Separation of Light and Middle-Heavy Rare Earths from Nitrate Medium by Liquid-Liquid Extraction

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ABSTRACT

Separation of light (LREEs) and middle-heavy (M-HREEs) rare earths from a nitrate medium was studied using a liquid-liquid extraction technique. Tri-*n*- butyl phosphate (TBP) in kerosene was used as the extractant. The effect of the TBP concentration (30–80% volume per volume; v/v), contact time (3–10 min) and shaking speed (100–200 rpm) on rare earth extraction were investigated. The distribution ratio and separation factor were determined to evaluate the extraction behavior and the separation possibilities of M-HREEs from LREEs. The results showed that the distribution ratio increased with increasing TBP concentration. The concentration of rare earth in the aqueous phase decreased as the contact time and shaking speed increased. The separation factor values for M-HREEs/LREEs markedly increased as the atomic number of the LREEs decreased. High separation factor values were observed for Y/Nd, Y/Pr, Y/La of 6.35, 11.15 and 13.95 respectively. The best conditions for the separation in this study were found to be: a TBP concentration of 50% v/v, a contact time of 5 min and a shaking speed of 200 rpm. Under these conditions, it was possible to separate M-HREEs (Sm, Gd, Y) from LREEs (La, Pr, Nd).

Keywords: separation, light rare earth, middle-heavy rare earth, liquid-liquid extraction, tri-*n*-butyl phosphate

INTRODUCTION

Rare earth elements (REEs) are the group of 15 metallic, chemical elements with atomic numbers from 57 to 71 and also scandium and yttrium (Hussein, 1996; Jorjani and Shahbazi, 2012). They are divided into three groups: the light (La, Ce, Pr, Nd), middle (Sm, Eu, Gd, Tb) and heavy (Y and Dy to Lu) rare earths (Preston *et al.*, 1996; Fontana and Pietrelli, 2009). The minerals bastnasite, monazite, xenotime, allanite, gadolinite, loparite and fergusonite are the source of REEs (Morais and Ciminelli, 2004; Radhika *et al*., 2010; Panda *et al*., 2013). Monazite is the major source of REEs in nature (Abreu and Morais, 2010). REEs play an increasingly crucial role in industrial applications and modern technologies. For example, their compounds are used in glass polishing, phosphors, lasers, magnets, batteries, high-temperature superconductors and optical glass and REEs are also used as catalysts in the production of petroleum and synthetic products (Kokare *et al*., 2010; Radhika *et al*., 2010; Miaomiao *et al*., 2013).

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The Thailand Institute of Nuclear Technology (TINT) has carried out activity to decompose monazite ore using an alkali process to separate and purify individual rare earths. This process was divided into three stages. In the first stage, monazite ore was digested with concentrated NaOH to convert the REEs and other minerals to hydroxides. In the second stage, the hydroxide cake was dissolved by concentrated HCl to separate uranium and thorium from the mixed rare earth elements. The third stage involved the separation of individual REEs. In the separation stage of individual REES, cerium was first separated from the other rare earths and then the light rare earth group (La, Pr, Nd) was separated from the middle and heavy rare earth group (Sm, Eu, Gd, Dy, Y, Yb) by liquid-liquid extraction. Finally, each group was separated by liquid-liquid extraction and then purified by an ion exchange technique to obtain a high purity of individual RREs. In the third stage (after cerium removal), it is extremely difficult to separate the light rare earth group from the middle and heavy rare earth group due to their similar physical and chemical properties.

Solvent extraction or liquid-liquid extraction is reported to be the most commonly used and efficient method for separating and purifying rare earth elements (Kim *et al*., 2012). This method offers the advantages of simplicity, fast kinetics, high capacity, high selectivity and low operating cost (Torkaman *et al*., 2013; Yin *et al*., 2013). The most frequently used extractant for separating rare earth nitrate is tri-*n*-butyl phosphate (TBP). TBP is an excellent solvent by means of which many inorganic salts having desirable properties are extracted. The metal nitrates can consist of rare earth nitrate, uranyl nitrate, thorium nitrate and salting agents. TBP offers distinct advantages over other extractants in operation, safety, physical properties and economics (Buchalova *et al*., 1990; Changkrueng and Chatsiriwech, 2011).

Some authors studied the separation of

REEs by liquid-liquid extraction using TBP as the extractant. Jorjani and Shahbazi (2012) studied the solvent extraction of yttrium, lanthanum, cerium and neodymium from nitric acid leaching of apatite concentrate using TBP as the extractant. The effect of the TBP concentration, pH, temperature, contact time and phase ratio on the extraction efficiency were investigated. The results showed that about 95, 90, 87 and 80% of neodymium, cerium, lanthanum and yttrium, respectively, can be extracted under the optimum conditions of a TBP concentration of 3.65 mol L^{-1}, [H$^+$] of 0.63 mol.L^{-1}, a contact time of 5 min, an organic to aqueous phase ratio of 2:1 and ambient temperature (25 °C). Buchalova *et al*. (1990) investigated the separation of rare earth elements (Sm, Pr and Nd) with TBP from nitrate solutions. The effect of the concentration of TBP from 15 to 100 volume % on the distribution ratio was studied. The extraction was carried out at room temperature (22 °C), the volume ratio of the organic to aqueous phase of 1:2 and a contact time of 5 min. It was found that the distribution ratio of each studied element increased with an increased concentration of TBP. Kraikaew *et al*. (2005) studied the solvent extraction of individual rare earths from nitrate medium using mixtures of TBP and di (2-ethylhexy)phosphoric acid (D2EHPA) in kerosene compared with 50% TBP in kerosene. The experiment was performed at room temperature (35 °C), a volume ratio of organic to aqueous phase of 1:1, a contact time of 10 min and a shaking speed of 200 rpm. The distribution coefficients of heavy rare earths using isomolar mixtures of TBP and D2EHPA were higher compared with 50% TBP in kerosene.

In the current work, the separation of light (LREEs) and middle-heavy (M-HREEs) rare earths from a nitrate medium was studied using a liquid-liquid extraction technique. TBP was used as the extractant. The extraction behavior and the separation possibilities of M-HREEs from LREEs were investigated by varying the extraction parameters of the TBP concentration, contact time and shaking speed. In this experiment, the

rare earth nitrate solution was obtained from the decomposition of monazite by an alkaline method of the Rare Earth Research and Development Center at TINT (Rare Earth Research and Development Center, 1996).

MATERIALS AND METHODS

Experimental materials

The rare earth nitrate solution $(RE(NO_3)_3)$ used as a raw material for the extraction experiment was obtained from TINT. The chemical composition of $RE(NO_3)_3$ is given in Table 1. Tri-*n*-butyl phosphate (TBP), 98% (British Drug Houses) was used as the extractant. Kerosene (Jet A-1, Shell) was employed as the organic diluent. The organic phase solution was prepared by dissolving the required amounts of TBP in kerosene.

Experimental method

The extraction experiment was carried out by shaking an equal volume (100 mL) of aqueous and organic phases using a mechanical shaker. After shaking, the phases were separated using a separation funnel. The aqueous phase was analyzed to determine the concentration of rare earths by inductively coupled plasma optical emission spectrometry (Optima 5300 DV, Perkin Elmer; Waltham, MA USA).

All experiments were carried out using triplicate determinations. The deviation from experimental data was within 5%.

The distribution ratio (D) and separation factor (SF) are defined by Equations 1 and 2, respectively (Torkaman *et al.*, 2013):

$$D = \frac{C_0 - C}{C} \qquad (1)$$

$$SF = \frac{D_1}{D_2} \qquad (2)$$

where C_0 and C represent the initial and final concentration of rare earths in the aqueous phase, respectively. D_1 and D_2 refer to the distribution ratios of metal ion 1 and metal ion 2, respectively.

RESULTS AND DISSCUSSION

Effect of tri-*n*- butyl phosphate concentration on rare earth extraction

The extractant concentration plays a significant factor in the extraction process. Normally, TBP is chosen as the extractant for separating individual rare earths in a nitrate medium due to both its excellent chemical stability and its physical properties. However, it is limited by its high viscosity and density. A diluent such as kerosene reduces the viscosity and density of the organic phase to improve the phase separation

Table 1 Chemical composition of rare earth nitrate solution.

Rare earth metal	Concentration ($\mu g.mL^{-1}$)
La	112,675
Pr	10,975
Nd	57,115
Sm	7,608
Gd	3,400
Y	3,194
Ce	<50
Eu	118
Dy	261
Yb	<50

characteristics. All of the rare earths typically exhibit in a trivalent oxidation state, while some of them can also occur in the divalent (Sm, Eu and Yb) and tetravalent (Ce and Pr) states. These states are always less stable than the trivalent state. In the divalent and tetravalent states, the elements exhibit markedly different chemical behavior compared with that in the trivalent state (Gupta and Krishnamurthy, 2005). The extraction of trivalent rare earth ions from nitrate medium with TBP can be represented by Equation 3 (Xie *et al.*, 2014):

$$Ln^{3+} + 3NO_3^- + 3\overline{TBP} \rightarrow \overline{Ln(NO_3)_3(TBP)_3} \quad (3)$$
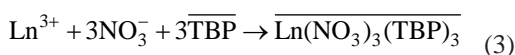
where Ln^{3+} denotes trivalent rare earth ions.

The effect of the TBP concentration on rare earth extraction was studied by varying the TBP concentrations from 30 to 80% volume per volume (v/v) dissolved in kerosene. The extraction experiments were carried out using a phase ratio of 1:1 (organic:aqueous), a contact time of 5 min and a shaking speed of 200 rpm. The results are shown in Figures 1 and 2. Figure 1 shows the effect of the TBP concentration on the distribution ratio. It is noted that the distribution ratio increased as the TBP concentration increased from 30 to 50%. However, a slight increase in the distribution ratio was observed when the concentration of TBP was increased from 50 to 80% and an increase in the extraction from La to Y was observed due to the difference in the acidity of these elements, which increases from La to Lu. This difference involves a decrease in the ionic radii of rare earth elements, known as the lanthanide contraction, which increases with the atomic number in the lanthanide series (Preston *et al.*, 1996; Morais and Ciminelli, 2004; Hongtao *et al.*, 2010; Radhika *et al.*, 2010). The separation factor (SF) values for the middle-heavy rare earths, M-HREEs (Sm, Gd, Y) from the light rare earths, LREEs (La, Pr, Nd) were calculated at various TBP concentrations as illustrated in Figures 2a, 2b and 2c which show that the SF value for Y/La increases from 5.21 to 13.95, when the TBP concentration is increased from 30 to 50% v/v. However, this SF value decreased to 11.53 after the TBP concentration reached 50% v/v. For other rare earth pairs, the same trend was observed but with lower values compared to Y/La. The decrease in SF values for M-HREEs/LREEs clearly followed the decrease in ionic radii of the LREEs, for La (117.2 pm), Pr (113 pm) and Nd (112.3 pm). The SF value of Sm/Nd was lower than that of Sm/Pr as was also reported by Buchalova *et al.* (1990). From the above results, it was concluded that the TBP concentration of 50% v/v efficiently separates M-HREEs from LREEs. Thus, it was chosen as the suitable concentration (Buchalova *et al.*, 1990).
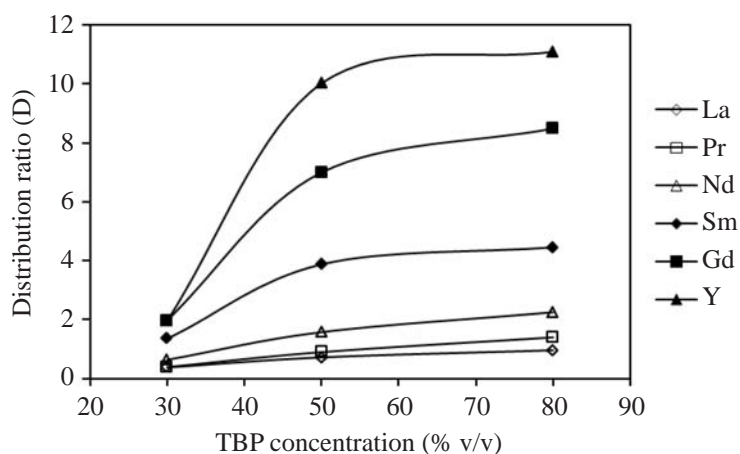

Figure 1 Effect of tri-*n*- butyl phosphate (TBP) concentration (percent volume per volume, % v/v) on distribution ratio with contact time of 5 min and shaking speed of 200 rpm.
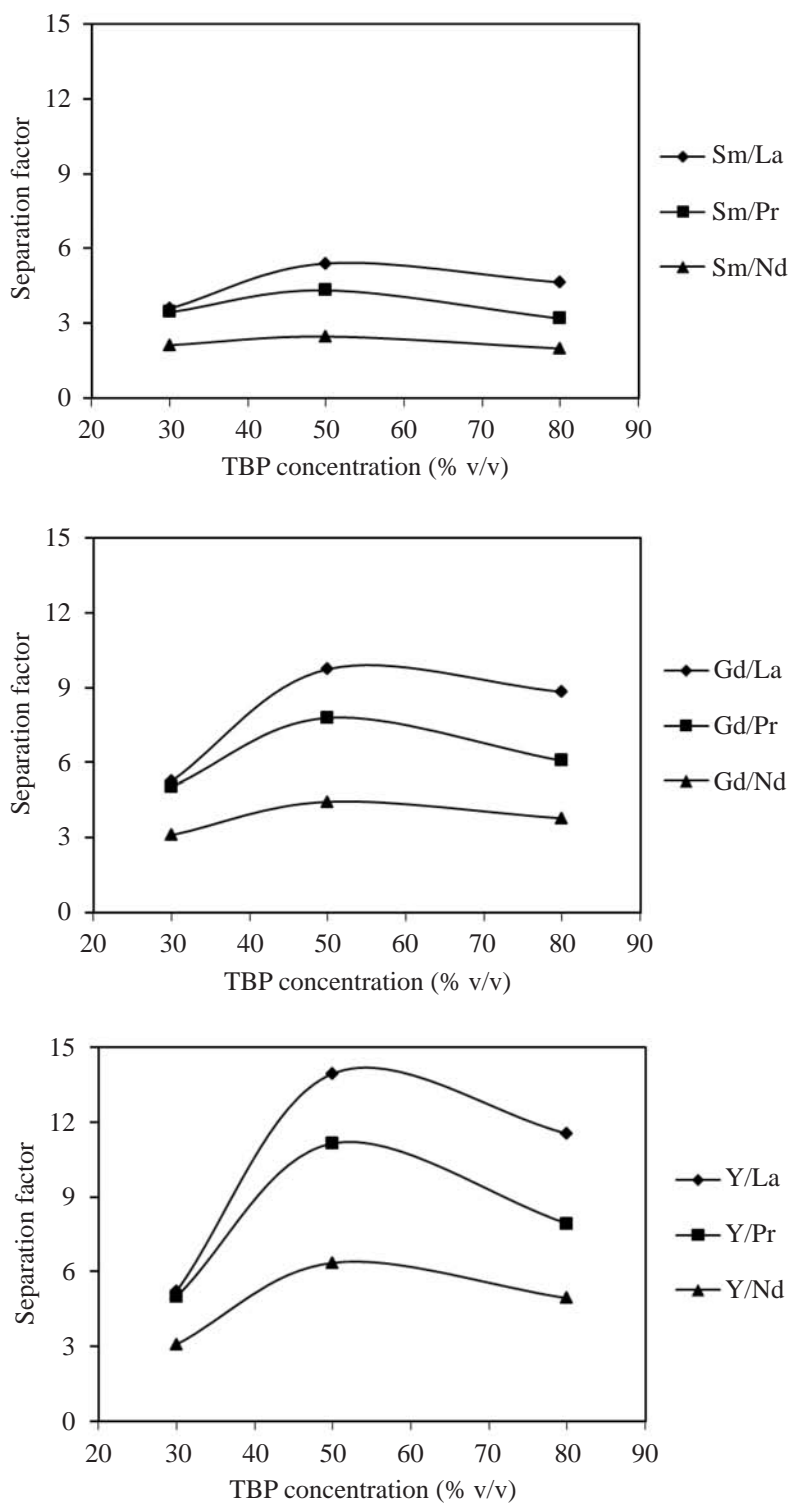
Figure 2 Separation factor for light rare earths (LREEs) at different tri-*n*- butyl phosphate (TBP) concentrations (percent volume per volume, % v/v): (a) Sm/LREEs; (b) Gd/LREEs; and (c) Y/LREEs.

Effect of contact time on rare earth extraction

It is well known that the contact time is one of the predominant factors governing extractability. The extraction of rare earths was conducted at different intervals ranging from 3 to 10 min. The other operating conditions were a phase ratio of 1:1 (organic:aqueous), a TBP concentration of 50% v/v and a shaking speed of 200 rpm. The effect of contact time on rare earth extraction is presented in Figure 3. It can be seen that an increase in the contact time from 3 to 5 min led to a decrease in the rare earth concentration in the aqueous phase. However, a further increase in the contact time after 5 min showed a very limited effect on the rare earth concentration in the aqueous phase. The SF values for M-HREEs/LREEs at different contact times are represented in Table 2 which shows that all SF values for M-HREEs/LREEs increased as the contact time

increased up to 5 min. However, when the contact time exceeded 5 min, the SF values were constant. The low values of SF for a short contact time (3 min) were due to the fact that the feed passed immediately into the solvent without separation. As the contact time increased, the solvent phase became rich in the feed and therefore, the SF increased. The SF values in the contact time range 3–10 min were below 15. The highest SF values were for the Y/La pair (8.93, 13.95 and 14.66 at contact times of 3, 5 and 10 min, respectively). At a contact time of 5 min, the SF values for Y/La, Y/Pr and Y/Nd were 13.95, 11.15 and 6.35, respectively, which were sufficient to reach equilibrium. These results were similar to Buchalova *et al.* (1990) and Jorjani and Shahbazi (2012). Therefore, the optimum contact time was considered to be 5 min for further studies.
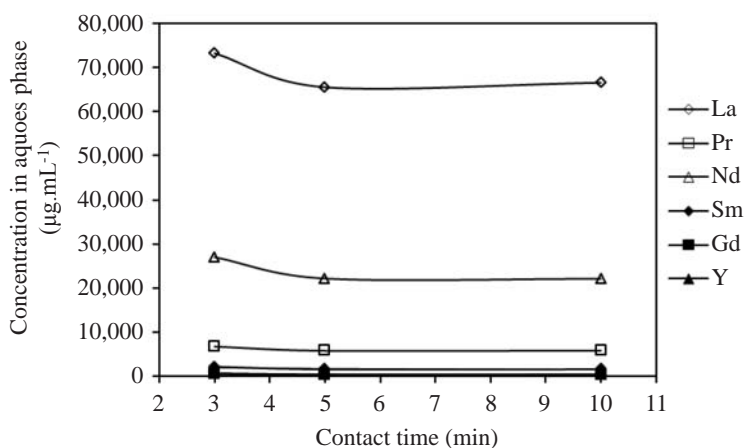

Figure 3 Effect of contact time on rare earth extraction with concentration of tri-*n*- butyl phosphate of 50% volume per volume and shaking speed of 200 rpm.

Table 2 Separation factors of rare earth pairs at different contact times.

Contact time (min)	Rare earth pairs								
	Sm/La	Sm/Pr	Sm/Nd	Gd/La	Gd/Pr	Gd/Nd	Y/La	Y/Pr	Y/Nd
3	4.69	4.00	2.26	7.64	6.52	3.69	8.93	7.61	4.31
5	5.40	4.31	2.46	9.74	7.78	4.43	13.95	11.15	6.35
10	5.61	4.37	2.45	10.11	7.87	4.41	14.66	11.42	6.40

Effect of shaking speed on rare earth extraction

The speed of shaking is a key factor that influences the rate of mass transfer from the aqueous phase into the organic phase. A higher shaking speed will result in enhanced mass transfer. At a higher shaking rate, the resistance to mass transfer is lower, and a larger mass transfer area is produced (small droplets). The influence of the shaking speed on rare earth extraction was evaluated at 100, 150 and 200 rpm. The extraction experiments were performed using a phase ratio of 1:1 (organic:aqueous), a TBP concentration of 50% v/v and a contact time of 5 min. As can be seen in Figure 4, the concentration of rare earth in the aqueous phase decreased with increased shaking speed because the higher shaking speed generated a large interfacial area between the sample and solvent, resulting in a very fast mass transfer. The SF values of rare earth pairs at different shaking speed are shown in Table 3. From Table 3, the

SF values in the range 2.19–13.95 resulted from a shaking speed ranging from 100 to 200 rpm. It can also be observed that with an increase in the shaking speed from 100 to 150 rpm, the SF values for Y/La, Y/Pr and Y/Nd increased markedly from 6.64, 4.25 and 3.45, respectively, to 12.91, 9.30 and 5.76, respectively. However, when the shaking speed was further increased to 200 rpm, the SF values for Y/La, Y/Pr and Y/Nd slightly increased to 13.95, 11.15 and 6.35, respectively. Similar trends in the SF values for the other rare earth pairs were observed, so the shaking speed of 200 rpm was selected for rare earth separation.

CONCLUSION

Liquid-liquid extraction was used to separate rare earths from a nitrate medium. The main variables affecting the separation of rare earths were investigated—namely, the TBP
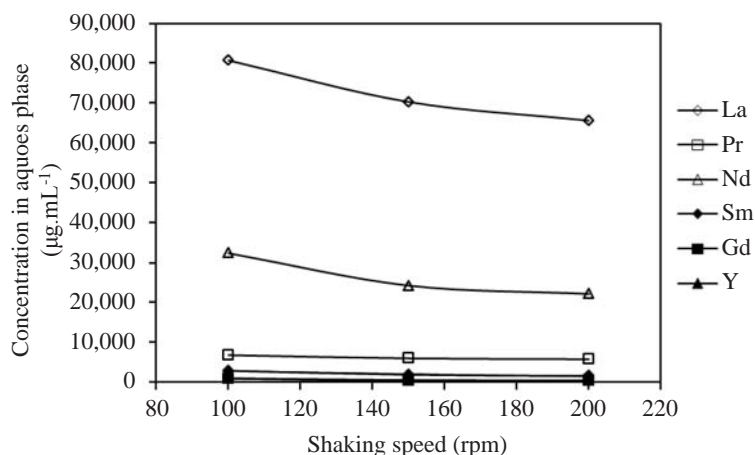

Figure 4　Effect of shaking speed (revolutions per minute, rpm) on rare earth extraction with concentration of tri-*n*- butyl phosphate of 50% volume per volume and contact time of 5 min.

Table 3　Separation factors of rare earth pairs at different shaking speeds.

Shaking speed (rpm)	Rare earth pairs								
	Sm/La	Sm/Pr	Sm/Nd	Gd/La	Gd/Pr	Gd/Nd	Y/La	Y/Pr	Y/Nd
100	4.21	2.69	2.19	6.40	4.10	3.33	6.64	4.25	3.45
150	5.14	3.70	2.29	9.53	6.87	4.25	12.91	9.30	5.76
200	5.40	4.31	2.46	9.74	7.78	4.43	13.95	11.15	6.35

concentration, contact time and shaking speed. The best conditions for the separation in this study were a TBP concentration of 50% v/v, a contact time of 5 min and a shaking speed of 200 rpm. Under these conditions, the middle-heavy rare earths (Sm, Gd, Y) could be separated from the light rare earths (La, Pr, Nd).

ACKNOWLEGEMENTS

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