Solvent Extraction and Stripping of Gadolinium (III) from Samarium (III) and Europium (III) Using D2EHPA as Extractant

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Abstract. Separation and purification of rare earth metals are still the major problem because of similar physical and chemical properties. Among various method, extraction and stripping are the most successful method for the separation of rare earth metals. In this study, we focused on separation of gadolinium from samarium and europium by extraction-stripping gradually methods using ligands di-2-ethylhexyl phosphoric acid (D2EHPA) extractant. The gadolinium, samarium and europium sample solutions were extracted using a ligand D2EHPA in *n*-hexane solvent and then were analyzed by ICP-OES to determined the distribution coefficient (Kd) of each complexes. Then, we performed the extraction-stripping of gadolinium from samarium and gadolinium from europium by using D2EHPA ligand in *n*-hexane solvent and nitric acid 6 M as the stripping agent. The efficiency of extraction were 81.23 % for Gd , 68.97 % for Sm, and 34.9 % for Eu. The efficiency of stripping were 36.2 % for Gd , 41.8 % for Sm and 83.6 % for Eu.

Keywords: rare earth metals, Extraction, Stripping, D2EHPA ligand

1 Introduction

Rare earth metals are lanthanide groups which have 14 members of the elements: Ce-Pr-Nd-Pm-Sm-Eu-Gd-Tb-Dy-Ho-Tr-Tm-Yb-Lu. Other metals often associated in the same minerals are Sc-Y-La. Usually these elements are used in a number of modern technologies such as permanent magnets, hybrid batteries, catalysts, generators, mobile phones, computers, Television and fiber optics [1].

Ligands or protective clusters are part of a coordinating compound located on the outside as an electron-pwatering so as to be called Lewis base[2]. The di-2-ethylhexyl phosphoric acid (D2EHPA) is an organophosphoric acid which has been widely used in the separation and purification of rare earth metals, where D2EHPA has 1 H atom which can be replaced by metal ions, so that this compound can be called an exchanger compound ion. In this state, each of them will engage in intra-moleecular hydrogen bonds with metal ions extracted by simply disconnecting one or two hydrogen bonds occurring within the dimer [3].

Liquid-liquid extraction or solvent extraction is a technique in which a solution (usually in water) is made in contact with a second (usually organic) solvent, essentially unmixed and gives rise or displacement of the solutes to the second solvent[4]. Generally metal ions are insoluble

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in non-polar organic solvents. The metal ions should be converted to moleecular shapes that are not charged with the formation of complexes so that the metal ions can be extracted into non-polar organic solvents[5].

The process of stripping or re-extraction is the process of metal recovery from the organic phase to the water phase with relatively pure results[6]. Factors affecting stripping efficiency are the type of acid, acid concentration, contact time, and the phase ratios of organic and aqueous phases[7]. In general, the greater the ability of a rare earth metal to be extracted, the harder it is stripped from the organic phase by the opposite reaction[8].

2 Materials and Methods

2.1 Materials

All materials that used in this study were used as received without further pufification. Di-2-ethylhexyl phosphoricacid (D2EHPA), gadolinium (III) oxide, samarium (III) oxide and euporium (III) oxide were purchased from Sigma Aldrich. Acetic acid, nitric acid, *n*-hexane, sodium acetate and ammonia hydroxide were purchased from Merck.

2.2 Methods

2.2.1 Determination of distribution coefficient (KD) of each ion Gd(III), Eu(III), and Sm(III)

About 20 mL aqueous solution of Gd(III) (pH 3) in separating funnel was extracted with 4 × 5.0 mL of *n*-hexane solvent containing D2EHPA ligand with a mole ratio of metal:ligand = 1: 3. The solution was then shaken for 15 minutes, until it forming 2 layers. After the two layers are separated, the water phase is analyzed by ICP-OES. The same procedures is used for determination of KD samarium (III) and europium (III) ions.

2.2.1 Extraction Methods - Stripping of Gd(III) from Sm(III) and Gd(III) from Eu(III)

About 10 mL aqueous solution of Gd(III) (5 ppm) and 10 mL aqueous solution of Eu(III) (5 ppm) were mixed and then adjusted the pH of the solution until 3 by acetate buffer. The solution was extracted with 4 × 5.0 mL of *n*-hexane solvent containing D2EHPA ligand with a mole ratio of metal:ligand = 1: 3. The solution was then shaken for 15 minutes, until it forming 2 layers. After the two layers are separated, the water phase is analyzed by ICP-OES. The organic phase was then stripping with 6 M HNO_3. Then the two phases were separated. The water phase generated from the stripping process (phase of water stripping) is analyzed by ICP-OES whereas the organic phase is treated with the stripping procedure. Extraction and stripping procedures are repeated four times in a row. The same procedure is also performed for Gd(III) and Sm(III).

3 Results and Discussion

3.1 Extraction of Gd(III), Sm(III), and Eu(III) with D2EHPA ligand

The determination of the distribution coefficient (KD) is performed to determine the ratio of solute concentration in the organic phase and water solvent (water phase) by extraction method. For the quantitative analysis, the ligands are required in the organic phase, the ligands that used are D2EHPA which is dissolved in *n*-hexane solvent with a mole ratio of metal: mole ligand = 1: 3 for Gd(III), Sm(III), and Eu(III) . The mole ratio of metal: mole ligand (1: 3) was designed to adopt the assumption that if the ligand concentration is higher then the formation of the complex will be more stable because the metal will bind more ligands so that the reaction will shift toward the formation of the product. In addition the mole ratio of 1: 3 because rare earth metals have +3 oxidation numbers which means a deficiency of 3 electrons so that requires 3 electrons can be obtained from the electron on the D2EHPA ligand. The *n*-hexane solvent is used because it qualifies as the organic solvent in the extraction method and produces the optimum condition for separation of Gd(III), Sm(III), andEu (III). Furthermore, the condition of standard solution Gd(III), Sm(III), and Eu(III) is set to be pH 3 as the optimum condition. The extraction was performed with each shuffling time for 15 minutes because it was sufficient time to reach the equilibrium state of Gd(III) extraction with D2EHPA ligand. Formation of complexes between metals with D2EHPA ligand in n-hexane solvent, with reaction as follows:

$$M^{(3+)}{}_{(a)} + 3H_2A_{2\,(o)} \rightleftharpoons M(H_3A_6)_{(o)} + 3H^+$$

$M^{(3+)}$ = metal ion
H_xA_x = D2EHPA ligand

3.2 Distribution coefficient (KD) for Gd(III), Sm(III), and Eu (III)

Before the measurements were made, a standard solution of Gd(III), Sm(III), and Eu(III) were prepared with 5 variations of concentration which are 1, 2, 3, 4 and 5 ppm. A linear regression equation for standard solution of Gd(III) is y = 12405x + 38.225, for Sm(III) is y = 12405x + 38.225, and Eu (III) is y = 3441.4x + 16.091. The value of distribution coefficient (KD) for each metal can be seen in Table 1, Table 2, and Table 3.

Table. 1 The distribution coefficient (K_D) data of individual Gd (III) simulation samples using ICP-OES instrument (initial concentration of Gd(III) = 4,9794 mg/L; *n*-hexane solvent; pH = 3; t = 15 minutes; V_{water} = 20 mL; $V_{organic}$ = 20 mL).

No	**Concentration (mg/L)**			**KD Gd (III)**
	[Gd]	**[Gd] in water phase**	**[Gd] in organic phase**	
1	4.9794	0.7755	4.2039	5.4208
2	4.9794	0.4703	4.5091	9.5877
3	4.9794	0.6018	4.3776	7.2742

KD serves to determine the ratio of metal concentrations Gd(III), Sm(III), and Eu(III) dissolved in organic solvents (organic phase) to form complexes into water (water phase). The concentration of Gd(III), Eu(III), Sm(III) funds attracted to the organic phase more than those attracted to the water phase, so that the value of KD> 1. If the value of KD>1 then means quantitatively distributed more in organic solvents to form complexes.

Table. 2 The distribution coefficient (K_D) data of Eu (III) individual simulation samples using ICP-OES instrument (initial concentration Eu (III) = 4,7797 mg / L; *n*-hexane solvent; pH = 3; t = 15 minutes; V_{water} = 20 mL; $V_{organic}$ = 20 mL)

No	**Concentration (mg/L)**			**KD Eu (III)**
	[Eu]	**[Eu] in water phase**	**[Eu] in organic phase**	
1	4.9794	2.0015	2.7782	1.3881
2	4.9794	2.2001	2.5789	1.1722
3	4.9794	2.5378	2.5419	1.0016

Table 3. The distribution coefficient (K_D) data of individual Sm (III) simulation samples using ICP-OES instrument (initial concentration of Sm (III) = 2.1939 mg / L; *n*-hexane solvent; pH = 3; t = 15 minutes; V_{water} = 20 mL; $V_{organic}$ = 20 mL)

No	**Concentration (mg/L)**			**KD Sm (III)**
	[Sm]	**[Sm] in water phase**	**[Sm] in organic phase**	
1	2.1939	0.57	1.6239	2.8489
2	2.1939	0.5094	1.6845	3.3068
3	2.1939	0.421	1.7729	4.2111

3.3 The Separation Factor (α) of Gd(III) to Sm(III) and Gd(III) to Eu(III)

To determine the value of the separation factor required the value of the distribution coefficient (K_D). Based on the data in Tables 4.4 and 4.5, it is found that the separation factor> 1 which indicates that in mixed systems for Gd(III) to Eu(III) ($\alpha_{Gd / Eu}$) and Gd(III) to Sm(III) ($\alpha_{Gd / Sm}$) at pH 3 with *n*-hexane solvent is possible to separate. The separation factor values of

Gd / Eu obtained is 3.9053, 8.1794, and 7.2624 while the value of the separation factor Gd / Sm obtained is 2.5804, 3.4685, and 2.9582..

Table 4. Separation factor (α) Gd (III) / Eu (III) in a simulated sample with D2EHPA ligand (mole metal: mole ligand = 1: 3)

No	**KD**		
	Gd (III)	**Eu (III)**	**α Gd(III)/Eu(III)**
1	5.4208	1.3880	3.9053
2	9.5877	1.1721	8.1794
3	7.2741	1.0016	7.2624

Table 5. Factor of **separation** (α) Gd (III) / Sm (III) in simulation sample with D2EHPA ligand (mole metal: mole ligand = 1: 3)

No	**KD**		**α Gd(III)/Sm(III)**
	Gd (III)	**Sm (III)**	
1	5.4208	2.1007	2.5804
2	9.5877	2.7641	3.4685
3	7.2741	2.4589	2.9582

3.4 Determination of Extraction Efficiency (%E) and efficiency of Strippping (%S) Gd (III), Sm (III), and Eu (III) on stripping extraction of Gd (III) mixtures of Eu (III) and Gd (III) Sm (III)

After performance of extraction and stripping to obtain the KD and α value, we continue to investigate the extraction efficiency and stripping efficiency. The results of analysis with ICP-OES for the extraction of Gd (III), Sm (III), and Eu (III) are shown in the Table 6 and 7.
The amount of metal ions extracted to the organic phase is expressed by the extraction efficiency or percent extraction (%E). Based on the data obtained in the table 6, %E Gd(III) with D2EHPA ligand is higher than Sm(III), with the value obtained is 81.2% while for Sm(III) obtained is equal to 68.9%. Based on the result as shown in table 7, the value of %E Gd(III) with D2EHPA ligand higher than Eu(III), with % E obtained is 71.7% while for Sm(III) obtained is 34.9%. T

The organic phase produced in the first extraction is stripped or re-extraction using 6 M nitric acid to re-extract the metal that forms the complex with the D2EHPA ligand in order to obtain the pure metal which will be drawn back to the water phase, with the reaction as follows:

$$MH_3A_{6\,(o)} + HNO_3 \xrightleftharpoons{Ka} M(NO_3)_{2\,(a)} + 3H_3A_{6\,(o)}$$

Table 6. Extraction efficiency data (%E) and **stripping** efficiency (%S) samples of Gd(II) and Sm(III) using ICP-OES instrument (*n*-hexane solvent; pH = 3; t = 15 minutes, V_{water} = 10 mL, $V_{organic}$ = 10 mL

Treatment		Gd(III) (ppm)	Sm(III) (ppm)
Initial concentration of metal		4.9794	2.1939
Extraction I	Water phase	23.998	0.5687
	Organic phase	25.796	16.252
Extraction I (Stripping)	Water phase	2.116	1.192
	Organic phase	0.4636	0.4332
Extraction II	Water phase	0.1381	0.1932
	Organic phase	12.619	0.2118
Extraction II (Stripping)	Water phase	1.056	0.138
	Organic phase	0.1657	0.128
Extraction III	Water phase	0.1381	0.1932
	Organic phase	12.619	0.2118
Extraction III (Stripping)	Water phase	1.056	0.138
	Organic phase	0.2059	0.0738
Extraction IV	Water phase	0.0647	0.0673
	Organic phase	0.9913	0.0707
Extraction IV (Stripping)	Water phase	0.892	0.025
	Organic phase	0.0993	0.0457
%E		81,20%	68,90%
%S		36,20%	41,80%

After the mixed samples of Gd (III) from Sm (III) and Gd (III) from Eu (III) were extracted-stripping 4 times, stripping water phase I extracted, Stripping extraction II, Stripping extraction III, and Stripping of IV extraction was analyzed using ICP-OES, then the stripping efficiency (%S) can be determined from comparison of water phase concentration divided by organic phase concentration obtained. %S is the strength of a concentrated acid released a complex bond between the metal and its ligand to form a new charged complex, wherein the acid used in this study is a 6 m HNO_3 which later releases a complex bond between metal and D2EHPA ligands to form a new charged complex $M(NO_3)_2$. The stripping efficiency value obtained of Gd(III) from Sm(III) is equal to 36.2% and Sm(III) 41.8% which means Gd(III) and Sm(III) is possibly to separated but not perfect because % S of both metals has not reached 0 and obtained the purity level of Gd(III) 72.8% and purity of Sm(III) 27.2%. While the stripping efficiency of Gd (III) and Eu (III) from extraction and stripping of Gd(III)-Eu(III) mixed metal ion was obtained to be 50.9% and 83.6%, respectively, so that Gd(III) and Eu(III) can be recovered with a purity level of 68.1% and 31.9%, respectively.

Table 7. Extraction efficiency data (%E) and stripping **efficiency** (%S) samples of Gd(II) and Eu(III) using ICP-OES instrument (*n*-hexane solvent; pH = 3; t = 15 minutes, V_{water} = 10 mL, $V_{organic}$ = 10 mL

Treatment		**Gd(III) (ppm)**	**Eu(III) (ppm)**
Initial concentration of metal (ppm)		4.9794	4.7797
Extraction I	Water phase	22.106	10.597
	Organic phase	27.688	3.72
Extraction I (Stripping)	Water phase	1.865	1.945
	Organic phase	0.9038	2.075
Extraction II	Water phase	0.853	0.5785
	Organic phase	1.012	10.665
Extraction II (Stripping)	Water phase	0.717	0.0445
	Organic phase	0.295	1.022
Extraction III	Water phase	0.1097	0.0216
	Organic phase	0.6073	0.0229
Extraction III (Stripping)	Water phase	0.437	0.0095
	Organic phase	0.1703	0.0134
Extraction IV	Water phase	0.0973	0.0077
	Organic phase	0.3397	0.0018
Extraction IV (Stripping)	Water phase	0.297	0.001
	Organic phase	0.0427	0.008
%E		71,70%	34,90%
ES		50.90%	83.60%

CONCLUSION

1. The extraction-stripping method of mixed metal ion using D2EHPA ligand in *n*-hexane, with the condition of mole ratio metal ion: ligand = 1: 3, stripping by 6 M HNO_3 and at pH 3, Gd(III) is possibly to separated and purified from Eu(III) and Sm(III).
2. The efficiency of extraction were 81.23 % for Gd(III) , 68.97 % for Sm(III) , and 34.9 % for Eu(III),. The efficiency of stripping were 36.2 % for Gd(III) , 41.8 % for Sm(III) and 83,6 % for Eu(III).

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