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Preparation of Liquid Emulsion Membranes for Separation of Gadolinium(III) from Samarium(III) with Tributyl Phosphate or Di-(2-Ethylhexyl) Phosphoric Acid Extraction Based on Emulsion Stability

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Abstract

Separation and purification of Rare Earth Elements (REEs) from their mixture are is not easy, because of their similar physico-chemical properties. Therefore, efforts to separate and purify them by the Emulsion Liquid Membrane (ELM) because of their simplicity, effectivity and efficiency. In this study, the emulsion was made by mixing Span-80 as a surfactant, the Tributylphosphate (TBP) or Di-2-Ethylhexylphosphate (D2EHPA) as extractants in N-Hexane, and Nitric Acid as the internal phase, followed by extraction with a mixture of Gd(III) and Sm(III) in nitric acid as an external phase. The emulsion was made using an experimental design with a two-level factorial design method to select parameters that had a significant influence on the response of swelling ratios and creaming number in the separation of Gd(III) from Sm(III). The results of the study showed that the parameters selected were: Internal acidic concentration (0.5 M), surfactant concentration (2.9%), ligand concentration (0.1%), emulsification stirring speed (10000 rpm), external acid concentration (5.8 M), type of ligand (1= ligand code D2EHPA), extraction stirring speed (500 rpm) Furthermore, the data obtained from the research results show that the swelling ratio value was 0,0007 and the creaming rate was -0.0082. The two response values approached the 0 (zero) value, meaning that the resulting liquid emulsion was stable and good for its use in the separation of Gd(III) from Sm(III) by the emulsion liquid membrane method.

Keywords: Gadolinium • Emulsion liquid membrane • TBP • D2EHPA • Experimental design • Creaming number • Swelling ratio

Introduction

Rare Earth Metals (REEs) is a lanthanide group consisting of 15 elements plus scandium and yttrium, which are actinides because they have the same physical and chemical properties [1]. REEs is an associated mineral that is commonly found in the earth's crust and has potential in various fields with high economic value, thus determining it in global competition, for example, Gadolinium (Gd) and Samarium (Sm), which is widely used in the health sector as a contrast agent in Magnetic Resonance Imaging (MRI) to wait for cancer, while Sm is widely used as a laser and magnetic making material [2,3]. An abundance of Gd and Sm in monazite sand is very much found, but not in a free and pure state. However, still mixed with REEs and other minerals to obtain pure Gd(III), it is necessary to carry out repeated separation stages. The abundance, potential and huge demand for REEs attracted the researchers to separate Gd(III) to obtain Gd(III) with high purity. The problem that is often experienced is the similarity of the properties of REEs and another which makes REEs very difficult to separate. Hence, it is necessary to choose the right and most efficient method in separating REEs to get high purity.

Several methods for separating REEs from each other, including crystallization, fractionation, ion-exchange chromatography, solvent extraction, and the membrane fluid [4,5]. Liquid-liquid extraction is often used in REEs separation, but this method has several drawbacks, such as large amounts of solvents and difficult separation between phases [6]. Khaldun Ibu [7] also stated that solvent extraction requires many steps for downloading to get optimum separation. As an alternative, separation is carried out using an emulsion liquid membrane [8]. The separation of REEs by the emulsion liquid membrane method is based on the transport of metal ions through the membrane in the form of a liquid containing ligands as a carrier [9]. The transportation of metal ions is the most crucial thing in separation from liquid membranes [10]. The ligands used in this research were Tributylphosphate (TBP) and Di-2-Ethylhexylphosphate Acid (D2EHPA) ligands, commercial ligands as a comparison. TBP and D2EHPA ligands are excellent organophosphorus derivative compounds to form chelate compounds with REE, so they are suitable for the Gd(III) separation process [11]. The D2EHPA ligand has been widely used as a carrier for the transport of REEs ions by the emulsion liquid membrane method [12]. In contrast, there has been no research on the separation of Gd(III) with TBP ligands using the emulsion liquid membrane method, so this study Separated Gd(III) from Sm(III) using an emulsion liquid membrane with TBP and D2EHPA ligands and with experimental designs, through the two-level factorial design method to obtain selected parameters, based on the creaming rate and the swelling ratio response to the emulsion stability [12] have separated Gd(III) with D2EHPA and TBP ligands by liquid-liquid extraction with an extraction efficiency of 93.92% with D2EHPA ligands and 90.06% with TBP ligands. The separation of Gd(III) from Sm(III) with the D2EHPA ligand was also carried out by Anni Anggraeni, et al. [13] using liquid-liquid extraction with an extraction efficiency of 87.1% for Gd(III) and 49% for Sm(III). Meanwhile, separation of REEs by liquid emulsion membrane was carried out by Raji Maliheh, et al. [14], which separated Nd(III) from Dy(III) with the CYANEX 572 ligand with an extraction efficiency of 98.99%. Davoodi-Nasab Payman, et al. [2] also separated Gd(III) from acidic solutions with D2EHPA ligands and surfactant Span-80 with an extraction efficiency of 99%. This research carried out, namely the separation of Gd(III) from Sm(III)

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with D2EHPA or TBP ligands as a comparison with liquid emulsion membranes and a two-level factorial design experimental design with the results of an extraction efficiency of 72.48% for Gd(III) and 88% for Sm(III). Based on the research that has been done, the liquid emulsion membrane method can be used in the separation of rare earth metals. The success of separating Gd(III) from Sm(III) by liquid emulsion membrane is not only determined based on the extraction and stripping efficiency but is determined based on the emulsion stability, which is seen based on the creaming rate response and the swelling ratio. The creaming rate, which is the joining of the internal phase into large granules, breaks through to the external phase and tends to create a solid layer on top of the sample. The swelling ratio is swelling of the emulsion because the external phase combines and is attracted to the internal phase to form larger granules. A good emulsion has a creaming rate and a swelling ratio equal to zero [15]. Emulsion stability is a problem in the emulsion liquid membrane which can make the emulsion easily damaged, so a suitable composition is needed to make a stable emulsion. so that there is no swelling, leakage and emulsion breakdown, so that the separation of Gd(III) from Sm(III) occurs properly [16-18]. This research was conducted to determine the parameters that significantly affect the stability of the emulsion used for the separation of Gd(III) from Sm(III). The parameters are tested as the surfactant concentration, the ligand concentration, the internal water phase concentration, the external water phase concentration, emulsion stirring speed, extraction stirring speed, extraction time, and the type of ligand.

Materials and Methods

Chemicals materials

The materials used in this research were samarium oxide, gadolinium oxide (all REES was purchased from SIGMA-ALDRICH 99.9%), distilled water, N-Hexane, Span-80 (Sorbitan Monooleate), D2EHPA (Di-2-Ethylhexyl Phosphoric Acid), TBP (TributylPhosphate) (all SIGMA-ALDRICH 99.9% product ingredients) and Nitric Acid. The tools used in the preparation of separation Gd(III) from Sm(III) with the emulsion liquid membrane method are glass tools, digital analytical balance, magnetic heaters and stirrers, ultraturrax, ICP- AES Agilent, design expert 10 to selected parameters.

Experimental Procedures

Experimental design parameter selection of REES with emulsion liquid membranes: The design for parameter selection used the two-level factorial method where the parameters used in the separation of Gd(III) from Sm(III) were eight parameters, as shown in Table 1.

Preparation of emulsion: Span-80 concentration variance of 2.5 or 4.5% (v/v) and 0.1 or 0.3% (v/v) D2EHPA or TBP ligands piped with micropipettes (according to the experimental design table) then dissolved with N-Hexane up to 25 mL in a measuring cup. Transfer it to a beaker and stir with an ultraturrax stirrer with a speed variation of 6000 or 10000 rpm (according to the experimental design) for 5 minutes. Furthermore, 25 mL of the nitric acid solution is added as the internal acid phase slowly with various concentrations of 0.5 or 2.5 M (according to the experimental design), while continuing to stir for 50 minutes until a milky white emulsion is formed.

Extraction of samarium (III) and gadolinium (III): Gd(III) and Sm(III) 1000 mg/L solutions were diluted to 25 mg/L and 75 mg/L respectively in 50 mL of nitric acid solution with various concentrations of 3 or 6 M (according to experimental design), then stirred with a magnetic stirrer with a variation of the speed of 200 or 500 rpm for a variation of the stirring time of 10 or 30 minutes (according to the experimental design). The solution (Gd(III)-Sm(III))-(emulsion) was moved to a separate area and waited for two phases to form, namely the external water phase at the bottom and the membrane phase at the top. After two phases have been formed, the external water phase is separated from the membrane phase and the volume is measured. The membrane phase is awaited again until complete Demulsification occurs until two phases are formed, namely the internal water phase at the bottom and the membrane phase at the top. The internal water phase is separated again by the membrane phase and the volume is measured.

Analysis by ICP-AES: Solution analysis was carried out after the Demulsification process. The solutions measured were the external water phase and the internal water phase, then the Gd(III) and Sm(III) concentrations were measured using ICP-AES, respectively.

Results and Discussion

Emulsion stability

According to Davoodi-Nasab Payman, et al. [19] emulsion liquid membranes are very useful in separating metals. Still, they are limited by the emulsion's stability, including leakage and swelling of the emulsion, so that the emulsion's stability is a crucial factor in the separation and purification of metal ions by emulsion liquid membrane. The emulsion is said to be a highlighter that does not break easily over a certain period of time. The longer the emulsion breaks, the more stable the emulsion will be. Emulsion swelling can be measured as a swelling ratio, and emulsion leakage is called creaming, which can be counted as a creaming number, where the value should be = 0, meaning that there is no change in the volume of the internal or external (constant) phase, which means that the emulsion does not swell or leak. Emulsion stability is affected by the diameter of the emulsion granules. The ideal emulsion grain diameter makes the emulsion more stable. The emulsion granule's diameter is too small, making the viscosity of the emulsion increase so that the emulsion is too stable and difficult at the demulsification stage [20]. The emulsion grain diameter is too large, resulting in low emulsion stability, so the emulsion is easily separated. According to Wang Jun, et al. [21], the ideal w/o/w emulsion granule diameter is around 20 nm - 2000 μm. The diameter of the emulsion beads obtained in this study varied around 3.2-19 μm, measured using a microscope connected to a camera and calibrated with a 20x, as shown in Figure 1.

Selection of emulsion making parameters by two factorial level

The composition and stages of making the emulsion on the emulsion liquid membrane significantly affect the emulsion's stability. The 8 parameters mentioned in Table 1 were selected using a first-order experimental design, namely a two-level factorial design with the response to be achieved, the swelling ratio, and creaming rate equal to 0 as shown in Table 2. Table 2 illustrates a two-level factorial design for the separation Gd(III) from

Table 1. Parameters for the two factorial level experimental designs.

Separation Factor	Code	Level	
		Low (-)	High (+)
Surfactant Concentration (%)	A	2.5	4.5
Ligands Concentration (%)	B	0.1	0.3
Extraction Stirring Speed(rpm)	C	200	500
Internal Water Phase Acid Concentration (M)	D	0.5	2.5
External Water Phase Acid Concentration (M)	E	3	6
Emulsion Stirring Speed (rpm)	F	6000	10000
Extraction Time (min)	G.	10	30
Types of ligands	H	TBP	D2EHPA

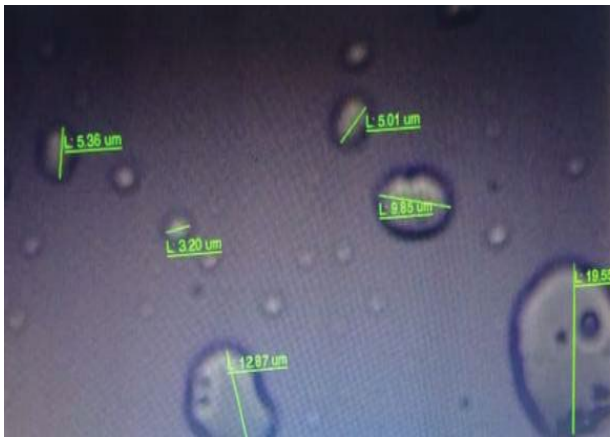

Figure 1. Size of the emulsion granule diameter using a microscope.

Table 2. Selection of emulsion membrane manufacturing parameters using two level factorial designs.

Parameters								Response	
C. Internal phase(M)	C. Surfactant (%)	C. Ligand (%)	V. Stirring speed emulsion (rpm)	C. External phase (M)	v. Stirring speed extraction (rpm)	t. Extraction (min)	Type of Ligand	Creaming rate	Swelling ratio
2,5	4,5	0,3	6000	6	200	10	-1	-0,39	-0,02
2,5	2,5	0,3	6000	3	500	10	1	0	-0,26
0,5	4,5	0,3	10000	3	500	10	-1	-0,04	-0,36
2,5	4,5	0,1	10000	3	200	10	1	0,16	0,04
0,5	2,5	0,3	10000	6	200	10	1	0	0,02
0,5	2,5	0,1	10000	3	500	30	1	-0,04	-0,43
2,5	4,5	0,1	6000	3	500	30	-1	0,02	0,04
0,5	4,5	0,1	10000	6	200	30	-1	0	-0,04
0,5	4,5	0,1	6000	6	500	10	1	0	-0,16
2,5	2,5	0,1	10000	6	500	10	-1	-0,04	-0,2
0,5	2,5	0,3	6000	6	500	30	-1	-0,04	-0,24
2,5	2,5	0,1	6000	6	200	30	1	0,18	0,2
0,5	4,5	0,3	6000	3	200	30	1	-0,01	-0,28
2,5	4,5	0,3	10000	6	500	30	1	-0,04	-0,16
2,5	2,5	0,3	10000	3	200	30	-1	0,38	-0,6
0,5	2,5	0,1	6000	3	200	10	-1	0,27	-0,6

Sm(III) in an emulsion liquid membrane, containing all parameters, such as internal acid phase concentration, external acid phase concentration, surfactant concentration, ligands concentration, the speed of stirring of the emulsion, the speed of the extraction stirring, the length of the extraction time and the type of ligand that will be selected with a variety of levels and also the response swelling ratio and creaming rate. Each parameter selected by design, each of which has minimum and maximum limits that are adjusted to previous studies, which still vary.

Selection results of emulsion liquid membrane extraction parameters

Based on the experimental results and data processing using ANOVA, the parameters that significantly affect the swelling ratio and the creaming rate response approaching 0 will be selected. The parameters selected included the internal phase acid concentration (0.5 M), surfactant concentration (2.9%), ligand concentration (0.1%), external phase acid concentration (5.8 M), type of ligand (1 = ligand code D2EHPA), extraction stirring speed (500 rpm) and emulsion stirring speed (10,000 rpm). The parameter that was not selected as the length of the extraction time was because these parameters did not significantly affect the swelling ratio or creaming rate response as shown in Figures 1 and 2. Parameter selection with a two-level factorial design, based on ANOVA-based data processing, selects the optimum conditions for each parameter both individually and the interaction between the chosen parameters by evaluating the p-value of less than 0.05 (<5%), as shown in Tables 3 and 4.

Table 3 data processing with ANOVA based on the swelling ratio response. Parameters that affect the response are surfactant concentration, ligand concentration, external phase acid concentration, and extraction stirring speed. Meanwhile, the interactions between parameters that affect the response are the interaction between the internal acid phase concentration and the surfactant concentration, the internal acid phase concentration and the stirring emulsion rate, the internal acid phase concentration and the external acid phase concentration, the internal acid phase concentration and the extraction time and the concentration of the internal acid phase with the type of ligand. This is acceptable because the p-value of the model is 0.0043 so that the model can be accepted. Based on the results of data processing using ANOVA, an equation regarding the effect of parameters on the swelling ratio response is obtained as follows:

$$y = 0.025652 + 0.008125\ X_1 - 0.063125\ X_2 - 0.043125\ X_3 + 0.021875\ X_4 - 0.066875\ X_5 - 0.048125\ X_6 + 0.030625\ X_7 + 0,005625\ X_8 - 0.033125\ X_1X_2 - 0.003125\ X_1X_3 + 0.059375\ X_1X_4 - 0.039375\ X_1X_5 - 0.000625\ X_1X_6 + 0.070625\ X_1X_7 + 0.035625\ X_1X_8$$

Table 4 is data processing using ANOVA based on the creaming rate response. Parameters that have an individual effect on the response are the internal acid phase concentration, the surfactant concentration, the ligand concentration, the external phase concentration, and the type of ligand. Meanwhile, the interactions between parameters that affect the response are

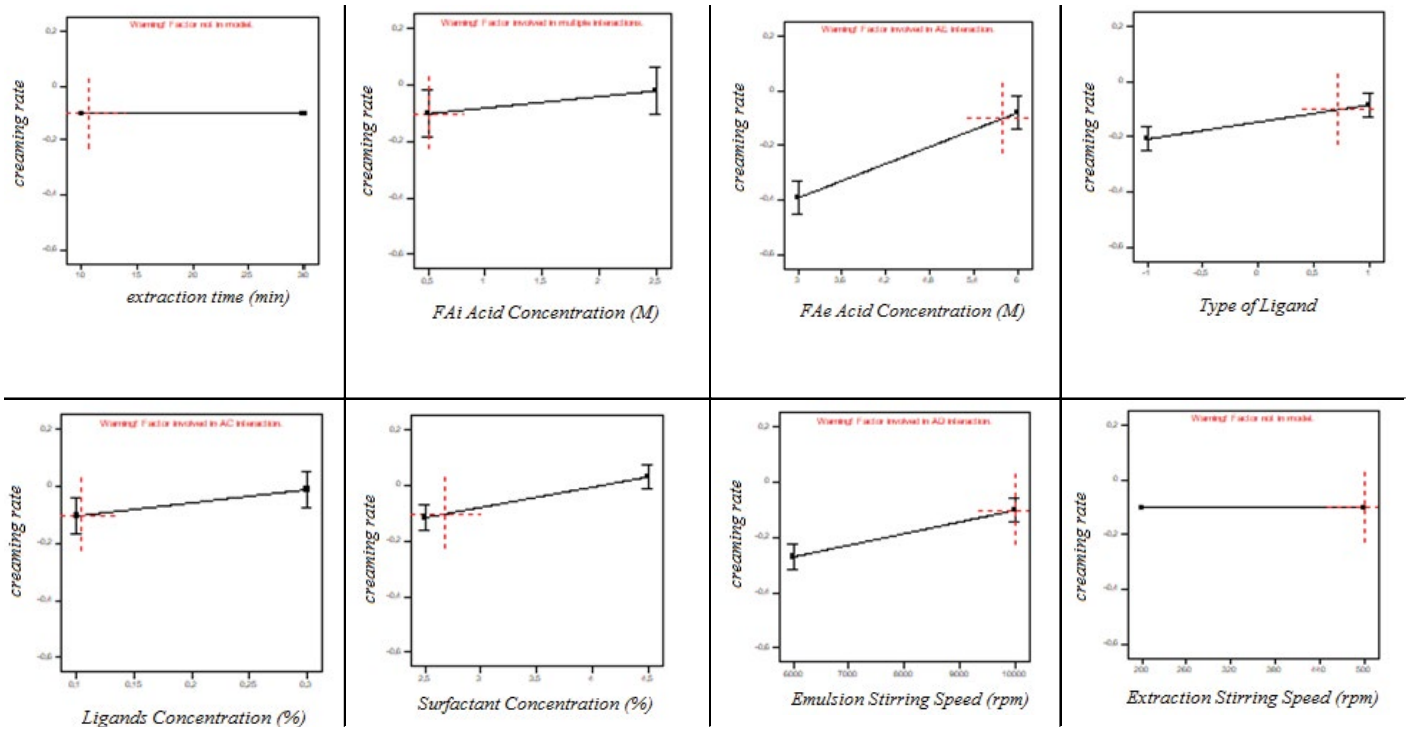

Figure 2. Graph of parameters relationship to creaming rate response.

Table 3. Analysis two level factorial design of parameter selection with swelling ratio response based on ANOVA.

Source	Sum of Total Squares	Degrees of Freedom	Average Square	F-Value	p-Value Prob>F	Information
Model	0,40	9	0,045	10,96	0,0043	**Significant**
B	0,064	1	0,064	15,69	0,0074	
C	0,030	1	0,030	7,32	0,0353	
E	0,072	1	0,072	17,60	0,0057	
F	0,037	1	0,037	9,12	0,0234	
AB	0,018	1	0,018	4,32	0,0829	
AD	0,056	1	0,056	13,88	0,0098	
AE	0,025	1	0,025	6,10	0,0484	
AG	0,080	1	0,080	19,63	0,0044	
AH	0,020	1	0,020	5,00	0,0668	
Residual	0,024	6	4,065E-003			

Information: A = Internal phase concentration; B = Surfactant concentration; C = Ligands concentration; D = Emulsion stirring speed; E = External phase concentration; F = Extraction stirring speed; G = Extraction time; H = Type of ligand

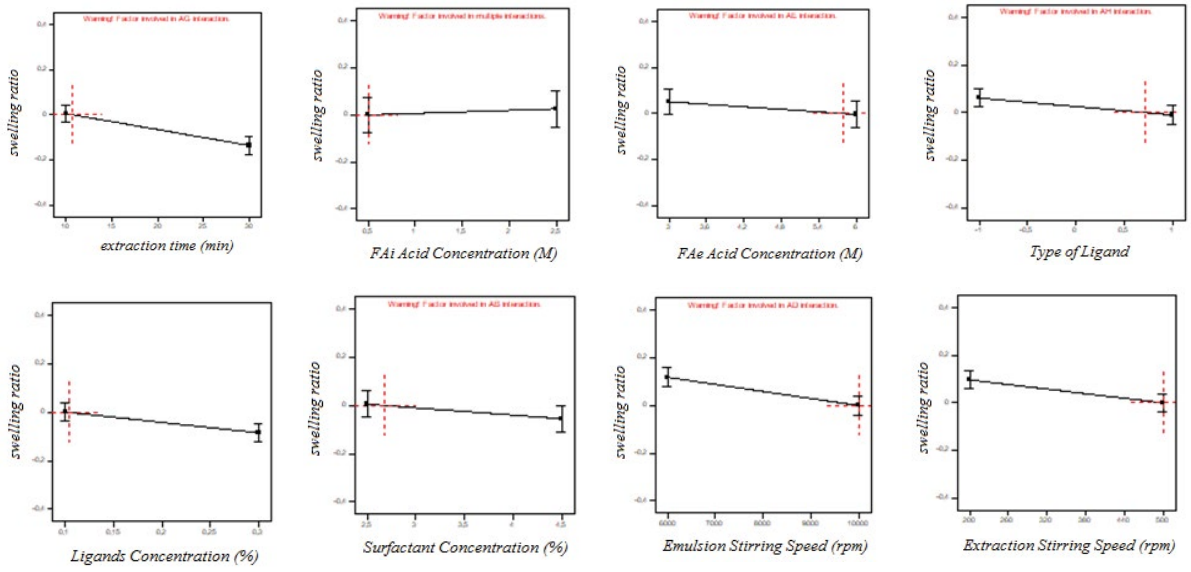

Figure 3. Graph of parameters relationship to swelling ratio response.

Table 4. Table of prediction parameter selection with creaming rate response based on ANOVA.

Source	Sum of The Total Squares	Degrees of Freedom	Average Square	F-Value	P-Value Prob>F	Information
Model	0,75	8	0,094	17,05	0,0006	**Significant**
A	0,080	1	0,080	14,42	0,0067	
B	0,086	1	0,086	15,46	0,0057	
C	0,035	1	0,035	6,35	0,0398	
E	0,21	1	0,21	38,65	0,0004	
H	0,061	1	0,061	11,07	0,0126	
AC	0,14	1	0,14	25,07	0,0016	
AD	0,11	1	0,11	20,58	0,0027	
AE	0,026	1	0,026	4,77	0,0652	
Residual	0,039	7	5,535E-003			

Information: A = Internal phase concentration; B = surfactant concentration; C = ligands concentration; D = emlusion stirring speed; E = External phase concentration; F = Extraction stirring speed; G = extraction time; H = Type of ligand

the internal phase concentration with the ligand concentration, the internal phase concentration with the stirring emulsion rate, and the internal phase concentration with the external phase concentration. This is acceptable because the p-value of the model is 0.0006 so that the model can be accepted. Based on the results of data processing using ANOVA, an equation regarding the effect of parameters on the response of the creaming rate is obtained as follows:

$$y = -0.190625 + 0.070625 X_1 + 0.073125 X_2 - 0.046875 X_3 - 0.025625 X_4 + 0.115625 X_5 - 0.030625 X_6 + 0.001875 X_7 + 0.061875 X_8 + 0.021875 X_1X_2 - 0.093125 X_1X_3 - 0.084375 X_1X_4 - 0.040625 X_1X_5 + 0.005625 X_1X_6 - 0.011875 X_1X_7 + 0.013125 X_1X_8$$

Based on a significant model predicted by design, the selected parameters have a significant effect on the response, namely:

Internal phase concentration parameters

The internal phase is made in acidic pH conditions using HNO_3, where hydrogen ions from HNO_3 in the internal phase will break the complex bonds between Gd(III) and ligands D2EHPA or TBP so that Gd(III) is free and dissolves in the internal phase because REEs is easily dissolved in acidic. There is a difference in acidic conditions between the internal and external phases, meaning that there is a difference in the hydrogen ion's chemical potential between the internal and external phases, which causes an increase in the driving force in the Gd(III) extraction. The concentration of HNO_3 in the internal phase used in this study was 0.5 or 2.5 M. Based on the data obtained from the experimental results, the HNO_3 concentration which affects the swelling ratio response and the creaming rate is close to 0, which is 0.5 M as shown in Figure 3. The internal phase concentration that is too high will cause the membrane phase which encloses the internal phase grains to become thinner, causing the emulsion to break more easily. Increasing pH or HNO_3 concentration causes the emulsion to swell so that the internal phase is diluted, resulting in a reduced Gd(III) stripping process. The graph of the relationship between the internal phase concentration parameters and the response to the creaming rate and the swelling ratio is shown in Figures 1 and 2.

External phase concentration parameters

The external phase is made under acidic pH conditions using HNO_3. The concentration of HNO_3 in the external phase used in this study is 3.0 or 6.0 M. Based on the data obtained from the experimental design, the HNO_3 concentration, which affects the swelling ratio and the creaming rate response is close to 0, which is 5.8 M as shown in Figure 3. The graph of the relationship between the externalphase concentration parameters and the creaming rate and the swelling ratio response is shown in Figures 1 and 2. The concentration of the external phase must be more acidic than the internal phase, it is intended that the Gd(III) diffusion process occurs from the external phase to the internal phase due to the concentration gradient. If the internal phase concentration is greater there will be swelling of the emulsion because the external phase breaks into the internal phase due to the influence of osmotic pressure [22].

Type of ligands parameters

Based on the design results, the D2EHPA ligand (code +1) was selected over the TBP ligand (code-1) because it significantly affected the response, as shown in (Figure 3). This shows that D2EHPA ligands form more complexes with Gd(III) than Sm(III) because the stability constant of Gd-D2EHPA complexes is greater than Sm-D2EHPA. The graph of the relationship between the type of ligand parameters to the creaming rate and ratio swelling is shown in Figures 1 and 2.

Ligand concentration parameters

The high concentration of ligands used will increase the performance of Gd(III) extraction from the external phase; however, if the ligand concentration is too high, the emulsion viscosity increases and reduces the complex diffusion process in the membrane phase [2]. The ligands concentration level in the emulsion preparation in this research was 0.1 or 0.3% (v/v). Based on the data obtained from the experimental results, the concentration of the ligands that affect the extraction performance of the emulsion liquid membrane and the ratio swelling and rate creaming response, which is close to 0, is 0.1%, as shown in Figure 1. Ligands must be used at optimum conditions so that the efficiency of the separation of Gd(III) from Sm(III) can occur properly, if the ligand concentration is too low or below the optimum value, causing the ligands to be insufficient to complex all the Gd(III) in the solution external phase. The graph of the relationship between the ligand concentration and the creaming rate and the swelling ratio response is shown in Figure 2.

Surfactant concentration parameters

Surfactants are organic compounds consisting of lipophilic (tail) and hydrophilic (head) groups so that the surfactants can dissolve in organic solvents and water. Surfactants will reduce the surface tension by absorbing the liquid-liquid (oil-water) interface. The decrease in the interfacial tension in both phases causes the emulgator to form a layer around the water phase so that water droplets are dispersed in the oil phase. The choice of surfactant is vital to determine the extraction process's success, reducing swelling and emulsion leakage in the emulsion liquid membrane. The selection of surfactant is based on the HLB value, where surfactants with a low HLB value of 1-10 are more soluble in oil than water and tend to make water/oil/water emulsions as this experimental. Meanwhile, surfactants with a high HLB value of 10-20 are more soluble in water so they can form emulsion oil/water/oil [23]. The surfactant used was Span-80 (sorbitan monooleate) because it had an HLB value of 4.3 [24]. The interface tension will decrease with increasing the surfactant concentration to a certain concentration level in the membrane phase, which can support the formation of more refined emulsion grains so that the emulsion is more stable, but increasing the surfactant concentration

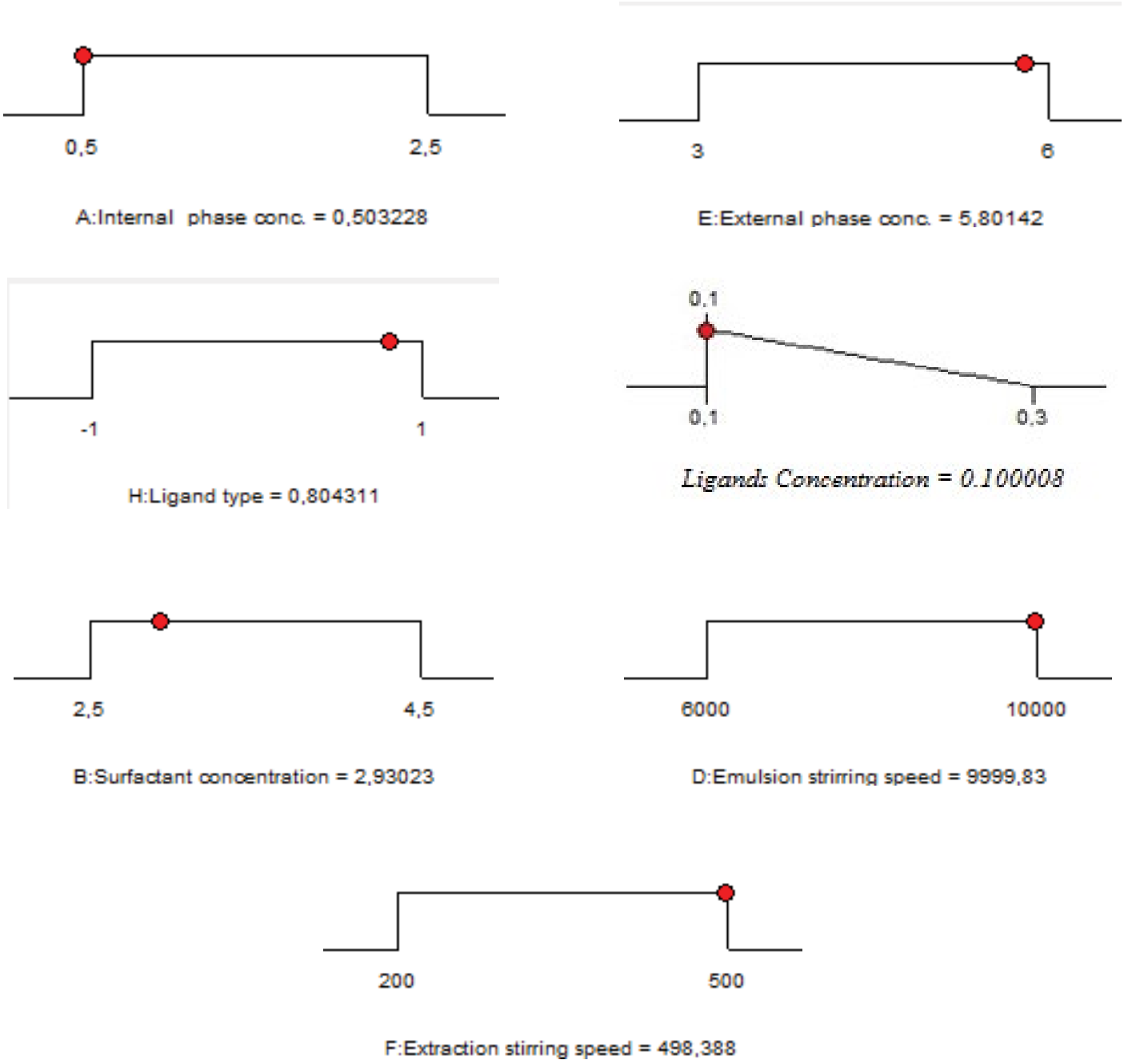

Figure 4. The results of each parameter are based on the prediction design.

further, cannot significantly reduce the interface tension. Too much surfactant in the membrane will increase the emulsion's viscosity, so it can slow down the diffusion of the complex in the membrane phase and cause swelling of the emulsion. Ideally, the emulsion is desired to be stable with the smallest possible thickness. The concentration level of the Span-80 surfactant used in the selection was between 2.5 or 4.5% (v/v). Based on the results of parameter selection, the span-80 concentration of 2.9% has a significant effect on the response, this is as shown in Figure 3 and is supported by a graph of the parameter related to the response in Figures 1 and 2.

Extraction time parameters

In this research, the extraction time used in the emulsion liquid membrane's extraction process was between 10 or 30 minutes. Based on the results of parameter selection, the extraction stirring time does not significantly affect the creaming rate response and swelling ratio as shown in Figures 1 and 3, so in this study, the extraction time of 10 minutes is quite optimal in separating Gd(III) from Sm. (III). The longer the stirring time can affect the emulsion's stability by increasing the water transport to the internal phase, which can lead to higher emulsion swelling. Therefore, the longer the contact time during the extraction, the more emulsion breakdown will be.

Emulsion stirring speed parameters

The speed at which the emulsion is prepared (emulsification) is critical in the emulsion's stability. In this study, the emulsion-making stirring speed used was between 6000 or 10000 rpm. Based on the results of parameter selection, the recommended stirring speed of the design is 10000 rpm because it has a significant effect on the swelling ratio and creaming rate response as shown in Figure 3 and the graph of the relationship between emulsion stirring speed to the creaming rate and swelling ratio response is shown in Figures 1 and 2. The low emulsification speed makes the emulsion lump size increase and the interface are available for mass transfer decreases. According to the higher the emulsification speed, the smaller the emulsion breakdown, which means the emulsion is more stable [25]. This occurs because the higher the emulsification speed, the smaller granules of the emulsion membrane phase and the internal phase formed, it takes a long time to form coalescence. Coalescence is the union of small grains into large grains and finally forming large lumps that

separate. If the stirring speed is too high, it can cause swelling and clots larger due to an increase in the rate of water transport in the internal phase direction. An excessive speed of emulsion stirring results in coalescence and breaks the emulsion granules to become unstable.

Extraction stirring speed parameters

The extraction stirring speed is important in the mass transfer rate of Gd(III) through the emulsion membrane and the emulsion's stability. In this study, the extraction stirring speed used was between 200 or 500 rpm. Based on parameter selection results, the extraction stirring speed has a significant effect on the creaming rate and swelling ratio response, at a speed of 500 rpm, as shown in Figure 3. The low extraction speed will cause the emulsion clot's size to increase, while the increase in the stirring speed's intensity will increase the interface area of the two phases so that the mass transfer rate of Gd(III) will increase and the emulsion less stable. The graph of the relationship between the extraction stirring speed and the creaming rate and the swelling ratio responseis shown in Figures 2 and 3.

Response swelling ratio and creaming rate

The extraction method's parameter selection using emulsion liquid membrane aims to obtain parameters that significantly affect the swelling ratio and creaming rate response is equal to 0, which means that there is no change in the volume of the membrane phase and the internal phase before and after extraction. Based on data processing from the two-level factorial design, the selected model's responses are a swelling ratio of 0.0007 and a creaming rate of -0.0825. This indicates that the emulsion made based on the design model is relatively stable because the resulting response is close to 0, meaning that the emulsion membrane leakage is insignificant, so it is suitable for use in separating Gd(III)-Sm(III) mixtures with the emulsion liquid membrane method. There is still no guideline for the maximum and minimum value limits on creaming rates and swelling ratios in determining emulsion stability. The determination of this range is still needed new research to specifically discuss the limitations of the creaming rate and the swelling ratio to emulsion stability 1. Selected parameters that have a significant effect on emulsion stability so that it is suitable for the separation of Gd(III) from Sm(III) are the concentration of the internal acid phase (0.5M), the concentration of surfactant (3%), the concentration of ligands as a carrier molecule (0.1%), the concentration of the external acid phase (5.8M), extraction stirring speed (500 rpm), emulsion stirring speed (10000 rpm), and type of ligands as carrier molecules (D2EPHA), as described at (Figure 4). The two-level factorial design produces two responses, namely the actual response value, and the predicted response value, where both have a correspondence that can be seen from the linear regression curve so that the selected design model must be known for its linearity, because by looking at the linearity, it can determine the relationship the suitability between the data predicted by the model and the actual data,with a correlation coefficient (r) = 0.9427 for the swelling ratio and (r) = 0.9512 for the creaming number [26].

Conclusions

- Selected parameters that have a significant effect on emulsion stability so that it is suitable for the separation of Gd(III) from Sm(III) are the concentration of the internal acid phase, the concentration of surfactant, the concentration of ligands as a carrier molecule, the concentration of the external acid phase, extraction stirring speed, emulsion stirring speed, and type of ligands as carrier molecules.
- The emulsion prepared in this study is stable because the response is close to zero, there are the swelling ratio is 0.0007 and the creaming rate is -0.0825. Thus, it is suitable for separating Gd(III) from Sm(III) by the liquid emulsion membrane method. This is also shown by the results of the extraction efficiency, which is 72.48% for Gd(III) and 38.36% for Sm(III).
- D2EHPA ligand as a carrier molecule has the same effect as TBP on the emulsion stability based on the design results.
- The liquid emulsion membrane method can be used in REES separation because it is more effective and efficient because the solvent can be reused, and the extraction and stripping process occurs in one stage compared to liquid-liquid extraction. However, the liquid emulsion membrane method is still limited in the stability of the emulsion.

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