial and final condition in BLM.

Transport	Feed phase		Receiving phase	
	Initial pH	Final pH	Initial pH	Final pH
BLM 1	5.01	4.84	1.07	3.56
BLM 2	5.01	4.61	1.07	2.15
BLM 3	5.01	4.42	1.07	1.98

Descriptions:
BLM 1: BLM with PEATM mass of 0.7 gram
BLM 2: BLM with PEATM mass of 0.5 gram
BLM 3: BLM with PEATM mass of 0.3 gram

The metal ions concentrations of the feed phase and the receiving phase were determined using AAS to prove the existence of the transport process. The results obtained can be seen in Table 2 below:

Table 2. Percentage (%) Result of Transported Metal Ions from Feed Phase to Receiving Phase by means of BLM technique

Transport	% Transport		
	Cu(II) ion	Cd(II) ion	Cr(III) ion
BLM 1	12.59	56.80	5.14
BLM 2	10.66	47.77	2.48
BLM 3	3.15	41.50	1.68

Descriptions:
BLM 1: BLM with PEATM mass of 0.7 gram
BLM 2: BLM with PEATM mass of 0.5 gram
BLM 3: BLM with PEATM mass of 0.3 gram

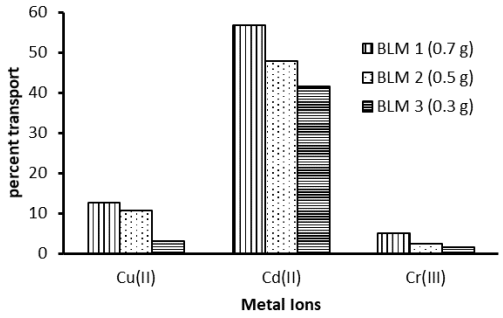

Figure 8. Diagram of Metal Ions Transport in the Receiving Phase.

Based on the results of the transport process obtained (Fig. 8), it can be known that in BLM 1, BLM 2 and BLM 3 the largest amount of metal transported was Cd^{2+} metal ion then followed by Cu^{2+} and Cr^{3+} metal ions. This indicates that the PEATM carrier is more selective towards the Cd^{2+} rather than Cu^{2+} and Cr^{3+} metal ions because the PEATM compound contains the S group. The S group belongs to the soft base group and thus forms a strong complex with the soft acid Cd^{2+} metal ion. This corresponds to the theory of HSAB (Hard Soft Acid Base). Compounds with soft donor atoms such as S atom will be selective towards soft metal ion such as Cd^{2+} [9]. Cd (II) is a soft acid metal ion that can bind to an active S ligand which is a soft donor atom that is stronger than other metal ions. It is not known certainly the bond between PEATM as a carrier compound with Cd^{2+} metal ion. It is estimated that the bond is as shown in Fig. 9.

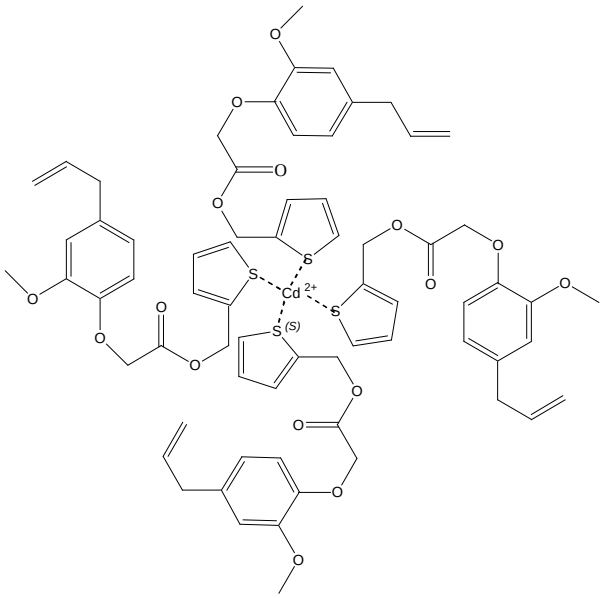

Figure 9. Estimation of ligand- metal ion complex form.

From the estimation of metal ligand complex form, it is deduced that the O atom became dysfunctional because of a steric hindrance that caused the O atom to not form complex with Cr^{3+} and resulted in small transport percentage of Cr^{3+}. The presence of Cu^{2+} metal ions that were transported to the receiving phase was due to the S ligand complex with Cu^{2+} ions which although weak in stability but was still prominent. Consequently, the most transported metal ion was Cd^{2+}, then Cu^{2+} and Cr^{3+}.

In this study we studied the effect of mass of the carrier compound on metal ion transport by comparing metal ion transport results using different PEATM membrane mass which were 0.7 g, 0.5g and 0.3 g. From the data obtained, it is known that BLM 1 that used 0.7 g of PEATM carrier compound gives greater percentage of Cd^{2+} transport compared to BLM 2 that used 0.5 g and BLM 3 that used 0.3 g of PEATM carrier compound. This shows that the bigger the mass of the liquid membrane used, the more metal ions are going to be transported to the receiving phase. This behaviour may be related to the greater chance of metal ions to bind with the carrier compound as its mass is proportionally greater.

5. Conclusion

Based on the research results it can be concluded that: Polyeugenocy Acetyl Thiophene Methanolate (PEATM) *carrier* compound was successfully synthesized from eugenol. PEATM has brownish-black thick colour in the form of liquid with molecular weight about 700 and the weight was 4 g (93.2 %). Separation of heavy metals Cu^{2+}, Cd^{2+}, and Cr^{3+} by BLM technique can be conducted using Polyeugenoxy Acetyl Thiophene Methanolate (PEATM) as a *carrier*. From the transport results it was

found that polyeugenoxy acetyl thiophene methanolate (PEATM) was more selective against Cd^{2+} than Cu^{2+} and Cr^{3+} with percentage of transported ions of 56.80%; 12.59%; 5.14% using PEATM mass of 0.7 g, 47.77%; 10.66%; 2.48%% using PEATM mass of 0.5 g and 41.50%; 3.15%; 1.68%% using PEATM mass of 0.3 g.

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