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# Investigation of performances of solvents D2EHPA, Cyanex272, and their mixture system in separation of some rare earth elements from a Nitric Acid solution

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**Abstract**

This work was aimed to evaluate and compare the performances of the solvents D2EHPA (Di-(2-ethylhexyl) phosphoric acid), Cyanex 272 (bis (2,4,4-trimethylpentyl) phosphinic acid), and a mixture system of D2EHPA and Cyanex272 in the separation of some rare earth elements (REEs) including lanthanum, gadolinium, neodymium, and dyspersym from a nitric acid solution. The results obtained showed that Cyane272 had the lowest separation factor in the separation of Dy, La, Nd, and Gd from each other. Also it was found that a mixture system of D2EHPA and Cyanex272 had the best performance in the separation of the investigated REEs, owing to the higher separation factors for Dy/Nd and Dy/Gd, as well as the lower extraction efficiencies for Gd (64.54%), La (30.07%), and Nd (26.47) from Dy (99.92). It was also determined that the separation factors for Dy/Nd and Dy/Gd were 720.05 and 3640.27, respectively, using their mixture system.

**Keywords:** *Rare Earth Elements (REEs), Separation Factor, D2EHPA, Cyanex272, Mixture System.*

## 1. Introduction

From the manufacturing viewpoint, the rare earth elements (REEs) are significant elements. They are an unusual group of metallic elements with unique properties such as the chemical, catalytic, metallurgical, magnetic, and phosphorescent ones, which consists of seventeen elements belonging to the lanthanides. They are widely used in the metallurgy, lasers, magnets, and batteries [1].

With the increasing demand for REEs, their separation and purification from each other have gained considerable importance. The separation of a mixture of REEs into its individual elements using the fractional crystallization, fractional precipitation, ion exchange, and solvent extraction techniques is very complicated due to their small differences in basicity [2]. Among all of these, solvent extraction is the most successful process used for the industrial separation of REEs [3]. Solvent extraction employs the separation of REEs in different acid solutions using various kinds of extractants including the acidic, basic, and neutral ones, and combinations of different kinds of extractants [4-8].

Solvent extraction has been widely employed as a flexible separation method for REEs in various fields such as hydrometallurgy due to its simplicity, speed, and applicability in the extraction and separation of REEs [9, 10].

Sun et al. (2005) have reported that a mixture of CA12 and bis (2,4,4-trimethylpentyl) phosphinic acid (Cyanex272) in n-heptane for separating Y (yttrium) of HRE (Ho, Er, Tm,Yb, and Lu) from chloride solutions have synergistic effects [11]. Sun et al. (2006) have reported that a mixture of Cyanex272 and sec-nonyl phenoxy acetic acid (CA-100) exhibits a significant synergistic effect in the extraction of Sc, Y, La, Ga, and Yb from chloride solutions in n-heptane [12]. Wang et al. (2011) have reported that the separation coefficient for yttrium and a heavy rare earth is more significant in the double solvent (CA12-Cyanex272-TBP) extraction system, compared with the single (CA12-TBP) extraction system [13]. Tri-n-butyl phosphate (TBP) was used above in the system as the phase modifier to achieve a fast phase separation, and to improve the organic phase stability.

The type of organic solvent used in the solvent extraction, pH value, concentration of solvent, solution type (hydrochloric acid, nitric acid, sulfuric acid or phosphate), and diluent (n-heptane, toluene, carbon tetrachloride or kerosene) influence the separation factor and selectivity of the solvent extraction. Meanwhile, no investigation was observed on the separation of REEs (including La, Gd, Nd, and Dy) from a nitric acid solution using Cyanex272, D2EHPA, and their mixture system. Hence, this research work was focused on the performances of D2EHPA, Cyanex272, and their mixture system in the separation of REEs from a nitric acid solution, and to select the best solvent or mixture system.

## 2. Experimental

### 2.1. Reagents and preparations

The commercial extractant Cyanex272 (bis(2,4,4-trimethylpentyl) phosphinic acid) ($C_{16}H_{35}O_2P$) with a purity of 90% was purchased from Aldrich Chemistry Co, and the commercial extractant D2EHPA (Bis (2-ethyhexyl) phosphate) ($C_{16}H_{35}O_4P$) with a purity of over 95% was purchased from Merck; they were used without further purification with the same purity.

Kerosene was applied as the diluent in the solvent extraction.

The $HNO_3$ and NaOH solutions were used to adjust the pH value for the aqueous phase. The pH-meter used in the experiments was RS323 interface AZ8601.

The oxides of REEs such as La, Nd, Gd, and Dy with purities over 99% were purchased from Merck to prepare the stock solution. The stock solution of REEs was prepared from their oxides (up to 99) by dissolving 0.1146 g of $Dy_2O_3$, 0.1166 g of $Gd_2O_3$, 0.1179 g of $Nd_2O_3$, and 0.1172 g of $La_2O_3$ in 10 mL of concentrated nitric acid ($HNO_3$, 65%) and 10 mL of distilled water. Also, for some of the insoluble REE oxides, the stock solution was heated up to 80 $^{o}$C on a hot plate, and then mixed by a magnetic stirrer (SHIN SAENO) for about 15 min. Then the stock solutions were analyzed using ICP (ICP-Varian, Geological Survey of IRAN), and their chemical compositions were tabulated in Table 1.

**Table 1. Chemical composition of stock solution.**

| Element | Dy | Gd | Nd | La |
|---|---|---|---|---|
| Chemical composition (ppm) | 184 | 176 | 166 | 153 |

### 2.2. Solvent extraction procedures

General extraction experiments were carried out in 100 mL glasses using a hot plate and a magnetic stirrer (450 rpm) at room temperature (299 ± 1k) by contacting equal volumes (10 mL) of the aqueous and organic phases in the solvent extraction (A/O = 1). Also all the preliminary experiments were carried out at a fixed contact time of 10 min. After extraction, the two phases were separated using a separation funnel. The metal ion concentrations in the aqueous phase were determined before and after extraction by ICP. The metal contents in the organic phase were also obtained by the mass balance.

The distribution ratio (D) that is the most important parameter involved in the solvent extraction, and the other parameter involved such as the extraction efficiency (E) and separation factor (SF) were determined using the formulas (1) to (3), respectively.

$$D = \frac{[M]_t - [M]_a}{[M]_a} \quad (1)$$

$$E = \frac{D}{D + (\frac{V_{aq}}{V_{org}})} \times 100 \quad (2)$$

$$SF = \frac{D_1}{D_2} \quad (3)$$

where $[M]_t$ and $[M]_a$ represent the initial and final concentrations of the metal ions in the aqueous phase, and $V_{aq}$ and $V_{org}$ are the volumes of the aqueous and organic phases. $D_1$ and $D_2$ denote the larger and the smaller RE distribution ratios, respectively.

## 3. Results and discussion

### 3.1. Solvent extraction with D2EHPA

In order to investigate the performance of D2EHPA, firstly, the experiments were carried out at the pH values of 1, 2, 3, and 4.5, with 0.05 molar of D2EHPA. Then the separation factors for REEs were compared, and the optimal pH value was obtained based on the highest separation factor. Thereafter, 10 mL of D2EHPA with concentrations of 0.2, 0.1, 0.05, and 0.025 molar were used to extract and separate the rare earth elements (La, Nd, Dy, and Gd) at the optimal pH value of 2. It was found that 0.05 molar was the best concentration at the pH value of 2. Subsequently, 10 mL of the organic phase (D2EHPA) was mixed with 10 mL of the aqueous phase for 10 min using a magnetic stirrer under the conditions of room temperature (298 K), concentration of 0.05 molar, and pH value of 2. Finally, after the extraction, the organic phase was separated from the aqueous phase using a separation funnel. The aqueous phase was analyzed by ICP. The distribution ratios and extraction efficiencies for REEs, calculated by D2EHPA, are presented in Table 2 and Figure 1.

**Table 2. Distribution ratios and extraction efficiencies for REEs usingD2EHPA at optimal conditions (0.05 molar, pH = 2).**

| Element | Distribution ratio | Extraction efficiency (%) |
|---|---|---|
| Dy | 1835.1 | 99.95 |
| Gd | 104.88 | 99.06 |
| Nd | 3.3 | 76.74 |
| La | 0.43 | 30.07 |

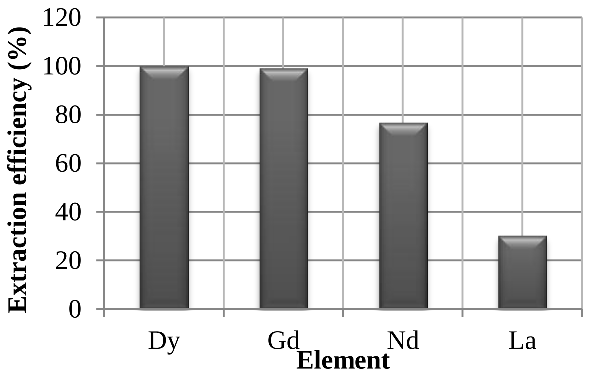


**Figure 1. Extraction efficiencies for REEsusing D2EHPA.**

According to the results obtained (see Table 2 and Figure 1), the following observations can be attained.

It was observed that the distribution ratio and extraction efficiency of the elements for Gd and Dy had values higher than those for Nd and La. The distribution ratios for Dy and Gd were obtained to be 1835.1 and 104.88, respectively. The extraction efficiencies for both Dy and Gd were obtained to be about 100% at the optimal conditions (0.05 molar, pH = 2). It was seen that La had the least distribution ratio (0.43) and extraction efficiency (30%). In addition, it can be observed that D2EHPA has the least ability to extract the element La.

### 3.2. Solvent extraction with Cyanex272

In investigating the ability of Cyanex272 as an extractant for the separation of REEs, similar to the extractant D2EHPA, separations of La, Nd, Dy, and Gd were carried out using Cyanex272 at the optimal conditions (0.05 molar, pH = 2). The results obtained for the distribution ratio and extraction efficiency of REEs are presented in Table 3 and Figure 2.

**Table 3. Distribution ratios and extraction efficiencies for REEs usingCyanex272 at the optimal conditions (0.05 molar, pH = 2).**

| Element | Distribution ratio | Extraction efficiency (%) |
|---|---|---|
| Dy | 0.19 | 15.97 |
| Gd | 0.014 | 1.38 |
| Nd | 0.14 | 12.28 |
| La | 0.41 | 29.08 |

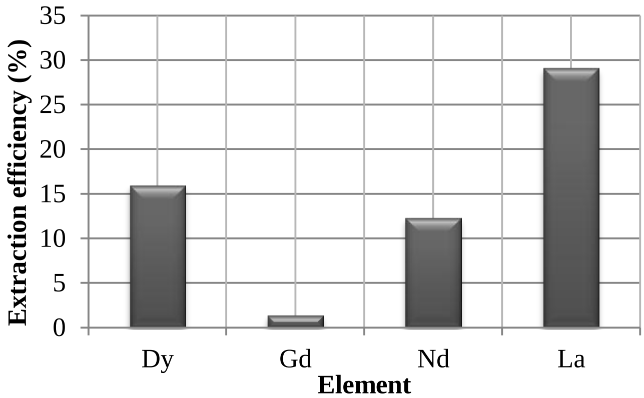


**Figure 2. Extraction efficiencies of REEs using Cyanex272.**

According to the data in Table 3 and Figures 3 and 4, the distribution ratios for La and Dy have higher values compared with Nd and Gd under the conditions of 0.05 molar of Cyanex272 and pH value of 2.

The distribution ratios for La and Dy were obtained to be 0.41 and 0.19, respectively. The extraction efficiencies for La and Dy were determined to be about 29.08 and 15.97%, respectively. Also it was found by Cyanex272 that Gd had the lowest distribution ratio (0.014) and extraction efficiency (1.38%). On the other hand, Cyanex272 had the least ability for extractiing Gd.

### 3.3. Solvent extraction using extractant mixture (Cyanex272 and D2EHPA)

In order to investigate the performance of the synergistic extraction, different volumes of the extraction solvents Cyanex272 and D2EHPA were used to extract and separate the rare earth elements La, Nd, Dy, and Gd under the optimal experimental conditions (0.05 molar and pH =,2) (Table 4).

**Table 4. Separation factors for REEs using different volumes of a mixture of Cyanex272 and D2EHPA.**

| Mixture of Cyanex272 and D2EHPA | Separation factor | | | | | |
|---|---|---|---|---|---|---|
| | Dy/Gd | Dy/Nd | Dy/La | Gd/Nd | Nd/La | Gd/La |
| 2 mL of Cyanex272 + 8 mL of D2EHPA | 1.04 | 261.41 | 2548.75 | 250.23 | 9.75 | 1050.83 |
| 4 ml of Cyanex272 + 6 mL of D2EHPA | 10.6 | 384.23 | 3670.2 | 73.94 | 4.68 | 346.04 |
| 6 mL of Cyanex272 + 4 mL of D2EHPA | 32.78 | 1700.5 | 3282.28 | 51.87 | 1.93 | 100.12 |
| 8 mL of Cyanex272 + 2 mL of D2EHPA | 720.05 | 3640.3 | 3047.67 | 5.06 | 1.19 | 4.23 |

As it can be seen in Table 4, the volumes 8 mL of Cyanex272 + 2 mL of D2EHPA had the highest separation factors for Dy/Nd and Dy/La. Hence, this mixture was used to compare with D2EHPA and Cyanex272 in the extraction and separation of REEs. Consequently, 10 mL of the aqueous phase was stirred with 10 mL of the organic phase (8 mL of Cyanex272 + 2 mL of D2EHPA) for 10 min using a magnetic stirrer at room temperature (298 K). After extraction, the aqueous phase was separated from the organic phase, and analyzed by ICP. The results obtained are demonstrated in Table 5 and Figure 3.

According to the results obtained (see Table 4 and Figure 3), the following observations were made for the extractant mixture (8 mL of Cyanex272 + 2 mL of D2EHPA).

It was observed that Dy had the highest distribution ratio and extraction efficiency (1310.5 and 100%, respectively). Also it was found that 8 mL of Cyanex272 + 2 mL of D2EHPA had the least ability for the extraction of Nd with the distribution ratio of 0.36 and extraction efficiency of 26.47(%).

Moreover, the results derived for the extractants were compared with each other (Table 6 and Figure 4). It was observed that Dy/Nd and Dy/Gd had the highest separation factors (3640.27 and 720.05, respectively) in the mixture system of Cyanex272 (8 mL) and D2EHPA (2 mL). On the other hand, D2EHPA had the highest separation factors for Dy/La (4267.67), La/Gd (243.91), Gd/Nd (31.78), and Nd/La (7.67).

It can be concluded that the mixture system of 8 mL Cyanex272 + 2 mL of D2EHPA had the highest performance in the separation of REEs, especially for Dy/Nd and Dy/Gd.

**Table 5. Distribution ratios and extraction efficiencies for REES using the extractant mixture (8 mL of Cyanex272 + 2 mL of D2EHPA) at the optimal conditions (0.05 molar, pH = 2).**

| Element | Distribution ratio | Extraction efficiency (%) |
|---|---|---|
| Dy | 1310.5 | 99.92 |
| Gd | 1.82 | 64.54 |
| Nd | 0.36 | 26.47 |
| La | 0.43 | 30.07 |

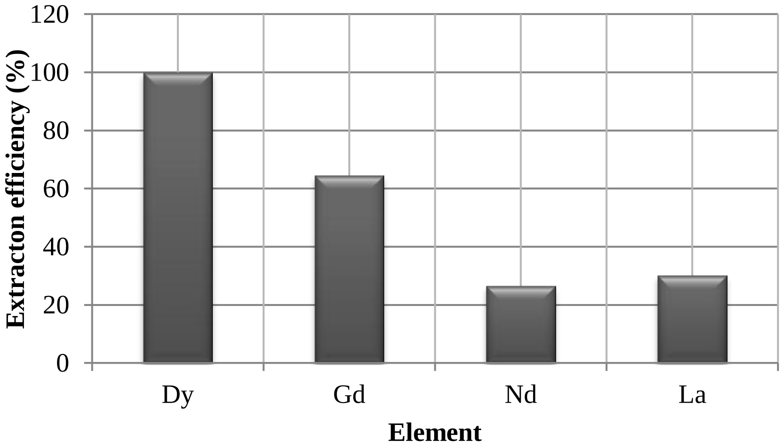


**Figure 3. Extraction efficiencies for REEs using the mixture (8 mL of Cyanex272 and 2 mL of D2EHPA).**

**Table 6. Comparison between separation factors of Cyanex272 and D2EHPA and mixture system of 8 mL of Cyanex272 and 2 mL of D2EHPA at optimal conditions (0.05 molar, pH = 2)**

| Solvent extrations | Separation factor | | | | | |
|---|---|---|---|---|---|---|
| | Dy/Gd | Dy/Nd | Dy/La | Gd/Nd | La/Gd | Nd/La |
| **8 mL of Cyanex272 + 2 mL of D2EHPA** | 720.05 | 3640.27 | 3047.67 | 5.06 | 4.23 | 1.19 |
| **0.05 molar D2EHPA** | 17.50 | 556.09 | 4267.67 | 31.78 | 243.91 | 7.67 |
| **0.05 molar Cyanex272** | 13.57 | 1.36 | 1.67 | 10.00 | 33.33 | 2.94 |

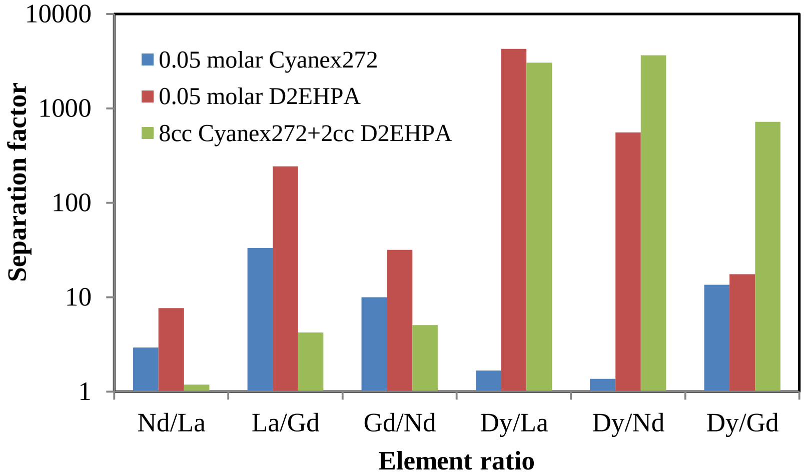


**Figure 4. Comparison between separation factors for Cyanex272 and D2EHPA, and their mixture (8 mL of Cyanex272 and 2 mL of D2EHPA).**

## 4. Conclusions

In this work, we investigated the separation factors for the extractants using D2EHPA and Cyanex272, and their mixture system in the separation of Dy, La, Nd, and Gd in the optimal conditions (0.05 molar and pH value of 2). The major conclusions based on this research work can be summarized as follow:

(1) 8 mL of Cyanex272 + 2 mL of D2EHPA had the highest separation factors for the separation of Dy/Gd and Dy/Nd with the separation factors of 720.05 and 3640.27, respectively.

(2) D2EHPA had the highest separation factors for Dy/La (4267.67), La/Gd (243.91), Gd/Nd (31.78), and Nd/La (7.67). Therefore, this solvent can be used as a suitable solvent for the separation of Dy/La, La/Gd, Gd/Nd, and Nd/La.

(3) Cyanex272 had the lowest separation factor and extraction efficiency for the separation of La, Gd, Dy, and Nd.

(4) It was found that the degree of performance of the systems in the separation of REEs was in the order of the mixture system of Cyanex272 (8 mL) and D2EHPA (2 mL) > D2EHPA > Cyanex272.

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# بررسی عملکرد حلال‌های آلی دپا، سیانکس ۲۷۲ و مخلوط آن‌ها در جدایش عناصر نادر از محلول اسید نیتریک

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**چکیده:**

این کار تحقیقاتی به‌منظور ارزیابی و مقایسه عملکردهای جدایش حلال‌های آلی دپا (دی ۲-اتیل هگزیل فسفوریک اسید) سیانکس ۲۷۲ (بیس ۲ و ۴ و ۴- تری متیل پنتیل (فسفینیک اسید)) و مخلوط دپا و سیانکس ۲۷۲ در جدایش عناصر نادر از قبیل لانتانیم، گادولینیم، نئودیمیم و دیسپروسیم از محلول اسید نیتریک مورد استفاده قرار گرفت. نتایج به‌دست‌آمده نشان داد که سیانکس ۲۷۲ دارای کمترین فاکتور جدایش در جدایش دیسپروسیم، لانتانیم، نئودیمیم و گادولینیم از همدیگر است، مخلوط دو حلال آلی دپا و سیانکس ۲۷۲ از نظر عملکرد جدایش، دارای بهترین عملکرد جدایش به خاطر فاکتورهای جدایش بالاتر دیسپروسیم به نئودیمی و دیسپروسیم به گادولینیم بوده است، درصدها استخراج گادولینیم (۶۴/۵۴٪)، لانتانیم (۳۰/۰۷٪)، نئودیمیم (۲۶/۴۷٪) و دیسپروسیم (۹۹/۹۲٪) در این سیستم ترکیبی به دست آمد و فاکتورهای جدایش عناصر نادر دیسپروسیم به نئودیمیم و دیسپروسیم به گادولینیم در این سیستم ترکیبی به ترتیب ۷۲۰/۰۵ و ۳۶۴۰/۲۷ رسید.

**کلمات کلیدی:** عناصر نادر، فاکتور جدایش، دپا، سیانکس ۲۷۲، مخلوط دو حلال.