

การกระจายของแลนทานัมและนีโอดีเมียม
ในกรดไดทุเอทิลเฮกซิลฟอสฟอริกและไตรบิวทิลฟอสเฟต

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1. ปัจจุบันศึกษาต่อในระดับปริญญาโท ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

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2. กองเคมี สำนักงานพลังงานปรมาณูเพื่อสันติ

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บทคัดย่อ

แลนทานัม และนีโอดีเมียม เป็นธาตุที่มีปริมาณสูงในแร่เอิร์ทผสม ซึ่งได้จากการย่อยแร่โมนาไซต์
กรรมวิธีการแยกที่นิยมกัน คือ การสกัดของเหลวด้วยของเหลว งานวิจัยนี้เป็นการศึกษาการกระจายของ
แลนทานัมและนีโอดีเมียมในสารเคมีที่ใช้ในการสกัด 2 ชนิด คือ กรดไดทุเอทิลเฮกซิลฟอสฟอริก [Di(2-
ethylhexyl) phosphoric acid] และ ไตรบิวทิลฟอสเฟต (Tributylphosphate) พบว่า นีโอดีเมียม
สามารถกระจายไปยังสารเคมีที่ใช้ในการสกัดได้ดีกว่าแลนทานัม ในสภาวะที่สารละลายเริ่มต้น มีความ-
เป็นกรดต่ำ ทั้งสองตัวจะกระจายไปยังสารเคมีที่ใช้ในการสกัด ได้ดีกว่าสภาวะที่สารละลายเริ่มต้นมี
ความเป็นกรดสูง จากการตรวจสอบอย่างหยาบและเร็ว โดยคำนวณอัตราส่วนของสัมประสิทธิ์การกระจาย
ของนีโอดีเมียมต่อแลนทานัม สำหรับสารเคมีที่ใช้ในการสกัดแต่ละอย่าง พบว่า กรดไดทุเอทิลเฮกซิล-
ฟอสฟอริก สามารถแยกแลนทานัมและนีโอดีเมียมออกจากกันได้ดีกว่าไตรบิวทิลฟอสเฟต

Distribution of Lanthanum and Neodymium
in Di(2-ethylhexyl) phosphoric acid and Tributylphosphate

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ABSTRACT

Lanthanum and neodymium are among the high quantity elements in mixed rare earth from monazite processing. The popular rare earth separation process is liquid-liquid extraction. This research was carried out to study lanthanum and neodymium distribution in two extractants, di(2-ethylhexyl) phosphoric acid and tributylphosphate. The experimental results show that neodymium distributes in both extractants better than lanthanum. The distribution of both elements are higher at low acidity than at high acidity. Quick and rough investigation by calculating the ratio of distribution coefficient of neodymium to lanthanum in each extractant indicated that La-Nd separation efficiency of Di(2-ethylhexyl) phosphoric acid is higher than that of tributylphosphate.

1. Introduction

Both lanthanum and neodymium are classified in the light rare earth elements group. Rare earths are the elements in Lanthanide series which include of 15 elements. In Thailand, the rare earths can be processed from monazite sand which is found in tin mine. From the survey of Department of Mineral Resources in 1979-1991, the reserve is about 17,792.8 metric tons and it costs 244.5 billion bahts or 13,737 bahts/metric tons⁽¹⁾. In 1990, world's rare earth consumption is about 37,000 metric tons⁽²⁾.

Because of the similar chemical properties of each individual rare earth, it is hard to separate and purify them. Liquid-liquid extraction process is one of the efficient and economic separation techniques to obtain high purity individual rare earth. There are two popular chemical systems in commercial scale⁽³⁾: HNO_3 -Tributylphosphate (TBP) and HCl -di(2-ethylhexyl) phosphoric acid (D2EHPA).

TBP was the main extractant that was used in rare earth separation processes for a long time by some giant companies such as Rhone-Poulenc, Thorium Ltd. (UK) and Indian Rare Earths⁽⁴⁾. In 1957, Peppard⁽⁵⁾ reported that the rare earth separation factor was as high as 2.5 in chloride and nitrate system by using D2EHPA as solvent while the highest separation factor of TBP- HNO_3 system was 1.9. In 1965, C. Battista, C. Mize and M. Smutz⁽⁶⁾ found that chloride system was more suitable than nitrate system and extraction should be done at lowest acidity. In 1967, Nair and Smutz⁽⁷⁾ extracted lanthanum from didymium chloride (45% La_2O_3 , 35% Nd_2O_3 , 10% Pr_6O_{11} and 5% Sm_2O_3) using D2EHPA and the yield obtained was as high as 99.8%. The equipment used was 14-stage-mixer-settler. In 1975, B.H. Lucas and G.M. Ritcey⁽⁸⁾ from Department of Energy, Mines and Resources, Canada, extracted yttrium from heavy rare earth and light rare earth by D2EHPA using sieve-plate pulse column. In 1979, Indian Rare Earths plant at Alwaye, India, extracted rare earths from mixed rare earth chloride obtained from monazite processing⁽⁹⁾ using D2EHPA and produced individual rare earths which concentrations of about 60-95%.

The objectives of this research are listed below:

- (1) to investigate individual rare earth distribution in 50% TBP and 1M

D2EHPA by using lanthanum and neodymium as examples because of their high amounts in mixed rare earth obtained from monazite processing.

(2) to study optimum conditions for extraction and scrubbing.

(3) to preliminary compare separation efficiency between two extractants: TBP and D2EHPA.

2. Materials and methods

2.1 Materials

- separatory funnels

- electronic shaker

- chemicals :

LaCl₃ (Fluka, assay > 99.0%)

NdCl₃.6H₂O (Fluka, 99.9% Nd)

La(NO₃)₃.6H₂O (Fluka, assay >99.0%)

Nd(NO₃)₃.6H₂O (Fluka, 99.9% Nd)

HCl, HNO₃ (A.R.grade)

Di(2-ethylhexyl) phosphoric acid (Sigma, minimum 95%)

Tributylphosphate (BDH, assay(GLC)98%)

kerosene (commercial grade)

2.2 Methods

The nitrate and chloride system were studied at some acidities and the extractants were 1M D2EHPA/kerosene and 50% TBP/kerosene. The commercial kerosene was washed by conc.H₂SO₄, 1N NaOH and H₂O, respectively. The extractant, 1M D2EHPA/kerosene is also washed by 6N HCl, 1N NaOH and H₂O respectively and TBP was washed by 5% Na₂CO₃ and then H₂O.

The equilibration was run between feed and extractant by shaking in separatory funnels. The ratio of feed to extractant was 1:1 and after 15 minutes shaking, the solution was kept 1 hour for phase separation and then was shaken again about 15 minutes. After that, it was kept 1 hour again for phase separation. This equilibration technique was done in order to eliminate

the effect of temperature. Samples from raffinates and feeds were taken for lanthanum and neodymium analysis by inductive coupled plasma emission spectrometer (ICP) model Plasma 1000 of Perkin-Elmer.

The conditions of both systems that used in this experiment were:

1. LaCl_3 (neutral) - 1M D2EHPA/kerosene
2. $\text{LaCl}_3/0.5\text{N HCl}$ - 1M D2EHPA/kerosene
3. $\text{NdCl}_3/0.05\text{N HCl}$ - 1M D2EHPA/kerosene
4. $\text{NdCl}_3/0.5\text{N HCl}$ - 1M D2EHPA/kerosene
5. $\text{La}(\text{NO}_3)_3/0.3\text{N HNO}_3$ - 50% TBP/kerosene
6. $\text{La}(\text{NO}_3)_3/5\text{N HNO}_3$ - 50% TBP/kerosene
7. $\text{Nd}(\text{NO}_3)_3/0.3\text{N HNO}_3$ - 50% TBP/kerosene
8. $\text{La}(\text{NO}_3)_3/5\text{N HNO}_3$ - 50% TBP/kerosene

From the distributions of La and Nd in these conditions, the distribution coefficients were calculated. The rough estimation of number of theoretical stages for single component extraction was done by means of Kremser equation (Appendix A) and the assumption of linear equilibrium line in the range of 200 g/l [La]/feed and 100 g/l [Nd]/feed. Both concentrations are estimated from concentrations of La and Nd in mixed rare earth feed obtained from monazite processing⁽⁹⁾. That is:

feed [rare earth]	400	g/l
compositions: [La] <small>estimated</small>	170	g/l
[Nd] <small>estimated</small>	70	g/l

The comparisons between these results were also carried out.

3. Results

3.1 Comparisons of the distribution coefficients of lanthanum and neodymium at the same acidity and same extractant are shown in Fig.3.1.1-Fig.3.1.4.

3.2 Comparisons of the distribution coefficients of lanthanum and neodymium in different extractants are shown in Fig.3.2.1-Fig.3.2.4.

3.3 Comparisons of ratios of distribution coefficients of neodymium to distribution coefficients of lanthanum in D2EHPA and TBP system are shown in Table 3.3.1.

3.4 Numbers of theoretical stage for single component extraction were calculated by graphical method of Kremser equation. The results are shown in Table 3.4.1. Nevertheless, the calculated values of solvent rate/ feed rate (S/F) with the extraction factor of 1.3 are also listed in this Table.

4. Discussion and conclusion

1. From Fig.3.1.1-Fig.3.1.4, the equilibrium results indicated that the distribution of neodymium to extractant is higher than the distribution of lanthanum to the same extractant. When the neutral or low acidity feed solution was used, lanthanum and neodymium can distribute to extractant better than when high acidity feed solution was used. So, the suitable extraction should be carried out with neutral or low acidity feed and then individual rare earths are scrubbed by more concentrated acid.

2. From Fig.3.2.1-Fig.3.2.4, the comparison of the distribution coefficients of lanthanum and neodymium between D2EHPA system and TBP system shows that:

(1) Extraction process

Extractant: 1M.D2EHPA/kerosene and 50%TBP/kerosene

- Lanthanum can distribute in D2EHPA system better than TBP system when [La]/feed is lower than 120 g/l. (Fig. 3.2.1)

- Neodymium can distribute in D2EHPA system better than TBP system when [Nd]/feed is lower than 85 g/l. (Fig. 3.2.2)

(2) Scrubbing process

Scrub solution: 0.5N HCl and 5N HNO₃

- Lanthanum and Neodymium can distribute to 5N.HNO₃ (TBP system) better than 0.5N.HCl (D2EHPA system). (Fig. 3.2.3 and Fig. 3.2.4)

3. The approximation for selectivity was done by investigation of the ratio of distribution coefficients of neodymium to lanthanum (m_{Nd}/m_{La}) between the two systems. The linear equilibrium lines are assumed in the range of 200 g/l [La]/feed and 100 g/l [Nd]/feed that are approximated from [La] and [Nd] in mixed rare earth feed obtained from monazite processing.

From Table 3.3.1, the results show that extraction and scrubbing in D2EHPA system give the higher ratio of m_{Nd}/m_{La} than in TBP system. So, D2EHPA can separate lanthanum from neodymium better than TBP.

Extraction: D2EHPA system; neutral or 0.05 N HCl	,	$m_{1,1}/m_{1,1}$	=	2.28
TBP system ; 0.3N HNO ₃	,	$m_{1,v}/m_{1,1}$	=	1.84
Scrubbing : D2EHPA system; 0.5N HCl	,	$m_{1,1}/m_{1,1}$	=	4.51
TBP system ; 5N HNO ₃	,	$m_{1,v}/m_{1,1}$	=	1.54

4. Quick and rough estimation of number of theoretical stages (N) by graphical method of Kremser equation indicated that 90% extraction can be achieved by using 4 stages and 99.9% extraction can be reached when 12 stages was used. This estimation was done for single component and the extraction factor was 1.3. The flow rate ratios of solvent/feed (S/F) obtained are not equal. But the optimum working conditions should be estimated from optimization between extraction factors, S/F and N.

Nevertheless, we can conclude from Table 3.4.1 that:

(1) At high acidity (system I'-TV'), S/F is high. These systems are not suitable for scrubbing process. Lanthanum is the one which is scrubbed into aqueous phase first because it distributes in 0.5N HCl or 5N HNO₃ better than neodymium.

(2) At low acidity (system I-IV), S/F is not high. The maximum value of S/F is 10.4. These systems are suitable for extraction process. Neodymium can be extracted better than lanthanum because of lower S/F value in the same extractant.

5. The experimental results also indicated that the distribution of rare earth to extractant is very low, so the extraction with reflux technique should be applied in order to concentrate individual rare earths.

5. Acknowledgement

We would like to thank Mr.Chouvana Rodthongkom, Director of Chemistry Division, Mr.Vibul Leenanupan, Head of Chemical Analysis Section, and Mr. Chavalek Chayavadhanangkur, for their help and assistance.

We also wish to thank for Chemical Analysis Section, for their equipments and laboratory. Thanks for Mr.Paprat Imkamon for some work in lanthanum and neodymium analysis and also thanks for Mr.Pruan Manyrut and Mr.Prechar Popromsri for some work in laboratory. At last, we would like to thank the officers of Library INIS (International Nuclear Information System) for their help and service.

6. Reference

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Appendix A

Kremser equation

$$N = \log \left[\frac{(X_F - Y_S/m)/(X_N - Y_S/m)(1-1/E) + 1/E}{\log E} \right]$$

N = number of theoretical stages

X_F = concentration of solute in feed

X_N = concentration of solute in raffinate

Y_S = concentration of solute in solvent

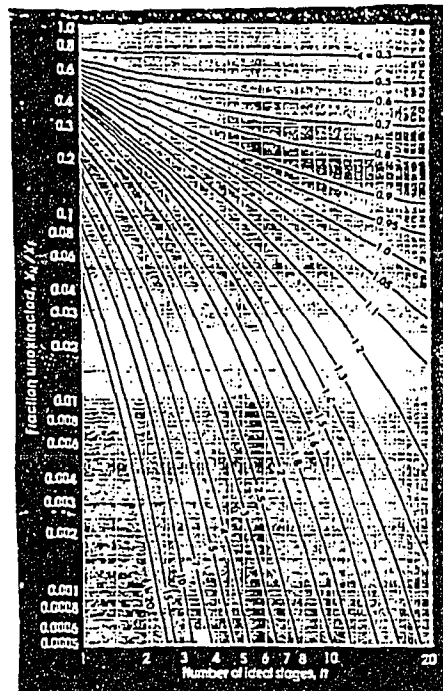
E = extraction factor = $m(S/F)$

m = distribution coefficient

S = solvent rate

F = feed rate

This equation can be shown by the graph below:



A quick way to find the number of ideal extraction stages
by graphical method based on the Kremser equation

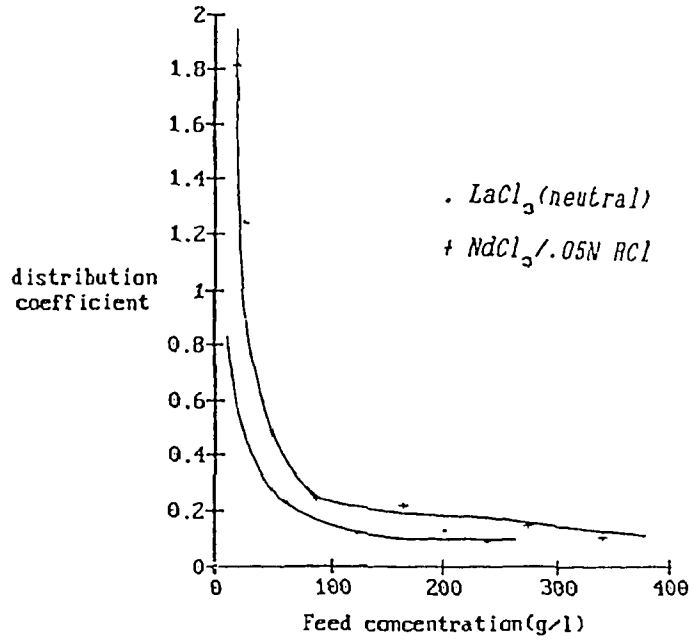


Fig.3.1.1 Distribution coefficient comparison between La and Nd in D2EHPA system using neutral or very low acidity feed

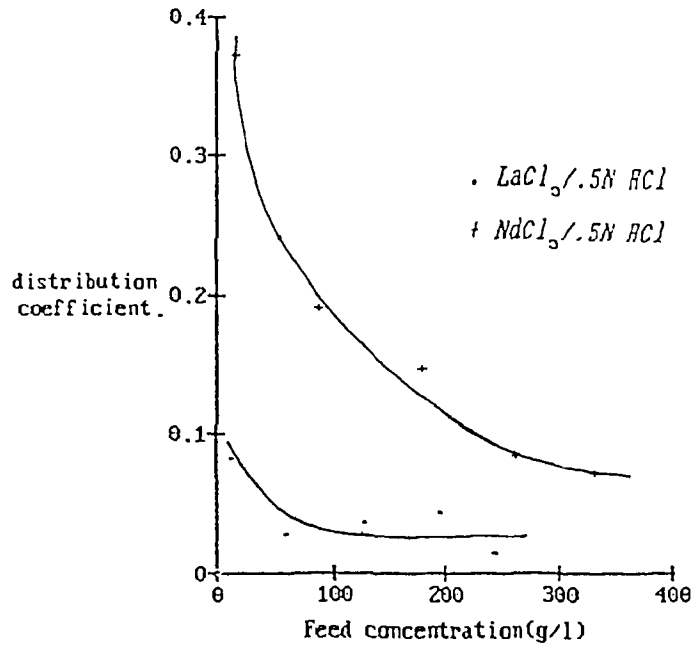


Fig.3.1.2 Distribution coefficient comparison between La and Nd in D2EHPA system using 0.5N HCl medium feed

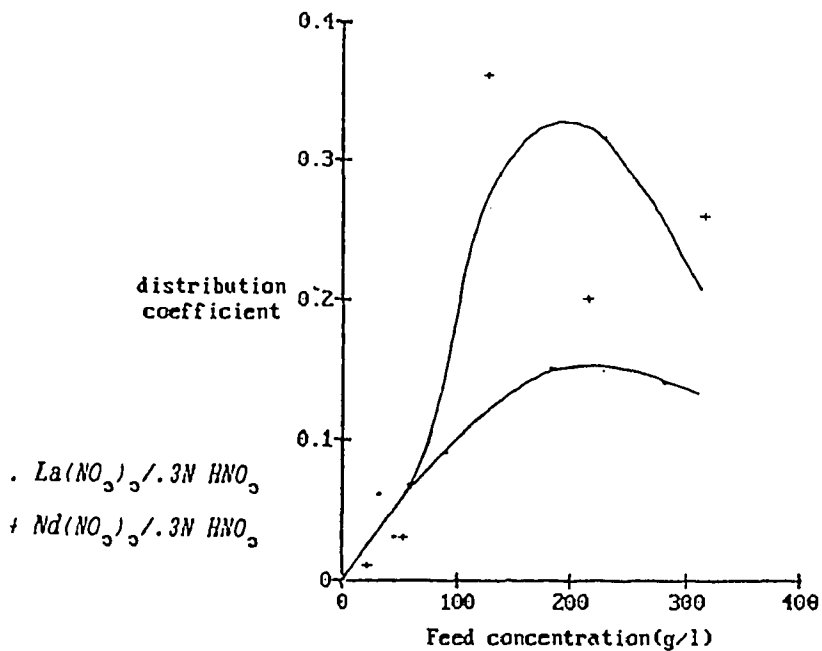


Fig.3.1.3 Distribution coefficient comparison between La and Nd in TBP system using 0.3N HNO_3 medium feed

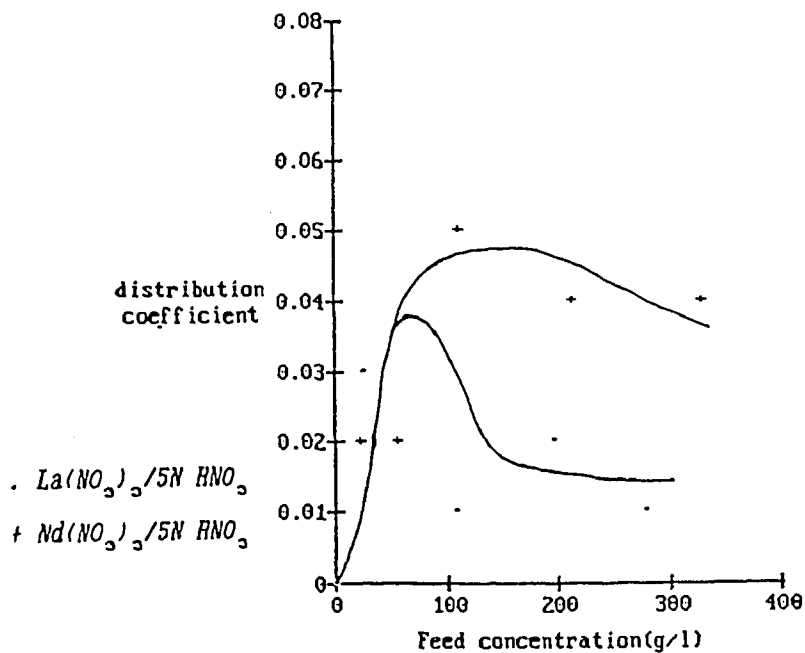


Fig.3.1.4 Distribution coefficient comparison between La and Nd in TBP system using 5N HNO_3 medium feed

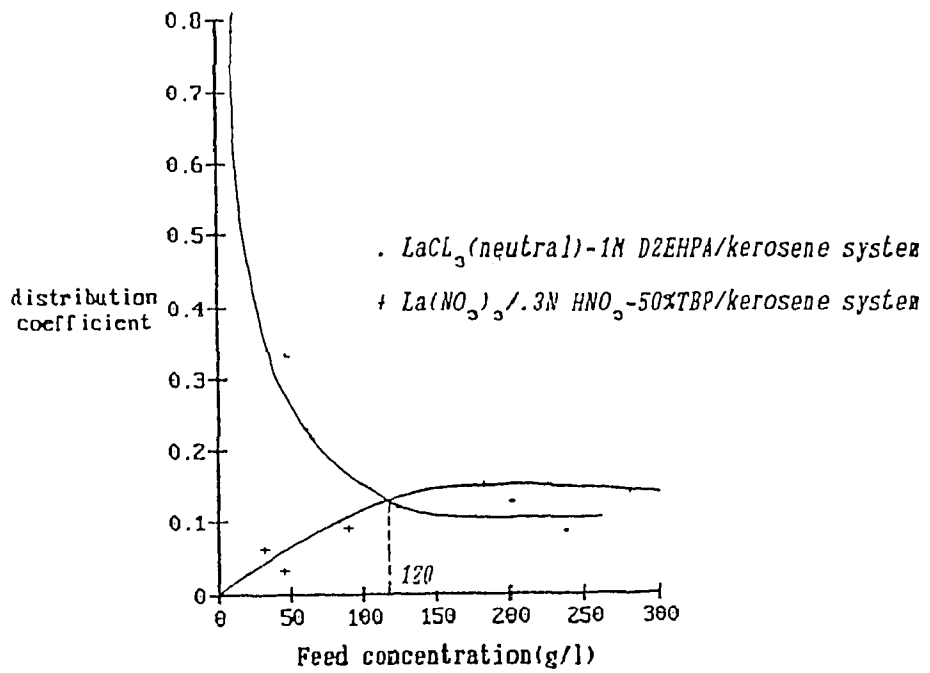


Fig.3.2.1 La distribution coefficient comparison between D2EHPA system using neutral feed and TBP system using 0.3N HNO_3 medium feed

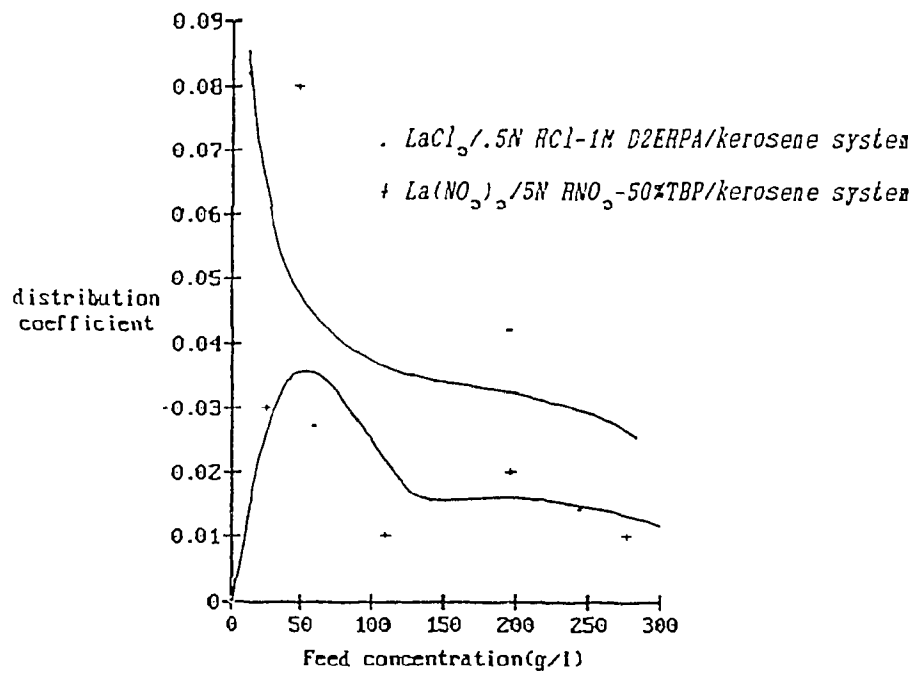


Fig.3.2.2 La distribution coefficient comparison between D2EHPA system using 0.5N HCl medium feed and TBP system using 5N HNO_3 medium feed

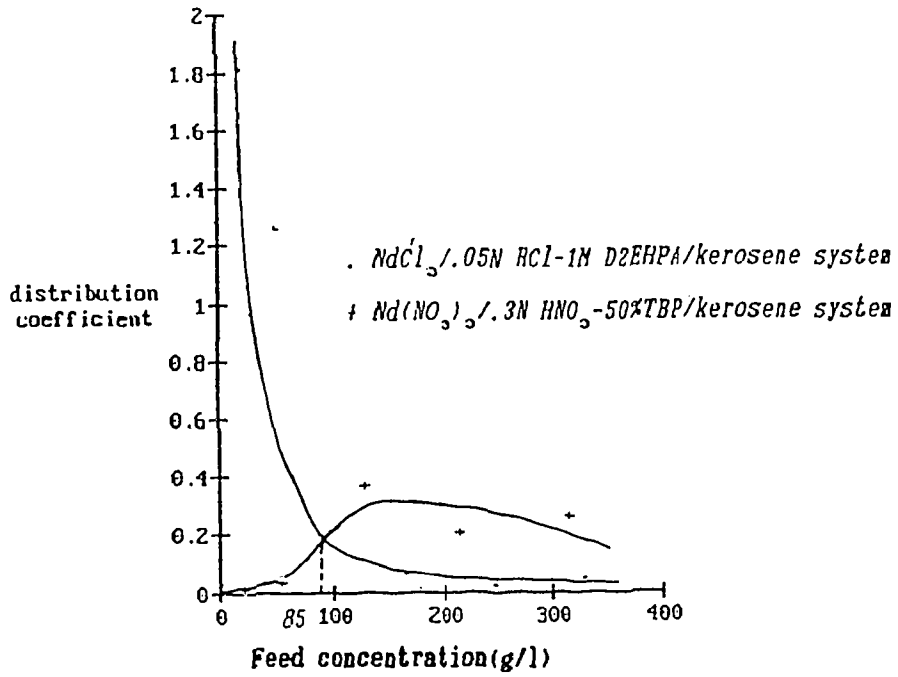


Fig.3.2.3 Nd distribution coefficient comparison between D2EHPA system using 0.05N HCl medium feed and TBP system using 0.3N HNO_3 medium feed

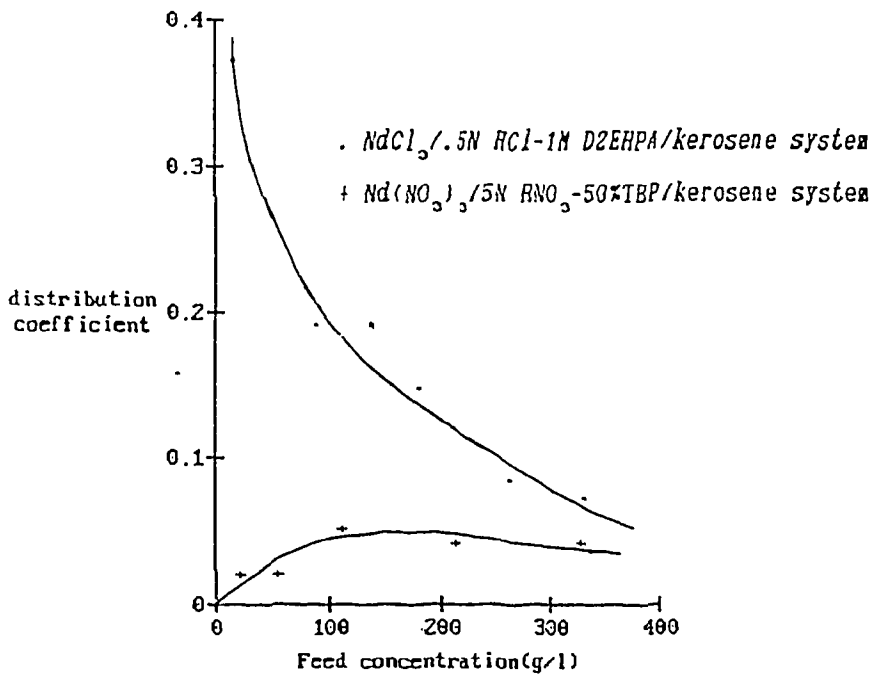


Fig.3.2.4 Nd distribution coefficient comparison between D2EHPA system using 0.5N HCl medium feed and TBP system using 5N HNO_3 medium feed

Table 3.3.1 Comparison of distribution coefficient ratio of neodymium to lanthanum in D2EHPA and TBP systems

System	Distribution coefficient	Remark
I. LaCl_3 (neutral)-1M D2EHPA/ kerosene	$m_{\text{I}} = 25/200$ $= 0.125$	
II. $\text{NdCl}_3/0.05 \text{ N HCl}$ -1M D2EHPA/ kerosene	$m_{\text{II}} = 28.5/100$ $= 0.285$	$m_{\text{II}}/m_{\text{I}} = 0.285/0.125$ $= 2.28$
III. $\text{La}(\text{NO}_3)_3/0.3 \text{ N HNO}_3$ -50% TBP/ kerosene	$m_{\text{III}} = 27.1/200$ $= 0.136$	
IV. $\text{Nd}(\text{NO}_3)_3/0.3 \text{ N HNO}_3$ -50% TBP/ kerosene	$m_{\text{IV}} = 25/100$ $= 0.25$	$m_{\text{IV}}/m_{\text{III}} = 0.25/0.136$ $= 1.84$
I'. $\text{LaCl}_3/0.5 \text{ N HCl}$ -1M D2EHPA/ kerosene	$m_{\text{I}'} = 8.1/200$ $= 0.041$	
II'. $\text{NdCl}_3/0.5 \text{ N HCl}$ -1M D2EHPA/ kerosene	$m_{\text{II}'} = 18.5/100$ $= 0.185$	$m_{\text{II}'}/m_{\text{I}'}$ $= 0.185/0.041$ $= 4.51$
III'. $\text{La}(\text{NO}_3)_3/5 \text{ N HNO}_3$ -50% TBP/ kerosene	$m_{\text{III}'} = 4.7/200$ $= 0.024$	
IV'. $\text{Nd}(\text{NO}_3)_3/5 \text{ N HNO}_3$ -50% TBP/ kerosene	$m_{\text{IV}'} = 3.7/100$ $= 0.037$	$m_{\text{IV}'}/m_{\text{III}'}$ $= 0.037/0.024$ $= 1.54$

Table 3.4.1 Calculated results of number of theoretical stages and solvent rate/feed rate of D2EHPA and TBP systems for single component extraction at extraction factor of 1.3

System	Distribu- tion coefficient	S/F	N (90% ex- traction efficien- cy)	N (99.9% extrac- tion ef- ficiency)
I. LaCl ₃ (neutral)-1M D2EHPA/ kerosene	0.125	10.4	4	12
II. NdCl ₃ /0.05 N HCl-1M D2EHPA/ kerosene	0.285	4.6	4	12
III. La(NO ₃) ₃ /0.3 N HNO ₃ -50% TBP/ kerosene	0.138	9.6	4	12
IV. Nd(NO ₃) ₃ /0.3 N HNO ₃ -50% TBP/ kerosene	0.25	5.2	4	12
I'. LaCl ₃ /0.5 N HCl-1M D2EHPA/ kerosene	0.041	31.7	4	12
II'. NdCl ₃ /0.5 N HCl-1M D2EHPA/ kerosene	0.185	7.0	4	12
III'. La(NO ₃) ₃ /5 N HNO ₃ -50% TBP/ kerosene	0.024	54.2	4	12
IV'. Nd(NO ₃) ₃ /5 N HNO ₃ -50% TBP/ kerosene	0.037	35.1	4	12