

การสกัดแยกแอร์เทียทกลุ่มหนักโดยการสกัดของเหลวด้วยของเหลว

Separation of Heavy Rare Earths by Liquid- Liquid Extraction

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บทคัดย่อ

การสกัดแยกแอร์เทียทกลุ่มหนัก (Gd, Dy, Y และ Yb) โดยกระบวนการสกัดของเหลวด้วยของเหลวได้ถูกตรวจสอบที่ 37 ± 1 องศาเซลเซียส ได้ศึกษาภาวะสมดุลของแอร์เทียทกลุ่มหนักที่ความเข้มข้นแอร์เทียทในเตรทต่าง ๆ กัน โดยมีสารสกัดคือ สารผสมไอโซโมลาร์ (isomolar) ของไตรบิวทิลฟอสเฟต (TBP) และกรดไดทูเอทิลเฮกซิลฟอสฟอริก (D2EHPA) ในน้ำมันก๊าด เปรียบเทียบกับ TBP ความเข้มข้น 50% ในน้ำมันก๊าด สัมประสิทธิ์การกระจาย (K_d) ของแอร์เทียทกลุ่มหนักโน้มเอียงที่จะลดลงเมื่อความเข้มข้นของแอร์เทียทในสารละลายป้อนเพิ่มขึ้น (K_{dY} และ (K_{dYb}) มีค่าประมาณ 20 เมื่อสารสกัดคือ D2EHPA ในน้ำมันก๊าด ความเข้มข้น 1 โมลาร์ แפקเตอร์การแยกของ Y ($\alpha_{Yb/Y}$, $\alpha_{Y/Dy}$ และ $\alpha_{Y/Gd}$) เพิ่มขึ้นเมื่อความเข้มข้นของ D2EHPA ในสารผสมไอโซโมลาร์ (TBP-D2EHPA) เพิ่มขึ้นในน้ำมันก๊าด เมื่อใช้สารสกัดคือ TBP ความเข้มข้น 50% ในน้ำมันก๊าด $\alpha_{Dy/Gd}$ มีค่าประมาณ 1.1-1.2 ที่ความเข้มข้นสารละลายป้อนสูง จึงเป็นไปได้ที่จะแยก Y ด้วยสารผสมไอโซโมลาร์ (TBP-D2EHPA) ในน้ำมันก๊าด และแยก Gd ด้วย TBP ความเข้มข้น 50% ในน้ำมันก๊าด

ABSTRACT

Solvent extraction of heavy rare earths (Gd, Dy, Y, and Yb) has been investigated at $37 \pm 1^\circ\text{C}$. The equilibrium of heavy rare earths at various rare earth nitrate concentrations with isomolar mixtures of tributylphosphate (TBP) and di-(2-ethylhexyl) phosphoric acid (D2EHPA) in kerosene as the extractant was examined and compared with 50% TBP in kerosene. The distribution coefficients (K_d) of heavy rare earths tend to decrease with the increasing of their concentrations in feed solution. (K_{dY}) and (K_{dYb}) are high, approximately 20, when 1 M D2EHPA / kerosene is applied as the solvent. The separation factors of Y ($\alpha_{Yb/Y}$, $\alpha_{Y/Dy}$, and $\alpha_{Y/Gd}$) increase with the increasing concentration of D2EHPA in isomolar (TBP-D2EHPA) / kerosene. When the solvent is 50% TBP / kerosene, $\alpha_{Dy/Gd}$ are around 1.1-1.2 at high feed concentration. It is possible to separate Y with isomolar (TBP-D2EHPA) / kerosene and separate Gd with 50% TBP / kerosene.

Key Words : Heavy rare earths, TBP, D2EHPA, liquid-liquid extraction

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Introduction

Monazite and xenotime are the by-product ores from the tin mining in the southern part of Thailand. Only monazite is processed in Rare Earth Research and Development Center (RRDC), Office of Atoms for Peace, Pathumthanee Province, to produce uranium, thorium, and rare earths. Uranium and thorium are reserved for nuclear fuel research and development. The light rare earths (atomic numbers 57 to 71) are separated from mixed rare earth nitrate solution by solvent extraction process. The remaining light and heavy rare earths (Gd to Lu, together with Y) are fed to ion-exchange process for separation and purification but it takes much time for separation and the throughput is low. (RRDC; Gupta, C.K. and N.Krishnamurthy, 1992)

Solvent extraction is less time consuming. It is available for high concentration feed solution and it is economical for handling large quantities of materials. Tributylphosphate (TBP) and di-(2-ethylhexyl)phosphoric acid (D2EHPA) are generally applied as the extractant for a long time. Commercially, TBP is used in Rhone-Poulenc, Thorium Ltd(UK), and Indian Rare Earths to separate individual rare earths from nitrate solution. D2EHPA extracts better from a chloride than from a nitrate medium. (Gupta, C.K. and N. Krishnamurthy, 1992; Kraikaew, J. et al. 1994)

In nitrate system, D2EHPA extracts well only heavy rare earths while TBP extracts satisfactorily both light and heavy rare earths (Kraikaew, J. and W. Srinuttrakul, 2004). The application of isomolar mixtures of TBP and D2EHPA in kerosene for separation of individual rare earths from nitrate system has been studied. The synergistic effect was found in Eu(III) and some other rare earth elements from 0.1 M HNO₃ + 3 M LiNO₃ (Jedináková, V. et al., 1992). The distribution coefficient (K_d) of Yb and Y remarkably increased (Kraikaew, J. et al., 2004). The maximum separation factor between Yb and Y ($\alpha_{Yb/Y}$) was found to be 4.7 when the solvent applied was (0.2 M TBP – 0.8 M D2EHPA) / kerosene and the aqueous was rare earth nitrate solution.

It was the purpose of this study to examine the equilibrium of heavy rare earths at various nitrate concentrations using isomolar mixtures of TBP and D2EHPA in kerosene as the extractant compared with 50%TBP in kerosene, which is used in rare earth separation processes at the RRDC. The distribution coefficients and the separation factors of heavy rare earths were calculated. The optimum condition, which was possible to separate and purify heavy rare earths, was determined.

Materials and Methods

1. Preparation of heavy rare earth nitrate solution

Five kilograms of mixed heavy rare earth hydroxide cake (0.615 % Gd, 0.149 % Dy, 0.677 % Y, and 0.004 % Yb), supported from the RRDC, were dissolved in nitric acid solution, heated on a hot plate, and mixed via magnetic stirrer. The solution obtained was filtered to remove impurities and undissolved precipitates.

2. Procedure

Free acidity of heavy rare earth nitrate stock solution was determined to be 0.6619 N by pH measurement method (Jiyavorrnanant, T. and S. Laoharojanaphand, 2001). The stock solution was diluted with de-ionized water to achieve 5 portions of feed concentration including stock solution concentration. The acidity of four diluted feed concentration was adjusted to 0.6619 N by 1 N HNO₃. The extractants, 50%TBP / kerosene and 1 M isomolar (TBP-D2EHPA) / kerosene, were prepared and the total of 7 solvents were obtained.

Equal volumes (20 ml) of the aqueous and organic phases were measured precisely by pipettes and were added together into a separatory funnel. Each concentration of the aqueous phase was equilibrated with 7 solvents of the organic phase. The equilibration was performed by mixing both phases in the separatory funnel using laboratory shaking machine at 200 rpm for 10 minutes at room temperature of 37±1 °C. Both phases were allowed 10 minutes to separate after mixing. After phase separation, the feed and raffinate were collected to analyze (duplicate) for heavy rare earths by ICP-AES (Inductively coupled plasma atomic emission spectrometry).

Concentration of heavy rare earths in the organic phase was calculated from the following equation.

$$[C]_{org} = [C]_F - [C]_{aq}$$

where, C = concentration

subscript "i" : individual rare earths (i = a, b, c,.....)

"org" : organic phase; "aq" : aqueous phase; "F" : feed

The distribution coefficient (K_d) and the separation factor ($\alpha_{a,b}$) were calculated from (Roger, W.C., et al, 1991):

$$K_d = [C]_{org}/[C]_{aq}$$

$$\alpha_{a/b} = (K_d)_a/(K_d)_b$$

3. Analysis

The pH measurement was applied to determine free acidity of heavy rare earth nitrate feed solution. The pH of (NH₄)₂SO₄ solution containing nitric acid with known pH, volume, and normality, was measured. The rare earth nitrate solution was added to this (NH₄)₂SO₄ solution and then pH of this solution was measured again. The free acidity of the sample was analyzed from the difference of pH measurement. (Jiyavorrnanant, T. and S. Laoharojanaphand, 2001)

All samples were analyzed in duplicate for heavy rare earth concentration by ICP-AES. The samples were diluted with 1%HNO₃ to lower their concentrations. The concentrations of rare earths in the samples were calculated automatically compared with the calibration curves of the standards. The results of each condition were calculated from the average values of two ICP-AES analyses.

Results and Discussion

Concentrations of heavy rare earth feed solutions are arranged in Table 1. The distribution coefficients, calculated from the equilibrium data, in various solvents, as a function of their concentrations in feed solutions, are illustrated in Figures 1-4. When the concentrations of heavy rare earths (Gd, Dy, Y, and Yb) in feed increase, their distribution coefficients (K_d) decrease. However, (K_d)_{Gd} increases with the increasing concentration of Gd in feed solution when the solvent is 50 %TBP / kerosene but they are less than “1” for all of the solvents. K_d of Dy, Y, and Yb are low, less than “1”, and almost constant when 50 %TBP/kerosene is the solvent. The highest distribution coefficient (K_d) of Y and Yb were around 20, when 1 M D2EHPA / kerosene is used.

Table 1 Concentrations of heavy rare earth feed solutions

Feed solution	Gd, g/l	Dy, g/l	Y, g/l	Yb, g/l	Total heavy rare earths, g/l
F1	4.3810	1.0570	4.8320	0.0204	10.2904
F2	8.7740	2.1190	9.6530	0.0505	20.5965
F3	13.6900	3.2980	14.9070	0.0837	31.9787
F4	18.4000	4.4320	20.0090	0.1157	42.9567
F5	21.3700	5.1450	23.2570	0.1349	49.9069

Because of the high percentage of Y in heavy rare earth cake, it is interesting to determine the optimum conditions to separate Y. The separation factors of Yb-Y, Y-Dy, and Y-Gd pairs ($\alpha_{Yb/Y}$, $\alpha_{Y/Dy}$, and $\alpha_{Y/Gd}$), as a function of concentration of isomolar mixture (TBP-D2EHPA) / kerosene at various feed concentrations, are shown in Figures 5-7. All of these values are higher than one. When concentration of D2EHPA in isomolar mixture (TBP-D2EHPA) / kerosene increases, their separation factors tend to increase. If concentration of heavy rare earths in feed increases, most of their separation factors decreases.

As a result, in order to separate Y with 1 M D2EHPA / kerosene, the feed concentration should not be high. Because $\alpha_{Yb/Y}$, $\alpha_{Y/Dy}$, and $\alpha_{Y/Gd}$ are higher than “1” when the solvent is 1 M D2EHPA / kerosene, it is possible to separate Yb-Y pair to organic phase while Gd and Dy remain in aqueous phase. Then, Yb will be separated from Y to organic phase while Y is still in aqueous phase.

When the solvent is 50%TBP / kerosene (Figure 8), $\alpha_{Yb/Y}$, $\alpha_{Y/Dy}$, and $\alpha_{Y/Gd}$ are less than one. The separation is poor and it shows that 50%TBP / kerosene is not suitable to separate Y. However, it is possible to separate Gd, which is also high in heavy rare earth hydroxide cake (0.615 %), by this solvent because $\alpha_{Dy/Gd}$ are around 1.1-1.2 at high feed concentration.

In order to find optimum condition to separate Y, stage numbers for Y extraction with 1 M D2EHPA / kerosene are calculated graphically from equilibrium curve as in Figure 9. The operating line slope, F/S (feed flow rate / solvent flow rate), is 2/3 and 90 % extraction efficiency is obtained with only two stages when the input feed concentration is 12 g/l.

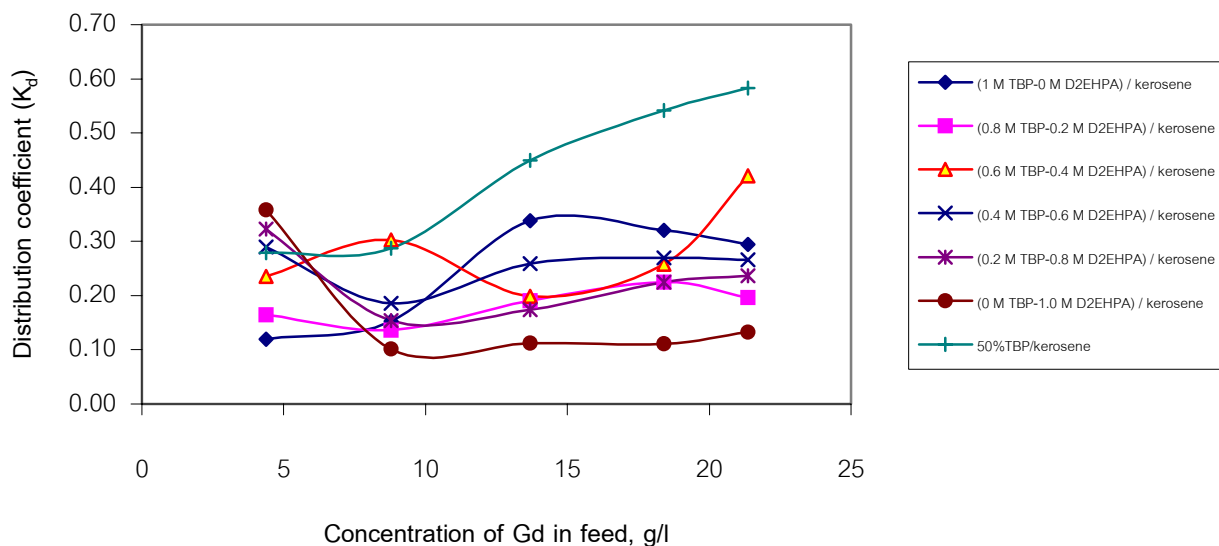


Figure 1 Distribution coefficient of Gd in various solvents as a function of Gd concentration in feed

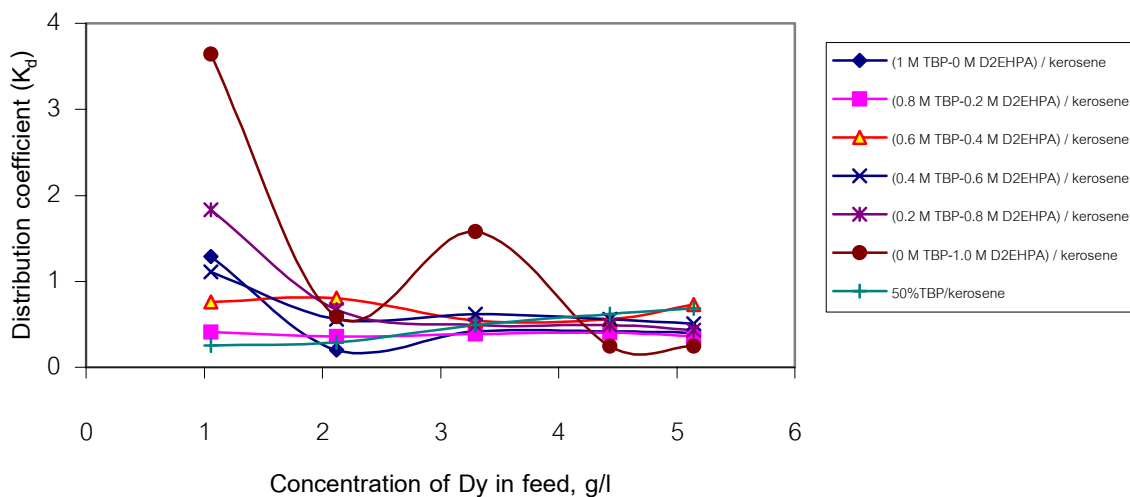


Figure 2 Distribution coefficient of Dy in various solvents as a function of Dy concentration in feed

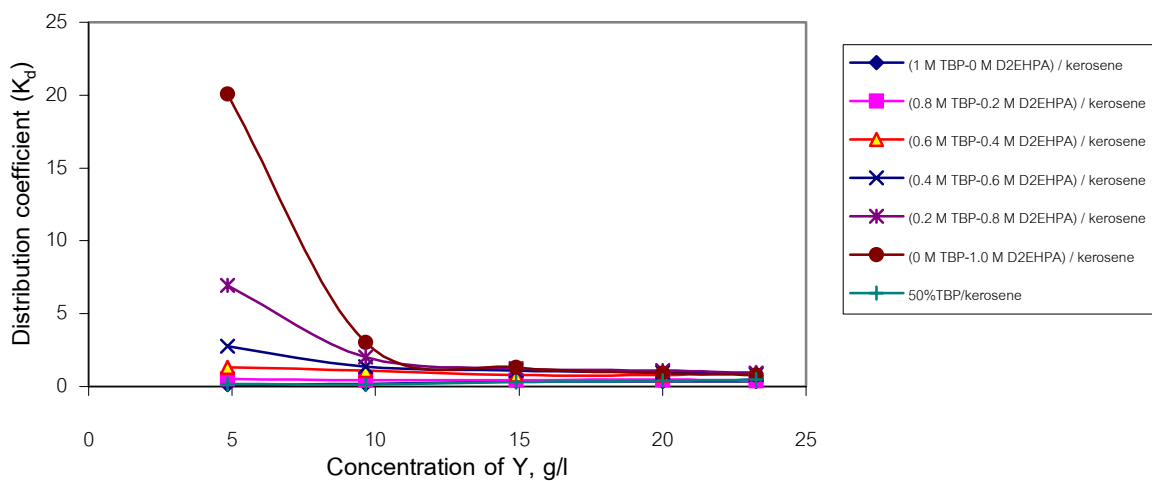


Figure 3 Distribution coefficient of Y in various solvents as a function of Y concentration in feed

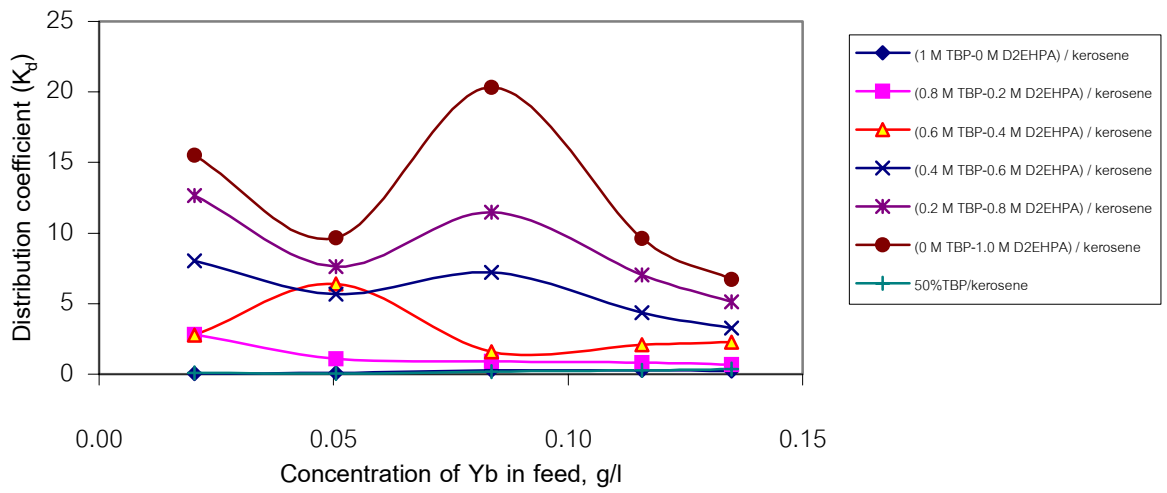


Figure 4 Distribution coefficient of Yb in various solvents as a function of Yb concentration in feed

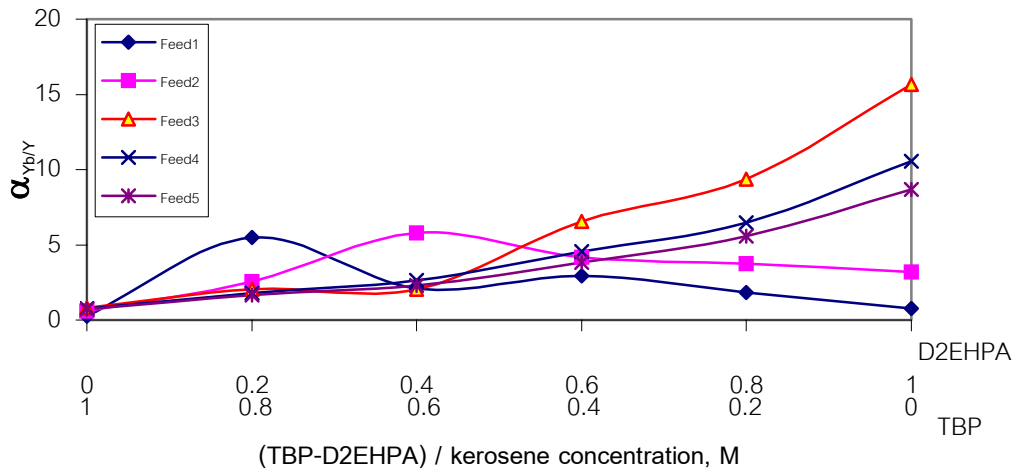


Figure 5 $\alpha_{Yb/Y}$ as a function of concentration of isomolar mixture(TBP-D2EHPA) / kerosene at various feed concentration

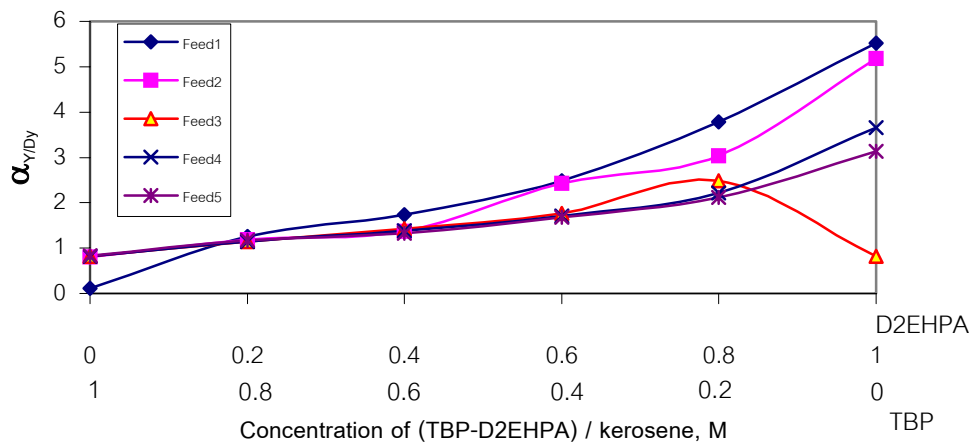


Figure 6 $\alpha_{Y/Dy}$ as a function of concentration of isomolar mixture (TBP-D2EHPA) / kerosene at various feed concentrations

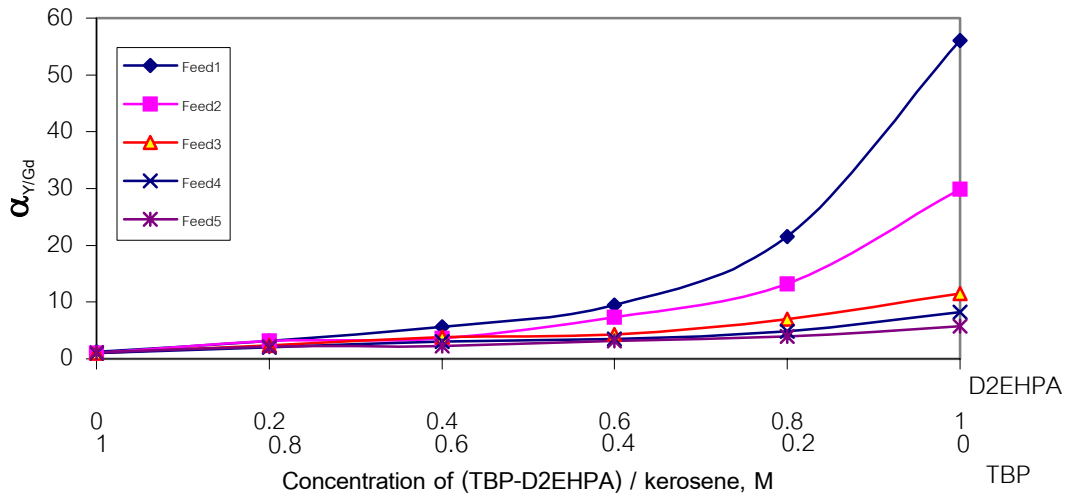


Figure 7 $\alpha_{Y/Gd}$ as a function of concentration of isomolar mixture (TBP-D2EHPA) / kerosene at various feed concentrations

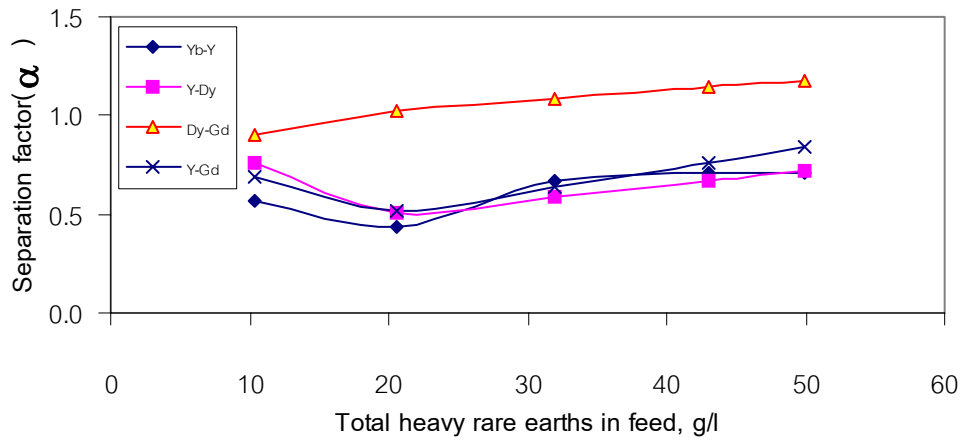


Figure 8 Separation factor of heavy rare earths as a function of total heavy rare earths in feed when the solvent is 50%TBP / kerosene

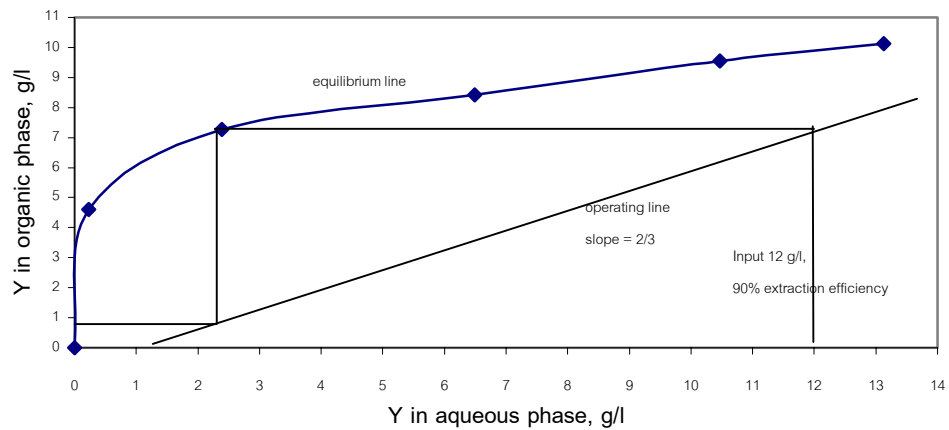


Figure 9 Stage calculation of the system $Y(NO_3)_3/dil.HNO_3 - 1 M D2EHPA / kerosene$

Conclusions

K_d of heavy rare earths (Gd, Dy, Y, and Yb) decreases with the increasing of their concentrations in feed. $(K_d)_{Gd}$ are less than one for all of the solvents. $(K_d)_Y$ and $(K_d)_{Yb}$ are high, around 20 when the solvent is 1 M D2EHPA / kerosene. The separation factors of heavy rare earths tend to increase with the increasing concentration of D2EHPA in isomolar (TBP-D2EHPA) / kerosene and $\alpha_{Yb/Y}$, $\alpha_{Y/Dy}$, and $\alpha_{Y/Gd}$ are higher than one. $\alpha_{Dy/Gd}$ are around 1.1-1.2 at high feed concentration when the solvent is 50 %TBP / kerosene. It is possible to separate Y and Gd, which their compositions are high in heavy rare earth hydroxide cake, by solvent extraction. Isomolar (TBP-D2EHPA) / kerosene can be applied to separate Y and 50 %TBP / kerosene is more suitable to separate Gd.

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