



## Effect of Different Types of Extractants in the Separation of Rare Earth Metals using Emulsion Liquid Membrane Method: A Review

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### Abstract

Rare earth metals (REMs) are minerals needed in modern technology because they have unique chemical, catalytic, electrical, and paramagnetic properties, so REMs have the potential in various field applications. The similarity in the physical and chemical properties of REMs causes the separation process from their parent minerals hard occurred. Emulsion liquid membrane is an effective and efficient method for REMs purification and separation because in practice it only requires a small amount of solvent, the diffusion rate, and mass transfer are high, fast, and simultaneous compared to the solvent extraction method which requires many extraction steps and requires many the solvents. In the emulsion liquid membrane method, one of the factors that can determine the success of the extraction process is the ligands/extractants selectivity used. The extractants should be highly selective against the target REM ions, both in the external aqueous phase and the internal aqueous phase. Therefore, this review aimed to determine various types of extractants selectivity, such as D2EHPA, Cyanex 302, Cyanex 572, (RO)<sub>2</sub>P(O)OPh-COOH, aniline, and TBP on extraction efficiency and stripping efficiency in the separation of rare earth metals through the emulsion liquid membrane method.

**Keywords:** Rare earth metals, emulsion liquid membrane, extractants

### Introduction

Rare earth metals (REMs), also known as lanthanide elements, are metals abundant in nature, but they are found in relatively small amounts and have limited distribution (Binnemans et al., 2013; Suprpto, 2009).

REM in its pure condition is high value because it has the potential to support modern technology so that in recent years the demand for REM has increased, this is due to its unique properties such as paramagnetic, optical, electrical, and special electronic structures that make REM potential for application in various fields (Pusztai et al., 2013; Larquet et al., 2017) including permanent magnets, metallurgy, autocatalysts, glass additives and ceramic applications (Asnani & Patra, 2013). In addition, it can be widely used in various high-tech products and industries such as aerospace, military systems, and wind turbines (Hoenderdaal et al., 2013; Srinivasan et al., 2017). However, REM has similar physical and chemical properties between one element to another, which causes the separation process from their parent minerals hard occur (Jolly, 1975). Therefore we need an effective and efficient separation method to obtain REM in its pure condition.

Conventional methods that can be used in REM separation are deposition, reverse osmosis, adsorption, ion exchange, and solvent extraction (Liang et al., 2011). Solvent extraction is the method most often used on an industrial scale (Kumbasar, 2008) because it is simple and the results of the separation are good, but this technique is less efficient because it requires many extraction stages, high operating costs, and high solvent consumption so that it is not environmentally friendly and uneconomical (Wang et al., 2017; Ritcey & Ashbrook, 1979). Therefore, the solvent extraction method is expanded into a liquid membrane-based technology using emulsion liquid membrane (ELM), where this method is economical because it only requires a small amount of solvent, simple operation with high-efficiency and selectivity, high diffusion rate and mass transfer, low energy consumption, simultaneous and fast because the extraction and stripping processes occur in one stage (Balasubramanian, 2017; Laki et al., 2015; Hirai & Orikoshi, 2004; Chaouchi & Hamdaoui, 2014). The ELM selectivity depends on the extractant used (Othman et al., 2006). ELM is a three-phase dispersion system, which consists of an external phase, a membrane, and an internal phase in the form of a double emulsion. The solute from

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the external phase is transported to the internal phase through the membrane phase. The membrane phase is an organic phase that contains a carrier (extractant) together with surfactants to stabilize the primary emulsion granules. The primary emulsion is made by dispersing the internal phase in the membrane phase. This emulsion is then dispersed under stirring to an external phase containing the solute to be separated (Kargari, 2013; Choudhury et al., 2010).

The solute in the form of metal ions contained in the external solution forms a complex with the extractant at the membrane-external phase interface. The complex formed is transported through the membrane phase to the internal-membrane phase interface leading to the internal phase. Selectivity for the desired metal is often increased by introducing a carrier/extractant that fits into the membrane.

Extractant selectivity affects the extraction yield. The extractants must be highly selective towards the target metal ions, both in the external and internal aqueous phases (Chakraborty et al., 2010). The extractant works as an activator to transport the desired solute from the feed phase to the internal phase. The carrier concentration has an important role in the transport behavior, membrane stability, selectivity, and extraction efficiency of the ELM process. Therefore, this review article discusses the effect of various types of extractants concentration based on their chemical properties to determine their selectivity to extraction yields in the separation of rare earth metals using the Emulsion Liquid Membrane method.

## Results and Discussion

### Extractants

Extractants known as ligands are electron donors that are selective towards the target metal ion, which is an electron acceptor, to form a complex compound (Sari, 2017). In the emulsion liquid membrane process, the extractants act as a carrier that facilitates the mass transfer of rare-earth ions from the feed solution to the receiving solution through the membrane for the separation process (Kolev, 2005).

Most of the extractants are viscous. Thus a diluent is needed to dissolve the extractant and ensure good contact between the extractant and the water phase. Examples of various types of diluents that are often used include kerosene, n-hexane, benzene, dichloromethane, and chloroform. Each diluent gives a different equilibrium constant value depending on the extraction mechanism (Zhang et al., 2016a).

The synthesis process or the selection of extractants must follow several criteria to obtain a good separation. Most importantly, the extractant must have at least one functional group and a relatively long hydrocarbon chain or ring-substituted element. Functional groups such as P, N, O, or S act as metal complexes with REM, while

carbon chains are used to intensify the extractant's solubility in the solvent used. In addition, a good extractant must have positive selectivity to the desired REM, excellent chemical stability, low density and viscosity, and large surface tension (Zhang et al., 2016a).

The most widely used extractants for the separation of REM are organophosphorus-based extractants. Organophosphorus acid extractants such as 2-ethylhexyl phosphoric acid mono 2-ethylhexyl ester (EHEHPA or also known as PC-88A), di-(2-ethylhexyl) phosphoric acid (D2EHPA), and bis-2,4,4-trimethyl pentyl phosphate acid (Cyanex 272) is widely used commercially for the separation and purification process of REM because of its low water solubility, also has good chemical stability and solvation properties. To obtain high selectivity, an extractant must have a very specific affinity for one component (Swain & Otu, 2011; Yoon et al., 2015; Anitha et al., 2015; Wannachod et al., 2015a; Wannachod et al., 2015b).

### Classification of extractants

Based on their chemical properties, extractants are broadly classified into the following three categories (Perera & Stevens, 2009; Zhang et al., 2016b).

#### Acid extractants

In general, the metal-binding mechanism with acidic extractants follows the cation exchange mechanism. Acid extractants consist of:

- Organophosphoric acid (for examples: Cyanex 272, DTPA, Cyanex 572, Cyanex 302, PC-88A/EHEHPA, D2EHPA/P204, Ionquest 801)
- Carboxylic acid (for example:  $(RO)_2P(O)OPh-COOH$ )

#### Anionic extractant

In anionic extractants, the extraction process depends on the ability of metal ions to form anionic species in the external phase. The metal is extracted as an ion pair by the amine salt. Anionic extractants consist of:

- Quaternary ammonium salt (for example, Aliquat 336 / TOMAC)
- Primary amines (for example, aniline)
- Tertiary amines (for example, TOA, TNOA, Alamine 336)

#### Solvent extractants

The solvent extractant competes with the aqueous phase as the first solvent shell around the metal ion, which facilitates the transfer of the metal ion complex into the membrane phase. The solvent extractant consists of:

- Phosphine oxides (for example: TOPO/ Cyanex 921)
- Phosphorus esters (for example: TBP).

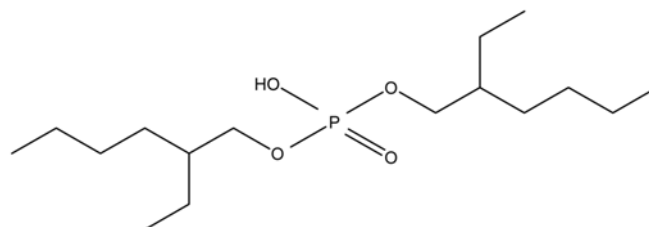
### Extractants types for REM separation in the ELM system

The following are various types of extractants that are commonly used based on their chemical properties for the separation of rare earth metals in the emulsion liquid membrane system: D2EHPA

The most commonly used extractant for REM separation from the organophosphorus group is di-(2-ethylhexyl) phosphoric acid or also known as D2EHPA/P204. This extractant is a colorless or yellowish liquid with non-polar properties.

D2EHPA can reduce the overall number of extraction steps required in REM separation (Ismail et al., 2019).

D2EHPA is also known as a cation-exchange extractant, which is similar to most other organophosphorus acids. This is because the metal replaces the hydrogen ions in the extractant and produces a dissolved organic complex that has a neutral charge. The compound structure of D2EHPA is shown in **Figure 1**.



**Figure 1.** D2EHPA structure (di-(2-ethylhexyl) phosphoric acid /P<sub>2</sub>O<sub>4</sub>: dioctyl phosphate

In his research, Sato (1989) concluded that REM with D2EHPA follows a cation exchange mechanism in low acidity and a solvent mechanism in high acidity. D2EHPA shows higher extraction efficiency for metals with a larger atomic number in the lanthanide series; La < Ce < Pr < Nd < Sm < Eu < Gd < Tb < Dy (~ Y < Ho < Er < Tm < Yb < Lu. This indicates that the extraction efficiency is proportional to the REM atomic number for a particular organophosphorus acid due to the anion extractants attraction effect and an increased electrostatic force that causes the size of the cations to be smaller (Gupta & Krishnamurthy, 2005).

In emulsion liquid membrane systems, the concentration of ligands or extractants plays a major role in the transport behavior and membrane stability, among all other parameters. The extractant concentration used must be optimized to obtain high extraction and stripping efficiency. Too high or too low extractant concentrations can reduce the extraction and stripping efficiency. The extraction efficiency and stripping efficiency in the emulsion liquid membrane method can be calculated through equations (1) and (2) as follows (Davoodi-Nasab et al., 2018b):

$$\%E = \left( \frac{(V_{Fa0} \cdot C_{Fa0}) - (V_{Fa} \cdot C_{Fa})}{(V_{Fa0} \cdot C_{Fa0})} \right) \times 100\% \quad (1)$$

$$\%S = \left( \frac{C_{Fa} \cdot V_{Fa}}{(V_{Fa0} \cdot C_{Fa0}) - (V_{Fa} \cdot C_{Fa})} \right) \times 100\% \quad (2)$$

Where  $V_{fa0}$  is the external phase volume before extraction,  $V_{fa}$  is the external phase volume after extraction,  $C_{fa0}$  is the external phase concentration before extraction,  $C_{fa}$  is the external phase concentration after extraction,  $C_{fa}$  is the final concentration of the internal phase, and  $V_{fa}$  is the final volume of the internal phase.

**Figure 2** shows the effect of D2EHPA extractant concentration on the Gd(III) extraction yield carried out by Davoodi-Nasab et al. (2018b). The extraction efficiency of Gd(III) can be increased by increasing the D2EHPA concentration from 0.005 to 0.05 M. It can be attributed to sufficient free extractant access and an unsaturated interface between the feed phase and the membrane for

extraction (Alpaydin et al., 2011; Othman et al., 2006).

Increasing the D2EHPA concentration further from 0.05 to 0.5 M did not improve the extraction performance and led to a decrease in the extraction efficiency of Gd(III). This is due to a decrease in the rate of the stripping reaction. Gd(III) remains uncomplicated in the membrane phase and causes a reduction in the final yield. In addition, increasing the extractant concentration could further decrease

the emulsion stability. According to Sabry et al. (2007), this occurs due to the nature of the extractant interface and the opposite nature of the extractant and surfactant. In addition, increasing the higher concentration of extractants can also increase the membrane viscosity, which leads to forming larger emulsion clumps, thus slowing the diffusion rate and causing membrane swelling, which can dilute the stripping phase (Kumbasar & Tutkun, 2006).

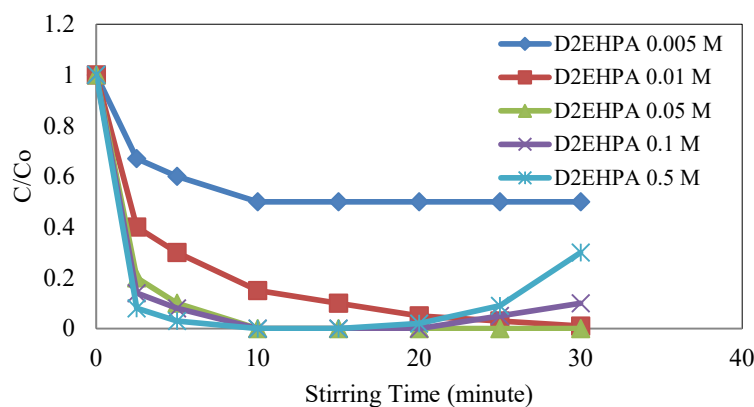


Figure 2. Effect of extractant concentration and stirring time on extraction Gd(III) (adopted from research Davoodi-Nasab et al., 2018a)

Based on an economic point of view, a lower concentration of extractants is more profitable (Chaouchi & Hamdaoui, 2015) because the extractant is the most expensive agent among the other components of the ELM system. Therefore, 0.05 M was determined as the optimal concentration value for D2EHPA as the extractant resulting in higher stability and extraction efficiency of Gd(III). The extraction efficiency and stripping efficiency of Gd(III) were 99 and 79 %, respectively.

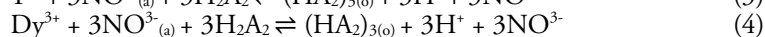
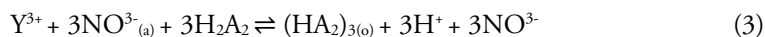
Raji et al. (2017b) also conducted an ELM study by varying the D2EHPA concentration in the range of 0.005 to 0.5 M against the Dy(III) extraction yield. The results show that the extraction efficiency of Dy(III) increases by increasing the D2EHPA concentration from 0.005 to 0.5 M.

It comes from the formation of more Dy-D2EHPA complexes at the outer interface between the feed phase and the membrane phase, resulting in increased diffusion of Dy(III) through the membrane (Raji et al., 2017b). The 0.05 M D2EHPA concentration was chosen as the best extractant concentration based on the experimental results. The maximum extraction efficiency and

stripping efficiency of Dy(III) were 99.6% and 85.22%, respectively.

Based on the research of Basuki & Pamungkas (2019), D2EHPA concentration was important to determine the metal transfer mechanism in the internal phase because, with the increased D2EHPA concentration, the internal phase concentration of the REM will be increase. Therefore, the reaction with D2EHPA and metal will be better. To determine the effect of REM transfer on the organic phase, it can be seen in the binding ability of D2EHPA and REM to be separated. REM is initially in the external aqueous phase in a complex form that is dissolved with water and aqueous solutions such as nitrates. Furthermore, the extraction process is replaced by D2EHPA because the D2EHPA ligand is in contact with H<sub>2</sub>O and forms a neutral complex in the organic phase. This shows that the more REM is extracted, the more neutral complexes are formed with D2EHPA in the membrane phase.

The following is an example of the reaction that occurs in the Y and Dy extraction process in each acidic medium, which can be written as equations (3) and (4) (Setyadji & Purwani, 2018):



The effectiveness of the entire process of the emulsion liquid membrane method can be seen by

looking at the distribution coefficient and separation factors of Y and Dy. The distribution

coefficient is the ratio of the concentration of a compound in an immiscible two-phase mixture at equilibrium. While the separation factor is identical to the ratio of the distribution factor of the organic phase into the aqueous phase.

Based on Basuki & Pamungkas's (2019) study, relatively good results were obtained at concentrations of 4 – 5% D2EHPA. The results showed that stripping efficiency increases due to the increasing number of complex compounds. The extraction efficiency and distribution coefficient for

Y and Dy were respectively 94.08% and 15.97 for Y and 67.85 % and 2.11 for Dy with the value of the Y-Dy separator factor of 7. 57.

#### Cyanex 302

Another type of extractant that is often used in the emulsion liquid membrane process in REM extraction is Cyanex 302. Laguel & Samar (2019) extracted Eu(III) using Cyanex 302 extractant as a carrier. The structure of the compound Cyanex 302 is shown in Figure 3.

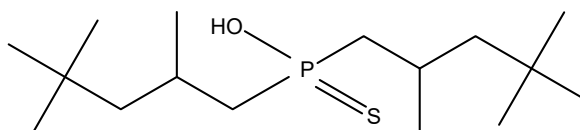


Figure 3. Structure of the compound Cyanex 302: bis-(2,4,4-trimethyl pentyl) monothiophosphate phosphate acid

The transport mechanism of Eu(III) by ELM method using Cyanex 302 as a carrier is shown in Figure 4.

In this case, the reactive compound (Cyanex 302) is in the membrane phase. The ligand is soluble in the membrane phase and insoluble in the external phase and the internal phase. In the outer phase/membrane phase interface, Cyanex 302 is formed selectively and reversibly with the solute Eu(III) forming a complex (Cyanex 302-Eu(III)) in the membrane (Figure 4). In the presence of a concentration gradient, the complex (Cyanex 302-Eu(III)) diffuses through the membrane towards the

internal membrane-phase interface. At this interface, the complex (Cyanex 302-Eu(III)) then reacts with the stripping agent present in the internal phase to form a complex with the transported solute Eu(III), which is more stable than the complex formed by the transporter (Cyanex 302). As a result of this reaction, there is a disconnection of the Cyanex 302-Eu(III) complex. Where the solute Eu(III) is permanently bound to the stripping agent, while the carrier (Cyanex 302) is regenerated and returned through the membrane to the external-membrane phase interface to transport the residual solute.

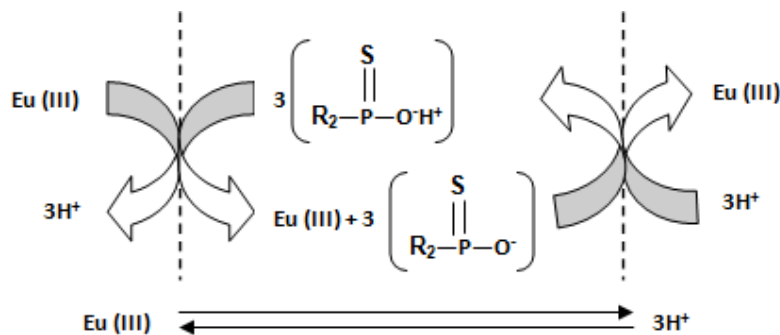


Figure 4. Eu(III) extraction mechanism in an emulsion liquid membrane system (adopted from research Laguel & Samar, 2019)

To study the effect of carrier concentration, Eu(III) ions were extracted using various Cyanex 302 concentrations. The Cyanex 302 concentration was varied from 0.05-0.9% (w/w) with the optimum Cyanex 302 concentration of 0.3% (w/w). The results obtained are shown in Figure 5.

From Figure 5 it has been proven that the carrier concentration has a significant effect on the recovery of Eu(III) from the aqueous phase. Thus, the extraction efficiency of Eu(III) using Cyanex 302 extractant was 92.68%.

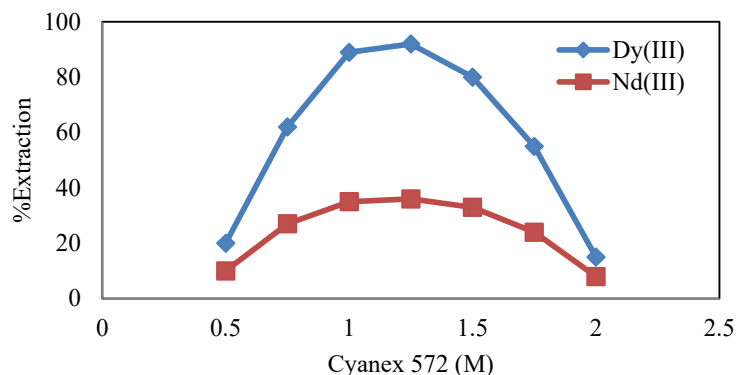


Figure 5. Effect of the carrier concentration on the extraction of Eu(III) in the ELM system (adopted from research Laguel & Samar, 2019)

#### Cyanex 572

Cyanex 572 is a new type of organophosphorus extractant consisting of a mixture of phosphoric and phosphonic acids, it is stable and specially formulated for the separation and purification of individual REM (Wang et al., 2015). Cyanex 572 used can affect the acid concentration in the REM stripping to be lower due to the slightly higher extraction pH. This, of course, leads to significant acid savings over time (Tunsu et al., 2016).

The extraction efficiency of REM can be increased by increasing the concentration of Cyanex 572 to a certain degree (Davoodi-nasab et al., 2018b). This can be explained by the presence of a free carrier at the feed-membrane phase interface and the unsaturated interface between the feed phase and the membrane phase, which results in the formation of more metal-Cyanex 572 complexes (Alpaydin et al., 2011; Othman et al., 2006).

The extraction efficiency and the REM separation factor are highly dependent on the acidity in the external phase solution. Extraction of REM occurs by replacing the extractant hydrogen ions. The difference in hydrogen ion concentration between the feed and stripping phases induces increased REM transport by increasing the pH value of the feed phase (Davoodi-nasab et al., 2018b). This shows that the rate of complexation of the REM ion with Cyanex 572 extractant as a cation exchanger is directly proportional to the acidity of the feed phase.

Raji et al. (2017b) conducted a study to determine the role of Cyanex 572 in the selectivity of Dy and Nd, using various concentrations of Cyanex 572 in the range 0.5 to 2 M with the optimum concentration of Cyanex 572 at 1.25 M. The variation of Cyanex 572 concentration on extraction efficiency shown in Figure 6.

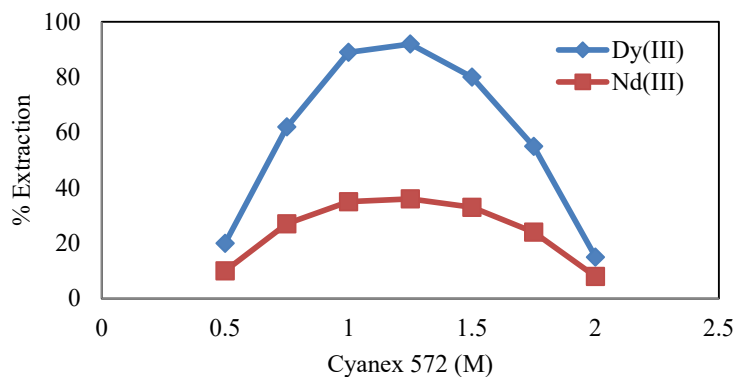


Figure 6. Effect of Cyanex 572 carrier concentration on Dy(III) and Nd(III) extraction (adopted from research Raji et al., 2017a)



In the concentration range of 0.5 - 1.25 M the extraction efficiency of Dy(III) increased from 22.16 to 95.98% and from 10.98 to 38.9% for Nd(III). This stems from the formation of many more extractant and metal complexes at the outer interface.

Furthermore, when the concentration was further increased from 1.25 to 2 M, the extraction efficiency and recovery value were lower. This can be attributed to an increase in membrane viscosity with an increase in extractant concentration leading to a lower diffusion of the metal complex through the membrane phase (Binnal & Hiremath, 2012; Kulkarni & Mahajani, 2002; Seifollahi & Rahbar-Kelishami, 2017). In addition, increasing the Cyanex 572 concentration can also increase membrane swelling, thereby diluting the stripping phase and decreasing the extraction efficiency and yield value of the ELM process (Kulkarni et al., 2000). According to these data, the maximum separation factor achieved when the concentration of Cyanex 572 was equal to 1.25 M. From Raji et al. (2017b) experiment, the extraction efficiency of Dy(III) was 98.99% and resulted in a good

separation with a value of 19.56 for Dy(III) and 2.7 for Nd(III).

In addition, Davoodi-Nasab et al. (2018b) have also performed selective separation of Gd(III) and Nd(III) using Cyanex 572 with optimum concentration at 0.75 M and obtained extraction efficiency of 67.45% for Gd(III) and 28.98% for Nd(III).

#### $(RO)_2P(O)OPh-COOH$

Carboxylic acid group extractants are quite stable in hydrocarbon solvents. However, in low polarity solvents, it tends to associate and result in more complex speciations (García et al., 2013). This type of extractant has practical uses for REM processing because it is relatively inexpensive compared to other common extractants, is easy to obtain, and has been used in commercial processes for various purposes (Vahidi & Zhao, 2017).

Chen et al. (2018), in their study, modified the D2EHPA extractant for obtained a new type of extractant  $(RO)_2P(O)OPh-COOH$ , which can show improved performance in the  $REM^{3+}$  extraction process. The structure of the compound  $(RO)_2P(O)OPh-COOH$  is shown in Figure 7.

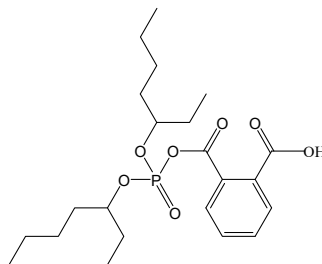


Figure 7. Structure of the compound  $(RO)_2P(O)OPh-COOH$

To produce an effective transport system, one of the factors that are considered important is the type of extractant (carrier) that is suitable. As a

comparison, the migration ability of D2EHPA, and  $(RO)_2P(O)OPhCOOH$  as carriers are shown in Figure 8.

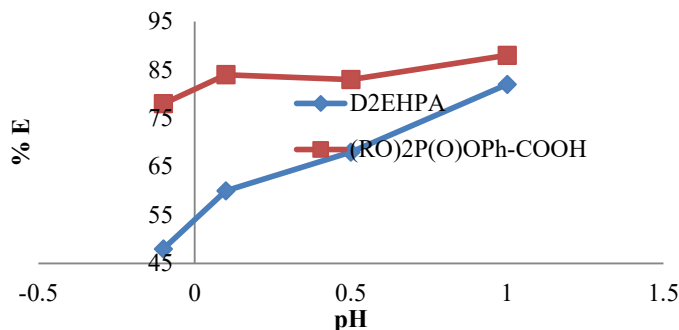


Figure 8. Effect of carrier and pH value on the extraction rate of  $REM^{3+}$  using ELM process (adopted from research Chen et al., 2018)

Figure 8 concluded that increasing the pH from -0.1 to 1.0 led to a significant increase in the

extraction efficiency of  $REM^{3+}$ . This means that the extraction is easier at a higher pH. The extraction

ability of D2EHPA under low acidity is determined by the acidity of the feed solution and is unstable in feed solutions with different acidities (Raji et al., 2017a; Hasan et al., 2009). The acidity  $(RO)_2P(O)OPh-COOH$  is stronger than D2EHPA. As a carrier,  $(RO)_2P(O)OPh-COOH$  is superior to D2EHPA because it can increase the atomic number distribution coefficient caused by the extraction of REM alkyl phosphoric acid with lanthanide elements, and its extraction capacity increases due to its benzene ring conjugation effect. When phthalic acid reacts with D2EHPA, it causes only one carboxyl reaction. The other carboxyl remains connected to the benzene, thereby increasing steric hindrance. Under highly acidic conditions, the electron density of the  $P=O$  bond increases, and this change can increase the extraction performance (Krea & Khalaf, 2000; Singh et al., 2004).

Based on Chen et al. (2018) study, the efficiency of  $REM^{3+}$  extraction using extractant  $(RO)_2P(O)OPh-COOH$  reached 82.68 %. Extractant  $(RO)_2P(O)OPh-COOH$  as a carrier has high selectivity for  $REM^{3+}$ . Even more, under the

optimal operating parameters, the demulsification (stripping) efficiency reaches more than 59%.

#### Aniline

Amine extractants consisting of primary ammonium (Aniline) to quaternary are very efficient in separating radioactive elements and rare earth elements (Zhang et al., 2015). Amine extractants performed well with light REM groups. A suggested route for separation by amine extractants is an anion exchange mechanism (Coleman, 1963).

The complex formation mechanism that can be extracted can only occur when the nitrate ions in the solution are high (Cerna et al., 1992). In addition, ion dehydration from REM ion stripping can also contribute to an increase in the number of complexes that can be extracted. Hydration is higher in the light REM group and may continue to decrease throughout the lanthanide series (Marcus & Abrahamer, 1961). The structure of the aniline compound is included in the primary amine shown in Figure 9.

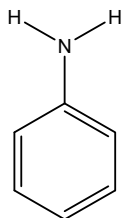


Figure 9. The structure of Aniline compound ( $PhNH_2$ )

In the study conducted by Zhang et al. (2016a) concentration, and the extraction rate of aniline,

D2EHPA, and PC-88A as comparison extractants showed in Figure 10.

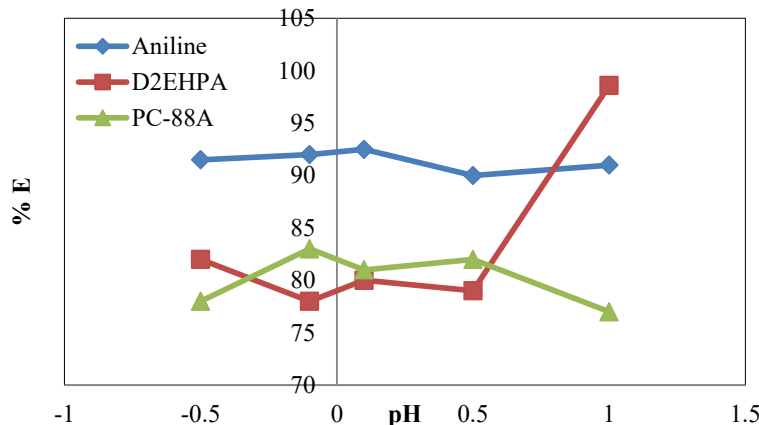


Figure 10. Extraction efficiency of  $REM^{3+}$  in the ELM system using D2EHPA

Figure 10 shows that the extraction efficiency of  $REM^{3+}$  in the ELM system using D2EHPA reaches

98.64 % at pH 1.0. However, the extraction rate decreases drastically at lower pH values. At pH - 0.5,



the extraction rate is 82.23%. While the variation in pH using PC-88A as a carrier has a small effect on ELM properties and the extraction efficiency fluctuates around 80%. Zhang et al. (2016a) chose Aniline as a carrier because the extraction abilities of D2EHPA and PC-88A were less stable than Aniline when the acidity of the REM solution was changed. this can be caused by a different reaction mechanism For D2EHPA and PC-88A with low acidity, H<sup>+</sup> which dissociates from the hydroxyl groups in D2EHPA and PC-88A can be exchanged for REM<sup>3+</sup>. In addition, the P=O bond tends to coordinate with REM<sup>3+</sup>. When the pH is set to a



The variation of aniline concentrations was carried out in the range of 4 – 14%, with the optimum concentration of Aniline, which was 6%, where the extraction efficiency obtained was 93.21%. Increasing the Aniline concentration beyond 6 % will decrease the extraction efficiency. Increasing the extractant (carrier) concentration within a certain range contributes to reducing the viscosity of ELM; however, an excessive concentration of the carrier will reduce the ELM stability (Yan & Pal, 2001; Clause et al., 1999).

#### TBP

TBP (tributyl phosphate) is a type of organophosphorus extractant that is widely used in

lower level (high acidity), there will be less H<sup>+</sup> in the solution to interact with REM<sup>3+</sup>. As for the extraction ability, D2EHPA is better than PC-88A because there are no C-P bonds in the molecular structure of D2EHPA, then it has lower electronegativity, and higher acidity Aniline is a primary amine. Under acidic conditions, the amine extractant will be protonated into ammonium cations then form an anion complex with the ammonium ion. The extraction mechanism using aniline extractant is explained by Equations (5) and (6) (Zhang et al., 2016a):

industry for the separation and purification of REM ions because of its high ability to extract, stable to acids, and easily obtained (Purwani & Biyantoro, 2013).

Tributyl phosphate (TBP) ligand has the chemical formula (C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>PO<sub>4</sub>, is in the form of a liquid, colorless, or faded yellow with a molecular weight of 266.318 g/mol and a specific gravity of 0.9727 g/mL. TBP is a neutral organophosphate compound, contains three butyl groups, and has 1 donor oxygen atom in the P=O group, which can coordinate with metal ions by donating its lone pair to the empty metal ion orbital to be separated (Aryadi, 2011). The structure of TBP is shown in Figure 11.

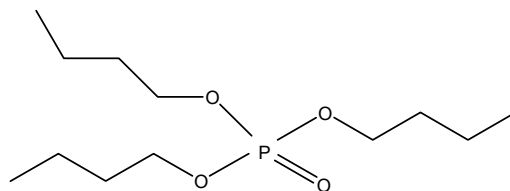
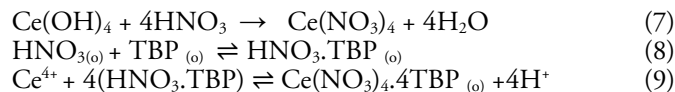


Figure 11. The structure of tributyl phosphate compound

In their research, Purwani & Biyantoro (2013) conducted Th-Ce separation using TBP extractant in the ELM system. The reaction that occurs

between REM in nitric acid and TBP extractant follows the cation exchange reaction as in equations (7), (8), and (9) as follows (Zhou, 2012):



While the reaction that occurs in the stripping phase with phosphoric acid is shown in

equation (10) as follows (Purwani & Biyantoro, 2013):



The concentration of TBP used greatly influenced the extraction of separated metals. In the Purwani & Biyantoro (2013) study, the TBP concentration was varied from 5-30%. Figure 12 shows the correlation between % TBP and the extraction efficiency of Ce and Th.

Figure 12 shows that the greater the % TBP, the better the extraction efficiency. This shows that the reaction between Ce and Th with TBP is getting more complete. However, when using % TBP exceeding 15%, the extraction efficiency does not increase. This can be due to the increased viscosity

of the organic phase, which can inhibit the mass transfer of Ce and Th from the feed phase to the

membrane phase. The correlation between % TBP and stripping efficiency is shown in Figure 13.

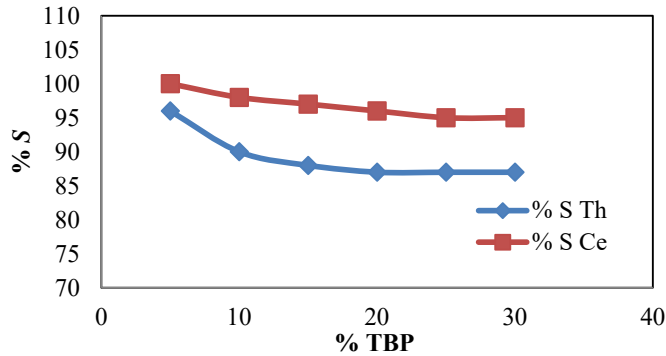


Figure 12. The correlation between % TBP and stripping efficiency of Th and Ce (adopted from research Purwani & Biyantoro, 2013)

Figure 12 shows that as the % TBP increases, the stripping efficiency tends to decrease. This can be since there is still an internal aqueous phase trapped in the membrane phase so that the volume of the internal aqueous phase decreases, which causes the amount of Ce and Th in the internal aqueous phase to be less. In addition, as the % TBP increases, the amount of Ce and Th in the

membrane phase increases. This can lead to a decrease in the stripping efficiency because the less amount of acid from the internal phase can react with Ce and Th, so there are only a few ions Ce and Th were stripped into the internal phase. The correlation between % TBP and the separation factor (SF) of Ce-Th is shown in Figure 14.

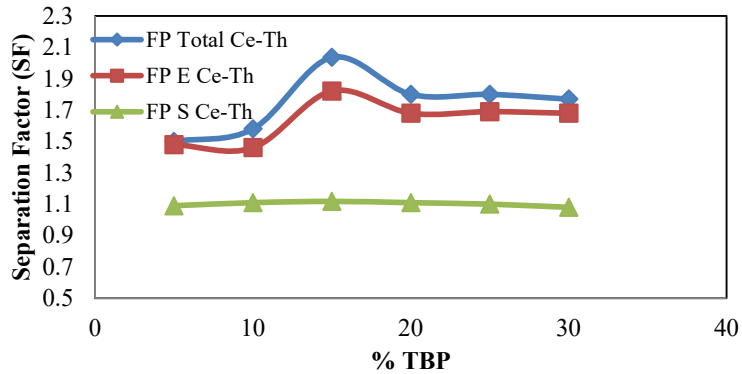


Figure 13. The correlation between % TBP and Ce-Th separation factor (adopted from research Purwani & Biyantoro, 2013)

Figure 13 shows that with 5 -15 % TBP concentration used, separation factor (SF) extraction and SF stripping Ce-Th increased so that the total SF Ce-Th also increased. However, when the TBP concentration exceeds 15 %, SF Ce-Th decreases. So it concluded that 15 % is the optimum concentration for TBP in the separation of Th from Ce. In this separation, %E Ce = 84.54 %, %S Ce = 98.05 % and %E Th = 46.41 %, %S Th = 87.68 %

were obtained. In addition, it was obtained SF of Ce-Th extraction = 1.8216, SF stripping Ce-Th = 1,1177, and total SF Ce-Th = 2.036.

Table 1 shows a summary of the various concentrations and types of extractants on the extraction and stripping efficiency in the separation of REM using the ELM (Emulsion Liquid Membrane) method.

Table 1. Types of extractants and various concentrations on REM separation

Methode	REM	Extractants Types	Extractants Concentration	% E	% S
	Eu(III) (Laguel & Samar, 2019)	Cyanex 302	0.3 % (w/w)	92.68	-
	Y(III) (Basuki & Pamungkas, 2019)	D2EHPA	4.5 % (v/v)	94.08	92.28
	Gd(III) (Davoodi-Nasab et al., 2018a)	D2EHPA	0.05 M	99	79
	Nd(III) Gd(III) (Davoodi-Nasab, et al., 2018b)	Cyanex 572	0.75 M	Gd = 67.45 Nd = 28.98	Gd = 89.04 Nd = 19.45
ELM	REM(III) (Chen, et al., 2018)	(RO) <sub>2</sub> P(O)OPh-COOH	12 % (v/v)	82.68	59
	Dy(III) (Raji, et al., 2017b)	D2EHPA	0.05 M	99.6	85.22
	Dy(III) (Raji, et al., 2017a)	Cyanex 572	1.25 M	98.99	-
	REM(III) (Zhang, et al., 2016)	Aniline	6 % (v/v)	93.21	-
	Th-Ce (Purwani & Biyantoro, 2013)	TBP	15 % (v/v)	Ce = 84.54 Th = 46.41	Ce = 89.05 Th = 87.68

## Conclusions

The separation process of rare earth metals in the emulsion liquid membrane (ELM) system is strongly influenced by the concentration of various types of extractants used because it plays an important role in the transport properties and membrane stability. The optimum extractant concentration ranges from 0.05 – 15 % v/v depending on the conditions of other parameters such as the pH of the feed phase, the time of extraction stirring, and the acidity of the stripping phase. The extractant concentration used must be optimized to obtain high extraction efficiency and stripping efficiency. The extraction efficiency of REM can be increased by increasing the extractant concentration to a certain degree. Too high or too low the extractant concentration can decrease the extraction and stripping efficiency. A good extractant must have a positive selectivity to the desired REM, excellent chemical stability, low density and viscosity, and low solubility in the aqueous phase.

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