Experimental and Theoretical Study on Sm/Eu-Gd Extraction by P204 and [A336][P204]

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Abstract. Extraction of rare earth using ionic liquid as extractant become an alternative practice to replace the common volatile organic solvents in recent years. In general, the work to extract rare earth element, require a large number of extraction stage, and different extractant used resulted in different number of extraction needed. Therefore an analysis on the theoretical number of stages is necessary prior to laboratory work. This study was designed to compare between the number of extraction stages required by 2-ethylhexyl phosphoric acid mono 2-the ester (P204), a common rare earth extractant with a bifunctional ionic liquid, and [A336][P204] in a counter-current extraction process for the separation of Sm in Sm-Eu-Gd mixed solution. The value of the separation factor ($\beta$) of both extractants, was obtained from the experimental work, while other process parameters were calculated using the counter-current theory developed by Xu Guangxian. Extraction of Sm using [A336][P204] was optimum in 3.0 M of nitric acid, with organic to aqueous (O/A) ratio of 4:1, while the optimum condition for P204 was when the medium was 2.0 M of hydrochloric acid and 7:3 of O/A ratio. The $\beta$ value for the optimized condition for P204 was lower compared to the condition for [A336][P204] at $\beta$:1.93 and $\beta$:2.81, respectively. To derive an optimum extraction condition to calculate the number of extraction stage, target purity and recovery ratio were set to 99.9% and 90%, respectively, for both extractants. As a result, [A336][P204] was able to reduce the number of extraction stage by 5 compared to P204. The result indicated that [A336][P204] is preferable over P204 from the viewpoint of economic efficiency.

1. Introduction
Rare earths (REs) are attracting attention as a high-tech material for industries in the 21st century. With rapid developments in hybrid vehicles, petrochemical catalysts, permanent magnets, optical glass, and wind power, the demand for REs has increased as the basic material for these green technology industry [1]. REs usually exist in mineral form and it is difficult to separate them into individual components due to their chemical similarity. So far, one of the methods that are able to separate RE components with high purity is solvent extraction (SX). This technique exploits the partition of a solute between two immiscible liquid phases for metal exchange and transport purposes. SX also enables continuous operation, with low processing cost, to be conducted. The type of extractant is another contributing factor in the extraction process. Some examples of common extractants that exhibit remarkable selectivity in RE extraction are 2-ethylhexyl phosphoric acid mono-2-ethylhexyl ester
(P507), di(2-ethylhexyl)phosphoric acid (P204), and bis (2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272) [2], [3]. P204 (Figure 1) is categorised as a cation-exchange extractant, which is similar to most of other organophosphorus acids. The metal/RE replaces the hydrogen ion in the extractant and produces a soluble organic complex that has a neutral charge. In excess, the combination of RE and extractant complexes produce an 8-membered pseudo-chelate by holding one of the hydrogens in the dimer, and releasing the other, while replacing it with a metal cation. In 1957, Peppard et al. studied the properties and application of P204 as an extractant in separating REs [4]. They explored the ability of P204 to form a dimer with RE$^{3+}$ ions, as shown in Equation 1. They concluded that P204 was a feasible extractant, with a high distribution ratio, apart from having the ability to lower the overall number of extraction stages needed in RE separation.

\[
\text{RE}^{3+}(\text{aq}) + 3(\text{HL})_2(\text{org}) = \text{RE}((\text{HL})_2)_3(\text{org}) + 3\text{H}^{+}(\text{aq})
\] (1)

Based on Equation 1, (HL)$_2$ refers to the dimeric species, (aq) is the aqueous phase, and (org) is the organic phase.

In recent years, a new group of sophisticated extractants based on ionic liquid was developed, such as tricaprylmethylammoniumdihexyldiglycolamate, [A336][DHDGA], and [triocetylmethylammonium][2,4,4-trimethylpentyl phosphinate] [A336/Cy272] [5],[6]. These extractants portrayed great extraction capabilities for RE extraction. Our previous paper revealed the prominent synergistic effect of [A336][P204] towards La(III), Sm(III), and Y(III) compared to the common P204 extractant due to the existence of the dual-functional group [7]. This effect could significantly enhance the extraction ability while providing a greener separation route with the elimination of the saponification process.

To recover a high purity RE from a solvent extraction technology, a multi-stage contact for the organic and aqueous phases using a mixer settler is often used. In addition, to avoid coagulation, the aqueous liquid phase and the organic phase are injected in the opposite direction, known as the countercurrent process. The extraction process starts when the RE in the acidic medium (aqueous phase) is mixed with the extractant (organic phase) in a container until the mixture reaches an equilibrium point. The mixture is then divided back into aqueous and organic phases in the settling stage, in which some of the RE from the aqueous phase is now entrapped in the organic phase, producing a metal-extractant complex. The process of mixing, settling, and dividing the organic and aqueous phases is repeated several times (1 to n times) until a satisfactory purity and recovery value of RE extraction is achieved (Figure 2). Each cycle is counted as one extraction stage.
Since the extraction process of RE is a problematic work with huge number of stages and different extractants involved, adoption of a procedure to surmise the number of extraction stages based on the extractant chosen is an excellent decision. The number of extraction stages obtained from the calculation could help determine feasibility of the process without wasting copious resources. Usually, the normal-concentration plot is used for calculating the number of extraction stages. However, this one-step singular analysis is lacking inaccuracy. Guangxian Xu providing a theoretical basis for the design and application of the liquid-liquid extraction for RE, including the algebraic calculation for extraction ratio, purity, and the number of extraction stages [9]. This theory is widely applied in China and has boosted the RE extraction industry until the country practically became the sole supplier of high purity REs in the world.

This paper examines the effect of different extractants on the number of extraction stages. An optimization study of P204 and [A336][P204] in various parameters, such as type and concentration of acid, as well as organic to the aqueous ratio of the solution, was explored. In this study, the theory proposed by Xu Guangxian was used in calculating the theoretical stages required to separate Sm from an Sm-Eu-Gd solution. The least number of extraction stages is preferred as it reflects the cost and the efficiency of the overall extraction process.

2. Theoretical background

Figure 3 shows the simplified design procedure to calculate the number of extraction stage based on the counter-current theory developed by Guangxian Xu in 1978. Each stage of the design procedure is discussed in the following sections. This theory was established based on five assumptions;

1. The extractability sequence of the RE is represented by A, B, and C, in which A is the element or group with the highest extractability.
2. Since counter-current extraction is comprised of a multistage extraction process, the average separation factor is used due to the different distribution ratios in different stages.
3. The extraction factor is kept constant.
4. RE composition in the aqueous feed and in the aqueous phase is assumed the same.
5. All extraction stages have a constant flow ratio.

![Diagram of a counter-current extraction](image)

**Figure 2.** Schematic diagram of a counter-current extraction

**Figure 3.** Simplified design procedure to calculate the number of extraction stage
2.1. Determination of Extraction System and Separation Factor
It is important to experimentally optimize an SX system by determining its parameters, such as the type and concentration of acid, the organic to aqueous ratio (O/A), and feed concentration. Once a suitable extraction system is determined, the distribution factor, $D$ and separation factor, $\beta$ are measured, as shown by Equation 2 and Equation 3. $D$ can be calculated when the RE distribution between the organic and aqueous phases has achieved an equilibrium state,

$$D_A = \frac{[A_{\text{org}}]}{[A_{\text{aq}}]}$$  \hspace{1cm} (2)$$

From the $D$, the separation factor, $\beta$ can be measured. $\beta$ is defined as the ratio of distribution between two adjacent rare earth metals (A and B) in the separation system,

$$\beta_{AB} = \frac{D_A}{D_B}$$  \hspace{1cm} (3)$$

2.2. Separation Target Specification
To calculate the number of extraction stages in one particular SX system, the mole fraction of metal A in the feed ($f_A$), the target purity of product A in the organic outlet ($P_{A(O)}$), and the target percentage of the product recovery of A ($Y_A$) must be determine beforehand. Based on the assumptions mentioned in Section 2, the REs are categorized based on their extractability in the SX system; A is the element/group of REs that are easily extracted, while B is the relatively difficult element/group to be extracted from the system. The $f_A$ and $f_B$ can be calculated using the following Equation 4:

$$f_A = \frac{\text{Total mole of A}}{\text{Total mole of B}}, \quad f_A + f_B = 1$$  \hspace{1cm} (4)$$

If A is the major product, then, the concentrating factor of A, $a$ can be calculated using Equation 5:

$$a = \frac{P_{A+n+m(o)}}{(1-P_{A+n+m(o)})} \frac{f_A/f_B}{f_B}$$  \hspace{1cm} (5)$$

And the concentrating factor for B can be calculated using Equation 6:

$$b = \frac{a-Y_A}{a(1-Y_A)}$$  \hspace{1cm} (6)$$

However, if the major product is B, then, the concentrating factor of B can be calculated using Equation 7:

$$b = \frac{P_{B_{1+}(o)}}{(1-P_{B_{1+(o)}})} \frac{f_B/f_A}{f_A}$$  \hspace{1cm} (7)$$

And the concentrating factor for A for the major product, B is calculated using Equation 8:

$$a = \frac{b-Y_B}{b(1-Y_B)}$$  \hspace{1cm} (8)$$

The solute fraction in the organic and aqueous outlets can be calculated using Equation 9, as follows

$$f'_A = \frac{f_A Y_A}{P_{A+n+m(o)}}, \quad f'_B = \frac{f_B Y_B}{P_{B_{1+(o)}}}, \quad f'_A + f'_B = 1$$  \hspace{1cm} (9)$$
2.3. Determination of Optimum Process Parameters
Next, the average extraction factors, $E_M$ and $E'_M$, were measured from the optimum conditions based on either the SX system is the extraction or scrubbing controlled, as shown in Table 1.

| Table 1. Determining the extraction factor from the optimum conditions |
|---------------------------------------------------------------|
| If $f'_B > \frac{\sqrt{\beta}}{\sqrt{\beta}+1}$, the SX system is extraction controlled |
| $E_M = \frac{1}{\sqrt{\beta}}$ (10) |
| $E'_M = \frac{E_M f'_A}{E_M f'_A}$ (11) |
| If $f'_B < \frac{\sqrt{\beta}}{\sqrt{\beta}+1}$, the SX system is scrubbing controlled |
| $E'_M = \sqrt{\beta}$ (12) |
| $E'_M = \frac{E_M f'_A}{E_M f'_A}$ (13) |

2.4. Determination of the Number of Stages
If B is the major component in the feed and targeted as a high purity product at the aqueous outlet, the number of extraction stage, $n$ can be calculated using the following Equation 14:

$$n = \log_b \frac{1}{\log\beta E_M}$$ (14)

However, if the targeted end product is a high purity A, and A is the major component in the aqueous feed, then, Equation 15 can be used:

$$n = \log_b \frac{1}{\log\beta E_M + 2.303 \log \frac{P_{A(a)}^{*} - P_{A(a)}}{P_{A(a)}^{*} - P_{A(a)}}}$$ (15)

3. Experimental Method
3.1. Chemicals and Reagents
Aliquat 336, (<99% purity, [A336]Cl) and di-(2-ethylhexyl) phosphate (P204) were purchased from Sigma Aldrich (USA). Nitric acid (HNO$_3$), sulphuric acid (H$_2$SO$_4$), hydrochloric acid (HCl), sodium hydroxide (NaOH), sodium chloride (NaCl), and sodium nitrate (NaNO$_3$) were purchased from Fischer Scientific. A stock solution consisting of Sm(III), Eu(III), and Gd(III) was prepared by dissolving their oxides (99.9%) in concentrated acid. All other chemicals used were of analytical grade.

3.2. Extraction Procedure
The [A336][P204] was prepared using the acid-base neutralization method, as described by Sun et al. [10]. The extractant was dissolved in n-heptane for extraction. 5 mL of the aqueous phase containing RE(III) and 5 mL of the organic phase containing the extractant were mixed and shaken for 1 h at 200 rpm using a mechanical shaker, which was sufficient for equilibrium. The pH of the aqueous mixture was maintained at pH 1–2 using sodium salt (either NaCl or NaNO$_3$). The mixtures were then centrifuged for 5 min at 8,000 rpm to enhance the separation between the aqueous and organic layers. The optimization work is done by varying the type of the acid medium (HNO$_3$ and HCl) at different concentration (1.5 M, 2 M, 3 M, 4 M and 5 M) and different ratio of acid to the organic solution (1:1, 3:2, 7:3, 4:1 and 9:1). The separation factor for each extraction process.
3.3. Calculating the Extraction Stages
Based on the value of the separation factor, the number of extraction stages was calculated in Microsoft Office Professional Plus Excel 2013 as described in the counter-current theory. For this study, the recovery was set to 90%, whereas the purity was fixed at 99.99%.

4. Results and discussion

4.1. System Optimisation and Determining the Separation Factor
Separation of Sm from Sm-Eu-Gd mixed solution was performed to determine the optimum condition based on the value of the separation factor. The results are shown in Figure 4 and Figure 5. Figure 4 shows the effect of HNO₃ and HCl on the extraction of Sm in both extractants, and expressed as log D versus concentration. The log D for [A336][P204] produced a higher value compared to the value for P204 in the same acidic condition. HNO₃ has better separation capabilities for the [A336][P204], but not for the P204. The order of the log D values are as follows; [A336][P204] in HNO₃ > [A336][P204] in HCl > P204 in HCl > P204 in HNO₃. A similar outcome was reported by Guo et al. showing a high separation of RE(III) in the nitrate medium compared to the chloride medium for light and heavy REs when [A336][P204] was used as the extractant [11].

![Figure 4. Effect of acid concentration on the separation of Sm from Sm-Eu-Gd mixed solution](image)

Sun et al. proposed that the main extraction mechanism for [A336][P204] in HNO₃ medium is neutral dissociation [12]. In their paper, the distribution ratio of Eu(III) in HNO₃ was 11 times higher than in HCl (DHNO$_3$ = 21.7, DHCl = 1.97). In this study, the highest distribution ratio for HNO₃ compared to HCl was only 2.9 times higher when using the same extractant. The changes in the extraction capabilities in a different medium were due to the property of the anion in the system (NO$_3^-$, Cl$^-$, and SO$_4^{2-}$), which regulate the stability and selectivity of the extractant in the system [11]. Although it can be confirmed that HNO₃ is the best medium for extraction, the detailed understanding of this mechanism is far from complete.

Figure 5 explores the effect of different O/A phase ratios on Sm separation. Since [A336][P204] produced the highest separation value in HNO₃, and in HCl for P204, as shown in the previous figures, the effect of O/A phase ratio was studied in their preferred medium. The extraction using [A336][P204] had constantly resulted in higher distribution ratios, regardless of the O/A phase ratio in comparison to P204. This observation indicates the ability of [A336][P204] to become a prominent extractant to
separate Sm from Eu-Gd mixed solution. Based on Figure 4 and Figure 5, the best condition for Sm separation using [A336][P204] ($\beta$: 2.81) would be in HNO$_3$, with O/A ratio of 4:1. Meanwhile, HCl and O/A ratio of 7:3 would be the best condition for Sm separation using P204 ($\beta$: 1.93).

**Figure 5.** Effect of O/A phase ratio on the separation of Sm from Eu and Gd mixed solution

### 4.1. Extraction Stages of P204 and [A33][P204]

To compare the efficiency for metal separation, two extractants were selected, namely, a common extractant, P204, and a synthesized bifunctional ionic liquid, [A336][P204]. The optimum condition for both extractants was explored and the value of $\beta$ was determined. Based on the experimental data, the number of theoretical extraction stages was calculated, as listed in Table 2. To separate Sm with 99.99% purity and 90% recovery, [A336][P204] required four full, continuous countercurrent extraction stages, while P204 required nine stages. Both processes were extraction controlled.

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Figure 6. Counter-current process of Sm/Eu-Gd separation by a)P204 b)[A336][P204]

Table 2. Simplified theoretical output for Sm separation from Sm-Eu-Gd mixed solution using P204 and [A336][P204] as the extractants

| STEP 1 | System condition | Extractant | P204 | [A336][P204] |
|--------|------------------|------------|------|--------------|
|        | System condition |            |      |              |
|        | Extractant       | P204       | [A336][P204] |
|        | Medium           | 2.0 M HCl  | 3.0 M HNO₃ |
|        | O/A phase ratio  | 7:3        | 4:1  |
| Group A| Sm              | Sm         |      |
| Group B| Eu and Gd       | Eu and Gd  |      |
|        | Separation Factor| β<sub>Sm/total</sub> | 1.93 | 2.81 |
|        |                  | f<sub>A</sub> | 0.30 | 0.31 |
|        |                  | f<sub>'A</sub> | 0.27 | 0.28 |
|        |                  | f<sub>B</sub> | 0.51 | 0.69 |
|        |                  | f<sub>'B</sub> | 0.73 | 0.72 |

| STEP 2 | Target purity of the product | P<sub>A</sub> | 0.9999 | 0.9999 |
|        | Percentage of the product recovery | Y<sub>A</sub> | 0.9 | 0.90 |
|        | Concentrating factor | a | 23,307.7 | 22,269.5 |
|        |                  | b | 9,999 | 9,9996 |

| STEP 3 | Average extraction factor | E<sub>'</sub> | 0.72 (extraction controlled) | 0.6 (extraction controlled) |

| STEP 4 | Number of extraction stage | n | ≈ 9 stages | ≈ 4 stages |
5. Conclusion

P204 and \([A336][P204]\) were used to separate Sm from Sm-Eu-Gd mixed solution. The optimum \(\beta\) was determined based on experimental work and applied to the Counter-current Theory. Under the optimized condition of 2.0 M of HCl and 7:3 of O/A, the \(\beta\) for the Sm separation using P204 was 1.93. For \([A336][P204]\), the \(\beta\) was 2.81, under the optimized condition of 3.0 M of HNO\(_3\) and 4:1 of O/A. \([A336][P204]\) showed better separation efficiency based on the value of the \(\beta\). The total number of theoretical extraction stages was calculated based on the \(\beta\) obtained in the experimental part. P204 required nine stages to extract Sm with 99.99% purity and 90% recovery, while \([A336][P204]\) required only four stages. In conclusion, the \([A336][P204]\) has provided better separation capabilities.

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