Separation of didymium from lanthanum by liquid-liquid extraction using organophosphorus acids and acetic acid

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ABSTRACT

Due to their many high-tech applications and the dominance of China as a supplier, rare earth elements (REEs) are considered to be critical materials by many countries. The motivation of this study arose from the need to obtain rare earth elements by a more efficient and sustainable process. REEs appear together in nature in different minerals, making their separation and purification necessary. Liquid-liquid extraction (SX) is the most widely used technique for this separation and organophosphorus acids are the most frequently used extractants in industry. Saponification of the extractant acid considerably improves the separation of REEs and is commonly used in industrial applications. Nonetheless, this practice generates wastewater containing sodium or ammonia ions, thus requiring treatment before disposal in the environment. An alternative to saponification that maintains high extraction and good separation is the addition of carboxylic acids to the rare earth feed solution. This article reports the separation of didymium (Pr + Nd) from lanthanum by liquid-liquid extraction using different organophosphorus acids as extractants and acetic acid as the carboxylic acid. The batch extraction assays were performed using the organophosphorus acids di-(2-ethylhexyl) phosphoric acid (D2EHPA), 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (P507) and bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex272). We evaluated the effect of pH variation of the feed solution and acetic acid concentration on extraction and separation. The results showed that the rare earth extraction and didymium/lanthanum separation factor increased as the feed solution's pH increased. The extraction of the lanthanides was favored when the acetic acid concentration increased. The lanthanum separation from didymium increased with rising acetic acid concentration values at pH 3.5. Cyanex272 was the most selective extractant. However, it was necessary to carry out the liquid-liquid separation from a less concentrated feed solution to avoid organic phase emulsification.

Keywords: solvent extraction, rare earths elements, acetic acid.
INTRODUCTION

Because of the variety of applications of rare earth elements (REEs), especially in high-tech industries, strong interest exists in many countries to produce these elements domestically. Among the most important applications of these elements are the production of magnets, fuel cells, hybrid vehicle batteries, photovoltaic panels, batteries to store energy from renewable sources and LEDs. In the near future, demand for rare earths will grow in Brazil due to the increasing production of electricity from renewable sources and greater capacity to refine hydrocarbons. Due to this outlook, efforts are under way to develop domestic sources of REEs. In this respect, the Ministry of Mines and Energy (MME) included rare earths as a priority in its National Mining Plan for 2030.

Liquid-liquid extraction, or solvent extraction, is the main method for industrial-scale separation and purification of rare earth elements. When coming into contact with organic extractants, some of these elements pass from the aqueous to organic phase in greater quantity than others, thus allowing their separation. In the case of organophosphorus acid extractants, the extraction mechanism consists of cationic exchange between the metal ions present in the aqueous phase and the hydrogen ions of the extractant acid. The extraction reaction using organophosphorus acids strongly depends on the pH of the aqueous solution. The higher the initial pH of the feed liquor, the more thorough the extraction reaction will be. However, the increase of the initial pH faces constraints because high pH levels can trigger unwanted precipitation of rare earth hydroxides.

Saponification of the extractant acids raises the extraction percentage and thus improves the separation of rare earth elements because the pH of the aqueous solution declines less drastically during the extraction process. However, the use of saponified extractants produces wastewater containing ammonium or sodium ions, making it necessary to treat this effluent before disposal in the environment or recycling for the industrial process. As an alternative to saponification, researchers have been investigating the addition of a complexing agent, such as lactic or citric acid, to the feed liquor, obtaining good extraction and separation results (Sun, Wang & Li, 2006; Yin et al., 2013).

The objective of this study was to evaluate the effect on the separation of didymium (neodymium + praseodymium) from lanthanum through liquid-liquid extraction, with the addition of acetic acid to the rare earth liquor. The extractants tested were the organophosphorus acids D_{2}EHPA, P507 and Cyanex 272, at pH of 3.5.

METHODOLOGY

Reagents

The extractant used to separate lanthanum from didymium were di-(2-ethylhexyl) phosphoric acid (D_{2}EHPA), 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (P507) and bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272), provided by Aodachem (China). The diluent used was commercial kerosene (isoparaffin), provided by Ypiranga (Brazil).

The aqueous feed solution used in the extraction tests was a synthetic solution of La, Pr and Nd with similar characteristics to a monazite leachate (21.0 g L^{-1} of La_{2}O_{3}, 4.87 g L^{-1} of Pr_{6}O_{11}, 17.47 g L^{-1} of Nd_{2}O_{3}), and the oxides (99.9% purity) were provided by Pacific Industrial Development Corporation. The total molar concentration of rare earth elements in the feed solution was 0.26 mol L^{-1}. All other chemicals had analytical grade.

Batch Test

The organophosphorus acids at 0.6 mol L^{-1} were used in all extraction experiments. The pH value of the aqueous phase was 3.5 and the acetic acid concentration varied between 0 and 1.5 mol L^{-1}.
The extractant and the feed solution were placed in contact during 15 minutes (initial experiments showed that equilibrium was achieved within 5 min). After mixing the phases, they were separated in a separatory funnel the concentrations of rare earth metals in the aqueous phase were determined. The extraction experiments were performed at room temperature and in triplicate. The standard deviations of all variables were calculated.

In the extraction tests with Cyanex 272, it was necessary to dilute the feed liquor due to the emulsification of the aqueous solution during the extraction process. The feed solution in the extraction tests with Cyanex 272 had the following composition: La 1.8 g L\(^{-1}\), Pr 0.41 g L\(^{-1}\) and Nd 1.5 g L\(^{-1}\).

**Chemical analysis**

It were determined the Pr and Nd concentrations in aqueous phase by UV-Vis spectrometry (HACH DR 6000 spectrophotometer) and the total REE concentration by complexometric titration with EDTA and xylene orange as indicator. The La concentration was calculated by the difference between the total concentration of REEs and Pr + Nd concentrations.

**Parameter Equations**

The accumulated extraction (%\(E_M\)) of the REEs was calculated from equation 1; as well as the metal concentrations in the loaded organic phase (equation 2). The distribution ratio of each element (D) is the ratio of the concentration of metal in the organic phase and aqueous phase at equilibrium (equation 3). The separation factor (\(\beta\)) indicates the degree of separation of two elements and was calculated from the distribution coefficient of two different metals (equation 4). Finally, the didymium purity in the loaded organic phase was determined by equations 5.

\[
E_M = \frac{[M]_{\text{feed}} - [M]_{\text{raffinate}}(a)}{[M]_{\text{feed}}} \times 100 \tag{1}
\]

\[
[M]_{\text{loaded(o)}} = [M]_{\text{feed}} - [M]_{\text{raffinate}} \tag{2}
\]

\[
D = \frac{[M]_{\text{loaded(o)}}}{[M]_{\text{raffinate}}} \tag{3}
\]

\[
\beta_{M1/M2} = \frac{D_{M1}}{D_{M2}} \tag{4}
\]

\[
\%\text{Didymium purity} = \frac{[\text{Pr}]_{\text{loaded(o)}} + [\text{Nd}]_{\text{loaded(o)}}}{[\text{Pr}]_{\text{loaded(o)}} + [\text{Nd}]_{\text{loaded(o)}} + [\text{La}]_{\text{loaded(o)}}} \times 100 \tag{5}
\]

In these equations, \([M]_{\text{feed}}\) represents the REE concentration in the feed solution, \([M]_{\text{raffinate}}\) is the REE concentration in the aqueous solution after extraction, \([M]_{\text{loaded(o)}}\) is the REE concentration in the loaded organic solution.

**RESULTS AND DISCUSSION**

Figure 1 shows the extraction of the REEs in function of acetic acid concentration for the extractants D2EHPA, P507 and Cyanex 272.
Figure 1. REE extraction values in function of the acetic acid concentration obtained with the extractants D2EHPA, P507 and Cyanex 272 with initial feed pH of 3.5.

It can be noted that for the same element and same extraction conditions, the extraction percentages obtained with D2EHPA were higher than those obtained with P507 and that the percentages obtained with P507 were higher than those obtained with Cyanex 272.

It can also be observed that under the conditions studied, there was greater extraction of neodymium in relation to praseodymium and of the latter in relation to lanthanum, demonstrating the extractant's preference for heavier REEs. Besides this, the addition of acetic acid caused an increase in the REE extraction percentages.

The preference of organophosphorus acids for heavier elements and the better extraction with D2EHPA in relation to P507 and of the latter in relation to Cyanex272 can be explained by Pearson's theory of hard and soft acids and bases (Pearson, 1963). According to this theory, hard bases have greater affinity with hard acids than soft acids, and soft bases have greater affinity for soft acids than hard
acids. The hard species are less polarizable and have higher charge states and smaller size, while the species that are more polarizable, with smaller charge and larger size, are considered soft.

The trivalent ions of the REEs and the conjugate bases of the extractant acids are considered hard acids and bases, respectively. The trivalent ions of the REEs are hard acids due to their high charge, while the extractants are hard bases for having oxygen atoms in their composition. The conjugate base of D2EHPA is considered to be the hardest base of all the extractants for having four oxygen atoms bound to the phosphorus, while P507, which has three oxygen atoms, is less hard than Cyanex272, which has two oxygen atoms. With relation to the metals, neodymium has a smaller radius than praseodymium, which in turn has a smaller radius than lanthanum, so that Nd is harder and La is softer.

Since according the Pearson scheme the acids can be ordered according to their hardness as Nd > Pr > La, the affinity between these and the extractants has the following order from weaker to stronger affinity: Nd > Pr > La. This order of affinity explains the order of extraction levels of Nd > Pr > La observed in the experiments. On the other hand, since the Pearson order of hardness of the bases is D2EHPA > P507 > Cyanex272, the extraction of the REEs with D2EHPA should be greater than that of P507, with both of these being greater than Cyanex272, as confirmed experimentally.

The increase of extraction with higher acetic acid concentration can be explained by the greater concentration of acetate ions (Ac\(^-\)) in aqueous solution as the acetic acid concentration in the feed solution rises. The process of ionization of acetic acid (HAc) can be represented by equation (4). The extraction reaction consists of a cationic exchange between the hydrogen ions of the extractant and the cations of the REE (equation 5). The H\(^+\) released in equation (5) to the aqueous phase reacts with the acetate (Ac\(^-\)), as shown in reaction (6), again forming acetic acid molecules. The higher the concentration of acetate ions in aqueous phase, the lower will be the decline in the aqueous solution's pH and the more extensive the extraction will be.

\[
\begin{align*}
\text{HAc}_{(aq)} &= \text{H}^{+}_{(aq)} + \text{Ac}^{-}_{(aq)} \quad (4) \\
\text{REE}^{3+}_{(aq)} + 3\text{H}_2\text{A}_{2(o)} &= \text{REE(HA)}_{3(o)} + 3\text{H}^{+}_{(aq)} \quad (5) \\
\text{H}^{+}_{(aq)} + \text{Ac}^{-}_{(aq)} &= \text{HAc}_{(aq)} \quad (6)
\end{align*}
\]

Figure 2 shows the praseodymium-lanthanum separation factor and didymium purity in organic phase in function of the concentration of acetic acid, for the extractants D2EHPA, P507 and Cyanex272.
Figure 2. Praseodymium-lanthanum separation factor and didymium purity in organic phase in function of the concentration of acetic acid, for the extractants D2EHPA, P507 and Cyanex272.

It can be noted that the addition of acetic acid favored the separation of lanthanum and praseodymium slightly in comparison to the reaction without addition of acetic acid. A substantial separation of Pr and La (b_{Pr/La} = 21.2 ± 3.8) was achieved only when Cyanex 272 and acetic acid 0.3 mol L⁻¹ were used. This reaction produced didymium with the greatest purity (95% ± 4%). Under the rest of the conditions studied, didymium was obtained with greater purity using P507 as the extractant.

CONCLUSION

In this study, we investigated the effect of adding acetic acid to the rare earth feed liquor on the separation of didymium and lanthanum using the liquid-liquid extraction technique. We observed that, for any of the elements and under the same conditions, the extraction with D2EHPA was greater than with P507, which in turn was greater than extraction with Cyanex 272. Likewise, we observed the preference of the organophosphorus extractants for the heavier REEs. Besides this, we noted that the addition of acetic acid enhanced the REE extraction percentages, and slightly increased the Pr-La separation factor. The best separation was obtained with Cyanex 272 and 0.3 mo L⁻¹ of acetic acid added in the feed liquor.

REFERENCES

