Effect additional pH on separation extraction gadolinium from terbium and europium with Di-2-(ethylhexyl)phosphate acid

S Budiman1, B Saputra1, A Hardian1, T Yuliana1, A Murniati1, V A Kusumaningtyas1, Nurdeni2, S Effendy3, A Mutalib4, A Anggraeni4 and H H Bahti1

1 Department of Chemistry, Jenderal Achmad Yani University, Cimahi, Indonesia.
2 Mathematics Education Study Program, Indraprasta PGRI University, Jakarta, Indonesia.
3 Department of Pharmacy, Al-Ghifari University, Bandung, Indonesia.
4 Department of Chemistry, Padjadjaran University, Jatinangor, Indonesia.

*Corresponding author e-mail: husein.bahti@unpad.ac.id

Abstract. Rare earth elements are strategic materials, difficult to obtain, and have wide uses. Currently, it is still difficult to separate and refine REE’s because it has similar physical and chemical properties. Solvent extraction is most successful method used for the separation of REE’s. Di-2-ethylhexyl phosphoric acid has been widely used in industry for the separation and of REE’s. Purpose of this study is effect of pH on basic parameters extraction which include distribution coefficient, extraction efficiency and separation factor in extraction gadolinium, terbium and europium through complex with D2EHPA. Determination effect pH is a parameter determined in process extracting standard solutions gadolinium, terbium and europium using D2EHPA with n-hexane. Basic parameters in extraction gadolinium, terbium and europium with D2EHPA at pH 4 are as follows KdGd = 89.90; αGd/Tb = 5.63, Gd/Eu = 1.83; %E = 98.90. KdTb = 15.94; αTb/Gd = 0.17; Tb/Eu = 0.32; % E = 94.10; KdEu = 1.40; αEu/Gd = 0.01,Eu/Tb = 0.08; %E = 98.29. From these values it can be concluded that gadolinium, can be separated from terbium and europium by the solvent extraction method by forming complex D2EHPA with best separation results obtained at pH 4.

1. Introduction

Rare earth elements (REEs) are found form phosphate and carbonate complex compounds [1]. Existence and availability of REEs has an important role for the advancement of high-tech industry and its sources are quite widely available in Indonesia because it is widely available on several islands, including Bangka Belitung and Singkpel which is a by-product of tin processing [2].

Rare earth elements (REEs) uses include superconductors, lasers, permanent magnets, electronic equipment and ceramics [3]. Rare earth elements are able to produce neomagnets, which are magnets that have a magnetic field better than ordinary magnets that allow the emergence of electric-powered cars that can be used for long trips. Therefore, electric cars are starting to be widely developed [4]. Separation of REEs mixtures has been widely used by means of crystallization, fractionation, ion exchange and solvent extraction techniques [5]. However, among all these separation methods, solvent extraction is the most common method best used for REE’s separation [6]. The development of REEs separation and analysis methods has attracted attention of many researchers because these elements are materials that support development of science and technology [3]. Separation of Sm, Gd and Dy can be done by solvent extraction method using D2EHPA acid as an extractant with n-hexane as solvent. Extraction of Gd(III) and Sm(III) through the formation of the D2EHPA ligand complex using n-hexane solvent with the parameters of metal mole ratio: ligand mole, shaking time and extraction pH. Optimum extraction conditions and success of extraction process were evaluated using ICP-OES [7]. Liquid solvent or liquid extraction methods with ligands were developed for separation and purification of
REE’s. Separation by extraction can be determined by distribution coefficient (Kd), concentrate dissolved in nitric acid and factor separation [8]. Parameters used were variations: % vol TBP, pH, stirring time and (Organic phase) : (Aqueous phase) [9]. In [10] performed REE’s extraction with EHEHPA ligands, Cyanex 272, Cyanex 572 and a mixture of EHEHPA with Cyanex 272, pH and concentration of extracts. Results show that Kd produces better separation. Performed separation extraction, Nd(III) from Dy(III), and Y(III) with Hydrochloric acid, D2EHPA and n heptane [11]. Separation of gadolinium with di-(2ethylhexyl)phosphoric acid (D2EHPA) and tributylphosphate (TBP) acid ligands by liquid-liquid extraction with organic solvent- kerosene. Solvent extraction and stripping stepwise on Th and Nd from monazite sand with parameters used: (Organic phase): (Aqueous phase), pH of nitric acid, TBP ligands and stirring speed. Stripping was carried out 3 times using distilled water with 5% oxalic acid [12].

2. Materials and Method
A total of 20 ml of solution standard gadolinium, terbium and europium 10 ppm were pipetted and placed in a Beaker and pH of solution was adjusted by adding a solution of sodium hydroxide or 1M nitric acid until it reached pH 2 and adding buffer according to pH conditions while solution was stirred. Solution was extracted with 20 mL of n hexane solvent containing D2EHPA. Solutions were shaken each for 15 minutes. Aqueous phase and organic phase formed are separated. Aqueous phase was analyzed with ICP-OES instrument. Meanwhile, organic phase was analyzed by means UV spectrophotometer. Same procedure was carried out for various extraction pH 3, 4 and 5.

3. Result and Discussion
3.1. Phase of Metal Extraction Analysis of Gd(III), Tb(III) and Eu(III) with ICP-OES instrument
Extracted aqueous phase was then analyzed using ICP-OES instrument, so that concentrations of Gd(III), Tb(III) and Eu(III) remaining in aqueous phase could be determined. Determination of aqueous phase metal ion concentration after extraction with the ICP-OES instrument was carried out at typical wavelengths of 342.246 nm for Gd (III), 397.197 nm for Eu(III) and 350.914 nm for Tb(III). First step to determine the concentration using ICP-OES is to determine standard curves of Gd(III), Tb(III) and Eu(III). Standard curve was made from 5 standard solutions with varying concentrations, namely, 1 ppm, 2 ppm, 3 ppm, 4 ppm and 5 ppm. Five standard solutions were then measured for their intensity. From standard curve Gd(III) above, the linear regression equation $y = 11273.8x + 153.0$ is obtained. From standard Tb(III) curve above, linear regression equation $y = 5809.5x + 50.0$ and from standard Eu(III) curve above, we get the linear regression equation $y = 39527.1 x + 242.6$.

3.2. Determination of concentration of Gd(III), Tb(III) and Eu(III) after extraction with n-hexane solvent
To determine optimum conditions of reaction for formation of complexes Gd-D2EHPA, Tb-D2EHPA and Eu-D2EHPA, an analysis of solution after extraction (aqueous phase) with ICP-OES will be carried out. Free metal intensity measured by ICP-OES instrument was then entered into linear regression equation from standard curve, so that concentration of free metal remaining in aqueous phase after extraction could be determined. Concentration of extracted Gd-D2EHPA, Tb-D2EHPA and Eu-D2EHPA complexes into organic phase can be determined by calculating difference between initial concentrations of Gd(III), Tb(III) and Eu(III) before extraction with concentrations of Gd(III), Tb(III) and Eu(III) remaining in aqueous phase after extraction. Data analysis of extraction results of Gd-D2EHPA, Tb-D2EHPA and Eu-D2EHPA with solvents n-hexane at each the pH variation can be seen in Table 1, Table 2 and Table 3.

There was an increase in % E in the extraction of Gd(III) using the D2EHPA ligand at a decrease in pH, so that the increase in % E was optimum at pH 5. The value of Gd(III) with dibuthyldithiophosphatic acid (DBDTP) ligand have extraction percentage increases as the pH in the solution increases. In lower pH, there is a decrease in the percentage of Gd(III) extraction compared to higher pH [13].
Table 1. Concentration of Gd(III) before and after extraction on extraction with solvent n-hexane at various pH.

| pH | [Eu(III)] early (ppm) | Water Phase | Organic Phase | % E |
|----|----------------------|-------------|--------------|-----|
| 3  | 10                   | 8.0895      | 89.89        |
| 4  | 10                   | 9.4509      | 94.51        |
| 5  | 10                   | 9.8881      | 98.88        |

Table 2. Concentration of Tb(III) before and after extraction on extraction with solvent n-hexane at various pH.

| pH | [Eu(III)] early (ppm) | Water Phase | Organic Phase | % E |
|----|----------------------|-------------|--------------|-----|
| 3  | 10                   | 5.8432      | 41.57        |
| 4  | 10                   | 9.9175      | 99.17        |
| 5  | 10                   | 9.6327      | 96.33        |

Figure 1. Concentration of Gd(III) before and after extraction at various pH.

Figure 2. Concentration of Tb(III) before and after extraction at various pH.

There was an increase in % E in the extraction of Tb(III) using the D2EHPA ligand at a decrease in pH, so that the increase in % E was optimum at pH 4. The value of Gd(III) with dibuthyldithiophosphjate (DBDTP) ligand have extraction percentage increases as the pH in the solution increases. In lower pH, there is a decrease in the percentage of Gd(III) extraction compared to higher pH [13].

Table 3. Concentration of Eu(III) before and after extraction on extraction with solvent n-hexane at various pH.

| pH | [Eu(III)] early (ppm) | Water Phase | Organic Phase | % E |
|----|----------------------|-------------|--------------|-----|
| 3  | 10                   | 8.9157      | 89.15        |
| 4  | 10                   | 9.9738      | 99.73        |
| 5  | 10                   | 9.9241      | 98.24        |

There was an increase in % E in the extraction of Eu(III) using the D2EHPA ligand at a decrease in pH, so that the increase in % E was optimum at pH 4. The value of Gd(III) extraction percentage increases as the pH in the solution increases. In lower pH, there is a decrease in the percentage of Gd(III) extraction compared to higher pH [13]. The physical and chemical properties of Gd(III) and Sm(III) are...
not much different so that the extraction efficiency values are not too far apart, therefore they are difficult to separate [14]. The % extraction is optimum at pH value of 4 in Gd(III) experiment.

After obtaining optimum pH for each complex Gd-D2EHPA, Tb-D2EHPA and Eu-D2EHPA extraction results. Extracted organic phase was analyzed using UV spectrophotometer. Comparable with spectrum of free D2EHPA ligands, such as show in Figure 4.

Figure 3. Concentration of Eu(III) before and after extraction at various pH.

Figure 4 Spectrum of the Gd-D2EHPA, Tb-D2EHPA and Eu- D2EHPA with a spectrum of free D2EHPA ligands.

When compared with spectrum of free D2EHPA ligand, absorption peak of Gd-D2EHPA complex experienced a maximum wavelength shift towards a lower energy (longer wavelength) or also called a red shift (batochromic) from a wavelength of 221.80 nm to a wavelength of 221.80 nm. 228.40 nm for Gd-D2EHPA complex, while the shift for Tb-D2EHPA complex from a wavelength of 221.80 nm to a wavelength of 229.00 nm. And for Eu-D2EHPA complex, it shows a wavelength shift from 221.80 nm to a wavelength of 227.00 nm. This shift is thought to originate from the extension of conjugation or delocalization of π electrons in structure of the compound formed. This proves that there has been a reaction between gadolinium and D2EHPA ligand. There was a shift in the absorbance spectrum of Gd-DBDTP shifting to a longer wavelength. This chemical shift originates in the elongation of the conjugate system or delocalization of π electrons from new molecule [13].

4. Conclusion

Distribution coefficient (Kd), separation factor (α) and extraction efficiency (%E) in extraction of gadolinium, terbium and europium metals through complex formation with D2EHPA ligand using a hexane-water pair can be determined. Kd_Gd = 89.90; Gd/Tb = 5.63, Gd/Eu = 1.83; %E = 98.90 %. Kd_Tb = 15.94; Tb/Gd = 0.17, Tb/Eu = 0.32; %E = 94.10 %; Kd_Eu = 1.40; Eu/Gd = 0.01, Eu/Tb = 0.08; %E = 98.29%. From these values it can be concluded that gadolinium, terbium and europium metals can be separated. The % Extraction is optimum at pH value of 4 in Gd(III) experiment.

References

[1] Suwargi E, Pardiarto B and Islah T 2010 Potensi logam tanah jarang di Indonesia Bul. Sumber Daya Geol. 5 131–40
[2] Suprapto S J 2009 Tinjauan tentang unsur tanah jarang Bul. Sumber Daya Geol. 4 36–47
[3] Christie T, Brathwaite B and Tulloch A 1998 Mineral commodity report 17 - rare earths and related elements New Zeal. Min. 27 1–13
[4] Rodliyah I 2015 Penelitian logam tanah jarang di Indonesia Maj. Energi 13 71–80
[5] Gupta C K and Krishnamurthy N 1992 Extractive metallurgy of rare earths Int. Mater. Rev. 37 197–248
[6] Brown C G and Sherrington L G 2007 Solvent extraction used in industrial separation of rare
[7] Anggraeni A, Sofyatin T and Bahti H H 2014 Ekstraksi gadolinium dan samarium dari mineral monasit secara ekstraksi dengan ligan etilendiamintrimetilen-fosfonat (EDTMP) Chim. Nat. Acta 2 166–72

[8] Thakur N V. 2000 Separation of rare earths by solvent extraction Miner. Process. Extr. Metall. Rev. 21 277–306

[9] Bintarti A N, Bambang E B B and Purwani M V. 2002 Ekstraksi untuk memisahkan unsur-unsur dalam konsentrat logam tanah dari pasir senotim Prosiding Pertemuan dan Presentasi ilmiah Penelitian Dasar Ilmu Pengetahuan dan Teknologi Nuklir P3TM-BATAN (Yogyakarta) pp 257–61

[10] Quinn J E, Soldenhoff K H, Stevens G W and Lengkeek N A 2015 Solvent extraction of rare earth elements using phosphonic/phosphinic acid mixtures Hydrometallurgy 157 298–305

[11] Mohammadi M, Forsberg K, Kloo L, Martinez De La Cruz J and Rasmuson Å 2015 Separation of ND(III), DY(III) and Y(III) by solvent extraction using D2EHPA and EHEHPA Hydrometallurgy 156 215–24

[12] Suyanti and Purwani M V. 2006 Pengaruh persentase surfaktan dan topo-kerosen pada ekstraksi membran emulsi terhadap konsentrat Ce(IV) Prosiding PPI - PDIPTN 2006 (Yogyakarta) pp 4–11

[13] Solihin R M, Mulyaningsih Y and Anggraeni A 2008 Extraction study of Gadolinium(III) by di-n-butylthiophosphate (DBDTP) ligand as complex agen Proceeding Int. Semin. Chem. 2008 2008 118–22

[14] Sofyatin T, Nurlina N, Anggraeni A and Bahti H H 2016 Penentuan koefisien distribusi, efisiensi ekstraksi dan faktor pemisahan pada ekstraksi gadolinium dan samarium dengan ligan dibutilditiofosfat Chim. Nat. Acta 4 47